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of energy either by evaporating a neutral atom and then ionizing it or by evaporating the charged components. If $W_1' - W_2'$ would be zero, then the galvanic potential difference would still not be given by the voltaic potential difference between the two metals, which is equal to the difference between the *Richardson constants for the electrons alone*, since the difference between the values of the Richardson constants for the positive ions has to be added, which in general is of the same order of magnitude. Still a certain parallelism between the voltaic and galvanic potentials could then be expected because the Richardson constants for the positively and negatively charged particles go somewhat parallel to each other.

Now the difference between the Richardson constants, being of the order of magnitude of 1 volt, cannot in general be considered to be large compared to the difference in the work done by immersing a charged ion into a liquid. The simple electrostatic considerations: work done by a sphere of radius a when transferred from a medium with the dielectric constant 1 to another with the dielectric constant D leads to values for $W_1' - W_2'$ which are of the same order of magnitude as the other terms in (6). There does not therefore exist any general theoretical principle which would justify the much discussed hypothesis of equivalence of voltaic and galvanic potentials. In a subsequent communication the authors intend to present what evidence can be derived from a study of ionic diameters and correlated quantities as to the magnitude of the work done by transferring ions from the gaseous into the liquid phase.

Rotating Polar Groups in "Organic" Molecules

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The temperature dependence of the electric moment, observed in the case of molecules with rotating polar groups, permits a quantitative explanation in terms of intra-molecular forces opposing free rotation of the groups. Specifically, the following questions have been raised and treated: I. The statistical weight to be associated with a configuration. II. Approximation of the periodic potential function by its first and second Fourier component. III. An application to 1,2-dichloroethane is given and a plausible potential of interaction between the two CH_2Cl groups is obtained. The result suggests the presence of repulsive forces between two bound chlorine atoms at distances as large as 4.0 Angstrom. IV. The related question of the thermal equilibrium ratio of the *cis* and *trans* isomers of dichloroethylene is discussed. A new explanation of the observed value is proposed, which attributes about equal heat of formation to both isomeric forms.

INTRODUCTION: STATEMENT OF THE PROBLEM

IT is now generally recognized that the deviations of the molar polarization *vs.* T^{-1} curves from a straight Debye line, as are observed with 1,2-dichloroethane, diacetyl, and similar molecules,[1] must be attributed to the presence of forces restricting free rotation of the polar groups around the single $C-C$ bond,[2,3] and that from the temperature variation of the dipole moment we can gather information with regard to these forces.[4,5,6] This information is important and, indeed, unique because in this particular phenomenon—unlike others where interatomic forces manifest themselves (second virial coefficient, friction in gases)—the groups approach each other under rigidly defined geometrical conditions which can be derived with great accuracy from x-ray and electron diffraction data.

[1] C. T. Zahn, Phys. Rev. **38**, 521 (1931); **40**, 291 (1932).
[2] L. Meyer, Zeits f. physik. Chemie **B8**, 27 (1930).
[3] Smyth, Dornte and Wilson, J. Am. Chem. Soc. **53**, 4242 (1931).
[4] Lennard-Jones and Pike, Trans. Faraday Soc. **30**, 830 (1934).
[5] Mizushima and Higasi, Proc. Imp. Acad. Japan **8**, 482 (1932).
[5a] Mizushima, Morino and Higasi, Physik. Zeits. **35**, 905 (1934).
[6] C. T. Zahn, Trans. Faraday Soc. **30**, 804 (1934).

As a refinement of the conceptions of free and restricted rotation, a distinction must be made with regard to the origin of the restricting forces.[7] In molecules like dichloroethane, the groups move under no restriction other than the one resulting from their own interaction. The single $C-C$ bond in itself gives no preference to any internal configuration. Molecules like ethylene represent the other extreme where practically complete inhibition of the internal motion is enforced by the presence of a double bond. The conception of quantum resonance has presented us with the possibility of an intermediate case of which diphenyl is perhaps representative. The shortening of the linkage between the two rings[3] and other arguments have led L. Pauling and his co-workers to suggest that, with the single bond character prevalent, there might be resonance with double bond structures of comparable energy. Thus the idea of a hybrid bond with features borrowed from the parent structures might offer a more adequate description.[9, 10] If so, one should expect a stiffening of the single bond, a possibility which—if established from dipole data of o,o'-dichloro-diphenyl, let us say —might constitute an experimental test of "whether the phenomenon of resonance exists to anything like the imagined extent"[11] and whether it is present in that particular structure. In order to be quantitative, such a test would have to cover a wide temperature range. However, on account of the high boiling point of the compound, one must either improve the sensitivity of the dielectric measurements and adapt them to low vapor pressures, or else resort to the molecular beam method with its theoretical complications.

The applicability of the method is not restricted to the interaction between groups. A study of electric fields in crystals may, for instance, be based on the observed temperature dependence of the polarization in cases where polar groups are rotating in such fields.

It is the intention of this paper further to develop the analytic tool for such studies. As a test case, the general results are applied to the dipole data available for 1,2-dichloroethane, where we believe we have a fair understanding of the controlling factors, and where more dependable vapor measurements over a wider temperature range are at hand than for other compounds relevant in this connection. This will perhaps justify the extensive and somewhat laborious treatment given this molecule in section III.

Mathematically, the problem is to determine the potential function $V(\varphi)$ from a knowledge of the temperature variation of the mean square of the dipole moment. This, as will be shown below, amounts to solve for $V(\varphi)$ from a given equation:

$$\overline{\cos \varphi} = \int_0^{2\pi} d\varphi \cos \varphi e^{-V(\varphi)/kT} \Big/ \int_0^{2\pi} d\varphi e^{-V(\varphi)/kT}.$$

It is plausible that this could be done provided the left side of the equation were known for the entire temperature range. In view of the inherent experimental limitations, however, the best that can be done is to set up plausible potential functions which, upon proper choice of one or more disposable parameters, will best account for the experimental data over the accessible temperature range.

Previous investigators have taken a cosine function

$$V = V_1 \cos \varphi \tag{1}$$

as the presumable expression for the potential energy. While this potential is suggested by the calculated mutual potential of the electric dipoles,[12] it is hardly one to do full justice to the complexity of the forces involved. The cosine shape of the electrostatic potential as calculated by Smyth, Dornte and Wilson[12] and given in a later part (curve C in Fig. 5), is enhanced if a flattening of the potential hill takes place as a result of a weakening of the bond moments by mutual induction. On the other hand, we shall find that electrostatic forces do not play a dominating part in dichloroethane, and that—

[7] E. Hueckel, Zeits. f. Physik **60**, 423 (1930).
[8] As N. V. Sidgwick remarks, a similar shortening has been observed with tetramethylbenzene in the link between the ring carbon and the methyl carbon, where resonance is obviously not a factor (See: discussion remark, Trans. Faraday Soc. **30**, 824 (1934)).
[9] Pauling and Sherman, J. Chem. Phys. **1**, 606, 680 (1933). For fuller references consult reference 10.
[10] Sutton, Trans. Faraday Soc. **30**, 789 (1934).
[11] Such doubts have been expressed with strong arguments by Bayley, Trans. Faraday Soc. **30**, 828 (1934).

[12] Smyth, Dornte and Wilson, J. Am. Chem. Soc. **53**, 4242 (1931).

except in a region which at moderate temperatures is effectively barred by forces of non-electrostatic origin,—their contribution stays within a few hundred calories/mole. The dominating forces arise in all probability from van der Waals attraction and from steric repulsion, and their potential remains yet to be calculated.

Considering, then, (1) as a first approximation suggested by the periodic character of the potential, we shall try the following as a second approximation:

$$V = V_1 \cos \varphi + V_2 \cos 2\varphi \qquad (2)$$

and shall derive the temperature dependence of the molar polarization resulting from (2). Since the more general assumption (2) puts two parameters at our disposal, we may expect a better agreement between theory and experiment, and more information than could be had on the basis of (1).

Before this derivation is given in section II, a point will be discussed in section I which has seemingly been neglected in past treatments. This concerns the statistical method of taking mean values of an assembly of systems possessing internal degrees of freedom.

I. THE STATISTICAL WEIGHT OF A CONFIGURATION

The formula for the statistical mean value of a quantity μ, averaged over an assembly of mechanical systems $\mathfrak{S}$ which move according to the laws of classical mechanics, calls for integration over the phase space of $\mathfrak{S}$:

$$\bar{\mu} = \frac{\int dq_1 \cdots dq_n \int dp_1 \cdots dp_n \mu e^{-H(p\,q)/kT}}{\int dq_1 \cdots dq_n \int dp_1 \cdots dp_n e^{-H(p\,q)/kT}}. \qquad (3)$$

In the case of rigid molecules, identical momentum integrals can be factored off both the denominator and the numerator so that integrations over configuration space only are required. When dealing with a molecule with internal degrees of freedom, the conventional omission of the integration in momentum space is no longer permissible. This point deserves attention with respect to the choice of the internal position variables, since it is the integration over their conjugate momenta which

makes the values of the integrals in (3) independent of the particular choice of variables. Equally important, though, perhaps, less obviously so, is the integration over the three "external" momentum variables, since, in general, the three moments of inertia of the molecule do not remain constant, but vary with the internal configuration.

It is perhaps not superfluous, in view of different uses of the terms in recent discussions,[13] to set down at this point the proposed way of distinguishing between external and internal motion. Kinematically, such division can be effected in a variety of ways. Uniqueness is attained if we require that external and internal degrees of freedom be separable from each other in the sense that no cross-terms between the two sets of variables occur in the Hamiltonian form of the kinetic energy. With this end in view we define a rigid, rectangular frame X_i attached to, and moving with, the molecule in a manner such that at any time the following expression vanishes:

$$\sum_i m_i [r_i \times v_i] = 0. \qquad (4)$$

Here, v_i is the velocity of the i'th particle relative to the moving frame and represents the part of the total motion referred to as internal. The remaining, external part is the motion $[r_i \times \omega]$ executed by the particle if it were rigidly attached to, and moving with the frame in its instantaneous relative position. Once given, the system X_i is determined at subsequent times by the equations:

$$dX_i/dt = [\omega \times X_i].$$

By ignoring translational degrees of freedom, the kinetic energy:

$$K = \tfrac{1}{2} \sum_i m_i V_i^2 = \tfrac{1}{2} \sum_i m_i (v_i + r_i \times \omega)^2$$
$$= \tfrac{1}{2} \sum_i m_i v_i^2 + \tfrac{1}{2} \omega^2 \sum_i m_i r_i^2 \sin^2 (r_i \omega)$$

is found to be free of cross terms between the two sets of variables because of (4) and:

$$\sum_i m_i v_i \cdot [r_i \times \omega] = \omega \cdot \sum_i m_i [\vartheta_i \times r].$$

[13] C. Eckart, in Phys. Rev. **46**, 383 (1934), defined the angular velocity by:
$$da_i/dt = [\omega \times a_i] \qquad (11)$$
and obtained cross terms in the kinetic energy. There, a_i is the unit vector along the i'th principal axis of inertia.

Eulerian angles θ, ψ, χ may be used to describe the motion of the rigid frame, and $(3N-6)$ internal parameters, preferably normal coordinates, may be chosen to describe the positions of the N particles relative to the frame.

Let us now consider a general system $\mathcal{S}$ with n rotational[14] degrees of freedom, the only restriction being that the kinetic energy K of $\mathcal{S}$ can be expressed as a quadratic form in the momenta p_i:

$$2K = \sum_{ik} a_{ik} p_i p_k. \qquad (5)$$

The momentum part of the integration required by (3) can then be carried out explicitly. Considering (5) and the fact that an n-dimensional ellipsoid with the equation:

$$\sum_{ik} b_{ik} x_i x_k = 1$$

has a volume v:

$$v = (\pi^{n/2}/\Gamma(n/2+1)) |C_{ik}|^{-\frac{1}{2}}$$

it is easily seen that:

$$\int \cdots \int dp_1 \cdots dp_n e^{-k/kT} = (2\pi kT)^{n/2} |a_{ik}|^{-\frac{1}{2}}.$$

Substituting this into (3) we arrive at the following formula:

$$\bar{\mu} = \int \cdots \int dq_1 \cdots dq_n \mu e^{(E-f)/kT} \qquad (6)$$

with

$$f \equiv v - kT \ln \left[(2\pi kT)^{n/2} |a_{ik}|^{-\frac{1}{2}} \right] \qquad (6a)$$

and

$$F \equiv -kT \ln \int \cdots \int dq_1 \cdots dq_n e^{-f/kT}$$
$$= \bar{\bar{H}} - TS. \qquad (6b)$$

F and S represent the rotational free energy and entropy of the system respectively. An expression for the entropy of a molecule with internal degrees of freedom is thus obtained as a by-product of the above calculation:

$$S = k \ln \int \cdots \int dq_1 \cdots dq_n$$
$$\times \ln \left\{ (2\pi e kT)^{n/2} |a_{ik}|^{-\frac{1}{2}} e^{(\bar{v}-v)/kT} \right\}. \qquad (7)$$

As an application, the part of the molar polarization $(P-P_0)$ which is due to the presence of rotating polar groups will be computed for a compound consisting of molecules with only one

internal degree of freedom, q_0. Let the potential energy be a function $V(q_0)$ in the absence of external fields, and $[V(q_0) - F\mu_z]$ in the presence of the homogeneous electric field F directed along the z axis. μ_z is a function of q_0 and represents the z component of the instantaneous electric moment of the molecule. According to (3), the mean value of the electric moment in the direction of the field is:

$$\overline{\mu_z(F)} = \frac{\int \cdots \int dq_0 \cdots dp_3 \mu_z e^{-H/kT}}{\int \cdots \int dq_0 \cdots dp_3 e^{-H/kT}}, \qquad (8)$$

where $H = H_0 - F\mu_z$ is the total energy of the system. Since in the approximation valid for the weak fields of the Debye theory:

$$e^{-H/kT} = e^{-H_0/kT} [1 + (F\mu_z/kT) + \cdots]$$

we have:

$$\overline{\mu_z(F)} = \overline{\mu_z(0)} + (F/kT) \left[\overline{\mu_z^2(0)} - \overline{\mu_z(0)}^2 \right]$$
$$= (F/3kT)\overline{\mu^2(0)}. \qquad (9)$$

The kinetic energy of the molecule may be expressed in terms of the angular momentum M, resolved in the three directions of its—instantaneous—principal axes:

$$2K = p_0^2/I(q_0) + M_I^2/A(q_0)$$
$$+ M_{II}^2/B(q_0) + M_{III}^2/C(q_0). \qquad (10)$$

It is not difficult to show that evaluation of the mean square of the electric moment $\overline{\bar{\mu}^2}$ according to formula (6) leads to the following expression for the molar polarization:

$$P - P_0 = \frac{4\pi N}{3} \frac{\overline{\mu(F)}}{F}$$
$$= \frac{4\pi N}{9kT} \frac{\int dq_0 \mu^2 (ABCI)^{\frac{1}{2}} e^{-v(q_0)/kT}}{\int dq_0 (ABCI)^{\frac{1}{2}} e^{-v(q_0)/kT}}, \qquad (11)$$

where N is the number of molecules per mole, $A(q_0)$, $B(q_0)$, $C(q_0)$ are the Eulerian moments of inertia and $I(q_0)$ is the generalized moment of inertia for the internal motion as defined by Eq. (10). Its functional relation to q_0 is such as to render Eq. (11) invariant under transformations from one internal parameter q_0 to another.

The weight factor which occurs in (11):

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[14] "Rotational" degrees of freedom are characterized by full excitation at the temperature considered and may include torsional vibrations of low frequency. The translational degrees of freedom are not interesting in this connection and we assume that they have been separated off.

$$W(q_0) = (ABCI)^{\frac{1}{2}} \qquad (12)$$

attributes weight to the individual configurations according to their moments of inertia. In a purely descriptive manner we may connect the variations of weight with pulsations of phase space as the volume element in momentum space occupied by a given range dK of kinetic energy changes with the changing configurations. This is the classical analog, in the sense of the correspondence principle, of the fact that the rotational energy levels are more widely spaced, and of lesser multiplicity in a certain definite energy range dK,[15] when the moments of inertia are smaller; an analog that could be made more convincing were it true that the system goes through a number of external revolutions before marked changes of the moments of inertia take place.

Before closing this section, the obvious limitations of the treatment will be emphasized:

(1) Integrals in phase space are used throughout as an approximation of the state sums. As 🜏 is in reality a quantized system, our results are valid only inasmuch as the separation between neighboring rotational levels $\Delta E \ll kT$.

(2) Our neglect of the vibrational degrees of freedom which the system may have, restricts the strict validity of the treatment to temperatures where practically all molecules are in their lowest vibrational state. At higher temperatures, Eqs. (6), (6a), (7) have to be modified so as to include the vibrational part of the entropy.

(3) Even with all the molecules in their lowest vibrational states the kinetic energy of vibration is not zero, and may vary from one configuration to the other. Inasmuch as the molecule vibrates in the neglected degrees of freedom at a much faster rate than it goes through the rotations and torsional vibrations, it is probably a good approximation to consider the interaction as an adiabatic transfer of zero-point energy to and from the other modes of motion; a picture which attributes to the zero-point energy a role similar to a potential opposing free rotation in q_0.[16]

The fluctuations of zero-point energy may be estimated as contributing amounts of the order of a few hundred calories to the opposing potential, in the case of compounds such as butane, dichloroethane and others, where the observed broadening and doubling of Raman shifts has been attributed to the internal motion.[17] As equipartition of kinetic energy is more nearly approached with rising temperature, the effect should vanish or, in any event, be drowned by the concurring influence of the higher states of vibration.

II. Approximation of the Potential Function by Its First Two Fourier Components

In order to extend the integrations required by (11) to the second Fourier component of the periodic potential $V(q_0)$, we replace it by its expression (2). In terms of the azimuthal angle φ between the two revolving groups, taken around the $C-C$ bond, the square of the instantaneous electric dipole moment in (11) is:

$$\mu^2 = [2\mu_1 \cos(\varphi/2)]^2 = 2\mu_1^2(1 + \cos\varphi), \quad (13)$$

where μ_1 is the group moment of either of the two alike groups, resolved at right angles to the $C-C$ bond. Thus it is seen that formula (11) leads to integrals of the following type:

$$I(m; x, y) \equiv (1/2\pi)\int_0^{2\pi} e^{(x\cos\varphi + y\cos 2\varphi)} \times \cos m\varphi \, d\varphi. \quad (14)$$

In terms of these integrals, we have:

$$\overline{\cos\varphi} = \frac{I(1; -v_1/kT, -v_2/kT)}{I(0; -v_1/kT, -v_2/kT)}. \quad (15)$$

Here, the single bar in $\overline{\cos\varphi}$ indicates that the weight factor $W(\varphi)$ has been omitted. It is practical to derive $\overline{\overline{\cos\varphi}}$ as a correction of $\overline{\cos\varphi}$ at a later stage, when $W(\varphi)$ has been determined for a particular molecule, by a procedure described at the end of this section.

By expanding the exponential in the integrand of $I(m; x, y)$ into powers of x, y:

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[15] This change of multiplicity results from the fact that, with the moments of inertia decreasing, rotational levels of lesser quantum number j (i.e., in the case of a simple rotator) and accordingly of lesser multiplicity $(2j+1)$ move into the contemplated energy range dK.

[16] This potential can be brought into a certain formal analogy with the binding potentials between atoms in a molecule where the quantized electronic energy varies with the internuclear distance. The variation of electronic energy provides the potential in which the nuclei are moving.

[17] F. Kohlrausch, Zeits. f. physik. Chemie **B18**, 61, also reference 5a. In typical cases, line doubling with about 100 wave numbers separation has been reported.

$$2\pi I(m; x, y) = \sum_{n,\ k} \frac{1}{n!}\binom{n}{k} x^{n-k}y^k \int_0^{2\pi} \cos^{n-k}\varphi(2\cos^2\varphi-1)^k \cos m\varphi d\varphi$$

$$= \sum_{n,\ k\ l}(-1)^{k-l}2^l x^{n-k}y^k \frac{1}{n!}\binom{n}{k}\binom{k}{l}\int_0^{2\pi} \cos^{n-k+2l}\varphi \cos m\varphi d\varphi$$

and changing from powers of the cosine to the cosine of the multiple angle[18] we have:

$$2\pi I(m; x, y) = \sum_{nklr}(-1)^{k-l}\frac{1}{2^{n-k+l}}x^{n-k}y^k \frac{1}{n!}\binom{n}{k}\binom{k}{l}\binom{n-k+2l}{r}\int_0^{2\pi} \cos(n-k+2l-2r)\varphi \cos m\varphi d\varphi.$$

This last sum of integrals contains only two nonvanishing contributions, namely the ones for which: $|n-k+2l-2r| = |m|$. That the two contributions are equal can be seen from the fact that, with n, k, l being fixed and $2r = n-k+2l\pm m$, the only expression which could depend on the sign of m would be $\binom{n-k+2l}{r}$. But this is also independent of the sign of m since, for every value of s, m:

$$\binom{s}{(s+m)/2} = \binom{s}{(s-m)/2}$$

if $(s-m)$ is even as in the present case. Thus, introducing a new summation index $i = (r-l)$ in place of l, and discarding all terms except the ones for which $(n-k+2l-2r) = \pm m$, we have:

$$2\pi I(m; x, y) = 2\sum_{kir}(-1)^{k+i-r}\frac{1}{2^{m+i+r}}x^{m+2i}y^k \frac{1}{(m+2i)!k!}\binom{k}{r-i}\binom{m+2r}{r}\int_0^{2\pi} \cos^{2|m|}\varphi d\varphi$$

and finally:

$$I(m; x, y) = \sum_{ik}a^m{}_{2i,\ k}x^{m+2i}y^k \qquad (16)$$

with

$$a^m{}_{2i,\ k} = \frac{(-1)^{i+k}}{2^{m+i}(m+2i)!k!}\sum_i{}^{i+k}\left(-\frac{1}{2}\right)^r\binom{k}{r-i}\binom{m+2r}{r}. \qquad (17)$$

No separate treatment is needed for $m=0$; in this case, the sum contains only one nonvanishing integral, but its value is 2π instead of π.

The numerical evaluation of the integrals $I(m; x, y)$ is greatly simplified by the aid of recurrence formulas:

$$a^0{}_{2i,\ k} = (1/2i)a'{}_{2i-2,\ k} \qquad \text{for } m=0 \quad (18)$$

$$a^{m+1}{}_{2i,\ k} = 2(m+2i+2)a^m{}_{2i+2,\ k} - a^{m-1}{}_{2i+2,\ k}$$

$$\text{for } m = \pm1, 2\cdots. \quad (19)$$

Only the formula for $m=0$ is needed here and

will be proved:[19] If the identity between binomial coefficients:

$$\left(-\frac{1}{2}\right)^{r+1}\binom{2r+2}{r+1} = \left(-\frac{1}{2}\right)^{r+1}\binom{2r+1}{r}$$

is multiplied on both sides with $\frac{(-1)^{i+k}}{2^i(2i)!k!}\binom{k}{r-i}$ and if the index r is summed from $r=i$ to $r=i+k$, Eq. (18) follows at once from a comparison of the result with Eq. (17).

The higher coefficients $a^m{}_{2i,\ k}$ can be expressed in terms of the a^0's with the aid of (18), (19).

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[18] It is readily verified that:

$$\cos^p x = (\tfrac{1}{2}p)\sum_{=0}^p\binom{p}{k}\cos(p-2k)x.$$

Including into the summation negative values of $(p-2k)$ takes automatic care of the various two-factors appearing in the formula as usually stated, and makes unnecessary the customary distinction between even and odd p.

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[19] The recurrence formula (18) for $m=0$ follows as a special case of (19) if use is made of the identity:

$$a^1{}_{2i,\ k} = a^{-1}{}_{2i+2,\ k}.$$

This, in turn, springs directly from a comparison of corresponding powers in the equation [see definition (14) of $I(m; x, y)$]:

$$I(1; x, y) = I(-1; x, y).$$
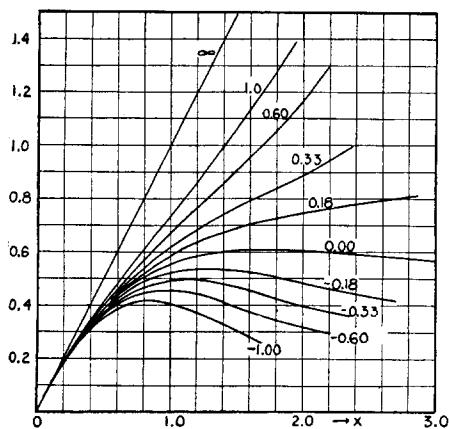
FIG. 1. $p_\nu(x)$.

Formula (18) reduces the numerical labor necessary for evaluation of $I(l; x, y)$ and $I(0; x, y)$ to exactly the half amount.

We are now ready to calculate the polarization (11), omitting the weight factor W for the time being. Substituting (13) into (11) we have:

$$P - P_0 = (8\pi N/9kT)\mu_1^2(1 + \overline{\cos \varphi}). \quad (20)$$

This shall be written:

$$p_\rho(x) = x[1 + I(1; x, \rho x)/I(0; x, \rho x)], \quad (21)$$

where

$$p_\rho(x) \equiv (9v_1/8\pi N\mu_1^2)(P - P_0),$$

$$\rho \equiv v_2/v_1, \quad x \equiv -v_1/kT$$

and

$$I(m; x, \rho x) = \sum_{ik}(a^m_{2i,\ k}\rho^k)x^{m+2i+k}. \quad (22)$$

The curves $p_\rho(x)$ have been calculated from (21), (16), (17) and are plotted in Fig. 1. The experimental values $(P - P_0)$ may now be plotted against T^{-1} in such a manner that, upon suitable choice of scale factors $a = 9v_1/8\pi N\mu_1^2$, $b = v_1/k$ the closest possible fit is attained between the points $a(P - P_0)$ plotted vs. bT^{-1} on one hand, and one of the curves $p_\rho(x)$ on the other. This matching fixes the numerical value of ρ and thus determines the shape of the potential (2). Its absolute magnitude, expressed by V_1, as well as the group moment μ_1, are determined simultane-

ously from the two scale factors a, b used in the process of matching. The curve $p_0(x)$, labeled 0.00 in Fig. 1, is the same as has been previously obtained by different workers. It permits expression in terms of Bessel functions:

$$p_0(x) = x(1 + iJ_1(ix)/J_0(ix)).$$

Because of the poor convergence of (22) for large x (low temperatures), the numerical evaluation of the curves $p_\rho(x)$ is quite laborious; up to 16 powers had to be used. Thus, a discussion of the asymptotic behavior of the curves for large x supplements the calculations in a helpful way. The position of the absolute minimum of the potential (2) decides the limiting value which the resulting dipole moment of the molecule approaches for low temperatures, and determines the limiting slope of the p curves for large x. Since, for $\rho < 0$, both terms of $V^\bullet$ have their minimum value at $\varphi = 180°$, the most stable position is always the trans position; hence no dipole moment and zero slope of the curves as x goes to infinity. In the case of positive ρ, however, a shift of the absolute minimum may take place. A distinction is found necessary between the two cases $\rho \lessgtr 0.25$.

(a) $\rho < 0.25$: At very low temperatures, practically all molecules are found in the immediate neighborhood of the trans position $\varphi = 180°$. A Taylor expansion around $\varphi = 180°$ shows that the potential there behaves qualitatively as in the case $\rho = 0.0$:

$$v(\pi - \epsilon) = -v_1(1 - \rho) + v_1(1 - 4\rho)\epsilon^2/2 + \cdots.$$

Correspondingly, it is found by a short calculation that the curves $p_\rho(x)$ go asymptotically to a constant value $1/2(1 - 4\rho)$.

(b) $\rho > 0.25$: In this case the minimum is shifted from $\varphi = 180°$ to two positions $\varphi = \arccos(-1/4\rho)$, symmetrically spaced around the trans position. Hence, the dipole moment approaches a lower limit

$$\overline{\mu(F)}/F = \overline{\mu^2}/3kT \rightarrow (2\mu_1^2/3kT)(1 - 1/4\rho)$$

and the limiting slope of the p-curves is found to be:

$$\lim_{x \to \infty} (d/dx)p_\rho(x) = (1 - 1/4\rho).$$

The Fig. 1 shows the different behavior of the curves in both cases quite markedly. It is hardly necessary to emphasize that our classical treatment does not really apply to the limiting case of low temperature, and gives consistently lower polarizations than would a quantum-mechanical treatment. In the experimentally accessible range of temperature, however, such deviations are, in all probability, very small.

A few words are necessary concerning the computation of $\overline{\cos\varphi}$. When the weight factor $W(\varphi)$ has been determined for a particular molecule, and provided its deviations from unity: $\Delta W = (W-1)$ are found small so that the influence of W on (11) has the character of a correction applicable to $\overline{\cos\varphi}$, it is expedient to carry out the integration (11) in the two steps indicated by the following:

$$\overline{\cos\varphi} = (I_1 + \Delta I_1)/(I_0 + \Delta I_0), \qquad (23)$$

where

$$I_0 + \Delta I_0 \equiv \frac{1}{2\pi} \int_0^{2\pi} d\varphi W(\varphi) e^{x \cos\varphi + y \cos 2\varphi}$$

$$= I(0; x, \rho x) + \frac{1}{2\pi} \int_0^{2\pi} d\varphi \Delta W e^{x(\cos\varphi + \rho \cos 2\varphi)},$$

$$I_1 + \Delta I_1 \equiv \frac{1}{2\pi} \int_0^{2\pi} d\varphi W(\varphi) \cos\varphi e^{x \cos\varphi + y \cos 2\varphi}$$

$$= I(1; x, \rho x) + \frac{1}{2\pi} \int_0^{2\pi} d\varphi \cos\varphi \Delta W \cdot e^{x(\cos\varphi + \rho \cos 2\varphi)}.$$

By a suitable choice of the integration parameter

TABLE I.

φ	A^*	B	C	$(ABC)^{\frac{1}{3}}$	I^*	W	ΔW
cis: 0°	154.8	219	70.7	1560	9.70	0.6827	−0.3173
15						.730	− .270
30	167.2	226.1	68.1	1600	13.9	.8363	− .1637
45						.960	− .040
60	204.9	248.6	59.5	1745	19.16	1.070	.070
75						1.150	.150
90	267.0	287	42.4	1800	22.64	1.200	.200
105						1.190	.190
120	320.5	327.3	31.7	1830	19.36	1.132	.132
135						1.023	.023
150	353.6	347.2	20.7	1600	18.24	.9557	− .044
165						.950	− .050
trans: 180	377	365.5	17.6	1560	19.70	.9650	− .035

*The moments of inertia in this table are expressed in the units: Hydrogen mass at one Angstrom distance. C is the moment around the principal axis closest to the C−C bond.

TABLE II.

φ	$\bar{\varphi}$	$d\varphi/d\bar{\varphi}$	$\overline{W}(\bar{\varphi})$
0	0	1.8	1.21
30	18	1.78	1.47
60	36	1.7	1.79
90	55	1.4	1.65
120	80	1.0	1.11
150	116.5	.7	.66
180	180	.3	.28

q_0, the corrections ΔI_0 and ΔI_1 can be kept small compared with the main terms $I(0; x, y)$ and $I(l; x, y)$, and can be found by graphical integration with sufficient accuracy to match the accuracy of the series expansion attainable for the main terms. The overall accuracy obtained with the combined use of explicit formulas and graphical integration was sufficient to compare with the accuracy of the best experimental results.

III. APPLICATION TO 1,2-DICHLOROETHANE

The results of the preceding two sections have been applied to dichloroethane with the help of graphical methods. The determination of the moments of inertia $A(q_0)$, $B(q_0)$, $C(q_0)$ is greatly facilitated if we note that the molecule has, for every one configuration, what may be termed an inversion axis X; i.e., an axis which permits rotation of the whole molecule by 180° as a covering operation. This property makes the axis X automatically a principal axis of inertia, since projections of the system into any plane containing X are symmetric with respect to X. On the strength of this fact, the process of locating the principal axes for a particular configuration of the molecule reduces to finding the two remaining ones, i.e., a problem in two dimensions.

The customary distances, namely 1.52A, 1.85A and 1.08A, were used for the distances between $C-C$, $C-Cl$ and $H-C$, respectively. It was assumed that the two CH_2Cl groups revolve around the $C-C$ bond with constant valence angles. Actually, considerable distortion of the tetrahedral angle $C-C-Cl$ would be necessary to let the two Cl atoms pass by each other in the *cis* configuration. I requires an increase of 7° to raise the distance of closest approach from
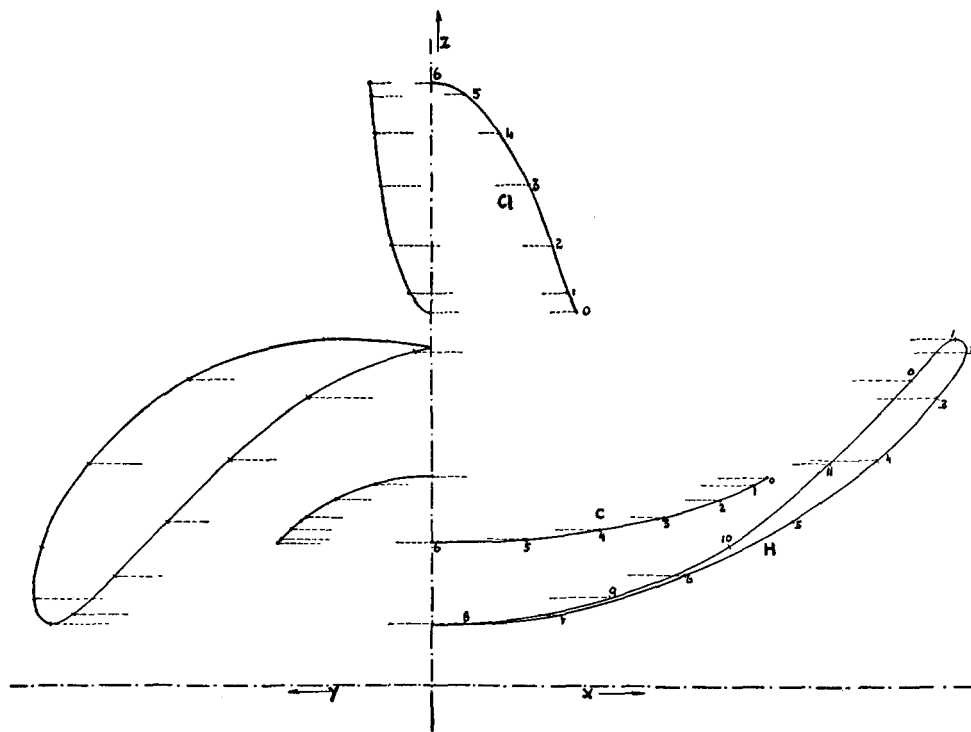
FIG. 2. Orbits of the constituent atoms of dichloroethane described in "internal" motion. The H orbit is the same for both hydrogen atoms in the same group, positions occupied simultaneously are: 0–0, 1–11, 2–10, etc.

2.7A to the observed 3.2A; a distortion which has been ignored here, both in the calculation of A, B, C as in the effect which it must have on the validity of Eq. (13). This neglect tends to raise the calculated polarization at high temperatures where distortion plays a part, as is born out, later on, by a comparison with the experimental values.

Next, the moment of inertia $I(\varphi)$ had to be determined. From its definition (10) it follows that:

$$K_{\text{int}} = p_\varphi{}^2/2I = (\dot\varphi^2/2)\sum_i m_i (dx_i/d\varphi)^2,$$
$$I(\varphi) = \sum_i m_i (dx_i/d\varphi)^2. \tag{24}$$

The derivatives $dx_i/d\varphi$ were determined graphically in the following manner: The orbits were constructed which the individual atoms of the molecule describe, relative to a reference frame $X_i = (X, Y, Z)$ defined by the Eq. (4). This

relative motion is the one which was referred to as "internal" motion in the earlier part of section I. The orientation of the frame relative to the molecule is completely described by two geometrical requirements: For any instantaneous configuration, the X axis can be identified with the inversion axis, and the Z axis taken as the straight line through the two centers of gravity of the two CH_2Cl groups. During the motion, the centers of gravity slide back and forth along the Z axis while equal and opposite revolutions around it are executed by the two groups.

During each complete revolution in space the molecule goes through two *cis* positions in the XZ plane, and through two *trans* positions in the YZ plane; two successive *cis* positions marking a full period 2π of the parameter φ. Thus it is seen that all orbits are symmetrically arranged with respect to any of the three coordinate planes. It is then sufficient for a full
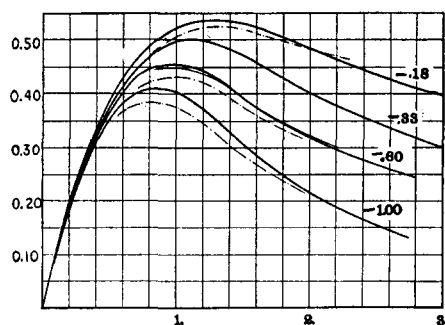
Fig. 3. Curves $p_\rho(x)$ with corrections $\Delta W'$ applied' (broken curves). The weak curve near $\rho = -0.60$ is corrected with ΔW.

Fig. 4.

description of the motion in space to present two views of one octant, using the conventional methods of descriptive geometry. The dots 0, 1, 2 $\cdots$ in Fig. 2 represent those configurations for which φ equals a multiple of 30°. A third view, looking down along the Z axis can be readily obtained and provides us with the functional relation between our parameter φ and the one used by Lennard-Jones and Pike in their treatment of the same problem. This latter parameter $\bar{\varphi}$ measures the azimuthal angle between the two C—Cl bonds around the Z axis; a list of corresponding values of φ and $\bar{\varphi}$ is given in Table II for later reference.

From Fig. 2 the coordinates x_i of the eight atoms in their positions 0, 1, 2 $\cdots$ have been measured and the derivatives $dx_i/d\varphi$ determined by numerical differentiation.[20] In terms of these, I was determined from (24) and is listed in Table I. W was next calculated and normalized so that:

$$\int_0^{2\pi} d\varphi W(\varphi) = 1,$$

The values of $W(\varphi)$ for odd multiples of 15° in Table I were then found by interpolating between the calculated ones. With the values ΔW determined, the weight factor could now be applied to the $p_\rho(x)$ curves, using (23).

The correction, when applied to $p_{-0.60}(x)$, results in the weak curve accompanying the fully drawn curve in Fig. 3. The correction is surprisingly small, so that it was considered
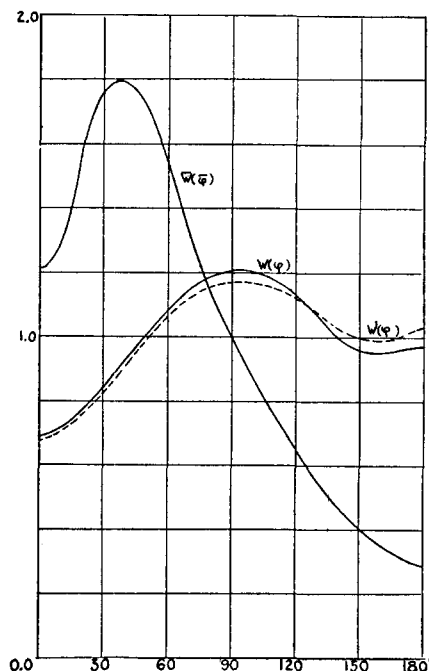
[20] Runge and Koenig, *Vorlesungen ueber numerisches Rechnen*, p. 76.

unnecessary to apply the same lengthy process to the other curves. That the weighing with W is, in general, an affair by no means trivial but results in noticeable corrections of the p curves, is demonstrated by setting up an artificial weight factor $W'(\varphi)$, Fig. 4, which, for demonstration's sake, has been given slight deviations from $W(\varphi)$. The corrections obtained for $p_\rho(x)$ with $W'(\varphi)$ are given for a few ρ values as the broken curves in Fig. 3, showing that small changes are not the rule but constitute a specific advantage of our choice of parameter.

Lennard-Jones and Pike,[4] have taken a different choice, arguing that the motion in space is not around the C—C bond and that the azimuthal angle should more properly be taken around the axis of revolution. A comparison of results of the two treatments is therefore in order. Clearly, this method is sufficiently general to permit the choice of either φ or $\bar{\varphi}$, since integration over the conjugate momentum makes the results invariant under transformations from one to the other. With this proviso, the question

TABLE III.

ρ	$\mu_1{}^{DU}$	$2V_1$
0.0	1.75	$2.06.10^{-13}$ erg
− .18	1.57	1.48
− .33	1.53	1.26
− .60	1.48	1.14
−1.00	1.46	0.96

reduces to one of mere convenience. However, attention must be given to the significance of the potential function V when comparing results, since obviously $V_1 \cos \bar{\varphi}$ means something quite different from $V_1 \cos \varphi$. If the values φ are substituted from Table II, the potential function $V_1 \cos \bar{\varphi}$ adopted by Lennard-Jones and Pike is a function of φ as pictured in Fig. 5, curve B. In the calculation of the polarization with a potential $V_1 \cos \bar{\varphi}$, a weight factor $\overline{W}(\bar{\varphi})$ should be used which follows from the formula:

$$\overline{W}(\bar{\varphi}) = W(\varphi)d\varphi/d\bar{\varphi}.$$

φ and $\bar{\varphi}$ in this formula are corresponding parameter values referring to the same configuration. Numerical evaluation has given the values $\overline{W}(\bar{\varphi})$ listed in Table II and plotted in Fig. 4. It would seem that omission of this

weight factor must modify the conclusions reached.

These advantages were found in choosing φ as our parameter: It permits a direct and physically significant expression of the potential; an expression which, in particular, does not depend upon the mass distribution in the molecule. The dipole moment μ bears a simple relation to φ and thus complications are avoided. The main advantage in working with φ is that it permits use of the p curves as polarization curves without laborious corrections.

Next it must be found which curve $p_\rho(x)$ gives the best agreement with Zahn's experimental values $(P-P_0)$ for dichloroethane.[1] To be acceptable, this choice must also lead to reasonable conclusions regarding μ_1 and $2V_1$. (It has been shown, above, how these two quantities are determined in the matching process.) Table III gives a list of values required to establish coincidence between the maxima of the experimental curve and the corresponding $p_\rho(x)$ curve.

Of the potentials (2) admitted for comparison, the following (Fig. 5, curve A) has been found to give closest agreement with Zahn's measurements:

$$V = (0.57 \cos \varphi - 0.34 \cos 2\varphi) \cdot 10^{-13} \text{ erg.} \quad (25)$$

It involves a ratio $\rho = -0.60$ and a group moment $\mu_1 = 1.48 \cdot 10^{-18}$ e.s.u. The temperature dependence of $(P-P_0)$ calculated with (25) is shown in Fig. 6, together with the experimental points.
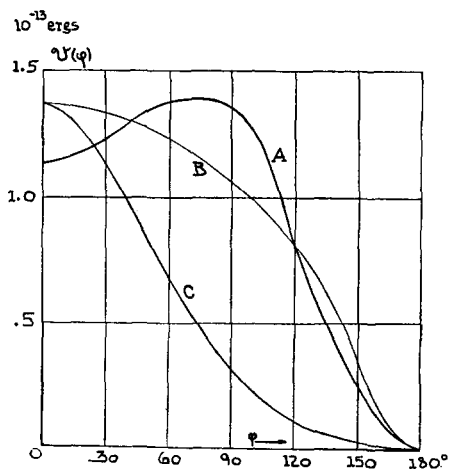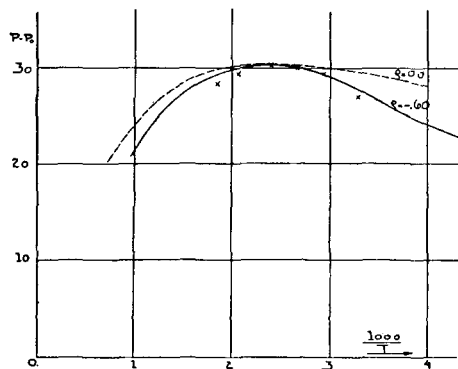

FIG. 5. Curve A: $V(\varphi) = 0.571 \cos \varphi - 0.34 \cos 2\varphi$; Curve B: Lennard-Jones and Pike's potential; Curve C: Electrostatic potential according to Smyth, Dornte and Wilson.

FIG. 6. Comparison between the measured values $(P-P_0)x$ and the calculated curves $p_0(x)$ and $p_{-0.60}(x)$.

Discussion of results

The improvement obtained with the incorporation of a second Fourier component is seen from a comparison with the broken curve in Fig. 6. This curve shows the best agreement that can be obtained on the basis of $p_0(x)$. Marked deviations result from the relative flatness of $p_0(x)$; deviations which are greatly reduced though not completely avoided when $p_{-0.60}$ is used instead. The deviations of $p_{-0.60}$ at high temperatures (small x) can in part be attributed to the neglect of valence angle distortion. In principle, however, they indicate to the author's mind a steeper potential rise, upon approaching the *cis* position, than is exhibited by (25). The potential V could rise more steeply from 90°, say, toward 0° without appreciable change of the statistical distribution at lower temperatures, where few groups penetrate into the near *cis* region anyway. At temperatures around 500°K, however, the configurations near the *cis* position gain in statistical weight. Failure of (25) to represent the potential rise in its full steepness must then raise the calculated values of the mean dipole moment. According to Fig. 6, this appears to be the case. Thus it is not likely that the potential minimum in the *cis* position is significant though it seemed to offer an interesting and tempting possibility, in view of other experimental data which had been interpreted in the past as proving the existence of two stable forms of dichloroethane.[21]

The rise of the potential from the *trans* position, ($\varphi = 180°$) is surprisingly steep. Up to about 150°, it must certainly be attributed to repulsion between either of the two Cl atoms and the closer H atom belonging to the other group. Upon further approach of the *cis* position, however, a very appreciable portion of the total repulsion must be due to $Cl - Cl$ repulsion. This

seems to establish the existence of repulsive forces between two bound Cl atoms at larger distances than is usually assumed; in fact, there must be considerable repulsion at a distance of $4.0A (\varphi = 120°)$. No further attempt is made here to interpret the potential (25) in detail. Calculations, based on such theoretical assumptions as can be made at present with regard to $Cl - Cl$, $Cl - H$ and $H - H$ interaction, yield a total potential V in fair agreement with (25). It is expected to present these calculations in a separate note.

IV. *Cis* and *Trans* Dichloroethylene

The results of section III are likely to throw new light on a problem which has arisen from other experimental sources, namely the question of the relative stability of the two isomers of dichloroethylene. The thermal equilibrium ratio of the two forms has been determined by Ebert and Büll[22] as 63 percent *cis* to 37 percent *trans* at 300°C, and has been interpreted as demonstrating that the potential energy of the *trans* form exceeds that of the *cis* form by approximately 600 cal/mole; a situation both unusual and unexpected in view of the strong intramolecular repulsion which manifests itself in the similar case of dichloroethane. Hence the present writer has felt reluctant to accept this interpretation, in spite of theoretical arguments brought forward by H. A. Stuart and intended to make plausible the greater energy of the *trans* form.[23] Stuart's omission of repulsive potentials other than electrostatic is a disputable point, considering that an appreciable part of the repulsive energy in dichloroethane had to be attributed to $Cl - Cl$ steric repulsion. To get some indication about the energy difference between the two forms by comparison with dichloroethane, we note that the $Cl - Cl$ distance in the latter is very nearly the same at $\varphi = 90°$ as in *cis*-dichloroethylene, and only slightly shorter at $\varphi = 180°$ than it is in *trans*-dichloroethylene. Obviously, only part of the repulsive forces active in dichloroethane

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[21] Wierl's contention that two stable forms exist was based on his electron diffraction data which seemed to suggest two definite spacings of $Cl - Cl$ at 3.2 and 4.4A. Ehrhardt's investigation of dichloroethane with x-rays, however, suggested a continuous distribution of spacings as a more likely alternative (Physik. Zeits. **33**, 605 (1932)). Also, the doubling of Raman shifts in molecules $X - CH_2 - CH_2 - X$, observed by Kohlrausch (Zeits. f. physik. Chemie **B18**, 61, originally attributed to the presence of essentially two configurations, can be reconciled with the idea of a continuous distribution, following an argument by Mizushima, Morino and Higasi, Physik. Zeits. **35**, 905 (1934).

[22] Ebert and Büll, Zeits. f. physik. Chemie **A152**, 451 (1931).

[23] H. A. Stuart, Physik. Zeits. **32**, 793 (1931); also the same author's book *Molekülstruktur*, Springer, Berlin. Stuart's calculation would give an even larger difference: $v_{trans.} - v_{cis} = 1150$ cal.

TABLE IV.

	ENERGY OF INTERACTION $\times 10^{14}$/ERGS			
CL – CL DISTANCE IN A	DIPOLE EFFECT	INDUCTION EFFECT	STERIC REPULSION MINUS VAN DER WAALS ATTRACTION:	TOTAL
cis: 3.6	+8.4	−7.7	+4.0 (−4.8)*	+4.7 (−4.1)
trans: 4.6	+4.9	0	0 (−1.1)	+4.9 (+3.8)
			Difference	− 0.2 (−7.9)

* The *trans* position is arbitrarily assumed as having zero "steric" potential.

will be found present in dichloroethylene, on account of the absence of two H atoms. Let us roughly assume that 30 percent of the repulsive energy of the former, taken at $\varphi = 90°$, is a conservative estimate for the increase in "steric" potential of dichloroethylene when going from the *trans* to the *cis* form. This would suggest the following changes in Table IV originally given by Stuart,[22] with his original figures retained in brackets for comparison where changes have been made. Thus we find the energies of the two forms equal within the accuracy of the estimates made. A possible difference in the vibrational zero-point energies may affect this result one way or the other by small amounts. Far from agreeing with the result reported by Ebert and Büll, this merely serves to accentuate the difficulty which Stuart wished to explain. The following has now occurred as a likely explanation: By reasoning in very much the same manner as in part I, one is led to the following formula for the equilibrium ratio r

between the two forms:

$$r = \frac{c_{cis}}{c_{trans}} = \frac{(ABC)^{\frac{1}{2}} \, cis}{(ABC)^{\frac{1}{2}} \, trans} e^{-\Delta v/kT}. \quad (26)$$

The principal moments of inertia have been determined, assuming a valence angle of 130° for $C = C - Cl$, and it was found that:

$$(ABC)^{\frac{1}{2}}_{cis} : (ABC)^{\frac{1}{2}}_{trans} = 1.65$$

$$= 62.3 \text{ percent} : 37.7 \text{ percent}.$$

This means that an isomeric equilibrium ratio which is very nearly equal to the one observed must be expected even in the complete absence of any heat of reaction ΔV. Generally, for temperatures high enough so that: $\Delta V \ll kT$, this ratio should represent a limiting value. It must not be forgotten, however, that here as in our previous discussions, the excitation of vibrational states is apt to modify the ratio. Among such effects are a possible change of the moments of inertia with T and the change of distribution of kinetic energy among the vibrational states at various temperatures.