In previous communications it has been shown that cohesion can be explained by the attractions between each molecule and its immediate neighbours. For the general case of a homogeneous isotropic substance the most convenient average arrangement of the molecules to be taken as mathematically representative of that of Nature is the cubical one, in which case each molecule has six nearest neighbours. Each molecule may be regarded as an electrized sphere analogous to the Earth as a magnetized sphere. It has an electric moment, which in several of my papers is denoted by $es$, originally used to indicate the simplest electric moment, that of two opposite electron charges $e$ at distance $s$ apart. But $es$ may be regarded as the symbol for the electric moment of the molecule, however produced. Outside of the molecule the electrization acts like an electric doublet of infinitely small axis but of finite moment $es$ placed at the centre of the molecule. For the sake of simplicity and without any real loss of generality we may imagine the electric axis of a molecule parallel to one set of the edges in our assumed cubical arrangement. Then in order that a molecule may attract its six immediate neighbours it must have its electric axis similarly directed to those of its two axial neighbours, and oppositely directed to those of its four lateral neighbours.

* Communicated by the Author.

The diagram represents these relations in perspective for a central molecule and its six neighbours. Let \( R \) be its distance from its neighbours. Then it attracts the two axial neighbours with a force \( 6e^2s^2/R^4 \) and its four lateral with a force \( 3e^2s^2/R^4 \). The mean attraction is \( 4e^2s^2/R^4 \). Concerning the forces between the central molecule and the more remote ones we see that they are either repulsions or attractions whose average effect can be calculated. I propose to treat it as negligible in comparison with the attractions of the six immediate neighbours. The reason for doing so is this. The molecules of Nature are in motion, the directions of their axes are changing. Our cubical arrangement of the molecules and the assumed directions of the axes becomes a closer representation of the facts of Nature, the smaller the multiple of \( R \) to which it is extended from a central molecule. Even for a molecule and its six nearest neighbours at any instant the cubical arrangement is not a true picture. The real state of affairs is a succession of distorted cubical arrangements with a strictly cubical arrangement for a mean. We deprive our schematic representation of plasticity if we make the one set of dividing planes apply to a large number of molecules. The best way of stating the position is to say that near a molecule the arrangement of other molecules is approximately cubical at any instant, but that the accumulated effects of small departure from the strict cubical arrangement make the relations between any molecule and those which are not its immediate neighbours not expressible by means of a single cubical arrangement. For these reasons then I propose to investigate molecular potential energy on
the following simple principle, that a molecule attracts its six nearest neighbours with a force \(4e^2s^2/R^4\), and that its effects on all other molecules may be neglected.

1. The so-called internal molecular pressure, the \(Kp^2\) of Laplace and the \(a/v^2\) of van der Waals.

The attraction of a molecule for one neighbour having the average value \(4e^2s^2/R^4\), the attraction per unit area of matter lying on one side of a plane exerted on that lying on the other is \(4e^2s^2/R^6\). If \(m\) is the mass of a molecule and \(\rho (=1/v)\) is the density of the substance, \(R^3 = m/\rho\), so we may write

\[
Kp^2 = a/v^2 = 4e^2s^2/R^6 = 4e^2s^2\rho^2/m^2 = 4e^2s^2/m^2\rho^2.
\]

(1)

2. The internal virial \(\frac{1}{2} \cdot \frac{1}{3} \Sigma \Sigma rf(r)\).

With \(f(r)\) to denote the attraction between two molecules at distance \(r\) apart, this evaluation becomes easy. Let us make it for unit mass of the substance consisting of \(n\) molecules in volume \(v\). For a molecule and each of its six immediate neighbours \(rf(r)\) becomes \(4e^2s^2/R^3\). The first \(\Sigma\) extends only to the six nearest neighbours, so

\[
\Sigma rf(r) = 24e^2s^2/R^3.
\]

Then

\[
\Sigma \Sigma rf(r) = 24ne^2s^2/R^3,
\]

and

\[
\frac{1}{2} \cdot \frac{1}{3} \Sigma \Sigma rf(r) = 6ne^2s^2/R^3 = 6npe^2s^2/m = 6npe^2s^2
\]

\[
= 6pe^2s^2/m^2 = 3Kp/2.
\]

(2)

3. Molecular potential energy.

The potential energy of a molecule and one nearest neighbour for an attraction \(4e^2s^2/R^4\) is \(4e^2s^2/3R^3\). For the six nearest neighbours it is \(8e^2s^2/R^3\), and for the \(n\) molecules in volume \(v\) it is \(n/2\) times this, the factor \(\frac{1}{2}\) being introduced to avoid counting the mutual energy of two molecules twice in the summation. So for the potential energy of unit mass we have

\[
4ne^2s^2/R^3 = 4npe^2s^2 \rho = 4pe^2s^2/m^2 = Kp.
\]

(3)

4. Surface energy.

First let us take the imaginary case of a substance whose surface is common with that of a vacuous space. A molecule on the surface has now only five nearest neighbours, if we carry our cubical scheme right up to the surface. The attraction of one nearest neighbour would be unbalanced by an equal opposite force. So a process of adjustment takes place in the surface layer of molecules. Part of the adjustment
consists of evaporation into the vacuum, but for the moment we may neglect the effects of this. The main part of the adjustment consists in a changed arrangement of the molecules in the surface layer, involving a change of density which is often small compared with the density because of the small compressibility of liquids and solids. To a first approximation we may say that a molecule in the surface layer has only \( \frac{5}{6} \) of the potential energy of a molecule in the body. If then we regard the potential energy of the whole mass as being due to compression brought about by the attractive forces between neighbours, then we must say that each molecule on the surface has superposed on this compressional energy a tensional supply which is \( \frac{1}{6} \) of the potential energy of a molecule in the body. So the surface energy per molecule is \( 4e^2s^2/3R^3 = 4ne^2s^2/3 \), and the surface energy per unit surface often denoted by \( \alpha \) is \( 4e^2s^2/3R^5 \). This will apply to a liquid in contact with its vapour whose density is small enough to be neglected. The case in which the effect of the vapour becomes appreciable can be treated as a special one of the following.

5. Surface energy at the contact of two substances.

Here the attraction between unlike molecules enters. Let the one substance be called 1, and have quantities assigned to it by the subscript 1, the other substance being 2. Then the average attraction between a molecule of 1 and a neighbouring molecule of 2 is \( 4e_1s_1e_2s_2/1R_2^3 \), where \( 1R_2 \) has still to be defined. It is the average distance between the surface layer of molecules of 1 and the surface layer of molecules of 2. Thus the representative cubical arrangement of six molecules of 1 round a central molecule in the body of 1 is to be replaced for a central molecule in the surface layer by five molecules of 1 in cubical order round it, and one molecule of 2 at distance \( 1R_2 \) in the sixth direction. So the surface energy of a molecule in the surface of 1 is \( 4(e_1^2s_1^2/1R_1^3 \) \( - e_1s_1e_2s_2/1R_2^3) /3 \), and for a molecule in the surface of 2 it is \( 4(e_2^2s_2^2/1R_2^3 \) \( - e_1s_1e_2s_2/1R_1^3) /3 \). Per unit surface the energies are \( 4(e_1^2s_1^2/1R_1^3 \) \( - e_1s_1e_2s_2/1R_2^3) /3R_1^2 \) and \( 4(e_2^2s_2^2/1R_2^3 \) \( - e_1s_1e_2s_2/1R_1^3) /3R_2^2 \), so for the total surface energy or tension \( \alpha \) we have

\[
3\alpha/4 = e_1^2s_1^2/R_1^4 - e_1s_1e_2s_2(1/R_1^2 + 1/R_2^2)/R_2^3 + e_2^2s_2^2/R_2^5. \tag{4}
\]

The conditions of statical equilibrium are not provided by our definition of \( 1R_2 \) and placing of molecules in the sixth direction. An adjustment takes place, whose effects are neglected.
6. Surface energy of a liquid in contact with its vapour.

Here there is more difficulty in specifying an artificial arrangement which will represent the average case of Nature. A molecule of the surface layer of the vapour in a cubical scheme has five nearest neighbours amongst the vapour molecules and one nearest amongst the surface molecules of liquid, but there are many surface molecules of the liquid which are almost as near as the nearest, half of these repelling and half attracting. But it seems to me that it is right to assume that the electrical adjustments to minimum potential energy which cause a molecule of vapour not at a surface to attract its six immediate neighbours, will likewise cause it, when it is in a surface layer, to determine in all the near molecules of the liquid surface such a total electric moment as attracts it as if the sixth vapour molecule were present alone in the place of the nearest liquid molecule. In Nature the surface molecule of vapour is not stationary in the average position, but it moves right up to the liquid surface, establishing for itself there liquid conditions, it may retreat, or its place may be taken by a molecule leaving the liquid. Our assumption averages the values of the force experienced during this motion, and supposes it to be equal to the force between two vapour molecules whose distance apart is the average distance of a surface molecule of vapour from the liquid surface. On this supposition there is no reason to expect any appreciable perturbation of the vapour density except in the layer quite close to the liquid. It leads to somewhat different results from those obtained in my paper “The Principle of Dynamical Similarity in Molecular Physics” (Boltzmann Festschrift, 1904, A. Barth, Leipzig) from similar considerations. By suitably changing the symbols in the last section with subscript 2 for vapour we get for the tensional surface energy of a molecule in the liquid \( 4e^2s^2\left(1/R_1^5 - 1/R_2^3\right)/3 \), and for the compressional surface energy of a molecule in the vapour \( 4e^2s^2\left(1/R_2^5 - 1/R_2^3\right)/3 \), the total per unit surface being

\[
\alpha = 4e^2s^2\left[\frac{1}{R_1^5} - \frac{1}{R_1^2 + 1/R_2^2}\right] - \frac{1}{1/R_2^3 + 1/R_2^5}\right)]/3. \quad (5)
\]

It has been assumed here that \( es \) remains constant during the change from liquid to vapour. It is possible that two molecules approaching one another might alter one another’s electric moments by a process of induction or otherwise. This is a very important matter in connexion with the electrization of molecules. In section 10 we shall be investigating a change of equal importance within each molecule due to
variation of its distance from its neighbours. Evidence bearing upon a real or apparent change of \( es \) with \( R \) will be discussed in the next section, the subject of the present section being resumed in 8.

7. The virial of molecular attraction expressed empirically.

In "The Laws of Molecular Force" (Phil. Mag. [5] xxxv. 1893, p. 211) it was shown from the extensive experiments of Amagat that the equation of van der Waals applies to the whole gaseous region of the element gases \( H_2, O_2, N_2 \), and to \( CH_4 \), down to and a little beyond the critical volume. Let us write that equation in its properly extended dynamical form for comparison with the equation of the virial of Clausius. It is

\[
\frac{3}{2} p v = \frac{3}{2} RT + \frac{3}{2} RT \frac{v}{v-b} - \frac{3}{2} \frac{a}{v} \ldots \ldots (6)
\]

The term on the left is the virial of the external pressure, the first term on the right is the translatory kinetic energy of the molecules, the second is the virial of the repulsive forces which act during molecular collisions, and the third is the virial of molecular attraction. The form of this third term when compared with (2) with \( \rho = 1/v \), shows that for the element gases and \( CH_4 \) the electric moment \( es \) does not vary with the distance between neighbour molecules either in reality or in effect. But in the same paper it was shown from Amagat's experiments on \( CO_2 \) and from those of Ramsay and Young on \((C_2H_6)_2O\) that for typical compounds the equation takes empirically not the form of that of van der Waals, but this

\[
\frac{3}{2} p v = \frac{3}{2} RT + \frac{2k}{2} \frac{v}{v+k} - \frac{3}{2} \frac{l}{v+k} \ldots \ldots (7)
\]

This applies from \( v=\infty \) to the critical volume which is nearly \( 7k/6 \), and it holds approximately down to \( v=k \). Here we have two remarkable differences from the equation of the van der Waals type. Originally I supposed these to be due to a pairing of the compound molecules, but in later papers attributed them to molecular entanglements during collision. We have now again to consider them more closely. In the first place the virial of the repulsive forces during collision takes the form \( 2k/(v+k) \) times, instead of \( b/(v-b) \) times \( 3RT/2 \). Now in the kinetic theory of gases \( v-b \) enters because under given conditions the mean free path of a molecule diminishes with increasing size of the molecule, the
effect of this in the dynamical calculation of the virial of the collisional forces is to subtract $b$ from $v$, the molecules being assumed to act during collision like perfectly resilient spheres. So the form $v + k$, in which $k$ is added to $v$, indicates that during the collision of compound molecules, there is some cause which lengthens the mean free path, or in other words, reduces the frequency of collisions. A temporary entanglement during collision is the probable cause of this effect. It must be remembered that though we assign a certain electric moment to the whole molecule, the atoms contribute to this electric moments of their own according to laws investigated in my papers on molecular attraction. The great distinction between the molecules of element gases and those of compound gases is this, that in the diatomic element gases the two atoms are identical. Although consisting of two atoms the molecule of an element gas, while not homogeneous, is more nearly homogeneous than that of a compound. When two compound molecules are colliding, the permanent electrical differences amongst the atoms may prevent the electric fields of the whole molecules from adjusting themselves as they do when the molecules are far apart. It may be more an affair of the atoms in contact than of the whole molecule. Thus the effective moments of the molecules in contact may be different from what they are when the molecules are separate. We can account for the virial of the attractions taking the form $3l/2(v + k)$ instead of $3l/2v$, if we write that form $(3l/2v)\left\{v/(v + k)\right\}$ and interpret the factor $v/(v + k)$ as expressing the change which takes place in the $\varepsilon^2s^2$ of $6\rho e^2s^2/m^2$ in (2) with changing distance between neighbour molecules, that is, with changing $v$. This change in $\varepsilon s$ may sometimes be partly of the nature of an effect of mutual induction, but it seems to me that in the collisional virial the change of form from $v - b$ to $v + k$ is suggestive rather of entanglement during molecular encounter, the atomic electric fields being thrown into a confusion which on the averages causes the colliding molecules to have smaller total electric moments effective than when they are free. The equation for ethylene shows the transition from the type for elements to that for compounds. As CH$_4$ ranges itself with the element gases, we infer that the electric fields of C and of H are united up into one simple field like that of the element gases. In the paper cited it is shown that down to $v = k$ the virial of molecular attractions has the form $l/(v + k)$ when the factor $3/2$ is omitted. When $v = k$ it is $l/2k$, and for values of $v$ less than $k$ it is $l/2v$. Thus in typical compounds $l$ in the virial of the attractions and in the
attractional potential energy has for the liquid state half the value for the gaseous. These points and many others will be cleared up only by a kinetic theory of liquids worked out as completely as the kinetic theory of gases. It is because of this form $l/(v + k)$ involving change of $l$ from $l$ to $l/2$ that I retain $l$ as the symbol for a quantity standing for the K of Laplace who puts $\rho = 1$, and the $a$ of van der Waals.

8. Surface energy of a liquid and its vapour

(continued from 6).

Having satisfied ourselves that for the element gases and CH$_4$ the value of $e^2s^2$ may be taken to be the same in the states of liquid and vapour, we can write for them the equation for surface tension $\alpha$

$$3\alpha/4 = e^2s^2\{1/R_1^5 - (1/R_1^2 + 1/R_2^2)/R_2^3 + 1/R_2^5\}. \quad (8)$$

For a typical compound, if we express the various effective values of $es$ in terms of that for the vapour when $v = \infty$ or $\rho = 0$ denoted by $e_g^2s^2$, then for the liquid $e^2s^2 = e_g^2s^2/2$, and for the vapour $e^2s^2 = e_g^2s^2(v + k) = e_g^2s^2/(1 + k\rho)$, so

$$3\alpha/4 = e_g^2s^2\{1/2R_1^5 - (1/R_1^2 + 1/R_2^2)/R_2^32(1 + k\rho)\}
+ 1/R_2^5(1 + k\rho). \quad (9)$$

Though empirically $k = 6v_0/7 = 6/7\rho_c$, where $\rho_c$ is the critical density, it simplifies matters to assume that in this connexion $k$ can be replaced by $1/\rho_c$, and then

$$3\alpha/4 = e_g^2s^2\{1/2R_1^5 - (1/R_1^2 + 1/R_2^2)/R_2^32(1 + \rho/\rho_c)\}
+ 1/R_2^5(1 + \rho/\rho_c). \quad (10)$$

This vanishes at the critical point, as it ought.

For the further development of this equation we can proceed as in the Boltzmann Festschrift, but more definitely and rigorously. Let us consider two typical neighbour molecules as regards the relative motion of approach and departure. Suppose one fixed while the other performs the relative motion. Its kinetic energy may be such as will just carry it to rest at infinity, or it may be more or less than that amount. The relative orbit may be one of infinite range with finite or zero velocity at infinity, or one of finite range. The most beautiful and familiar instances of these three classes of relative orbits are those described under a force varying inversely as the square of the distance, as in the case of comets under the influence of the sun. The hyperbola is the orbit open at infinity on account of there being
more kinetic energy at any point than just suffices to carry the comet to infinity, the parabola is the orbit of infinite range with zero velocity at infinity, the ellipse the orbit of finite range because nowhere is the kinetic energy equal to that acquired by falling from rest at infinity. By this consideration of orbits we can give a dynamical definition of the states of vapour and liquid. In a vapour the relative orbit of two neighbour molecules is an arc of a curve of infinite range open at infinity, in a liquid the relative orbit is one of finite range. At the critical point the orbit is a transitional form, like the parabola, between these two, being of infinite range but closed at infinity. Liquefaction is the gathering together of neighbours of relative orbits of finite range, evaporation is the segregation of neighbours whose relative orbit is of infinite range. When a liquid is in contact with its vapour we have just seen from statical considerations that the surface layer of molecules in the liquid is in tension, as if at less pressure, while the surface layer of molecules of vapour is in compression, as if at higher pressure than prevails away from the surface. Let us state the facts with the aid of the James Thomson ABCD curve, which replaces the straight line AD of condensation at constant saturation pressure. The state of the surface layer of the liquid is expressed by a point between A and B, let us say at B. The state of the surface layer of vapour is represented by a point between D and C, let us say at C. The states represented by points between B and C are unstable. The two surface layers of molecules consist of subsaturated liquid and supersaturated vapour. The two layers might be replaced by a single homogeneous medium occupying the same space in a state represented by the point E, the instability being interpreted as a continual change of state, both condensation and evaporation, occurring at the transition from liquid to vapour.
Dynamically we may regard this medium as consisting of molecules so moving that the relative orbit of two neighbours is a closed orbit of infinite range similar to the parabolic orbit of comets. Let the liquid and vapour be at absolute temperature $T$, then the difference between this fictitious medium of transition and the substance at the critical temperature $T_c$ is that at kinetic energy corresponding with $T$, and at density associated with $1 R_2$ two neighbour molecules in the medium could just separate to an infinite distance apart and come to rest. Let $\rho_s$ be the density associated with $1 R_2$, then $\rho_s$ corresponds with that distance between neighbours which allows their kinetic energy proportional to $T$ just to give them a relative orbit of infinite range, while $\rho_s$ corresponds with that distance between neighbours at the critical point which allows their kinetic energy proportional to $T_c$ just to give them a relative orbit of infinite range. Thus the difference of the potential energy of a molecule in our fictitious medium of density $\rho_s$, and that of a molecule in the critical state is equal to that of their kinetic energies. Let us now return to equations (8) and (10) and derive from them the average potential energy of a molecule amongst those in the surface layer of liquid and the surface layer of vapour, namely

$$4 \pi^2 (1/R_1^2 - 2/1 R_2^3 + 1/R_2^3)/6,$$  \hspace{1cm} (11)$$

and

$$4 \pi^2 \{1/2 R_1^3 - 2/1 R_2^3 (1 + \rho/\rho_s)^3 + 1/R_2^3 (1 + \rho/\rho_s)\}/6.$$  \hspace{1cm} (12)$$

The first and the last terms taken together are the mean energy of a molecule in the liquid and a molecule in the vapour, which we may identify with the potential energy of a molecule in our fictitious medium of density $\rho_s$. Again the middle term becomes the potential energy of a molecule at density $\rho_s$, if we identify $1 R_2$ with $m/\rho_s$ in elements, and with $m/2(1 + \rho/\rho_s)^3 \rho_s$ in compounds. To this definition of $1 R_2$ I have been led by the consideration that it is the simplest one which will give the relation discovered by Eötvös, which we shall obtain at once, for the last expression is now equal to the difference between the kinetic energy of a molecule at $T_c$ and at $T$. So, passing from molecules to gram-molecules, we have the result that the surface energy or tension per gram-molecule $\alpha(M/\rho)^{2/3}$ is equal to the difference between the translatory kinetic energy of $N^{2/3}$ molecules ($N$ being the number of molecules in a gram-molecule) at $T_c$ and at $T$, namely $3R(T_c - T)/2N^{1/3}$ where $R$ is the gas constant when
and Electronic Potential Energy.

The energy is expressed in ergs for a gram-molecule, having the value

\[ 1,014,000 \times 22430/273 = 83 \times 10^6, \]

and

\[ N = 2.77 \times 10^{19} \times 22430. \]

Thus

\[ \alpha(M/\rho)^{2/3} = 1.46(T_\text{c} - T). \ldots \ldots (13) \]

This is the relation discovered by Eötvös (Wied. Ann. xxvii. 1886, p. 448) by means of the principle of corresponding states enunciated by van der Waals. In his experiments Eötvös found 2.23 to be the numerical coefficient in place of the 1.46 just found. For 36 normal compounds Ramsay and Shields found 2.121 to be the mean value of this constant of Eötvös. For Cl₂ it is 1.91, O₂ 1.66, and N₂ 1.53 (Boltzmann Festschrift, p. 384). The agreement between the theoretical coefficient and these experimental values is sufficiently close to justify the reasoning of this section and the assumption

\[ 1R_2 \approx \frac{m}{\rho_c} \text{ in elements, and } \frac{m}{2\rho_c}(1 + \rho/\rho_c)^3 \text{ in compounds,} \]

or in other words that at the passage from the surface layer of the liquid to the surface layer of the vapour the critical density prevails in elements, and a closely related density in compounds. The chief reason for the difference between 1.46 and 2.12 is that in our reasoning, by confining our attention to the kinetic energy and the attractive potential energy, we have neglected the energies associated with the external pressure and with the collisional forces, that is, the energies corresponding to the virials \( 3p/2 \) and \( 3RT/2(v - b) \) or \( 3RT2k/2(v + k) \). These approximately neutralize one another so long as we can use the equation \( pv = RT \) approximately, and that is why we have been able to reason successfully as if the molecules were planets and comets free from external force and free from collisions. At the critical point and near it the approximation \( pv \approx RT \) is too rough, whence the discrepancy between 1.46 and 2.12. It would lead us too far from the present subject to discuss the inclusion of these two neglected terms. The chief object of the present section is to show how the classical statitical theory of surface tension, developed by Laplace, Young, and Gauss, in the days before the kinetic theory of matter, is connected with the more recent discoveries made in the light of that theory. Closely connected with the discovery of Eötvös is that made by Caillietet and Mathias (Comptes Rendus, cii. 1886, p. 1202) which I have discussed in the Boltzmann Festschrift. With temperature as abscissa and density as ordinate they plotted the densities of liquid and saturated vapour right up to the critical point, forming two branches of a curve which merged
into one another at the critical point. When the points of mean density are marked they yield a straight line inclined to the axes. The mean density is a linear function of the temperature. That is the discovery made by Cailletet and Mathias. S. Young (Phil. Mag. [5] l. 1900, p. 291) has shown that there is a small departure from linearity. The relation of Cailletet and Mathias is expressed completely by the equation

\[ \rho_1 + \rho_2 - 2\rho_c = 2c(T_c - T), \ldots \]  

(14)

to which S. Young adds on the right a small term in \( T_c^2 - T^2 \).

By the principle of corresponding states \( c \) is a parameter such that \( cT_c/\rho_c = 1 \), the actual values calculated by S. Young ranging from 0.932 for fluorobenzene to 1.061 for ethyl formate. For \( \text{C}_2\text{H}_4 \) the value rises to 1.30, and for \( \text{N}_2\text{O} \) to 1.49. For \( \text{Cl}_2 \) it falls to 0.7675. If we return to equation (10) with our interpretation of it, we can write it

\[ \frac{\rho_1^2 + \rho_2^2 - 2\rho_c^2}{2\rho_c^2} = 1.46 \text{ (or } 2.12) \frac{T_c - T}{T_c}. \]  

(15)

Since by the principle of corresponding states we derive from this \( (\rho_1 + \rho_2 - 2\rho_c)/2\rho_c = (T_c - T)/T_c \) which is the law of Cailletet and Mathias, it follows that

\[ \rho_c^2 \frac{2}{3} = 3 \times 1.46 \text{ (or } 2.12) \frac{T_c}{8\rho_c N^{2/3}}. \]  

(16)

The law of Cailletet and Mathias is identical with that of Eötvös by virtue of the relations which we have adopted between \( R_1, R_2, R_3 \) on the one hand and densities on the other. The equations just given contain the fourth and fifth methods of calculating the attractional virial parameter \( l \) as developed in “The Laws of Molecular Force” (Phil. Mag. [5] xxxv. 1893, p. 211), namely, from the data of the critical point and from surface tension.

9. The surface energy of mixed liquids.

Here an interesting kinetic point is raised in connexion with our principle that molecules can be treated as though each attracted only its six immediate neighbours. Consider a mixture of liquids 1 and 2 containing 100 molecules of 1 to 1 of 2. Then in a permanent uniform distribution of the molecules, no molecule of 2 has another molecule of 2 amongst its six immediate neighbours, for it is surrounded by more than 100 molecules of 1. In a purely sttical theory with the assumption of permanent uniform distribution the mutual
energy of two molecules of 2 would not enter into the expression for the potential energy of any molecule or of an average molecule.

Then again the cubical arrangement seems an unsuitable one to assume for a mixture of unlike molecules unless the volume occupied by a molecule of each is the same. Nevertheless, by the application of kinetic principles we get over these two difficulties in the following way. If \( \rho \) is the density of a mixture containing \( n_1 \) molecules of 1 per unit mass, it will contain \( n_1 \rho \) per unit volume. It contains \( n_2 \) of 2 per unit mass and \( n_2 \rho \) per unit volume. Let \( n_{01} \) denote the number of molecules of 1 per unit mass in the pure liquid, \( n_{02} \) being the number for 2. Then according to the statistical principles used in the kinetic theory we state that the time for which a molecule of 1 in the mixture is one of the immediate neighbours of a molecule of 1 is the fraction \( n_1 \rho / n_{01} \rho_1 \) of the corresponding time for the pure liquid 1. Now from (3) we know that the average potential energy of a molecule of 1 having molecules of 1 for its neighbours all the time is \( 4e_1^2 \theta_1^2 / R_1^3 \). Hence the potential energy of a molecule of 1 and the other molecules of 1 in the mixture is \( 4n_1 \rho e_1^2 \theta_1^2 / R_1^3 n_{01} \rho_1 \); so the mutual potential energy of the \( n_1 \) molecules is \( 4n_1^2 e_1^2 \theta_1^2 / R_1^3 \rho_1 \).

In this way by making our cubical arrangement the standard of reference where it was geometrically possible we have been able to pass to the case of mixtures where it is impossible.

As to the mutual potential energy of the \( n_1 \) and the \( n_2 \) molecules we can find it most simply by considerations of symmetry from the result just obtained. When \( n_1 \) and \( n_2 \) are large, the number of pairs of a molecule of 1 with a molecule of 1 is \( n_1^2 / 2 \) nearly, while the number of possible pairs of a molecule of 1 with a molecule of 2 is \( n_1 n_2 \). Hence for the desired result there needs only to replace in \( 4n_1^2 e_1^2 \theta_1^2 / R_1^3 \rho_1 \) the \( n_1^2 \) by \( 2n_1 n_2 \) and \( e_1^2 \theta_1^2 \) by \( e_1 e_2 \theta_2 \), obtaining \( 8n_1 n_2 e_1 e_2 \theta_1 \theta_2 \rho_1 \). If we desire to get this from first principles we may return and analyse the product \( 4n_1 (e_1^2 \theta_1^2 / R_1^3)(n_1 \rho / n_{01} \rho_1) \) in the following manner. As \( R_1^3 n_{01} \rho_1 = 1 \), we have \( n_1 \rho / n_{01} \rho_1 \) equal to the total volume of the molecules of liquid 1 in unit volume of the mixture or to \( n_1 \rho / 2 \) times the volume of a pair of molecules of 1 when they are neighbours. Thus the mutual potential energy of the \( n_1 \) molecules is equal to three times the energy of a pair of them as neighbours \( 4e_1^2 e_2^2 / R_1^3 \) multiplied by \( n_1 \rho / 2 \) times the volume of a pair as neighbours, multiplied by \( n_1 \). Let \( R_2 \) be the distance between a molecule of 1 and of 2 in their average positions as neighbours, then the mutual potential energy of one molecule of 1 and
all the molecules of 2 is $4e_1 e_2 s_1 s_2 / R_2^2$ multiplied by $n_2 \rho / 2$ times $2, R_2^2$, so for the $n_1$ molecules the factor $n_1$ is introduced and a factor 2 introduced because of the contrast pointed out above between $n_1^2 / 2$ and $n_1 n_2$. Thus we arrive at the same result as before. For the total potential energy of the $n_1 + n_2$ molecules in unit mass of mixture we have

$$4\rho (n_1 e_1 s_1 + n_2 e_2 s_2)^2 = 4\rho (p_1 e_1 s_1 / m_1 + p_2 e_2 s_2 / m_2)^2,$$

(17)

where $p_1$ and $p_2 = 1 - p_1$ are the masses of liquids 1 and 2 in unit mass of the mixture.

The attractional virial for such a mixture is $3/2$ times the potential energy. As to the surface energy we shall consider only the case where the effect of the vapour is negligible. Then by similar reasoning to that just used in calculating the potential energy of unit mass we find that liquid 1 in the mixture contributes the fraction $(n_1 \rho / n_0 \rho_1)^2$ of its surface energy per unit area as a pure liquid to the surface energy of the mixture, and so

$$\alpha = (n_1 \rho / n_0 \rho_1)^2 \alpha_1 + 2(n_1 n_2 \rho / n_0 n_2 \rho_1 \rho_2) \alpha_1 \alpha_2 + (n_2 \rho / n_0 \rho_2)^2 \alpha_2,$$

\[ \vdots \alpha / \rho^2 = (p_1 \alpha_1 / \rho_1 + p_2 \alpha_2 / \rho_2)^2. \] 

(18)

This equation was verified (Phil. Mag. [5] xxxviii. 1894, p. 188; xl. 1895, p. 1) by the same experiments as proved the formula corresponding with $4e_1 e_2 s_1 s_2 / R_2^4$ for the force of attraction between two unlike molecules. If this formula were to hold in a purely statical theory of surface energy it would imply that the distribution of the mixed sets of molecules was a purely random one. Any regular distribution favouring the existence of a minimum potential energy would be excluded. Such a result is highly improbable, and therefore the formula just established may be regarded as evidence in favour of the active motion of the molecules in a liquid. This kinetic method of investigating mixed liquids has been neglected in the past, but it has many useful applications.

By means of the results of this section we can explain the remarkable fact that so many ordinary liquids mix with so little contraction or expansion and so small an evolution of heat. Such cases as the rise of temperature on mixing water with sulphuric acid or with ethyl alcohol are marked exceptions. For the change of potential energy on mixing a mass $p_1$ of liquid 1 with $p_2 = 1 - p_1$ of liquid 2 we have

$$4\rho (p_1 e_1 s_1 / m_1 + p_2 e_2 s_2 / m_2)^2 - 4\rho p_1 e_1 s_1 / m_1^2 - 4\rho p_2 e_2 s_2 / m_2^2.$$

In "Further Studies on Molecular Force" (Phil. Mag. [5] xxxix. 1895, p. 1) it was shown that for most elements in
their compounds, except the metals, $es$ for the atom is nearly proportional to the volume of the atom, so for the molecules of most ordinary liquids $es$ is proportional to the volume $m/p$. So the change of energy on mixing is proportional to

$$4\rho(p_1/p_1 + p_2/p_2)^2 - 4p_1/p_1 - 4p_2/p_2.$$ 

If this is 0, then

$$1/\sigma = p_1/p_1 + p_2/p_2,$$

which states that mixture occurs without change of volume. Thus the absence of change of volume and of thermal effect connected with potential energy are related. As the limiting volume of the molecule is proportional to its electric moment, and as the molecules of ordinary liquids at ordinary temperatures occupy nearly their limiting volumes, we may conclude that constancy of volume on mixing and constancy of electric moment are connected.

10. The relation of Mills.

This has been discussed recently in "The Electric Origin of Molecular Attraction" (Phil. Mag. [6] xvii. 1909, p. 657), but requires to be considered further in the present connexion. In the simplest case the change of attractional potential energy for an element gas when unit mass is changed from liquid to saturated vapour is $4e^2\delta(\rho_1 - \rho_2)/m^2$. For a typical compound the change is

$$4e^2\delta^2[\rho_1/2 - \rho_2/(1 + kp_2)]/m^2,$$

or nearly

$$4e^2\delta^2[\rho_1/2 - \rho_2/(1 + \rho_2/\rho_c)]/m^2.$$

The simplest hypothesis that we could make concerning the internal latent heat of vaporization would be to equate it to these changes of potential energy. For an element gas at different temperatures we should have the internal latent heats proportional to the difference of the densities of liquid and saturated vapour, and for a typical compound proportional to $\rho_1/2 - \rho_2/(1 + kp_2)$, or nearly to $\rho_1/2 - \rho_2/(1 + \rho_2/\rho_c)$. But the relation of Mills makes latent heat proportional to $\rho_1^{\frac{3}{2}} - \rho_2^{\frac{3}{2}}$. The interpretation of these results leads to an important principle concerning the motion of the electrons which form a molecule. In an investigation of the nature of dielectric capacity (Phil. Mag. [6] xix. 1910, p. 1) the molecule was treated as made of pairs of opposite electrons, each pair having an electric moment $es$. The sum of the components of $es$ parallel to the axis of electrization of the whole atom or molecule forms $es$. For the maintenance of this state of affairs we must imagine each pair of electrons in motion.
round the axis of electrization. If we imagine the axes of magnetization and of rotation in the Earth to coincide, it will furnish a large mechanical model of the pair of electrons, magnetization replacing electrization. The pair of electrons is a gyrostat electrized parallel to the axis of rotation. The electrons of a pair do not move round one another in a plane, but each may be treated on the average as moving in a plane at right angles to the axis of electrization. The figure illustrates the conception. PN is the axis of electrization, the positive electron moving in a circle round P as centre in the direction shown by an arrow, and the negative electron round N. The components of the attraction between \( \# \) and \( \hat{\text{p}} \) along \( \hat{\text{P}}\hat{\text{N}} \) and \( \hat{\text{N}}\hat{\text{P}} \) keep \( \# \) and \( \hat{\text{p}} \) in their circular orbits, while the components of the attraction along \( \hat{\text{NP}} \) equilibrate the forces acting on \( \# \) and \( \hat{\text{p}} \) on account of the electric field of the whole molecule parallel to \( \hat{\text{NP}} \). The length of \( \hat{\text{NP}} \) is \( \sigma \). Other rotational motions of these electric gyrostats may have to be considered in other connexions, but at present the motion postulated suffices. The independence of electric moment in the molecules of the element gases both of temperature and density indicates that \( \hat{\text{P}}\hat{\text{N}}\hat{\text{P}} \) and \( \hat{\text{N}}\hat{\text{P}}\hat{\text{N}} \) are small compared with \( \hat{\text{NP}} \), and that the rotatory energy of a pair of electrons is a constant like its electric moment. Probably the same statements apply to compounds, the change associated with the replacing of \( v \) in the attractional virial by \( v + k \) being probably apparent rather than real. Imagine an element gas so compressed that there is no gap between molecule and molecule, the whole mass being a uniform collection of pairs of electrons at distance \( r_1 \) apart, each pair having an electric moment \( \varepsilon \sigma_1 \) proportional to \( r_1 \). Imagine
the whole expanded till it fills the volume which it would have as saturated vapour. Let the distance between neighbour pairs be \( r_1 \), and suppose the electric moment \( e\sigma_2 \) now proportional to \( r_2 \), so that the medium in its second state is geometrically similar to what it was in the first, then on account of \( e\sigma \), and therefore \( e\sigma \) changing in the proportion of \( r_1 \) to \( r_2 \), and therefore of \( R_1 \) to \( R_2 \) the corresponding molecular distances, the change of attractional potential energy is not proportional to \( \rho_1 - \rho_2 \) but to \( \rho_1^{1/3} - \rho_2^{1/3} \). Now in the second state suppose that the electrons fall together in groups so as to form the actual molecules of the saturated vapour. The potential energy lost in this collapse will be converted into translatory kinetic energy of the electron pairs, for we have seen that their rotational energy seems to be constant. The relation of Mills shows that none of this kinetic energy appears as heat, for our imaginary operations have simply converted the liquid into vapour at the same temperature. The loss of potential energy during the imagined collapse has become kinetic energy required by the pairs of electrons to maintain dynamical equilibrium in the non-uniform state when they are collected in groups to form molecules. This kinetic energy may be regarded as internal molecular potential energy. When there is a change of molecular state the total change of potential energy is equal to the difference of the changes occurring when all the electrons forming the molecules fall from one and the same imaginary uniform distribution to each of the non-uniform distributions forming a molecular state. The total energy required to change one heterogeneous distribution of pairs of electrons into another is equal to the differences between the changes required to transform the heterogeneous states into the same homogeneous one, it is equal to the work required to change the distance apart of the molecules from the one heterogeneous state to the other against the attraction of neighbours according to the inverse fourth power law, together with the supply of internal energy required to maintain dynamical equilibrium under the changed conditions of heterogeneity. The sum of these two quantities of energy forming the total internal latent heat is subject to the law discovered by Mills. This law could be explained by itself by supposing that each molecule attracts its six immediate neighbours with a force varying inversely as the square of the distance between them, and that no internal change takes place in molecules when their distance apart is changed. But the large mass of evidence gathered in my papers on molecular attraction is quite against this simple hypothesis, while it all supports the

The law of force expressed by $4e^4R_x$. The true significance of the relation of Mills seems to me to be the indication of broad simple dynamical law in the kinetics of electrons forming atoms. These ideas lead at once to the following speculation.

11. The nature of chemical potential energy.

If the view proposed in the last section is correct, namely, that a part of the latent heat of vaporization of a liquid is kinetic energy supplied to the electrons of atoms to establish dynamical equilibrium under changed conditions of heterogeneity, it follows that the heat of chemical reactions is energy given out because of changed heterogeneity of the electrons in the reacting atoms. Is it possible that the pairs of electrons of two chemically combined atoms mingle like the molecules of two mixed liquids? Even if such mixture does not take place, the close approach of two different swarms of pairs of electrons may produce instability in the dynamical equilibrium of each and a fall into a new position of equilibrium with evolution of heat in the process. The internal energy of the radium atom is of the type here supposed to reside in all atoms as kinetic energy of the constitutive pairs of electrons.

Melbourne, April 1910.

XXI. On the Forces at the Surface of a Needle-Point discharging in Air. By A. P. Chattock, Professor of Physics in the University of Bristol.*

The strength of the field at a spherically ended electrified needle-point may be measured in terms of the pull of the lines of force upon its surface †, if the pull is due to the lines of force alone; a condition which is only strictly fulfilled when the point is not discharging.

In 1897, while attempting to extend this method to a discharging point, I tried the effect of supplying the latter with ions of opposite sign to itself obtained from a second point in its neighbourhood. Some rather interesting effects were observed in air at atmospheric pressure; but as at the time no explanation of them was forthcoming their discussion was postponed, and they remained unpublished.

Recently while looking over the record of the experiments

* Communicated by the Author.