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On the Nature of the Interaction between Starch and Iodine¹

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(1) It is postulated that the interaction between starch and iodine in the amylose-iodine complex is of dipolar nature.

(2) A model for such dipolar interaction is proposed and the necessity for a cooperative effect is discussed.

(3) The interaction energy is calculated as a function of a parameter α and it is shown that this parameter possesses a critical value at which a "condensation" of iodine into the complex occurs.

(4) It is demonstrated that it is physically reasonable for this parameter to attain its critical value.

(5) It is shown that additional stabilization may occur as a result of the formation of a resonating "polyiodine" chain at high dipolar interaction having a I—I distance and heat of formation which compares favorably with experiment.

(6) Application of the theory is made in discussing the stability of the polyvinyl alcohol-iodine complex.

(7) The color of these complexes is discussed in terms of the theory.

INTRODUCTION

THE configuration of the starch-iodine complex has been the subject of several previous papers.⁴⁻¹⁰ On the basis of x-ray diffraction measurements, studies of iodine activity, crystal birefringence and dichroism, flow dichroism, light absorption and chemical properties, a model for the complex has been proposed in which the iodine molecules are arranged in a linear array, enclosed within and parallel to the axis of an amylose helix (Fig. 1).

Several attempts have been made¹⁰⁻¹³ to

explain the nature of the interaction between the starch and the iodine on the basis of this structure. These explanations fall into two categories: (a) those which propose adsorption of iodine or solid solution formation, and (b) those which propose the formation of a new "compound" or phase of definite composition. However, potentiometric titrations of amylose with iodine⁴ show that iodine activity remains essentially constant during the precipitation of the complex from amylose. Moreover, on adding half the amount of iodine necessary to precipitate completely the amylose from a solution, it is found¹⁰ that half of the amylose is precipitated completely while the remaining half is unaffected. These phenomena would be difficult to explain by any but the latter mechanism.

Also stoichiometric considerations (on the basis of steric requirements) of the displacement of other complexing agents (i.e., fatty acids) from amylose by iodine have strongly favored a complex of definite composition. It is the purpose of this paper to consider quantitatively the implications of a dipole interaction mechanism which would explain the type of forces involved in the formation of such a complex phase.

It has been pointed out¹⁰ that many of the high molecular weight materials forming complexes with iodine of the starch-iodine type have

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⁴ F. Bates, D. French, and R. E. Rundle, *J. Am. Chem. Soc.* **65**, 142 (1943).

⁵ R. E. Rundle and R. R. Baldwin, *J. Am. Chem. Soc.* **65**, 554 (1943).

⁶ R. E. Rundle and D. French, *J. Am. Chem. Soc.* **65**, 558 (1943).

⁷ R. E. Rundle and D. French, *J. Am. Chem. Soc.* **65**, 1707 (1943).

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⁹ R. R. Baldwin, R. S. Bear, and R. E. Rundle, *J. Am. Chem. Soc.* **66**, 111 (1944).

¹⁰ R. E. Rundle, J. F. Foster, and R. R. Baldwin, *J. Am. Chem. Soc.* **66**, 2116 (1944).

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¹² F. F. Mikus, R. M. Hixon, and R. E. Rundle, *J. Am. Chem. Soc.* **68**, 1115 (1946).

¹³ K. Freudenberg, E. Schaaf, G. Dumpert, and T. Ploetz, *Naturwiss.* **27**, 850 (1939).

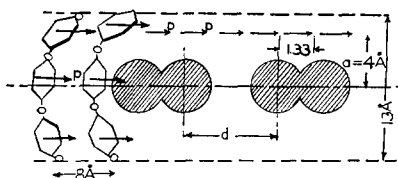


FIG. 1. The model of the iodine-filled amylose helix.

two significant properties in common; that (a) the repeating unit of the structure has a residual component of dipole moment resulting in a linear array of dipoles in the polymer, and (b) a "channel" is available in the structure adjacent to and parallel to the array of dipoles of suitable dimensions to accommodate a chain of iodine molecules. Structural analysis has indicated that both the helical modification of amylose⁷ and oriented polyvinyl alcohol^{14,15} meet these qualifications.

In addition to iodine, alcohols, fatty acids, and nitro compounds may serve as complexing agents.^{16,17} These all have in common either a high polarizability or a permanent dipole moment. This would indicate that the forces associated with complex stability are of dipolar origin.

If one considers the similarity of structure of the iodine, alcohol, and fatty acid complexes,^{7,8,12} and the ease of replaceability without alteration of the basic amylose structure, it does not seem probable that any type of common valence force could be operative other than secondary binding.

Therefore, in the light of this evidence we shall consider only dipolar interaction between the iodine and the amylose helix.

It has been found that the iodine repeat distances along the helix, if it is regular, is probably incommensurate with the repeat distance of the helix itself.⁷ West has found repeat distances for halogens in many halogen-polymer complexes^{15b,35} which are incommensurate with the polymer spacings. This is added evidence that the influence of the polymers on the halogen molecules is not specific in nature and does not

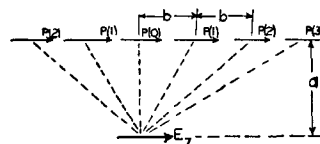


FIG. 2. The dipoles contributing to the field of the helix

involve either direct chemical bonds or even hydrogen or dipolar bonds to the halogen in which the halogen molecule must be located in a specific position with respect to some polymer group.

Another experimental observation is useful in formulating an interaction theory. That is, one finds that the stability of the complex increases with helix length. Therefore, the origin of the attractive forces cannot be local but must be characteristic of the entire helix. They cannot be of the nature of a hydrogen bond which is local and capable of being saturated, but must be of a cooperative nature with the force on a particular iodine enhanced by the presence of other iodines. This, for example, could result from an "extended Silberstein Effect" due to the greater-than-additive polarizability of a chain of iodine molecules.

Similarly, a variation in intensity and wavelength of light absorption by the complex is observed with increasing helix strength^{9,10} for the amylose complex. This also could be interpreted on the basis of increasing local field with increasing iodine chain length.

PROPOSED MODEL—THE FIELD OF THE HELIX

X-ray studies of the amylose helix have indicated that a turn of the amylose helix contains six glucose residues. Because of the helical structure, it is probable that the dipole moments of all the hydroxyl groups of the glucose residues will not cancel, and that there will be a residual component of dipole moment directed along the axis of the helix.¹⁰ We have assumed, for purposes of calculation, that there is a residual moment of one hydroxyl group per glucose residue. The helix has an external van der Waals diameter of 13 Å and a hole down the center having an effective diameter of about 6 Å. Since the residual moment will represent an average between these radii which is weighted with

¹⁴ R. C. L. Mooney, *J. Am. Chem. Soc.* **63**, 2828 (1941).

¹⁵ (a) S. E. Sheppard and P. T. Newsome, *J. Chem. Phys.* **12**, 513 (1944). (b) C. D. West and E. H. Land in Alexander, *Advances in Colloid Chemistry* (Reinhold Publishing Corporation, New York, 1946).

¹⁶ R. Bear, *J. Am. Chem. Soc.* **66**, 2122 (1944).

¹⁷ R. Whistler and G. Hilbert, *J. Am. Chem. Soc.* **66**, 1721 (1944).

respect to an inverse high power of the radius, it would seem reasonable to assume that these average dipoles are located on the circumference of a cylinder of 8Å diameter.

Because of the cylindrical symmetry, residual radial components of the dipole moments are neglected. It is possible that this radial field may be important in perturbing the iodine energy levels and thus influence the color of the complex. As a result of this symmetry property, one may consider these dipoles to be confined to a linear array rather than being distributed over the entire circumference of the cylinder. The resulting model is shown in Fig. 2, where $b = (8\text{Å per loop}/6 \text{ glucose residues per loop}) = 1.33\text{Å}$ and $a = 4\text{Å}$.

The first stage of the calculation is the computation of the axial component of field at a particular point on the axis of the helix resulting from this array of dipoles. From elementary electrostatic field considerations, it may be shown that the component of field at a point on the axis originating from a dipole, \mathbf{P} , located a distance, z , (along the axis) from the point is¹⁸

$$\mathbf{E}_z = \mathbf{P} \left[\frac{1}{(a^2 + z^2)^{3/2}} - \frac{3z^2}{(a^2 + z^2)^{5/2}} \right]. \quad (1)$$

The total field from the entire array at point z' located a distance kb from the end of the helix of N glucose residues is

$$\mathbf{E}_z = \mathbf{P} \sum_{h=-k}^{N-k} \left(\frac{1}{(a^2 + h^2 b^2)^{3/2}} - \frac{3h^2 b^2}{(a^2 + h^2 b^2)^{5/2}} \right). \quad (2)$$

This field has been evaluated for helices of $N = 50$, 100, and 500, Fig. 3. It is seen that the field at the center is actually smaller for longer helices, as opposed to the observed variation of complex stability with chain length. However, it shall be seen that this tendency is more than overcome because of the greater enhancement of induced dipole moment in the longer helices.

INTERACTION OF THE IODINE MOLECULES WITH THE FIELD OF THE HELIX

If iodine molecules are now placed inside of these helices, they will become polarized by this

¹⁸ See for example Frank, *Introduction to Electricity and Optics* (McGraw-Hill Book Company, Inc., New York and London, 1940), Chapter I.

field. Secondary polarization will result through interaction of the resulting induced dipoles. In an attempt to evaluate the resultant field, we shall make the following assumptions:

(a) The iodine molecule exists in the helix as a molecular entity having its usual polarizability, van der Waals' radius, and constant inter-atomic distance.

(b) The iodine molecules are linearly arranged along the axis of the helix which they completely fill, and may be assumed, for purposes of calculation, to be equidistant. The distance between iodine molecules may be determined by equating the van der Waals, electrostatic and resonance attractive forces to the usual van der Waals repulsive forces.

(c) The dipolar forces originate only with the helix with which the iodine is associated.

(d) The electrostatic forces arise from (1) the field of the helix and (2) the field of neighboring induced dipoles.

(e) The dipole interactions may be considered from a classical viewpoint, with the dipole considered as definite point charges, the magnitude and separation of which may be determined from consideration of polarizability and light absorption frequency.

(f) The effect on the field of the surrounding polarizable matter is neglected.

A set of equations for the field on a particular iodine molecule is set up. The field \mathbf{E}_1 on the first iodine molecule is

$$\mathbf{E}_1 = \mathbf{E}_1^0 + x_0 \mathbf{E}_2 + x_0' \mathbf{E}_3 + \dots \quad (3)$$

where \mathbf{E}_1^0 is the axial field of the helix acting at the location of iodine molecule (1), \mathbf{E}_2 , \mathbf{E}_3 , etc. are the total fields at the location of iodine

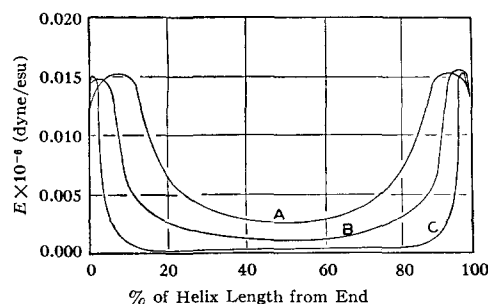


FIG. 3. The field of the amylose dipoles along the axis of the helix—A—50 glucose residues, B—100 glucose residues, C—500 glucose residues.

molecules (2), (3), etc. and $x_0, x_0', x_0'',$ etc. are the respective dipole interaction coefficients. The magnitudes of these coefficients depend upon the "coupling" of the respective dipoles which, in turn, is a function of the polarizability and the proximity of the particular iodine molecules. Therefore, they will not be constant but will vary with the field. However, it is convenient to write the equations in this form because of the ease in solving the resulting set of linear simultaneous equations, and because of the ease of determining the physical conditions requisite for a cooperative effect. These coefficients will be evaluated in terms of physical properties of the system in a later section.

Equation (3) may be simplified if it is noted that in the range of fields encountered, the ratio of the series of dipole interaction terms to the

term representing nearest neighbor interaction is essentially constant. Therefore, if this ratio is called β , we may rewrite Eq. (3) as

$$\mathbf{E}_1 = \mathbf{E}_1^0 + \beta x_0 \mathbf{E}_2, \quad (4)$$

where

$$\beta = (x_0 \mathbf{E}_2 + x_0' \mathbf{E}_3 + \cdots) / x_0 \mathbf{E}_2. \quad (5)$$

Similarly, for the second iodine molecule

$$\mathbf{E}_2 = \mathbf{E}_2^0 + x_0 \mathbf{E}_1 + \beta x_0 \mathbf{E}_3. \quad (6)$$

Generally, further in the helix where end effects are negligible,

$$\mathbf{E}_n = \mathbf{E}_n^0 + \beta x_0 (\mathbf{E}_{n-1} + \mathbf{E}_{n+1}). \quad (7)$$

By solving this set of equations simultaneously (substituting Eq. (6) in (4), etc.), the following recursion formula may be derived:¹⁹

$$E_n = \left\{ \mathbf{E}_n^0 + x \mathbf{E}_{n+1} + \frac{x}{G_{n-1}} \left(\mathbf{E}_{n-1}^0 + \frac{x}{G_{n-2}} [\mathbf{E}_{n-2}^0 + \cdots + \mathbf{E}_1^0] \cdots \right) \right\} / G_n, \quad (8)$$

where

$$x = \beta x_0 \quad (9)$$

$$G_n = 1 - x^2 \frac{1 - x^2}{1 - x^2}, \text{ etc., for } n \text{ "layers."}$$

It is obvious from symmetry considerations that the resulting field must be symmetrical about the center of the helix. That is

$$\mathbf{E}_{(N/2)-1} = \mathbf{E}_{(N/2)+1},$$

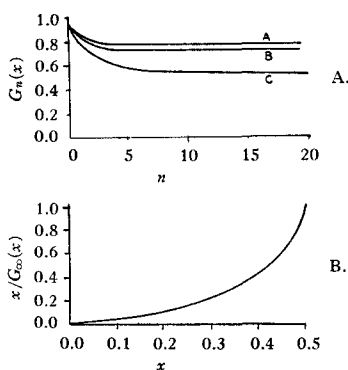


FIG. 4. Some properties of $G_n(x)$: 4A. the convergence of $G_n(x)$ A. $x=0.41$; B. $x=0.45$; C. $x=0.50$; 4B. the variation of $x/G_\infty(x)$ with x .

so that

$$\mathbf{E}_{N/2} = \frac{\mathbf{E}_{N/2}^0 + 2\mathbf{Q}_{(N/2)-1}}{G_{N/2}[1 - (x^2/G_{N/2}G_{(N/2)-1})]}, \quad (10)$$

where

$$\mathbf{Q}_N = \frac{x}{G_N} \left\{ \mathbf{E}_N^0 + \frac{x}{G_{N-1}} [(\mathbf{E}_{N-1}^0 + \cdots + \mathbf{E}_1^0) \cdots] \right\}.$$

Also, $\mathbf{E}_1 = \mathbf{E}_N$ so that

$$\mathbf{E}_N = \frac{\mathbf{E}_N^0 + \mathbf{Q}_{N-1}}{G_N}.$$

The complete field distribution may then be obtained by application of Eq. (8).

The nature of x .—An examination of these equations reveals that the field at any point is an expansion in terms of successive powers of the parameter x . It is seen that in order for a cooperative effect to exist where an appreciable contribution is made by higher powered terms representing more distant dipoles, x/G must be close to unity. The function G is seen to converge rather rapidly (Fig. 4a) so that its properties will

¹⁹ This set of equations will be recognized as constituting a set of difference equations having variable coefficients. If the coefficients, x , are represented as an analytic function of the field, \mathbf{E} (determined by the balancing of forces between iodines), a direct analytic solution of the problem should be possible.

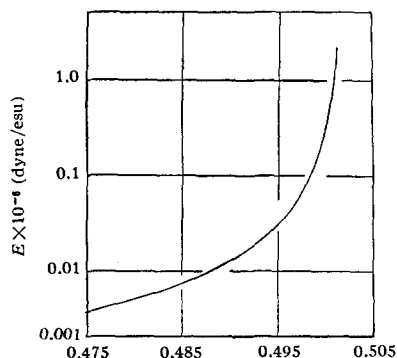


FIG. 5. The variation of the total field along the axis of a 200 glucose residue helix with the interaction coefficient x .

be determined largely by its limiting value, G_∞ . In Fig. 4b, x/G_∞ is plotted against x . It is seen that at a critical value of $x=0.5$, x/G_∞ rapidly increases, passing through unity. Therefore, we should expect that the physical restraints require x to lie in this region for the amylose-iodine configuration.

In Fig. 5 the total field at the center of the helix is plotted logarithmically against x . As expected, the field increases greatly at $x=0.5$. Actually, for an infinitely long helix, the field would become infinite at this point, while for a finite helix, x may slightly exceed the critical value. It shall be seen that the physical limitations on x keep the field within reasonable bounds.

It is interesting now to examine the variation of the field with helix length (Fig. 6). We have plotted the field variation along a 200 glucose helix (corn amylose) and a 500 glucose helix (potato amylose) for an arbitrarily chosen value of $x=0.5$. It is seen here that, as a result of the cooperative effect, the field now increases with helix length. This presumably would explain the experimentally observed decrease in iodine activity with helix length as well as the intensification of light absorption.

THE EVALUATION OF THE INTERACTION COEFFICIENT

The magnitude of the dipole moment induced in an iodine molecule residing in an electrostatic field may be expressed in terms of the polarizability tensor of the iodine. As a first approximation, the secondary force field originating from this dipole could then be expressed as a function

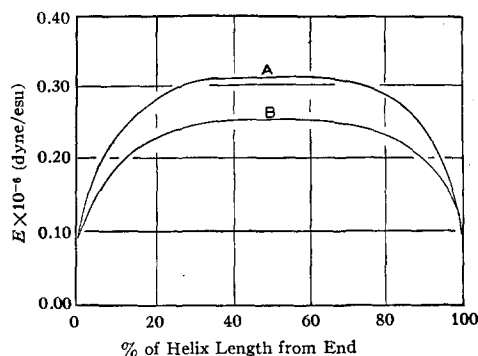


FIG. 6. The variation of the axial field of the completely filled helix with the helix length (assuming $x=0.5$): A—500 glucose residues; B—200 glucose residues.

of this dipole moment. Such an expression, however, involves the assumption that the separation of charges in the dipole is small as compared with the distance between the dipole and its point of action. As applied to this calculation, one finds that in the region where the cooperative effect becomes significant, this assumption is not valid. Therefore, a refinement is required.

We have chosen to represent the dipole as two equal finite point charges located symmetrically on the principle axis of the iodine molecule. The polarizability is no longer adequate in characterizing this system since both the magnitude and the displacement of the charges must be specified. A possible means of very roughly specifying the charge displacement independently of its magnitude is to relate it to the light absorption. If it is assumed that the absorption of light by the iodine results from the natural harmonic vibration of the same electrons involved in polarization, then the frequency of maximum absorption may be related to the force constant for the electronic displacement by the usual relationship,

$$\nu_0 = 1/2\pi(k/m)^{1/2}.$$

The displacement of the electrons l may then be related to the field strength and the electronic charge e , since

$$Ee = kl,$$

so that

$$l = e/(4\pi^2\nu_0^2m)E = KE. \quad (12)$$

One finds from the absorption spectra of iodine in the helix that $K = 5.55 \times 10^{-4} \text{ A/unit field}$.

Obviously, the assumption of a linear restoring

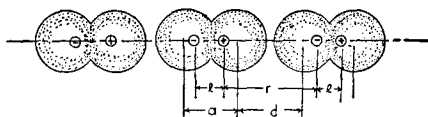


FIG. 7. Arrangement of the induced dipoles of the iodine molecules in the helix.

force on the electrons cannot be applicable at higher fields. It actually must become more difficult to separate the charges further as the separation becomes large. However, there appears to be no simple way to characterize completely this restoring force, and it must be realized that our solutions in regions of high fields may be in error as a result of this approximation.

Thus, it is seen that the solution of the problem involves the evaluation of the field of a system of displaceable point charges (Fig. 7), the spacing of which is determined by the balancing of the associated forces. In considering the separation of charges caused by the polarization of an iodine molecule, one is confronted with the problem of assigning a point in the molecule at which an effective average polarizing field acts. However, we may safely assume that such a point is on the axis of the molecule, not too far from its center, and closest to the polarizing dipole. Its location also will vary with the extent of polarization. As a working assumption, we have assumed that this point is located at a distance $r+l/3$ from the closest charge of the polarizing dipole.

We then may set up an equation for the total field at the n th iodine molecule,

$$\begin{aligned}
 E_n &= E_n^0 + \sum_i \frac{qi}{r_{in}^2} \\
 &= E_n^0 + q \left\{ \left(\frac{1}{(r_n')^2} - \frac{1}{(r_n' + l_{n-1})^2} \right) \right. \\
 &\quad + \left(\frac{1}{(r_{n+1}')^2} - \frac{1}{(r_n' + l_{n+1})^2} \right) \\
 &\quad + \left(\frac{1}{(r_n' + r_{n+1}' + l_{n+1})^2} - \frac{1}{(r_n' + r_{n+1}' + l_{n+2})^2} \right) \\
 &\quad + \left(\frac{1}{(r_n' + r_{n-1}' + l_{n-1})^2} \right. \\
 &\quad \left. \left. - \frac{1}{(r_n' + r_{n-1}' + l_{n-1} + l_{n-2})^2} \right) + \dots \right\} \quad (13)
 \end{aligned}$$

where $r' = r + l/3$. Then

$$E_n = E_n^0 + \frac{\alpha\beta}{K} \left\{ \left(\frac{1}{(r_n')^2} - \frac{1}{(r_n' + l_{n-1})^2} \right) + \left(\frac{1}{(r_{n+1}')^2} - \frac{1}{(r_n' + l_{n+1})^2} \right) \right\}, \quad (14)$$

where β is defined by Eq. (5) and $q = (\alpha l/E)/(l/E) = \alpha/K$. Since the variation in l will be much greater than the variation in r , we may assume that all of the r 's are equal in this equation. Expanding:

$$\begin{aligned}
 E_n &= E_n^0 + \frac{\alpha\beta}{K} \left\{ \left(\frac{1}{(r')^2} \right) - \left(\frac{1}{(r')^2} - \frac{2l_{n-1}}{(r')^3} \right. \right. \\
 &\quad + \frac{3l_{n-1}^2}{(r')^4} + \dots \left. \right) + \left(\frac{1}{(r')^2} \right) - \left(\frac{1}{(r')^2} \right. \\
 &\quad \left. \left. - \frac{2l_{n+1}}{(r')^3} + \frac{3l_{n+1}^2}{(r')^4} + \dots \right) \right\} \\
 &= E_n^0 + \frac{2\alpha\beta}{(r')^3} \left\{ \left(E_{n+1} - \frac{3KE_{n+1}^2}{2r'} \right. \right. \\
 &\quad + \frac{2K^2E_{n+1}^3}{(r')^2} - \frac{5K^3E_{n+1}^4}{2(r')^3} + \dots \left. \right) \\
 &\quad + \left(E_{n-1} - \frac{3KE_{n-1}^2}{2r'} + \frac{2K^2E_{n-1}^3}{(r')^2} \right. \\
 &\quad \left. \left. - \frac{5K^3E_{n-1}^4}{2(r')^3} + \dots \right) \right\} \\
 &= E_n^0 + x(E_{n-1} + E_{n+1}),
 \end{aligned} \quad (15)$$

where

$$x_n \cong \frac{2\alpha\beta}{(r')^3} \left\{ 1 - \frac{3}{2} \left(\frac{KE_n}{r'} \right) + 2 \left(\frac{KE_n}{r'} \right)^2 - \frac{5}{2} \left(\frac{KE_n}{r'} \right)^3 + \dots \right\}. \quad (16)$$

It has been assumed in writing down the expression for x that (in this factor) it is permissible to set $E_{n-1} = E_n = E_{n+1}$. This assumption is probably not too serious since, over most of the length of the helix, E varies rather slowly, and since E enters into this series only into the relatively negligible higher powered terms.

Evaluation of β .— β is defined in Eq. (5) and may be numerically evaluated in terms of the above theory. The complete equation (including further neighbor fields) for the field is given by

$$\beta = \frac{\left(\begin{aligned} &[1/(r+(l/3))^2 + 1/(2r+(4/3)l)^2 + 1/(3r+(7/3)l)^2 + \dots] \\ &- [1/(r+(4l/3))^2 + 1/(2r+(7/3)l)^2 + 1/(3r+(10/3)l)^2 + \dots] \end{aligned} \right)}{\{1/(r+(l/3))^2 - 1/(r+(4/3)l)^2\}}.$$

The numerator of this equation may be expressed as

$$\sum_{n=1}^{N/2} [(an - \frac{2}{3}l)^{-2} - (an + \frac{1}{3}l)^{-2}]$$

where $a = r + l$. Expanding these terms, this becomes

$$\begin{aligned} &\sum_{n=1}^{N/2} \{ [(an)^{-2} + (4/3)l(an)^{-3} + (4/3)l^2(an)^{-4} + (32/27)l^3(an)^{-5} + (80/81)l^4(an)^{-6} + \dots] \\ &- [(an)^{-2} - (2/3)l(an)^{-3} + (1/3)l^2(an)^{-4} - (4/27)l^3(an)^{-5} + (5/81)l^4(an)^{-6} + \dots] \} \\ &= (1/l^2) \left\{ 2(l/a)^3 \sum_1^{N/2} (1/n^3) + (l/a)^4 \sum_1^{N/2} (1/n^4) + (4/3)(l/a)^5 \sum_1^{N/2} (1/n^5) + (25/27)(l/a)^6 \sum_1^{N/2} (1/n^6) + \dots \right\}. \end{aligned}$$

Therefore,

$$\beta = \frac{\{ [1/l^2] [2.404(l/a)^3 + 1.082(l/a)^4 + 1.382(l/a)^5 + 0.941(l/a)^6 + \dots] \}}{\{1/(r+(1/3)l)^2 - 1/(r+(4/3)l)^2\}}.$$

In Table I we have evaluated β for several values of the field.

It is seen that β does not vary significantly and that its application as an approximation is very well justified.

The solution for x .—It is seen from Eq. (16) that x is a function of the field E and the distance between dipoles r . Also, from the solution from the set of cooperative effect equations we have shown that the field is a function of x . In order to obtain a solution for the three variables, a third relationship is necessary.

An examination of these variables reveals that we may interrelate r and E by considerations of the force equilibrium. In the absence of a field, the distance between iodine molecules is determined by the van der Waals distance, d_0 , which results from the balancing of the van der Waals (dispersion) attractive force against the repulsive forces. In the presence of a field, there is an additional attractive force resulting from electrostatic attraction of the induced dipoles. This will reduce the van der Waals distance to a new

Eq. (13). For purposes of evaluating β , it is sufficiently accurate to consider all of the l 's and r 's to be identical in this equation. Therefore, β may be given by

value, d . If d is reduced sufficiently so as to become comparable with the interatomic distance a it is possible that the interatomic and intermolecular bonds characterizing particular iodine molecules lose their identities and that additional stabilization may result from the resonance energy. In these processes, a also will presumably change but to a lesser extent than does d .

A relationship then may be obtained between the reduced van der Waals radius and the field. It is obvious from Fig. (7) that r is given by

$$r = d(E) + a - l = d(E) + a - KE. \quad (17)$$

We have, then, our desired third relationship among the three variables, x , r , and E . These

TABLE I.

$E \times 10^{-6}$	β
0.568	1.17
0.360	1.16
0.050	1.18

may be solved simultaneously to give the solution for the state of the system.

THE FORCE BALANCE

The repulsive force.—The repulsive force function may be estimated from the Morse curve by a method due to Eyring.²⁰ The force between two iodine atoms united in a molecule may be obtained by differentiating the Morse function²¹ with respect to the distance between them, d . This gives

$$F = 2D\alpha(e^{-2\alpha(d-a)} - e^{-\alpha(d-a)}).$$

For I_2 , the constants are given²² as $D = 2.47 \times 10^{-12}$ erg, $\alpha = 1.85A^{-1}$, and $a = 2.67A$. The first term in the expression represents a repulsive force while the second represents attraction. The attractive force, if considered quantum mechanically from the point of view of the London theory,²³ may be expressed as a sum of Coulombic integrals and exchange integrals. If the two iodine atoms are not bound in a molecule, it is found that the exchange integrals no longer contribute to the attractive force but represent a repulsion equal in magnitude to $\frac{1}{2}$ of their former attraction. Then, the force will be

$$F_{\text{repulsive}} = 2D\alpha \left(e^{-2\alpha(d-a)} - \left(\frac{\% \text{ Coulombic}}{2} - \frac{\% \text{ Exchange}}{2} \right) e^{-\alpha(d-a)} \right). \quad (18)$$

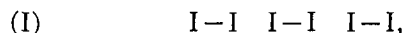
For the purposes of this calculation, it was assumed that the I—I bond is 86 percent Coulombic.

The van der Waals attractive force.—The van der Waals attractive force has been shown²⁴ theoretically to vary inversely with the seventh power of the distance between centers of the attracting atoms. If an expression of this type is equated to the above type equation for the repulsive force for the case of $d = d_0$, the unperturbed van der Waals distance (4.3A for iodine),

$$F_{\text{repulsive}} = F_{\text{attractive}} = (A/d_0^7), \quad (19)$$

the proportionality constant A may be evaluated. For iodine, A was found to be equal to 4104×10^{-4} dyne/A⁷.^{24a}

Resonance stabilization.—The possibility of resonance between structures of the type.



must also be considered.

If d is the unperturbed van der Waals distance, the exchange integrals between the atoms separated by this distance will be small, and the contribution of structures of type (II) will be negligible. However, as d is reduced through operation of electrostatic attraction, these integrals become increasingly more important, and an increasing resonance energy exists due to interaction between types (I) and (II) structures. The variation of resonance energy with d results in an attractive force which serves to reduce d further.

The secular equation for a set of resonating structures of this type is identical to that arising from the description of the π electrons of a long conjugated hydrocarbon. These have been treated by means of the valence bond method by Pauling and Wheland,²⁵ Wheland,²⁶⁻²⁹ and Pauling and Sherman,³⁰ and by the molecular orbital method by Huckel³¹ and Lennard-Jones.³² For our purposes the treatment of Lennard-Jones appeared most useful.

He considers the general problem of a conjugated hydrocarbon where the bond lengths alternate and is successful in obtaining a general solution for the associated secular equation. He

^{24a} An alternate method for calculating the van der Waals and repulsive forces would be to calculate explicitly the absolute attractive force between iodines from the London formula and using an empirical inverse twelfth power or exponential repulsive force.

²⁵ L. Pauling and G. W. Wheland, *J. Chem. Phys.* **1**, 362 (1933).

²⁶ G. W. Wheland, *J. Chem. Phys.* **2**, 356 (1934).

²⁷ G. W. Wheland, *J. Chem. Phys.* **2**, 474 (1934).

²⁸ G. W. Wheland, *J. Chem. Phys.* **2**, 230, 365 (1935).

²⁹ G. W. Wheland, *J. Am. Chem. Soc.* **63**, 2025 (1941).

³⁰ L. Pauling and J. Sherman, *J. Chem. Phys.* **1**, 679 (1933).

³¹ Huckel, *Zeits. f. Physik* **70**, 204 (1931); **72**, 310 (1931); **76**, 628 (1932).

³² J. E. Lennard-Jones, *Proc. Roy. Soc.* **158A**, 280, 297 (1937).

²⁰ Henry Eyring, *J. Am. Chem. Soc.* **54**, 3191 (1932).

²¹ P. Morse, *Phys. Rev.* **34**, 57 (1929).

²² G. Hertzberg, *Molecular Spectra and Molecular Structure, I. Diatomic Molecules* (Prentice-Hall, Inc. New York, 1939), p. 488.

²³ F. London, *Zeits. f. Elektrochemie* **35**, 552 (1929).

²⁴ R. Eisenschitz and F. London, *Zeits. f. Physik* **60**, 491 (1930).

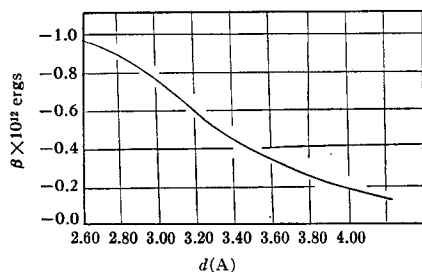


FIG. 8. The variation of the molecular orbital exchange integral with the intermolecular distance (for constant $a = 2.67\text{\AA}$).

obtains the following equation for the orbital energy for a chain having 2ν atoms:

$$\mathcal{E} = 2\beta_a \sum_{r=1}^{\nu} \{1 + 2(\beta_d/\beta_a) \cos \theta_r + (\beta_d/\beta_a)^2\}^{\frac{1}{2}}, \quad (20)$$

where

$$\theta_r = \frac{2r\pi}{2\nu+1} - \frac{1}{2\nu+1} \left(1 - \frac{\beta_d}{\beta_a}\right) \tan \frac{r\pi}{2\nu+1}.$$

β_d and β_a are the molecular orbital exchange integrals across the distances d and a , respectively. It is assumed that exchange integrals between other than adjacent atoms are negligible, and that there are sufficient atoms in the chain so that all of the diagonal terms in the secular determinant may be considered identical (end effects are negligible). The expression given for θ_r is a first approximation and is only accurate if a and d are not too different.

The exchange integrals cannot be directly evaluated as no thermochemical or spectroscopic data is available for polyiodine type compounds. However, comparison reveals²⁴ that the results of the molecular orbital and valence orbital methods are surprisingly consistent. The ratio of the molecular orbital exchange integral β to the valence orbital exchange integral α is fairly constant and approximately equals 0.45 for long conjugated chains. α may be evaluated rather readily as it is approximately a constant fraction (0.86) of the energy (given by the Morse function) which may be obtained from the exact treatment of simpler molecules. Therefore, a plot of β as a function of d calculated in this way is given in Fig. 8.

The resonance energy is obtained by subtracting from the orbital energy, the orbital

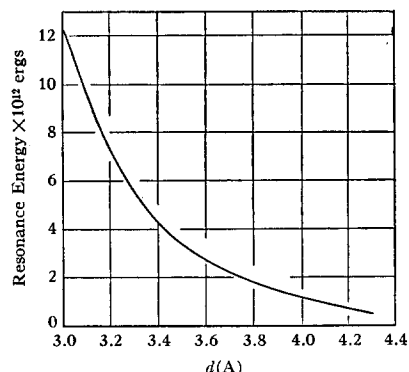


FIG. 9. Variation of resonance energy with intermolecular distance (keeping a constant $a = 2.67\text{\AA}$).

energy of the static, unexcited structure, $2\nu\beta_a$. We have calculated this resonance energy as a function of d (with a held constant at 2.67\AA) for a chain of 40 iodine molecules (Fig. 9). This would roughly correspond to a filled helix of 200 glucose residues. The slope of this curve is equal to the force caused by the resonance energy.

Electrostatic attractive force.—The electrostatic attractive force is a result of (1) the Coulombic potential resulting from the attraction and repulsion of the charges representing the dipoles and (2) the potential energy expended in separating the charges in forming the dipole. That is

$$F_{\text{electrostatic}} = \sum_i \sum_j \frac{q^2}{r_{ij}^2} - \sum_i \frac{\partial}{\partial d} \left(\frac{p_i^2}{2\alpha} \right)$$

where p_i is the dipole moment of the i th dipole. It has been shown³³ (to the approximation that the forces may be represented by interactions between dipoles) that the charge separation term is opposite in sign and equal in magnitude to half of the first (Coulombic attraction) term. Therefore,

$$F_{\text{electrostatic}} = \frac{1}{2} \sum_i \sum_j \frac{q^2}{r_{ij}^2} = \frac{\beta q^2}{2} \left(\frac{1}{r^2} + \frac{1}{(r+2l)^2} - \frac{2}{(r+l)^2} \right), \quad (22)$$

where β , as before, corrects for further neighbor interaction.

³³ See, for example, O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940), Appendix III.

TABLE II.

	Energy (kcal./mole of I ₂)
Repulsive	15.5
van der Waals attraction	-10.6
Electrostatic attraction	-28.7
Resonance attraction	-3.12
Total energy	-26.9

To solve for the relationship between d and E , the equation,

$$F(d) = \frac{\beta\alpha^2}{2K^2} \left(\frac{1}{(a+d-KE)^2} + \frac{1}{(a+d+KE)^2} - \frac{2}{(a+d)^2} \right), \quad (23)$$

where

$$F(d) = F_{\text{repulsive}} - F_{\text{van der Waals}} - F_{\text{resonance}},$$

was solved graphically. The resulting plot of d against E is given in Fig. 10.

THE SOLUTION OF THE SIMULTANEOUS EQUATIONS

The following procedure was followed in obtaining the solution of the three simultaneous equations: (a) For a given value of x , E was obtained from Eq. (10); (b) using the value of x and E , Eq. (16) was solved graphically for r ; (c) d was then calculated using Eq. (17), and d was plotted against x . (See, for example, curve A of Fig. 11); (d) another plot of d against x was obtained from the solution of Eq. (23) (curve B of Fig. 11). The intersection of these two curves is the desired solution.

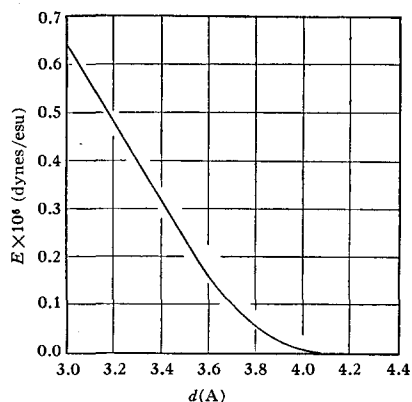


FIG. 10. The force balance—Variation of interatomic distance with field strength.

The curves of Fig. 11 represent a solution for the center of a 200 glucose residue helix. It is seen that the intersection occurs at $x=0.5005$, $d=3.13\text{\AA}$, and $E=0.50 \times 10^6$ dynes/unit charge. One observes that another intersection occurs at about $x=0.2$. This, however, represents a negligibly small field with d at the unperturbed van der Waals distance. This would correspond to a state having much higher free energy than the high field solution and would be unstable with respect to it.

The stabilization energy corresponding to this solution may be readily computed. The contributions of the interactions making up this energy are tabulated in Table II.

While the configurational stabilization energy appears rather high, its order of magnitude is not too unreasonable. Qualitative observations indicate that the stability of the iodine in the complex is comparable with that of iodine held by weak primary valence bonds. The heat of formation of the complex indicated by the electrode potential is -19.6 kcal. per mole of iodine at 25°C .³⁴ It is expected that this value should be lower than that of the dry complex because it has formed in solution, and there is the possibility of ion or solvent inclusion which would interrupt the iodine chain.

It should be noted that while the ordinary van der Waals distance for I_2 is 4.3\AA , the intermolecular distance is as short as 3.54\AA in the I_2 crystal. In view of this, the shortening of the van der Waals distances in the iodine complexes predicted by our theory is not as unreasonable as it might appear.

In this treatment, changes in a resulting from resonance and from unequal electrostatic forces on the two iodine atoms of the molecule have been neglected. This change is probably rather small because of the "stiffness" of the primary bond and is probably no more than a few hundredths of an angstrom unit. It presumably would affect the solution because of the following effects: (a) increasing a would decrease the polarizability, (b) increasing a would decrease K , (c) increasing a would affect the location of the average dipole. As the atoms become separated, the electrons spend less of their time between

³⁴ Harvey Dube, Thesis, Iowa State College (1947), p. 81.

the two atoms and it probably would not be correct to locate the dipole in the center of the molecule, but it should be considered to reside in the individual atoms. This is especially true if d and a are close together and resonance results in loss of molecular identity.

The absolute value of this stabilization energy should not be taken too seriously because of the uncertainty of the many assumptions necessary for solution. However, we believe that we have shown that it is possible by this mechanism to obtain a solution having the correct order of magnitude to account for the stability and qualitative behavior of the complex.

It is interesting to discuss the formation of a complex of definite composition in terms of this mechanism. It is seen that a long uninterrupted iodine chain is necessary for the manifestation of a cooperative effect. The enhancement of the interaction energy is a function of this chain length. Therefore, the decrease in energy per iodine molecule added will be greater, the more iodine already in the helix. There will then be a greater tendency for iodine to keep going into a helix once it has started than for it to start filling an empty helix. This process would be more energetically favorable as it proceeds until the helix is filled.

OTHER HALOGEN-POLYMER COMPLEXES

Recently, West^{15,35} has found that many hydrophilic, organic polymers form complexes with iodine, bromine, and iodine-bromide. Aside from the amylose-iodine complex, the most notable iodine complex is probably that of polyvinyl alcohol.

Polyvinyl alcohol is known to form a complex with iodine which is similar in appearance and behavior to the starch-iodine complex. This complex appears to be very stable—it is not possible to measure the vapor pressure of iodine above it by ordinary methods.¹⁵ Preliminary evidence indicates that the complex is also a *molecular compound* rather than a result of ordinary adsorption or solid solution formation.

The structure of crystalline polyvinyl alcohol has been determined by Mooney¹³ and has been recently criticized by Bunn.³⁶ Mooney has

³⁵ C. D. West, J. Chem. Phys. 15, 689 (1947).

³⁶ Bunn, in *Advances in Colloid Science* (Interscience Publishers, New York, 1946), Vol. II, pp. 121-3.

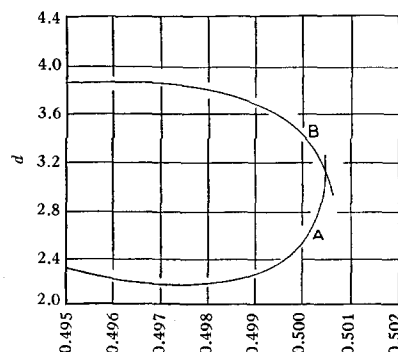


FIG. 11. The solution of the simultaneous equations.

postulated a structure consisting of parallel hydrocarbon chains interlinked by hydrogen bonds between the hydroxyl groups (Fig. 12). From considerations of complex forming ability, the most striking feature of this structure is that the hydroxyl groups are held in such a way that each contributes a re-enforcing component of dipole moment along the fiber axis. This would give rise to a field similar to that of the amylose helix. Also, there are channels parallel to this array of dipoles. Preliminary x-ray studies indicate that the iodine actually does reside in these channels.

West has found that the polymer halogen complexes studied produce x-ray reflections characteristic of a one-dimensional lattice with periods 3.10 (iodine), 2.70 (bromine) and 2.90 Å (iodine bromide) essentially independent of the polymer. He has interpreted these spacings as interatomic distances in linear polyhalogen chains.

As we have seen, equally spaced iodines are allowed by our theory only if there is complete resonance of the bond between nearest neighbors in the linear array. In this case each bond would have an electronic density of half an electron pair (bond number $\frac{1}{2}$ in Pauling's nomenclature)³⁷ and the expected bond distance is 2.85 Å (calculated in accordance with Pauling's rule, $R(1) - R(n) = 0.300 \log n$, where n is the bond number and R the radius of the atom).³⁷ This is far shorter than West's spacing, which corresponds to a bond number of only 0.17 (again by Pauling's rule).

It seems very difficult to understand how the iodine-iodine bond in a polyiodine chain could have so low a bond number. Indeed, the bond

³⁷ Pauling, J. Am. Chem. Soc. 69, 542 (1947).

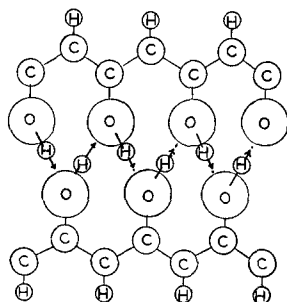


FIG. 12. The structure of polyvinyl alcohol (Mooney).

number is so low that halogen-halogen bonding appears to have nearly disappeared if West's interpretation is accepted. There is no chemical evidence to indicate that bonding to the polymer has replaced the original I—I bond in I_2 and, in fact, since the x-ray spacing of the halogen is unrelated to the fiber spacing of the polymer, polymer-iodine bonding is hardly possible.

Actually, the x-ray data are not sufficient to assure that the iodine atoms are equally spaced in the linear array. Only three orders of the spacing are observed even in "favorable circumstances," and it may well be that these are the even orders of a spacing twice as great (6.2Å). (The fact that West has not observed a doubling of the spacing for the iodine-bromide complexes is further evidence that the data cannot be accepted as evidence for equally spaced, equivalent halogens.)

If we allow unequal spacings between iodine molecules, then a shortened van der Waals distance (our calculated value for the particular field assumed for the starch helix goes as low as 3.2Å), and a normal, or more probably a somewhat lengthened, single bond distance could easily account for a 6.2Å spacing. Of the first few x-ray reflections, only even orders could be visible. Indeed, the observed spacing is near enough to that which our calculations would predict as to tend to confirm the general validity of our procedure.

The observed spacings in bromine and iodine bromide complexes also correspond roughly to bond numbers of 0.17. Again, it appears more probable that the halogen atoms are unequally spaced, corresponding to halogen molecules separated by rather short van der Waals distances. It appears from the observed spacings

that no known complexes have reached the limiting value of equally spaced halogens, though we should again emphasize that this possibility is not excluded.

Both the helical form of amylose and the usual form of polyvinyl alcohol provide polymer dipole fields in accord with the demands of the present proposal. It seems not unreasonable to suppose that these demands are met by other polymers forming halogen complexes, and that the mechanism, proposed here, aside from the very particular points peculiar to amylose structure can be carried over to explain the halogen complexing powers of other polymers.

It should be noted that the theory only strictly applies to the formation of the complex with dry amylose or polyvinyl alcohol and iodine in the vapor phase. In solution several additional complications arise. A consideration of the effect of the dielectric constant of an imbibing medium has been neglected. This approximation will be serious in aqueous solution where the fields may be materially reduced by polarization of the water. Also ions will enter the helix in solution and, as has been experimentally demonstrated,⁴ will affect the stability of the complex.

It is somewhat disturbing that water which has a higher (macroscopic) dielectric constant than iodine does not preferentially enter the helix. Possibly water in the helix would exhibit a different structure from its macroscopic structure and would not orient to give a high polarization necessary for complex formation. It seems quite possible that through hydrogen bonding for specific hydroxyl groups, its action could be entirely local.

This model for the complex offers an explanation for the enhancement of the color of the iodine. It has been pointed out that the color of iodine in solution varies with the nature of the solvent. This probably results from the perturbation of the energy levels of the iodine molecule by the field of the solvent molecules in such a manner as to allow previously forbidden transitions. The same effect could obviously result from the action of the strong fields in the helix. Also, the resonance energy contribution may lower the energy levels sufficiently so as to shift the wave-length of absorption. While we calculate that resonance energy is only about 10

percent of the total binding energy, it should be noted that the resonance energy is a very sensitive function of inter-iodine distance in this region so that a slight error in calculation may materially change the resonance contribution.

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The Molecular Structure of Nitrogen Dioxide. A Reinvestigation by Electron Diffraction*

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An investigation of the structure of the nitrogen dioxide molecule has been made by the electron diffraction method. The interpretation of the photographs, which showed rings extending to values of q of nearly $100(q = 40/\lambda \sin\theta/2)$, leads to the following structural parameter values: $N-O = 1.20 \pm 0.024$, $\angle O-N-O = 132 \pm 3^\circ$. These values are discussed briefly and compared with those obtained by other methods.

INTRODUCTION

IN recent years the molecular structure of nitrogen dioxide has been the subject of numerous investigations but, aside from general agreement on a non-linear symmetrical structure with a wide bond angle and a multiplicity corresponding to only the odd electron, the conclusions have been surprisingly divergent. This is true of the dielectric constant measurements on the $NO_2-N_2O_4$ system, which have lead variously to the conclusions that both nitrogen dioxide and nitrogen tetroxide have small constant dipole moments of the order of 0.4×10^{-18} e.s.u., that of nitrogen tetroxide being the greater,^{1,2} and that nitrogen dioxide has a moment of this magnitude which decreases with increasing temperature while nitrogen tetroxide has a zero moment.³ It is especially true of the bond angle and bond distance estimates and determinations, which naturally concern us directly. However, Giauque and Kemp's⁴ comprehensive considerations of the

equilibrium measurements⁵ on the dissociation of nitrogen dioxide in connection with spectroscopic data for nitric oxide,⁶ oxygen,⁷ and nitrogen dioxide rule out the suggestion of Zeise⁸ that the molecule has a multiplicity of 4. This suggestion is likewise ruled out by the results of the magnetic susceptibility measurements of Havens,⁹ as was pointed out by Harris and King.¹⁰

From consideration of an assumed electronic structure Pauling¹¹ predicted 1.18A for the nitrogen-oxygen distance and 140° for the angle $O-N-O$. On the assumption of a valence potential function and a frequency assignment suggested by the infrared spectrum Penney and Sutherland¹² obtained the value 114° for the bond angle. With a similar assumption but a slightly

* Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 1156.

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⁴ W. F. Giauque and J. D. Kemp, *J. Chem. Phys.* **6**, 40 (1938).

⁵ Especially those of M. Bodenstein and Lindner, *Zeits. f. physik. Chemie* **100**, 82 (1922).

⁶ H. L. Johnston and A. T. Chapman, *J. Am. Chem. Soc.* **55**, 153 (1933).

⁷ H. L. Johnston and M. K. Walker, *J. Am. Chem. Soc.*, **55**, 172 (1933).

⁸ H. W. Zeise, *Zeits. f. Elektrochemie* **42**, 785 (1936).

⁹ G. G. Havens, *Phys. Rev.* **41**, 337 (1932).

¹⁰ L. Harris and G. W. King, *J. Chem. Phys.* **8**, 775 (1940).

¹¹ L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1940), second edition, p. 270.

¹² W. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc. A* **156**, 654 (1936).