

to prolonged heating it loses hydrazine very slowly at 120°, ultimately yielding the anhydrazinous salt. On the modified Maquenne block¹⁰ the monohydrazinate was found to decompose immediately, with explosive violence, at about 308°, and less rapidly at lower temperatures.

Summary

Two hydrazinates of calcium trinitride have been isolated and described. The *dihydrazinate*, $\text{Ca}(\text{N}_3)_2 \cdot 2\text{N}_2\text{H}_4$, prepared by crystallization from anhydrous hydrazine, is empirically isomeric and possibly identical with the calcium derivative of either of the two hitherto unknown hydronitrogens *pentazene-1*, $\text{HN}=\text{NNHNHNH}_2$, and *pentazene-2*, $\text{HN}(\text{NH}_2)\text{N}=\text{NNH}_2$ (*orthohydrazonitrous acid*). It may be possible, for example, that the terminal nitrogens of the pentazene-1 groups form coördinate linkages with the calcium atom, yielding a spiro structure of two six-membered rings. The *monohydrazinate* was prepared by gradual dehydrazination of the disolvate.

The chemical identity of the two compounds was definitely established by means of pressure-concentration and pressure-temperature curves.

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ELECTRIC MOMENT AND MOLECULAR STRUCTURE.

VI. THE VARIATION OF ELECTRIC MOMENT WITH TEMPERATURE

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Status of the Problem

When electric moments were first investigated, the question of their possible dependence upon temperature was considered. In the cases of the simpler moments, there seemed no reason to believe that change of temperature would alter the moment of a molecule unless it caused some molecular rearrangement or a large shift of energy level. The substances which were measured over a wide range of temperature showed no departure from the linear relation between the polarization and the reciprocal of the absolute temperature required by the Debye theory that could not be attributed to the effects of molecular association or experimental error. The moments calculated from the temperature variation of the polarization of gases and liquids agreed satisfactorily with those obtained at one temperature only.¹

In these past investigations, as in the present work, the polarization, P , was calculated as

¹ Smyth, *Chem. Rev.*, 6, 549 (1929).

$$P = \frac{\epsilon - 1}{\epsilon + 2} \frac{M}{d} = a + \frac{b}{T} \quad (1)$$

in which ϵ is the dielectric constant, M , the molecular weight, d , the density; $a = P_E + P_A$, the sum of the electronic polarization, P_E , and the atomic polarization, P_A , $b = 4\pi N\mu^2/9k$, N being the Avogadro constant, 6.061×10^{23} , μ , the electric moment, and k , the molecular gas constant, 1.372×10^{-16} , and T is the absolute temperature. In the case of liquids, it is necessary to measure the polar substance 2 in dilute solution in the non-polar 1 and calculate the polarization P_2 of the polar substance from the polarization P_{12} of the solution, use being made of the equations

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{c_1 M_1 + c_2 M_2}{d} \quad \text{and} \quad P_2 = \frac{P_{12} - P_1}{c_2} + P_1 \quad (2)$$

in which c_1 and c_2 are the mole fractions and the other symbols are obvious in their meaning. The effect of association is eliminated as far as possible by plotting P_2 against c_2 and extrapolating to infinite dilution, that is, $c_2 = 0$, to obtain P_∞ .

Zahn² found that acetic acid, with increasing temperature, showed an apparent increase in moment, which he attributed to change in the molecules to a higher energy state, but subsequent measurements upon formic and propionic acids have led him to attribute this apparent change in moment to the effect of molecular association.³ Bramley⁴ has thought to find evidence of an increase in the moment of bromine vapor with rising temperature due to the raising of the molecules to a higher energy level, but his experimental data do not appear adequate for the drawing of such a conclusion.

Werner⁵ reported that hydroquinone diethyl ether showed a variation of electric moment with temperature, the values being 1.72×10^{-18} at 20° , 1.92×10^{-18} at 40° and 2.00×10^{-18} at 60° . However, Meyer⁶ and Hassel and Naeshagen⁷ found no variation of the moment with temperature, the value, 1.73×10^{-18} , found in both investigations being in excellent agreement with those found by Weissberger and Sängewald⁸ in four different solvents, and with the result of an earlier measurement by Williams.⁹ Hassel and Naeshagen also found no variation with temperature in the electric moment of the similar molecule of hydroquinone-dimethyl ether.

The absence of temperature variation in the moments of the hydroquinone ethers is in accord with the theoretical predictions of Meyer,⁶ who

² Zahn, *Phys. Rev.*, **35**, 1047 (1930).

³ Zahn, *ibid.*, **37**, 1516 (1931).

⁴ Bramley, *J. Franklin Inst.*, **210**, 421 (1930).

⁵ Werner, *Z. physik. Chem.*, [B] **4**, 393 (1929).

⁶ Meyer, *ibid.*, [B] **8**, 27 (1930).

⁷ Hassel and Naeshagen, *ibid.*, [B] **8**, 357 (1930).

⁸ Weissberger and Sängewald, *Physik. Z.*, **30**, 792 (1929).

⁹ Williams, *ibid.*, **29**, 271 (1928).

used classical mechanics to calculate the potential energy of a system in which two dipoles were rotating around a line with which their axes made an angle θ . The effective moment of the molecule is obviously the resultant of the projections of each of the two moments upon a plane perpendicular to the line about which the dipoles are oscillating. When these projections point in the same direction, that is, when the angle between them is zero, the moment of the molecule is a maximum and the potential energy is also a maximum. When the projections point in opposite directions, making an angle of 180° with one another, the moment is a minimum, zero if the two dipoles are identical and the potential energy is a minimum. When the potential energy is of the order of magnitude of kT , free rotation is hindered and an increase in the electric moment is to be expected, as increasing oscillation caused by rising temperature tends to overcome the effect of the mutual potential energy of the dipoles. For the case in which both dipoles have the moment m , the constant b of the Debye equation becomes, according to the treatment of Meyer, a variable

$$b = \frac{4\pi N}{3} \frac{2(m \sin \theta)^2}{3k} (1 - x) \quad (3)$$

in which

$$x = \frac{\frac{\alpha}{kT} + \frac{\beta}{(kT)^2} + \frac{\gamma}{(kT)^3} + \dots}{m + \frac{n}{kT} + \frac{o}{(kT)^2} + \frac{p}{(kT)^3}} \quad (4)$$

α , β , γ , m , n , o and p are functions of the geometrical structure of the molecule. The limiting value of the moment of the molecule, μ , obtained when $x = 0$, that is, when there is complete freedom of rotation, is evidently

$$\mu = \sqrt{2} m \sin \theta \quad (5)$$

which is identical with an equation derived by Williams¹⁰ for the case of two freely rotating dipoles.

In the hydroquinone ethers, Meyer shows that the separation of the dipoles is such that their mutual potential energy is too small to cause a temperature variation of the moment. In acetic acid the dipoles are so close together that Meyer calculates a temperature of $20,000^\circ$ to be necessary for completely excited rotation. Because of the uncertainty caused by molecular association in the results for acetic acid,¹¹ it has seemed desirable in the present work to study ethyl acetate, which should resemble acetic acid.

Meyer has made a detailed investigation of ethylene chloride. He found that, in benzene solution, the moment did not vary appreciably with temperature, the value remaining approximately constant at 1.83×10^{-18} in satisfactory agreement with the value 1.86×10^{-18} obtained by Gross¹²

¹⁰ Williams, *Z. physik. Chem.*, **138**, 75 (1928).

¹¹ Smyth and Rogers, *THIS JOURNAL*, **52**, 1824 (1930); Zahn, *Phys. Rev.*, **35**, 1047 (1930).

¹² Gross, *Physik. Z.*, **30**, 504 (1929).

and 1.75×10^{-18} obtained by Williams¹⁰ from measurements at one temperature only. Meyer found that, in benzene solution, the polarization of the ethylene chloride was much higher than in other solvents, the value interpolated at 26° being 85 as compared to 64 in cyclohexane and in carbon tetrachloride and 62 in hexane at the same temperature. The electric moment calculated from measurements in hexane solution increased from 1.26×10^{-18} at -75° to 1.42×10^{-18} at 40°.

This behavior was in accordance with the calculations for ethylene chloride made by Meyer by means of his equation. According to these, the potential energy between the dipoles is such that a temperature of 5000 or 6000° is necessary for completely excited rotation, which would give the limiting value of 2.4×10^{-18} for the moment.

The measurements of Ghosh, Mahanti and Sen Gupta¹³ gave a moment of 1.56×10^{-18} for ethylene chloride vapor with no departure from the linear relation between polarization and the reciprocal of the absolute temperature. In view, however, of discrepancies in similar measurements, little weight can be attached to this evidence. In very recent measurements upon the vapor, Sanger¹⁴ has obtained a value 1.01×10^{-18} , which he regards as too low, stating that the moment probably lies between 1.2 and 1.4×10^{-18} . Certain of Sanger's polarization values show a decided deviation from a linear dependence upon $1/T$, which he attributes to the effect of molecular association. Meyer,¹⁵ however, has pointed out that it would require an abnormally great molecular association to produce this deviation, while ethylene chloride in heptane solution shows very little association. Sanger's results must be regarded as inconclusive, although they might be interpreted as indicating a variation of the moment with temperature.

In view of the conflicting evidence in regard to this important question of the temperature variation of electric moment, measurements were made a year ago upon ethylene bromide¹⁶ and have been continued in the present investigation upon ethylene chloride, ethylene chlorobromide and diethyl succinate, which latter substance had been found to show a moment of 2.14×10^{-18} at 25° and 2.21×10^{-18} at 50°.¹⁷ A preliminary notice of these results has appeared in a communication to the Editor.¹⁸

Mathematical Discussion

Because of the conflicting experimental results in the literature and because of the fact that Meyer has not published many of the details of the

¹³ Ghosh, Mahanti and Sen Gupta, *Z. Physik*, **54**, 711 (1929).

¹⁴ Sanger, *Physik. Z.*, **32**, 21 (1931).

¹⁵ Meyer, *ibid.*, **32**, 260 (1931).

¹⁶ Smyth and Kamerling, *THIS JOURNAL*, **53**, 2988 (1931).

¹⁷ Smyth and Walls, *ibid.*, **53**, 527 (1931).

¹⁸ Smyth and Dornte, *ibid.*, **53**, 2005 (1931).

derivation of his equation, it has seemed desirable to investigate the effect of intramolecular rotation upon the moment of a molecule of the type of ethylene chloride, first, by means of classical mechanics and then by quantum mechanics.

The geometry of the problem is shown in Fig. 1, where C_1 , C_2 represent the centers of the two carbon atoms, while P and Q are the points at which

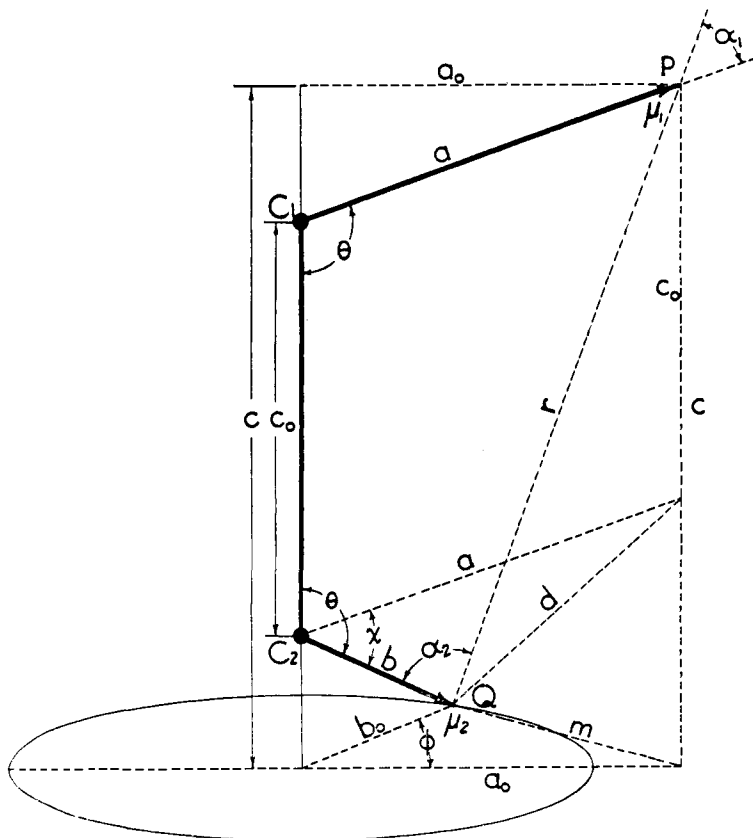


Fig. 1.—Molecule containing two rotating dipoles.

the dipoles of moment μ_1 and μ_2 are assumed to be localized, Q lying behind the plane of the paper. PQ, or r , is the distance between these points and, of course, varies with the rotation. θ is the angle, assumed to be constant, between the direction of the dipole and the C_1-C_2 axis, which is also the axis of rotation. c_0 is the C_1-C_2 separation. a and b are the distances of the dipoles from their respective carbon atoms. ϕ is the angle between the projections of the two dipole axes on a plane perpendicular to the C_1-C_2 axis.

The expression for the mutual potential energy of two dipoles is¹⁹

$$U = \frac{\mu_1 \mu_2}{r^3} (\cos \chi - 3 \cos \alpha_1 \cos \alpha_2) \quad (6)$$

where μ_1 and μ_2 are the moments of the two dipoles, r is the distance between them, χ is the angle between them, and α_1 and α_2 are the angles between the dipole axes and the line PQ joining them. We wish to transpose this formula into an expression involving only constant geometrical quantities and the variable angle ϕ . The symbols for various distances used are evident in Fig. 1. To find r we note that r , c and m form a right triangle, so that

$$\begin{aligned} r^2 &= m^2 + c^2, \text{ but} \\ m^2 &= a_0^2 + b_0^2 - 2a_0b_0 \cos \phi \end{aligned}$$

therefore

$$\begin{aligned} r^2 &= a_0^2 + b_0^2 + c^2 - 2a_0b_0 \cos \phi \\ &= K + B \cos \phi \end{aligned}$$

where $K = a_0^2 + b_0^2 + c^2$ and $B = -2a_0b_0$. To obtain the angle χ , use is made of the triangle of which a , b and d are the sides, whence

$$\cos \chi = \frac{a^2 + b^2 - d^2}{2ab} \quad (7)$$

The other necessary quantities are obtained in similar fashion, so that

$$\begin{aligned} \cos \alpha_1 &= \frac{a^2 + r^2 - b_0^2 - (c_0 - b \cos \theta)^2}{2ar}, \text{ and} \\ \cos \alpha_2 &= -\frac{b^2 + r^2 - a_0^2 - (c_0 - a \cos \theta)^2}{2br} \end{aligned} \quad (8)$$

Substitution in equation (6) and algebraic reduction gives

$$U = \frac{\mu_1 \mu_2}{(K + B \cos \phi)^{3/2}} [D_0 + D_1 \cos \phi + D_2 \cos^2 \phi] \quad (9)$$

where

$$K = c_0^2 + a^2 + b^2 - 2c_0(a + b) \cos \theta + 2ab \cos^2 \theta$$

$$B = -2ab \sin^2 \theta$$

$$D_0 = ab(3 + \cos^4 \theta) + 2 \cos^2 \theta (c_0^2 + a^2 + b^2) - c_0 \cos \theta (a + b) (\cos^2 \theta + 3)$$

$$D_1 = \sin^2 \theta [-2(a^2 + b^2) + c_0^2 - 2ab \cos^2 \theta + (a + b)c_0 \cos \theta]$$

$$\text{and } D_2 = ab \sin^4 \theta = -\frac{1}{2} B \sin^2 \theta$$

In the case of ethylene chloride, Meyer neglected the effect of the hydrogens and assumed but two rotating dipoles, one located in each of the two C-Cl lines, one-eighth of the distance from the chlorine nucleus to the carbon. The moment of each dipole was taken as that of the C-Cl bond, 1.5×10^{-18} , calculated by Eucken and Meyer.²⁰ For the sake of comparison, we have used the same moment, 1.5×10^{-18} , for the dipole in the C-Cl line, but have attempted to take into account the effect of the hydro-

¹⁹ Cf. Jeans, "Electricity and Magnetism," Cambridge University Press, Cambridge, 1920, p. 354.

²⁰ Eucken and Meyer, *Physik. Z.*, **30**, 397 (1929).

gens by placing a dipole of moment 0.5×10^{-18} in each of the C-H lines. This latter is an uncertain procedure and we have used a larger moment than that calculated by Eucken and Meyer for the C-H bond in order to calculate the maximum possible effect of the hydrogens. These dipoles are located at a distance from the carbon nucleus equal to the value for the radius of the carbon atom, 0.77 \AA .²¹ The C-Cl and C-C nuclear separations are taken as 1.85 \AA . and 1.55 \AA . and the valence angle θ as 110° . A second calculation has been made with the C-Cl dipoles assumed to be located at distances of 0.77 \AA . from the carbon nuclei instead of at 1.62 \AA . as given by the assumptions used in the first calculations. This location of the dipoles at the imaginary atomic surfaces was successfully used by Smallwood and Herzfeld²² in calculating the mutual inductive effects of moments.

It is evident that, in these calculations, $\mu_1 = \mu_2$ and $a = b$. In using equation (9) to calculate the potential energy of the system of dipoles constituting the molecule, it is necessary to consider what may be called the phase relations of the various dipole interactions. Equation (9) is for one pair of dipoles only, while, in ethylene chloride, the dipoles may be paired in nine different combinations. The total energy U corresponding to any value of ϕ may, therefore, be obtained as the sum of nine energies, each calculated by means of equation 9, that is

$$U = U_{\text{Cl-Cl}}(\phi) + 2U_{\text{H-H}}(\phi) + U_{\text{H-H}}(120 - \phi) + U_{\text{H-H}}(120 + \phi) + 2U_{\text{H-Cl}}(120 - \phi) + 2U_{\text{H-Cl}}(120 + \phi) \quad (10)$$

in which $U_{\text{Cl-Cl}}$ is the energy between two dipoles in the C-Cl line, $U_{\text{H-H}}$ that between two in the C-H line, and $U_{\text{H-Cl}}$ the energy between a dipole in the C-H line and one in the C-Cl line, the angle between the dipole projections being given in parentheses after each. In Table I, the first column gives the value of ϕ , the second the value of $U_{\text{Cl-Cl}}$ in ergs $\times 10^{14}$ when the dipoles are at a distance of 1.62 \AA . from the carbon nuclei, the

TABLE I

MUTUAL POTENTIAL ENERGIES OF THE DIPOLES (ERGS $\times 10^{14}$)

ϕ	$U_{\text{Cl-Cl}}$	U_1	U_2	ϕ	$U_{\text{Cl-Cl}}$	U_1	U_2
0°	13.43	12.35	73.2	100°	6.80	0.88	64.9
10°	13.20	12.02	72.8	110°	6.47	0.13	64.8
20°	12.61	11.21	72.0	120°	6.18	-0.36	64.7
30°	11.88	10.02	70.5	130°	5.97	-0.79	64.2
40°	10.94	8.48	68.8	140°	5.78	-1.02	63.9
50°	10.02	6.93	67.3	150°	5.65	-1.19	63.0
60°	9.16	5.46	66.0	160°	5.58	-1.28	62.2
70°	8.41	4.06	65.4	170°	5.52	-1.29	61.9
80°	7.79	2.79	65.1	180°	5.50	-1.34	61.5
90°	7.25	1.79	65.0				

²¹ Huggins, *Phys. Rev.*, **28**, 1086 (1926).²² Smallwood and Herzfeld, *THIS JOURNAL*, **52**, 1919 (1930).

third column the total energy U_1 under these conditions, and the fourth column the total energy U_2 when the C-Cl dipoles are supposed to lie at the imaginary surfaces of the carbon atoms like the C-H dipoles. As ϕ increases from 180 to 360° in the execution of a complete revolution, the course of the energy change is simply reversed so that, in Fig. 2, the potential energy curves obtained by plotting U_1 and U_2 against ϕ are symmetrical. The ordinates used in plotting U_2 are shown at the right.

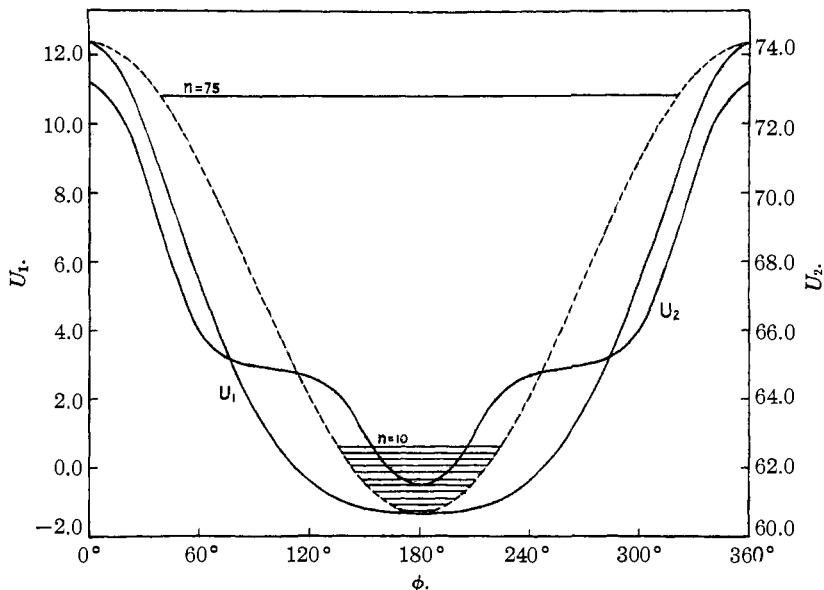


Fig. 2.—Mutual potential energies of the dipoles.

The U_1 curve is very similar to the potential energy curve obtained by Meyer. The smaller distance between the C-Cl dipoles used in calculating the U_2 curve greatly increases the potential energy and alters somewhat the shape of the curve, but the energy difference between the *cis* and the *trans* positions is but little different from that in the case of the U_1 curve. Evidently, the introduction of the C-H dipoles into the calculation makes no fundamental difference in the character of the results. The importance of the exact location of the dipoles is obvious, but we may conclude that, qualitatively, these results are similar to those of Meyer.

In treating the problem by means of the wave mechanics, use is made of the Schrödinger equation

$$\frac{d^2\psi}{d\phi^2} + \frac{8\pi^2I}{h^2} (W - U)\psi = 0 \quad (11)$$

in which ψ is the Schrödinger probability function, I is the moment of inertia of one-half of the molecule, *e. g.*, $-\text{CH}_2\text{Cl}$, around the C-C axis,

h is the Planck constant, and W is the total intramolecular rotational energy. In order to facilitate the calculation, we shall express U as a function of ϕ and use what amounts to the first terms of the Fourier expression

$$U = \frac{U_0}{2}(1 + \cos \phi) \quad (12)$$

That this relation gives a rough empirical representation of the dependence of U upon ϕ is shown by the dotted line which represents it in Fig. 2. The value of U_0 is obtained as the total depth of the U_1 curve in Fig. 2. Substituting for U in (11) the expression for it given by (12), and setting $x = 1/2\phi$, $\alpha = (8\pi^2 I/h^2)(W - 1/2 U_0)$, and $q = (\pi^2 I U_0)/h^2$, we obtain

$$\frac{d^2\psi}{dx^2} + (4\alpha - 16q \cos 2x)\psi = 0 \quad (13)$$

which is known as Mathieu's equation. As this equation has been studied by Goldstein,²³ we may use his expressions to calculate the values of the energy levels, W , given in Table II, which shows in the second column the energy in ergs $\times 10^{14}$ measured from the lowest point of U for the first eleven energy levels and a few higher levels as examples, the numbers of the levels n being given in the first column. The first eleven and the seventy-fifth level are represented by the horizontal lines in Fig. 2. The relative numbers of molecules in the different levels may be calculated from the simple Maxwell-Boltzmann equation

$$\frac{n_1}{n_2} = \frac{\omega_1}{\omega_2} e^{-\Delta E/kT} \quad (14)$$

in which ΔE is the energy difference and $\omega_1 = \omega_2$. The third and fourth columns in Table II give the number of molecules calculated to be in each level when there are 100 in the zero level at 223 and at 323°A.

TABLE II

ENERGY (ERGS $\times 10^{14}$) OF LEVELS AND DISTRIBUTION OF MOLECULES							
n	W	No. of molecules		n	W	No. of molecules	
		223°A.	323°A.			223°A.	323°A.
0	0.09	100	100	8	1.59	61	71
1	.28	94	96	9	1.78	58	68
2	.47	89	92	10	1.96	54	66
3	.66	83	88	20	3.76	30	44
4	.84	78	85	30	5.47	17	30
5	1.03	74	81	40	7.12	10	20
6	1.22	69	78	75	12.18	2	6
7	1.41	65	75				

As the energy levels are very closely spaced, differing by amounts small in comparison with kT , which is 4.11×10^{-14} ergs at 300° A., it is evident that a classical treatment such as that of Meyer should be adequate. Since the actual curve for U designated as U_1 is wider than the approxima-

²³ Goldstein, *Trans. Cambridge Phil. Soc.*, **23**, 303 (1927).

tion represented by the dotted line, the actual energy levels must be even more closely spaced. As the lower levels are nearly equally spaced, the motion in that region is approximately equivalent to a simple harmonic oscillation of the two halves of the molecule (*e. g.*, $-\text{CH}_2\text{Cl}$) about the position of minimum energy. Since, as in all such problems, quantum mechanics gives a lowest level which is not one of rest and since the total depth of the potential energy curve (*ca.* 14×10^{-14} erg) is not very large in comparison with kT (*ca.* 4×10^{-14}) at ordinary temperatures, the moment of the molecule would never be zero and, at ordinary temperatures, would be appreciable. Figure 2 shows that oscillation in the molecules in the seventy-fifth level occurs through an angle of about 300° , thus falling considerably short of complete rotation. As Table II shows that the proportion of the molecules which are in this level is very small at ordinary temperatures, it is evident that the number of molecules in an energy level sufficiently high to give an oscillation of the halves through an angle of 360° , that is, complete rotation, is very small in the neighborhood of room temperature. We may, therefore, conclude that equation (5), which should apply to the limiting case where there is complete freedom of rotation of the dipoles, is quite inapplicable to the ethylene chloride molecule at ordinary temperatures. At these temperatures the great majority of the molecules are in the low energy levels, where the dipoles, to a considerable extent, oppose and cancel one another, so that the mean moment observed experimentally for the molecule is low. Table II shows how rising temperature increases the proportion of the molecules in the high levels where the greater oscillation gives greater moment so that the observed moment should increase. If the separation of the dipoles is much greater or the moment much smaller, U is too small to have appreciable effect, equation (5) may apply, and the observed moment will not vary with temperature. On the other hand, if the moments and the separation of the dipoles are such that U is very large, the change of oscillation with temperature in the region experimentally attainable may be insufficient to cause an experimentally observable change of moment with temperature.

The uncertainty in regard to the exact location of the dipoles in the molecule and the importance of the effect of this location have been pointed out. Other factors which have, of necessity, been neglected in the treatment are the inductive effects of the moments upon one another, the attractive and repulsive forces between the charges which cannot be wholly represented by dipoles located at points, and the distortion of the valence angles as a result of these forces and of the centrifugal forces arising from the rotatory oscillation about the C-C line. In view, therefore, of the approximations necessary in the discussion, an exact quantitative treatment does not appear justified, but the qualitative predictions of the preceding paragraph, which are in accord with Meyer's theory, appear to be

warranted. These predictions may now be examined in the light of the experimental data.

Preparation of Materials

Heptane.—Normal heptane obtained from the Ethyl Gasoline Corporation had the correct refractive index (n_D^{20} 1.38777) and was used without purification.

Kerosene.—A high grade kerosene was supplied through the courtesy of Dr. J. Bennett Hill of the Atlantic Refining Company. It had been washed with sulfuric acid and water, dried and fractionally distilled; b. p. 217–230°; n_D^{20} 1.45317. Its dielectric properties showed it to be a non-polar substance so it was used without further treatment.

Ethyl Acetate and Diethyl Succinate.—These materials were the same as used in previous work.¹⁷

Ethylene Chloride.—Ethylene chloride from the Eastman Kodak Company was washed with dilute sodium hydroxide and water, dried over calcium chloride, and fractionally distilled; b. p. 83.5–83.7°; n_D^{20} 1.44476.

Ethylene Chlorobromide.—Ethylene chlorobromide obtained from the Eastman Kodak Company was purified by the method given for the ethylene chloride; b. p. 106.8–107.0°; n_D^{20} 1.49174; d_4^{20} 1.7392.

Experimental Results

The dielectric constants and densities were measured with the apparatus used in previous work,²⁴ the former being determined at a wave length of 600 meters. The values of these constants in Table III were determined at the indicated temperatures so that no interpolation was necessary, and the values of P_2 , the polarization of the polar substance, were calculated from them. These values were extrapolated to $c_2 = 0$ to obtain the values of P_∞ listed in Table IV, except in the case of ethylene chloride where, as P_2 showed no definite variation with concentration in the dilute region, P_∞ was obtained by averaging the P_2 values for the more dilute solutions. For ethylene chloride $P_E + P_A$ was taken as the polarization of the solid substance, 23.9, determined by Mr. C. S. Hitchcock. The value $P_E + P_A$ for ethylene chlorobromide was estimated from that of the chloride by comparison of the refractions, MR_D for the chlorobromide being 23.9. The error in this estimated value should be no more than one unit. The determination of $a = P_E + P_A$ in this way makes possible the direct calculation of the moment at each temperature. The values of $(P_\infty - a)T = b$ and the moments calculated from them are shown for the chloride and the chlorobromide in Table IV. For the calculation of the moments of ethyl acetate and diethyl succinate, an approximation is made by setting a equal to the molar refraction, MR_D . From equation (1), by insertion of the values of the universal constants, we then obtain

$$\mu = 0.127 \times 10^{-18} \sqrt{(P_\infty - MR_D)T}$$

²⁴ (a) Smyth, Morgan and Boyce, *THIS JOURNAL*, **50**, 1536 (1928); (b) Smyth and Morgan, *ibid.*, **50**, 1547 (1928); (c) Dornite and Smyth, *ibid.*, **52**, 3546 (1930).

In the case of ethyl acetate, P_∞ varies in approximately linear fashion with $1/T$, thus permitting the calculation of the values of a , b and μ given below

TABLE III
DIELECTRIC CONSTANTS AND DENSITIES OF SOLUTIONS AND POLARIZATIONS OF POLAR COMPONENTS

Heptane-Ethylene Chloride							
Mole fr. of $C_2H_4Cl_2 =$ $t, ^\circ C.$	0.0000	0.0322	0.0508	0.0698	0.0878	0.5024	1.0000
-90	2.075						
-70	2.048	2.099	2.135	2.172			
-50	2.020	2.072	2.107	2.146	2.178		
-30	1.992	2.050	2.079	2.116	2.148		14.17
-10	1.966	2.021	2.050	2.087	2.117	3.824	12.43
10	1.939	1.991	2.018	2.054	2.084	3.613	11.03
30	1.910	1.963	1.988	2.021	2.050	3.415	9.87
50	1.879	1.926	1.951	1.982	2.008	3.241	8.87
70	1.848	1.888	1.913	1.938	1.971	3.092	8.02
d							
-90	0.7748						
-70	.7585	0.7681	0.7744	0.7809			
-50	.7421	.7520	.7582	.7644	0.7704		
-30	.7259	.7354	.7414	.7475	.7535		1.326
-10	.7095	.7187	.7248	.7306	.7363	0.9098	1.297
10	.6926	.7013	.7071	.7133	.7190	.8860	1.268
30	.6756	.6846	.6902	.6958	.7013	.8666	1.239
50	.6581	.6671	.6723	.6778	.6832	.8446	1.209
70	.6398	.6491	.6539	.6594	.6646	.8214	1.181
P_1		P_2					
-90	34.11						
-70	34.17	58.0	59.6	60.3			
-50	34.22	59.6	61.0	62.1	61.3		
-30	34.27	65.9	62.5	62.3	62.3		60.8
-10	34.33	66.2	63.1	64.3	63.0	76.5	60.4
10	34.38	67.3	63.3	64.2	63.3	70.0	60.1
30	34.44	67.9	63.3	64.0	63.2	67.8	59.7
50	34.49	62.5	60.7	61.9	61.0	66.1	59.2
70	34.55	55.4	57.3	57.4	60.1	67.1	58.7
Heptane-Ethylene Chlorobromide							
Mole fr. of $C_2H_4BrCl =$ $t, ^\circ C.$	0.0530	0.0705	0.1095	1.0000			
-50	2.082	2.102					
-30	2.059	2.076	2.126				
-10	2.032	2.052	2.098	7.98			
10	2.004	2.023	2.069	7.41			
30	1.978	1.999	2.042	6.92			
50	1.941	1.964	2.008	6.47			
70	1.905	1.927	1.974	6.08			
90	1.872	1.893	1.937	5.69			

TABLE III (Continued)

Mole fr. of $C_8H_8BrCl =$ $t, ^\circ C.$	TABLE III (Continued)				
	0.530	0.0705	0.1095	1.0000	
-50	0.7755	0.7871			
-30	.7590	.7700	0.7958		
-10	.7418	.7527	.7780	1.7939	
10	.7245	.7350	.7600	1.7579	
30	.7068	.7170	.7415	1.7211	
50	.6886	.6987	.7225	1.6837	
70	.6698	.6800	.7030	1.6463	
90	.6506	.6600	.6828	1.6080	
	P_2				
-50	50.8	48.3			
-30	51.8	49.9	49.7		
-10	53.2	52.2	50.5	55.9	
10	54.4	53.0	51.5	55.6	
30	56.6	55.8	52.8	55.3	
50	53.7	54.7	52.9	55.0	
70	51.2	52.7	53.0	54.8	
90	50.6	52.3	52.1	54.4	
	Heptane-Ethyl Acetate				
Mole fr. of $CH_3COOC_2H_5 =$ $t, ^\circ C.$	Heptane-Ethyl Acetate				
	0.0347	0.0442	0.0585	0.0843	0.1059
-90		2.276	2.339	2.439	2.518
-70	2.193	2.233	2.292	2.384	2.448
-50	2.152	2.190	2.234	2.326	2.397
-30	2.112	2.147	2.184	2.269	2.334
-10	2.074	2.106	2.140	2.218	2.277
10	2.040	2.064	2.098	2.171	2.224
30	2.000	2.024	2.055	2.127	2.170
50	1.956	1.979	2.008	2.076	2.113
70	1.913	1.934	1.962	2.025	2.057
	d				
-90		0.7808	0.7850	0.7868	0.7908
-70	0.7631	.7648	.7674	.7706	.7744
-50	.7468	.7483	.7496	.7535	.7576
-30	.7304	.7317	.7338	.7375	.7400
-10	.7136	.7152	.7172	.7205	.7236
10	.6968	.6983	.7000	.7033	.7062
30	.6796	.6811	.6827	.6859	.6888
50	.6619	.6633	.6649	.6680	.6705
70	.6438	.6451	.6465	.6494	.6529
	P_2				
-90		123.5	119.1	113.9	108.5
-70	120.7	119.1	116.7	110.5	103.9
-50	115.4	115.0	110.0	106.6	102.5
-30	110.4	110.5	103.9	101.7	99.0
-10	106.4	106.1	100.0	98.3	95.2
10	105.9	101.2	96.1	95.8	92.8
30	98.9	98.6	93.4	94.0	89.4
50	89.7	89.7	87.9	90.0	85.5
70	80.2	82.2	82.3	85.8	80.7

TABLE III (Concluded)
Kerosene-Diethyl Succinate

Mole fr. of ($-\text{CH}_2\text{COOC}_2\text{H}_5$) ₂ = <i>t</i> , °C.	0.0000	0.0383	0.0518	0.0638	0.0869	0.1075
0	2.154	2.247		2.308	2.367	2.411
20	2.134	2.220	2.251	2.277	2.334	2.377
40	2.108	2.191	2.215	2.246	2.302	2.343
60	2.084	2.160	2.182	2.217	2.265	2.308
80	2.059	2.132	2.156	2.183	2.234	2.272
100	2.032	2.110	2.133	2.155	2.206	2.239
120	2.013	2.086	2.103	2.125	2.168	2.205
140	1.991	2.055	2.073	2.095	2.135	2.176
160	1.963	2.032	2.044	2.068	2.098	2.141
180	1.934	1.996	2.015	2.034	2.065	2.105
200	1.908		1.972	1.996	2.027	2.055
d						
0	0.8297	0.8374		0.8414	0.8451	0.8484
20	.8171	.8225	0.8246	.8265	.8301	.8333
40	.8025	.8079	.8098	.8117	.8152	.8182
60	.7880	.7931	.7950	.7968	.8002	.8031
80	.7735	.7784	.7801	.7818	.7851	.7880
100	.7585	.7636	.7651	.7669	.7697	.7725
120	.7436	.7484	.7500	.7515	.7543	.7570
140	.7286	.7328	.7345	.7361	.7388	.7413
160	.7134	.7173	.7190	.7205	.7231	.7257
180	.6975	.7015	.7032	.7048	.7066	.7099
200	.6815		.6875	.6890	.6894	.6939
P ₁						
0	61.98	133.6		133.0	133.2	130.0
20	62.09	135.0	133.3	132.5	132.3	129.9
40	62.20	133.2	129.2	131.7	132.4	129.8
60	62.31	130.0	125.3	132.0	130.3	129.1
80	62.42	128.8	126.8	129.0	130.2	127.9
100	62.53	133.1	130.9	129.5	131.7	127.7
120	62.64	138.6	129.6	129.3	128.6	127.1
140	62.75	135.2	128.3	128.6	127.6	128.2
160	62.86	140.2	127.7	130.2	124.4	127.2
180	62.97	131.1	127.5	126.8	123.7	126.5
200	63.08		113.1	119.6	120.6	117.4

the other data. As it has been found in previous measurements that polarization values not far from the boiling points of the solution are generally low because of loss of material by evaporation or formation of gas bubbles between the condenser plates, the values at the highest temperatures are put in parentheses. The values at the lowest temperature for ethylene chloride and ethyl acetate are probably a little low, as slight cloudiness of the solutions at this temperature indicated the separation of a very small amount of these substances.

TABLE IV
VALUES OF $(P_\infty - a)T$, $(P_\infty - MR_D)T$ AND THE MOMENT

$C_2H_4Cl_2$ ($P_E + P_A = 23.9$)				C_2H_4ClBr ($P_E + P_A = 27.5$)		
$T, ^\circ A.$	P_∞	$(P_\infty - a)T$	$\mu \times 10^{18}$	P_∞	$(P_\infty - a)T$	$\mu \times 10^{18}$
203	(59.3)	(7095)	(1.07)			
223	61.0	8280	1.16	50.8	5200	0.92
243	63.3	9580	1.24	51.8	5900	0.98
263	64.1	10,550	1.31	53.2	6760	1.05
283	64.5	11,500	1.36	54.4	7620	1.11
303	64.5	12,300	1.41	56.6	8820	1.19
323	62.5	12,480	1.42	54.4	8660	1.18
343	(57.6)	(11,560)	(1.36)	53.0	8750	1.19
363				(52.4)	(9040)	(1.21)

$CH_3COOC_2H_5$ ($MR_D = 22.3$)				$(-CH_2COOC_2H_5)_2$ ($MR_D = 42.4$)			
$T, ^\circ A.$	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$	$T, ^\circ A.$	P_∞	$(P_\infty - MR_D)T$	$\mu \times 10^{18}$
183	(134.9)	(20,600)	(1.82)	273	134.0	25,000	2.01
203	128.8	21,650	1.87	293	133.5	26,700	2.08
223	122.1	22,250	1.90	313	132.8	28,300	2.14
243	117.9	23,200	1.93	333	132.0	29,800	2.19
263	111.7	23,500	1.95	353	131.0	31,300	2.25
283	106.6	23,800	1.96	373	130.0	32,700	2.30
303	104.1	24,800	2.00	393	129.0	34,000	2.34
323	(92.2)	(22,600)	(1.91)	413	128.0	35,400	2.39
343	(84.0)	(21,200)	(1.85)	433	127.0	36,600	2.43
				453	126.0	37,850	2.47
				473	(122.0)	(37,650)	(2.46)

$a = 53.9, b = 15,190, \mu = 1.57 \times 10^{-18}$

Discussion of Results

The polarizations of ethylene chloride present a very striking behavior in that they increase with rising temperature in the dilute solutions and decrease in the concentrated region, while the change of polarization with concentration is surprisingly small. For the sake of comparison, one may mention ethyl bromide, which has a moment of 1.86×10^{-18} , values of P_∞ , 143.5 at -90° and 100.2 at 30° , and values of P_2 for the pure liquid, 54.24 at -90° and 55.07 at 30° .^{24b} Even chloroform with its small moment 1.05×10^{-18} has values of P_∞ , 58.9 at -60° and 48.8 at 30° , and values of P_2 for the pure liquid, 47.85 at -60° and 44.35 at 30° . The falling off of the polarization with increasing concentration of these substances has been shown to be due to intermolecular action or association, which decreases with rising temperature. The increase in polarization of the ethylene chloride with rising temperature is positive evidence of the increase in moment which is shown by the values of $(P_\infty - a)T$ and those of μ calculated from them. The values of μ are in excellent agreement with those obtained by Meyer in hexane solution, 1.26×10^{-18} at -75° increasing to 1.42×10^{-18} at 40° , the inclusion of P_A in our calculation tending to make the values slightly lower than those of Meyer. The change of moment with

temperature is thus in excellent agreement with the qualitative predictions of the theoretical treatment.

The considerable difference between the polarizations of ethylene chloride in benzene and in heptane and other solvents, which has been previously mentioned, and a similar difference in the case of ethylene bromide¹⁶ may be due to a weakening of the forces between the oscillating dipoles by the presence of the benzene.^{6,25} It has been found that benzene reduces the forces between the dipoles in different molecules of the alcohols more than do hexane, cyclohexane and heptane.²⁶ If such a reduction extended to the interior of the molecule, the mutual energy of the dipoles in the ethylene chloride would be reduced, the observed moment and polarization would be increased, and the variation of the moment with temperature probably reduced. If benzene can have such an effect, there appears to be no reason why ethylene chloride molecules should not affect one another in similar fashion. If this were so, the polarization of ethylene chloride should tend to increase with increasing concentration, but the intermolecular action increasing with increasing concentration tends to decrease the polarization as in the cases of ethyl bromide and chloroform. The two opposing effects may nearly cancel one another and thus render the change of polarization with concentration small as observed. As the moment of the molecule in the pure liquid should accordingly be closer to the limiting value given by equation (5), the increase of the moment with temperature may be too small to overcome the decrease in polarization caused by rising temperature according to equation (1).

The behavior of ethylene chlorobromide is exactly analogous to that of the chloride. The apparent absence of any appreciable change of moment from 30° up in both cases is probably due to the experimental difficulties on account of which the highest temperature values have been enclosed in parentheses. As might be expected, the moment of the chlorobromide is intermediate between that of the bromide¹⁶ and that of the chloride, the values for the three substances being 0.79, 0.98 and 1.24×10^{-18} at -30° and 1.04, 1.19 and 1.41×10^{-18} at 30°. It was thought, at first, that the lowering of moment caused by replacing chlorine by bromine might be due in part to increase in the repulsion between the halogens as a result of the larger size of the bromine, but calculation showed that the nuclear separation of the halogens in the *cis* position increased by an amount slightly more than proportional to the increase in atomic radius from chlorine to bromine. The moment of methyl chloride is²⁷ 1.86×10^{-18} and that of methyl bromide is about 1.6×10^{-18} .^{28,16} Evidently, therefore, the mo-

²⁵ Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

²⁶ Smyth and Stoops, *THIS JOURNAL*, **51**, 3312 (1929).

²⁷ Fuchs, *Z. Physik*, **63**, 824 (1930); Sanger, *Helv. Phys. Acta*, **3**, 161 (1930).

²⁸ Morgan and Lowry, *J. Phys. Chem.*, **34**, 2385 (1930).

ment in the C-Br line is lower than that in the C-Cl line, although the difference observed between the moments of the methyl halides is, perhaps, not enough to account entirely for the differences between the ethylene halides. Probably the greater lowering of the moments of the bromide dipoles by mutual induction, which would be greater because of the greater polarizability of the bromine,²⁹ would account for the rest of the difference between the ethylene halides.

The values of $(P_{\infty} - MR_D)T$ for ethyl acetate and those of the moment calculated from them show a small increase with rising temperature. However, when P_{∞} is plotted against $1/T$, the low values at the high and low temperatures being omitted, a straight line is obtained. The value of b obtained as the slope of this line is decidedly lower than the values of $(P_{\infty} - MR_D)T$ and the value of μ calculated from b is somewhat lower than previously reported values, while, at the same time, the high value of a gives a value of P_A which is presumably too large. The values of the polarization are somewhat larger than those found in benzene solution,¹⁷ which causes the values of μ calculated from $(P_{\infty} - MR_D)T$ to be higher. These values are probably a little high because of the neglect of P_A in their calculation, while the value calculated from the slope of the straight line, which gives a very high value of P_A , is probably too low. The mean of the average of the high values and the low value agrees well with the unpublished value 1.76×10^{-18} determined by Dr. C. T. Zahn from measurements upon the vapor. It is evident that the temperature variation of the moment is insignificant. As in the case of the C=O and O-H dipoles of acetic acid treated theoretically by Meyer, the dipoles of the C=O and O-C₂H₅ groups should have a large mutual potential energy, which may be so large that the change of oscillatory energy produced by the rise of temperature employed experimentally may be insufficient to produce a detectable change of moment.

Kerosene was used as a solvent for diethyl succinate in order to extend the temperature range of the measurements as much as possible, the temperatures used running higher than any heretofore employed in moment determinations of liquids. The polarization decreases much more slowly with rising temperature than would be expected of a substance possessing a moment as great as 2×10^{-18} , which would lead one to expect the uniform rise in moment observed. The results are in excellent agreement with the values of the polarization and the moment at 25 and 50° in benzene solution¹⁷ previously mentioned. The value of the moment at 180° is almost identical with that found for diethyl sebacate, 2.50×10^{-18} , and that for the diethyl ester of hexadecamethylenedicarboxylic acid, 2.48×10^{-18} , in both of which compounds the -COOC₂H₅ groups are so far separated that they should not affect one another.¹⁷ It was pointed

²⁹ Cf. Smyth, *Phil. Mag.*, **50**, 361 (1925).

out in the discussion of the results just mentioned that the ease of anhydride formation of succinic acid and the abnormal viscosity and temperature coefficient of the rotatory power of its esters combined with the low value of the moment of the diethyl ester to indicate a bending of the molecule in such a way that the dipoles of the $-\text{COOC}_2\text{H}_5$ groups were brought close together so as to cancel one another partially. The increase in vibrational energy with rising temperature should enable more and more of the molecules to overcome the forces of dipole attraction and open out to an extended structure in which the $-\text{COOC}_2\text{H}_5$ groups are independent of one another. The coincidence of the value of the moment at 180° with those of the very long chain esters indicates the disappearance of the bent ring structure at this temperature. However, it would be necessary to show an absence of further change in the values at still higher temperature before the conclusion could be definite.

It has been shown that the moments of ethylene chloride and bromide, which vary with temperature in heptane solution, are lower than the values in benzene solution, in which they vary little, if at all, with temperature. The moment of diethyl succinate is approximately the same in benzene solution and in kerosene solution and varies with temperature in both solvents, while the moment of ethyl acetate appears slightly higher in heptane than in benzene solution, although it shows no significant variation with temperature in either. It is evident that the moments of molecules containing two or more dipoles, the axes of which may alter their positions relative to one another, may be affected considerably by temperature and environment. The change of moment with temperature is in qualitative agreement with the predictions of both the classical and the quantum mechanics.

The writers wish to express their gratitude to Professor E. U. Condon for his assistance in the mathematical part of this paper.

Summary

The question of the variation of the electric moment of a molecule with temperature has been discussed and the energy of a system of dipoles rotating about a common axis has been calculated in terms of the classical mechanics and of the wave mechanics. Both treatments lead to the conclusion that the moment of a molecule containing such a system may vary with temperature.

The electric moments of ethylene chloride and ethylene chlorobromide, the molecules of which contain such systems of dipoles, are found to vary markedly with temperature. The electric moment of the ethyl acetate molecule shows no significant variation with temperature, probably because of the high mutual potential energy of its dipoles. The moment of the diethyl succinate molecule increases as the temperature rises from 0 to

180°, probably because increasing vibrational energy enables more and more of the molecules to open out to an extended structure in which the $-\text{COOC}_2\text{H}_5$ groups are independent of one another, the moment at 180° being identical with those of the very long chain dicarboxylic acid esters.

As three of these substances and also ethylene bromide, which has been studied previously, show moments in heptane solution different from those found in benzene solution, it is evident that the moment of a molecule containing two or more dipoles, the axes of which may alter their positions relative to one another, may be affected by both temperature and environment.

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[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE THEORY OF THE GLASS ELECTRODE¹

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Introduction

The practical utility of the glass electrode for measuring the hydrogen activity or P_{H} of biological fluids has been well demonstrated in the past.² More recently it has been used with excellent success for precision acid-base titrations in the presence of oxidizing and reducing potentials,³ and for the determination of the P_{H} of such widely unrelated systems as growing tissue cultures,⁴ ferric oxide sols⁵ and tanning liquor extracts,⁶ to mention a few.

The theoretical significance of the glass electrode is equally interesting and important particularly from the standpoint of phase boundary, interfacial, semi-permeable membrane and liquid junction potentials. There is no doubt that a complete understanding of the glass electrode would throw considerable light not only on the vexing and elusive problem of the boundary potentials mentioned above, but also on the nature and origin of

¹ The beginnings of the theoretical treatment of the glass electrode presented in this paper were conceived by the author while employed as an assistant at the Rockefeller Institute for Medical Research, New York. He wishes to express to Dr. W. J. V. Osterhout and Dr. D. A. MacInnes of that Institute his appreciation of their interest in this work.

² A complete bibliography is given in "The Determination of Hydrogen Ions," W. M. Clark, Williams and Wilkins Co., Baltimore, 1928.

³ D. A. MacInnes and Malcolm Dole, *Ind. Eng. Chem., Anal. Ed.*, **1**, 57 (1929).

⁴ As carried out by the author in coöperation with Dr. Alexis Carrel. See D. A. MacInnes and Malcolm Dole, *J. Gen. Physiol.*, **12**, 805 (1929).

⁵ Fred Hazel and C. H. Sorum, *THIS JOURNAL*, **53**, 49 (1931).

⁶ D. H. Cameron and G. D. McLaughlin, *J. Am. Leather Chem. Assoc.*, **25**, 325 (1930); D. H. Cameron, *ibid.*, **26**, 7 (1931).