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## The Derivation of a General Kinetic Equation for Reaction Between Ions and Dipolar Molecules

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An equation has been derived for the reaction rate constant in the case of ion-dipole reactions. Section II contains the extension of Debye-Hückel's theory of ionic atmospheres to the case of dipoles surrounded by ions, coupling it with Onsager's theory of electric moments of molecules in liquids. Section III applies the potential constructed to the derivation of the rate constant by the kinetic procedure of Christiansen and Scatchard. The result is substantiated by existing data both from concentration and dielectric constant dependence of the rate of reaction between ions and dipoles (Section IV).

### I. INTRODUCTION

SINCE the formulation of the law of mass action and the promulgation of the theory of temperature coefficients, the two outstanding contributions to the theory of the kinetics of reactions in solution have been the application by Brönsted<sup>1</sup> of the theory of Debye and Hückel to reaction rates, and Scatchard's<sup>2</sup> development of the effect upon reaction velocities of changing solvent insofar as this effect is due to changing dielectric constant. These two contributions were applicable to the case of reactions between ions and led to the general kinetic equation

$$\ln k = \ln k_{\infty} - \frac{z_A z_B e^2}{DkT r_0} + \frac{z_A z_B e^2}{DkT} \frac{\kappa}{1 + a\kappa}, \quad (1)$$

which has become so familiar to those who read kinetic literature.

The authors, studying the reactions between charged ions and dipolar molecules, have become convinced that a similar equation expressing the concentration and dielectric effects upon ion-dipole reactions in solution should be available to kineticists. This paper has as its object, therefore, the derivation of such an equation together with its experimental verification insofar as existing data permit.

### II. THE IONIC ATMOSPHERE AROUND A DIPOLAR MOLECULE

In determining the ionic atmosphere around a dipolar molecule we shall disregard the inter-

action between dipoles. Under this restriction the differential equation for the potential  $\psi_0$  in the neighborhood of any one dipolar molecule will be the same as for the potential around an ion. It is only with regard to the boundary conditions at the surface of the molecule that the two problems differ.

We shall assume that there are  $s$  different species of ions. Let  $z_i$  be the valency of the species  $i$  and let  $n_i$  be their number per  $\text{cm}^3$ . Then the differential equation for  $\psi_0$  becomes, with the usual restriction to small values of  $\psi_0$ ,

$$\nabla^2 \psi_0 = \kappa^2 \psi_0, \quad (2)$$

where  $\kappa$  is the well-known parameter of the theory of Debye-Hückel<sup>3</sup> and is of the dimension of a reciprocal length:

$$\kappa^2 = (4\pi e^2 / DkT) \sum_{i=1}^s n_i z_i^2. \quad (3)$$

Here  $e$  signifies the elementary charge and  $D$  the dielectric constant of the solvent.

As the Eq. (2) can be "separated" in spherical coordinates it is easy to obtain a general solution which can be adapted to any distribution of point charges within the molecule. However, we shall be satisfied to treat the dipole as a point singularity. Then a suitable particular solution of (2) can be obtained in a very direct way by "polarizing" the solution of Debye and Hückel. This is, for the case of an ion,

$$\psi_0 = A_0 e^{-\kappa r} / r. \quad (4)$$

<sup>1</sup> J. N. Brönsted, *Zeits. f. physik. Chemie* **102**, 169 (1922); **115**, 337 (1925).

<sup>2</sup> G. Scatchard, *Chem. Rev.* **10**, 229 (1932).

<sup>3</sup> P. Debye and E. Hückel, *Physik. Zeits.* **24**, 185 (1923). See also Hans Falkenhagen, *Elektrolytes*, English translation by R. P. Bell (Clarendon Press, Oxford, 1934), Chapter VII.

Let the position of the dipole coincide with the origin and its direction with the positive  $z$  axis. Let, furthermore, the shape of the dipole-molecule be idealized by a sphere of radius  $a$ . Then we obtain an adequate solution for  $r \geq a$ , i.e., a solution that has the same angular dependence as a dipole-potential, by differentiating (4) partially with regard to  $z$ . Doing this and substituting in the result for  $z$  the expression  $r \cos \vartheta$  (the angle  $\vartheta$  being counted from the positive  $z$  axis) we obtain

$$\psi_0 = A(e^{-\kappa r}/r^2)(1 + \kappa r) \cos \vartheta, \quad r \geq a. \quad (5)$$

As for the interior of the dipole molecule we might follow the procedure of Debye and Hückel by determining  $\psi_i$  there from the differential equation

$$\nabla^2 \psi_i = 0, \quad r \leq a \quad (6)$$

and retaining the constant value  $D$  also for the interior. The condition to be imposed on  $\psi$  in this domain is that it should be continuous except for a singularity at the origin corresponding to a dipole of the given strength.

If this is done a reasonable formula for the ionic atmosphere is obtained. However, a comparison with experimental kinetic data (see Section IV) shows that, in order to obtain agreement, the dipoles have to be chosen of the order  $10 \times 10^{-18}$ , i.e., five to ten times too large. The reason for this discrepancy is evidently that in the indicated procedure the interaction between the dipole and the dielectric solvent is not properly accounted for.

From Onsager's theory of electric moments of molecules in liquids<sup>4</sup> it follows that any one immersed dipole acts upon distant charges with an "external moment" different from its moment in vacuum. The intervening medium has the effect of "enhancing both the permanent and the induced dipole moments." We are, therefore, going to combine Debye-Hückel's theory of ionic atmospheres with Onsager's model of a dipole immersed in a dielectric liquid.

In accordance with Onsager we retain the spherical shape of the molecule and characterize it by its permanent moment  $\mu_0$  (in vacuum) and its polarizability  $\alpha$ . This is to be related to an

"internal refractive index  $n$ " by

$$\alpha = ((n^2 - 1)/(n^2 + 2))a^3. \quad (7)$$

The problem to be solved is the following: a solution of (6) having a dipole singularity at  $r=0$  has to be joined to our solution (5) in the proper way (see reference 4, p. 1488) at  $r=a$ . This involves a determination of the external characteristic moment  $\mu^*$  such as it becomes under the action of the polarization created by itself.

First we solve the problem which presents itself if a rigid dipole of moment  $m$  is introduced into a cavity of radius  $a$ . For the exterior the solution given by (5) is to hold; for the interior the solution

$$\psi_i = (m/r^2 + Br) \cos \vartheta, \quad r \leq a \quad (8)$$

meets the requirements. From the usual boundary conditions for the electrostatic field the constants  $A$  and  $B$  are determined as

$$A = 3me^{\kappa a}/(D(2 + 2\kappa a + \kappa^2 a^2) + (1 + \kappa a)) \quad (9a)$$

and

$$B = -(m/a^3)(D(2 + 2\kappa a + \kappa^2 a^2) - 2(1 + \kappa a))/(D(2 + 2\kappa a + \kappa^2 a^2) + (1 + \kappa a)). \quad (9b)$$

Now  $m$  remains to be determined as a function of  $\mu_0$  and  $n^2$ . This determination has to be based on the "condition for internal equilibrium" (Onsager, reference 4, p. 1488):

$$m = \mu_0 + \alpha F_z, \quad (10)$$

where the force  $F_z$  is the force acting on the dipole owing to the polarization created by itself. This force is found to be

$$F_z = -\frac{\partial}{\partial z}(\psi_i - m \cos \vartheta/r^2) = -B. \quad (11)$$

Making use of (7) and (9b) we obtain

$$m = \mu_0(n^2 + 2)(D(2 + 2\kappa a + \kappa^2 a^2) + (1 + \kappa a))/3(D(2 + 2\kappa a + \kappa^2 a^2) + n^2(1 + \kappa a)). \quad (12)$$

With this value introduced into (9a) the potential of the ionic atmosphere around a dipolar molecule of moment  $\mu_0$  can finally be written in the form

$$\psi_0 = (\mu^* e^{-\kappa r}/Dr^2)(1 + \kappa r) \cos \vartheta, \quad (13)$$

<sup>4</sup> L. Onsager, J. Am. Chem. Soc. 58, 1486 (1936).

where  $\mu^*$ , the "external moment," is given by

$$\mu^* = \mu_0(n^2 + 2)De^{\kappa a} / (D(2 + 2\kappa a + \kappa^2 a^2) + n^2(1 + \kappa a)). \quad (14)$$

In the absence of an ionic atmosphere, i.e., for  $\kappa \rightarrow 0$ , this solution and the corresponding one for  $\psi_i$  reduce to Onsager's solution, as they should. For  $n^2 \rightarrow 1$  Eqs. (13) and (14) represent the simpler case where the molecule has a permanent dipole but no polarizability.

### III. THE KINETIC EQUATION

We shall now apply the potential constructed in Section II to calculate the rate of formation of an intermediate complex  $X$  formed out of a dipole molecule  $A$  of moment  $\mu_0$  and an ion  $B$  of charge  $\epsilon z_B$ . In doing so we are going to follow the procedure of Christiansen and Scatchard.<sup>5</sup> However, it must be taken into account that the potential does not depend on  $r$  only but also on  $\vartheta$ .

Let  $C_x$ ,  $C_A$ , and  $C_B$  be the concentrations of  $X$ ,  $A$ , and  $B$ , respectively, and let us introduce polar coordinates  $r$ ,  $\vartheta$ ,  $\varphi$  about the center of a dipole  $A$ . The probability of finding an ion  $B$  in a specified element of volume characterized by the limits  $r$  and  $r+dr$ ,  $\vartheta$  and  $\vartheta+d\vartheta$ ,  $\varphi$  and  $\varphi+d\varphi$ , will then, by Boltzmann's theorem, be proportional to

$$C_A C_B \exp(-\psi_0 \epsilon z_B / kT) r^2 \sin \vartheta dr d\vartheta d\varphi. \quad (15)$$

In order to obtain the rate of formation of  $X$ , and thereby the velocity of reaction, some criterion for the formation of  $X$  must be established. This can be done in two different ways. Either it is assumed that there are "sensitive zones" on the exterior of the molecule. Whenever one of these areas is touched by an ion  $B$  the formation of  $X$  ensues. Or it is assumed that there is a critical distance for each direction.

Let us follow the first alternative. This amounts to assuming that  $r$ ,  $\vartheta$ ,  $\varphi$  have to assume specified values between comparatively narrow limits:  $r_0$  and  $r_0 + \Delta r_0$ ,  $\vartheta_0$  and  $\vartheta_0 + \Delta \vartheta_0$ ,  $\varphi_0$  and  $\varphi_0 + \Delta \varphi_0$ . We shall assume rotational symmetry of the molecule about the  $z$  axis. Then  $\varphi$  need not be specified and (15) can be integrated with regard

to  $\varphi$ . Consequently the expression for the concentration of the complex becomes

$$C_x = 2\pi k' C_A C_B r_0^2 \sin \vartheta_0 \Delta r_0 \Delta \vartheta_0 \times \exp(-\epsilon z_B \psi_0 / kT), \quad (16)$$

where  $k'$  is a constant.<sup>6</sup>

Setting

$$K = 2\pi k' r_0^2 \sin \vartheta_0 \Delta r_0 \Delta \vartheta_0 \quad (17)$$

we obtain

$$\ln(C_x / C_A C_B) = \ln K - \epsilon z_B \psi_0(r_0, \vartheta_0) / kT. \quad (18)$$

In the limiting case  $\kappa \rightarrow 0$  this reduces to

$$\ln(C_x^0 / C_A^0 C_B^0) = \ln K - \epsilon z_B \mu_0^* \cos \vartheta_0 / DkTr_0^2, \quad (19)$$

where  $\mu_0^*$  is Onsager's value

$$\mu_0^* = \mu_0(n^2 + 2)D / (2D + n^2). \quad (20)$$

From (18) and (19) we finally obtain for the speed of formation

$$\ln k = \ln k_{\kappa=0}$$

$$+ \frac{\epsilon z_B \cos \vartheta_0}{DkTr_0^2} (\mu_0^* - \mu^* e^{-\kappa r_0} / (1 + \kappa r_0)). \quad (21)$$

This formula for ion-dipole reactions corresponds to formula (1) in the case of ion-ion reactions.

In the second alternative Eq. (15) has to be integrated to give the resultant probability of formation. In the most general case the critical distance will be a function of the angles  $\vartheta$  and  $\varphi$  and this functional relation constitutes the "shape of the molecular dipole." It is, however, required that  $r$  is, in all directions, larger than  $a$  as otherwise  $\psi_0$  is not the valid potential throughout. The further procedure, after (15) has been integrated follows the same lines as above.

It is easy to perform the calculations if  $r$  is assumed constant, i.e., between  $r_0$  and  $r_0 + \Delta r_0$ , and if  $\vartheta$  is unrestricted. This means that the ion has to approach, *in all directions*, the same critical distance  $r_0$ . Such a behavior would be rather astonishing for a molecular dipole. As a matter of fact, this assumption leads to the wrong sign for the dependence of  $k$  on concentration and dielectric constant.

<sup>5</sup> J. A. Christiansen, *Zeits. f. Physik. Chemie* **113**, 35 (1924); G. Scatchard, *J. Am. Chem. Soc.* **52**, 52 (1930); *Chem. Rev.* **10**, 229 (1932).

<sup>6</sup> It should be mentioned that, according to the kinetic theory,  $k'$  is still proportional to  $T^{\frac{1}{2}}$  but this is of no importance for what follows.

A more adequate assumption would be that the critical surface is a prolonged spheroid with the dipole in one of the foci directed along the long axis. We have carried through the calculations for this case restricting ourselves to weak potentials (as in the derivation of Debye's Eq. (2)). The result is of a similar nature as (21) and coincides, for small values of  $\kappa$ , with (21). The only difference which remains is that  $\cos \vartheta_0$  is replaced by  $\epsilon$ , the eccentricity of the spheroid. This shows that the result may be chosen with the required sign according to whether the positive or the negative side of the dipole is nearer the surface.

We do not want to stress these calculations which involve a spheroidal form for the following reason. A spheroid would partake of the heat motion with rotations and these would have such a high frequency that the ionic atmosphere would not be able to follow them owing to its considerable time of relaxation.

However, these calculations show that it is legitimate to choose  $\vartheta_0$  and  $r_0$  as *critical average values* which are characteristic of the molecule. In this sense we are going to understand them and, consequently, use formula (21).

It will be seen in Section IV that  $\cos \vartheta_0$  has to be chosen as  $+1$  if we want to obtain agreement with empirical data for positive ions, i.e., an increase of  $\ln k$  with an increase of  $1/D$ . This means, in the spheroidal model, that the negative charge of the dipole has to be nearer the surface if the ion is positive. Furthermore, we assume that the critical distance  $r_0$  coincides with the radius  $a$  used in Section II.

Introducing the dimensionless variable

$$z = \kappa a = \kappa r_0 \quad (22)$$

and the dimensionless quantity

$$W = (\ln k - \ln k_{\kappa=0})(2DkTr_0^2)/\epsilon z_B \mu_0^* \cos \vartheta_0 \quad (23)$$

we can write our result in the final form

$$W = z^2 / (1 + z + z^2/2 + (n^2/2D)(1 + z)). \quad (24)$$

This formula brings out the dependence of  $k$  on concentration in a general way. Whatever the valency of the  $B$  ion, and whatever the nature of the other (admixed) ions contributing to the ionic atmosphere, the relationship between  $W$  and  $z$  ought to be the same.

As for the dependence of the reaction rate on  $D$ , the dielectric constant of the solvent, an additional remark should be made. Starting from the idea that  $k_{\kappa=0}$ , as used above, may still depend on the value of  $D$ , several authors<sup>7</sup> have split off from  $k_{\kappa=0}$  the part  $k_{\kappa=0}^{D=\infty}$  measuring thus the  $D$  dependence of  $k$  from a point of reference defined by the double transition  $\kappa=0$  and  $D \rightarrow \infty$  (see Eq. (1)). This procedure has proved to be successful in the case of ion-ion reactions. However, in our case it would lead to the result that the change of  $k$  with  $1/D$  should be in the opposite sense to the change with  $\kappa$ . This is contradicted by all available empirical data.

It should be taken into account that, in our case, the situation is very different from what it is in ion-ion reactions. In the latter case the electric attractions tend towards zero as  $D$  increases indefinitely. However, for a dipolar molecule, the "external moment" increases with increase of  $D$ . Therefore, though the  $\lim_{D \rightarrow \infty} \mu^*$  exists, the point  $D = \infty$  is certainly not an adequate point of reference since it accentuates rather than eliminates the effect of the dielectric constant.

In the case of ion-dipole reactions, owing to the argument just presented, the point  $\kappa=0$  can be interpreted as the ideal limiting case in which *all* electrostatic actions have disappeared. For this reason it seems to us that this point represents the adequate point of reference. Anyway we are going to introduce this as a special assumption. Then our formula (21) will express the complete dependence of  $k$  on  $D$  as on concentration.

Again it is useful to introduce dimensionless variables. If we set

$$\kappa^2 = \lambda^2 / D \quad (25)$$

$\lambda$  will still be of the dimension  $\text{cm}^{-1}$ , but free from  $D$ . Setting then

$$\zeta = \lambda a = \lambda r_0 \quad (26)$$

and

$$W' = (\ln k - \ln k_{\kappa=0})(2kT)/\epsilon z_B \mu_0^* \lambda^2 \cos \vartheta_0 \quad (27)$$

we have the general relation

$$W' = (1/D^2)(1/(1 + \zeta/D + \zeta^2/2D)). \quad (28)$$

<sup>7</sup> V. K. LaMer, J. Frank. Inst. **225**, 709 (1938); E. S. Amis and V. K. LaMer, J. Am. Chem. Soc. **61**, 905 (1939); J. C. Warner, Ann. N. Y. Acad. Sci. **39**, 345 (1940).

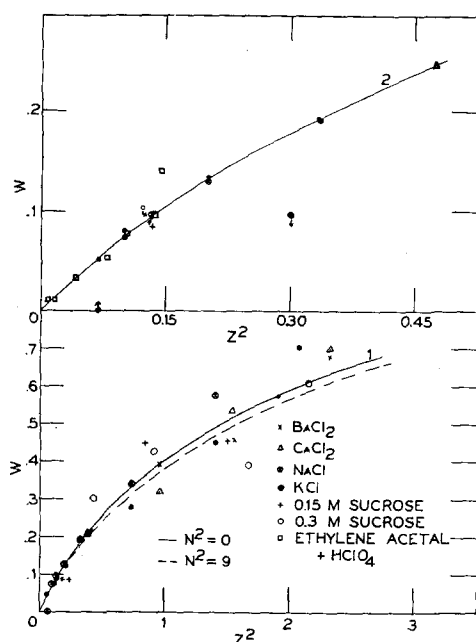


FIG. 1.

It shows that, in the limit  $\lambda \rightarrow 0$ ,  $W'$  will change as  $1/D^2$ . For larger concentrations the increase will become less and depends on the parameter  $\zeta$ . It should be mentioned that  $z^2$  as well as  $\zeta^2$  are, by their definitions (3) and (25), proportional to the ionic strength.

#### IV. APPLICATIONS

Equation (21) may be tested as to the effect of ionic strength upon reaction rate by putting it into the non-dimensional form given by Eq. (24) and plotting a theoretical curve  $W$  vs.  $z^2$ . As a good approximation the term  $(n^2/2D)(1+z)$  may be omitted in making the plot. In Fig. 1 the solid line is the theoretical curve for  $n^2=0$  and the broken line that for  $n^2=9$ . It can be seen that for these extreme values of  $n^2$  the plots do not vary a great amount.

Experimental values of  $(\ln k - \ln k_{\kappa=0})$  plotted against ionic strength will confirm the theoretical curve if they can be made to fit it by change of scale, for  $z^2$  is proportional to the ionic strength. From the change of scale of the abscissae a reasonable value of  $r_0$  ought to result. Further, from two given values of  $\log k$ , corresponding to two given values of  $W$ , a reasonable value of the enhanced moment  $\mu_0^*$

should be calculable according to the relation

$$\mu_0^* = (4.606 D k T r_0^2 \Delta \log_{10} k) / \epsilon z_B \cos \vartheta_0 \Delta W. \quad (29)$$

In the following calculations  $\cos \vartheta_0$  was always chosen as +1 (see Section III).

We may test Eq. (21) for the dielectric dependence of the rate by transforming it into the dimensionless form given by Eq. (28), and plotting  $W'$  against  $1/D^2$ . Various theoretical curves will be obtained depending on the value of the parameter  $\zeta$  chosen. The curves in Fig. 2 are for the two values  $\zeta=3.2$  and  $\zeta=6.0$ . Experimental data agreeing with theory should fit a theoretical curve depending on reasonable values of  $r_0$  and  $\mu_0^*$ .

There is not a great amount of data available for testing Eq. (21). It is unfortunate that no author has investigated thoroughly the influence of both the ionic atmosphere and the dielectric constant of the solvent upon the rate of any reaction between ions and dipoles.

#### (a) Dependence on Concentration

In Fig. 1 are plotted on curve 1 the data of Fales and Morrell<sup>8</sup> for the inversion of sucrose in various concentrations of HCl, and the data of Kautz and Robinson<sup>9</sup> for the inversion of sucrose in 0.1M HCl containing various concentrations of different salts. In curve 2 of Fig. 1 the part of curve 1 up to an ionic strength of 0.1 has been reproduced and enlarged. In curve 2 has also been plotted the data of Brönsted and Grove<sup>10</sup> for the hydrolysis of ethylene acetal by perchloric acid. The theoretical curves average these points very well. It might be mentioned that in the case of the data of Fales and Morrell the points corresponding to the lowest acid concentrations (below about 0.01M  $C_{H^+}$ ) were omitted since they were entirely inconsistent with the rest of the data. In the case of inversion, observed by Kautz and Robinson, in the presence of NaCl two points are seen to be evidently in error.

In column 2 of Table I are given the  $r_0$  values

<sup>8</sup> H. A. Fales and J. C. Morrell, J. Am. Chem. Soc. **44**, 2071 (1922).

<sup>9</sup> C. F. Kautz and A. L. Robinson, J. Am. Chem. Soc. **50**, 1022 (1928).

<sup>10</sup> J. N. Brönsted and Clinton Grove, J. Am. Chem. Soc. **52**, 1397 (1930).

used in fitting the various data to the theoretical curves in Fig. 1. It will be observed that these values are always reasonable and are always identical for the same type of atmosphere. In column 3 of this table are given the enhanced moments calculated according to Eq. (29). Column 4 contains the value of  $n^2$  (the internal dielectric constant) necessary to reduce the enhanced moment to  $3.4 \times 10^{-18}$  in the case of sucrose<sup>11</sup> and to  $4 \times 10^{-18}$  in the case of ethylene acetal. No value of the moment for ethylene acetal was found recorded in literature so the value  $4 \times 10^{-18}$  was arbitrarily chosen. In the fifth column of this table is a key as to the value of the ionic strength to which this theory held for each charge type of ionic atmosphere. It will be observed that for sucrose inversion, when the atmosphere was made up of univalent ions, the theory held to a value of ionic strength  $>3$  which is as far as the data extended. However, when there were bivalent ions in the atmosphere, the theory applied up to a value of the ionic strength of about 0.6. This is similar to the case of reactions between ions where the presence of higher valence ions in the ionic atmosphere causes a departure from theory at lower ionic strengths than is the case for an ionic atmosphere of univalent ions. The data for the hydrolysis of ethylene acetal extended only to an ionic strength of about 0.08.

### (b) Dependence on Dielectric Constant

In two instances there have been extensive studies made of the influence of the dielectric

TABLE I. Constants used in plotting the curves of Fig. 1.

(1)	(2)	(3)	(4)	(5)	(6)
Substances	$r_0(\text{\AA})$	$10^{18}\mu_0^*$	$n^2$	$z^2$ at ionic strength = 1 for curve 1	$k_{\infty=0}$
Sucrose + HCl					
+ BaCl <sub>2</sub>	6.0	6.65	1.91	3.867	$4.02 \times 10^{-4}$
Sucrose + HCl					
+ CaCl <sub>2</sub>	6.0	9.05	3.32	3.867	$4.02 \times 10^{-4}$
Sucrose + HCl					
+ KCl	2.5	14.0	6.24	0.670	$3.95 \times 10^{-4}$
Sucrose + HCl					
+ NaCl	2.5	10.5	4.18	0.670	$4.30 \times 10^{-4}$
Sucrose (0.15 M)					
+ HCl	3.5	10.3	4.06	1.35	$2.17 \times 10^{-4}$
Sucrose (0.3 M)					
+ HCl	3.5	7.15	2.21	1.35	$2.16 \times 10^{-4}$
Ethylene acetal					
+ HClO <sub>4</sub>	4.0	18.6	7.3 ( $\mu_0 = 4 \times 10^{-18}$ )	1.70	$4.15 \times 10^{-4}$

<sup>11</sup> E. Landt, Naturwiss. 22, 809 (1934).

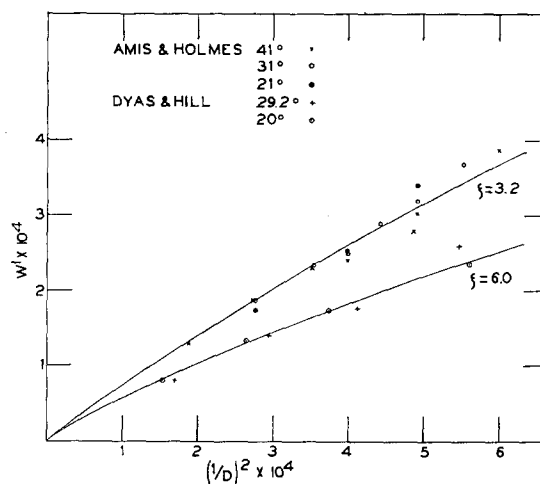


FIG. 2.

constant of the solvent upon the reaction rate. Amis and Holmes<sup>12</sup> have studied the inversion of 0.1000N HCl catalyzed sucrose in ethyl alcohol-water and in dioxane-water solvents. Since the data for alcohol-water media were shown from energy considerations to be in opposition to the predictions of electrostatics, they would not be pertinent here. However, the data for dioxane-water should fall in line with the requirements of Eq. (21). Dyas and Hill<sup>13</sup> investigated the mutarotation of glucose by HCl in methanol-water solvents. That part of the mutarotation brought about by the oxonium ion is a reaction of the ion-dipole type and should meet the requirements of our theory. The results of these authors are reduced to unit normality.

In Fig. 2 we have plotted the data of Amis and Holmes and also those of Dyas and Hill. The theoretical curves for  $z=3.2$ , corresponding to a value of  $r_0$  of about 3.5 Å used in the calculations on atmosphere effects, averages these data well. However, the values for pure water as the solvent at 21° and 31° were omitted from the graph since they were so inconsistent with the rest of the data that they must be grossly in error. The Dyas and Hill data fitted the same curve remarkably well but led to a  $r_0$  value in this case of only slightly more than 1 Å. The authors felt that the  $r_0$  value for the glucose-

<sup>12</sup> E. S. Amis and F. C. Holmes, J. Am. Chem. Soc. 63, 2231 (1941).

<sup>13</sup> H. E. Dyas and G. G. Hill, J. Am. Chem. Soc. 64, 236 (1942).

TABLE II. Constants used in plotting the curves of Fig. 2.

(1) Substances	(2) $r_0(\text{\AA})$	(3) $10^{18}\mu_0^*$	(4) $n^2$	(5) Temp. $^{\circ}\text{C}$	(6) $k_{\kappa=0}$
Sucrose + HCl	3.5	14.6	6.59	21	$4.95 \times 10^{-4}$
Sucrose + HCl	3.5	14.7	6.65	31	$2.00 \times 10^{-3}$
Sucrose + HCl	3.5	14.3	6.42	41	$6.76 \times 10^{-3}$
Glucose + HCl	2.0	8.07	2.04 ( $\mu^0 = 2 \times 10^{-18}$ )	20	$2.95 \times 10^{-1}$
Glucose + HCl	2.0	8.13	2.07 ( $\mu_0 = 2 \times 10^{-18}$ )	29.2	$7.59 \times 10^{-1}$

oxonium reaction would conceivably be less than the  $r_0$  value for the sucrose-oxonium reaction. However, the difference between 1.0A and 3.5A for  $r_0$  seemed rather large, so the choice of an  $r_0$  value of 2.0A gave the very satisfactory results shown by the curve for  $\zeta = 6.0$  in Fig. 2.

In Table II, column 3 are given the enhanced moments calculated for the sucrose and glucose molecules. The values of  $\mu_0^*$  for sucrose are of the same order of magnitude and compare favorably in actual value with those obtained from the concentration data of entirely different authors when the same value of  $r_0$  is used in the

two cases. The  $\mu_0^*$  values for both sugars are very consistent at the different temperatures which is in accordance with theory because in the approximation  $(n^2/2D) \ll 1$  used by us the ratio  $\mu_0^*/\mu_0$  depends only on  $n^2$  and, therefore, ought to be independent of temperature. The values of  $\mu_0^*$  in Table I are less consistent; these variations may be due to a change in the nature of the molecule in different surroundings.

Column 4 of Table II contains the value of  $n^2$  for the moment of sucrose to be  $3.4 \times 10^{-18}$  and that of glucose  $2 \times 10^{-18}$ . The latter value was chosen arbitrarily as no value for the moment of glucose was found recorded in the literature. The values of  $n^2$  are very consistent for either molecule, and those values for sucrose compare favorably with values found by the rate dependence upon ionic strength.

It might be pointed out that our derivation of the potential  $\psi_i$  in Eq. (8) contains a theory for the activity coefficient of molecular dipoles, analogous to that of Debye and Hückel for ions.