TEXT FLY WITHIN
THE BOOK ONLY

STUDIES IN
MOLECULAR FORCE.

STUDIES IN

MOLECULAR FORCE.

BY

HERBERT CHATLEY, D.Sc. (Engineering), Lond.,

ASSOCIATE OF THE INSTITUTE OF PHYSICS, FELLOW OF THE PHYSICAL SOCIETY OF LONDON, MEMBER OF THE INSTITUTION OF CIVIL ENGINEERS.

LONDON:

CHARLES GRIFFIN AND COMPANY, LIMITED;

42 DRURY LANE, W.C. 2.

1928.

"Have not the small Particles of Bodies certain Powers, Virtues, or Forces, by which they act at a distance, not only upon the Rays of Light, for reflecting, refracting and inflecting them, but also upon one another for producing a great part of the Phænomena of Nature?

"Perhaps electrical attraction may reach to such small distances, even without being excited by friction.

"The Parts of all homogeneal hard Bodies which fully touch one another, stick together very strongly. . . . I infer from their cohesion, that their Particles attract one another by some Force, which in immediate contact is very strong, at small distances performs the chymical Operations above mentioned, and reaches not far from the Particles with any sensible effect. . . . All Bodies seem to be composed of hard particles. . . . And how such very hard Particles which are only laid together and touch only in a few Points, can stick together and that so firmly as they do, without the assistance of something which causes them to be attracted or pressed towards one another, is very difficult to conceive."—*Optics*, Sir Isaac Newton, Third Book, Query 31, pp. 350 and 363, in the Second Edition, 1718.

"Cohesion, then, in my opinion, is . . . to be ascribed to the limit-points in the curve of forces, where there is a passage from a repulsive force at a small distance to an attractive force at a greater distance; that is to say, this is the cause of cohesion between two points, for here a repulsion prevents decrease, and an attraction increase, of distance; and so the points preserve the distance at which they are."—*Philosophiæ Naturalis Theoria*, R. J. Boscovich, 1763 (Child's Translation, 1922).

PREFACE.

A peculiar mystery lies over the whole subject of cohesion. Gravitation, which links the celestial bodies, and electrostatic force, which links the atoms in chemical bonds, are relatively straightforward problems, but the linkage of neutral atoms and molecules in bulk still awaits a complete solution.

The practical importance of such a solution cannot be over-estimated. Stronger materials, better cements, having higher resilience and decreased deterioration, are all conceivable useful results arising from a real knowledge of the physical basis of material strength.

These notes represent a digest of some fifteen years' work on the subject and will, it is hoped, prove useful in the further exploration of a much neglected field of study.

The puzzling problem as to the penetration of molecular force beyond molecules adjacent to the one considered is very vital to the whole question. Prof. Edser has apparently demonstrated that such penetration does occur, and I am much indebted to him for certain ideas on the matter.

HERBERT CHATLEY.

SHANGHAI, *January*, 1928.

CONTENTS.

CHAPTER I.

The Magnitude of Molecular Force.

CHAPTER II.

The Effective Range of Molecular Force.

CHAPTER III.

Molecular Potential and the Space Variation of the Force.

CHAPTER IV.

Molecular and Atomic Spacing in Solids and Liquids.

CHAPTER V.

Hypotheses as to Molecular Force.

CHAPTER VI.

Intermolecular Repulsion.

CHAPTER VII.

Viscosity and Internal Friction.

STUDIES IN MOLECULAR FORCE.

CHAPTER I.

THE MAGNITUDE OF MOLECULAR FORCE.

In order to obtain any adequate notion of molecular forces, it is obviously necessary to have some idea of their absolute magnitude, even though it involves all the logical objections to the idea of "*force*" as a persistent reality. Fortunately this magnitude is fairly well determinable, but, as these forces vary in some way with the distance between the molecules upon which they act and also change in magnitude with the angular position of the molecules with respect to one another, some general proviso must be made as to the relative positions of the molecules with which any prescribed forces occur. A further difficulty lies in the fact that it is usually impossible to deal experimentally with single pairs of molecules. As to this, however, it will be seen later that the contribution of adjacent molecules to the force between any particular pair is not necessarily very large, and for the present, therefore, may be neglected. A further confusing factor is that, in the solid state of matter, the word "molecule" may simply mean an arbitrary group of atoms and not a real structural unit.

With these reservations, a general statement as follows may be made :—

The force of attraction or repulsion between two average simple molecules in a solid or dense liquid state usually lies between one hundredth of a microdyne and one hundred microdynes. (A microdyne is one millionth of a dyne or one thousand-millionth of a gram weight.)

For purposes of comparison, it may be mentioned that the electrical repulsion or attraction between two centrally-charged molecules in similar positions is about one hundred microdynes, and their gravitational bond is about one sextillionth (10^{-36}) of a dyne. In these cases, however, adjacent molecules must also be considered, as the additive effects are not at all negligible.

From an abstract point of view, molecular energy is a much more absolute quantity than molecular force, but fails to express the geometrical conditions.

The actual force differs according to the distance between the centres of the molecules (which has here been taken as $10^{-7 \cdot 5}$ cms. $= 3 \cdot 2 \times 10^{-8}$ centimetres) and the chemical character of the molecules. In this general statement, the molecules are assumed to be simple atoms or diatomic or triatomic molecules.

Evidence in favour of these values may be obtained from very many sources, the principal of which are discussed in the following paragraphs :—

Surface Tension in Fluids.—It is well known that capillary attraction indicates the presence of something equivalent to a surface film on a fluid, in a state of tension. In the case of a homogeneous liquid this film is a mathematical abstraction,* the actual forces being difference effects, but as surface-tension in bubbles and drops is the most noticeable case of molecular force in fluids, there is no need here to consider anything more than the apparent facts. (See, however, Chap. VIII.)

Various reasons (optical and thermodynamic) indicate that the effective thickness of the film is not much more than the diameter of one molecular field (*i.e.*, the distance between the centres of two adjacent molecules) which is between 3 and 4 times 10^{-8} cms. for water, but the range of the forces is greater than this distance.

At just above the melting-point, the surface-tension in water is 73·2 dynes per centimetre, so that the tension per molecule-pair across an imaginary line in the film is $73 \cdot 2 \times$ (say) $3 \cdot 5 \times 10^{-8} = 2 \cdot 6 \times 10^{-6}$ dynes.

In mercury, at 0° C., the surface-tension is 577 dynes per cm. The size of the molecular-fields is about the same as in

* Langmuir has shown that the surface molecules of a fluid are polarised and oriented with respect to the surface, so that a weak structural film may actually exist, but, in view of the continuous exchange of molecules with the vapour above the structure, it must be a very unstable one.

water, so that the molecular-linkage is about $1{\cdot}4 \times 10^{-5}$ dynes. Edser indicates that this surface-tension is one-half the *gross* attraction.

As the temperatures are raised the surface-tension diminishes, and becomes zero at the critical temperature. At the boiling-point the volume (under atmospheric pressure) has expanded about 4 per cent., so that the molecular-fields have expanded over 1 per cent. It cannot, however, be argued that the molecular-force has vanished with this small expansion, since the heat-energy in the liquid produces repulsive forces, which, at the boiling-point, neutralise both the molecular attraction and the external air-pressure. An ambiguity is introduced by the fact that in water there is both association and dissociation of H_2O molecules, but this may be neglected for the purpose of this approximation.

Strength of Materials (Cohesion and Adhesion).—The strength of liquids is small in tension, but, in the absence of gas (*i.e.*, very active molecules), may rise to several atmospheres (Newton, Osborne Reynolds). The *adhesion* of the liquid to the walls of the containing vessel is a confusing factor.

The strength of solids is not known to have exceeded some 25 tonnes/cm.^{2} or $2\frac{1}{2} \times 10^{10}$ dynes/cm.^{2} The diameter of the molecular-fields of the ferro-carbon compounds which occur in tool-steel is probably more than $3{\cdot}2 \times 10^{-8}$ cm., so that less than 10^{15} molecules occur per square centimetre, and the maximum bond per molecule-pair across the plane of tension is more than

$$2{\cdot}5 \times 10^{10}/10^{15} = 2{\cdot}5 \times 10^{-5} \text{ dynes.}$$

A cohesion of one atmosphere, such as often occurs between polished surfaces (two atmospheres of gross adhesion), corresponds to a molecular bond of 10^{-9} dynes.

Since most solids break under tension with only a very small increase of volume, it is obvious that a molecular stress-resisting tension decreases appreciably after a certain minute separation has been produced. The weakening effect of "hair-cracks" is similar evidence. Superficial scratches and angularities are points of weakness from which fractures originate.

Microscopic study of fractures in solids shows that the constituent crystals fail by shearing on planes of crystallisation, so that at maximum stress the whole section is not effective, and the molecular-bonds are, therefore, rather higher than the figure given above. Also, as will be seen later, it is necessary to consider the idea that the bonds are really often atomic and not molecular. In most solids the structure is a most complex meshwork of minute and imperfect crystals, so that the strength varies enormously from point to point, even although it may be fairly constant for an area of, say, one square centimetre.

Fusion of Solids.—At the melting temperature heat must be applied to cause fusion of solids over and above that which would, in the solid state, produce the requisite difference of temperature. This is termed the latent heat of fusion, and may be regarded as the work done in separating the particles.

When cooling from the liquid to the solid state, this amount of heat is liberated as " heat of crystallisation." A difficulty here occurs in that the solid, or rather the crystalline state is apparently an atomic structure, while the liquid is molecular, so that volumetric changes are irregular. Thus ice contracts when melting, ice being a regular and rather open structure of hydrogen and oxygen atoms, while water is a collection of dihydrogen-monoxide (H_2O), tetra-hydrogen dioxide ($2H_2O$), and more complex molecules. Grey cast iron and bismuth behave similarly. It is possible, however, to show that the magnitudes are concordant. Thus copper has a latent heat of fusion of 43 calories per gram or $1{\cdot}8 \times 10^9$ ergs. There are about 10^{22} atoms per gram of copper, so that the energy of fusion per atom is $1{\cdot}8 \times 10^{-13}$ ergs. The linear expansion from the solid to the liquid state is less than 10^{-8} cms. per *atom*, so that the bond is more than

$$1{\cdot}8 \times 10^{-13}/10^{-8} = 1{\cdot}8 \times 10^{-5} \text{ dynes.}$$

The melting point is some indication of the cohesion of a substance.

Expansion of Solids with Heat.—If the heat required to cause a certain degree of expansion is reduced to molecular terms, some indication of the force overcome can be obtained, although, of course, the energy is almost wholly kinetic. Thus iron has a specific heat of 0·11 (small calories per gram per C.°). In one gram there are $6 \times 10^{23} \div 56$ atoms, or, say, 10^{22}. The specific heat per atom (structure assumed to be monatomic, as stated by Bragg) = approx. 10^{-23} calories or approx. 5×10^{-16} ergs. Each pair of atoms is separated per C. ° by 10^{-5} of the atomic interval, or, say, 3×10^{-13} cms. Disregarding the complications due to lateral effects and superposition of fields, the force per atom is of the order of

$$\frac{5 \times 10^{-16}}{3 \times 10^{-13}} = 1{\cdot}7 \times 10^{-3} \text{ dynes},$$

if the whole heat energy is absorbed in causing expansion (which is *not* the case).

At low temperatures this computation is disturbed by "quantum" conditions, but at normal temperatures the average result is correct.

Change in Compressibility.—Solids and liquids under hydrostatic pressure show a decrease of compressibility with increase of pressure which conforms to the general principles outlined here, and is discussed later in connection with the change of force with distance.

Vaporisation of Liquids.—Just as in the melting of solids, so in the boiling of liquids, "latent" heat must be supplied, but in this case a new difficulty arises from the fact that the molecules suddenly separate widely under the kinetic repulsions. There is, however, a certain minimum liquid density for each substance below which it is essentially vaporous (the so-called "critical" density). Thus water at 100° C. requires 542 calories or $2{\cdot}3 \times 10^{10}$ ergs per gram to convert it into steam. Water vapour cannot have a density greater than 0·4 grm./c.c. (special pressure and temperature is actually required to produce this, but that is immaterial to the present rough computation), so that we may fairly assume that when the volume of water has increased $2\frac{1}{2}$ times the molecular attractions have been virtually overcome. Since the molecular-field for water at boiling point is about 4×10^{-8} cms. diameter, the densest possible vapour has a molecular-field the cube root of $2\frac{1}{2}$ times this size, or, say, $5{\cdot}4 \times 10^{-8}$ cms., and the linear expansion as a liquid becoming vapour is $1{\cdot}4 \times 10^{-8}$ cms. per molecular pair. One gram of water contains about $2{\cdot}3 \times 10^{22}$ molecules, so that the energy of vaporisation per molecule is $2{\cdot}3 \times 10^{10}/2{\cdot}3 \times 10^{22} = 1{\cdot}0 \times 10^{-12}$ ergs. Dividing this by the expansion, we get $1{\cdot}0 \times 10^{-12}/1{\cdot}4 \times 10^{-8} = 7{\cdot}1 \times 10^{-5}$ dynes as the mean force.

It has been argued that a small (1 or 2) integral number of " quanta " of energy are absorbed per molecule at vaporisation (1 quantum $= 6{\cdot}7 \times 10^{-27} \times$ fundamental frequency of vibration per sec.) ergs. The frequency for water is about 10^{13} per second.

Expansion of Gases.—Hirn and Van der Waals devised a partially empirical formula to allow for the deviation of actual gases from the ideal gas formula $p\,v = \mathrm{R\,T}$ (where p is the gas pressure in dynes per sq. cm., v is the volume, c.c. per gram-molecule, $\mathrm{R} = 8{\cdot}3126$ (or $8{\cdot}33$) $\times 10^7$, T = absolute temperature in Centigrade degrees), which is as follows :—

$$(p + \tilde{\omega})\,(v - b) = \mathrm{R\,T},$$

where $\tilde{\omega}$ is the " molecular " pressure in dynes per sq. cm., and b is the effective volume in cubic centimetres per gram molecule of the molecules. According to this formula

$$\tilde{\omega} = \frac{\mathrm{R\,T}}{v - b} - p.$$

If we substitute the " critical values " and the minimum volume for water, we have

$$\tilde{\omega} = \frac{8{\cdot}3 \times 10^7 \times 647}{(45 - 18)} - (10^6 \times 217{\cdot}5) = 1{\cdot}7 \times 10^9 \text{ dynes/sq. cm.}$$

Since the diameter of the molecular-field at the critical state is $5{\cdot}4 \times 10^{-8}$ cm., the force per molecule is

$$(1{\cdot}7 \times 10^9)\,(5{\cdot}4 \times 10^{-8})^2 = 5{\cdot}0 \times 10^{-6} \text{ dynes.}$$

Van der Waals, from a consideration of the ability of ideal spherical molecules to pass between one another, has deduced that the quantity b has a value $4\,.\,(\frac{4}{3}\,\pi\,r^3)\,.\,\mathrm{N}$, where r is the " real " radius of a molecule and N is the number of molecules per gram-molecule.*

Since b is supposed to be the effective molecular volume at absolute zero, when almost perfect rigidity is probable, the writer has not adopted Van der Waals' formula for b. It must, however, be admitted that the numerical results obtained with that formula agree rather better with those obtained from viscosity and thermal conductivity data.

* If $\dfrac{d^3}{\sqrt{2}} = 4\left(\dfrac{\pi\,\delta^3}{6}\right)$, $d = 1{\cdot}44\,\delta$.

Some of the same fundamental assumptions underlie the latter determinations. Probably the spheres equivalent to the irregular-shaped molecules monopolise nearly all the geometrically available space in the solid state.

Kinetic Theory of Gases.—It has been established that the mean kinetic energy of a free molecule is

$$E = 3\,R\,T/2\,N,$$

where N is the number of molecules per gram-molecule ($6{\cdot}06 \times 10^{23}$), and also that the mean free path of a molecule in a gas, at atmospheric pressure, is $7{\cdot}6 \times 10^{-6}$ cms. E is approximately equal to $2 \times 10^{-16} \times T$ ergs., and for a gas at 0° (273° on the absolute scale) it has a value

$$5{\cdot}62 \times 10^{-14} \text{ ergs.}$$

If we suppose that all this energy is converted into potential by a molecule in traversing the mean free-path in a gas at normal temperature and pressure, the mean force overcome is $5{\cdot}62 \times 10^{-14}/7{\cdot}6 \times 10^{-6}$, or approx. $7{\cdot}0 \times 10^{-9}$ dynes.

Since the property of cohesion is only very slight in such gases, it follows that in the liquid or solid state the force per molecule must considerably exceed this value.

Differential Attraction of Ions.—It is shown in electrical theory that two unlike ions with a unit-valency, one centimetre apart, have a mutual attration of

$$2{\cdot}3 \times 10^{-19} \text{ dynes.}$$

If they are brought to within a distance (centre to centre) of $3{\cdot}2 \times 10^{-8}$ cms. (the usual diameter of a molecular-field), the force is $2{\cdot}3 \times 10^{-19}/10^{-15}$ or $2{\cdot}3 \times 10^{-4}$ dynes.

If an arrangement of ions is such that their electrical effect at an appreciable distance is zero, but they have *differential effects* at small distances, a net attraction at such small distances of, say, 10 per cent., the forces between individual pairs can easily be conceived to occur, so giving possible net attractions per molecule-pair of, say, 10^{-5} dynes. Such differential effects vary approximately as the inverse fourth power of the distance, except at very small distances.

Magneton Pairs.—A magneton is a hypothetical magnetic-unit consisting of an electron revolving in a circular orbit of, say, 10^{-8} cm. (or less) radius with a frequency of some 10^{14} times per second (10^{14} is the frequency of infra-red light waves which can be produced from many solids below the melting-point). If two such magnetic circuits are placed parallel at $3{\cdot}0 \times 10^{-8}$ cm. apart, the mutual attraction is about $4{\cdot}0 \times 10^{-8}$ dynes.

It is difficult to say how much or little importance should be attached to this example, but it is interesting to compare it with the others. (See later as to Parsons' hypothesis.)

Chemical Dissociation.—The energy required to separate the atoms in a molecule is not very well known, since the free or "nascent" atoms are difficult to produce in large numbers, but it is probable that at a temperature of 1,620° C. about 50 per cent. of the molecules of iodine-gas are split into atoms. Taking the specific heat at about 0·03, this means that some 100 calories or $4{\cdot}2 \times 10^9$ ergs per gram are required to dissociate all the atoms. There are about $2{\cdot}3 \times 10^{21}$ molecules per gram of iodine, so that the energy of dissociation per molecule is

$$4{\cdot}2 \times 10^9/2{\cdot}3 \times 10^{21} = 1{\cdot}8 \times 10^{-12} \text{ ergs.}$$

If the distance between the atom-centres is $3{\cdot}5 \times 10^{-8}$ cms., this means a force between the atoms of 5×10^{-5} dynes, the atoms up to the moment of dissociation being practically in contact.

Now, in the fluid-state, when the molecules are almost in contact, "fluid-crystal" effects occur which give way to the atomic forces when true (solid) crystals are formed. Hence the molecular-bond is probably somewhat, but not greatly, inferior to 10^{-5} dynes.

This case is, of course, similar to that of the ions previously discussed, but, being based on heat instead of electric phenomena, affords an interesting quantitative confirmation.

There are various other phenomena besides the above-mentioned, which include the presence of molecular forces of considerable magnitude. Among these may be remarked :—

(*a*) *The occlusion of gases by liquids and solids*, without any chemical change. The "compression" which occurs in the occluded gases, allowing for cubical elasticity, indicates molecular pressures of some thousands of atmospheres. (1,000 atmospheres equals 10^9 dynes/sq. cm.)

Similar compression effects occur in solutions, but it is there difficult to distinguish between the compression of the solute and that of the solvent.

(*b*) *The stability of disperse systems* of one phase or state of matter in another (the so-called "colloidal" solutions of minute solid particles suspended in liquids, dust-particles in air, jellies, froths, etc., are examples) indicates :—

(1) The adsorption or adhesion of a liquid to solid particles or of a gas to a liquid or solid.
(2) Viscosity or a general cohesion between the moving particles of a fluid or a solid.
(3) Electrostatic charges on the dispersed particles.

These may result in a neutralisation of the gravitational forces by opposing molecular forces, the only condition being that the heavier substance shall be so finely divided that the weight of each particle compares with the molecular force on it.

Computation shows that a very large degree of adsorption is required to explain the very slow settlement of minute particles, but the general viscosity plays a part which is proportionately considerable unless the gravitational forces are sufficient to rupture the fluid.

(*c*) *Aggregation of Particles.*—The velocity which water must possess to wash away very small particles of, say, mud from a mass is greater than would readily remove a fairly coarse sand, thus indicating that something more than mere weight and roughness-friction is overcome. (Chatley, *Min. Proc. Inst. C.E.*, 1921, paper 4380; $v = \frac{0{\cdot}02}{d}$ in c.g.s. units.) The great tensile strength developed by powdered material or polished surfaces under mere pressure indicates that close proximity of particles means appreciable attraction. The proximity must, however, be very great, and in many cases actual interpenetration is necessary. The smoothness of "soft" powders (*e.g.*, talc) appears to be due to sliding of the flakes.

It is an interesting but unsolved question whether any substance whatever has its strength reduced by uniform (say hydrostatic) pressure. Of course, an open material (with internal voids), like wood, will lose strength when the cellular structure is destroyed by pressure, but the density can be further increased so as to form a new and stronger solid-like celluloid.

In this connection it is interesting to notice that a pressure of 10^{11} dynes per sq. cm. (100 tonnes per sq. cm.) is comparable with the force of crystallisation, and will, therefore, make any unconfined material flow freely. This corresponds to the "isostatic" level in the earth (say 100 kilometres deep).

(*d*) *Planetary and Solar States of Matter.*—The mean densities which have been computed for the planets and the sun, together with the very high internal temperatures, indicate unusual material conditions. In all cases it would appear that the temperatures in the interior of the celestial bodies are such that the so-called "critical" condition is far exceeded, and the substances are, therefore, technically speaking, "gases." On the other hand, the densities are considerably greater than the "critical" values. Thus, at the centre of the earth, the pressure is probably some 10^{12} dynes/sq. cm., the temperature upwards of 10,000° C., and the density about 10 times that of water. The rigidity, as shown by the transmission of earthquakes and the absence of internal tidal effects, is comparable with that of steel.

Again, in the Sun, the central density must, at least, be five, the pressure some 10^{15} dynes/sq. cm., and the temperature some millions of degrees.

We see, then, in these cases gravity acting on an enormous scale and producing in gases densities and viscosities which correspond to those of solids, and we can logically argue that in actual solids the molecular forces are somewhat similar to these prodigious gravitational forces.

To conclude these introductory remarks as to the magnitude of molecular forces, it may be observed that, on the theory that atoms are constituted of whirling electrons, it can be shown that the centripetal force which holds an electron in place is of a comparable magnitude to those previously mentioned.

Wien's rule for the frequency of ethereal vibrations* of maximum energy content shows that at the temperature of the earth's surface, the frequency is over 10^{13} per second. The mass of an electron is about 10^{-27} grams, and the radius of an atom is about 10^{-8} cms., so that the centripetal force must be at least—

$$\text{Mass} \times 4\pi^2 \times \text{frequency}^2 \times \text{radius}.$$
$$10^{-27} \times 40 \times 10^{26} \times 10^{-8} = 4 \times 10^{-8} \text{ dynes}.$$

The deeper lying electrons have higher frequencies and smaller orbits, so that the forces are much greater. Also, according to Bohr's theory, the orbital frequencies exceed the radiation frequency.†

Similarly, if the molecules are *oscillating* with a frequency of 10^{13} per second, as is indicated by the energy content and also by spectroscopic observations on light absorption by fluids, through distances of about 10^{-9} cm., as we shall see later is probably the case, the force acting on them may be roughly computed from the well-known equation for harmonic oscillations :—

$$\text{Displacing force} = 4\pi^2 \times \text{displacement} \times \text{mass} \times \text{frequency}^2 = 40 \times 10^{-9} \times 10^{-23} \times 10^{26} = 4 \times 10^{-5} \text{ dynes}.$$

Again, in liquids, it may be shown that the mean free-path of a molecule is of the order of 10^{-9} cms., and the velocity of the molecule about 10^5 cm. per second, so that the number

* Wien's law is that the frequency of maximum radiant energy varies inversely as the absolute temperature of the radiating body. For an ideal perfect radiator (" black body ") $\lambda T = 0{\cdot}2879$; $f = c/\lambda = 3 \times 10^{10}/\lambda = 10^{11} . T$, where λ = wave length in cms. ; T = abs. temperature ; f = frequency per sec. ; c = velocity of light = 3×10^{10} cms./sec. At 300° abs., $f = 3 \times 10^{13}$. The actual frequency may be roughly computed by Sutherland's rule, $f = v/\delta$, where v is the velocity of sound in the body and δ is the molecular distance (centre to centre). This implies that the infra-red " heat " vibrations are identical in kind with the sound vibrations, which diminish in amplitude and increase in frequency until the two are completely identical.

The collision frequency in gases is of the same order, indicating similar forces during the moments of close proximity of the molecules.

† Thus, according to Bohr, the normal frequency of the hydrogen electron is $6{\cdot}6 \times 10^{15}$ per second ; radius of orbit is $0{\cdot}55 \times 10^{-8}$ cms., so that the centrifugal force is of the order of 10^{-3} dynes. In remoter orbits, the centrifugal force falls off as the inverse square of the radius, becoming comparable with atomic bonds at radii 10 or more times that of the smallest orbit.

of collisions is 10^{14} per second, and the kinetic energy per molecule being 5×10^{-14} ergs, the mean force during collision is $5 \times 10^{-14}/10^{-9} = 5 \times 10^{-5}$ dynes.

None of these computations professes to be at all exact, but they certainly serve to confirm the general statements made at the beginning of the chapter.

CHAPTER II.

THE EFFECTIVE RANGE OF MOLECULAR FORCE.

ONE of the most remarkable features of molecular force is the apparently minute range. Quincke, in his study of surface-tension (*vide* Clerk-Maxwell on "Capillary Action," in the *Encyclop. Britt.*, IXth edition), estimated the distance within which surface-tension ceased to be effective at $4{\cdot}0 \times 10^{-6}$ cms., and subsequent research has tended to reduce this figure, possibly even to 10^{-8} cms. (Lewis, "System of Physical Chemistry").

A fairly definite indication of the smallness of the range is seen in the fact that only minute changes of volume occur when solid materials are broken by tension and in the weakening effect of minute cracks. It is true that there may be an appreciable extension before fracture (rubber, for example, will stretch over 100 per cent., but even this could only double the molecular interval), but this is accompanied by a lateral contraction, so that the molecular spacing is, in fact, only very slightly enlarged (rarely more than 1 per cent.).

Again, it will be found that, unless surfaces are very highly polished, they do not adhere (a false adhesion may occur due to atmospheric pressure or "suction"), and cementing materials where no chemical effects occur require to be very finely subdivided or suspended in a fluid medium. Highly polished and accurately planed steel or glass surfaces will give an adhesion of two to thirty atmospheres net, but this is greatly inferior to the cohesive strength of the materials themselves.*

*** The C. E. Johannson Co., of Eskilstuna, Sweden, makes gauges which have a tolerance of only one hundred-thousandth. The smallest are about 0·1 inch thick, and the National Physical Laboratory has certified the accuracy of individual gauges up to 4 inches thick as within 0·00001 inch. These hardened carbon steel gauges when wrung together will adhere if the surfaces are free from moisture or grease under**

The very existence of liquids at almost the same temperature as the corresponding solids, with only a slightly greater volume, shows how rapidly the cohesion diminishes with separation.

Similarly, in gases at temperatures only slightly higher than those of the corresponding liquids, there is almost complete freedom with a molecular separation of less than 10^{-6} cms.

Nevertheless, seeing that the existence of resistance to compression indicates a repulsive force parallel to the attractive force, so that the actual cohesion is only the algebraic sum of the two, neither surface-tension nor simple cohesion provides conclusive evidence of a minute range in the attracting forces, *per se*.

As will be seen later, the question of range is a vital factor in any hypothesis as to the rate of diminution of the force with distance.

The most conclusive evidence on the point of effective range is to be found in the kinetic theory of gases. It appears certain that the mean kinetic energy of a free molecule is

$$\frac{3\,R\,T}{2\,N} = 2{\cdot}058 \times 10^{-16} \times T \text{ ergs.}$$

In order that gas molecules shall not cohere to a liquid or solid, the energy of the free molecules must be equal to or more than the energy of bondage. It has, however, been shown already that the net force of cohesion per molecule is between 10^{-9} and 10^{-5} dynes, so that the effective range must be less than from 10^{-11} to 10^{-7} times T centimetres, so that if T is, say, 300° absolute, it is not probable that the effective range exceeds 10^{-5} centimetres.

a normal stress of even 30 kilograms per square centimetre. The slightest visible greasiness, or a separation of the order of tolerance, prevents adhesion.

Similarly, it will be found that adhesives become effective when the interstices between the particles are of this same order of magnitude.

Griffith has shown recently that minute depressions and grooves on the surface of test pieces or internal flaws may, in fact, greatly reduce the strength, and that perfect structures formed under ideal conditions may temporarily have tensile strengths ten or twenty times greater than the usual ultimate values. Brittleness is probably associated with the instability of specially strong forms, and is well known to occur in connection with great hardness.

To put it in another way, if we suppose two molecules linked together, they may jointly possess a kinetic energy $2{\cdot}06 \times 10^{-16} \times T$. (This follows from the principle of the equipartition of energy according to which all free systems tend to have the same kinetic energy.) If now heat is applied, they will eventually separate, and each will possess the energy $2{\cdot}06 \times 10^{-16} \times T_2$, where T_2 is a higher temperature. If now they are cooled back to the original temperature, in the separated state they jointly possess twice as much energy as at first, so that they have an increase of energy $2{\cdot}06 \times 10^{-16} \times T$, which is obviously that which was required to separate them, or, technically speaking, to give them the "cohesion-potential." Thus, if the vaporising temperature is 300° absolute, the cohesion potential is

$$6{\cdot}18 \times 10^{14} \text{ ergs},$$

and if the force of attraction at close proximity is 10^{-8} dynes, the effective range is

$$6{\cdot}18 \times 10^{-14}/10^{-8}, \text{ or } 6{\cdot}18 \times 10^{-6} \text{ centimetres.}$$

Still another way of considering the matter is by the behaviour of the so-called "fixed" gases. These are so nearly perfect that the volume occupied by one gram-molecule is almost exactly that for a perfect gas, or 22,412 c.c. at normal temperature and pressure. There are $6{\cdot}06 \times 10^{23}$ molecules in this volume, so that the volume occupied by one molecule is $22{,}412/6{\cdot}06 \times 10^{23}$, or $37{\cdot}0 \times 10^{-21}$ c.c.

The diameter of the molecular field, using dodecahedral spacing, is then $\sqrt[3]{\sqrt{2} \times 37{\cdot}0} \times 10^{-7} = 3{\cdot}74 \times 10^{-7}$ cms.*

By means of Van der Waals' equation and actual measurement of the volume at atmospheric pressure, the "molecular pressure" can be computed, and it will be found to be very small (say 10^{-10} dynes per molecule) as compared with that in the critical liquid state. In other words, at a distance of 4×10^{-7} cms. the molecular pressure (net attraction) is negligibly small.

A similar result will be found if we assume any reasonable hypothesis for the space-variation and compare the forces at different distances. Thus, even if the variation is inversely

* Rhombic dodecahedral spacing is the densest and most uniform possible arrangements of equal spheres. Also termed "face-centred cubic packing."

as the square of the distance, since molecular distances are of the order of 10^{-8} cms., the force at 10^{-7} cms. is only one hundredth that at close proximity. As a matter of fact, the inverse square law is not directly true (as will be seen later), although it may be so in a differential sense.

Another line of argument follows from assumptions to the law of force. If we write the molecular attraction and repulsion as equal at the state of no external "stress,"

$$t_2 = t_1,$$

and then consider how the tensile stress increases with increasing separation ("strain"), it will be found that for forms

$$t_2 = a\, d^{-n}\,;\ t_1 = b\, d^{-m},$$

the differential $d\,(t_2 - t_1)/d\,d$ is a maximum in fact for values of d between much less than two times the equilibrium-value under no stress. [n may be from 2 to perhaps 13 ; m is more than n], thus showing that stress is a maximum for separation of the molecules much less than 100 per cent.—*i.e.*, one molecular interval (less than 10^{-7} centimetres), and generally less than 10^{-8} cms.

Laplace and others since his time have held that there is a fairly **definite** radius of molecular action. It seems to the writer probable that the distance at which the molecular force is so exceeded by other forces that it becomes imperceptible must vary widely according to the conditions of the case.*

The hypothesis that the cohesion is due to the electrical reactions of alternately positive and negative charges of atoms (or of atoms and valence electrons) leads to the conclusion that the effective cohesion-range may not much exceed one atomic diameter, since the resultant fields practically neutralise one another at about this distance outside the boundary of the whole group.

Hence we may reasonably conclude that the **net attractive molecular force is ineffective at distances greater than about one millionth of a centimetre, and, wherever we find it appreciably acting, the actual particles which experience it must come, temporarily or permanently within this minute distance.**

* Edser (*Brit. Ass. Rep. Colloid. Chem.*, No. 4, p. 93, 1922) finds that molecular attraction of liquids varies inversely as the fifth power of the distance of a molecule from a plane surface, and is not less than the weight of the molecule at distances of the order of 10^{-5} cms.

CHAPTER III.

MOLECULAR POTENTIAL AND THE SPACE-VARIATION OF THE FORCE.

As will be seen when we come to consider the theories as to molecular force, there are several conceivable types of function relating the force to the distance.

The early investigators, influenced by the analogy of gravitation and static electricity, favoured an inverse-square rule, but there are many fundamental objections to this conception. If it were true, the force must be a new one, since otherwise it would be completely identical in its effects with one of those two forces, and, apart from this, it would have a much wider range than is experimentally known to exist.

The next alternative is that of a central force (*i.e.*, one focussed in the geometrical centre of each of the mutually attracting molecules) varying as some higher inverse power of the distance or (as the writer has elsewhere suggested) as a varying power of the distance. If in this case the force is a total effect of similar forces from the *parts* of the molecule, it cannot be a truly "central" one focussed to a point, and would *de facto* imply a quasi-polarity in the molecules, since only the inverse square rule permits a true centralisation under such conditions, and then only for spherical bodies.

A third and most probable hypothesis regards the force as a differential one, being a resultant of attractive and repulsive fields following each an inverse square rule, with respect to a certain point, which resultant would be attractive at small distances and zero at large distances. The molecular field is then complex, and the resultant force cannot be described as central.

This can, however, be conveniently expressed *approximately* as an equivalent central force following a rule other than the inverse square, and this will be done in this chapter, although this overlooks the very important fact of angular-variation (vectorisation) which occurs in all differential fields, and also the possibility of sub-centres of intense local effect.

It will be understood that in this analysis the gross attraction (*i.e.*, the net or effective attraction, plus the gross repulsion) must be considered. In cases where there is equilibrium the net attraction is zero, so that the ratio of the gross attraction to the net attraction (which is all that we can measure in some cases) may be indefinitely large, but there appears no reason to suppose that the gross attraction at close proximity is much more than four times the maximum *net* attraction at fracture in solids. This question will become clearer when the repulsion has been studied. In the meantime, it should be observed that if the differential theory of molecular attraction is adopted, care must be taken to distinguish between the repulsion (electrical, in all probability) which, acting against a similar attraction, leaves a resultant gross molecular attraction, and the repulsion (largely if not wholly kinetic) which often neutralises the latter. The net attraction per unit area is what engineers call " tensile stress."

On the assumption of a central force (which assumption is probably not very wrong for isolated pairs of atoms or molecules, except perhaps for very minute distances), the work done by the gross molecular attractive force in drawing together two molecules from infinity to contact is

$$E = -\int_{d_0}^{\infty} t_2 \, . \, d\,r,$$

where t_2 is the gross molecular force at a distance r and d_0 is the distance between the centres at absolute contact.

If we suppose that t_2 is of the form A/r^n, then

$$E = -A\int_{d_0}^{\infty} r^{-n} \, . \, d\,r = -A\left[\frac{r^{1-n}}{1-n}\right]_{d_0}^{\infty} = -\frac{A\,d_0^{\,1-n}}{1-n}.$$

Since the force at contact

$$t_0 = A/d_0^n$$

the energy

$$E = -t_0 \, . \, \frac{d_0}{1-n}.$$

If we suppose the mean kinetic energy of a molecule at 0° C. (known by the kinetic theory of gases to be $5{\cdot}6 \times 10^{-14}$ ergs) to be entirely due to the loss of molecular potential, we have the expression

$$- t_0 \cdot \frac{d_0}{1 - n} = 5{\cdot}6 \times 10^{-14}.$$

Our previous reasoning indicates that t_0 is something of the order of 10^{-5} dynes, and that d_0 is about $2{\cdot}8 \times 10^{-8}$ cms.

Using these values, we have

$$- (10^{-5}) \cdot \frac{2{\cdot}8 \times 10^{-8}}{1 - n} = 5{\cdot}6 \times 10^{-14},$$

or

$$- 5 = 1 - n, \text{ so that } n = 6.$$

The following table of values shows how different determinations of t_0 affect n (d, of course, may also differ, but not to anything like the same extent) :—

t_0 (dynes).	n
10^{-4}	51
10^{-5}	6
6×10^{-6}	4
2×10^{-6}	2
10^{-6}	1·5
10^{-7}	1·05
zero	1·00

Thus, on the hypothesis of central forces diminishing as the n-th power of the distances between the centres of the molecules and the probable values of the molecular-bond at contact (absolute zero condition), the kinetic energy of a molecule, regarded as due to molecular potential, agrees with some power of n between unity and fifty. It should be observed that the inverse-square rule is possible, but there are other reasons which will be discussed later against it.*

* Edser (*Fourth Report Coll. Chem.*, p. 42) gives the following references :—

Inverse square, . . Mills, *Journ. Phys. Chem.*, 1902-9.
Inverse fourth, . . Sutherland, *Phil. Mag.*, 1887-1893.
Leduc, *Comptes Rendus*, 1909-11.
Amagat, *Comptes Rendus*, 1909.
Inverse fifth, . . Kleeman, *Phil. Mag.*, 19, 783 (1910).
Higher powers, . . Tyrer, *Phil. Mag.*, 23, 101 (1912).

He himself deduces 8 as the minimum value for n.

Van der Waals' equation for gases, previously referred to, has the form

$$\left(p + \frac{a}{v^2}\right)(v - b) = \mathrm{R\,T},$$

and is nearly, but not quite, true for gases which liquefy without association; * a/v^2 is the "molecular pressure," formerly denoted by the symbol $\tilde{\omega}$.

Since v^2 with unchanged system of packing varies as d^6, where d is the intermolecular distance (c. to c.), the molecular pressure of the whole volume acting on one molecule is approximately

$$t = \frac{a \,.\, d^2}{v^2} = \frac{a}{\mathrm{N}^2 d^4}\ \left[\text{or } \frac{2a}{\mathrm{N}^2 d^4} \text{ with rhombic-dodecahedral packing}\right].$$

This, then, indicates that for any one kind of molecule n is equal to 4, which would correspond according to the previous reasoning to a value of t when $d = 2{\cdot}8 \times 10^{-8}$ cms., equal to 6×10^{-5} dynes, and a would be of the order of 10^{12} (when v is the gram-molecular volume).

The following values of a are computed from the critical values of the temperature and pressure, and the assumption that the effective molecular volume b is one-third that of the critical volume per gram-molecule :—

* It has been suggested (*Engineering*, July 17, 1925, "Kinetic Theory of Gases") that the term a/v^2 is fictitious, that association always occurs, and that an addition should be made to v to allow for the contraction of volume to compensate for the association of the molecules. Carroll (*Phil. Mag.*, Aug. 1926) discusses association as indicated by the experimental deviations of pressure and volume from the Van der Waals' formula.

The first assumption leads to very high values for the association in the critical state. If changes in b are disregarded and the classical form of Van der Waals' formula is used, the association at the critical state halves the number of molecules (*i.e.*, every two are conjoined). If the quantity b is also changed the number of molecules is reduced to one-third (*i.e.*, every three are conjoined). These ratios seem very improbable, but this possibility should be not disregarded. Corrected forms of the Van der Waals' formula give still higher association values.

Substance.	a (dynes per cm.^{2} for volumes per gram-molecule in cc.)
Hydrogen, H_2, . .	$2{\cdot}1 \times 10^{11}$ ($1{\cdot}26$ to $3{\cdot}19 \times 10^{11}$)
Carbon dioxide, CO_2, .	$3{\cdot}6 \times 10^{12}$ ($3{\cdot}56$ to $4{\cdot}37 \times 10^{12}$)
Nitrogen, N_2, . .	$1{\cdot}6 \times 10^{12}$
Methane, CH_4, . .	$2{\cdot}9 \times 10^{12}$
Water, H_2O, . .	$5{\cdot}5 \times 10^{12}$
Sulphur dioxide, SO_2, .	$6{\cdot}8 \times 10^{12}$ ($6{\cdot}74$ to $7{\cdot}84 \times 10^{12}$)
Tin chloride, $SnCl_4$, .	$2{\cdot}7 \times 10^{13}$ ($2{\cdot}72$ to $3{\cdot}07 \times 10^{13}$)

Dr. H. P. Mathews' values for a for gram-molecules in dynes $\times 10^{-12}$ are as follow in the table. His formula is (*vide infra*) :—

$$a = N^2C\,(M \times \text{Val.})^{\frac{2}{3}}$$

$N = 6{\cdot}06 \times 10^{23}$, $C = 3{\cdot}201 \times 10^{-37}$

M = mol. wt., Val. = total number of valencies of all the atoms.

	Various Computations.	Mathews' Formula.	Van Laar's Formula.	M.
Hydrogen, . .	0·254–0·319	0·298	0·126	2
Nitrogen, . .	1·58 –1·79	1·72	1·33	28
Oxygen, . .	1·56 –1·81	1·88	1·33	32
Carbon monoxide,	1·70 –1·81	1·72	1·41	28
Methane, . .	2·63 –2·92	2·99	2·21	16
Nitrous oxide, .	4·02 –4·90	4·29	3·56	44
Carbon dioxide, .	4·08 –4·37	4·29	3·56	44
Acetylene, . .	4·91 –5·16	4·79	4·35	26
Ethylene, . .	5·26 –5·93	5·59	4·44	28
Ethane, . .	6·19 –6·71	6·60	5·33	30
Chlorine, . .	7·27 –7·66	7·37	5·85	70·9
Sulphur dioxide, .	7·48 –7·84	7·53	6·74	64
Methyl formate, .	11·10–12·14	11·45	11·91	60
Bromine, . .	12·49	12·68	. .	159·9
Carbon bisulphide,	12·35–18·00	13·40	12·14	76
Methyl acetate, .	15·74–17·11	16·28	15·77	74
Ethyl formate, .	15·27–17·38	16·28	. .	74
Ether, . .	18·52–19·34	19·12	17·40	74
n-Pentane, . .	20·68–21·05	20·52	19·12	72
Isopentane, .	19·88–20·47	20·52	19·12	72
Benzene, . .	19·17–20·95	20·73	18·72	78
Fluor-benzene, .	21·51–24·18	23·81	17·90	96
Ethyl acetate, .	20·47–23·23	21·46	20·49	88
Propyl formate, .	21·37–23·33	21·46	20·49	88
Methyl propionate,	21·11–23·27	21·46	19·91	88

Table continued on page 22.

Continued from previous page

	Various Computations.	Mathews' Formula.	Van Laar's Formula.	M
Carbon tetrachloride, . .	21·27–22·54	21·44	19·69	153·8
Hexamethylene, .	23·93–24·73	24·30	16·18	84
n-Hexane, . .	26·26–27·90	25·90	24·93	86
Di-isopropyl, .	25·30–25·96	25·90	24·92	86
Chlor-benzene, .	27·26–28·10	27·62	29·38	112·45
Methyl butyrate,	26·07–29·56	26·97	26·34	102
Methyl iso-butyrate	25·58–28·68	26·97	26·34	102
Propyl acetate, .	26·01–30·45	26·97	26·29	102
Ethyl propionate,	25·86–29·22	26·97	26·34	102
Stannic chloride, .	29·48–30·69	30·40	27·19	260·8
Brom-benzene, .	30·48–31·46	33·05	25·70	156·96
n-Heptane, . .	32·30–36·23	31·58	27·64	100
Iodo-benzene, .	35·48–36·97	39·34	29·89	203·85
n-Octane, . .	38·95–44·46	37·54	36·39	114
Di-isobutyl, .	37·65–41·56	37·54	33·42	114
Di-isoamyl, .	52·79	50·20	..	142·2
Mesitylene, . .	37·41	37·82	..	120·1
Cymene, . .	44·44	44·03	..	134·1
Diphenyl methane,	63·16	57·33	..	168
[$C_{18}H_{38}$] octodecane	[melts at 28° C.]	[about 100]		250

When a is of the order of 100×10^{12}, the substance is generally solid at normal temperature and pressure.

Traube's* values for the "molecular pressure" of various metals result as follows :—

K	Atomic Volume. $\frac{M}{\rho}$	Monatomic Value of a. $K\left(\frac{M}{\rho}\right)^2 = a$.
Pb, $5·08 \times 10^{11}$ dynes/cm.², . .	18·17	$1·69 \times 10^{14}$
Sn, $7·22 \times 10^{11}$, ...	16·19	$1·89 \times 10^{14}$
Ag, $1·60 \times 10^{12}$, ...	10·	$1·6 \times 10^{14}$
Cu, $2·33 \times 10^{12}$, ...	7·16	$1·19 \times 10^{14}$
Fe, $3·20 \times 10^{12}$, ...	7·18	$1·65 \times 10^{14}$
Ni, $3·20 \times 10^{12}$, ...	6·60	$1·39 \times 10^{14}$

Slightly different results are obtained, if the critical pressure

* F. G. Thompson, "The Elastic Strength of Metals," *Trans. Farad. Soc.*, vol. xi., 1915, Pt. 1.

and volume, or critical temperature and volume, are used, showing that Van der Waals' rule is not perfectly consistent. The most satisfactory method is to assume b as the gram-molecular-volume in the fluid state just above the melting-point and relate the molecular pressure to the observed molecular volumes at given temperatures.

Van der Waals has computed the molecular pressure in water as 5,000 atmospheres, or

$$5 \times 10^{9} \times 10^{-15} = 5 \times 10^{-6} \text{ dynes per molecule.}$$

More recent work by Tinker gives values five times greater, but as there is some uncertainty as to the mean size of the water-molecule, and also as to whether there is chemical association or not, no final conclusion can be drawn.

Van der Waals' formula is not so accurate that great reliance can be placed on it as a means of deducing n, but at least it indicates that in the dense gas state n is not less than 4.

Clerk-Maxwell, in his investigation as to surface-tension (vide *Encyclop. Britt.*, 9th edition, on "Capillary-Action") has employed the form

$$m_1 \, . \, m_2 \, . \, \varphi\,(d)$$

for the attraction between the molecules of masses m_1 and m_2 at a distance d from centre to centre.

He proceeds to discuss the potential in a film on this basis, and finally adopts Van der Waals' expression a/v^2 for this molecular pressure. He definitely recognises the inadequacy of Newtonian gravitation to explain surface-tension.

There is, however, a vital objection to his expression—viz., if cohesion is a function of the product of the masses, it should be related to gravitation. On the assumption that this must be done, the space function is a complex one, and the present writer, in a series of papers contributed to the Physical Society of London (1915 to 1918), has formerly suggested the empiric form

$$t_2 = \frac{G \, m_1 \, m_2}{d^{2 + (4/k)}},$$

where G is the Newtonian constant of gravitation ($6{\cdot}6 \times 10^{-8}$ dynes) and k is the ratio d/d_0 of the molecular field under the prescribed conditions of temperature, etc., to the molecular-field at the contact conditions of absolute zero.

If we assume similar molecules and a form

$$C \,.\, m^2/d^n,$$

we may connect it to the Van der Waals' expression.

The Van der Waals' "molecular pressure" on *one* molecule being about

$$\frac{2a}{N^2 d^4},$$

if this is assumed to be due wholly* to the radially adjacent molecules (as will probably be nearly the case if the space-rate of change of the force is great), and we equate it to the Maxwell form :—

$$C\, m^2/d^n,$$

then $$a = \frac{C}{2} \,.\, N^2 \,.\, d^{4-n} \,.\, m^2.$$

If now we substitute $d = \left(\frac{\sqrt{2}\,M}{N\,D}\right)^{\frac{1}{3}}$ and $m = \frac{M}{N}$.

[M = molecular weight ; N = Avogadro's number = mols. per gram-molecule ; D = density ; $N\,d^3/\sqrt{2} = v = M/D$].

$$a = \frac{C}{2} \,.\, N^2 \left(\frac{\sqrt{2}\,M}{N\,D}\right)^{\frac{4-n}{3}} \left(\frac{M}{N}\right)^2$$

$$= \frac{C}{2} \left(\frac{\sqrt{2}}{N}\right)^{\frac{4-n}{3}} \,.\, D^{-\frac{4-n}{3}} \,.\, M^{\left(2+\frac{4-n}{3}\right)}.$$

In the fully gaseous state d is almost constant, but in the critical state the condensation is appreciable.

By varying n, we can obtain a series of expressions connecting a with D and M.

* According to Edser's analysis the force between individual molecules has an inverse index at least four units greater than that of the total force of the gas on one internal molecule.

n	a varies as	n	a varies as
1	$D^{-1} M^{3}$	7	$D . M$
2	$D^{-\frac{2}{3}} M^{\frac{8}{3}}$	8	$D^{\frac{4}{3}} M^{\frac{2}{3}}$
3	$D^{-\frac{1}{3}} M^{\frac{7}{3}}$	9	$D^{\frac{5}{3}} M^{\frac{1}{3}}$
4	M^{2}	10	D^{2}
5	$D^{\frac{1}{3}} M^{\frac{5}{3}}$	13	$D^{3} M^{-1}$
6	$D^{\frac{2}{3}} M^{\frac{4}{3}}$		

The mere occurrence of solids alternating with gases in the series of elements shows that no simple relation of a to D and M exists, but by studying the series of elements of zero valency reasonably comparable conditions are provided, without unsymmetric electric (*i.e.*, chemical) effects.*

There certainly is a tendency in homologous series for a to increase fairly regularly with the molecular weight. Unfortunately, the only complete simple series is the zero-valent one, concerning which the data are rather scanty.

Saturated hydrocarbons are somewhat analogous, especially the paraffins :—

	Paraffin Series.	Melting Point.	Boiling Point.
	a		
Methane, . .	$2{\cdot}63 \times 10^{12}$	−186°	−164°
Ethane, . . .	$6{\cdot}19 \times 10^{12}$	−172°	− 84°
n-Pentane, . .	$20{\cdot}68 \times 10^{12}$	..	+ 38°
n-Hexane, . .	$26{\cdot}50 \times 10^{12}$	..	+ 71°
n-Heptane, . .	$32{\cdot}84 \times 10^{12}$	..	+ 99°
n-Octane, . .	$39{\cdot}72 \times 10^{12}$	..	+125°
n-Nonane, . .	..	− 51°	+149·5°
n-Decane, . .	..	− 32°	+173°
n-Pentadecane, .	..	+ 10°	+270·5°
Octodecane [$C_{18}H_{38}$],	Say 100×10^{12}	+ 28°	+317°

* It is possible that the conditions may be nearly satisfied by writing C as a function of the valency relations. This has been done by Mathews, *Journ. Phys. Chem.*, 17 (1913), 18 (1914), 20, (1916), who concludes that a varies as $(M \times Val.)^{\frac{2}{3}}$, where Val. is the total number of valencies in the molecules. This value of Mathews corresponds in the above table to $n = 8$, which is also Edser's value, but as Mathews' expression does not involve D, it is doubtful if any significance attaches to this coincidence. Mathews' expression is meaningless for the zerovalent elements. Isomers may be covered by the volume changes.

Elements.	Atomic Wt. M	Atomic Number.	Critical Density. Dc	*Van der Waals' Constants. a Atmospheres.	b Normal Volumes.
He	3·99	2	0·066	0·00005	0·0001
Ne	20·2	10	?	?	?
A	39·88	18	0·509	0·00259	0·00135
Kr	82·92	36	0·775	0·00462	0·00175
Xe	132·20	54	1·155	0·00818	0·00230
Nt (Rd)	222·4	86	?	?	?

A sufficient comparison may be made by taking $n = 1$, $n = 4$, $n = 7$, $n = 10$, and $n = 13$.

n	1	4	7	10	13
Element.	$\frac{a\,D}{M^3}$	$\frac{a}{M^2}$	$\frac{a}{D\,M}$	$\frac{a}{D^2}$	$\frac{a\,M}{D^3}$
He	·000000064	·0000039	·0002335	·01412	·6942
A	·000000021	·0000016	·0001276	·00998	·7834
Kr	·000000006	·0000007	·0000719	·00769	·8230
Xe	·000000004	·0000005	·0000544	·00613	·7018

It is obvious from these figures that if the attraction varies as m^2, the inverse index of space variation is very high (or not constant). This fact, coupled with a *temperature* discrepancy in the coefficient, which is alluded to later, and the certainty that, in elements and compounds of *active* valency, the value of "*a*" varies quasi-periodically with the atomic weight, practically puts out of court the m^2 function. The applicability of the d^{-4} form to gases of moderate rarity (where d is fairly constant for all gases under the same pressure and temperature and "*a*" alone is variable) confirms the idea that molecular pressure is an electrical and not predominantly a mass effect.

* These can be converted to gram-molecular (gram-atomic in this case) values in dynes by multiplying by 5×10^{14}, so that for He the value is about $2{\cdot}5 \times 10^{10}$ dynes, about 10 per cent. that for H_2.

SUMMARY OF DATA RELATING TO THE INERT GASES.

	Helium.	Neon.	Argon.	Krypton.	Xenon.	Radon or Niton.
Atomic number, ...	2	10	18	36	54	86
Atomic weight, ...	4	20	40	83	130	222
Melting temperature on absolute scale, .	1·15°	20	84	104	133	202
Boiling temperature, absolute, . . .	4·25	27	87	121	163	208
Critical temperature, ...	5·25	44	151	210	289	377
Critical pressure, atmospheres, . . .	2·26	27	48	54·3	57·2	62·4
Critical density, gms./c.c., . . .	0·07	?	0·509	0·775	1·155	1·5 ?
Critical volume, c.c./gm.-atom, . . .	57 ?	26 ?	78	78 ?	113	?
Van der Waals' "a," atoms and unit vols., referred to N.T.P., ...	0·00005	0·0006 ?	0·00259 *	0·00462	0·00818	?
Do., dynes/cm.² vols. in c.c./gm.-at., . .	0·025 × 10¹²	0·3 × 10¹² ?	1·3 × 10¹²	2·3 × 10¹²	4·1 × 10¹²	?
Van der Waals' "b" in unit vols., . .	0·0007	0·001 '	0 001348	0·001776	0·00230	0·003 ?
Do., c.c./gm.-atom, ...	19 ?	9 ?	26	40	52	?
Density as gas, gms./litres, . . .	0·1785	0·9002	1·7809	3·708	5·851	10 ?
Atomic diameter—Bragg, ...	1·98 Å.	1·3 Å.	2·05 Å.	2·35 Å.	2·70 Å.	?
" —Davey, ...	3·00 ?	2·3	2·87	3·42	3·95	?
" —Simon, ...	..	..	3·82	..	..	..
Density under 15,000 atm. press., . .	0·340	..	(1·62 at	40° abs.)	..	..
4 × critical density, ...	0·28	?	2·036	3·100	4·62	6·0 ?
Latent heat (of evaporation), . . .	..	..	1·32 (kg. cal. per gram-atom at — 162° C.)			
Heat of fusion, kg. cal./gm.-atom, . .	<0·004	0·08	0·268 ?	0·33	0·43	0·65
Analogous ionic couple, ...	LiH = 8 (not exact anology)	NaF=42	KCl= 74·56	Rb, Br = 165·37	CsI = 259·74	?
Melting temp. of same, abs., . . .	..	1,253	1,045	956	894	..
Density of same as solid, ...	..	2·766	1·994	3·21	4·51	..

* Edser's value of a (for volumes per gram) $= 1{\cdot}7083 \times 10^9 (1 - 0{\cdot}039\ T^{\frac{1}{2}})$ reduced to 0° C. multiplied by 40^2 and divided by $5 \times 10^{14} = 0{\cdot}00194$ [1 Å $= 10^{-8}$ cms.].

If we equate the Clerk-Maxwell expression for mutual-mass-attraction in the form. (*Note.*—γ is not Edser's.)

$$G\, m^2 \,.\, d^{-\gamma}$$

to the Van der Waals' molecular-pressure-term

$$2\, a \,/\, N^2\, d^4,$$

substituting for a the form

$$\frac{9}{8}\, R\, T_c v_c,$$

we have

$$\frac{9\, R\, T_c v_c}{4\, N^2 d_c^4} = \frac{G\, m^2}{d_c^{\gamma}} = \frac{G\, (\rho_c d_c^3)^2}{d_c^{\gamma}}$$

$$v_c = \frac{N\, m}{\rho_c} = \frac{N\, \rho_c d_c^3}{\rho_c} = N\, d_c^3$$

$$d_c^{\gamma} = \frac{4\, G\, \rho_c^2\, N^2 \,.\, d_c^{10}}{9\, R\, T_c N\, d^3} = \frac{4\, G\, \rho^2 N}{9\, R\, T_c} \,.\, d_c^7,$$

whence

$$d_c^{\gamma} = \frac{4}{9} \cdot \frac{G\, N}{R} \cdot \frac{\rho_2^{\,2}}{T_c} \cdot d_c^7$$

and

$$\gamma = 7 + \frac{\log\left(\frac{4\, G\, N}{9\, R}\right) + 2 \log \rho_c - \log T_c}{\log d_c}.$$

In this expression

$$\log\left(\frac{4\, G\, N}{9\, R}\right) = 8{\cdot}33.$$

ρ_c may be anything between, say, 0·3 and 10·0, so that 2 log ρ_c is — 1·0 to 1·0.

T_c may be from, say, 100° abs. to perhaps 4,000°, so that log T_c = 2·0 to 3·6.

d_c may be from $5{\cdot}0 \times 10^{-8}$ to perhaps 10^{-6}, so that log $d_c = \bar{8}{\cdot}7$ to $\bar{6}{\cdot}0$.

If these values are substituted, γ will be found to vary between 5 and 7, averaging about 6.

The use of the Newtonian constant here is arbitrary and open to question. Without this assumption the term involving the coefficient which may need to be substituted for G remains unknown, and beyond the general indication of 7 as a limit for the value of γ, nothing further can be said.

From a consideration of Van der Waals' formula and Clausius and Berthelot's empirical modifications thereof, a fair notion can be obtained of the molecular attraction which would follow at absolute zero from his hypothesis.*

According to Van der Waals, the molecular pressure is

$$\tilde{\omega} = a/v^2,$$

where $a = 3p_c v^2{}_c$ (p_c is the critical-pressure and v_c is the critical volume of a gram-molecule), so that

$$\tilde{\omega}_c = 3p_c$$

at the critical state.

The molecular-bond at the critical state is then at least

$$t_{2c} = \tilde{\omega}_c \cdot \frac{\pi}{4} \cdot d_c{}^2 = 3p_c \cdot \frac{\pi}{4} d_c{}^2.$$

As already shown, Van der Waals' formula indicates that the force varies as the inverse-fourth power of the spacing. It also leads to the result that the effective molecular-volume at absolute zero is $v_c/3$, so that

$$\frac{d_0}{d_c} = \frac{1}{\sqrt[3]{3}},$$

and at absolute zero, it follows that

$$t_{2o} = 3^{1\cdot 333} \,.\, 3p_c \,.\, \frac{\pi}{4} \,.\, d_c{}^2.$$

If we take water, for example :—

$p_c = 2\cdot175 \times 10^8$ dynes/cm.^{2}
$d_c = 5\cdot958 \times 10^{-8}$ cms. (computed from the critical density, Avogadro's constant and close packing)

and $t_{20} = 7\cdot87 \times 10^{-6}$ dynes.

* Edser (*Brit. Ass. Fourth Report on Colloid Chemistry*) asserts that molecular-attraction in fluids varies as the inverse eighth (or higher) power of the distance, and that the mass-effect on a single molecule varies as the inverse fifth (or higher) power. The Van der Waals result that a mass of N molecules acts on a molecule (in the mass) with a force which varies as the inverse *fourth* power is also reconcilable. He suggests that the inverse eighth form is due to the reaction of two double-doublets.

Clausius and Berthelot's revised formulæ for molecular pressure involve the absolute temperature—*i.e.*,

$$\tilde{\omega} = a_1/v^2\mathrm{T}.$$

(Clausius actually wrote $a_1/(v + c)^2\ \mathrm{T}$, but c is rather indeterminate.)

Clausius' value for a_1 is

$$3p_c \,.\, v_c^2 \,.\, \mathrm{T}_c,$$

and Berthelot's is

$$5{\cdot}33p_c \,.\, v_c^2\ \mathrm{T}_c,$$

so that

$$\tilde{\omega}_c = 3 \text{ or } 5{\cdot}33p_c.$$

Clausius' value is then the same as Van der Waals', while Berthelot's is greater in the ratio 16/9. Berthelot also considers that b is $v_c/4$, so that Berthelot's value for the molecular force at maximum density (again following the inverse-fourth rule) is

$$t_{20} = 4^{1\cdot333} \,.\, \frac{16}{3} \,.\, p_c \,.\, \frac{\pi}{4} \,.\, d_c^2,$$

which for water is $2{\cdot}053 \times 10^{-5}$ dynes.

If we suppose that Clausius' and Berthelot's form applies below the critical-temperature, then the molecular pressure at absolute zero is infinite. Hammick has developed some results which show a linear diminution of the coefficient of molecular pressure "a" with temperature, being about twice the critical-temperature value at absolute zero. Edser makes it four times, since he writes $a = a_0 \left(1 - \frac{\mathrm{T}^{\frac{1}{2}}}{2\mathrm{T}_c^{\frac{1}{2}}}\right)^2$, so that $a_c = \frac{a_0}{4}$.

According to Young ("Stoichiometry") for critical-values experiment indicates

$$p_c v_c = \mathrm{R}\ \mathrm{T}_c/3{\cdot}75,$$

and

$$b = v_c/4,$$

whence the critical-molecular-pressure

$$\tilde{\omega}_c = a/v_c^2 = 4p_c$$

i.e., *the molecular pressure at the critical state is four times the critical pressure.*

If
$$t_2 \propto \frac{a}{N^2 d^4}$$
at absolute zero, *disregarding temperature changes* in a,
$$\tilde{\omega}_{max} = \frac{a}{b^2} = \frac{16a}{v_c{}^2} = 16\omega_c = 64p_c.$$
Therefore, at absolute zero the molecular pressure is at least sixty-four times the critical pressure.

The table below shows how " a " changes according to the various methods of reckoning.

If $\tilde{\omega}$ be calculated from the equation
$$\tilde{\omega} = \frac{\mathrm{R\,T}}{v - b} - p,$$
using as *constant* the values of b which apply for the pressures above the critical, Amagat's values of p and v for CO_2 and C_2H_4 lead to the conclusion that $\tilde{\omega}$ deviates *widely* from the a/v^2 form for the volumes below the critical and increases slowly with temperature for these substances.

TABLE OF MEAN DEVIATIONS OF $\tilde{\omega}$ FROM a/v^2 FOR CO_2 and C_2H_4 (0° – 137° C.).

$\frac{v}{b}$	1·00	1·1	1·5	2·0	3·0	4·0
$\frac{\tilde{\omega}}{\tilde{\omega}_{3b}}$	∞	28·0	5·49	2·58	1·00	0·58
$\left(\frac{v}{3b}\right)^{-2}$	9·0	7·44	4·00	2·25	1·00	0·56

Assuming a *as constant*, b increases with v and changes slightly with temperature. Some authorities write $b = \left(b_1 - \frac{b_2}{v}\right)$, but this can only be an approximation. Such a change in b is certain if $\tilde{\omega} = a/v^2$. A reduction in b of 25 per cent. at minimum volumes is consistent with Van der Waals' $b_{max} = \frac{v_c}{3}$, and the fact that b_{min} may be only $= \frac{v_c}{4}$.

TABLE OF VALUES OF "a"—VAN DER WAALS' COEFFICIENT OF MOLECULAR PRESSURE.

Arguments.	a (independent of T).					$a_1 = a$ T.		
	Form.	Coefficients k.				Form.	Coefficients c.	
		Van der Waals.	$p_c v_c = \frac{R\,T_c}{3{\cdot}75}$, $b = v_c/4$	$p_c v_c = \frac{R\,T_c}{3{\cdot}75}$, $b = v_c/3{\cdot}75$	Berthelot $p_c v_c = \frac{9\,R\,T_c}{42}$, $b = v_c/4$		Berthelot.	Van der Waals and Clausius.
R, T_c, p_c	$k_1 \cdot \frac{R^2 T_c^2}{p_c}$	$\frac{27}{64}$	$\frac{64}{225}$	$\frac{1539}{5280}$	$\frac{303}{1024}$	$c_1 \frac{R^2 T_c^3}{p_c}$	$\frac{27}{64}$	$\frac{27}{64}$
v_c, T_c, p_c	$k_2 \cdot p_c v_c^2$	3	4	3·62	3·74	$c_2 \cdot p_c v_c^2 T_c$	$5{\cdot}\dot{3}$	3
v_c, R, p_c	,,	,,	,,	,,	,,	$c_3 \cdot \frac{p_c^2 v_c^3}{R}$	$\frac{512}{27}$	8
v_c, R_2, T_c	$k_4 \cdot R\,T_c v_c$	$\frac{9}{8}$	$\frac{16}{15}$	$\frac{171}{165}$	$\frac{101}{96}$	$c_4 \cdot R\,T_c^2 v_c$	$\frac{3}{2}$	$\frac{9}{8}$

NOTES TO TABLE.

If p is in atmospheres and v in litres per gram-molecule, R = 0·02707 per 1° C.

If p is in dynes per sq. cm. and v in c.c. per gram-molecule, R = $8{\cdot}3162 \times 10^7$ ergs per 1° C. ($8{\cdot}33 \times 10^7$ is a more recent value.)

v is sometimes expressed in litres or c.c. per *gram* (in which case R must be divided by M).

Sometimes p is in atmospheres and v in volume *relative* to that at normal temperature and pressure, so that $p\,v$ at 0° C. for a perfect gas is unity. (R = 0·00367.)

Whence $a_{\text{dynes/cm.}^2} = 1{\cdot}013 \times 10^6 \times (22{,}412)^2 \times a_{pv=1} = 5{\cdot}086 \times 10^{14}\,* \times a_{pv=1}$ in which 22,412 (or less) is the volume in cm.^{3} of one gram-molecule of the gas at N.T.P.

* Mathews gives $4{\cdot}923 \times 10^{14}$.

In gases at N.T.P., d is nearly constant = $3{\cdot}74 \times 10^{-7}$ cms.

$t_2 = (a_{pv=1})\,d^2 = 1{\cdot}398 \times 10^{-18} \cdot (a_{pv=1}) \times 1{\cdot}013 \times 10^6$ dynes $= 1{\cdot}445 \times 10^{-7} \times (a_{pv=1})$ dynes.

These latter expressions are only applicable when the gas is moderately rarefied at N.T.P.

Equation of Dieterici.—Another form of the "Equation of state" is Dieterici's :—

$$p\,(v - b) = \mathrm{R\,T}\,\varepsilon^{-\frac{\mathrm{A}}{\mathrm{RT}v}}$$

Where A is the work done per unit-mass of the gas at the boundary against cohesion.

From this it appears that

$$b = \frac{v_c}{2}, \text{ which is very incorrect.}$$

$$\mathrm{A} = 4\,b\,\mathrm{R\,T}_c = 2\,v_c\mathrm{R\,T}_c$$

$$p_c = \frac{\mathrm{A}}{4\,b}\,\varepsilon^{-2}$$

$$\frac{\mathrm{R\,T}_c}{p_c v_c} = \tfrac{1}{2}\,\varepsilon^2 = 3{\cdot}695,$$

which agrees well with experiment.

Writing

$$(p + \tilde{\omega})\,(v - b) = \mathrm{R\,T},$$

and substituting, we find that

$$\frac{\tilde{\omega}}{p} = \varepsilon^{+\frac{\mathrm{A}}{\mathrm{RT}v}} - 1,$$

and substituting the critical values

$$\left(\frac{\tilde{\omega}}{p}\right)_c = \varepsilon^2 - 1 = 6{\cdot}389,$$

much more than Van der Waals' value of 3.

The Dieterici form by its disagreement with Van der Waals' value for critical pressure, and its large disagreement in respect to the molecular-volume, does not show itself as a preferable form for deductions as to molecular force.

Dieterici had an alternative form $\left(p + \frac{a}{v^k}\right)(v - b) = \mathrm{R\,T}$, where $k = \frac{5}{3}$. Analogous is Fessendens' form

$$\left(p + \frac{c}{v^{\frac{4}{3}}}\right)(v - b) = \mathrm{R\,T},$$

which makes the molecular force vary as the inverse-square of the distance, the arguments against which are given elsewhere.

Hundreds of different forms of the "Equation of State" have been developed, none being a great improvement on Van der Waals', or rather Hirn's, original form, except perhaps for convenient use at low pressures, with which we are not here concerned. Some physicists consider that "*a*" is a function of temperature and diminishes with increase of temperature.* The apparent anomaly of an attraction being affected by temperature may be explained in two possible ways :—

(1) There are electromagnetic-repulsions which increase with the temperature on account of the increased kinetic-energy of the charges.

(2) The change in "*a*" may be really due to the increase of a repulsion-term arising from the change of energy. The equation of state represents a family of isothermal-changes, whereas the attraction-term can only be a simple function of space if the changes are isentropic—*i.e.*, adiabatic. It seems, however, possible that the irregularities are due to the changes in the *v* function rather than in the value of "*a*," so that the whole "molecular pressure" is not necessarily a function of temperature, but a more complex function of volume than a/v^2.†

* Edser says that *a* in Van der Waals' formula should be $a_0(1 - \gamma T^{\frac{1}{2}})^2$ for non-metals, where $\gamma = \frac{1}{2T_e^{\frac{1}{2}}}$; T_e being the critical temperature, and *l* the latent heat of vaporisation per gram.

$$\frac{l}{\rho - \rho_1} = a_0(1 - \gamma T^{\frac{1}{2}}). \quad (\rho, \rho_1, \text{ density of liquid and vapour}).$$

From the expression $a = a_0(1 - \gamma T^{\frac{1}{2}})^2$ and $\gamma = \frac{1}{2} T_c^{-\frac{1}{2}}$, we find that $a_c = a_0/4$ and $\frac{a_0}{b^2} = 108\, p_c$; assuming $b = v_c/3$.

† An attempt has been made (*Engineering*, 17th July, 1925, vol. cxx., "The Kinetic Theory of Gases") to show that the "molecular pressure" term is simply due to the effect of "periods of contact" during the collision of molecules—*i.e.*, a partial association. This appears to be a method of presentation rather than an abolition of molecular force, and leads to extraordinarily high values for the degree of association. M. F. Carroll (*Phil. Mag.*, Aug. 1926, p. 385, on "Molecular Association and the Equation of State") computes association from the deviations from Van der Waals' rule, and finds quite large values in certain cases. It seems doubtful if Van der Waals' rule is sufficiently exact to warrant such computations of association.

The table, pp. 36, 37 (Chatley, in *Proc. Phys. Soc.*, Feb. 25, 1918) gives rough indications of the quantitative values under consideration for five common substances.

If it be supposed, as has been done by Sutherland, Born, Landé, Fajans, and others that the attractive term in molecular-force is principally the difference-effect of the electrostatic attraction and repulsion between neighbouring electric doublets, each pole of which is an electron, we have the following results in the position of maximum attraction :—

$$f_2 = \frac{e^2}{s^2}\left[\frac{1}{(c-1)^2} + \frac{1}{(c+1)^2} - \frac{2}{c^2}\right]$$
$$= \frac{2e^2}{s^2}\left[\frac{c^2+1}{(c^2-1)^2} - \frac{1}{c^2}\right],$$

where e is the unit electron-charge ($4{\cdot}8 \times 10^{-10}$ electrostatic units),

s is the distance between the electrons in the doublet,
d is the distance between the centres of the doublets,
c is the ratio d/s.

This may be reduced to the form $\dfrac{6e^2}{s^2} \cdot \dfrac{1}{c^4 - \dfrac{5c^2}{3} + \dfrac{4}{9 - \dfrac{s}{c^2}}}$,

so that, for large values of c, the attraction is $\dfrac{6e^2}{s^2c^4} = \dfrac{6e^2s^2}{d^4}$.

For small values of c (say between 1·1 and 5), the attraction may be written

$$A\ e^2s^2/d^\Upsilon,$$

where, with $\gamma = 4$, A diminishes with c to 6 ; the value of γ for constant value of A gradually falls from a very high value to the limiting value of 4.

The agreement of this form with Van der Waals' expression is very striking, and the fact that the original equation arises directly from an inverse square relation is important from the point of view of simplicity.

One difficulty in regard to the above hypothesis is that, although there is a mutual torque between the molecules which tends to bring them into the position of mutual maximum attraction (which position has been assumed above),

SUBSTANCE.	H_2.	H_2O.	CO_2.	SO_2.	$SnCl_4$.
1. Molecular weight,	2·0155	18·0155	44·00	64·10	260·3
2. Critical pressure : atmospheres,	13·4	217·5	72·9	77·70	36·95
3. Critical temp. : absolute,	31·0	647·0	304·1	430·3	591·8
4. Critical volume : v_c cubic cm.,	60·54	45·00	98·22	125·00	351·00
5. Ditto from V. der W.s' equat.,	72·10	91·50	128·30	170·30	492·60
6. a from p_c and T_c,	$0·21 \times 10^{12}$	$5·537 \times 10^{12}$	$3·651 \times 10^{12}$	$6·853 \times 10^{12}$	$27·32 \times 10^{12}$
7. b from p_c and T_c,	24·03	30·49	42·77	56·7	164·2
8. b_1 = one-third critical volume,	20·15	15·00	32·74	41·67	117·0
9. b_2 = volume at abs. zero,	22·4	18·02	$<29·33$	$<44·83$	$<114·1$
10. Critical density, D_c,	0·033	0·4	0·448	0·513	0·7419
11. Density at abs. zero, D_0,	0·09	1·0	1·5	$>1·43$	$>2·28$
12. $D_c/D_0 = v_0/v_c = B$,	0·36	0·4	0·299	$<0·263$	$<0·232$
13. $p_c v_c / R\,T_c = K$,	0·3217	0·1845	0·2869	0·2749	0·2670
14. A, from K and B,	3·856	8·036	3·980	3·935	3·876
15. $p_c \div p'_c$,	0·2059	0·1107	0·2008	0·2027	0·2051
16. $p'_c \div A\,p_c$,	1·26	1·125	1·251	1·254	1·258
17. $\sqrt[3]{1/B} = d_c/d_0$,	1·397	1·257	1·489	1·561	1·628
18. $d_c = \sqrt[3]{v_c/N}$,	$3·331 \times 10^{-8}$	$4·203 \times 10^{-8}$	$5·451 \times 10^{-8}$	$5·907 \times 10^{-8}$	$8·835 \times 10^{-8}$
19. d_0,	$1·673 \times 10^{-8}$	$3·344 \times 10^{-8}$	$3·660 \times 10^{-8}$	$3·784 \times 10^{-8}$	$5·121 \times 10^{-8}$
20. m = M/N, gr.,	$3·326 \times 10^{-24}$	$2·973 \times 10^{-23}$	$7·259 \times 10^{-23}$	$1·058 \times 10^{-22}$	$4·294 \times 10^{-22}$
21. G m^2 dynes,	$7·30 \times 10^{-55}$	$5·833 \times 10^{-53}$	$3·557 \times 10^{-52}$	$7·387 \times 10^{-52}$	$1·53 \times 10^{-50}$
22. G N m^2 dynes,	$4·415 \times 10^{-31}$	$3·536 \times 10^{-29}$	$2·156 \times 10^{-28}$	$4·417 \times 10^{-28}$	$9·27 \times 10^{-27}$
23. $r_c = \sqrt[3]{3v_c/4\pi}$ cm.,	2·453	2·207	2·866	3·101	4·376
24. $F_2 = G\,N\,m^2/r^2$ dynes,	$7·336 \times 10^{-32}$	$7·259 \times 10^{-30}$	$2·624 \times 10^{-29}$	$4·593 \times 10^{-29}$	$4·841 \times 10^{-28}$
25. $F_1 = A\,p_c d_c^2$ dynes,	$1·127 \times 10^{-8}$	$3·130 \times 10^{-6}$	$8·744 \times 10^{-7}$	$1·079 \times 10^{-6}$	$1·009 \times 10^{-6}$
26. $F_1 \div F_2$,	$1·535 \times 10^{24}$	$4·311 \times 10^{23}$	$3·332 \times 10^{22}$	$2·35 \times 10^{22}$	$2·084 \times 10^{21}$
27. $\gamma = 2 + (4d_0/d_c)$,	4·869	5·183	4·692	4·563	4·458

28. $F_3 = G\,m^2/d_c\,\gamma$ dynes,	$1{\cdot}299 \times 10^{-29}$	$9{\cdot}961 \times 10^{-15}$	$4{\cdot}280 \times 10^{-18}$	$7{\cdot}122 \times 10^{-19}$	$5{\cdot}538 \times 10^{-19}$
29. $\nu_1 = F_1/F_3$,	$8{\cdot}672 \times 10^{21}$	$3{\cdot}142 \times 10^{8}$	$2{\cdot}043 \times 10^{11}$	$1{\cdot}516 \times 10^{12}$	$1{\cdot}822 \times 10^{12}$
30. ν_1/N,	$1{\cdot}430 \times 10^{-2}$	$5{\cdot}183 \times 10^{-16}$	$3{\cdot}370 \times 10^{-13}$	$2{\cdot}500 \times 10^{-12}$	$3{\cdot}004 \times 10^{-12}$
31. $F_4 = a/N^2 d_0^4$ dynes,	$4{\cdot}645 \times 10^{-7}$	$1{\cdot}206 \times 10^{-5}$	$5{\cdot}537 \times 10^{-6}$	$9{\cdot}093 \times 10^{-6}$	$1{\cdot}076 \times 10^{-5}$
32. $F_5 = G\,m^2/d_0^6$ dynes,	$5{\cdot}35 \times 10^{-10}$	$4{\cdot}176 \times 10^{-8}$	$1{\cdot}122 \times 10^{-7}$	$2{\cdot}517 \times 10^{-7}$	$8{\cdot}285 \times 10^{-7}$
32. $\nu_2 = F_4/F_5$,	868	288·8	49·33	10·01	12·99

In the above table, the following comments apply to the lines from 14 downwards :—

Line 14. A is the ratio of the " molecular-pressure " at the critical state to the external critical-pressure.
15. The ratio of the critical-pressure to the total pressure (critical and molecular).
16. The ratio of the total pressure to the molecular-pressure.
17. The ratio of the molecular diameter at the critical-volume to that at absolute zero.
18. The molecular-diameter at critical-volume assuming cubic spacing.
19. The molecular-diameter at absolute zero.
20. The mass of a molecule.
21. The Newtonian gravitation of two molecules 1 cm. apart.
22. The Newtonian gravitation of 1 gram-molecule upon one molecule 1 cm. away.
23. The radius of a gram-molecule at the critical-state.
24. The Newtonian gravitation of one gram-molecule upon one molecule at the radius (23).
25. The molecular-pressure upon one molecule at the critical state.
26. The ratio of (25) to (24).
27. Hypothetical index of quasi-Newtonian gravitation.
28. Quasi-Newtonian gravitation of two molecules using the index (27).
29. The ratio of (25) to (28).
30. The same ratio (29) divided by Avogadro's number
31. Molecular-pressure per molecule at absolute zero.
32. Quasi-Newtonian gravitation at absolute zero as for (28).
33. The ratio of (31) to (32).

It will be observed that the quasi-Newtonian formula is fairly correct for absolute zero conditions, but errs in a ratio of the order of N for critical volumes.

it is hard to see how this position can be maintained in the gaseous state, where there are incessant collisions. In the opposite position there is repulsion instead of attraction, so that, in rarefied gases at least, one might expect the molecular pressure to be nil, which does not appear to be the case. The attractive position is, however, more stable than the repulsive, and as the mutual torque varies as the inverse-third power of the distance, the doublets will tend to revolve into the position of stability. There will be a consequent variation of strength with strain. The condition of a *mat* of magnetised filings may be compared. Quantitatively the expression is of the right order, and since the "free charge" may vary from one to seven electrons per atom, while "*s*" may differ considerably in different kinds of atom, the result is quite plausible.

From both Van der Waals' rule and the electrostatic hypothesis molecular force would immensely exceed Newtonian gravitation at very considerable distances for individual pairs of isolated molecules, so that in the formation of aggregations of molecules in space, molecular-attraction could play an important part, but the reduction of mutual torque with distance decreases the tendency to form attractive configurations, so that repulsion becomes more important.

Sir J. J. Thomson has suggested an arrangement whereby in a solid (crystal) the atoms are linked by electrons (corresponding in number to the valency). In this case the cohesion will, for individual bonds, vary as the inverse square, but since on any section the charges will be alternately positive and negative, the effective fields will be almost confined to the pairs concerned. M. Born has made his calculations on the basis of the equilibrium of cubic crystal structures (alkaline halides) of alternately positive and negative atoms equidistant, using certain reasonable assumptions as to the electrons and their motions, and checking the result by comparison with the compressibility and vibration period. Madelung has developed the computation of the electrostatic potential of the atoms in a cubic grating * of alkaline halides.

* *Phys. Z.*, **19**, p. 524, 1918: Madelung's rule is that the lattice potential $= 13{\cdot}94\, e^2/\delta$, where δ is the distance between *similar* ions in a cubic grating. The "lattice potential" is reckoned per unit cube. A unit cube contains one complete $\pm$ ion, eight $\mp$ ions shared with eight cubes = one $\mp$ ion, twelve $\pm$ ions shared with four cubes = three

Some further light is shed on the question of space-variation by a consideration of the reinforcement of adjacent molecules upon the bond between one pair according to the degree of variation taken. It will be seen that if the inverse square (or even in a slighter degree, the inverse cube) rules are taken, the cohesion in a mass would vary with the volume (like gravitation). If the inverse sixth is used, only the molecules immediately adjacent (not more than six on one side of a median plane) have any appreciable effect, and in this case the bond in mass is a small number of times that of an isolated pair.

The method of arriving at this result is as follows :—

Let there be a molecule situated on the boundary of a plane surface of a mass of matter which extends indefinitely or to prescribed limits in one direction, then a semi-spherical shell one molecule thick, described about the centre of the molecule, is equidistant from it, and the radial attraction of all the molecules in the shell upon the central one is the same. The sum of the components of the attractions normal to the plane surface is the total attraction of the shell in the direction of the normal, and the integral of all such shell-attractions to infinity or the prescribed boundaries is the total attraction on the molecule.

Consider any elementary ring in the shell, parallel to the median plane, of radius $r \,.\, \sin\theta$. The volume of half this ring, for infinitesimals, is

$$(r \,.\, \delta\theta)\,(\delta r)\,(\pi r \,.\, \sin\theta).$$

If the attraction per unit-volume is p (r, the distance from the central molecule, being constant for any one shell) the total radial-tension in half the conical surface centred at the molecule is

$$\pi p r^2 \,.\, \sin\theta \,.\, d\theta \,.\, \delta r,$$

$\pm$ ions, six $\mp$ ions shared with two cubes = three $\pm$ ions, totalling eight ions or four atom pairs. The mutual potential of such pairs *considered as isolated* is $\frac{e^2}{\delta/2}$, so that the potential per unit cube on this basis is $\frac{4e^2}{\delta/2} = 8e^2/\delta$. Madelung's computation increases this in the ratio $\frac{13{\cdot}94}{8} = 1{\cdot}74$ on account of the effects of the ions in pairs other than the one directly conjoined.

and the total force from the quarter-shell, in the direction of the normal, is

$$\pi p r^2 . \sin\theta . d\theta . \delta r . \cos\theta.$$

The total radial force for the quarter-shell is

$$P = p . \delta r . \pi r^2,$$

and the normal component is

$$\int_0^{+\frac{\pi}{2}} \pi p r^2 . \sin\theta . \cos\theta . d\theta . \delta r = \pi p r^2 \delta r \int_0^{\frac{\pi}{2}} \sin\theta . \cos\theta . d\theta,$$

so that the ratio of the normal component to the total radial attraction is

$$\int_0^{\frac{\pi}{2}} \sin\theta . \cos\theta . d\theta = \tfrac{1}{2} \int_0^{\frac{\pi}{2}} \sin 2\theta . d\theta = \tfrac{1}{2} \left[\tfrac{1}{2} \cos 2\theta \right]_0^{\frac{\pi}{2}} = \tfrac{1}{2}.$$

If δr, the diameter of one molecule, the number of molecules in one hemispherical shell, is approximately

$$m = \frac{2\pi r^2 . \delta r}{(\delta r)^3} = \frac{2\pi r^2}{(\delta r)^2}.$$

If we write $\delta r = d$ and $\frac{r}{\delta r} = n$

$$m = 2\pi n^2 = 6{\cdot}28\, n^2.$$

In a close (rhombic dodecahedral) packing twelve spheres may be placed round one central one and mutually in contact, so that instead of 2π we may write $12/2 = 6$ for the first shell, and, disregarding the slight interpenetration of the spheres into the shells outside the central dodecahedron, say that in each half-shell there are $6n$ molecules.

The ratio of the total force to the bond of a single molecular pair is then as follows, according to the linkage-formula $t \propto d^{-\gamma}$.

n	m	γ 2	3	4	5	6
1	6	3	3	3	3	3
2	24	3	1·5	0·75	0·375	0·1875
3	54	3	1·0	0·3333	0·1111	0·0555
4	96	3	0·75	0·1875	0·0469	0·0117
5	150	3	0·60	0·12	0·024	0·0048
6	216	3	0·50	0·0833	0·0138	0·0023
7	294	3	0·4128	0·0589	0·0084	0·0012
8	384	3	0·375	0·469	0·0058	0·0007
9	486	3	0·3333	0·0333	0·0033	0·0003
10	600	3	0·3000	0·0300	0·0030	0·0003
n	$6n^2$	$\frac{6}{2}n^0$	$\frac{6}{2}n^{-1}$	$\frac{6}{2}n^{-2}$	$\frac{6}{2}n^{-3}$	$\frac{6}{2} \cdot n^{-4}$
Sum to infinity,		∞	∞	6·0	4·0	3·4286

According to the constants in the linkage formula, the ratio becomes

$$q = \Sigma_1^n 3n^{-(\gamma-2)}.$$

The series

$$1 + \frac{1}{2^p} + \frac{1}{3^p} + \frac{1}{4^p} + \quad . \quad . \quad . \quad \frac{1}{n^p}$$

is less than

$$1 + x + x^2 + x^3 + \quad . \quad . \quad . \quad x^u,$$

where x is $\frac{2}{2^p}$, and this series totals $\frac{1}{1-x}$ to infinity if x is fractional, so that if

$$\begin{array}{llll} \gamma = 4, & p = 2, & x = \frac{1}{2}, & \text{and } q = 6 \\ 5, & 3, & \frac{1}{4}, & 4 \\ 6, & 4, & \frac{1}{8}, & 3\frac{3}{7}. \end{array}$$

If γ is 2 or 3, the total is infinite, the value for n shells increasing uniformly if γ is 2, and at a slowly decreasing rate if γ is 3.

Hence the values of q are

γ	2	3	4	5	6
q	∞	∞	6	4	3·42857

For any higher power than 6, or if the power varies from 6 downwards, q is practically 3.

For cubic packing these values are practically halved.

The fact that the sum of such attractions to infinity is infinitely great for a value of $n = 3$, which implies an increase of strength of a test piece with size, indicates that $n > 3$. Edser by analogous reasoning shows successively that $n > 4$, 5, 6, and 7.

A recent interesting attempt to deduce a law for molecular attraction is that of Edser (*Brit. Ass. Fourth Report on Colloid Chemistry*, 1922, pp. 40-114). His main conclusions are that the molecular attraction in non-associating liquids (except mercury) behaves as if there were a central force between the molecules which varies inversely as the eighth power of the distance between their centres.

The main experimental basis of his argument is an empirical equation deduced from Young's data on the latent heat of vaporisation of numerous substances, as follows :—

$$\frac{l}{\rho - \rho_1} = a\,(1 - \gamma\,T^{\frac{1}{2}}),$$

where l = latent heat of vaporisation, ergs per gram,
ρ = density in liquid state at temperature T (abs.),
ρ_1 = density in vapour state at temperature T (abs.).
a = coefficient,
$\gamma = \frac{1}{2T_c^{\frac{1}{2}}}$, where T_c is the critical temperature (abs.).

He contends that the omission of the factor $(1 - \gamma\,T^{\frac{1}{2}})$ is the fallacy which underlies Mill's reasoning (see p. 59).*

By a process of integration of the molecular attraction (assumed to have the form $f = c\,r^{-n}$, where n is an unknown integer and f is the attraction between two isolated molecules whose centres are r apart) between a radius equal to the *diameter* δ of a spherical-molecular-field of repulsion and infinity, he obtains expressions for the " cohesion " (Van der Waals' $a\,v^{-2}$), surface-tension and latent heat. From the equation for the latent heat and the form given above and the dimensions of the molecules, he deduces that $n = 8$, and shows

* To facilitate reference Edser's symbols have been used, except for his N, which I have written N_1, to show that it is *not* Avogadro's number, but that number divided by the molecular weight.

that the results are consistent with the experimental values of the surface-tension, compressibility, and thermal expansion.

He also concludes that molecular force is appreciable through a considerable number of molecular diameters, and may compare with gravity at distances of the order of 10^{-5} cms.

The integration is the most important part of the analysis, and involves the assumption of the continuity of all the matter external to a sphere of radius δ enclosing the individual molecule. This assumption is not statically sound, but he claims that the averaging effect of the *motions* of the molecules renders it applicable.

His main results are as follows :—

(1) Van der Waals' coefficient "a" when v = volume of *one* gram of non-metallic liquid is

$$\left[\frac{\pi c \,.\, N_1^2 \,.\, v^2}{6\,\delta^4}\right] . (1 - \gamma T^{\frac{1}{3}})^2 = K\, v^2 \text{ (dynes/cm.}^2\text{)},$$

where N_1 is the number of molecules per c.c. and v is the vol. in c.c. per gram ; K = cohesion, dynes/cm.^{2}.

$$N_1 = \frac{2{\cdot}016 \times 10^{24}}{3{\cdot}24 \times M\, v}, \text{ where M is the molecular weight,}$$

$$\left(N_1 = \frac{N}{M\,v}, \text{ where N is Avogadro's number}\right).$$

(2) Surface-tension, neglecting vapour density

$$S = \frac{K \,.\, S}{4}, \text{ where } K = \frac{a\,(1 - \gamma T^{\frac{1}{3}})^2}{v^2},$$

a being the term in the left bracket in expression (1).

Not neglecting vapour density

$$S_{12} = \frac{a\,(1 - \gamma T^{\frac{1}{3}})^2 \,.\, \delta}{4} \,.\, (\rho - \rho_1)^2 \text{ dynes/cm. or ergs/cm.}^2$$

(3) The resultant force exerted on a molecule at a distance x from the surface of a liquid is

$$\frac{2\,\pi\, c\, N_1}{35\, x^5} \text{ dynes.}$$

(4) The cohesion K (disregarding temperature changes)

$$= \frac{\pi c N_1^2}{6 d^4} \text{ dynes/cm.}^2\text{, so that } c = \frac{6 \delta^4 . K}{\pi N_1^2}.$$

(5) 94 per cent. of the surface-tension energy in a liquid is within the surface-layer one molecule thick, whilst the remainder is located at a greater distance.

The case where the molecules are in general contact is of great interest, but Edser's theory must not be extrapolated to the immobile state without reservation.

Taking his expression (assuming constant temperature),

$$K = \frac{\pi c N_1^2}{6 \delta^4},$$

there may be substituted for N_1 the expression $\sqrt{2}/d^3$, where d is the *mean* distance from centre to centre of the molecules, so that

$$K = \frac{\pi c}{3 \delta^4 d^6} \text{ dynes}$$

and

$$f = \frac{c}{d^8} = \frac{3K \delta^4}{\pi d^2} \text{ dynes.}$$

If $$d = \delta, f = \frac{3K \delta^2}{\pi} \text{ dynes,}$$

which shows that the force between an individual pair of molecules may even exceed the integrated effect $K . \frac{\pi}{4} \delta^2$! This raises a doubt if the assumption of continuity in molecules proximate to the selected ones in the integration is justifiable. Edser, however, does not claim his formula to apply when the *free* space is less than *three* times the net volume of the molecules.

He lays great stress on the *motion* of the molecules.

General Conclusion.—From what has been said above, it is clear that **the molecular force between two molecules in a mass varies approximately as an inverse power of the distance**

not less than four,* and increases with the mass of the molecules when the chemical constitutions are analogous, but varies widely for different chemical types. The contribution of other molecules to the attraction between two is relatively small.

* In the case of ionised compounds—*e.g.*, the alkaline halides—the bonds between *adjacent atoms* vary inversely as the square of the distance from centre to centre, but alternate from attraction to repulsion for each atom paired with any one. Bragg (*Phil. Mag.*, Sept. 1926) says, "The actual law of force is probably much more complex than that of a simple inverse power of the interatomic distance." He lays special emphasis (Lectures "Concerning the Nature of Things," 1925) on the tendency to shear on planes of crystallisation.

CHAPTER IV.

MOLECULAR AND ATOMIC SPACING IN SOLIDS AND LIQUIDS.

Two important conclusions have been discovered in recent years which lead to definite results in connection with atomic spacing.

(1) From various sources it has been found that the number of molecules in a gram-molecule is :—

$$N = 6{\cdot}062 \times 10^{23} \text{ (Avogadro's number)},$$

or, in other words, the weight of a molecule is

$$\frac{\text{Molecular weight in grams}}{6{\cdot}062 \times 10^{23}}.$$

(2) In crystals the *atoms* are the units, and are spaced in a lattice (cubical, hexagonal or rhombohedral) frame with the atoms at the intersections of the bars.

Common salt or sodium chloride (NaCl, mol. wt. = 58·46, spec. grav. = 2·1741), which crystallises in cubes, has been shown by Von Laue and the Braggs' X-ray diffraction spectrum method to consist of alternate atoms of sodium and chlorine, and it is an easy matter to compute the distance from centre to centre of the atoms.

The volume of a gram-molecule of NaCl is :—

$$\frac{58{\cdot}46}{2{\cdot}1741} = 26{\cdot}88.$$

This volume contains 2N atoms, so that the side of the unit cubes is

$$d = \sqrt[3]{\frac{26{\cdot}88}{2 \times 6{\cdot}062 \times 10^{23}}} = 2{\cdot}809 \times 10^{-8} \text{ cms.}$$

(double or $\sqrt{2}$ or $\sqrt[3]{2}$ times this value can be compared with Sutherland's figure for a chlorine-molecule, computed from viscosity data = $3{\cdot}74 \times 10^{-8}$ cms.).

The interatomic (chemical or electrostatic) bond is then :—

$$\frac{e^2}{d^2} = \frac{(4{\cdot}774 \times 10^{-10})^2}{(2{\cdot}809 \times 10^{-8})^2} = 2{\cdot}888 \times 10^{-4} \text{ dynes.}$$

Since there are equal numbers of sodium and chlorine atoms, the external electrostatic effect is zero, but owing to the juxta-position of unlike atoms, there is a mutual attraction which may be found by computing the differences between the total attraction and repulsion across an imaginary plane between any two internal atoms and normal to the lines joining those centres. This amounts to over 10^{-5} dynes, and appears to account for cohesive strength. Madelung and Max. Born have elaborated this calculation and shown that it agrees with the compressibility and an inverse tenth of repulsion. Madelung's rule for energy for elementary cube (four atoms) $= -\frac{13{\cdot}94\, e^2}{\delta_0}\left(1 - \frac{1}{n}\right)$, where δ_0 = side of cube (*two* molecular diameters), n = inverse index of repulsion.

A reasonable hypothesis is that in fluids the higher kinetic-energy keeps all but the immediate pairs separate, so that these pairs (NaCl molecules) are held together by the above-mentioned bond of about 3×10^{-4} dynes, unless the atoms are more separated in the fluid-molecule.

Since the electrostatic-force is simply an inverse square one, the work (heat) of dissociation necessary is :—

$$\int_d^{\infty} \frac{e^2}{r^2} \,.\, d\,r = -\frac{e^2}{d} = \frac{(4{\cdot}774 \times 10^{-10})^2}{2{\cdot}809 \times 10^{-8}}$$

$$= 8{\cdot}11 \times 10^{-12} \text{ ergs per bond.}$$

The value in calories per gram is :—

$$\frac{0{\cdot}811 \times 10^{-22} \times 6{\cdot}062 \times 10^{23}}{58{\cdot}46 \times 4{\cdot}24 \times 10^7} = 1{,}984.$$

The specific heat of sodium-chloride gas is unknown, but if it is, say, 0·5, this means that at a temperature of

$$\frac{1{,}984}{0{\cdot}5} = \text{say } 4{,}000^\circ \text{ absolute}$$

all the molecules will be dissociated.

Such a temperature occurs in the atmosphere of the sun, so that the computation indicates the presence of nascent Na and Cl atoms in the sun. It appears that in temperatures of upwards of 10,000° only nascent atoms and electrons can exist, but under great pressure molecules may be reformed (Arrhenius).

A further interesting conclusion from the crystal-theory is that *molecules* are not spherical, but consist of geometrical configurations. Since atoms are not the same size, the molecule-skeletons do not form simple geometric figures. The atoms themselves are also probably not spherical, since valency shows that they are polarised. The cubic arrangement of atoms in crystal shows, however, that some kinds may be about equal in three diameters, and that different elements may have almost equal diameters. The *planes* of crystallisation are a source of weakness.

The mean atomic diameter varies (disregarding variation in the geometrical packing) as the cube-root of the atomic volume. The atomic-volume varies from 3 (carbon) to 120 (gadolinium) cubic centimetres, so that the diameter varies from 1 to 5 times that of a carbon atom.* Molecular volumes vary from less than 10 to over 250 c.c., so that mean molecular diameters vary from 2 to, say, 8 times the diameter of a carbon atom ($2 \cdot 0 \times 10^{-8}$ cms.).

For simple cubic atomic packing, the mean atomic diameter is

$$d = \sqrt[3]{\frac{w}{\text{N D}}} = 1 \cdot 183 \times 10^{-8} \,.\, \sqrt[3]{v_a}\ \text{cms.}$$

w = atomic wt.; D = density; N = Avogadro's number; v_a = at. vol. $= \frac{w}{\text{D}}$.

For rhombic dodecahedral packing, which is the densest possible for equal spheres (" face-centred cube ")

$$d = \sqrt[3]{\frac{2 \,.\, w}{\text{N D}}}.$$

Substituting m, the molecular weight, for w, this formula can be used to compute the mean molecular diameter, but it must be observed that the molecules may be spindle-shaped, discoid, hollow, or cruciform.

True separable molecules do not seem to occur in inorganic crystalline solids, but may do so in colloidal solids.

*** Bragg (*Phil. Mag.*, 7, vol. 2, 1926, p. 258, September, 1926) indicates that the atomic radius depends on the electrical structure. Anion pairs may be $0 \cdot 7 \times 10^{-8}$ further apart than cation-anion pairs.**

Disperse or colloidal solutions seem to have molecules surrounded by "adsorption" shells of the "solvent."

Imperfectly crystalline solids, such as cast and wrought metal, have a granular structure. Each grain seems to be internally truly crystalline, but the surfaces are distorted, imperfect, or ruptured, and the cohesion strength depends on the degree to which atom-pairs are dispersed in the common faces. Amorphous solids may also be regarded as solid colloids if the grains are very minute. Most amorphous solids consist of an interlocking meshwork of small crystals of most variable structure.

The application or removal of heat causes a difference in the equilibrium position of the particles of a solid. The addition of heat causes expansion, implying an increase in the mutual repulsion, diminution in the attraction, or both. This phenomenon, together with certain others, has led physicists to believe that heat in solids consists in a vibration of the particles, the kinetic energy of varying with the total heat. If the absolute zero of temperature is also the zero of heat, the mean kinetic energy of the particle varies approximately as the absolute temperature.

If it is assumed that the vibrations are linear, simple, harmonic oscillations (an assumption which is certainly not quite true), then we may write approximately :—

Total heat = number of molecules × mean kinetic energy per molecule.

$$J\,M\,s\,\theta = n^3\,\frac{m\,.\,\pi^2\,\Delta^2}{T^2},$$

where M = mass of unit volume, *i.e.*, density, $= n^3 m$,

s = mean specific heat from zero absolute to θ,

θ = temperature (absolute) Centigrade,

J = mechanical equivalent of heat, ergs per gram-calorie,

n^3 = molecules in unit volume,

m = mass of a molecule,

Δ = mean amplitude of oscillation (= half-swing),

T = mean periodic time of oscillation.

$$\frac{\Delta}{T} = \frac{1}{\pi}\sqrt{J\,s\,\theta.}$$

The mean velocity of the particles is $\frac{4\,\Delta}{T}$.

For example, steel at temperature of 300° absolute (27° C., 80° F.)

$$\frac{\Delta}{T} = \frac{1}{\pi} \sqrt{4 \cdot 2 \times 10^7 \times 0 \cdot 11 \times 300} = 11{,}850 \text{ cm./sec.}$$

$$v = \frac{4\,\Delta}{T} = 47{,}400 \text{ cm./sec.}$$

A dull *red* heat corresponding to a temperature of about 600° C. (say 900° abs.) will then involve a velocity of about 1·7 times the above, say 2,500 ft./sec., or 80,000 cms./sec. Optics shows that the vibrations in light of that colour have a frequency of about 400×10^{12} per second, so that on these assumptions

$$\Delta \text{ at } 900° \text{ abs.} = \frac{80{,}000}{400 \times 10^{12} \times 4} = 0 \cdot 5 \times 10^{-10} \text{ cms.}$$

2Δ, the molecular swing, would then be of the order of $1 \cdot 0 \times 10^{-10}$ cms.

Strong arguments may be adduced for locating the heat-energy principally in mobile electrons, but a sufficient fraction of the energy stored is probably in the mere "wobble" of the atoms about their centres to make these results of the right order.

Relation of Frequency to Temperature in a Solid.

From formula above,

$$f = \frac{\sqrt{J\,s\,\theta}}{\pi\,\Delta} \text{. writing } \Delta = \Delta_0\,[1 + m\,\theta],$$

where Δ_0 = molecular amplitude at abs. zero.

$$f = \frac{\sqrt{J\,s\,\theta}}{\pi\,\Delta_0\,[1 + m\,\theta]}.$$

Example.—Iron, $s = 0 \cdot 11$. If $\theta = 900°$ $f = \dfrac{20{,}523}{\Delta_0\,[1 + 0 \cdot 01]}$. Taking $\Delta_0 = 10^{-8}$, $f = 2 \cdot 0 \times 10^{+12}$ at 900° abs. and $0 \cdot 5 \times 10^{12}$ at 450° abs. If $f = 4 \cdot 0 \times 10^{14}$ at 900° abs., $\Delta_0 = 0 \cdot 5 \times 10^{-10}$.

Generally, if $\Delta_0 = 10^{-8}$,

$$f = \frac{684\,\sqrt{\theta}}{10^{-8}\,[1 + m\,\theta]} = \text{say } 7 \times 10^{10}\,\sqrt{\theta}.$$

Cf. Lindemann's formula (Nernst, "Theory of Solid State," p. 49) for atomic frequency.

$$f = 3{\cdot}08 \times 10^{12} \sqrt{\frac{T_s}{m\, v^{\frac{2}{3}}}} = \text{from 1 to 50 times } 10^{12}$$

for most monatomic solids, where T_s is melting temperature, v is vol. in cubic centimetres of m grammes, m is atomic-weight.

The general conclusions as to molecular spacing are then :—

(*a*) **In crystalline solids the spacing is atomic, the distances from centre to centre varying from 2 to 8 times 10^{-8} cms.**

(*b*) **In colloidal solids and in liquids the molecules are stable and the distances between their centres vary from 4·0 to 16·0 $\times 10^{-8}$ cms.**

CHAPTER V.

HYPOTHESES AS TO MOLECULAR FORCE.

THERE have been numerous hypotheses as to the nature and law of molecular forces. The principal are the following :—

(1) Gravitation (Kelvin, de Tunzelmann).
(2) Kinetic (Tolver-Preston).
(3) Unique (Bayma, Mills).
(4) Electro-chemical :—

(a) *Major Valencies* (Nernst and Schönflies, J. J. Thomson).
(b) *Partial Valencies* (Thiele, Veles, Svedberg, Langmuir, Abegg).
(c) *Residual Field* (Madelung, Sutherland, Born, Landé, Fajans, Werner).

1. Multipolar systems.
2. Alternate-point systems.

(5) Electro-magnetic (Crehore, Langmuir, Parson, etc.).
(6) Enhanced gravitation (Maxwell).
(7) The granule and similar sub-atomic theories (Reynolds, Lodge, etc.).

These theories are all inter-related to various hypotheses to atomic and molecular constitution. The following fundamental assumptions have been made as the atomic theory has advanced :—

(a) Immaterial points with repulsion from the central point to a certain limit, beyond which there is attraction (Boscovich). Now considered to be a metaphysical abstraction, but of value as a mathematical device. Boscovich imagined a series of alternations of repulsion and attraction ranges, ending in Newtonian attraction.

(b) Essentially attractive and repulsive centres in concentric shell structures statically balanced, but oscillating and pulsating (Bayma). The idea of universally attractive and repulsive elements has not proved consistent with facts, and is purely speculative.

(*c*) Mutually attractive cores surrounded by ether envelopes, which are attracted to the cores, but mutually repulsive (Pictet, Redtenbacher). A vague form of the next hypothesis.

(*d*) Quasi-planetary systems with positively electrified nucleus or sphere of influence and numerous negative electrons in shells or rings, the outer units of which are detachable (Thomson, Rutherford, Bohr, Bjerrum, Debye).

It is practically now accepted that the atom consists of a core of " protons " or unit positive charges equal in number to the atomic weight, cemented by " nucleus electrons " equal in number to the excess of the atomic weight over the atomic " number." This core is very small (of the order of 10^{-13} centimetres). Surrounding it is an " atmosphere " of planetary electrons, equal in number to the " atomic number." The outermost shell or ring of these are the " valency " * electrons, eight or less in number, which give the chemical properties. These outer electrons are in a state of rotation or oscillation, and when sufficiently agitated give off radiation. According to the Bohr theory, the radiation is given off in discrete " quanta," the orbit of the electron shrinking by a definite distance for each quantum given off. When the atoms are linked in pairs they are bound together by the attraction of the excess positive charge (deficiency of an electron) on one side upon the excess negative charge (surplus of an electron) on the other. It may happen that there is no effective charge on the individual atoms when separated, and they are simply linked by the attraction of the core of one upon prominent electrons in the other. There is still a great deal of uncertainty as to the electro-magnetic effect of the moving electrons, and until this is cleared up the theory will be incomplete in its relations to cohesion. It is, however, as certain as can be under the circumstances that the electrostatic charge of the atoms, with or without the electrodynamic effects of the electrons, is the cause of the mutual attraction.

* " Valency " is an artifice evolved by chemists to indicate the fact that atoms tend to limit their mutual combinations to simple ratios. Expressed in terms of hydrogen, the limit is 8, but in actual hydrides the limit is 4. While very useful, the conception is not wholly consistent.

The twin charges of linked atoms form a doublet, and such doublets could cause a residual molecular attraction in gases, as indicated by Van der Waals' formula.

In the case of solids the conditions are rather different.

If the solid is a single crystal the linkage is between the structural units which are the atoms themselves, and is of the same kind as is alluded to above in a pair of atoms in the gas molecule, but *every* juxtaposed pair seems to cohere to some extent. On some planes the cohesion may be much weaker than on others. If the solid is amorphous—*i.e.*, consists of minute crystals with interstitial films—the cohesion conditions change at the boundaries of the minute crystals. In the films there is probably a chain arrangement of the molecules extending from face to face, and along these chains possibly the inverse fourth rule applies, but only within a distance not much greater than the diameter of a molecule, and at the ends of the chains there is an atomic linkage with the nearest atom of the crystal. This is expressed in the terminology of metallurgy by saying that the grains are connected with super-cooled "liquid" films. These films are the main source of the strength of an ordinary solid, and the crystals often fracture before the cementing films. Large crystals behave in a manner quite differently from aggregations of small crystals, shearing rather freely on the grating planes.

In the case of "gels" the stiffness and tenacity is similarly due to the rigidity of the thin water films, the criterion being apparent that the thickness of the film must be small enough to compare with the effective range of the molecular forces, so that a "mechanical" linkwork from surface to surface can form. Surface-tension films are inclined to be of this character also.

Analysis along these lines for crystals indicates two possible types of cohesive structures :—

(*a*) A lattice of atoms each acting as a point charge located *at its centre*, attracting dissimilarly charged atoms and repelling similarly charged atoms (with some additional peripheral effects due to the electric fields).

(*b*) A lattice of multipolar atoms (at least doublets of two charges) with force centres *at or near the periphery* and geometrical centres respectively, with similar peripheral repulsions.

Strong arguments of a quasi-metaphysical character have often been urged in favour of a general inverse-square law (particularly on the score of simplicity). Such a law could only be applicable to cohesion if the resultant were a differential of attractions *and repulsions* following the law, although Rayleigh favoured a differential effect which itself varies inversely as the square of the distance.

(1) **The Gravitational Hypothesis.**—So great a physicist as Kelvin (*Trans. Roy. Soc. Edin.*, April 21, 1862, vol. iv.; Pop. Lect., vol. i.) held the Newtonian gravitation view, considering that the molecules attracted very strongly at close proximity owing to their density. He does not seem to have made any computations, but apparently his idea was that great density in the atomic masses (*i.e.*, minute volumes) would permit close approximation, but there is a paradox in this that the general density of the solid would also be increased. Newton does not seem to have held a gravitational view of cohesion.*

No conceivable modification of the internal distribution of the mass can really be adequate, since the gravity bond is a function of the masses *and* molecular distances *which are inter-related.*

In order that two molecules shall cohere with forces actually known to exist in the molecules of minute drops (when the effect of the whole mass is relatively small), say, even as little as 10^{-8} dynes, the distance between the centres needs to be as little as 10^{-23} cms., millions of times smaller than the diameter of an electron. This argument is conclusive as against the identification of cohesion with Newtonian gravitation (see Chatley, *Phil. Mag.*, vol. xl., Aug. 1920).

* "He (*i.e.*, Newton) supposed that there was such an attraction, which, as the distances were diminished, increased in such a manner that at contact it was exceedingly great; and when the primary particles touched one another along continuous planes, and thus in an infinite number of points, this attraction became infinitely greater than when primary particles touched primary particles in a definite number of points."—Boscovich, *Phil. Nat. Theoria*, 1763, § 409.

"The attractions of gravity, magnetism, and electricity reach to very sensible distances, and so have been observed by vulgar eyes, and there may be others which reach to so small distances as hitherto escape observation; and perhaps electrical attraction may reach to such small distances, even without being excited by friction."—Newton, "Optics," Supplementary Questions, p. 351, Second Edition, 1718.

The only manner in which gravitation can be conceived to produce a force sufficient to account for cohesion is if the mass of the atom is concentrated in a number $\left(\geqq 6\right)$ of minute *peripheral* points which cohere to their similar neighbours on other atoms. (Electrical forces can be involved to hold them together within the atom, but, if so, the electrical effects on the neighbours in other atoms would vastly exceed the gravitational ones.)

Thus, if we suppose that the cohesive strength of iron is 10^{-5} dynes per atom, and the mass of the atom (say 10^{-22} grams) is concentrated in six peripheral spherulets, which are each in contact with a similar spherulet on the neighbouring atom, a gravitational force of 10^{-5} dynes between such a pair of spherulets will suffice for cohesion between atoms, *although it in no way explains the stability of the atom itself.*

Writing

$$\frac{\mathrm{G}\, m^2}{d^2} = 10^{-5},$$

we have

$$d = \sqrt{\frac{6{\cdot}6 \times 10^{-8} \times (10^{-22})^2}{36 \times 10^{-5}}} = \text{approx. } 10^{-24} \text{ cms.}$$

The effect of other spherulets upon the pair is negligible, as they are at distances of the order of 10^{-8} cms.

The diminution of cohesion with separation is at an enormous rate, and quite irreconcilable with actual experience. This consideration, together with the entire absence of any explanation of the structure of such atoms, is decisively adverse to the hypothesis.

The only case in which gravitation can produce stresses comparable with the bonds which actually exist in material is at considerable depths in a very large mass. Thus, disregarding the variation in gravity (which varies approximately as radius from the centre), at a depth in the earth where the superincumbent weight per unit area is equal to the stress, that stress will be produced by gravitation. Using $g = 981$ and $\rho = 2{\cdot}5$,

$$981\, \rho\, h = 10^9 \; (= 1 \text{ ton/cm.}^2),$$

or, say, $\rho\, h = 10^6$; $h = 4 \times 10^5$ cms. $= 4$ kilometres.

At such and greater depths substance is liable to be crushed if there is space for lateral motion, and at a somewhat greater depth the crystallising forces are neutralised so that atomic structure may be there modified by the pressure, apart from temperature considerations.

Tait (" Properties of Matter," p. 145, 1890) points out that a body with a radius of 400 miles could have a gravitational mean stress on a diametrical plane equal to the tenacity of steel.

(2) **The Kinetic Hypothesis.**—Tolver-Preston * had a theory that cohesion is due to kinetic energy analogous to the mutual attraction of vibrating tuning forks. Except in so far as an electro-magnetic field might be regarded in this way, such an idea is at once disproved by the fact that cohesion varies in an inverse manner with the temperature, and is apparently a maximum at absolute zero.

(3) **Hypothesis of an Unique Energy.**—This is a perfectly reasonable idea, but its probability is reduced by the consideration of Ockham's razor (*i.e.*, the argument from simplicity). If it could be shown that cohesion followed the inverse-square law at all distances, it would be necessary, but is inconsistent with the existence and intensity of gravitation.

The most recent hypothesis as to cohesion which involves an inverse-square rule for the attraction is that of J. E. Mills (*Journ. Phys. Chem.*, **6**, 209, 1902; **8**, 383 and 593, 1904; **9**, 402, 1905; **10**, 1, 1906), quoted by Young (" Stoichiometry," 1908), and Edser (*Brit. Ass. Rep. Four. Coll., Chem.*, pp. 42-44, 1922).

Mills calculated the heats of vaporisation of a large number of substances over a wide range of temperature by means of the standard thermodynamic formula

$$L = \frac{T}{J}(V_v - V_L)\frac{dp}{dt}$$

where L is the latent heat (per unit mass),
T is the temperature,
J is the equivalent of heat ($4{\cdot}2 \times 10^7$ ergs per small calorie),
V_v is the volume of unit mass in vapour state,
V_L is the volume of unit mass in liquid state,
dp/dt is the rate of change of vapour-pressure with temperature,

* " Physics of the Ether," 1875; also various papers in the *Phil. Mag.*, 1877-1881.

and showed that the formula below obtains

$$(\mathrm{L} - \mathrm{E}_1)\ (\sqrt[3]{s_{\mathrm{L}}} - \sqrt[3]{s_v}) = \text{constant}\ (\mu^1),$$

where E_1 is the external heat-work, s_{L} and s_v are the densities of vapour and liquid.

Only small divergencies from experiment were noticed. By substitution of the molecular distance for the densities this expression is seen to have the form of the potential of a central molecular force varying as the inverse square of the molecular distances.

$$\lambda_1 = \mathrm{L} - \mathrm{E}_1 = \mu^1\,(\sqrt[3]{s_{\mathrm{L}}} - \sqrt[3]{s_v}) = \mu^1\left(\frac{1}{\sqrt[3]{v_{\mathrm{L}}}} - \frac{1}{\sqrt[3]{v_v}}\right)$$

$$= \mathrm{M}\left(\frac{1}{d_{\mathrm{L}}} - \frac{1}{d_v}\right).$$

Mills argued that, if the molecules are evenly distributed, if the number does not change with vaporisation, if no energy is spent in intra-molecular work, and if the attraction does not vary with the temperature, it necessarily follows that "the law of molecular attraction is similar to that of gravitation as far as the variation of the force with the distance is concerned."

The discrepancy with the other lines of argument is very grave, and, as a matter of fact, there is a current expression due to Bakker,

$$\lambda_1 = a\left(\frac{1}{v_{\mathrm{L}}} - \frac{1}{v_v}\right),$$

which is in absolute contradiction to Mills' formula and agrees with Van der Waals'.

The corrections to Van der Waals' equation for many substances do imply some change of the molecular attraction with temperature, and although the present writer has suggested that perhaps no such correction is necessary under adiabatic conditions, this probably explains the disagreement between Mills and Bakker. Still another suggestion is that in the process of vaporisation it is only the surface tension which has to be overcome, and it may be that this causes a fictitious resemblance to an inverse-square attraction acting through the volume expansion from the liquid to vapour states.

Young says :—

" J. E. Mills has brought forward strong evidence in favour of the view that the force, like that of gravity, varies inversely as the square of the distance, but it has generally been considered that the distance must be raised to a higher power.

" It has been suggested by Lord Rayleigh that there are two forces acting between molecules, one of attraction, the other of repulsion, and that the force of repulsion varies inversely as a higher power of distance than that of attraction. In that case the resultant force simulates a single force varying inversely as the (approximate) square of the distance."

This supposition seems, however, most improbable. The forces at the same distances are prodigiously greater than those of gravitation, and yet if they diminish according to the same rule they should be equally effective at the same distance—*i.e.*, they should be identical in all respects. Also, in such case strength should increase with the size of the test piece, whereas the tendency is rather the reverse.*

It seems certain that there is some flaw in the reasoning of Mills (see p. 42 as to Edser's criticism, which indicates that Mills is in error by reason of neglecting temperature changes). Rayleigh (*Phil. Mag.*, 1890; *Sci. Pap.*, **3**, 397) concluded that n was indeterminate by integration methods, but Edser has shown that this is not true if the molecular interval is taken as a limit.

(4) **Electrochemical Hypothesis.**—Since cohesion is a paramount property of solid crystals which consist of atomic lattices, it is reasonable to suppose that the force of cohesion is only one phase of the interatomic force of chemical affinity. This is known to be principally electrostatic. Some difficulties arise, however. If atoms are capable of forming bonds in all directions (or at least with six adjacent atoms along three conjoint axes), it is difficult to understand why free molecules in gases are so frequently diatomic. This problem is still more complicated if we regard the atomic bonds as taking place only through as many free electrons as the valency.†

* If all interatomic bonds are electrostatic the inverse square law applies as between any pair, but the distances are not necessarily equal to the atomic interval, and the linkages being alternately attractive and repulsive, the cohesion cannot be said to follow an inverse square law.

† It is quite certain that under some conditions atoms cohere in a number in excess of the valency. Moreover, zero-valent atoms cohere at low temperatures.

Abegg has, it is true, suggested that there are altogether eight possible valencies, and Thiele has postulated split or "partial valencies" to account for certain anomalies of stereo-chemistry. Stark first conceived an atom which had from one to eight free electrons polarising its surface. Lewis and Langmuir have elaborated the idea of polar atoms with much success.

As has been shown, cohesive attractions as computed from latent heat are of the order of one-hundredth or less of inter-atomic attractions as computed from electrochemistry, and we can well suppose that there is a stray field at small distances due to the non-coincidence of otherwise neutralising charges.

Sutherland suggested that molecules consist of doublets whose mutual attraction (like that of small magnets) is the source of cohesion. One difficulty here is that there is an equal likelihood of repulsion if the doublets are oppositely presented, even though the minimum potential condition favours cohering forms. If, on the other hand, the positive and negative charges are supposed to act centrally in the various atoms, certain cohesion configurations can be conceived, but this condition only occurs in certain types of compound.

The first complete exposition of the electrochemical theory of cohesion is that of W. Sutherland (Melbourne), which is contained in a series of papers contributed to the *Philosophical Magazine*, as follows :—*

5. xxii. (1886, Aug., Pt. I., No. cxxxv., p. 81).—" On the Law of Attraction amongst the Molecules of a Gas."
5. xxiv. (1887, July and Aug., No. cxlvii., pp. 113 and 168).—" On the Law of Molecular Force."
5. xxvii. (1889, p. 305).—" On Molecular Refraction."
5. xxxii. (1891).—" A Kinetic Theory of Solids."
5. xxxv. (1893, p. 211).—" The Laws of Molecular Force."
5. xxxvi. (1893, pp. 150 and 507).—" The Laws of Molecular Force."
5. xxxix. (1895).—" Further Studies in Molecular Force."
5. xl. (1895).—" Fundamental Atomic Laws of Thermochemistry."
6. ii. (1901).—" The Cause of the Structure of Spectra."
6. iv. (1902).—" The Electric Origin of Molecular Attraction."
6. vii. (1904).—" The Dielectric Capacity of Atoms."

---

* See also J. P. Kuenen, " Die Zustandsgleichung der Gäse und Flussigkeiten " (Wissenschaft Series) and Van der Waals, " On the Continuity of the Liquid and Gaseous States of Matter," *Phys. Soc.*, " Physical Memoirs," vol. i., Part III., 1888.

6. vii. (1904, May).—" The Electric Origin of Rigidity and Consequences."
6. xiv. (1907).—" Ionisation in Solution and Two New Types of Viscosity."
6. xvii. (1909).—" The Electric Origin of Molecular Attraction " and " Molecular Diameters."
6. xviii. (1909, Sep.).—" The Ions of the Gases."
6. xix. (1910, Jan.).—" The Fundamental Constant of Atomic Vibration and the Nature of Dielectric Capacity " and " Molecular Diameters."

Sutherland's earliest papers are very clear as to his hypothesis that " *the molecules of a gas attract one another with a force inversely proportional to the fourth power of the distance between them and directly proportional to the product of their masses*," and that a similar relation obtains in liquids and solids. In the later papers he passes from a *mass* relation to an *electrostatic* one, on the assumption that the molecules are electric doublets which will mutually react in much the same manner as small bar magnets.

It is obvious that a pure mass relation cannot hold in conjunction with the simple inverse fourth rule for the distance, since if it did so it must be substituted for the Newtonian law universally, as the coefficient is even larger than the Newtonian coefficient. Strange to say, Sutherland, while specifying that his first molecular force rule only applied within " the range of molecular force " in the Laplace sense (say equal to the thickness of a capillary film), did not attempt to explain why it should be so limited.*

On the assumption of doublets, the rule of attraction will be that of the inverse fourth as between any two molecules (together with a mutual torque tending to produce a tractative

* In order that a mass effect following the inverse fourth power of the distance shall be small compared with Newtonian gravitation at ordinary distances, a limit must be placed on the coefficient which makes it too small to account for molecular force.

Example.—If cohesion is negligible compared with gravitation at 1 mm. distance

$$\frac{G}{(0{\cdot}1)^2} > \frac{K}{(0{\cdot}1)^4}\,; \text{ i.e., } K < \frac{G}{100}.$$

If molecular distance $= 10^{-8}$ cms. and mass $= 10^{-20}$ gr., the attraction is less than

$$\frac{6{\cdot}6 \times 10^{-8}}{100} \times \frac{10^{-40}}{10^{-32}} = 6{\cdot}6 \times 10^{-18} \text{ dynes,}$$

which is much too small, even when allowance is made for the additive effects of a large number of molecules.

attitude, which torque follows an inverse cube rule, and is, therefore, more effective at a distance than the attraction), but as the mutual presentation of the molecules is indifferently attractive or repulsive, the external resultant of a group of molecules is practically zero. In the case of crystals, where the atoms are the units and are, broadly speaking, alternately positive and negative, there are some configurations in which the space rate of decrease is not quite so rapid; in general, while it may be true that the force varies as the inverse fourth within a distance of one molecular diameter, it must diminish at a much greater rate for greater distances, except for isolated pairs of molecules as in a rare gas.

An apparent mass relation may occur for any one substance, even if the electric charges are the real seat of force, by reason of the fact that the number of charges varies as the mass, but this, of course, is not true as between different substances.

Sir J. J. Thomson (*Phil. Mag.*, April, 1922) shows very plausibly that the crystalline state may be logically explained on the assumption that the atoms are linked by superficial electrons, corresponding in number per atom to the valency, so that a kind of crystal lattice system applies to these valency electrons as well as to the atoms. The electrostatic forces which form the basis of cohesion will then be identical with the chemical ones, except that there is a residual cohesion affinity in a neutral group, due to the non-coincidence in space of the mutually neutralising charges.

The most important features of Sutherland's later theory are that the atoms or molecules are polarised, the poles being unit electric charges (" electrons "), which may or may not be separable, but are not coincident or concentric in the particle, so that they have a moment. The characteristic parameter of molecular attraction is M^2l, where M is the molecular mass and l is two-thirds the " virial " parameter for unit mass of substance. With an inverse fourth relation for the mutual attraction of molecules which exists at small distances $l\rho$ is the potential energy of unit mass of substance of density ρ. If m is the mass of a molecule, it may be replaced for M, and the following equation be written

$$m^2l = e^2s^2,$$

where e is the electron charge ($4{\cdot}8 \times 10^{-10}$ e.s. units), and
s is the distance between the two charges.

If there is a dielectric of specific inductive capacity K

$$m^2 l = e^2 s^2 / \mathrm{K}.$$

Rigidity at absolute zero is electrostatic, but its variation with temperature is kinetic,

$$\frac{n}{\mathrm{N}} = l - \left(\frac{\theta}{\mathrm{T}}\right)^2,$$

where n is rigidity at absolute temperature θ,
T is melting temperature (absolute),
N is rigidity at absolute zero.

The following relations hold good :—

$$\frac{21\,\mathrm{N}\,b\,\mathrm{M}}{\mathrm{J}\,c\,\mathrm{M}} = 4{\cdot}6\,\rho\,; \quad \mathrm{M}^2 l = 0{\cdot}61\,\mathrm{J}\,(\mathrm{M}/\rho)/b\,; \quad c\,\mathrm{M} = 6{\cdot}4\,;$$

$$\mathrm{N} = 2{\cdot}3\,\frac{\mathrm{M}^2 l}{(\mathrm{M}/\rho)^2} = \frac{2{\cdot}3}{\mathrm{K}} \cdot \frac{e^2 s^2}{(m/\rho)^2},$$

where b is the coefficient of linear expansion,
M is the atomic mass,
c is the specific heat,
ρ is the density,
J is the mechanical equivalent of heat.

Sutherland gives the periodic time of vibration of an atom as

$$\frac{2\,a}{\delta\,(2/\rho\,\mathrm{K})^{\frac{1}{2}}},$$

where a is the radius of an atom containing the doublet, and

δ the electric surface density $= \sqrt{\dfrac{3\,\mathrm{K}\,\mathrm{N}}{2\,\pi}}$.

He states that the quantity l mentioned above is equivalent to Van der Waals' "a," and employs the following equation in Van der Waals' original form :—

$$l = \frac{27\,\mathrm{R}^2\,\mathrm{T}_c^{\,2}}{64\,p_c}.$$

On the question of the stability of molecular configurations, Sutherland says :—

"In matter contiguous molecules adjust their axes so that these form axial lines, along each of which the axes are similarly directed, whilst the axial lines are oppositely polarised. This arrangement is one of minimum electric potential energy, and causes each molecule to attract its six nearest neighbours with repulsions and attractions beyond these six tending towards an average null effect. At the same time it gives no electric moment to any ordinary piece of matter, the sum of the electric moments of all the molecules being nothing." —(*Phil. Mag.*, **6**, xix., I., p. 19).

It is not quite clear how Sutherland's hypothesis is affected by the modern concept of the atom as a complex of electrons. Apparently he considers that only the superficial negative electron (or electrons), and that part of the positive nucleus charge which neutralises it (or them) are effective, but it is not easy to see why all the other negative electrons, which may also have an electric moment, do not enter into the problem.

Sutherland and also Madelung suggest that the elastic forces resisting mechanical strain are identical with those which determine the optical vibrations of a solid material, and indicate the frequency of the infra-red vibration as being determined by the quotient of the velocity of sound in the solid divided by the molecular interval. In other words, " the vibrations of the highest frequencies (*i.e.*, the molecular vibrations) are perceptible to our senses, not as sound vibrations, but as light vibrations, and that the highest possible frequency is the highest frequency in the infra-red shown by the absorption spectrum of the body " (N. Campbell).

So far as this can be tested, it appears to be correct, the molecular frequencies in transparent solids being of the required order, 10^{12} to 10^{13} per second. Since optical vibrations in the ether are fundamentally electromagnetic, continuity seems to require that the vibrations in the originating solid shall also be electric in character, but, of course, this argument is equally applicable to electromagnetic hypotheses as to cohesion.

Sutherland refers to two writers as having anticipated him as to general principles :—

R. A. Fessenden (*Phys. Rev.*, x., 1900).
Reinganum (*Phys. Zeit.*, 1900, and also vol. ii., 1901, p. 241; *Ann. der Phys.*, **4**, x., 1903; Drude's *Annalen*, x., 1903, p. 331).

Fessenden used an " equation of state "

$$\left(p + \frac{c}{v^{\frac{4}{3}}}\right) (v - b) = \mathrm{R\,T},$$

and refers to articles in the *Electrical World*, Aug. 8/22, 1891, and in *Science*, July 22, 1892, and March 3, 1893.

He says :—

" The phenomena of rigidity, elasticity, and tensile strength are quite well explained by supposing the atoms are electric doublets and have charges on them of the same size as those called for by Faraday's laws of electrolysis."

Fessenden gives formulæ for elasticity and strength in terms of the atomic volumes, based on the above equation of state, which is obviously founded on an inverse square law ($v^{-\frac{4}{3}} \propto d^{-4}$, which multiplied by d^2 for area $= d^{-2}$). As this disagrees entirely with Van der Waals' gas law, the expression cannot be regarded as correct.

Sutherland held that gravitational attraction was a distinct effect, not to be associated with molecular attraction which becomes zero for large separations. He conceived that unlike charges attract to a degree which exceeds the repulsion of like charges in the ratio $1 + 10^{-43} : 1$. This, of course, is no explanation of gravitation at all, but merely a method of expressing it, except in so far as it identifies mass with charge.

One of the most vital features in the discussion of Sutherland's hypothesis of molecular attraction is the question as to the ratio of the distance between the constituent charges " s " and the distance between the centres of the molecules, or, in other words, the extent to which the molecules occupy space in a solid. If the ratio does not differ much from unity, then the law of diminution of attraction follows a higher power than the fourth of the reciprocal of the distance. If the ratio is small, as some theories of atomic structure suggest, then the inverse fourth is fairly correct, and there is a good agreement with Van der Waals' equation of state.*

* Edser (1922) maintains that Van der Waals' form is reconcilable with a form

$$f = c\,d^{-8}$$

as between individual pairs of molecules of non-metallic fluids which are not associated in the liquid state.

Still another difficulty lies in the question of the motion of the electrons. Madelung, Born, Landé, and Fajans (see *Science Abstracts*, 1919, *et seq.*) * in recent years have shown that there is a repulsion which follows for alkaline halides an inverse tenth power of the interionic distances; perhaps this should be identified with the kinetic repulsion which brings the molecule to equilibrium in the solid state.

Apropos of the electro-chemical theory of cohesion, something should be said of the Lewis-Langmuir "octet" theory. According to this, the electrons in the "atmosphere" of each atom are arranged in concentric shells. The most stable configuration of electrons in each shell is that of eight, and when this occurs naturally the element is of zero valency (neon, argon, etc.). Such elements do not combine chemically, and are gaseous except at very low temperatures. If the peripheral number is not eight, atoms brought close together tend to form groups of eight electrons—*e.g.*, Sodium, which has eleven electrons, loses one to chlorine, which has seventeen, so that the shells which are originally as follows :—

Sodium (neutral) . 2........8........1
Chlorine (neutral), 2........8........7

become

Sodium (positive), 2........8........0
Chlorine (negative), 2........8........8

This leaves each set a complete octet and with an electrical charge, and these charges being of opposite sign, there is a mutual attraction which, in the case of a number of atoms, allows a configuration of alternate atoms to form a cubic "lattice."

If it is numerically impossible for each such complete sets of independent "octets" to be formed by the transference of electrons,† atoms may share certain *pairs* of electrons in common so as to form octets—*e.g.*, N_2O and CO_2 :—

* M. Born, "Der Aufbau der Materie," Berlin, 1922; Born and Landé, *Verh. d. D. Phys. Soc.*, **20**, p. 210, 1918; E. Madelung, *Phys. Zeit.*, **19**, p. 524, 1998; M. Born. *Verh. d. D. Phys. Ges.*, **21**, p. 13, 1919.

† The so-called "*co-valency*" bonds. This rule only applies to very stable "resting" molecules such as N_2O, CO_2, H_2O, NH_3.

$$\begin{array}{lll} 2N, & \left\{\begin{array}{l} 2\ldots.5 \\ 2\ldots.5 \end{array}\right\} & \\ O, & 2\ldots.6 & \end{array} = \begin{array}{l} 2 \\ \quad\ldots.8 \\ 2 \\ \quad\ldots.8 \\ 2 \end{array} \qquad \begin{array}{lll} C, & 2\ldots.4 & \\ 2O, & \left\{\begin{array}{l} 2\ldots.6 \\ 2\ldots.6 \end{array}\right\} & \end{array} = \begin{array}{l} 2 \\ \quad\ldots.8 \\ 2 \\ \quad\ldots.8 \\ 2 \end{array}$$

In these cases three atoms form only two octets. These bonds are much stronger than those in the previous type, but are more localised, so that, whereas some kind of central force law *may* apply to the first class (called "polar" or "heteropolar" compounds), the second class (called "non-polar" or "homopolar") has strong vectorisation.

The fact that elements of zero valency still cohere under certain circumstances *may* be explicable by electrostatic variations of field, but many students invoke additional forces—*e.g.*, electromagnetic forces due to the motion of the electrons. According to Bohr, the electron structures are stable configurations of *orbits* or orbit planes, not of fixed electrons. Such orbit planes would normally have electromagnetic fields.

N. Campbell ("Modern Electrical Theory," 1913) remarks :—

"The force which one atom exerts on another is likely to be greater if the valency electron is not very near to the atom to which it is attached, so that the system of atom and electron forms an electric doublet of considerable moment. Sutherland has attempted to work out a complete theory of the mechanical properties of substances on the view that the forces between the molecules are those between electric doublets, and he finds, of course, that the tensile strength should be greater the greater the moment of the doublets. If the doublets are those formed by the valency electrons and the positive charges to which they are attached, the intimate connection between chemical and mechanical properties is explained at once. Indeed, the 'molecular forces' of a substance are to be regarded as differing only in degree and not in kind from its chemical forces."

Benjamin Moore and others have pleaded strongly for true "molecular affinities" between internally atomically saturated molecules. Such molecular affinities, according to this hypothesis, explain water of crystallisation, biogen structure, the behaviour of colloid particles, and also cohesion. In this connection it should be pointed out that Langmuir, the

Braggs, Kossel, and others hold that there are three kinds of chemical bond :—

(1) Between atoms with excess and deficiency of electrons.
(2) Between atoms and electrons in other atoms.
(3) Between atoms merely in virtue of stray field.

Werner's "co-ordination" hypothesis lays great stress on the last kind.

The consistency of the Lorenz-Fitzgerald-Einstein theory of the (apparent) contraction of rapidly moving bodies also is consistent with electrical intermolecular forces.

From a dimensional point of view, the argument for an electro-chemical nature for the cohesive attraction is very strong, and may be briefly stated as follows :—

(*a*) Chemical affinity is known by all the phenomena of electro-chemistry to be due to the separation of unit charges.

(*b*) All the evidence points to the electrostatic magnitude of these unit charges being about 5×10^{-10} e.s. units, so that the forces which act at atomic distances of the order of 10^{-8} centimetres are of the order of 10^{-3} dynes.

(*c*) The net forces of cohesion are of the order of 10^{-5} dynes per atom at the usual maxima.

(*d*) Non-coincident pairs of charges of equal and opposite magnitudes attract one another, but are, as a whole, neutral at a distance of a few times their mutual distance.

(*e*) The attractive forces in the neighbourhood of such pairs of non-coincident charges may easily be as small as one-hundredth the direct attraction between them, and can vary tremendously with radial or angular displacement.

(*f*) The forces of cohesion are frequently of the order of one-hundredth the forces of chemical affinity, and similarly the latent heat of fusion tends to be of the order of one-hundredth the heat of chemical combination.

(*g*) THEREFORE, the forces of cohesion are dimensionally of a magnitude which could arise in connection with a satisfied chemical affinity in the immediate neighbourhood of the neutralising atoms, and, since there is no other adequate cause available, on the principle of the economy of principles, this is the cause.

The only weak point * in this argument is that the know-

* The cohesion of the zero-valent elements in the solid form shows that either these elements have a rudimentary chemical action or that a low value of cohesion may be due to non-chemical causes.

ledge of the positions and motions of the unit charges is not DEFINITE, and there is also an uncertainty as to whether, on such a minute scale, the charges really follow the simple laws of electrostatic force between imaginary point charges. The possible or rather probable existence of rapid motion in the charges introduces the question of electromagnetic action. This aspect of the question is, however, best considered in connection with the hypotheses which regard electromagnetism as the major factor.

(5) **Electromagnetic Hypothesis.**—The effects of electromagnetism on surface tension of fluids are considerable. It has been shown by Svedberg that in a liquid complex chain molecules set themselves parallel or athwart the magnetic field. Langmuir also found from chemical considerations that the surface molecules in films of complex organic liquids are oriented towards the surface so that surface tension is due to congruous configuration of molecules and its modification by electromagnetism indicates a connection between the two.

Attention has been drawn by Parson ("A Magnetic Theory of the Structure of the Atom," *Smithsonian Misc. Coll.*, vol. lxv., No. 11, 1915) to postulated "ring electrons," each of which consist of an annular charge revolving with the speed of light, and have a bipolar magnetic field. The superficial ring electrons of an atom will arrange themselves to form a stable structure, and the joint electrostatic and electromagnetic effects cause both chemical affinity and cohesion. In the case of eight superficial electrons (as in gas of zero valency) the electromagnetic residual field is the principal cause of cohesion. This hypothesis agrees rather well with chemical requirements, which somewhat favour a static balance of electrons, but is difficult to reconcile with many atomic phenomena (*e.g.*, penetration of atoms by alpha rays, etc.), which are more consistent with the Bohr theory of orbit systems whose planes pass through the nucleus.*

Some argument in favour of cohesion being electromagnetic is provided by the very existence of fixed magnetism, but this is purely speculative. If the hypothesis were correct, it

* According to the elaborations of the Bohr theory, the orbit planes may be arranged systematically, and so have a general electromagnetic field. This may perhaps be invoked to explain the cohesion of the zero-valent elements as in Parson's theorv.

would appear that primary attraction (chemical affinity) is electrostatic and secondary attraction (cohesion) electromagnetic. There is, however, a higher probability that both forms of energy play a part in both phenomena. An electromagnetic source for repulsion is very probable, but here also kinetic effects of a purely mechanical character must also figure, together with the electrostatic repulsion of similar charges. The action of a capillary electrometer shows that surface tension can be affected by purely electrostatic forces. The modifications of light passed through transparent stressed solids (Coker's method) indicate electromagnetic forces in connection with mechanical stress. Magnetic pairs (like electric doublets) at close proximity attract or repel according to the inverse fourth power of the mutual distance, and also have a reciprocal torque which follows the inverse third power of the distance.

Dr. Crehore has set forth an electrical theory of gravitation (*Electrical World*, 1912; *Scientific American Supplement*, No. 1,893, April 13, 1912, p. 238), in which, by assuming that the velocity of the electrons in their orbits about the centre of the atoms differs only slightly from the velocity of light, he arrives at a formula for the mutual attraction of two atoms which may be reduced to the form

$$t_2 = \frac{G \, . \, m^2}{(d^2 - a^2)},$$

where a is the radius of the electronic orbit.

His hypothesis as to the electronic velocities does not receive confirmation from spectroscopic analysis,* but his formula is an interesting type.

He states that his equation (the electrical one from which the above is reduced) is true for both great and small distances, but "it must be remembered that in deriving this formula the magnetic induction in the sheet accompanying the corpuscle was considered to be uniform throughout the volume of the positive sphere of the attracted atom. When the distance is very small, the induction should be integrated throughout the volume, and the expression must not be used in case d is nearly equal to a."

* In the Bohr system the spectroscopic vibrations are not direct indicators of the orbital frequencies, as was the case with "classical" electrodynamics.

Even accepting his postulates, the last-mentioned reservation makes the application of the formula to cohesion rather doubtful, and in any case the difficulties of a " mass squared " formula apply to this type, although they might be to some extent masked by the changes in the denominator for different atoms at equal spacing.

Crehore's later hypotheses (*Physical Review*, June, 1917) give a form

$$t_2 - t_1 = \frac{f_1(v)}{d^4} - \frac{f_2(c)}{d^6},$$

where f_1 (v) is a function of the velocity of the infra-atomic electrons, and

f_2 (c) is a function of the charges on the atoms.

Crehore makes certain rather arbitrary assumptions, which may or may not be warranted.

(6) **Enhanced Gravitation.**—Almost from the time of Newton investigations have favoured a cohesion hypothesis closely analogous to the Newtonian law of gravitation, but with a high index of variation. The main difficulty is, however, to see why two methods of joint mass action following different rules should exist, and the present writer formerly endeavoured to make the two continuous by writing the index of variation as a function of the distance, thus :—

$$t_2 = \frac{G\, m^2}{d^{2 + \frac{n\, d_0}{d}}}$$

where d_0 is the value of d at absolute zero temperature, or

$$t_{20} = \frac{G\, m^2}{d_0^{\,2 + n}}.$$

If n is 4, which value does approximately satisfy some of the conditions, then t_{20} varies as s_0^2, where s_0 is the maximum density. This is approximately true for analogous chemical forms, but is *not* generally true for all forms.

A kind of polarity in a mass can occur with this equation, since for all integrated laws of central action other than the inverse square the equivalent focus is not geometrically central, but depends on the position of the attracted body.

The rate of diminution of attraction agrees fairly well with some cases of strength of solid materials, but is much too rapid for the gas state. This flaw would not matter if "molecular pressure" in gases could be proved to be a fiction due to association (see p. 20).

Reference may be made to the writer's papers to the Physical Society of London from 1915-1924.

If we assume that the tensile resistance in a solid is due to the attraction between adjacent molecules only, and that those molecules attract according to an expression

$$\frac{G\,m^2}{d^\gamma},$$

where G is the Newtonian constant,
 m is the mass of a molecule, and
 d is the distance (centre to centre) apart of the molecules,

then we may equate the maximum tensile stress f acting on one molecule as follows :—

$$t_2 = f\,d^2 = \frac{G\,m^2}{d^\gamma} = \frac{G\,(\rho\,d^3)^2}{d^\gamma},$$

and so find that (ρ = density).

$$\gamma = 4 + \left\{ \log\left[\frac{G\,\rho^2}{f}\right] \Big/ \log d \right\} = 5{\cdot}5 \text{ to } 6.$$

Since

$$G = 6{\cdot}6 \times 10^{-8};\ \log G = \bar{8}{\cdot}8195 = -7{\cdot}1805.$$
$$\rho = 1{\cdot}0 \text{ to } 23;\ \log\rho = 0{\cdot}0 \text{ to } 1{\cdot}36;\ 2\log\rho = 0{\cdot}0 \text{ to } 2{\cdot}72.$$
$$f = 1{\cdot}0 \text{ to } 25{,}000 \times 10^6;\ \log f = 6 \text{ to } 10{\cdot}4.$$
$$d = 1{\cdot}0 \text{ to } 10 \times 10^{-8};\ \log d = -7 \text{ to } -8.$$

$$\therefore \quad \log\left(\frac{G\,\rho^2}{f}\right) \Big/ \log d = \frac{\log G + 2\log\rho - \log f}{\log d}$$

$$= \frac{-(7{\cdot}1805) + \left\{\begin{matrix}0{\cdot}0\\ \text{to}\\ 2{\cdot}72\end{matrix}\right\} - \left\{\begin{matrix}6\\ \text{to}\\ 10{\cdot}4\end{matrix}\right\}}{-7 \text{ to } -8} = 1{\cdot}5 \text{ to } 2{\cdot}0.$$

(7) The "Granule" and Similar Sub-atomic Theories.— There are several abstruse speculations as to ultra-atomic structure which indirectly supply hypotheses as to the cause of cohesion.

In "The Sub-Mechanics of the Universe" (Cambridge University Press, 1903), Osborne Reynolds deduced that cohesion and gravitation can be explained by the mutual attraction of "inequalities" (*i.e.*, deficiencies) in a universally diffused granular medium of "negative mass." He says :—

"Cohesion between the singular surfaces of negative inequalities results from the terms which were not taken into account in the first approximation which corresponds to gravitation. These secondary terms involve the inverse distance to the sixth power, and, therefore, have a very short range, and so correspond to efforts of cohesion of the singular surfaces as well as surface tensions having no effect unless the singular surfaces, or molecules, are within a distance very small compared with the diameter of the singular surface" (I., par. 85).

"In the analysis for the effort of attraction of negative inequalities the ratio of the volume of the grains absent divided by the volume enclosed by the singular surface has been neglected, and it is this simplification only which renders the law of attraction—as the inverse square—the law of attraction of the singular surface at a distance.

"But this in no way limits the variation of the stresses over those portions of the space in and between the parts of the two singular surfaces which are within indefinitely small distances of each other. Such limits can only be determined by taking into account the higher terms which have been neglected.

"This analysis I have not attempted. But it seems to me very important to notice this omission, as it appears that the attractions expressed by the higher powers of $1/r$, when the surfaces are indefinitely near, must be of great intensity, so that, owing to sudden variations, the work done in separating the surfaces must be extremely small.

"These characteristics are those of cohesion and surface tension, and they promise to account by mechanical considerations for the hitherto obscure cohesion between the molecules as belonging to the attractions resulting from the finite diameter of the molecules divided by the curvature resulting from distortion, or we might say the complement of gravitation" (xiv., par. 227, slightly abridged).

Reynolds' theory has never been accepted by physicists as an adequate theory of matter, partly on the ground of an alleged instability of the configurations which he deduced, but it was a most elaborate and interesting speculation. In relation to the present subject, his references to the inverse sixth power of the distance and the effect of the curvature of the surfaces of the molecules are very interesting. In so far as the mass relations of gravitation are retained, the same objection applies to this hypothesis of cohesion as to others containing the same mass condition.

Eddington in 1919 revived interest in Reynolds' granule as a physical concept related to gravitation in connection with the general theory of relativity.

The modern theories of atomic constitution throw considerable doubt upon the reality of the apparently simple character of almost all the fundamental concepts of physics. The inverse square rule is doubted for distances comparable with the diameter of an electron, the latter is doubted as a simple charge, energy is thought to be in discrete parcels or quanta, mass is variable with velocity, etc. All these refinements, which may not improbably lead into another "plane" of substance, lower than that of the atoms, are as yet to some extent mutually inconsistent, but some at least are real, and it may well be that part or even the whole phenomena of mutual attraction arises from differential effects which are as yet only suspected.

One of the most remarkable suggestions along these lines is that of Sir Joseph Thomson,—viz., that the force between two point charges is of the form

$$f = e^2 \,.\, u^2 \,.\, \sin (c\,u)/c\,u,$$

where e is the value of the charge, u is the reciprocal of the distance between the centres, and c is a constant. For small values of $c\,u$ (*i.e.*, relatively large values of the distance) $\sin c\,u/c\,u$ is unity, and the formula becomes the ordinary inverse square form, but for values of $c\,u$ more than 1·57 the ratio periodically changes from positive to negative through zero. The illustrious physicist suggested that these points of equilibrium correspond to the various oscillation positions indicated by the series of lines in spectra, and that the energy required to displace one charge from one such position to another is the standard quantum.

Obviously if point charges come into sufficient proximity this formula would indicate attractions towards positions of equilibrium which could only be disturbed by integral quanta of energy. Boscovich had an analogous hypothesis in the eighteenth century.

Still another idea is that of Sir Oliver Lodge, who once suggested an atom whose neutral or inactive part consisted of a mat of positive and negative electrons. Two such atoms brought into positions where positive electrons faced negative ones would experience attractions, while a slight lateral displacement would produce conditions of repulsion.

Since information of this character can only be arrived at by statistical methods and rather extreme extrapolation, it is not very reliable until it has been checked along several different lines of argument and experiment.

Rankine (1924) considers that no central force rule can express cohesion, since it depends on the mutual presentation of multipolar atoms, and the complex planetary electron swarms cannot behave simply. This does not, however, exclude the possibility of a central force rule as a fair approximation.*

Conclusion.—It will thus be seen that **there is still some doubt as to the real nature of molecular force, but there are unmistakeable indications that it is electrical, and not greatly inferior in magnitude to the electrostatic forces of chemical affinity.**

* Sir W. Bragg emphasises the tendency to shear on planes of crystallisation in pure substances and large crystals, and suggests that interlocking meshes of spicular crystals give the strongest mass. This leads to the idea that cohesion is most effective at certain points on the periphery of the atom. Hence central force rules referred to atomic intervals will have little value in the solid state, and cohesive strength varies tremendously within minute distances. Perhaps some success is possible if inverse square rules are applied to hypothetical doublet separations smaller than the atomic intervals.

CHAPTER VI.

INTERMOLECULAR REPULSION.

SINCE molecules exist in gases and liquids at appreciable distances apart, and even in solids the atoms are not in absolute contact, it is obvious that the mutual attractions are usually neutralised by equal and opposite repulsions (Edser's "intrinsic pressure"). When the molecules exert actual pressure on the surfaces which confine them, the repulsive forces must exceed the attractive. This is especially the case with the gaseous state, but is equally true of hydrostatic pressure or internal stress.

The force of repulsion in gases under relatively small pressures is given by the gas law as equal and opposite to the pressure, the force of attraction being neglected, as follows :—

$$f = p = \mathrm{R\,T}/v,$$

where R is the gas constant,
T is the absolute temperature,
v is the volume occupied by a gram molecule of the gas, and
p is the pressure.

Expressed in molecular terms, approximately

$$t_1 = p \,.\, d^2 = \mathrm{R\,T} \,.\, d^2/v.$$

Substituting for v, N $d^3/\sqrt{2}$, where N is the number of molecules per gram molecule and $d^3/\sqrt{2}$ is the volume occupied by a spherical molecule with equidistant spacing (rhombic dodecahedral), we have

$$t_1 = \sqrt{2}\,\mathrm{R\,T/N}\,d.$$

In other words, at low pressures and constant temperature the net repulsion between two molecules varies inversely as the distance between their centres.

In dense gases, using Van der Waals' equation, the gross repulsion equals the pressure plus the attraction or " molecular pressure " already discussed :—

$$t_1 = (p + \tilde{\omega}) \cdot d^2 = \mathrm{R\,T} \cdot d^2/(v - b),$$

where b is the volume of a gramme molecule at absolute zero (or, what is almost the same thing, in the solid state).

If the volume is written $v = k^3 \cdot d_0{}^3 \cdot \mathrm{N}/\sqrt{2}$, where $\mathrm{N}\,d_0{}^3/\sqrt{2}$ equals b,

$$t_1 = \sqrt{2}\,\mathrm{R\,T} \cdot k^2 \cdot d_0{}^2/\mathrm{N}\,d_0{}^3\,(k^3 - 1)$$
$$= \sqrt{2}\,\mathrm{R\,T} \cdot k^2/\mathrm{N}\,d_0 \cdot (k^3 - 1),$$

which is approximately equal, for values of k not greatly exceeding 1, to

$$\sqrt{2}\,\mathrm{R\,T/N}\,d_0 \cdot 3\,(k - 1).$$

In liquids the repulsion exceeds the attraction by at least the vapour pressure, and we may write

$$t_1 = (\tilde{\omega} + p_v) \cdot d^2.$$

A gas pressure higher than the vapour pressure compresses the liquid and causes increased repulsion to correspond.

In solids, where there is no stress, the attraction balances the repulsion. Any difference corresponds to " stress," so that tensile stress in molecular terms is represented by the expression :—

$$\text{Tension, per molecular pair} = t_2 - t_1,$$

and compression similarly :—

$$\text{Compression per molecule pair} = t_1 - t_2.$$

These stresses can only be produced in conjunction with strain—*i.e.*, change in the distance between the centres of the molecules.

As an example of the magnitude of the gross repulsion, if we use the formula

$$t_1 = \sqrt{2}\,\mathrm{R\,T/N}\,d_0 \cdot 3\,(k - 1)$$

and substitute the values $d_0 = 3{\cdot}3 \times 10^{-8}$ and $k = 1{\cdot}05$,

$$t_1 = 4{\cdot}0 \times 10^{-8} \times \mathrm{T}\ \text{dynes};$$

i.e., if a substance expands linearly from absolute zero 5 per cent. at a temperature T, the intermolecular repulsion is

$4{\cdot}0 \times 10^{-8} \times T$ dynes. Thus, if T is 300° (27° C.), the force is $1{\cdot}2 \times 10^{-5}$ dynes. If the substance is solid at this temperature, this is also the magnitude of the gross molecular attraction.

It should be observed that this formula is of the same order of magnitude as that previously given for the attraction.

A similar but not identical formula for the repulsion can be derived in the following manner :—

The kinetic energy of a molecule is reputed to average

$$3\,R\,T/2\,N.$$

If, then, a molecule collides with another, and they come into contact (*i.e.*, the distance between their centres is d_0), but were originally at distance $(k - 1)\,d_0$, between the centres, the mean force acting is

$$3\,R\,T/2\,N\,d_0\,.\,(k-1).$$

This expression only differs in the coefficients from the former one, and is obviously only an approximation, since it assumes a repulsion varying from zero to twice the mean, whereas in actual fact the force varies from the equilibrium value or somewhat less to an indefinitely large value.

In the solid state there is an equilibrium value of both forces for an unstrained position,

$$t_2 - t_1 = 0.$$

Compression of a solid causes resistance, so that t_1 (the repulsion) increases with proximity more than t_2. Similarly tension causes tensile stress, so that t_2 must decrease more slowly with separation than t_1.

Clerk-Maxwell has used (only for illustration) a form—

$$\text{Tensile stress} = A\,.\,d^{-4} - B\,.\,d^{-7}.$$

Grüneisen similarly has a form—

$$A\,.\,d^{-3} - B\,.\,d^{-3n},$$

where n is 3 or more.

In regard to the mathematical form of the expression for the repulsion, it should be observed that the form

$$t_1 \text{ varies as } 1/d_0\,(k-1)$$

cannot be exactly reconciled with the inverse relation

$$t_1 \text{ varies as } 1/(k\,d_0)^m,$$

since if k is large, m is unity, and if k is unity m is infinity.

Max Born, Landé, and Fajans have adduced data to show that, in addition to the repulsion between unlike charges which reduces the electrochemical attraction of nascent atoms to marginal cohesion effects, there is also a repulsion between ions varying inversely (for the alkaline halides) as the tenth power of the distance—*i.e.*, with a potential varying as the inverse ninth power of the distance. This somewhat corresponds to Grüneisen's second term or to the writer's kinetic repulsion.

Crehore, as already mentioned, has a repulsion term

$$f(e)/d^6,$$

where $f(e)$ is a function of the charges.

If it is observed that the Van der Waals' formula presupposes isothermal conditions during volume changes, the possibility that the molecular pressure is a function of the temperature might be explained by an additional repulsion term due to the liberation or absorption of energy, so that in an adiabatic expansion the molecular pressure would *not* be a function of temperature—*e.g.*, if

$$\left(p + \frac{a_1}{\mathrm{T}\, v_i^2}\right) = \left(\frac{\mathrm{R\,T}}{v_i - b}\right) \text{ (Clausius)},$$

and for adiabatic change

$$\left(p + \frac{a}{v_a^2}\right)(v_a - b)^\gamma = \text{constant},$$

the second form for the molecular pressure may be a true spacial relation and the difference

$$\left[\frac{a}{v^2} \sim \frac{a_1}{\mathrm{T}\, v^2}\right]$$

may be a thermal energy effect. Contrariwise, Edser has shown that temperature changes in a are reconcilable with a high inverse power of the distance for the molecular attraction function.

Some suggestive but not final ideas as to the law of repulsion have been based on analysis of viscosity (see Chap. VIII.). On the dynamic theory of gases, viscosity can be written

$$f(m, n, \bar{v}, a),$$

where m is the mass of a molecule,
n is the number of molecules per unit volume,
$\bar{v}$ is the root-mean-square velocity,
a is the radius of the molecule.

As in an actual gas the "mean free path" (average distance travelled by a molecule before collision with another) is great compared with the radius of the molecule, the mean free path varies inversely as n. The viscosity being proportional to both these quantities is then independent of either as long as the other quantities defining the system remain unchanged. If the mutual repulsion is of a form

$$k \,.\, m^2 \,.\, d^{-s},$$

where k and s are constant and d is the distance between the centres of the molecules, the dimensions of k are

$$M^{-1} \,.\, L^{s+1} \,.\, T^{-2}.$$

We may then write the viscosity varies as

$$M^x \, v^y \, k^z,$$

provided that

$$M \,.\, L^{-1} \,.\, T^{-1} = M^x \, (L \, T^{-1})^y \, (M^{-1} \, L^{s+1} \, T^{-2})^z,$$

which is satisfied by

$$x - z = 1 \,;\; y + 2^z = 1 \,;\; y + (s + 1) \, z = -1,$$

so that

$$z = -2/(s-1) \,;\; y = (s+3)/(s-1) \,;\; x = (s-3)/(s-1).$$

On this basis the viscosity varies as

$$m^{\frac{s-9}{2s-2}} \, k^{-\frac{2}{s-1}} \, \theta^{\frac{s+3}{2s-2}}.$$

Thus, if the viscosity of gases varies as θ, s is equal to 5, while if the index of variation of θ is $\frac{3}{4}$, s is 9.

Clerk-Maxwell, who is responsible for this analysis, considered that experiment indicates that the index of variation of the temperature is unity, so that he deduced s to be 5, but there is some uncertainty about this temperature relation, and in any case the whole argument falls to the ground if the force does not vary as the square of the mass of the molecule.*

Some planetary electron hypotheses of atomic structure involve a repulsion between atoms varying inversely as the sixth power of the distance, but no finality attaches to these without further confirmation as to the structure of the electric fields.

Magnetic and electric doublets repel one another in certain positions in the same manner as they attract in other positions —*i.e.*, the repulsion varies as the inverse fourth power of the distance except for close proximity, and the torques vary as the inverse third power of the distance.

The mechanical reaction of a thermally activated electron moving through a distance 10^{-8} cms. is of the order of 10^{-6} dynes.

The only general conclusion that can be drawn as to the repulsion is that such repulsion **is a direct function of the temperature and decreases with separation of the molecules more rapidly than the attraction.**

* Sutherland regarded molecules as infinitely rigid spheres. Jones (*Proc. Roy. Soc.*, 106 A, pp. 441-477) deduces that the inverse index of repulsion is high, of the order of 20. Hasse and Cook (*Phil. Mag.*, May, 1927) deduce that Sutherland's spheres must be replaced by point centres with a central rapidly diminishing repulsion. Bragg (*Phil. Mag.*, Sept. 1926) considers that the law of repulsion must be more complex than that of a simple inverse power of the distance.

CHAPTER VII.

VISCOSITY AND INTERNAL FRICTION.

The resistance to deformation shown by fluids and their internal friction arise from one or both of two causes :—

(1) The action of molecular attractions.
(2) The interchange of momentum between colliding molecules moving at different speeds.

The former agent figures principally in liquids in sub-critical steady flow, and the latter in supercritical or turbulent flow. In gases the second predominates always, since the molecules are free to diffuse among one another.

The first cause decreases with rise of temperature, largely owing to the separation of the molecules and the consequent diminution of the attraction as well as the increased repulsion. The second increases with temperature, because the molecules move faster. It is, therefore, in some cases difficult to distinguish between them, and it is perhaps doubtful if the same method of measurement is rightfully applied to both.

The viscosity is that quantity which, if multiplied by the space rate of change of the velocity normal to the direction of the velocity, gives the friction per unit area on the fluid surface.

$$\mu = f_s/(d\,v/d\,y).$$

It has the dimensions M/L T.

For water the viscosity has the value

$$\frac{0{\cdot}01776}{(1 + 0{\cdot}03368T + 0{\cdot}000221T^2)} \text{ dynes-seconds/cm.}^2 \text{ or “poises,”}$$

or, according to other authorities

$$\frac{0{\cdot}017944}{(1 + 0{\cdot}023121\ T)^{1{\cdot}5423}} \text{ poises.}$$

(In each case T is the Centigrade temperature.)

For gaseous air, the value is given by Maxwell as

$$0{\cdot}00018226^* + 0{\cdot}000000584\,T - 0{\cdot}00000000124\,T^2.$$

It will be noticed that the value for air at 0° C. is only about one hundredth that for water, whereas the densities are in the ratio of one to eight hundred. In considering the effect of viscosity on motion, the kinematic viscosity, or viscosity per unit mass, is more useful even than the viscosity. The ratio of the kinematic viscosities for air and water is as follows :—

T	0° C.	60° F. = 15·5° C.	100° F. = 37·7° C.
$(\mu_a/\rho_a)\,/\,(\mu_w/\rho_w)$	7·37	13·1	24·6

By extrapolation it would appear that gases are extraordinarily more viscous (mass for mass) than liquids at very high temperatures. This partially explains the solar state of matter.

TABLE OF VISCOSITIES IN DYNE-SECONDS PER SQUARE CENTIMETRE = "POISES."

Substance.	Temperature (C°).	Viscosity.
Ether vapour,	0·0	$6{\cdot}89 \times 10^{-5}$
Air,	0·0	$1{\cdot}733 \times 10^{-4}$
Argon,	0·0	$2{\cdot}104 \times 10^{-4}$
Mercury gas,	270·0	$4{\cdot}89 \times 10^{-4}$
Air (liquid),	−192·3	$1{\cdot}72 \times 10^{-3}$
Acetaldehyde,	20·0	$2{\cdot}31 \times 10^{-3}$
Water,	20·0	$1{\cdot}00 \times 10^{-2}$
Mercury,	20·0	$1{\cdot}547 \times 10^{-2}$
Light oil,	100·0	$4{\cdot}9 \times 10^{-2}$
Heavy machinery oil,	15·6	6·606
Glycerine,	2·8	42·2
Sulphur,	187·0	560·0
Venice turpentine,	18·3	1,300·0
Shoemaker's wax,	8·0	$4{\cdot}7 \times 10^{6}$
London clay, fluid under pressure,	20·0	About $1{\cdot}0 \times 10^{7}$
Metals,	0·0	1 to 10×10^{8}
Pitch,	0·0	$1{\cdot}3 \times 10^{10}$
Soda glass,	175·0	$1{\cdot}1 \times 10^{13}$
Glacier ice,	0·0	$1{\cdot}2 \times 10^{14}$

* 0·0001711 (at 0° C.) (Millikan).
$0{\cdot}00017155 + 0{\cdot}0000004718\,T - 0{\cdot}00000000005833\,T^2$ (Holman).
0·0001733 (at 0° C.) (Smithsonian Tables).

"Fluidity" is the reciprocal of the absolute viscosity, as measured above. According to Bingham, fluidity is a more significant quantity than viscosity.

"Kinematic viscosity" is the absolute viscosity divided by the specific gravity.

"Specific viscosity" is the ratio of the absolute viscosity to that of a standard substance. In view of the close approximation of the viscosity of water at 20·0° to one hundredth of a poise, the absolute viscosity in centipoises is frequently used as a convenient measure.

VISCOSITY OF WATER AT DIFFERENT TEMPERATURES.

0·0°,	1·7921 centipoises	
50·0°,	0·5494 ,,	
100·0°,	0·2838 ,,	
100·0°,	0·0132 ,,	(vapour)

VISCOSITY OF AIR AT DIFFERENT TEMPERATURES.

−192·3,	$1{\cdot}72 \times 10^{-3}$ poises	(liquid)
−21·4,	$1{\cdot}63 \times 10^{-4}$,,	(gas)
0·0,	$1{\cdot}73 \times 10^{-4}$,,	
99·1,	$2{\cdot}20 \times 10^{-4}$,,	
302·0,	$2{\cdot}99 \times 10^{-4}$,,	

Many authorities hold that the viscosity of solids is infinite, and that the expression should only be used when the solid is under a stress greater than that required to make it flow plastically. Viscosity may then be considered in terms of the *excess* stress. This idea greatly reduces the viscosity values for the solids named.*

* Phillips (*Nat. Acad. Sci. Proc.*, 7, pp. 172-177, June, 1921) gives for liquids; *Sci. Abs.*, 286, 1922.

$$\mu = \frac{n\,\mathrm{N}\,h}{2\mathrm{M}\,(v - \delta)},$$

where n = 6 ; N = Avogadro's constant,
h = Planck's quantum, $6{\cdot}27 \times 10^{-27}$,
M = mol. wt. of liquid in gas phase,
v = vol. per gram.,
δ = co-volume (of molecules in gram).

Viscosity of liquids is greatly increased by *large* pressures. That of gases is also increased by high temperatures.* Hence for both reasons the viscosity of central parts of planets and stars must be high, comparable with that of "Solids," so that the distinction of state is arbitrary. Neither Boyle's law nor that of nil molecular pressure or low viscosity apply to such gases.

O. E. Meyer ("Kinetische Theorie der Gase," Breslau, 1877) has deduced the following equation for diffusive viscosity in gases :—

$$\mu = \frac{m\,\mathrm{N}}{3}\,\bar{\omega}\,l,$$

where μ = viscosity,
N = molecules per c.c. ; $m\,\mathrm{N} = \rho$;
$\bar{\omega}$ = mean velocity of molecules (cm./sec.),
l = mean free path,

and $$l = \frac{4}{\sqrt{2}\,.\,\mathrm{N}\,.\,\pi\,d^2} = \frac{2}{\pi}\left(\frac{\Delta}{d}\right)^2 . \,\Delta,$$

where d = effective diameter of molecule,
Δ = mean distance from c. to c. of molecules.

Since

$$l \text{ varies as } 1/\mathrm{N},$$

Meyer's equation indicates that

$$\mu \text{ varies as } \bar{\omega}.$$

According to the kinetic theory of gases,

$$\bar{\omega} \text{ varies as } \sqrt{\mathrm{T}}\,;\ \text{and hence } \mu \text{ should vary as } \sqrt{\mathrm{T}},$$

but this only agrees with experimental results for medium pressures. T is here the absolute temperature.

Sutherland in his 1893 paper deduced that

$$\mu_{\mathrm{T}} = \mu_0 \cdot \frac{273 + \mathrm{S}}{\mathrm{T} + \mathrm{S}} \cdot \left(\frac{\mathrm{T}}{273}\right)^{\frac{3}{2}} \left[\text{or } \mu \propto \frac{\mathrm{T}^{\frac{1}{2}}}{1 + \frac{\mathrm{S}}{\mathrm{T}}}\right]$$

where μ_0 is the viscosity at 0° C. ; T is the absolute temperature, and S is a constant for any one gas. (According to the

* When viscosity is a minimum: mutual attraction = diffusive effect.

Smithsonian Tables, S is 80 for helium, 124 for air, and 313 for nitrous oxide.) [S is the Sutherland constant which modifies Meyer's expression so as to allow for molecular attraction.]

The deviation of experiment from the kinetic theory form

$$\mu_T = \mu_0 \left(\frac{T}{273}\right)^{\frac{1}{2}}$$

corresponds to the molecular attraction effect.

Kamerlingh Onnes finds for low temperatures the following expression to be fairly exact :—

$$\mu_t = \mu_0 \left(\frac{T}{273}\right)^n,$$

where n is 0·647 for helium, 0·754 for air, and 0·93 for nitrous oxide.

Maxwell considered that

$$\mu_t = \mu_0 \left(\frac{T}{273}\right)$$

(see p. 78 on " Intermolecular Repulsion ").

Chapman (*Phil. Trans. Roy. Soc.*, 211A, pp. 433-483, 1912, and do., 216A, 1916) gives a formula

$$\mu = (1 + \varepsilon_a) \frac{5m}{64\,\pi^{\frac{1}{2}}\sigma^2} \left(\frac{R}{m}T\right)^{\frac{1}{2}} \frac{1}{1 + \frac{S}{T}},$$

where S is Sutherland's constant,
R is the gas constant,
m is the mass of a molecule,
σ is the radius of the molecular sphere,
ε_α is a tabular quantity less than $<$ 0·02.

Further investigation by Stefan and others has shown that these results are only approximate, but the equation of Meyer can be used for computing d with moderately consistent results.

So far as the writer is aware, no great success has been obtained in correlating μ for fluids with molecular quantities,* but the following considerations may indicate some steps towards that end. (It should be observed that if the change

* See, however, Phillips' formula above.

of μ with T is considered to be due *solely* * to volume changes, μ varies as a tremendously high inverse power of n, which diminishes as v increases.)

The resistance to the motion of fluids changes with increasing velocity gradually from a purely " viscous " form to a " turbulent " type at a certain " critical " velocity which depends on the dimensions of the body moving in the fluid or those of the channel through which the fluid is moving.

The simplest case is perhaps that of a sphere falling through a liquid by its own weight. The following formula indicates the equilibrium of forces :—

$$\frac{4}{3}\pi r^3 . s - \frac{4}{3}\pi r^3 . z = 0{\cdot}25\,\pi \frac{v^2}{g} . r^2 + 0{\cdot}06 . \pi \frac{v}{g} . r,$$

Weight — Buoyancy = Hydrodynamic resistance. + Viscous resistance.

whence

$$v = \sqrt{\frac{16}{3} r g (s - z) + \left(\frac{0{\cdot}12}{r}\right)^2} - \frac{0{\cdot}12}{r},$$

which converges towards the value

$$v = 22{\cdot}\dot{2}\, g\,(s - z)\, r^2,$$

when r is small, and converges to the value

$$v = \frac{16}{3} g\,(s - z)_r,$$

when r is large.

If we assume that the particle carries with it a shell of attached fluid, one of two alternative hypotheses may be adopted :—

(*a*) That the viscous resistance is due to the hydrodynamic resistance on the attached fluid shell (*i.e.*, all the resistance is really hydrodynamic).

This leads to the expression for the radius of the shell

$$r_1 = \sqrt{r^2 + \frac{0{\cdot}24\, r}{v}},$$

which is very large for small values of r.

* Macleod (*Faraday Soc.*, 1924) suggests that $\mu \propto \frac{1}{x}$, where x is the " free space " between the molecules.

(*b*) That the hydrodynamic resistance is due to viscous resistance on the shell (*i.e.*, that all the resistance is really viscous).

This leads to the form

$$r_1 = 4{\cdot}1\dot{6}\, r^2 v + r,$$

which is very large for moderately large values of r, and is equal to r for small values of r.

The ratio of v to r, if $s - z$ is 1·5, varies from zero for enormous values of r to a maximum at the critical velocity when r equals 0·025 cm., then having a value about 400, and diminishes again to zero for small values of r.

The viscous friction per unit area of particle varies as v/r, and per superficial molecule at the critical velocity is about $2{\cdot}5 \times 10^{-14}$ dynes.

It seems logical to suppose that in the viscous state the various fluid molecules roll and slide over one another without separation or collision, whereas in the turbulent condition the momenta imparted are such that the molecules stream through the general mass and collide with others, so that there is a field within which a general circulation or diffusion is taking place surrounded by a volume in which only viscous sliding and rolling is occurring.

In the turbulent condition there is always a "wake," "discontinuity," or "dead water," within which the pressure is less than normal, and into which the fluid flows with vortex motions. These vortices expand, losing kinetic energy by collision and viscosity until the moving body is sufficiently remote for the fluid currents, which it causes, to have no longer enough energy to separate the molecules.

Internal friction in solids, damping out oscillations, would appear to consist in the transformation of the oscillation energy into vibrations of high frequency (ultimately heat). No satisfactory method of calculating the values from first principles has yet been devised, but the coefficients of internal friction as applied to the exponential decrease of oscillations of standard pieces form a criterion.*

* Elastic vibrations are parallel and of relatively low frequency and are evanescent; heat vibrations are indiscriminate as to direction, with high and constant frequency. Internal friction represents the force causing the parallel vibrations to become indiscriminate.

True interfacial friction corresponds to the force required to raise the one piece over the interpenetrating rugosities between the two or to shearing stress (beyond the limits of stable cohesion) or to a combination of the two. Adhesion on piles in cohesive mud has two stages; (*a*) actual elastic cohesion and (*b*) slipping, a plastic motion in which the material is flowing. (See Forsell, "Jordtryck sasom ett elasticitetfenomen," Stockholm, 1917.) Friction of the latter class rises with great pressures to the regular shearing stress value for solid material. At low pressures, if the surfaces are highly polished or the material is soft, a slight tangential cohesion exists.

An analogy between viscous stress in liquids and shearing stress in a strained solid has been developed by regarding the viscous liquid as able to exert a certain amount of shearing stress, but continually breaking down under that stress.

An equation is written

$$\mu/E_s = \tau,$$

where E_s is the coefficient of rigidity (modulus of shear elasticity) and τ is the "relaxation time"—*i.e.*, the time taken for the shear to disappear from the substance when no fresh shear is applied to it.

CHAPTER VIII.

SURFACE TENSION.

THE dominant fact in the phenomenon of surface tension is that wherever two "phases" of the same substance or two different substances are in contact there is a storage of strain energy at the common surface, and if one of the phases is liquid the presence of this strain energy is shown by the deformation of the liquid surface principally at its margin. It is as if the liquid were covered with a thin skin in which there is a tensile stress. As one cannot readily conceive of such a skin actually existing unless it consist of the material itself in a state of compression, it is more logical to proceed at once to the study of the possibility of such a compression, but, nevertheless, for convenience, it is usual to postulate such a tangential surface effort as a prime cause.*

One of the simplest cases of surface tension is that of a bubble formed of a continuous liquid film enclosing a gas. On the hypothesis of the presence in this film of a tensile stress, the pressure within the bubble exceeds that outside, and the energy in the film is equal to the said excess pressure p acting through the distance $d\,r$ over the whole area of the bubble A, such energy being stored as strain energy, which is the product of the surface tension per unit length into the change of area of the bubble.

$$p \,.\, d\,r \,.\, A \text{ equals } T \,.\, d\,s.$$

T is here the sum of tensions *on both* faces of the film.

If the bubble is spherical, we can write (r is radius)

$$d\,s/d\,r = d\,(4\,\pi\,r^2)/d\,r = 8\,\pi\,r.$$

*** Langmuir and Bragg consider that films of special substances (*e.g.*, soap) may have a special structure oriented with respect to the surface, so that in such cases the film is a real coherent thing. Even in a homogeneous fluid the surface layer is *condensed* and perhaps polarised.**

Substituting for $d\,s$, we then have

$$p \,.\, 4 \pi r^2 \,.\, d\,r = \mathrm{T} \,.\, 8 \pi r \,.\, d\,r,$$

whence

$$\mathrm{T} = p\,r/2.$$

This result is also true for any spherical surface, and from experiment it appears that with the same liquid and gas T is constant, at any one temperature.

If the film is a curved surface with two different curvatures in two mutually perpendicular planes, it may be shown that

$$\mathrm{T} = \frac{p}{\left(\frac{1}{\mathrm{R}_1} + \frac{1}{\mathrm{R}_2}\right)}.$$

From this formula, the equilibrium forms of bubbles of various kinds can be computed.

If the pressure is raised until the bubble becomes about two molecules thick, the surface tension fails to maintain the film. Increase of the temperature reduces the surface tension, which becomes zero at the critical temperature.

With the critical thickness of the bubble it appears that the strain energy equals half the latent energy of the fluid in a gaseous form.

The conditions are more complex when the fluid is in mass in contact with a gas (or another liquid) and a solid. This is the case of drops lying on a surface, capillary sheets or threads between plates or in tubes. The current hypothesis here imagines that there is a surface tension tangential to the mutual surface of each pair of substances or phases, and considers the equilibrium at the common cusp, as if all three tensions acted on the liquid particles there. This notion seems highly artificial, but has some practical utility. If the three imaginary tensions are T_1, T_2, and T_3, then by the balance of forces

$$\mathrm{T}_2 - \mathrm{T}_3 - \mathrm{T}_1 \,.\, \cos\theta = 0,$$

and

$$\cos\theta = \frac{\mathrm{T}_2 - \mathrm{T}_3}{\mathrm{T}_1}.$$

Experiment indicates that at a given temperature, and under the same mechanical conditions, the angle of contact between any one pair of fluid and solid in the presence of a particular gas is constant. If three phases are in contact, and the tension between one pair exceeds the sum of the tensions between the other two pairs, the enclosed phase will spread out until a critical state is reached. In the case of a fluid, this means almost molecular thickness if no boundary is met by the spreading film.

In a tube a fluid will rise or fall above the general surface to a mean height

$$h = \frac{2\,T \,.\, \cos\theta}{\rho\, g \,.\, r},$$

where ρ is the density and r the radius of the tube. There is here an apparent total force

$$2\pi r \,.\, (T \cos\theta)$$

acting against or with gravity.

Between parallel plates the rise or fall is

$$\frac{2\,T \,.\, \cos\theta}{\rho\, g \,.\, a},$$

where a is the distance between the plates.

The capillary surface in such cases is in profile an " elastica."

In fluids where θ is less than 90° a drop may be retained in the end of a tube by the surface tension, provided the radius of the tube is less than a certain critical value.

A thin film of fluid between two plates may cause great mutual pressure, which is, *ex hypothesi*, owing to the tensions at the edge of the film. In all probability this is putting the cart before the horse.

The force is

$$\frac{2\,A\,T \,.\, \cos\theta}{d} + B\,T \,.\, \sin\theta,$$

where A is the area of the film,
d the thickness of the film at the edge,
B the circumference of the film.

Some such action as this is probably the basis of the initial process of fluid and cement adhesion, the pressure bringing the particles into intimate contact.

Excepting mercury, water has the highest surface tension of any substance liquid at ordinary temperatures, and various motions of the bounding surface occur when fluids of other surface tensions are added to it.

The surface tension of mercury is very variable, according to the amount of oxide present, and is greatly affected by potentials of a few millivolts. This is the basis of the Lippmann capillary electrometer, which consists of two mercury electrodes which are separated in a capillary tube by a bubble of acidulated water. The displacement of the bubble in the presence of a small difference of potential (*e.g.*, 0·01 volt) indicates an appreciable change of the surface tension, while the potential is quite insufficient to produce any dissociation.

Quincke has suggested the use of what is termed "specific cohesion," defined by the expression

$$C = 2\,T/g\,\rho = (K - k)^2,$$

where K is the height of a globule of the fluid resting on a standard surface, and k is the height of the vertical part of the bulge of the bubble.

He found that the following quantities roughly hold good :—

(All at just above fusion temperature.)

Bromides and iodides, ... C =	0·04
Nitrates, chlorides, sugar, fats, lead, bismuth, mercury, and antimony, ...	0·08
Carbonates, sulphates, phosphates, platinum, gold, silver, cadmium, tin, copper, water, .	0·16
Zinc, iron, and palladium, ...	0·24
Sodium, ...	0·48

A convenient method, which is largely used for determining the surface tension, is the "drop weight" method, in which, by choosing a suitable size of capillary tube, the drops that form are proportional in weight to the intensity of the surface tension.

Most recent students of surface tension have found it convenient to employ the "molar surface energy" as a standard of surface tension. This is the product of the surface tension into the area of a sphere of the liquid whose mass is just one gramme-molecule. This area, the "molar surface," varies as the two-thirds power of the "molar volume," which is the gram-molecular weight divided by the density. It should be observed that the energy per unit area is numerically equal to the force per unit of length.

Eötvös claims to have found that the temperature rate of change of the molar surface energy is constant, being independent of the temperature and the nature of the fluid, and Ramsay and Shields have deduced from this and further experiment the expression :—

$$T \cdot V_0^{0 \cdot 67} = k_s (t_c - t - 6),$$

where T is the surface tension, dynes per cm.,
V_0 is the molar surface,
k_s is a coefficient,
t_c is the critical temperature, C.°,
t is the temperature.

This expression is not exact if $t_c - t$ is less than 36°.

Some recent experiments by Jaeger indicate that these conclusions are not exact at high temperatures.

Walden has also indicated that the molar surface energy varies inversely as the melting and boiling temperatures, but Jaeger also casts doubt on these results at high temperatures.

Dealing with organic compounds, Jaeger finds that the molar surface energy increases with molecular weight, and that unsaturated compounds have higher values than saturated ones. "Aromatic" compounds have higher values than meta- and ortho- forms. Stereo-isomerides especially differ in this respect. A comparison of the molar surface energy with temperature for anisotropic liquids shows a curve with two branches, a sharp minimum marking the point where the substance passes from the anisotropic or "liquid crystal" state into the liquid condition.

Jaeger noticed many irregularities in the relation to the atomic weight, the alkali halides decreasing with increasing atomic weight, as well as other discontinuities.

One may presumably generalise in regard to the chemical relations of surface tension to the extent of saying that it is a function of the molecular structure, and, observing especially the greater values in the case of unsaturated compounds, deduce with a fair show of reason that the force is differentially atomic. This, of course, agrees with what has been said elsewhere as to molecular force.

Kelvin, in his "Popular Lectures" (vol. i.) mentions that the periodic time of vibration of a sphere of water due to surface tension is

$$\frac{1}{4} a^{1\cdot5} \text{ seconds,}$$

where a is the radius of the drop in cms.

If we substitute for a the quantity $1{\cdot}6 \times 10^{-8}$, which has elsewhere been suggested as the half-diameter of the water molecule, we get the periodic time as

$$5 \times 10^{-13} \text{ secs.}$$

or a frequency of 2×10^{12}.

Infra-red absorption of heat rays indicates somewhat similar frequency in water molecules, showing that the molecular forces controlling oscillation are of the same order as surface tension.*

The molar surface energy of water at 0° C. is about 1,000 calories, or 55 calories per gram, but if the surface is enlarged until it is one molecule thick, the energy is of the same order as that required to produce vaporisation, and according to thermodynamic theory is exactly half that quantity.

Plateau (" Statique experimentale et théorique des liquides," Ghent, 1873) showed that two important conditions hold good for liquid films :—

(*a*) Only three films can meet on an edge, and they must make angles of 120° with each other.

(*b*) Only six films can meet at a point, and the adjacent edges must make angles of 109° 28′ with each other.

From Plateau's conditions Kelvin (*Proc. Roy. Soc.*, 1894, vol. lv., p. 1 ; and " Collected Papers," vol. v., p. 333) showed that foam cells tend to be fourteen-walled or tetrakaidecahedra with 8 faces hexagonal, and 4 quadrilateral ; 36 edges, each face being common to two cells. A condition of minimum surface makes the faces have a slight double curvature.

The notion of skin or surface tension between all pairs of phases as outlined above, while it gives consistent results, is difficult to visualise, even if we suppose each surface to be covered with a film of " adsorbed " molecules, and a more

* Taylor, an American writer, has endeavoured to show that the molecules themselves have surface tension, but this a mere tour-de-force which involves the unnecessary introduction of surface tension as a fundamental physical concept without relation to other forces.

rational line of reasoning has been advocated by many physicists. It is argued that the molecular attractions (which at the free surface are practically unbalanced) are so tremendous that appreciable differences of density occur with a resultant flow in the liquid and a condition of expansion ("tensile stress") in the surface layer. It is on this basis that many seek to explain the capillary meniscus. Thus it is held that between water and glass there is a force of, say, 10^{-5} dynes per molecule pair or 10^{10} dynes per square centimetre, equal to ten thousand atmospheres. The compressibility of water at ordinary pressures is about 1/22000 of the volume per atmosphere, so that even if, as is certain, the compressibility is much less for high pressures, the density of the surface layer will be increased. The molecular pressure extends through several tens of molecules, and squeezes the liquid laterally, and the meniscus (or sheet, as the case may be) is produced. Edser shows by a simple argument that the surface tension tends to be one-half the molecular pressure.

We may even go further and say that the compression produces a lateral expansion or tension from one-half to one-quarter the compression (according to the rigidity), and it will be found that, if this tension is supposed to be mainly confined to a layer one molecule thick, it is quantitatively of the same order as the nominal surface tensions which actually occur. *Complete* analysis on these lines transcends the powers of mathematics, especially as long as the law of cohesional attraction is unknown, but Gauss and Laplace* have made some useful investigations. Edser has also succeeded in explaining the phenomena of surface tension in terms of molecular attraction.

It would certainly seem very improbable that there should be a tension in the surface of a liquid as a prime factor, whereas as the result of a compression it seems reasonable. The real difficulty lies in appreciating just what the real conditions of equilibrium are at the surface of a fluid.

Phenomena similar to surface tension can occur between two liquids or between a liquid and a solid in the general volume of a liquid. It is these which explain the stability of emulsions and all those peculiarities which are now grouped under the name of "colloid." Ostwald considers that this surface energy is somewhat different in character from

* "Mécanique Céleste." Supplement to xth Book.

ordinary surface tension, but, nevertheless, he regards it as the product of molecular forces acting through compressions of molecular dimensions, so that on each and every surface of separation there is a condition of strain energy, which, when the amount per particle is comparable with the gravitational or other forms of energy possessed by the particle, can play an equilibrating or predominating part.

It is not commonly realised that surface energy can be as it were petrified, but such is the case whenever solids are crystallised rapidly. Metal castings have always a skin which is differently structured from the interior, and there is in that skin a tension which, although neutralised externally by an opposing compression in the interior, shows itself in the phenomenon of brittleness, which is seen *par excellence* in Prince Rupert's glass drops.

Frictional electricity is also a surface strain energy effect, and Ostwald has suggested a brilliant generalisation to the effect that all chemical changes are really surface energy phenomena carried to the point of ultra-molecular subdivision.

Surface energy is again observable in the radiation effects of the celestial bodies. The mass increasing with the cube of the diameter, while the surface only increases with the square, the essentially mass effects, such as gravitation, stored heat, and possibly radio-activity, are seen to become more and more important as the dimensions increase, until in the vast nebular systems almost anything may be conceived to happen. Lubrication (concerning which, see Osborne Reynolds' "Scientific Papers," and the general discussion in the *Proceedings of the Physical Society of London*, No. 182, vol. xxxii., Part II., 1920, and various papers by Sir W. Hardy to the Royal Society) raises many interesting questions as to cohesive force.

In the case of copious lubrication, films of lubricant can be maintained under pressures up to about 200 kilogrammes per sq. cm. The resistance is then a function of the viscosity.

In the case of small quantities of lubricant, various puzzling phenomena occur. Efficient lubrication can under such conditions happen with films perhaps only one molecule thick, and the most decisive question is whether the lubricant "wets" the solids or not. Animal and vegetable lubricants have more "oiliness" than mineral lubricants, such "oiliness" not being proportionate to viscosity. The "wetting" or adhesion effect is probably a result of surface tension pressure referred to above, and this again is probably dependent on an orientation of the molecules in the film due to polarisation or "incomplete saturation" (residual charge), but no very simple relations have yet been discovered. The condition of the molecules of the wetted solid is also exceedingly important, since the wetting is a reciprocal effect between the solid and the liquid, and the "liquid" gel solidifies in such small thicknesses. Such films are almost certainly condensed by the molecular pressure.

An excellent study of "Surface Tension and Surface Energy" is Messrs. Willows and Hatschek's recent book under that title, published by Messrs. J. & A. Churchill.

The following important points are especially discussed :—

(*a*) There is a marked parallelism between the temperature coefficient of surface tension and the coefficient of expansion.

(*b*) High intrinsic (*i.e.*. molecular) pressure is accompanied by high surface tension.

(*c*) High surface tension is accompanied by low compressibility.

(*d*) Total surface energy (tensile strain energy plus heat stored) varies with the latent heat of the liquid and the temperature.

(*e*) The change of vapour pressure over a curved liquid surface varies with the curvature, and is very appreciable for minute drops of fluid in a gas.

(*f*) Similar changes of osmotic pressure occur over minute solid particles in a liquid.

(*g*) Surface tensions of solids have high values (*e.g.*, 4,000 dynes per cm. for $BaSO_4$).

(*h*) The variation of the tensile strength of the cementing material between the grains of metals, etc., is partly related to the surface energy in the smaller particles.

(*i*) Chemical reaction in thin films may be modified by surface tension.

(*j*) There is a transition layer about one molecule thick of intermediate density between two phases.

(*k*) Changes of concentration between two phases (adsorption) are the resultant effects of surface tension, osmotic pressure, and electric charge.

With respect to the last question, one wonders whether the distinctions made are not somewhat arbitrary, and if all these effects are not simply residual electrostatic and kinetic energy phenomena.

CHAPTER IX.

THE STRENGTH, ELASTICITY, AND RIGIDITY OF SOLIDS.

THE most obvious case of cohesion is that of the strength and elasticity of materials. All solids will resist a certain amount of applied force without breaking, but there is always a compression, expansion, or distortion " strain " accompanying this resistance. Measured as a force per unit area, this resistance is termed " stress." In " rigid " materials the strain is almost wholly temporary, provided that a certain maximum stress is not exceeded, but a small amount of permanent " set " does usually occur in most materials. Below a fairly definite " elastic limit " the ratio of stress to strain for an " elastic " material is practically constant (" modulus of elasticity "). Above that limit the ratio diminishes, and, in manufactured materials such as steel, a critical or " yield " point is reached at which most of the strain becomes permanent. There is, however, no real fracture at this stage, and the process may be repeated *de novo* with, if anything, higher limits. If, however, the stress continues to increase, the strain increases at a still greater rate, until an " ultimate " stress is reached. The material then " flows " freely, and as the stress increases (usually automatically by the reduction of the area stressed) fracture occurs. Up to the elastic limit the volume is slightly increased (or decreased, in the case of compression) by the strain, but above the yield point the volume remains practically unchanged. Engineers are very familiar with this series of phenomena in connection with metals, but it should be observed that two complexities occur, which make it doubtful whether all the features are characteristic of homogeneous solids. The one is that the material has, during manufacture, been subjected to processes which generally leave it in a state of internally balanced stress. The other is that, when solidifying from the molten state, owing to the formation of different molecular structures at different temperatures, a granular condition exists. Microscopic examination seems to show that the peculiarities of set and yield are partly due to relative displacements of the grains, as well as to those of the substance within the grains along their planes of crystallisation.

For "brittle" materials (*e.g.*, cast metals, rock, etc.) the elastic limit is lower and less definite. High tensile stresses can occur with gradual loading in such materials, but there is little or no "flow" except under very high compressive stress.

With "plastic" materials there is very little elasticity, and flow occurs under a constant low stress.

Stresses are classed as tensile, compressive, and shear. Shear may be considered as compounded of joint tension and compression on two planes oblique to the shearing plane. Compression applied equally in all directions cannot produce failure, except temporarily in materials containing voids (*e.g.*, wood, bone). Some theorists are inclined to regard failure as always occurring through shear, but it is probably most correct to say that all failure is ultimately tensile, although true shearing is not inconceivable, especially on planes of crystallisation.

When compression does cause failure, the piece either tears by the tension induced through bending (as in a column), bursts laterally by sideward expansion, or slides over itself obliquely. In such cases the compression is acting in one direction and the failure occurs in another direction.

The lateral or bursting stress which arises in connection with uni-directional compressive stress is from one-quarter to one-half the magnitude of the compressive stress, according to the rigidity of the materials.

For many years engineering writers, when speaking of "stress," have referred in a vague manner to molecular forces as the source of stress, but it is very doubtful if they had any real notion of what they meant. Physical research in recent years has partially cleared up the question, and there is now no reason why an engineer should not have a fairly clear picture of "stress" as due to molecular reaction.

The description of a few simple experiments will help to lead up to the main ideas. If two fairly smooth metal plates are laid on one another there is no apparent tendency to adhere. If they are wetted or well greased they do adhere with a tenacity of about one atmosphere tension (1 kilogram per sq. cm.). This is obviously due to the tendency of the lower plate to fall, so creating a vacuum between the plates, which allows the external air pressure to show a "suction" effect. If, however, certain fluids are used or the plates are extremely smooth and true, a tenacity of even 30 kilograms per sq. cm. appears, which cannot possibly be explained by "suction."

Similarly, if two soft materials are pressed together, they often become as one piece. Two freshly cut lead surfaces will recombine in this way. Cohesion is, therefore, dependent on propinquity of a very high order.

Again, an ordinary tension test of material shows that the net cohesion increases with separation up to a limit, and that, in most cases, fracture happens long before the piece is stretched to twice its original length, which indicates that when the constituent and almost inexpansible particles have been separated by a distance much less than their own diameter the net cohesion between them is a maximum. In the case of rubber, gum, soft metal, or other plastic materials, which do stretch more than 100 per cent. before rupture, it is found that the lateral contraction of area is keeping pace with the extension, so that the longitudinal bonds are reinforced by the lateral drawing together of the particles. Postulating that cohesive strength does arise from molecules (or atoms), ordinary experience with solids thus shows that the *net* attraction between the molecules is the greatest when they are separated much less than two times the ordinary equilibrium distance between centres (about 1·01 times is usual).* The cohesive strength referred to the actual sectional area rises to a maximum (for special steels) of about 150 tons per sq. in. (say 25 tonnes per sq. cm.) $= 25 \times 10^9$ dynes per sq. cm. If the number of molecules on a sq. cm. is 10^{15}, this means a force of $2{\cdot}5 \times 10^{-6}$ dynes per molecular pair. This is the net cohesion or difference between gross attraction and gross repulsion at the separation corresponding to the strain.

So long as we are ignorant of the exact arrangement of the

* The expansion of a *melting* solid (without change of temperature) rarely exceeds 10 per cent. by volume, so that the linear expansion for dissolution of the structure is usually less than 3 per cent.

molecules (or atoms) and the true laws of their repulsion and attraction, it is almost impossible to say exactly what ratio there is between the actual bond along a line between two molecules and that which there would be if two were isolated. The ratio cannot be less than unity, but is not more than, say, 10, unless the index of inverse space variation is low. If the index were two the ratio is very large, but, as we have already seen, this value for the index is most improbable. Taking the ratio as unity, let us consider two isolated molecules.

There is a repulsion between them which varies in some inverse sense with the distance from centre to centre. There is also an attraction which varies in an analogous manner, but in the position of equilibrium the two forces are balanced. If they are brought closer together, repulsion prevails to an extent which increases continuously with proximity. It cannot become infinite, since chemical (*i.e.*, electrical) change may occur so that the atoms re-arrange themselves (possibly even interpenetrate), but still closer proximity than this will involve enormous resistance from the dynamic repulsion of the extremely energetic electron systems.

A formula of the type

$$t_1 = k_1 d^{-n_1}$$

may serve approximately for the repulsion, where t_1 is the repulsion (negative attraction), k_1 is a coefficient, d is the intermolecular distance, centre to centre, and n_1 is an index appreciably more than unity.

The net or effective attraction during separation does not increase in this way, but, on the contrary, approaches a limit within a distance considerably less than $2d_0$, where d_0 is the distance at equilibrium. Outside this range it diminishes, and presumably becomes indistinguishable from gravitation at a distance a few times d_0. (See section on the effective range of molecular force.)

If we consider the effective bond to be the resultant of an attraction and a repulsion, we have

$$t = t_2 - t_1,$$

and it appears that t_2 (the molecular attraction) may also be written in a form

$$k_2 \, . \, d^{-n_2},$$

and agree broadly with the experimental facts.

Hooke's law of elasticity shows that for small strains in the neighbourhood of d_0, t is of the form $c\,x$, where c is a constant. The conditions will be approximately satisfied if the curve representing t_1 is asymptotic to the d axis more rapidly than that representing t_2, and is asymptotic to the ordinate axis (or perhaps to one parallel thereto) less rapidly than that of t_2.

Since at equilibrium $t_1 = t_2$ and d_0 is common,

$$k_1 d_0^{-n_1} = k_2 d_0^{-n_2},$$

and, since the slope of the t_1 curve exceeds that of the t_2 curve,

$$-\,n_1 k_1 d^{-(n_1+1)} \text{ exceeds } -\,n_2 k_2 d^{-(n_2+1)},$$

and since

$$d^{-(n+1)} = d^{-n}/d$$

for the value d_0,

$$-\,n_1\,(k_1 d_0^{-n_1}/d_0) > -\,n_2\,(k_2 d_0^{-n_2}/d_0),$$

and since

$$k_1 d_0^{-n_1} = k_2 d_0^{-n_2},$$

n_1 exceeds n_2.

For functions of this type there is an equilibrium value below which the first term exceeds the second, and above which the second exceeds the first. If the coefficient k_1 is increased the equilibrium point is advanced. If the coefficient k_1 is decreased the equilibrium point is retracted. This corresponds to the effect of heat in causing expansion and contraction. Similarly, by sufficiently increasing k_1, the equilibrium point may be abolished, corresponding to the gaseous state.

The resultant curve in the neighbourhood of d_1 corresponds to the stress-strain curve obtained in the experiments on materials reduced to the case of a single pair of molecules. To convert it into a unit area stress-strain diagram the indices must be increased by 2, so as to allow for the area of the molecular fields. On the compression side of the curve there is an apparent discrepancy in the indefinite increase of the stress-strain ratio, but it should be observed that the curve refers to pure contraction without any shear. There is no very satisfactory way of arriving at the values of the indices except along the lines which have been already outlined in the previous chapters, but in the author's paper to the

Physical Society of London (" Cohesion " (vi.), *Proc. Phys. Soc.*, vol. xxxvi., Part iv., June 15, 1924, p. 336) an attempt has been made to show that if n_1 has the value 10, which appears to be required by Born's investigations on the alkaline halides,* and n_2 has the value of four which is involved in Van der Waals' gas rule, the resultant curves agree moderately well with both the actual maximum stable strains and also with the increase in the bulk elasticity with stress.†

The following general equations are derivable from the original one :—

(1) Normal equilibrium :—

$$k_1 d_0^{-n_1} - k_2 d_0^{-n_2} = 0.$$

(2) Elastic strain of small amount :—

$$n_1 k_1 d_0^{-(n_1 + 1)} - n_2 k_2 d_0^{-(n_2 + 1)} = \mathrm{E}_1,$$

where E_1 is the modulus of elasticity (tension per molecular pair/strain).

(3) Maximum stress :—

$$t_{max} = k_2(c\, d_0)^{-n_2} - k_1\, (c\, d_0)^{-n_1}\, ;$$

$$n_1 k_1 c^{-(n_1 + 1)}\, d_0^{-(n_1)} - n_2 k_2 c^{-(n_2 + 1)}\, d_0^{-(n_2)} = 0\, ;$$

$$n_1 c^{-(n_1 + 1)} - n_2 c^{-(n_2 + 1)} = 0.$$

(c is ratio of extension under maximum stable stress).

(4) Liquefaction :—

$$- a = k_2(c_1 d_0)^{-n_2} - m\, k_1(c_1 d_0)^{-n_1}.$$

* From the equation $\mathrm{K} = \dfrac{9\, \delta_0^4}{a\,(n_1 - 1)}$, where K = compressibility of crystals ; δ_0 = grating constant (distance between like ions) ; a = Madelung's constant 13·94 e^2.

† Two other forms are conceivable—

(1) $$\frac{a}{d^{n_1}} - \left(\frac{b}{d^2} - \frac{c}{d^2}\right),$$

corresponding to lattice potentials varying as $\frac{1}{d}$.

(2) $$\frac{a}{d^{n_1}} - \frac{b}{d^8},$$

corresponding to Edser's rule for molecular attraction, which is, however, only supposed to apply to liquids.

(a is atmospheric pressure per molecule in direction of the bond; c_1 is the coefficient of expansion at the temperature of liquefaction; m is the ratio of the coefficient of repulsion at this temperature to that at normal temperature).

(5) Pure compression :—

$$-t = k_2 d^{-n_2} - k_1 d^{-n_1},$$

which must be negative and equal to infinity when d is 0.

The oscillation theory of repulsion is complicated by the fact that it will not simultaneously explain cohesion and temperature effects without including a potential energy store in addition to the kinetic energy. Thus, a piece of material compressed becomes heated, but when it has lost its excess of temperature by radiation and conduction it might appear that the amplitude of the oscillations had decreased, and that the frequency, after temporarily rising, had fallen to its original value. This would indicate that the kinetic energy had decreased, but, nevertheless, if the material is elastic, it contains stored strain energy. Similarly, as Kelvin has shown, tension can cause cooling. India-rubber is distinctly peculiar in this respect, as it contracts when heated and expands when cooled. Vulcanised rubber can store 14,600 ft.-lbs., per inch cube, of strain energy as compared with 95 ft.-lbs. for spring steel.

Some means of storing potential energy must be postulated in such cases unless we can suppose the frequency to remain at a higher value than before straining, and yet not indicate any appreciable temperature effect.

The expansion before liquefaction is a rough indicator of the manner in which the net attraction falls away, but this is complicated by the increase of repulsion due to the heat taken up. (Ratio of expansion, Pb 1·099, Sn 1·068, Zn 1·11, Ag 1·113; Bi is anomalous. These ratios include the expansion from 0° C.)

The increase of cohesion with cooling is another source of information. When cooled to absolute zero from normal temperature, steel has a linear contraction of about 0·003. It possesses a greater cohesion at such low temperatures,* a fact which may be due to the reduction of the repulsion or to the increase of the attraction or to both.

*** Iron is about doubled in tenacity at − 180° C., according to Dewar.**

The volume expansion from absolute zero up to melting point averages about 0·065, and to boiling point about 0·13. The tensile strength diminishes roughly according to a formula

$$f = f_{\text{abs. zero}}\left(\frac{T_m - T}{T_m}\right)^{1.5},$$

where T is the temperature and T_m is the melting temperature, both on the absolute scale.

The variation of ultimate stress with temperature raises some difficult questions in the formulæ. The attraction varies inversely as the first or some lower power of the temperature. The repulsion varies directly as the first or some higher power of the temperature, but, in order that the repulsion shall exceed the attraction for all values of the interval above the melting value, the space rate of change of either the attraction or repulsion or both must change a little, so that at the melting state both may follow the same rule and be equal at all intervals until vaporisation commences.

Solids may be classified as—

Elastic gels—*e.g.*, rubber.
Plastic semi-gels—*e.g.*, mud, clay, wax.
Granular accretions—*e.g.*, metals, rock, cement.
Structural formations—*e.g.*, wood, bone, crystals.

From a physical point of view the first three forms may be regarded to some extent as "liquids," but, in so far as the molecular forces cause a certain degree of rigidity (*i.e.*, shear resistance at zero velocity of shear), they come within the ordinary class of solids. A true gel appears to consist of very large molecules whose residual affinities are such that appreciable cohesive forces exist and can act through a relatively large range.*

Mud and clay (whose properties largely depend on water content; 10 per cent. of water generally gives firmness and high cohesion; 30 per cent. gives softness and plasticity)

* Wax is a very interesting case. Paraffin wax, which is plastic at temperatures slightly above the normal, consists of a mixture of molecules of the form C_nH_{2n+2}, where n exceeds 16, so that the number of atoms in the molecule exceeds 50, and the molecules have a mean dimension exceeding $\sqrt[3]{50} \times 1{\cdot}6 \times 10^{-8}$. Probably the molecules are rod-shaped and rather more than n times the diameter of a carbon atom in *length*.

have very similar properties to rubber, but the range of strain, the elastic limit, and the resilience are much smaller. In the case of rubber only minute changes of volume occur, so that the bulk elasticity under "fluid stress" is large, but the rigidity ("shear elasticity") is relatively small. The lateral expansion of rubber under simple compression is about one-half the axial compression, whereas in more rigid materials it is only one-quarter. If this ratio (Poisson's) is written $1/m$, the lateral stress to prevent lateral expansion due to simple uni-directional compression p is $p/(m-1)$, being thus equal to that stress for materials whose m is 2 and one-third for very stiff materials for which m is 4.

The well-known equations between the three moduli of elasticity (linear, shear, and cubic) must be considered in endeavouring to arrive at a general theory of molecular stress, and it should be observed that if lateral strain is entirely prevented the longitudinal strain is less, and the material behaves as if there were a modulus of linear elasticity

$$\frac{E \,.\, m\,(m-1)}{(m-2)\,.\,(m+1)}.$$

All the processes of the mechanical handling of materials are based on molecular (or residual atomic) forces. It should be observed that these processes are most effective in metals which, generally speaking, are energised *above* the ordinary "resting" state of natural chemical compounds. Furthermore, it should be noticed that most materials in their commercial form are "amorphous"—*i.e.*, aggregates of minute and probably crystalline grains. The rationale of "hardening" may vary from the toughening of metals by hammering to the consolidation of powders by pressure. In all cases there is a pressure applied in all directions, the lateral and upward forces in the case of hammering being obtained by reaction from the surrounding material. With solid metal a slight increase of density occurs in hammered as compared with the cast state, and microscopic observation often shows that the grains are distorted (shearing on slip planes or atomic sheets). Skew crystallisation shows that this is quite compatible with interatomic linkage, and it is to be presumed that in the process the intergranular faces are brought into better contact, so increasing the tenacity.

In the consolidation of powders the density may be increased as much as 100 per cent. Thus a dry powdered clay may have a bulk density of 1·25, and be compressed until the density is 2·5. The tenacity is greatly increased during the latter stages of the pressure, thus showing that the molecular forces vary as a high inverse power of the distance. The tenacity is generally much less than the stress required to produce it, indicating that the forces resisting the re-arrangement of the particles (which particles have the full density of the consolidated product and are not appreciably compressible) are considerably greater than the residual attractions, which keep the grains in place when they are re-arranged.

In some cases it happens that the tenacity is wholly in the external part or skin of a mass, owing to the greater facility which the particles there have for becoming arranged in a stable configuration. The inner parts are then under a permanent compressive stress or excess of mutual repulsion, which causes fracture directly the crust is broken.

It seems fairly certain that permanent tenacity does not occur in a powder much before there is a stress capable of producing flow—*i.e.*, a rolling or sliding of the particles on one another. This is supported by the fact that powders as such are more easily consolidated when they are wetted, the particles moving more easily into place at first, and the fluid being then forced out by the stress.

The property of ductility is to some extent related to the chemical nature of the substances. Lothar Meyer, one of the originators of the periodic system, notes that the most ductile metals lie near the peaks and troughs of the atomic volume-atomic weight curve. Tammann holds that ductility is dependent on the mutual shearing of the grains in the direction of the extension. According to him, "ductility is not dependent on any definite form of space lattice, but seems to be connected with the occurrence of only one kind of atoms, and those are not bound together by active valencies in the lattice of their crystals. When the valencies become active, as in alloys, the tendency to the formation of slip bands is checked, and the ductility is diminished" (*Engineering*, Aug. 1918). Bragg suggests that in impure substances—*e.g.*, alloys—the planes of crystallisation are bumpy owing to the different sizes of the various atoms.

Hardness, as measured by impact or impression methods, shows periodic changes like those of the atomic valume, but quantitatively follows the melting temperature rather than any other physical characteristic.

Studies of the constitution of metals (Desch, "The Solidification of Metals from the Liquid State," *Inst. of Metals*, Sept. 11, 1919) have thrown considerable light on the question of granular structure. It appears fairly certain that the grains tend to form space-filling solids (rhombic or trapezoid dodecahedra), but that, owing to the poor equilibrium of the surface tension films of the liquid matrix, foam forms (Kelvin's tetrakaidecahedra) tend to be the final result. The setting liquid cements the grains together, and the surface tension in the films is largely a determinative factor in the strength of the solid metal.* Similarly, in setting cements, there are inert centres or grains surrounded by concentric rings of gel and finally spicular crystals radiating from each grain forming a rigid meshwork ("Theoretical and Applied Colloid Chemistry," Ostwald and Fischer). This explains why finely grained cements are preferable.

There are thus two types of molecular force in solids, the surface residuals of the crystallising forces in the grains and the skin tensions in the cementing materials. Seeing that the crystallising forces are polarised with respect to the "optical" axes of the crystals, and that these axes will generally meet the interfaces of the grains (which are necessarily in most cases incomplete crystals) obliquely, it may be that the so-called surface tensions are nothing more than the tangential resultants of the crystallising forces on the individual grains. Beilby has shown very successfully that in polishing materials the molecules are drawn out in liquid fashion to form a continuous smooth surface.

These complexities make it almost impossible to lay down at present any definite relation between the chemical constitution and cohesive strength. On the face of it, such cohesive strength involves three conditions :—

(1) A comparatively wide separation of the electric doublets so that their differential attractions are potent at a range considerably exceeding the radius of the atoms. This is a chemical condition.

*** Clerk Maxwell ("Constitution of Bodies," *Encyc. Brit.*, 9th edition) saw clearly that the strength of solids depends very much on the existence of configurations of various degrees of stability.**

(2) A dense packing of the molecular atom-groups. This is a physico-chemical condition which is well illustrated by the varying strengths of the allotropic forms of the elements.

(3) A low oscillation range in the atoms—*i.e.*, high frequency and high atomic weight.

It is interesting in this connection to observe that the gases and liquid and metalloid elements are to some extent clustered in the periodic table as usually written, the electro-positive and more characteristic metallic forms tending towards the right bottom corner of the table.

A further observation is that chemical affinity is not necessarily concomitant with great cohesion, and that the artificial products which have great strength are chiefly artificial, endothermic, and unstable.

We are thus led to conclude that many of the most obvious properties of solid matter are functions of atomic structure, so that until the latter is fully understood the former cannot be fully explained.

There are numerous practical problems in connection with the strength of materials which would doubtless be partially or wholly solved by a complete theory of cohesion. Among these the principal are the following :—

(1) The best conditions for cementation, including the questions of adhesion to various materials, the effect of the size of the grains, the quantity of water for hydration of cements, the expansion or contraction of the cement, etc.

(2) The production of maximum strength per unit volume —*i.e.*, material of absolute maximum strength (*e.g.*, areo-steel).

The solution in this case is probably to be found in the elimination of internal minute flaws. A. A. Griffith (*Phil. Trans. Roy. Soc.*, 1921, 221A, p. 163) * has shown that glass and similar material has a possible but unstable state, in which the cohesive strength is enormous, say ten times that under ordinary circumstances. Large crystals, however, appear to have less strength than aggregates of small crystals, if the planes of crystallisation are simple, and the larger the crystals the weaker are the septa between them in a mass. The ideal cohesion is the full crystallising tension, provided the tendency to shear on the planes of crystallisation can be avoided.

*** This paper, "The Phenomena of Rupture and Flow in Solids," is a most valuable contribution to the present subject.**

(3) The production of maximum strength per unit weight —*i.e.*, material of maximum strength combined with lightness (*e.g.*, wood, bone, papier-mâché, etc.). This is a question of structure. Doubtless an open fibrous fabric in which each molecule could exert its full tension with a minimum number of molecules per unit volume is the ideal, and has probably been almost realised in organic skeletons.

(4) The limitations of and the best conditions for fine grinding.

(5) The manipulation of material by heat, including welding, annealing, hardening, tempering, casting, surface treatment, etc.

(6) The stability and strength of alloys and other heterogeneous granular materials.

(7) The control of gels and gelled solids—*e.g.*, gelatine, mud, cement, etc.

(8) The production of material of maximum resilience.

(9) The ageing of materials.

(10) The improvement of material to resist alternating stress.

(11) The development of magnetic retentivity in ferromagnetic materials.

It seems perfectly clear that as time goes on it will be necessary for the structural engineer to have a much greater familiarity with analytical and physical chemistry than is generally the case at the present time. Our whole study tends to show that cohesion—*i.e.*, the strength of materials—is to a great extent a chemical form of energy, and, therefore, those who seek to exploit it must be *au fait* with the chemical constitution of the materials they use.

NAME INDEX.

SUBJECT INDEX.