Molecular Weights of Polymers.

On progressive growth of linear macromolecules we have seen that the van der Waals' forces increase, true molecular dispersion in any solvent becomes more difficult and the tendency for micelle formation increases. Application of the usual colligative methods for determination of the molecular weight is thus rendered difficult, for extremely dilute solutions must be employed. If chemical methods are employed based upon analysis of the end groups it is important to ensure that no cross-linkage can occur. When the macromolecule is of the order of 1000 or more monomeric units the presence of one part in a thousand of an impurity capable of forming a cross-link could evidently link the macromolecules to each other and, if no statistical distribution of the molecules of impurity occurred, the whole system would be locked up into one chemical unit. Such a system would be relatively unstable and easily broken down, and the true molecular weight would vary with the mechanical treatment to which the material had been subjected before examination, the isolated macromolecular units being ultimately obtained. When viscosity methods are employed for determining molecular weight we must ensure not only that the solution is sufficiently dilute to disperse all micelles to single macromolecules, but also that the macromolecules are capable of rotational movement in the solution without interference. If we take the case of a eucolloid of a polyprene of molecular weight 100,000 the spiral cylinder of length about 1000 Å.U. will require a volume of 4×10^9 Å.U.[3] for each molecule, so that we see that the dilution would have to be some 25×10^6 litres per gm. mol., *i.e.* about 10^{-8} molar for such measurements.

THE INFLUENCE OF VAN DER WAALS' FORCES AND PRIMARY BONDS ON BINDING ENERGY, STRENGTH AND ORIENTATION, WITH SPECIAL REFERENCE TO SOME ARTIFICIAL RESINS.

By J. H. de Boer.*

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Part I. The Calculation of Sublimation Energies.

1. The Expression for the Van Der Waals Reciprocal Energy.

The general forces of cohesion, or van der Waals' forces, play an important part in the building up of natural as well as artificial resins. Investigations carried out during recent years have greatly deepened our insight into the nature of the van der Waals forces. In particular, the mutual attractive forces between two or more electrically neutral and dipole-free atoms or molecules have in many cases become admissible of calculation.

Owing to the short-period movement of the electrons in the atoms and molecules, which exist even at absolute zero, there exist in all atoms dipoles, which change continually in magnitude and direction. Although

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* Translated from the manuscript by Mrs. H. E. Teves-Acly.

the atoms or molecules under consideration are electrically neutral and symmetrical on the whole over a given period of time, the continually changing dipoles induce dipoles in other neighbouring atoms and vice versa, in such a way that at each moment an attractive force results from the reciprocal action between the induced and the inducing dipoles. The reciprocal energy between an induced dipole in an atom having a polarisability α and the inducing dipole with a moment μ situated in another atom at a distance R from the first, is proportional to $\frac{\alpha\mu^2}{R^6}$. We may, therefore, also expect that the binding energies due to van der Waals' forces will vary in inverse proportion to R^6.

In this article we shall make use of the following expression for the reciprocal binding energy due to van der Waals' forces:

$$E = -\frac{C}{R^6},$$

where C represents a constant, which may be evaluated in two ways. C may be calculated from the approximation formula of London:[1]

$$C = \tfrac{3}{4}\alpha^2 h\nu_0$$

in which α is the polarisability, and $h\nu_0$ a characteristic amount of energy, which corresponds to the chief specific frequency ν_0 taken from the dispersion equation of the atom under consideration (in many cases the ionisation energy or a slightly higher energy value). C may also be calculated by means of the approximation formula of Slater and Kirkwood:[2]

$$C = 1{\cdot}36 n^{\frac{1}{2}} \alpha^{3/2} a_0^{3/2} E_0,$$

where n is the number of electrons in the outermost shell of the atom under consideration, a_0 is the radius of a hydrogen atom (0·53 Å.), and E_0 is the energy of a hydrogen atom in its normal state. According as E_0 is expressed in ergs per molecule, electron volts, or kg. cal. per gram molecule, the reciprocal energy is represented by the following three formulæ respectively:

$$\begin{aligned} E &= -\frac{11{\cdot}25 \times 10^{-24} n^{\frac{1}{2}} \alpha^{3/2}}{R^6} \text{ ergs/molecule} \\ &= -\frac{7{\cdot}07 \times 10^{-12} n^{\frac{1}{2}} \alpha^{3/2}}{R^6} \text{ electron volts} \\ &= -\frac{163 \times 10^{-12} n^{\frac{1}{2}} \alpha^{3/2}}{R^6} \text{ kg. cal./gram molecule.} \end{aligned}$$

2. Orientation caused by Van Der Waals' Forces.

The magnitude of the van der Waals forces is in the first instance independent of the direction. The value of the reciprocal energy of a given atom with respect to a large number of other atoms can be obtained by simply adding the reciprocal energies with respect to each of these other atoms individually. Because of its great dependence on distance, the magnitude of the reciprocal energy will be determined chiefly by those atoms, which can make the closest approach to the atom under discussion. Because of this circumstance, two molecules which attract

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[1] F. London, *Z. Physik*, 1930, **63**, 245; *Z. physikal. Chem.*, 1931, **11B**, 222.

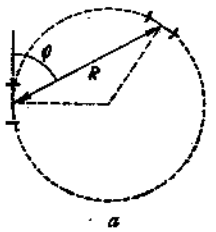
[2] J. C. Slater and J. G. Kirkwood, *Physic. Rev.*, 1931, **37**, 682.

each other by means of van der Waals' forces will always have a tendency to orient themselves into such a position, that the largest possible number of atoms are in contact with each other. Thus hydrocarbon chains will show a tendency to be oriented so that their long axes are parallel and two benzene molecules will prefer to lie with their flat sides together.

Very many molecules are anisotropic as regards their polarisability, and, in general, the direction of the greatest polarisability corresponds to that of the axis of length of the molecule. In the case of the molecules of special interest to us at this moment, this is found to be true: with the hydrocarbon chains the direction of the greatest polarisability is the same as of the axis of the molecule. In the case of benzene the polarisability in the direction perpendicular to the plane of the ring is the smallest, and it is greatest in the plane of the ring. In general, this anisotropy opposes the above-mentioned orientation due to the tendency of the atoms to secure as many neighbours as possible. If anisotropy should exist in the case of spherical molecules, so that the polarisability in one direction were greater than in the other two perpendicular directions, then two such molecules would have a tendency to orient each other in such a way that the directions of the greatest polarisability would form a straight line, since in that position the mutual energy is greatest. A dipole with a moment μ attracts an atom with a polarisability α, at a distance R in such a way that the mutual energy is:

$$E = -\frac{\alpha\mu^2}{2R^6}\{2\cos^2\phi - \sin^2\phi\}^2$$

in which ϕ is the angle which the dipole makes with the line joining it to the atom (Fig. 1*a*). When the inducing dipole is perpendicular to the line joining it to the atom ($\phi = 90°$), then the induced dipole also lies perpendicular to that line (Fig. 1*b*), and the mutual energy E equals $-\frac{\alpha\mu^2}{2R^6}$. If the direction of the inducing dipole is the same as that of the line joining the two atoms, then the induced dipole has the same direction (Fig. 1*c*) also and the reciprocal energy E is $-\frac{4\alpha\mu^2}{2R^6}$. In the case of binding by means of van der Waals' forces we are concerned with alternating inducing dipoles whereby all possible directions occur. Those directions which are the same as the line joining the atoms give rise to energies which are four times as great as the values due to dipoles perpendicular to the joining line. With infinite anisotropy, therefore, an orientation whereby the directions of greatest polarisability lie in each other's extensions, would give a van der Waals' reciprocal energy which is four times as great as that arising from an orientation whereby the direc-



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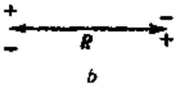

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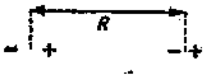

c

FIG. 1*a*.—One dipole inducing another dipole on an atom at a distance R, ϕ being the angle which the original dipole makes with the line joining it to the atom.

FIG. 1*b*.—When the inducing dipole is perpendicular to the line joining it to the atom, then the induced dipole also lies perpendicular to that line.

FIG. 1*c*.—When the inducing dipole lies in the same direction as the line joining it to the atom, then the induced dipole has the same direction.

tion of greatest polarisability of both atoms is perpendicular to the line joining them.

In the case of the molecules of interest to us at present, the orientation caused by the tendency of the atoms to gather as many neighbours as possible dominates over the effect of the anisotropy. We shall illustrate this more clearly with reference to the reciprocal energy between two benzene molecules.

3. The Reciprocal Energy between Two Benzene Molecules; Orientation of the Benzene Molecules.

The average polarisability of a benzene molecule α_0 is $10{\cdot}3 \times 10^{-24}$, the anisotropy is fairly great, the polarisability perpendicular to the plane of the ring α_c (see Fig. 2) is $6{\cdot}35 \times 10^{-24}$ and in the plane of the ring

$$\alpha_a = \alpha_b = 12{\cdot}3 \times 10^{-24}.^3$$

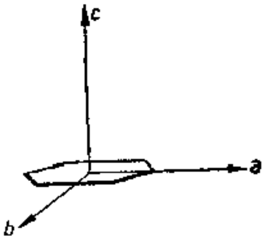

FIG. 2.—Co-ordinates are chosen in three diections *Oa*, *Ob* and *Oc*, in order to take into account the anisotropy of the polarisability.

In calculating the reciprocal energy, a benzene molecule should not be considered as a single centre of attraction; the action of the six $=$ CH groups must be investigated separately. The following polarisabilities may be credited to these $=$ CH groups, whose centres of gravity lie at the centres of the C atoms: $\alpha_0 = 1{\cdot}71 \times 10^{-24}$; $\alpha_c = 1{\cdot}06 \times 10^{-24}$; $\alpha_a = \alpha_b = 2{\cdot}05 \times 10^{-24}.^4$

Let us consider first two benzene molecules with respect to each other, as is represented in Fig. 3 (case I.). On the basis of the known data about organic molecules we may assume that the mutual distance between the two closest C atoms (bound by van der Waals' forces) will be about 3·5 Å. The reciprocal energy is obtained by adding the mutual energies of all the centres of the one molecule with those of all the centres of the other molecule:

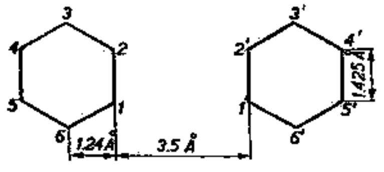

FIG. 3.—Two benzene molecules, lying in the same plane.

$$E_I = \sum -\frac{C}{R^6}.$$

In the case represented in Fig. 3, R varies from the value 3·5 Å. (between the atoms 1 and 1') to 8·59 Å. (between the atoms 4 and 5'). The summation gives:

$$E_I = -0{\cdot}0026 \times 10^{48}C.$$

Let us now consider two benzene molecules situated at a distance of 3·5 Å. from each other, with the planes of the rings parallel as in Fig. 4

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[3] H. A. Stuart, *Molekülstruktur*, Berlin, 1934, p. 225; H. A. Stuart and H. Volkmann, *Z. Physik*, 1933, **80**, 107.

[4] Strictly speaking α_a for a single $=$ CH group is not equal to α_b of that group, as here, too, the polarisability in the direction pointing towards the neighbouring atoms is somewhat greater than in the other directions lying in the plane of the benzene ring. For the sake of simplicity, however, we may consider for the individual $=$ CH groups too $\alpha_a = \alpha_b$.

(case II.), then the summation gives :

$$E_{\mathrm{II}} = -0{\cdot}0100 \times 10^{48} C,$$

a value almost four times the first, if C remains unchanged.

If the anisotropy with respect to the polarisability should be such that for each pair of centres there was a polarisability only in the direction of the joining line, then, as a consequence, the value of C in position I. would be four times as great as in position II. (see § 2), and because of this there would be no preference for either position. Because of the actual presence of an anistropy the difference in energy between position I. and position II. is, as a matter of fact, slightly lessened, but in any case the energy content of position II. is always three times as great as of position I.[5]

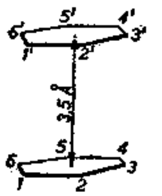

FIG. 4.—Two benzene molecules, lying in parallel planes.

We must therefore expect that benzene molecules will exhibit a tendency to orient each other in the manner represented by position II. (Fig. 4). This agrees completely with the result obtained by Briegleb,[6] that benzene molecules (as well as many other molecules for which similar considerations hold) direct each other in such a manner that the axes of greatest polarisability lie parallel to each other.[7] This result also agrees with the conclusion, which may be drawn from the X-ray analysis of liquid benzene, whereby the observed periodicity of about 3·6 Å. is correlated with a disk orientation.[8]

In this connection it is interesting to point out that in artificial resins of the type phenol or cresol formaldehyde condensation products the

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[5] For the calculation of the values of C, instead of the formula mentioned in § 1

$C = \frac{3}{4}\alpha^2 h\nu_0$, we use the expression $C = \alpha_0^{\frac{1}{2}}(\alpha_x^{3/2} + \alpha_y^{3/2} + 4\alpha_z^{3/2})\frac{h\nu_0}{8}$,

in which α_0 is the average polarisability and α_x, α_y and α_z are the polarisabilities in the x, y and z directions respectively, whereby the z direction is the same as that of the line joining the atoms. (*Cf.* an article of G. Heller and J. H. de Boer, to appear shortly in *Physica*). In case I. we then obtain

$$C_{\mathrm{I}} = \alpha_0^{\frac{1}{2}}(\alpha_a^{3/2} + 4\alpha_b^{3/2} + \alpha_c^{3/2})\frac{h\nu_0}{8} = 2{\cdot}58\, h\nu_0 \times 10^{-48}$$

and the energy content

$$E_{\mathrm{I}} = -0{\cdot}0026 \times 10^{48} \times 2{\cdot}58 \times 10^{-48} h\nu_0 = -0{\cdot}0067\, h\nu_0.$$

In case II. we calculate for the reciprocal energies of the combinations of atoms : 1-1′, 2-2′, 3-3′, etc.

$$C_{\mathrm{II}} = \alpha_0^{\frac{1}{2}}(\alpha_a^{3/2} + \alpha_b^{3/2} + 4\alpha_c^{3/2})\frac{h\nu_0}{8} = 1{\cdot}68 h\nu_0 \times 10^{-48},$$

while for the combinations : 1-2′, etc.,

$$C'_{\mathrm{II}} = \tfrac{3}{4}\alpha_0^2 h\nu_0 = 2{\cdot}19 h\nu_0 \times 10^{-48}.$$

The summation gives

$$E_{\mathrm{II}} = -(0{\cdot}00328 C_{\mathrm{II}} + 0{\cdot}00675 C_{\mathrm{II}}') \times 10^{48} = -(0{\cdot}0055 + 0{\cdot}0148) h\nu_0 = -0{\cdot}0203 h\nu_0,$$

an energy content three times as great as in case I.

[6] G. Briegleb, *Z. physikal. Chem.*, 1931, 14B, 97 ; 1932, **16**, 249.

[7] Briegleb concludes this from the decrease in the anisotropy of dipole-free molecules during transition from the gaseous state to the liquid, and from the decrease in the molar Kerr constant with increasing concentration of dissolved dipole-free molecules in a heptane solution.

[8] J. Selman, *Diss.*, Amsterdam, 1932, p. 105.

same periodicity is again observed,[9] a fact which may indicate that in the amorphous structure of these resins also a similar parallel orientation of benzene (or rather phenol) groups often occurs.

4. The Influence of Repulsive Forces.

In the bond between two or more atoms the distance by which they remain separated from each other is determined by the equilibrium between attractive and repulsive forces. If the repulsive force is expressed as an exponential function according to Born and Mayer,[10] then the expression for the mutual energy with van der Waals' attraction becomes :

$$E = -\frac{C}{R^6} + be^{-\frac{R}{\rho}}$$

where b and ρ represent constants, of which ρ may be given the value $0{\cdot}345 \times 10^{-8}$ cm., at least in the case of the reciprocal action of the binding forces (electrostatic and van der Waals' together), which act in the alkali halides. The constant b can be calculated from the equilibrium condition :

$$\left(\frac{\partial E}{\partial R}\right)_{R=R_0} = 0 = \frac{6C}{R_0{}^7} - \frac{1}{\rho}be^{-\frac{R_0}{\rho}}$$

(R_0 is the distance between the bound atoms, and therefore the value of R at the minimum of energy). Then for the binding energy it follows that

$$E_0 = -\frac{C}{R_0{}^6}\left(1 - \frac{6\rho}{R_0}\right)$$

With $\rho = 0{\cdot}345 \times 10^{-8}$ cm. and R_0 about 3·5 Å., this becomes

$$E_0 = (\text{about}) - 0{\cdot}4\,\frac{C}{R_0{}^6}.$$

With the aid of the approximation formula for C mentioned in § 1, London [11] has calculated the sublimation energies of a great many gases in the solid state, and obtained results which are in good agreement with known experimental data. London neglects, however, the repulsive forces. Born and Mayer [10] point out that when account is taken of the repulsive forces the agreement with experiment is much less exact. It must here be noted that the approximation formula of Slater and Kirkwood also gives good results for the sublimation energies of molecular lattices, when the repulsive forces are neglected. For example, the sublimation energy for solid argon according to London's formula is found to be 2·08 kg. cal./mol., according to Slater and Kirkwood it is 2·35 kg. cal./mol., while the experimental value is 2·03 kg. cal./mol. If we choose another example from the hydrocarbons, we find that the sublimation energy of solid methane [12] according to London's formula is 2·3 kg. cal./mol., according to Slater and Kirkwood's formula it is 2·7 kg. cal./mol., while the experimental value is 2·7 kg. cal./mol. Such examples may be multiplied, so that it seems as if the potential contri-

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[9] R. Houwink, *Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934, p. 179.

[10] M. Born and J. E. Mayer, *Z. Physik*, 1932, **75**, 1.

[11] F. London, *Z. physikal. Chem.*: 1931, **11B**, 222.

[12] The lattice distance for the face-centred methane lattice is : $d = 5{\cdot}89$ Å., *cf.* H. H. Mooy, *Proc. Amsterdam*, 1931, 34, 660 ; *Nature*, 1931, **127**, 707. London used a slightly lower value.

bution of the repulsive forces is much smaller than the formula of Born and Mayer would lead one to think. It may be that, at the relatively great distances caused by van der Waals' bonds, the repulsive forces obey a different relation. One might be able to work formally with the expression b/R^n, often used previously, whereby very high values [13, 14] would have to be ascribed to n.

Another possibility is that the approximation formulæ used give a value for the van der Waals attraction, which is too small at the distances with which we are concerned. In a recent article Pauling and Beach [15] calculate the van der Waals interaction of hydrogen atoms and use not only the terms in $1/R^6$, but also those in $1/R^8$ and $1/R^{10}$. At a distance of 3·5 Å. this further approximation gives an energy value one and one-half times as large as that given by the previously used formulæ. If this result is capable of generalisation, it means in the case we are considering that the increase of energy given by the closer approximation is just about compensated for by the repulsive forces.

For the present we shall make use of the approximation formulæ of London or of Slater and Kirkwood for the calculation of the energy magnitudes, without taking into account the repulsive forces, while in the calculation of tensile strengths in Part II. we shall include the repulsive forces in our calculations (in order to obtain a maximum in the distance-force curve), and thus have the assurance that our calculated values represent minima.

5. The Sublimation Energy of Benzene.

Since the van der Waals binding energy of benzene molecules can throw light on the particular problems connected with the bond in many artificial resins, we shall in this section examine whether or not the result obtained in the previous section is valid in the calculation of the sublimation energy of solid benzene, that is to say, whether or not the energy value is adequately represented by the approximation formulæ given in § 1, no account being taken of the repulsive forces.

The crystal structure of solid benzene is not known with absolute certainty: the structure as determined by Cox,[16] however, offers sufficient points of contact for our calculations. The unit cell (at − 22° C.) of the rhombically crystallising benzene contains four molecules, and has the following dimensions: $a = 7{\cdot}4^4$ Å., $b = 9{\cdot}6^5$ Å., $c = 6{\cdot}8^1$ Å. The position of the molecules is probably similar to that shown in Fig. 5. The shaded molecules lie at a distance $b/2$ below and above the plane of the drawing. The distance between the centres of the molecules A and B is 5·04 Å., that between A and C, 5·90 Å., between A and D, 6·1 Å., and between A and A', 6·8 Å. The molecules make an angle of about 40° with the 100 plane. In the calculation we shall use 45°. The respective positions of molecules A and B become those represented schematically in Fig. 6. Molecule A is in this way surrounded by four other molecules. The CH centres 1 and 6', and 2 and 3' lie closest to each other (3·87 Å.), the greatest separation is that of 4 and 6', and 5 and 3' (6·62 Å.). The relative positions of A and C are then represented by

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[13] K. Wohl, *Z. physikal. Chem.*, 1931, **14B**, 36.

[14] G. Heller mentioned the possibility that for atoms, like argon, where the valence electrons have an orbital momentum, the valence forces give an attraction rather than a repulsion at these distances.

[15] L. Pauling and J. Y. Beach, *Physic. Rev.*, 1935, **47**, 686.

[16] E. G. Cox, *Proc. Roy. Soc.*, 1932, **135A**, 491.

the position shown schematically in Fig. 7, in which the molecule C' must be imagined to lie 2·52 Å. above the plane of the drawing. The shortest distance between two centres is then 3·9 Å. (1-5′ and 2-4′). The positions of A and C' are taken as representative also for A and D in

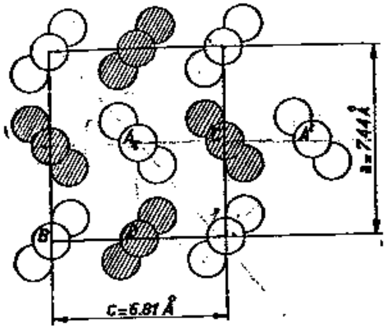

FIG. 5.—Diagram representing the crystal structure of solid benzene, according to E. G. Cox, *Proc. Roy. Soc.*, 1932, **135A**, 491.

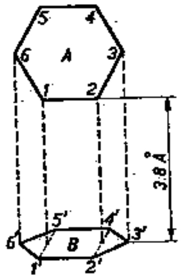

FIG. 6.—Relative positions of molecules A and B of Fig. 5.

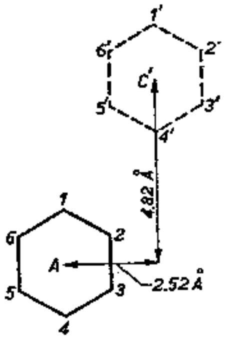

FIG. 7.—Relative positions of molecules A and C or A and D of Fig. 5; the molecule C' must be imagined to lie 2·52 Å. above the plane of the drawing.

Fig. 5. The relative positions of A and A' are represented by Fig. 8, in which molecule A' must be imagined to lie 5·04 Å. above the plane of the drawing. The shortest distance between two centres is then 5·66 Å. (1-5′ and 2-4′). Molecule A is thus surrounded by four molecules whereby the relative position is as of A to B, by eight molecules with relative position A to C', by four with the relative position A to A', etc. The mutual energy of the six groups of molecule A with respect to the groups of the surrounding molecules is now added for all groups within the distance 6·81 Å. (408 terms), and then the mutual energy with respect to the remaining groups is calculated by integration from 6·81 Å. on

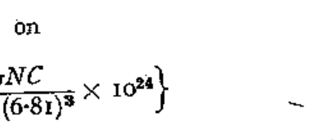

FIG. 8.—Relative positions of molecules A and A' of Fig. 5; the molecule A' must be imagined to lie 5·04 Å. above the plane of the drawing.

$$E_A = -\left\{ \sum_{R=3\cdot87}^{R=6\cdot81} \frac{C}{R^6} + \frac{8\pi NC}{6 \times (6\cdot81)^3} \times 10^{24} \right\}$$

where N is the number of centres of attraction (— CH groups) per cm.^{3} ($0{\cdot}049 \times 10^{24}$). The evaluation gives:

$$E_A = -\{0{\cdot}0270_5 C + 0.0006_5 C\} \times 10^{48} = -0{\cdot}0277\, C \times 10^{48}.$$

The value of C is calculated by means of the Slater-Kirkwood approximation formula mentioned in § 1:

$$C = 163 \times 10^{-12} n^{\frac{1}{2}} \alpha^{3/2},$$

in which $n = 5$ and $\alpha = 1{\cdot}71 \times 10^{-24}$ (in this case, because of the relative positions of the molecules no account need be taken of the anisotropy).

The sublimation energy S is equal to half the reciprocal energy of one molecule with respect to the rest of the lattice. Thus we may write:

$$S = -\frac{E_A}{2} = \frac{0{\cdot}0277}{2}C = 11{\cdot}3 \text{ kg. cal./gram molecule.}$$

The experimentally found value of the sublimation energy of solid benzene at 0° C. is 10·67 kg. cal./gram molecule, so that we see here again that the approximation formula of Slater and Kirkwood gives a correct result when the potential due to the repulsive forces is neglected.

Part II. The Tensile Strength and Van Der Waals' Forces in Polymers.

6. The Tensile Strength of Sodium Chloride.

It is a well-known fact that the tensile strength of a crystal like that of common salt is much smaller than the value calculated by means of the lattice theory from the electrostatic forces. If the temperature is chosen such that practically no plastic deformation occurs (in any case below 200° C.), values of from 0·4 to 0·6 kg/mm^2 are found for the tensile strength, while the calculation by means of the lattice theory gives a value[17] of about 200 kg/mm.^{2}. This great discrepancy between the experimental and the theoretical values is ascribed chiefly to the "notch effect," which may arise from the presence of incidental small cracks[18] on the surface, but which is due especially to the more or less regularly distributed defects of the crystal structure (*Lockerstellen*).[19] In particular, the investigations of Smekal[20] and his co-workers have shown how many properties of crystalline matter are dependent upon these internal defects of the crystal structure (properties sensitive to structure). Zwicky[21] had previously given a possible explanation in his conception of the mosaic structure of crystals. According to this conception a "secondary" lattice is superposed on the "primary" lattice, in such a way that lattice planes occur at regular distances in the lattice having a separation from the other planes differing from that between the primary crystal planes. In this manner the crystal would be divided into blocks with the dimensions in the three directions varying from 100 to 1000 times the separation of the ions. While these blocks may be considered as ideal lattices, the forces which act between the blocks are, however, much weaker than in the lattice. Although this concept has experienced much opposition[22] it is nevertheless desirable, in studying the artificial resins, to find out what a calculation of the forces indicates in this connection. If such a secondary structure actually existed, one could assume that the electrostatic reactions among the various blocks would be neutralised, while the van der Waals forces would, however,

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[17] F. Zwicky, *Physikal. Z.*, 1923, **24**, 131.

[18] A. F. Joffé, *The Physics of Crystals*, New York, McGraw Hill, 1928.

[19] *Cf.* for example, A. Smekal, *Physikal. Z.*, 1933, **34**, 633, and also a very recent survey by W. G. Burgers and J. M. Burgers, in the *First Report on Viscosity and Plasticity*, Royal Acad. Amsterdam, 1935.

[20] *Cf.* for example, A. Smekal in *Handb. d. Physik 2e Auflage*, 1933, Band 24, 2, pp. 795-923, and also J. H. de Boer, *Electron Emission and Adsorption Phenomena*, Cambridge, 1935, chap. X.

[21] F. Zwicky, *Helv. Physic. Acta*, 1930, **3**, 269, and more recent literature.

[22] See, among others: E. Orowan, *Z. Physik*, 1932, **79**, 573; *Helv. Physica Acta*, 1933, **7**, 285.

continue to function. We must therefore investigate the influence of the van der Waals' forces on the tensile strength.

7. The Influence of Van Der Waals' Forces on the Tensile Strength of Sodium Chloride.

In order to study the influence of van der Waals' forces on the tensile strength of sodium chloride, we must successively calculate the tensile strength when (*a*) only electrostatic forces and repulsive forces are acting, (*b*) when electrostatic, van der Waals' and repulsive forces act, and (*c*) when only van der Waals' and repulsive forces act.

(a) Only Electrostatic and Repulsive Forces.

Imagine a section through a crystal of sodium chloride parallel to a face of the cube. The electrostatic attractive force which is experienced by an ion at a distance r from a 100 plane can be calculated with the aid of a formula given by Hückel :[23]

$$F_{\text{el.}} = \frac{\epsilon^2}{a^2} 2\pi \times 16 e^{-2\pi\sqrt{2}\frac{r}{a}},$$

in which a is the lattice distance (the distance between two similarly charged ions, 5·628 Å.) and ϵ is the charge on an ion. This force decreases with increasing distance so rapidly that an ion at a distance $r = a$ experiences practically no more attraction. For the calculation of the tensile strength, therefore, it is sufficient to take into account only the first layer of ions, which are situated at a distance of $r_0 = \frac{1}{2}a$ from the imaginary plane.

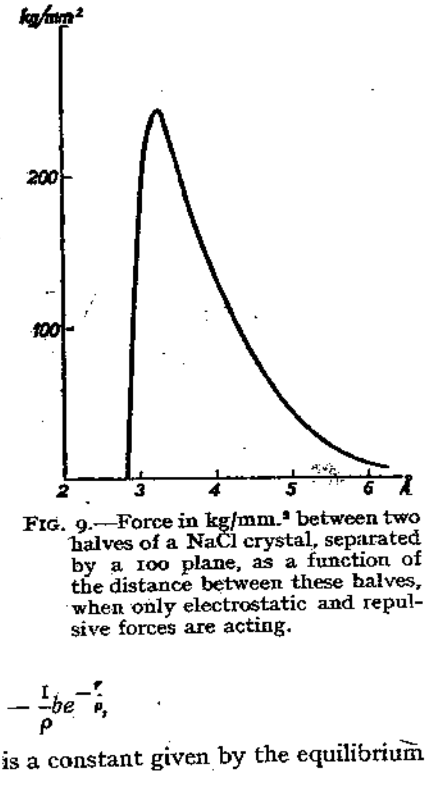

FIG. 9.—Force in kg/mm.² between two halves of a NaCl crystal, separated by a 100 plane, as a function of the distance between these halves, when only electrostatic and repulsive forces are acting.

The repulsive forces may be expressed by the following formula according to Born and Mayer :[10]

$$F_{\text{rep.}} = -\frac{1}{\rho} b e^{-\frac{r}{\rho}},$$

where $\rho = 0{\cdot}345 \times 10^{-8}$ cm. and b is a constant given by the equilibrium condition ($r_0 = 2{\cdot}814$ Å.) :

$$(F_{\text{el.}} - F_{\text{rep.}})_{r=r_0} = 0 = \frac{\epsilon^2}{a^2} 2\pi \times 16 e^{-2\pi\sqrt{2}\frac{r_0}{a}} - \frac{1}{\rho} b e^{-\frac{r_0}{\rho}}.$$

If we substitute the value of b thus obtained, we have for the total force acting upon an ion

$$F = \frac{\epsilon^2}{a^2} 2\pi \times 16 e^{-\pi\sqrt{2}} \left\{ e^{2\pi\sqrt{2} \times \frac{r_0 - r}{a}} - e^{\frac{r_0 - r}{a}} \right\}.$$

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[23] E. Hückel, *Adsorption und Kapillarkondensation*, Leipzig, 1928, p. 125.

The force acting over 1 cm.^{2} is obtained[24] by multiplying by N_2, the number of ions per cm.^{2} ($0{\cdot}126 \times 10^{16}$). This force $N_2 \times F$ is represented in Fig. 9. It reaches a maximum at a distance $r_{max.}$, which is given by the relation

$$\left(\frac{\partial F}{\partial r}\right)_{r=r_{\max}} = 0.$$

The calculation gives $r_{max.} = 3{\cdot}27$ Å., while the maximum value of N_2F, that is of the tensile strength is found to be:

$$N_2F_{\mathrm{max.}} = 238 \text{ kg./mm.}^2$$

a value which agrees very well with that calculated by Zwicky.[25]

(b) Electrostatic Attractive Forces, Van der Waals' Attractive Forces and Repulsive Forces.

If we again consider an ion opposite a 100 plane, the van der Waals attractive force which is experienced by the ion due to the portion of the crystal limited by the 100 plane, is calculated by the addition of the components of the van der Waals forces perpendicular to the plane, which forces are exercised by the individual centres of attraction of the portion of the crystal under consideration (see Fig. 10):

$$F_{\mathrm{ion}} = \sum \frac{6C}{R^7} \cos \phi$$

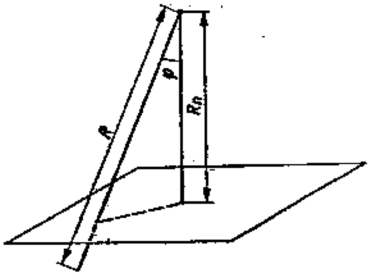

FIG. 10.—An ion opposite to a 100 plane has a distance R_n from that plane; the distance from an arbitrary ion of the portion of the crystal limited by the 100 plane is denoted R, ϕ being the angle between the direction to that ion and the normal to the plane.

This summation can be carried out in the case of sodium chloride, but since, in a similar connection, in the case of artificial resins the summation cannot be made because of the unoriented amorphous character of the resins, we shall replace the summation in this case already by an integral

$$F_{\mathrm{ion}} = \iiint \frac{6C}{R^7} \cos \phi N_3 dV = \frac{\pi N_3 C}{2R_n^4},$$

in which expression N_3 is the number of ions per cm.^{3} of sodium chloride and R_n the shortest distance from the ion under consideration to the plane.

If we now consider the whole row of ions which lie along a single line perpendicular to the 100 plane, then, in order to calculate the van der Waals force experienced by the row of ions, we would have to make a summation over the row

$$F_{\mathrm{row}} = \Sigma F_{\mathrm{ion}}.$$

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[24] We shall use N_1 for the number of ions or atoms per cm. and N_3 for the number of ions or atoms per cm.^{3}

[25] In this calculation and in the others further on in this paper we neglect the small influence of the lateral contraction.

In view of the calculations to follow in the case of artificial resins, we again replace this summation by an integral

$$F_{\text{row}} = \int \frac{\pi N_3 C}{2R_n^4} N_1 dR_n = \frac{\pi N_3 N_1 C}{6r^3}$$

in which N_1 is the number of ions per cm. (of a row) and r is the shortest distance of the closest ion to the 100 plane. Since in addition there are N_2 of these rows per cm.^{2}, we obtain for F_w, the van der Waals attractive force perpendicular to a 100 plane between two halves of a crystal of 1 cm.^{2} section:

$$F_w = \frac{\pi N_3 N_2 N_1 C}{6r^3} = \frac{\pi N_3^2 C}{6r^3},$$

since $N_2 \times N_1 = N_3$.
The total force per cm.^{2} is now given by

$$F = F_{\text{el.}} + F_w - F_{\text{rep.}} = N_2 \frac{\epsilon^2}{a^2} 2\pi \times 16 e^{-2\pi\sqrt{2}\frac{r}{a}} + \frac{\pi N_3^2 C}{6r^3} - N_2 b \frac{1}{\rho} e^{-\frac{r}{\rho}}.$$

With the aid of the equilibrium condition

$$(F)_{r=r_0} = 0$$

one can express $\frac{N_2 b}{\rho}$ in the other terms. The magnitude C is calculated by means of the approximation formula of Slater and Kirkwood (§ 1):

$$C = 11{\cdot}2^5 \times 10^{-24}\, n^{\frac{1}{2}}\, \alpha^{3/2} \text{ ergs} \times \text{cm.}^6$$

Again in order to allow analogy with the resins we use for α an average value, such as can be calculated directly from the molar refraction of sodium chloride[26]

$$\frac{3{\cdot}25}{2} \times 10^{-24} = 1{\cdot}6 \times 10^{-24}$$

while further $n = 8$. For C we find

$$C = 64{\cdot}5 \times 10^{-60} \text{ ergs} \times \text{cm.}^6$$

If we substitute this value as well as those for N_2, r_0, a and ρ, and let $N_3 = 0{\cdot}0448 \times 10^{24}$, then we obtain for F:

$$F = 9{\cdot}13 \times 10^{12}\, e^{-1{\cdot}575\times 10^8 r} + \frac{0{\cdot}068 \times 10^{-12}}{r^3} - 3{\cdot}86 \times 10^{14}\, e^{-2{\cdot}9\times 10^8 r} \text{ dynes/cm.}^2$$

This function is of course zero when $r = r_0 = 2{\cdot}814$ Å., and reaches a maximum when r is about 3·25 Å. The tensile strength is about 262 kg./mm.^{2} The van der Waals forces have thus a not unimportant influence on the tensile strength; actually their influence is still very much greater since we have here integrated over regions where this is not permissible, and have used an average[27] value of α in the calculations. The

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[26] *Cf.* J. H. de Boer and J. F. H. Custers, *Z. physikal. Chem.*, 1934, 25B, 233.

[27] Substitution of the average value of α by the true values of α for the ions (Cl': $\alpha = 3{\cdot}55 \times 10^{-24}$; Na^+: $\alpha = 0{\cdot}20 \times 10^{-24}$, see A. E. van Arkel and J. H. de Boer, *Chemische Bindung*, Leipzig, 1931, p. 91), but retention of the integration has only a slight influence. Instead of the value of C used ($64{\cdot}5 \times 10^{-60}$ ergs cm.^{6}) three values of C enter the calculations: $C_{\text{Cl-Cl}} = 221 \times 10^{-60}$, $C_{\text{Na-Na}} = 3{\cdot}03 \times 10^{-60}$ and $C_{\text{Cl-Na}} = 25{\cdot}9 \times 10^{-60}$, and the van der Waals force becomes 10 per cent. greater.

actual value of the van der Waals attractive forces at 3·25 Å. is even greater [28] than 160 kg./mm.^{2}, so that the theoretical tensile strength of sodium chloride is probably greater than 400 kg./mm.^{2} The origin of this relatively great influence compared with that of the electrostatic forces in the case of the tensile strength, notwithstanding the fact that the influence of the van der Waals forces on the lattice energy is only slight, may be ascribed chiefly to the circumstance that the electrostatic forces to a great extent neutralise each other.[29]

(c) Only Van der Waals' Forces and Repulsive Forces.

Let us imagine that the electrostatic action between two 100 planes in sodium chloride is completely neutralised. These two planes will then seek a new equilibrium position with respect to each other. The separation at equilibrium will become greater than $r_0 = 2{\cdot}814$ Å. since it would be determined only by van der Waals' and repulsive forces. If we determine the shape of the function

$$F' = F_w - F_{\text{rep.}}$$

or in numerical values

$$F' = \frac{0{\cdot}068 \times 10^{-12}}{r^3} - 3{\cdot}86 \times 10^{14}\, e^{-2{\cdot}9\times10^{8} r} \text{ dynes/cm.}^2$$

we obtain the curve shown in Fig. 11. $F' = 0$ when $r =$ (about) 4·55 Å., and it reaches a maximum when $r =$ (about) 5·2 Å. The two planes under consideration would thus be situated at about 4·55 Å. from each other, while the force acting between the two parts of the crystal would be about 3·7 kg./mm.^{2} The force actually prevailing is again very much greater, since here again integration gives much too small values [30] and, moreover, at these relatively great distances either the influence of the repulsive forces is probably much smaller than is assumed in the calculation, or here again the van der Waals force is much greater than is given by the approximation formulae (§ 4).

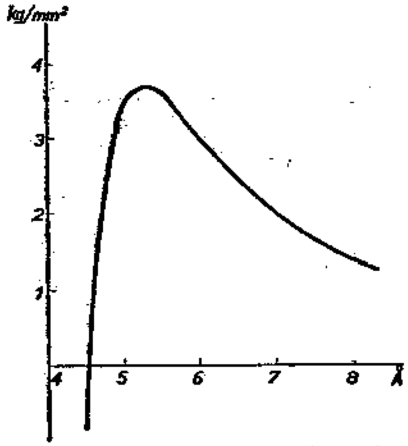

FIG. 11.—Force in kg/mm.^{2} between two halves of a NaCl crystal, separated by a 100 plane, as a function of the distance between these halves, when only van der Waals' and repulsive forces are acting.

If, according to Zwicky's hypothesis, blocks exist between which smaller electrostatic forces

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[28] One arrives at this value if a summation is made separately for the Na$^+$ ions and the Cl$^-$ ions and if the α-values for these ions are used. It is possible that further approximation of the van der Waals reciprocal energy would give still greater values (see § 4).

[29] The binding energy of an ion at a normal distance from a 100 plane is only about 0·04 of the binding energy in a lattice; *cf.* for example, J. H. de Boer, *Electron Emission and Adsorption Phenomena*, Cambridge, 1935, p. 41.

[30] If, for example, no integral is substituted for the summation for F_{row}, an equilibrium distance is found at $r < 4{\cdot}5$ Å., a maximum at about 5·0 Å., and a force of about 7·2 kg/mm.^{2}

act, then these blocks must always remain at a distance of $< 4{\cdot}5$ Å. from each other owing to the van der Waals forces, while the force in every case is $\gg 3{\cdot}7$ kg./mm.^{2} In the occurrence of a rupture due to tension in the case of cubic blocks the surface obtained per half crystal may be up to three times the cross section, so that a certain force must be employed in order to slide the blocks along each other. The force will probably be hereby increased by about 20 per cent., so that a value for the tensile strength of certainly $\gg 4{\cdot}5$ kg./mm.^{2} is obtained, and in view of the method of calculation probably a value of > 20 kg./mm.^{2} An hypothesis of a regular division into blocks cannot therefore explain the low experimental values of the tensile strength.

8. Certain Numerical Values necessary for the Calculation of the Tensile Strength of Phenol and *m*-Cresol Formaldehyde Condensation Products.

As examples of artificial resins whose tensile strengths we shall attempt to calculate we are taking the phenol-formaldehyde condensation product and the *m*-cresol-formaldehyde condensation product, both of which are resins which can react in three dimensions. We shall take as structural unit of the phenol-formaldehyde condensation product $C_6H_2OH(CH_2)_{3/2}$, or rather twice this unit, namely $(C_6H_2)_2(OH)_2(CH_2)_3$, with an equivalent weight[31] of 224. Such a unit has 17 centres of attraction (C, CH, CH_2 and OH groups), which can manifest themselves in the van der Waals attractive forces. We shall only consider those of the direct C—C linkages (" primary bonds ") between the phenyl groups and the CH_2 groups since these are weaker than the bonds in the benzene ring itself, and will therefore be the first to give way when a rupture takes place. Table I. contains the data necessary for the calculations :—

TABLE I.

	Phenol-formaldehyde Condensation Product.	*m*-cresol-formaldehyde Condensation Product.
Structural unit . . .	$(C_6H_2)_2(OH)_2(CH_2)_3$	$(C_6H)_2(CH_3)_2(OH)_2(CH_2)_3$
Attraction centres per unit .	17	19
" Primary bonds " per unit .	6	6
Density	1·3	1·2
Equivalent weight . .	224	252
Attraction centres per cm.^{2} (N_3)	6×10^{22}	$5{\cdot}5 \times 10^{22}$
Attraction centres per cm.^{3} (N_2)	$15{\cdot}3 \times 10^{14}$	$14{\cdot}4 \times 10^{14}$
Attraction centres per cm. (N_1)	$3{\cdot}9 \times 10^{7}$	$3{\cdot}8 \times 10^{7}$
" Primary bonds " per cm.^{2}	$7{\cdot}6 \times 10^{14}$	$6{\cdot}7 \times 10^{14}$
Index of refraction . .	1·65	1·62
Equivalent refraction . .	62·5	74
α per structural unit . .	$24{\cdot}7 \times 10^{-24}$	29×10^{-24}
α per attractive centre . .	$1{\cdot}45 \times 10^{-24}$	$1{\cdot}53 \times 10^{-24}$
$\bar{n}$ (average number of electrons for the Slater-Kirkwood formula)	5	5

9. Theoretical Tensile Strength due to " Primary Bonds."

Just as in the calculation of electrostatic bonds, the heat of combination cannot be taken as a measure of the strength of the bond, but the

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[31] *Cf.* R. Houwink, *Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934, p. 118.

Coulomb force itself must be calculated, so also in the case of the C—C bond. In the carbon bond the starting-point is not the normal carbon atom, but an excited carbon atom with a high energy. In the description of the change in energy content, therefore, one does not start from the ground energy level, but from a much higher (7 to 7·5 electron volts) energy level. If the C—C bond between two aliphatic C atoms is considered by itself, the energy content of the bond [32] is 6·95 electron volts (160 kg. cal./gram equivalent = 11 × 10^{-12} erg/bond).

In order to trace the potential curve of such a bond use is made of the formula proposed by Morse,[33] which expresses the energy content Q as a function of the energy content Q_0 at the minimum of the potential curve, and of the distance r.

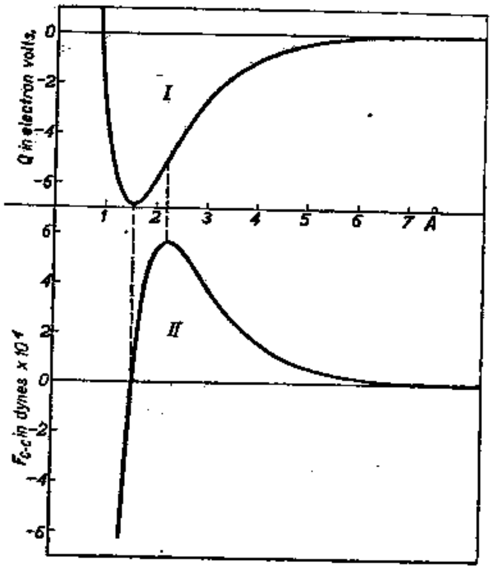

FIG. 12.—Potential energy (in electron volts) and force (in dynes) between two aliphatic bound carbon atoms as a function of the distance between these atoms.

$$Q = Q_0 e^{-2a(r-r_0)} - 2Q_0 e^{-a(r-r_0)},$$

in which r_0 is the equilibrium distance, and a is a constant given by the formula

$$a = \sqrt{\frac{8\pi^2 c\mu\omega_0 x}{h}}.$$

In this formula c is the velocity of light, μ the so-called reduced mass, ω_0 the specific frequency of the bond, and x a so-called anharmonic factor. In our case $\mu = 9{\cdot}95 \times 10^{-24}$ gram, $\omega_0 = 810$ cm.$^{-1}$ (0·1 electron volt), while x follows from Morse's relation $Q_0 = \frac{\omega_0^2}{4\omega_0 x}$, and is found to be 36×10^{-4}. When c and h are substituted, we obtain $a = 1{\cdot}025 \times 10^8$ cm.$^{-1}$. The curve which represents Q as a function of r is illustrated by curve I. in Fig. 12. The force between the two C atoms can be calculated from Q.

$$F_{C-C} = \frac{\partial Q}{\partial r} = -2aQ_0 e^{-2a(r-r_0)} + 2aQ_0 e^{-a(r-r_0)}.$$

Curve II. in Fig. 12 gives F as a function of r, the value is maximum for a $r_{max.}$ value given by :

$$\frac{\partial F}{\partial r} = 0 = 4\, a^2 Q_0 e^{-2a(r_{max.}-r_0)} - 2a^2 Q_0 e^{-a(r_{max.}-r_0)},$$

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[32] R. Serber, *J. Chem. Physics*, 1935, 3, 81. The heat of combination calculated from heat of combustion is 71 kg. cal./gram equivalent.

[33] P. H. Morse, *Physic. Rev.*, 1929, 34, 57.

or

$$r_{max.} = \frac{ar_0 + \ln 2}{a}.$$

With the value of a calculated above as $1{\cdot}025 \times 10^8$ cm.$^{-1}$ and the value of $r_0 = 1{\cdot}55 \times 10^{-8}$ cm. (the distance between two C atoms directly bound) one may calculate for $r_{max.}$.

$$r_{max.} = 2{\cdot}23 \text{ Å}.$$

With this value the force

$$(F_{C-C})_{max.} = 2aQ_0\{e^{-\ln 2} - e^{-2\ln 2}\} = \frac{aQ_0}{2},$$

or numerically

$$(F_{C-C})_{max.} = 5{\cdot}64 \times 10^{-4} \text{ dynes}.$$

If we now assume that the phenol-formaldehyde condensation product and the *m*-cresol-formaldehyde condensation product are built up entirely by "primary bonds" which have resulted wholly from condensation reactions, in other words, if we assume that an entire object forms as it were a single large molecule (as may be done with an ideal crystal of common salt), then the tensile strength of phenol-formaldehyde condensation product is about 4300 kg./mm.^{2} and of *m*-cresol-formaldehyde condensation product about 3800 kg./mm^2.

The actual theoretical values are still somewhat higher, since in the calculations in this section no account has yet been taken of the van der Waals forces. These latter raise the values in this case relatively only slightly.

As appears from the communication of R. Houwink [34] to this Discussion the experimental values, in this case, just as in the case of sodium chloride, are only of the order of magnitude of $\frac{1}{1000}$ of the theoretical.

10. Theoretical Tensile Strength Due to Van der Waals' Forces.

In the case of these artificial resins one may assume that the whole is built up of relatively large regions, within which the constituents are bound by primary bonds, and which are themselves fastened to each other by means of van der Waals' forces.[35] Apart from the irregularity of the "blocks" in this case, the structure may to a certain extent be compared with that which was discussed in reference to sodium chloride.[36] One may now ask whether or not the repulsive forces used in the previous section which are valid for the direct C—C linkage, may also be used here. With sodium chloride such a method was applied in § 7, but in that case the electrostatic as well as the van der Waals forces prevailed for all ions and we were concerned with centres with separate shells of electrons, which in a certain sense had maintained their individuality with respect to each other. For the van der Waals forces in artificial resins this is also the case, but for the C—C linkages of the previous section it is not so, since these latter occur only between certain atoms which possess common electrons. If, notwithstanding this, we apply the repulsive forces of the C—C linkages from the previous section to all cases of van der Waals' reciprocal action, we obtain

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[34] R. Houwink, *This No.*, p. 128.

[35] In reality, in the case of the thermo-setting resins under consideration, regions will be partially glued to each other by primary bonds, while in addition van der Waals' forces also act, *cf.* § 12.

[36] Still better, it could be compared with a crystalline conglomerate which has been sintered, see Fig. 5 of the communication of R. Houwink. *This No.*, p. 129.

an improbably great "equilibrium distance" for the van der Waals bond, *viz.*, about 6 Å.

We know from experience with organic molecular lattices and fluids, that when there is a van der Waals linkage of aromatic remainders the molecules remain apart by from about 3·5 to 3·7 Å. The phenol and cresol-formaldehyde condensation products as regards their X-ray diagrams[9] and their optical behaviour[37] correspond exactly to the phenol, so that it is permissible to apply the same distances for the van der Waals bond between two individuals. For phenol-formaldehyde condensation product we choose 3·5 Å. and for *m*-cresol-formaldehyde condensation product 3·6 Å., on the basis of the X-ray diagrams for these materials.

On the basis of the results of Lennard-Jones and of Wohl[38] the repulsive forces will be taken into account by means of the usual formula

$$F_{\text{rep.}} = \frac{k}{r^n}$$

where n is a number[39] greater than 10. If we combine this with the expression for the van der Waals forces derived in § 7, then we obtain as force per cm².

$$F_{\text{cm}^2} = (F_w)_{\text{cm}^2} - (F_{\text{rep.}})_{\text{cm}^2} = \frac{\pi N_3{}^2 C}{6r^3} - \frac{B}{r^n}.$$

From the equilibrium condition

$$(F)_{r=r_0} = 0 = \frac{\pi N_3{}^2 C}{6r_0{}^3} - \frac{B}{r_0{}^n}$$

a value of B is found, so that the expression becomes:

$$F_{\text{cm}^2} = \frac{\pi N_3{}^2 C}{6r^3}\left\{1 - \left(\frac{r_0}{r}\right)^{n-3}\right\}.$$

We are interested only in the maximum value of this force; concerning this maximum we have

$$\frac{\partial F}{\partial r} = 0 = \frac{3\pi N_3{}^2 C}{6r^4_{max.}} - \frac{n\pi N_3{}^2 C r_0{}^{n-3}}{6r^{n+1}_{max.}}.$$

From this follows

$$\frac{3}{r^4_{max.}} = \frac{n r_0{}^{n-3}}{r^{n+1}_{max.}}$$

or

$$\left(\frac{r_0}{r_{max.}}\right)^{n-3} = \frac{3}{n}.$$

For the maximum force per cm². we therefore obtain

$$(F_{\text{cm}^2})_{max.} = \frac{\pi N_3{}^2 C}{6r^3_{max.}}\left\{1 - \frac{3}{n}\right\}.$$

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[37] J. H. de Boer, R. Houwink and J. F. H. Custers, *Rec. trav. chim. P.B.*, 1933, 52, 709.

[38] J. E. Lennard-Jones, *Proc. Physic. Soc.*, 1931, 43, 461 and earlier literature. K. Wohl, *Z. physikal. Chem.* 1931, 14B, 36; *Bodenstein Festband*, 1931, p. 807.

[39] *Cf.* also A. E. van Arkel and J. H. de Boer, *Chemische Bindung*, Leipzig, 1931, p. 52 ff. in which earlier literature, particularly that of J. E. Lennard-Jones, is cited.

Since we may write $n > 10$

$$(F_{\text{cm}^2})_{max.} > 0{\cdot}7\,\frac{\pi N_3{}^2 C}{6 r^3_{max.}},$$

and $r_{max.} < 1{\cdot}19\,r_0$.

Therefore

$$(F_{\text{cm}^2})_{max.} > 0{\cdot}7\,\frac{\pi N_3{}^2 C}{6(1{\cdot}19 r_0)^3}.$$

The necessary data for the calculation of C are found in Table I. For phenol-formaldehyde condensation product $C = 43{\cdot}9 \times 10^{-60}$ ergs cm^6. and for *m*-cresol-formaldehyde condensation product $C = 47{\cdot}6 \times 10^{-60}$ ergs cm^6. Using these values we can calculate the force per cm^2. for phenol-formaldehyde condensation product to be greater than 8 kg./mm.^{2} and for *m*-cresol-formaldehyde condensation product, greater than 6·4 kg./mm^2.

For very many reasons the actual forces are still many times greater than those here proposed. As in the case of common salt the chief reason is the substitution of an integral for the summation. With sodium chloride a summation was possible, but not in this case. If we desire to know the order of magnitude approximately, we may imagine the mass of the artificial resin to be replaced by a point lattice, in which the centres of attraction lie at a distance of $\frac{1}{N_1}$ from each other. If we then calculate the force between two such lattice blocks situated at a distance $r_{max.} = 1{\cdot}19 r_0$ from each other, after introducing the factor 0·7 once more to account for the repulsive force, we find

$$(F_{\text{cm}^2})_{max.} > 0{\cdot}7 \sum \frac{6C}{R^7} \cos\phi.$$

In the case of phenol-formaldehyde condensation product this becomes > 39 kg./mm^2 and for *m*-cresol-formaldehyde condensation product > 32 kg./mm.^{2} In every case the figures are many times greater than 8 kg./mm^2. and 6·4 kg./mm^2. respectively.

11. Comparison with Experimental Values.

As appears from the communication of R. Houwink [40] in this General Discussion, the values of the tensile strength are found experimentally to be the following at liquid air temperature:

phenol-formaldehyde resin (C stage) about 7·8 kg./mm^2.
m-cresol-formaldehyde [41] (C stage) about 3·8 kg./mm^2.

Just as with sodium chloride, the experimental values of the tensile strengths are not only several orders of magnitude smaller than the theoretical when it is assumed that work must be done against the primary bonds, *but the experimental values are at least one order of magnitude smaller than the theoretical values assuming only van der Waals' forces to be overcome.* Houwink therefore draws the conclusion that, just as in sodium chloride and other crystal lattices of heteropolar structure, the values here are also dominated by the notch effect, which arises

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[40] R. Houwink. This vol., p. 126.

[41] It must be remembered that the cresol resin consisted of about 60 per cent. meta cresol resin, the remainder being para and ortho.

perhaps from cracks in the surface, but especially from defects within the material.

It is, however, very remarkable that the arrangement of the figures, theoretical as well as experimental, is the same, as may be seen from Table II.

TABLE II.

Substance.	Tensile Strength in kg/mm.^{2}		
	Theoretical for Primary Bonds.	Theoretical for for V. d. Waals' Forces only.	Experimental.
Sodium chloride . . .	400	> 20	0·6
Phenol formaldehyde resin .	4300	> 39	7·8
m-Cresol formaldehyde resin .	3800	> 32	3·8

Possibly this means that in every case the arrangement of the strength of the individual bonds of one single "centrum of attraction" is found, as by working with the mechanism of the notch effect too these individual bonds must be loosened.

K. H. Meyer and H. Mark [42] estimate the tensile strength of cellulose fibres at 800 kg./mm^2., assuming that primary bonds are actually broken. In § 9 we saw the force to be overcome for one primary bond is $5{\cdot}64 \times 10^{-4}$ dyne. Since there are 4×10^{14} primary bonds per cm^2. in cellulose fibres, the theoretical tensile strength may be calculated to be 2260 kg./mm^2. As Meyer and Mark, however, rightly remark, in this case also only the van der Waals forces are overcome by the rupture. The tensile strength is here composed of the force necessary for tearing loose certain van der Waals linkages and the force necessary to cause the stretched molecules to slide over one another. If the maximum force is overcome in the process of rupture, at that moment 4×10^{14} atoms per cm^2. are removed from the influence of van der Waals' attraction, while in the most favourable case 2×10^{14} chains are displaced over a certain distance along other chains. Only a small force is necessary to cause one centre of attraction of a given chain to slide along the surrounding chains, since only enough force must be applied to shift such a centre from place to place. Because of the large number of centres of attraction in one chain, which must all be displaced at the same time, a large force is, however, necessary for the displacement. As Meyer and Mark show, the greatest strength is obtained by the favourable mutual orientation in the fibre. We can estimate the force necessary to tear loose an attraction centre A or B in Fig. 13 (the surface

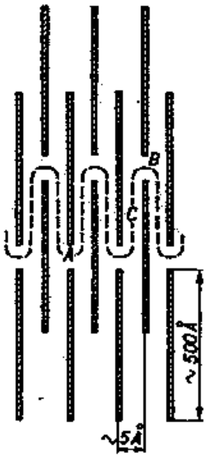

FIG. 13.—Diagram representing some long chain molecules with a favourable mutual orientation.

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[42] K. H. Meyer and H. Mark, *Der Aufbau der hochpolymeren organischen Naturstoffe*, Leipzig, 1930, p. 152 ff.

obtained by rupture is indicated schematically by the dotted line) as of the order of magnitude of 10^{-6} dyne, while the force necessary to shift an atom C will be of the order of magnitude of several times 10^{-7} dyne (for instance 4×10^{-7} dyne when each chain is surrounded by four others). If the chains have the length of 300 centres of attraction, 150 of them must be displaced in the most favourable case. Then we obtain for the tensile strength $4 \times 10^{14} \times 10^{-6} + 2 \times 10^{14} \times 150 \times 4 \times 10^{-7}$ dyne/cm². $= 4 \times 10^{8} + 120 \times 10^{8} = 124 \times 10^{8}$ dynes/cm². The tensile strength is thus estimated at about 124 kg./mm². in the case of the most favourable orientation. In this case the observed tensile strength is of the same order of magnitude and not, as in the cases of the phenol-formaldehyde and the *m*-cresol-formaldehyde condensation products, one order of magnitude lower.

12. The Modulus of Elasticity (Young's Modulus).

We may now attempt to calculate Young's modulus on the basis of the results in the previous sections. This value is given by the following expression :

$$E = \left(\frac{\partial F}{\partial r}\right)_{r=r_0} \times r_0 \times (1 - 2m)$$

where m is Poisson's ratio. $1 - 2m$ may have the value of about 0·4. If the primary bonds considered in § 9 determine the elasticity, we obtain in the case of phenol-formaldehyde resin the following result :

$$\left(\frac{\partial F}{\partial r}\right)_{r=r_0} \times r_0 = 2a^2 Q_0 r_0 = 35{\cdot}8 \times 10^{-4} \text{ dyne per bond.}$$

Multiplying this by the number of primary bonds per cm²., we obtain for Young's modulus

$$E = 7{\cdot}6 \times 10^{14} \times 35{\cdot}8 \times 10^{-4} \times (1 - 2m)$$
$$= 272 \times 10^{10} \times 0{\cdot}4 \text{ dynes/cm}^2.$$
$$= \text{about } 11{,}000 \text{ kg./mm}^2.$$

a value which is much too high.

In the case of the elasticity, the much weaker van der Waals linkages too will be of importance. If we include in the calculations only the van der Waals bonds, we obtain the following :

$$E = \left(\frac{\partial F}{\partial r}\right)_{r=r_0} = > (n - 3)\frac{\pi N_3{}^2 C}{6 r_0{}^4} \times r_0 (1 - 2m)$$

in which we have used the $>$ sign because the formula was obtained by integration. Remembering that $n > 10$

$$E \gg 7 \times \frac{\pi N_3{}^2 C}{6 r_0{}^3}(1 - 2m)$$

For phenol-formaldehyde condensation product this becomes

$$E \gg 114 \times (1 - 2m) \text{ kg./mm}^2. = \gg 45 \text{ kg./mm}^2.$$

From the communication of R. Houwink[43] it appears that a value of about 595 kg./mm². is found at room temperature, and about 1050 kg./mm². at − 180° C. From this figure we may draw the conclusion that, in accordance with Houwinks view, both primary bonds and van der Waals' bonds play a rôle in the resins under consideration.

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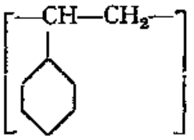
[43] R. Houwink, *Trans. Faraday Soc.* This No., p. 126.

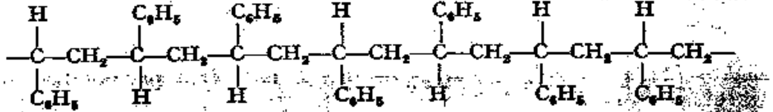
Part III. Some Remarks on the Mutual Orientation of the Benzene Nuclei in Polystyrene.

13. The Formula of Polystyrene.

The chemical formula of polystyrene is relatively simple. Apart from the end groups the molecules are built up of structural units of the formula $C_6H_5 . CH . CH_2$, so that the molecular formula may be schematically written [44]



This formula is in good agreement with the optical properties of polystyrene, especially with the absorption spectrum, which resembles that of an alkyl-benzene.[37] The long threadlike molecules are, according to Staudinger, built up irregularly with respect to the distribution of phenyl groups, a fact which he connects with the lack of a tendency to crystallisation.[45] This irregular distribution depends upon the possibility of various stereoisomers, a fact which is illustrated by the following formula:



$$-\underset{C_6H_5}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{H}{\overset{C_6H_5}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{H}{\overset{C_6H_5}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{C_6H_5}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{H}{\overset{C_6H_5}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{C_6H_5}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2-\underset{C_6H_5}{\overset{H}{\underset{|}{\overset{|}{C}}}}-CH_2-$$

In the following sections we shall examine whether any conclusions may be drawn as to the mutual orientation of the benzene nuclei.

14. Potential Curves of Two Benzene Molecules.

In § 3 we saw that two benzene nuclei will try to orient each other by means of van der Waals' forces, that is to say, *two free* benzene rings will prefer to take up positions so that the rings are perpendicular to the line joining them (see Fig. 4). As is shown from the crystal structure of solid benzene (§ 5, Fig. 5), this position is changed when a large number of benzene molecules come together; it may also change when the benzene molecules are not entirely free to determine their mutual separations. This latter is the case with polystyrene and we must first find out the distance up to which two benzene radicals will be able to approach each other without mutual repulsion. In § 3 we assumed, with a mutually parallel orientation, a separation of 3·5 Å. for the two benzene rings. This distance, which is confirmed by the structural data of many aromatic substances, results from the reciprocal influence of all the individual CH groups on each other when the mutual influence of two individual aromatic CH groups is such that their equilibrium position is at a distance of 3·7 Å. from each other. In Fig. 14 curve *a* represents the potential curve of two such CH groups, and it is so constructed that the value of the potential energy at the minimum is given by the van der Waals attractive energy (see § 4), while the right-hand branch of curve *a*

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[44] *Cf.* H. Staudinger, *Die hochmolekularen organischen Verbindungen*, Berlin, 1932, p. 163.

[45] H. Staudinger, *loc. cit.*, [44], pp. 114, 165.

is identical with the curve (curve b) for the van der Waals attractive energy, for distances greater than 4 Å., and while further it is assumed, on the basis of data for other molecules [46] that, when the equilibrium distance, *i.e.*, the position of the potential minimum lies at 3·7 Å., the energy content is again zero at 3·4 Å. In the calculation (curve b) the van der Waals reciprocal energy is set equal to $\frac{C}{r^6}$, whereby C is calculated according to the Slater-Kirkwood approximation formula when an average value $\alpha_0 = 1{\cdot}7 \times 10^{-24}$ is taken for the polarisability. Thus

$$C = 805 \times 10^{-48}\,\text{kg. cal.} \times \text{cm.}^6.$$

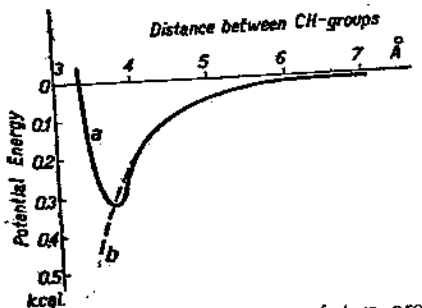

FIG. 14.—Potential energy of two aromatic CH groups as a function of the distance between the groups (curve a). Curve b gives the course of the van der Waals attractive energy.

If we let the two benzene rings approach each other along a line perpendicular to both rings then the six CH groups which are closest to each other (the pairs $1 - 1'$, $2 - 2'$, etc. in Fig. 4) will be in unfavourable positions with respect to the anisotropy of the polarisability. In order to take this into account, we use the formula mentioned in § 3:

$$C = \alpha_0^{\frac{1}{2}}(\alpha_a^{3/2} + \alpha_b^{3/2} + 4\alpha_c^{3/2})\frac{h\nu_0}{8}$$

for which we calculate $h\nu_0$ by substituting for C the value of C according to the approximation formula of London, $C = \frac{3}{4}\alpha_0^{2}h\nu_0$ and for S the experimental value ($S = 10{\cdot}67$ kg. cal./mol.) in the expression

$$S = \frac{0{\cdot}0277}{2}\,C \quad (\text{Cf. § 5}).$$

We thus obtain $h\nu_0 = 353$ kg. cal. In Fig. 15, curve a represents the respective reciprocal energy of the six pairs of CH groups which lie opposite each other, calculated with the aid of a value of C which takes into account the anisotropy ($C = 592 \times 10^{-48}$ kg. cal. × cm⁶.), while curve b gives the total reciprocal energy of both benzene molecules, whereby, as in § 3, no account is taken of the anisotropy for pairs of CH groups, which do not lie opposite each other ($C' = 770 \times 10^{-48}$ kg. cal. × cm^6.). Although,

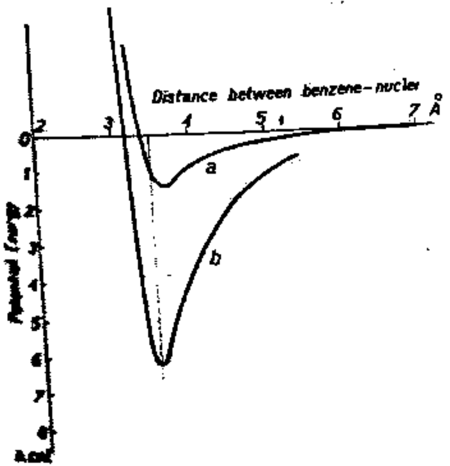

FIG. 15.—Potential energy of two benzene molecules, lying in parallel planes, as a function of the distance between the molecules (curve b). Curve a represents the reciprocal energy of the six pairs of CH groups which lie opposite each other.

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[46] *Cf.* table in H. A. Stuart's *Molekülstruktur*, Berlin, 1934, pp. 36 and 262.

therefore, at distances slightly less than 3·7 Å. the pairs of CH groups directly opposite each other are situated upon the repulsion branch of the potential curve, the molecules taken as a whole nevertheless attract each other with increasing force until the potential minimum for the whole molecules is reached at 3·5 Å. It is evident, further, that at a mutual separation of 3·2 Å. the energy content is still only slightly negative, while at 3·1 Å. the repulsion is already so great that 3 to 4 kg. cal. would be necessary to cause the molecules to approach to this distance.

Therefore, if two or more benzene rings in a molecule must be brought so close to each other, this occurs at the cost of the energy content of the molecule. It may be that the easy dissociability of hexaphenylethane into two triphenyl-methyl radicals is partially due to this effect. In this case the energy of dissociation is about 12 kg. cal., while on the contrary 71 kg. cal. are necessary to separate two normally bound aliphatic carbon atoms.[47] We must keep this repulsion strictly in mind in the discussion of the orientation in polystyrene.[48]

15. Positions of the Benzene Rings in Polystyrene, Assuming a Structure of the Aliphatic Carbon Chain like that in Solid Paraffins.

If we assume that the aliphatic carbon chain in polystyrene has the same structure as the aliphatic chains in the solid paraffins, and if we imagine the phenyl groups substituted on the carbon atoms *0, 2, 4,* etc., then we may distinguish several cases **A, B,** and **C.**

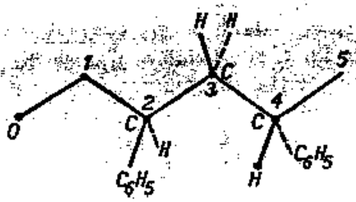

FIG. 16.—Part of a polystyrene molecule; the C_6H_5 group on the second and the H atom on the fourth carbon atom of the chain stick out from the figure; the H atom on the second and the C_6H_5 group on the fourth carbon atom lie behind the plane of the drawing.

A. The phenyl groups on the second and fourth carbon atoms are situated on different sides of the carbon chain. This is indicated schematically in Fig. 16 in which the C_6H_5 group on the second, and the H atom on the fourth carbon atom must be imagined to stick out from the figure, and the H on the second and the C_6H_5 on the fourth carbon atom must be imagined to lie behind the plane of the drawing. We consider the three following positions under this case:

(*a*) That in which both benzene rings lie perpendicular to the direction of the carbon chain (Fig. 17).

(*b*) That in which both benzene rings lie parallel to the direction of the carbon chain (Fig. 18).

(*c*) That in which one of the benzene rings is perpendicular and one parallel to the carbon chain (Fig. 19).

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[47] In the case of still larger aliphatic groups, naphthyl, etc., the dissociation is still easier.

[48] Additional phenomena, connected with the repulsion between two phenyl groups which are very close to each other in the molecule, are the stretched-out form of diphenyl, and the relatively large valence angle (142° ± 8°) of diphenyl ether.

If we keep in mind that, in all positions (especially in position **A** *c*, Fig. 19), the CH groups of the benzene rings which have approached closest to each other, do not attract each other with the maximum force, but even repel each other appreciably, we come to the conclusion that the benzene rings attract each other in all three positions and that binding energies are :

Position *A a* about 2·4 kg. cal.
" *A b* " 2·3 "
" *A c* " 1·8 "

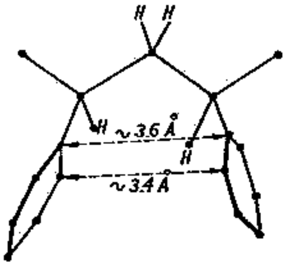

FIG. 17.—Part of a polystyrene molecule; positions as in Fig. 16; both benzene rings perpendicular to the direction of the carbon chain.

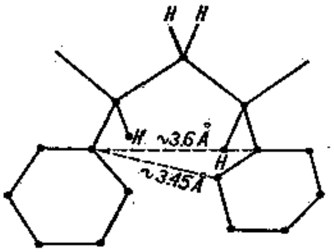

FIG. 18.—Part of a polystyrene molecule; positions as in Fig. 16; both benzene rings parallel to the direction of the carbon chain.

If, further, we remember that in position **A** *b* the distance between the H atom, which is also attached to carbon atom *4*, and the closest CH group of the benzene ring attached to carbon atom *2* is only about 1·8 Å. (calculated to the nucleus of the C atom of the CH group. If the H atom is calculated separately the repulsion becomes still much greater), we see that the combining energy in position **A** *c* and especially in position **A** *b* will thereby be much smaller than the above-mentioned quantities indicate (the energy content of the system of two H atoms and two benzene radicals will probably even be positive in these positions because of the strong repulsion between the H atoms and the closest CH groups of the benzene nuclei).[49]

The differences in energy among the three above-mentioned positions therefore become greater than the average kinetic energy at room temperature, so that we arrive at the result that case **A** *a* is not only by far the preferred one, but also that the benzene radicals, in the cases of linkages which fall under case **A**, will execute oscillations about position **A** *a*.

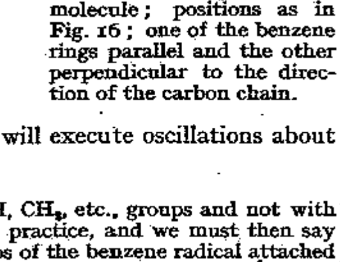

FIG. 19.—Part of a polystyrene molecule; positions as in Fig. 16; one of the benzene rings parallel and the other perpendicular to the direction of the carbon chain.

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[49] Up to now we have worked only with CH, CH_2, etc., groups and not with individual H atoms. We might continue this practice, and we must then say that the distance between the closest CH groups of the benzene radical attached to carbon atom *2*, for example (in position **A** *b* or **A** *c*) is only about 2·6 Å. away from CH group *4*, so that these two groups will exhibit a strong repulsion.

B. The phenyl groups attached to the second and fourth carbon atoms are situated on the same side of the carbon chain. Since the distance between carbon atoms *2* and *4* is only 2·54 Å., all orientation leads to repulsion, but that in which the benzene rings both lie perpendicular to the direction of the carbon chain, to the smallest extent. One might imagine that the angle at carbon atom *3* would be forced to greater values than 110° by this repulsion. In the completely stretched state, however, the second and fourth carbon atoms are still 3·1 Å. away from each other, so that with parallel orientation the phenyl groups still repel each other slightly. In this latter case the energy content of this grouping would be strongly positive because of the energy necessary for the widening of the angle at carbon atom *3* (this energy would be of the order[50] of magnitude of 15 kg. cal., while the repulsion would add 3 to 4 kg. cal. more).

C. The phenyl groups attached to the second and sixth carbon atoms are situated on the same side of the carbon chain. The position in which the benzene rings lie parallel to the carbon chain leads here also to a repulsion, since the distance between the closest CH groups is only 2·58 Å. If both benzene rings are oriented perpendicular to the carbon chain, they attract each other (binding energy about 1·1 kg. cal.), while the most favourable position is that in which one benzene ring is perpendicular and the other parallel to the carbon chain (binding energy about 2·5 kg. cal.). This position is, however, unfavourable as regards the phenyl group attached to the intermediate carbon atom *4* (see under **A**).

Summarising, we come to the conclusion that when the aliphatic carbon chain is similar to that found in the solid paraffins, the most favourable position of the phenyl groups is that in which they lie alternately to the right and to the left of the chain and perpendicular to the direction of the chain. This is, however, only possible when the other, equally possible stereoisomers cannot be formed during polymerisation. If these latter are formed, and if the chain form is also retained, then the benzene rings certainly lie perpendicular to the direction of the chain, and a weaker spot occurs at that point in the chain.

16. Positions of the Benzene Rings in Polystyrene, Assuming Another Structure of the Aliphatic Carbon Chain.

Another possibility is, however, that when the two phenyl groups on carbon atoms *2* and *4* lie on the same side of the chain, the chain will take another form. If one rotates the groups attached to carbon atom *3* about the line joining *2* to *3* by 180°, for example, the configuration of Fig. 20 results. In this case the groups attached to carbon atom *4'* will be repelled by the two H atoms on carbon atom *1*, but in any case the benzene ring will again take up a position perpendicular to the direction of the chain.

If only these of all possible stereoisomers should occur one might imagine a chain as in Fig. 21. The benzene rings would certainly all be perpendicular to the direction of the chain (the closest CH groups are then about 3·5 Å. apart) so that a strong attraction prevails between the phenyl groups; the intermediate CH_2 groups, however, exercise a strong repulsion).

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[50] *Cf.* H. A. Stuart, *Molekülstruktur*, Berlin, 1934, pp. 85, 86.

Another possibility may also be reviewed, *viz.*, that whereby the carbon chain is wound in a spiral, so that the seventh carbon atom comes above the first, etc. Because of the van der Waals reaction between the members of the chain themselves, they will have a tendency to seek a mutual separation of about 4 to 4·5 Å. The benzene rings must then be perpendicular to the axis of the spiral.

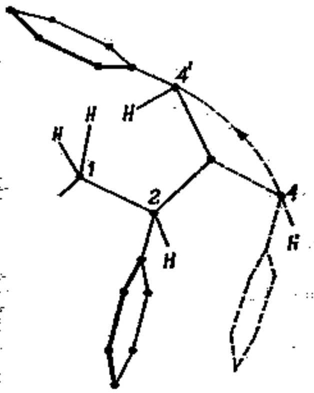

FIG. 20.—Part of a polystyrene molecule; when the two phenyl groups on carbon atoms *2* and *4* lie on the same side of the chain another form of the chain is possible. In reality a position between the two here denoted is very probable.

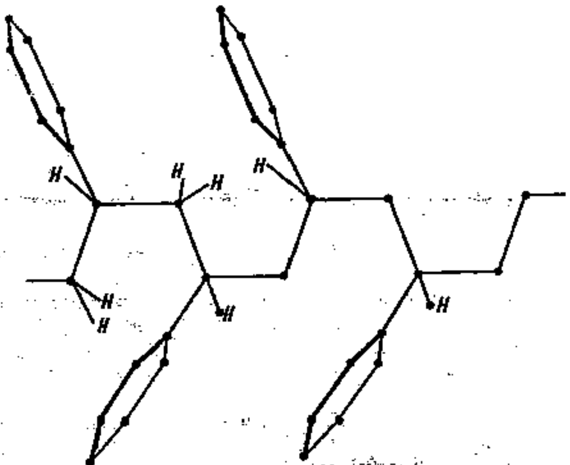

FIG. 21.—A repetition of the positions given in Fig. 20.

17. Conclusion.

We may expect that various configurations of polystyrene occur due to the various possible stereoisomers in different parts of the carbon chain. Common to all these configurations, however, will be a preference of the benzene ring to take up a position perpendicular to the carbon chain, or at least to execute oscillations about equilibrium positions, in which the benzene ring is perpendicular to that direction. If we remember that the polarisability of benzene in the direction perpendicular to the plane of the ring is only about half that in the plane of the ring, we see that an anisotropy will be present in the polystyrene chain, which will completely dominate that of the carbon chain itself. The carbon chain itself would cause an anisotropy such that the polarisability in the direction of the chain would be greater than in the perpendicular direction. Because of the benzene rings which lie perpendicular to the chain, however, the former anisotropy of the chain itself will be more than compensated for and we obtain the smallest polarisability in the direction of the chain, and therefore also the smallest index of refraction. In our opinion herein lies the explanation of the strongly negative double refraction caused by flow of polystyrene,[51] which must be ascribed to the individual polystyrene molecules.[52]

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[51] R. Signer, *Z. physikal. Chem.* 1930, **150A**, 257.

[52] R. Houwink, *Physikalische Eigenschaften und Feinbau von Natur- und Kunstharzen*, Leipzig, 1934, pp. 155, 165.

Summary.

PART I.

The question of the mutual orientation of molecules under the influence of van der Waals' forces is discussed. In general there are two opposing factors, namely: the tendency of the atoms to gather as many neighbours as possible, and the anisotropy of the polarisability. The first of these tendencies practically always dominates over the second. This fact is illustrated with reference to two benzene molecules. In the calculation of the reciprocal energy in the equilibrium state, good results are by chance obtained when use is made of the approximation formula of London or of Kirkwood and Slater, and when the influence of the repulsive forces is neglected. The sublimation energy of benzene, for example, may be satisfactorily calculated in this way.

PART II.

The theoretically calculated value of the tensile strength of common salt is very much greater than the value found experimentally. In the theoretical calculation the influence of the van der Waals forces has been thus far neglected. When this is not done, the theoretical value obtained is still much greater, about 400 kg./mm.^{2}. If a secondary structure is assumed, such as has been proposed by Zwicky, and if it is likewise assumed that there are no electrostatic forces of any description between the "blocks," the value obtained for the theoretical tensile strength is still much too great. In this case the value obtained is > 20 kg./mm.^{2}, while the experimental value is 0·6 kg./mm.^{2}. This low experimental value must be ascribed to a notch effect arising from defects in the lattice, and not to a regular secondary structure.

In the case of artificial resins of the phenol-formaldehyde type and the *m*-cresol-formaldehyde type similar relations between calculated and observed values are encountered. If such an artificial resin is completely polymerised throughout its whole mass and all the $C-C$ linkages possible are actually formed, the theoretical tensile strength may be calculated to be about 4000 kg./mm.^{2}. If (irregular) "blocks" are assumed in this case also, and if these blocks are assumed to cohere only by means of van der Waals forces, then the theoretical value of the tensile strength is about > 35 kg./mm.^{2}. The experimental value is, in this case as with sodium chloride, very much smaller, *viz.*, about 7·8 kg./mm.^{2} for the phenol-formaldehyde resin, so that here also an influence of a notch effect is probable. On the other hand, in the case of well-oriented cellulose derivatives, the correct order of magnitude for the tensile strength may be obtained by theoretical calculations.

Young's modulus of elasticity is also dependent on the van der Waals bonds present in the artificial resin.

PART III.

The potential curve for the bond between two benzene molecules is examined on the basis of the effects due to the individual CH groups. When the minimum lies at 3·5 Å., the energy content at a separation of 3·2 Å. is only slightly negative, while at 3·1 Å. the repulsion is already so great that 3 to 4 kg. cal. would be necessary to cause the molecules to approach to within this distance.

The relative positions of the benzene rings in polystyrene are investigated, and the conclusion may be drawn that there will be a preference on the part of the benzene ring to lie perpendicular to the direction of the aliphatic carbon chain. This makes understandable the strongly negative double refraction caused by flow.

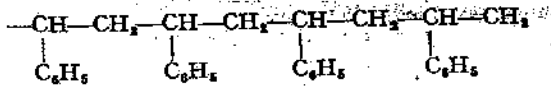
Many thanks are due to Mr. G. Heller for his valuable suggestions concerning Part I. Part II. owes its existence to several discussions with Dr. R. Houwink, and I am greatly indebted to him for his kindness in putting his experimental figures at my disposal.

(*Natuurkundig Laboratorium der N. V. Philips,*
Gloeilampenfabrieken,
Eindhoven-Holland.)

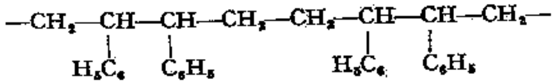
GENERAL DISCUSSION

Professor J. E. Lennard-Jones (*Cambridge*) said: While I agree that Van der Waals' fields play an important rôle in the phenomena discussed by Dr. de Boer and that it is very desirable to estimate their magnitude, I should like to ask the author whether he thinks the theory sufficiently developed at present to make reliable quantitative calculations. I think the formula given by London was intended only for spherically symmetrical systems and even for them it is only approximate. While it gives the right order of magnitude for the inert gases, it is not yet certain that there is not an error by a factor of two. But the error may be greater in the case of aromatic molecules owing to their lack of symmetry and to their special electronic structure in that they contain "non-localised" electrons. Is it not likely that these will require special treatment?

Professor H. Staudinger (*Freiburg i. Br.*) said: The question whether in the polystyrene molecule, the single styrene molecules are linked according to formula 1 or formula 2 is answered in favour of formula 1 by the following experiments: [58]

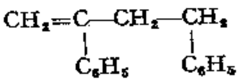


$$-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH}-CH_2 \quad . \quad . \quad (1)$$



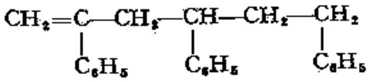
$$-CH_2-\underset{H_5C_6}{CH}-\underset{C_6H_5}{CH}-CH_2-CH_2-\underset{H_5C_6}{CH}-\underset{C_6H_5}{CH}-CH_2- \quad . \quad . \quad (2)$$

Polystyrene, as is well known, depolymerises very easily, reforming chiefly the monomer, but also some dimer, trimer and higher polymers. The yield of the latter products can be increased by performing the depolymerisation *in vacuo*. The formula of the dimer is



$$CH_2=\underset{C_6H_5}{C}-CH_2-\underset{C_6H_5}{CH_2} \quad . \quad . \quad . \quad . \quad (3)$$

and that of the trimer



$$CH_2=\underset{C_6H_5}{C}-CH_2-\underset{C_6H_5}{CH}-CH_2-\underset{C_6H_5}{CH_2} \quad . \quad . \quad . \quad (4)$$

It follows that formula 1 and not formula 2 must be attributed to polystyrene. Decomposition products which should occur in the decomposition of a product of the formula 2 could not be observed.

However, as was originally supposed, the constitution of the polystyrenes is more complicated. According to viscosity measurements, products prepared with the aid of catalysts have the constitution of formula 1, for in this case determinations of the molecular weights cryoscopically and by viscosity measurements agree well. The end groups of these molecules remain, however, unknown. The meso- and eucolloidal polystyrenes

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[58] Compare H. Staudinger and A. Steinhofer, *Annalen*, 1935, **517**, 35.

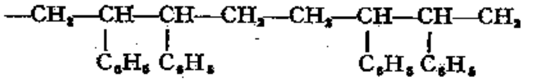
obtained by heat polymerisation have a more complicated structure than the hemicolloidal; the molecular weight determined by the viscosity method is smaller than that given by Svedberg's method,[54] and by the osmotic method.[55] In this case unknown branching must have occurred in the formation of the high polymer. By increased temperature of polymerisation these side reactions take place to a greater extent. For this reason it will be difficult to make final calculations on the relations between the size of the molecules and the tensile strength, unless the structure of the molecules is previously elucidated.

Professor K. H. Meyer (*Genève*) said: De Boer has calculated the modulus of elasticity of an artificial phenol-formaldehyde resin with only primary valencies. The value of 11,000 kg./mm.^{2} found is far beyond the observed value.

Lotmar and I recently calculated the modulus of a cellulose-chain according to our spacial model, taking into account both the valency-oscillations and the deformation-oscillations (*Knickschwingung*). The calculated value was 10,000 ± 2000 kg./mm.^{2} We measured the modulus of well-orientated natural cellulose fibres by an acoustic method, and found that all the fibres tend to a value of about 11,000 kg./mm.^{2} This experiment is certainly the most direct proof in favour of the primary valency chain formula of cellulose.

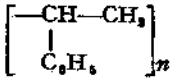
Dr. J. H. De Boer (*Eindhoven*), said, in reply to Professor J. E. Lennard-Jones: It is perhaps possible that some other attractive forces are present in the reciprocal action of two benzene molecules; indeed benzene molecules are not directly comparable with inert gas atoms or with aliphatic hydrocarbons, as they have one electron per C-atom left. But, on the other hand, we see that the same procedure which leads to the right order of magnitude of the heats of sublimation of the inert gases, hydrogen, oxygen, nitrogen, aliphatic hydrocarbons and the like, leads to the right value for the heat of sublimation of solid benzene.

In reply to a question by Dr. J. R. Katz: The distance of 10 Å. in polystyrene resulting from the X-ray investigations of Dr. Katz has puzzled me too. Perhaps it is related to a distance between two different polystyrene molecules in a special direction. In every case my steric formulæ, supplementing the formula of Staudinger and based upon it, allow the distance of 10 Å. to the same extent as the formula of Staudinger does. There are no arguments in favour of the formula :—



$$-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-\underset{C_6H_5}{\underset{|}{CH}}-CH_2-CH_2-\underset{C_6H_5}{\underset{|}{CH}}-\underset{C_6H_5}{\underset{|}{CH}}-CH_2$$

In addition to the arguments in favour of the common formula :—



$$\left[-\underset{C_6H_5}{\underset{|}{CH}}-CH_2\right]_n$$

given above by Professor H. Staudinger, I mention the absorption spectrum * of polystyrene which is identical to that of æthyl benzene.

The remark of Professor K. H. Meyer is very valuable; it shows that, as also in the case of the tensile strength, the experimental values found with cellulose fibre fit very well with the values given by theory.

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[54] Compare this vol., No. 18 (R. Signer).

[55] Compare this vol., No. 6 (H. Staudinger).

* J. H. de Boer, R. Houwink and J. F. H. Custers, *Rec. tr. chim. P. B.*, 1933, **52**, 799.