PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

A Chain Model for Polyelectrolytes. IX. The Effects of Chain Length and Charge on the Friction Constant

BY GEORGE THOMSON,[1a] STUART A. RICE, AND MITSURA NAGASAWA[1b]

RECEIVED MARCH 8, 1963

In this paper we report measurements of self-diffusion and viscosity as a function of chain length and charge for some protonated and unprotonated amines and for some disulfonate ions. It is found that: (a) The Peterlin theory of diffusion of short-chain molecules is an accurate description of real systems. (b) The Peterlin theory of viscosity is qualitatively correct but quantitatively in error by a factor of two. (c) The placement of two charges on an ethylenimine leads to an extended molecular configuration. (d) The possibility of hydrogen bonding between uncharged ethylenimines and the water leads to zero slip between molecule and solvent. Therefore, classical hydrodynamic conditions are satisfied and the system behaves differently (larger friction constant) from what would be expected from other studies in nonhydrogen bonding solvents. (e) When charges are placed on the ion the local water structure is modified, decreasing the efficacy (or even possibility) of hydrogen bonding. There is a range of variables wherein the friction constant per bead drops on going from the neutral molecule to the bolion because of the change in solvent interactions. (i) The transition from simple ion to polyion requires more than five charges per ion and longer chain lengths than considered herein.

I. Introduction

Among the interesting and little understood aspects of the solution behavior of charged macromolecules are:

(a) What is the nature of the transition from small molecule behavior to large molecule behavior, and how does the charge distribution on the solute molecule influence the transition? (b) How do the frictional properties of a given polymer-solvent system alter when the polymer becomes charged?

It is the purpose of this paper to describe experimental studies of diffusion in the systems ethylenediamine, diethylenetriamine, ..., polyethylenimine-water. The experiments are designed to answer, at least in part, the two questions cited.

Examination of the literature reveals that there have been very few studies directed toward understanding the transition between small molecule and macromolecule solution behavior. For the case of uncharged polymers in a low molecular weight solvent, the following should be cited: (a) Holtzer, Benoit, and Doty[2] showed that the effective bond length of cellulose trinitrate in acetone solution decreases when the degree of polymerization becomes small. The studies could not be carried to very low molecular weights and therefore the transition region could not be examined in detail. From the available data, however, it can be estimated that the transition is reached when the degree of polymerization exceeds 500.

(b) Peterlin has developed a theory of the diffusion and viscosity of small chain molecules.[3a,b] Attempts to test this theory have not heretofore been completely successful because data for very short chains have not been available. Peterlin's analysis of the viscosity of

cellulose nitrate[4] indicates a long transition region with long-chain behavior not reached until the degree of polymerization exceeds 500. Rice has shown[5] that the Peterlin theory can be applied quantitatively to the description of the limiting conductance of flexible bolions, but the available data do not permit examination of any possible transition region.

(c) Brönsted and Koefoed[6] have studied the thermodynamic properties of mixtures of paraffin hydrocarbons. The results indicate that for molecules as small as dodecane (in hexane) the thermodynamic properties of the solution are adequately described by the same molecular model that fits the thermodynamic properties of high molecular weight solute in the same solvent. Although this result might be interpreted to indicate that any transition region must lie below a degree of polymerization of 12, it is a more likely explanation that the gross thermodynamic properties are sufficiently insensitive to molecular configuration that no differentiation of behavior is observable.

(d) McCall and co-workers[7] have made extensive studies of self-diffusion as a function of chain length in the paraffin hydrocarbon and linear dimethylsiloxane series. Comparison with solution studies is difficult because the "solvent" changes from compound to compound. Nevertheless, the data are interesting. In the case of the linear dimethylsiloxanes, it is found that the rate of change of self-diffusion coefficient with increasing chain length becomes much smaller for molecules containing more than five silicon atoms than for smaller molecules. The analogous transition in the

(1) (a) NRC-NBS Postdoctoral Research Associate, National Bureau of Standards, Washington, D. C. (b) Permanent address: Department of Synthetic Chemistry, University of Nagoya, Nagoya, Japan.

(2) A. M. Holtzer, H. Benoit, and P. Doty, J. Phys. Chem., **58**, 635 (1954).

(3) (a) A. Peterlin, J. chim. phys., **47**, 669 (1950); (b) **48**, 13 (1951).

(4) A. Peterlin, J. Polymer Sci., **8**, 173 (1952).

(5) S. A. Rice, J. Am. Chem. Soc., **80**, 3207 (1958).

(6) J. N. Brönsted and J. Koefoed, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd., **22**, No. 17 (1946).

(7) D. W. McCall, D. C. Douglass, and E. W. Anderson, Phys. Fluids, **2**, 87 (1959); J. Chem. Phys., **30**, 771 (1959); D. C. Douglass and D. W. McCall, J. Phys. Chem., **62**, 1102 (1958); D. W. McCall, E. W. Anderson, and C. M. Huggins, J. Chem. Phys., **34**, 804 (1961).

Table I
Chemical Analysis of Various Amine Hydrochlorides

	———Carbon, %———		———Hydrogen, %———		———Chlorine, %———		———Nitrogen, %———	
	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.	Calcd.	Fnd.
ED·2HCl[a]	18.06	18.25	7.58	7.56	53.31	53.41	. . .	. . .
DT·3HCl[a]	. . .	. . .	. . .	. . .	50.04	50.10	19.77	19.63
TT·4HCl[a]	. . .	. . .	. . .	. . .	48.56	48.33	. . .	. . .

[a] The abbreviations ED, DT, and TT represent ethylenediamine, diethylenetriamine, and triethylenetetramine, respectively.

paraffin hydrocarbon series occurs at somewhat larger chain lengths. From studies of the temperature dependence of the self-diffusion coefficient it may be estimated that long-chain behavior is achieved for carbon chains containing more than 20–30 carbon atoms. It is interesting to note that the length of the transition region, as well as its position on the scale of chain length, may depend on the solvent. Thus, McCall notes that studies of the pressure dependence of mutual diffusion in mixtures of *n*-hexane, *n*-octane, and *n*-decane with polyethylene suggest that the same molecular configuration is required for diffusion in each case. This is, in our opinion, likely to be a reflection of the dominant role of the solvent in determining the frictional force acting on a solute molecule. It should also be noted that the flexibility of the linear dimethylsiloxanes is much greater than that of the linear paraffin hydrocarbons. In turn, the flexibility of the hydrocarbons greatly exceed that of cellulose and cellulose derivatives. It is therefore to be expected that in solution in a low molecular weight solvent any transition region will be at a higher degree of polymerization for cellulose molecules than for paraffin molecules, and for paraffin molecules than for siloxane molecules. Further, it is to be expected that the liquid structure of the dimethylsiloxanes will be more disordered than that of the corresponding paraffin hydrocarbons (where a parallelism of molecules is slightly favored) and therefore that any transition from small to large molecule behavior (as exhibited, say, in self-diffusion) will be in a range of smaller chain length.

(e) Longsworth[8] has made an extensive study of the relationship between the mutual diffusion coefficient and the solute molecular volume for the case of compact molecules. Some similar studies have been made by McCall[9] of self-diffusion, and the extensive data on the limiting conductance[10] of ions in water can also be used to provide correlations of molecular friction with molecular volume.

Further examination of the literature reveals that even fewer studies have been made of the small molecule–polymer transition when the molecule is charged. For the case of compact ions we have already cited conductivity studies. For the case of linear molecules, Lapanje, Haebig, Davis, and Rice[11] showed that, in aqueous solutions of polyethyleneimine hydrochloride, both the counterion activity coefficient and the extent of counterion binding indicated the transition region to lie at a degree of polymerization (now referred to charges) greater than 5. There is a slight indication in their data that at a degree of polymerization of 5, the transition is just beginning or is not far off. Nothing is known of the relationship between solute charge distribution and the transition to polymeric behavior.

There is very little information available with which to answer the second of the questions posed. It is clear that any changes in the frictional properties of

the molecule due to charging involve changes both in the solute–solvent interaction and in the local structure of the solvent. Despite extensive studies of the properties of small spherical ions, the only generalization to emerge from studies of aqueous solutions is an empirical correction to Stokes' law.

The results of the investigation presented herein show that: (a) The Peterlin theory of diffusion of short-chain molecules is an accurate description of real systems. (b) The Peterlin theory of viscosity is qualitatively correct but quantitatively in error by about a factor of two. (c) The placement of two charges on an ethyleneimine leads to an extended molecular configuration. (d) The possibility of hydrogen bonding between uncharged ethyleneimines and the water leads to zero slip between molecule and solvent. Therefore, classical hydrodynamic conditions are satisfied and the system behaves differently (larger friction constant) from what would be expected from other studies in nonhydrogen bonding solvents. (e) When charges are placed on the ion the local water structure is modified, decreasing the efficacy (or even possibility) of hydrogen bonding. There is a range of variables wherein the friction constant per bead drops on going from the neutral molecule to the bolion because of the change in solvent interactions. (f) The transition from simple ion to polyion requires more than 5 charges per ion and longer chain lengths than considered herein.

II. Experimental Details

Ethylenediamine (ED), diethylenetriamine (DT), triethylenetetramine (TT), and tetraethylenepentamine (TP) were purchased from the Eastman Kodak Co. The ethylenediamine was 95 to 100% Eastman Grade; the others were technical grade chemicals. Ethylenediamine and diethylenetriamine were distilled at atmospheric pressure; their boiling ranges were 115.5 to 116.5° and 250 to 251°, respectively. Triethylenetetramine and tetraethylenepentamine were distilled at reduced pressure; their boiling ranges were 122 to 123° and 250 to 251°, respectively, at a pressure of about 6 mm. The exhaustively protonated salts (herein referred to as completely quaternized) were prepared by adding concentrated hydrochloric acid to the pure amine after it had been frozen in Dry Ice–acetone cooling mixture. These salts were then precipitated five times from aqueous solution with cold 95% ethanol. The precipitates were filtered by suction and dried in a vacuum oven at 40 to 50°. The results of microanalyses are displayed in Table I. The partly quaternized salts were prepared by adding 2 N hydrochloric acid to amine solutions of convenient concentrations.

The polyethylenimines (PEI) were a gift from the Chemirad Corporation. They were said to be anhydrous and to have estimated molecular weight ranges of 19,000 to 25,000, 25,000 to 35,000, and 36,000 to 48,000. The first sample was light yellow, but the others were white. The properties of one older sample of the polymer with a molecular weight of 3,600 were also studied. It is necessary to mention that the manufacturer's estimate of the molecular weights was found to be grossly in error. From measurements of freezing point depressions and viscosities the number average and weight average molecular weights were found to be 275 and 680 for the 19,000 to 25,000 sample, 540 and 1,100 for the 25,000 to 35,000 sample, and 550 and 2,600 for the 36,000 to 48,000 sample. The molecular weight of the older sample is believed to be correct at 3,500, but it had been depleted before freezing point and viscosity measurements were started. It should be noted that the polymers are quite polydisperse, M_w/M_n ranging from about two to about five. Although viscosity measurements could provide useful information, the diffusion was dominated by the low-molecular-weight tail of the distribution, and only the diffusion coefficient for the lowest degree of polymerization could be used. In the earliest stages of this investigation an attempt was made to synthesize the octamine and the decamine, but the yields were so poor that this

(8) L. G. Longsworth, *J. Am. Chem. Soc.*, **75**, 5705 (1953).

(9) D. W. McCall, D. C. Douglass, and E. W. Anderson, *J. Chem. Phys.*, **31**, 1555 (1959).

(10) See, for example, R. Robinson and R. Stokes, "Electrolyte Solutions," Butterworths, London, 1955.

(11) S. Lapanje, J. Haebig, H. T. Davis, and S. A. Rice, *J. Am. Chem. Soc.*, **83**, 1590 (1961).

TABLE II

DIFFUSION COEFFICIENTS OF UNCHARGED MOLECULES

Compound	$D \times 10^6$, cm.^{2}/sec.
ED	10.5
DT	6.95
TT	6.25
TP	5.80
PEI (N = 47)	3.90
PEI (N = 240)	1.60

TABLE IIIa

DIFFUSION COEFFICIENTS OF BOLAFORM SALTS

Salt	$D \times 10^6$, cm.^{2} sec.$^{-1}$
ED·2HCl	13.8
DT·2HCl	12.2
TT·2HCl	10.3
TP·2HCl	9.60
BDS·K$_2$	12.0
BPDS·K$_2$	10.25
TPDS·K$_2$	9.50

TABLE IIIb

DIFFUSION COEFFICIENTS OF BOLAFORM IONS

Ion	$D \times 10^6$, cm.^{2} sec.$^{-1}$
ED·H$_2$$^{++}$	8.40
DT·H$_2$$^{++}$	6.78
TT·H$_2$$^{++}$	5.19
TP·H$_2$$^{++}$	4.68
BDS$^=$	6.80
BPDS$^-$	5.22
TPDS$^-$	4.69

TABLE IV

VISCOSITIES OF BOLAFORM ELECTROLYTES

Compound	[η] (100 cc./g.)	$F(\lambda\delta)$
ED·2HCl	5.8×10^{-3}	3.62
DT·2HCl	1.3×10^{-2}	2.03
TT·2HCl	1.9×10^{-2}	1.32
TP·2HCl	2.5×10^{-2}	0.98

TABLE Va

DIFFUSION COEFFICIENTS OF HIGHLY CHARGED SALTS

Salt	$D \times 10^6$, cm.^{2} sec.$^{-1}$
DT·3HCl	12.7
TT·3HCl	11.2
TP·3HCl	11.0
TT·4HCl	10.8
TP·4HCl	10.8
TP·5HCl	9.3

TABLE Vb

DIFFUSION COEFFICIENTS OF HIGHLY CHARGED IONS

Ion	$D \times 10^6$, cm.^{2} sec.$^{-1}$
DT·3H$^+$	5.97
TT·3H$^+$	4.78
TP·3H$^+$	4.63
TT·4H$^+$	3.75
TP·4H$^+$	3.75
TP·5H$^+$	2.51

approach was abandoned. Preliminary values of the diffusion coefficients of these two compounds are in agreement with the deductions based on the data obtained from the measurements of the diffusion coefficients of the smaller amines. Because sufficient material could not be prepared to check the measurements, the values obtained are not reported here. Since the polymers could not be purified as such, they were used as received. The preparation of the hydrochlorides of the polymers was similar to the preparation of the salts of the simple amines. A quantity of polymer was cooled in a Dry Ice–acetone mixture, 0.024 equivalent of concentrated hydrochloric acid was added for each gram of polymer, the mixture was allowed to warm to room temperature, and it was heated until the polymer had dissolved completely. The solutions were then stirred while 95% ethanol was slowly added until the polymer gelled; the gel was broken up and stirring was continued. The alcohol was poured off, the salts were dissolved in water, and the solutions were freeze-dried in a Rinco evaporator.

Samples of potassium p-benzenedisulfonate (BDS), potassium p,p'-biphenyldisulfonate (BPDS), and potassium p,p''-terphenyldisulfonate (TPDS) were obtained from Professor Gordon Atkinson of the Chemistry Department of the University of Maryland. His kindness is greatly appreciated.

Except for the solutions of the partially neutralized amines which were used as prepared, all solutions were made up on a weight/volume basis.

The diffusion experiments were performed at 25.04 ± 0.01° using a Spinco Model H diffusion apparatus as a Rayleigh interferometer. The thermostat of this instrument is designed to maintain a temperature near 0°, so a heater was installed and operated continuously with the thermoregulator and refrigerating unit of the instrument used to control the temperature. As a routine procedure, the boundary was sharpened using a long blunt-ended syringe needle. For a typical run nine or ten photographic exposures were made at intervals ranging from 15 min. to 3 hr.; 4 in. by 5 in. Kodak type M glass photographic plates
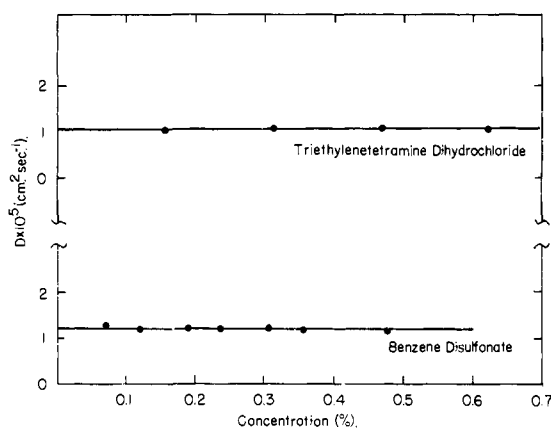

Fig. 1.—Diffusion coefficients of triethylenetetramine dihydrochloride and potassium benzenedisulfonate as a function of concentration.

were used. They were developed in Kodak D-19 developer and fixed in Kodak acid fixer. The plates were measured with a Mann type 829A comparator. Usually five (or more) patterns were measured giving apparent diffusion constants at five times (or more). A least squares line through the points on a diffusion coefficient vs. $1/t$ plot was extrapolated to $(1/t) = 0$ to find the diffusion coefficient at infinite time. The slope of this line is $D_0\Delta t$, where Δt is the time correction. Application of this correction changes the slope of the line to zero but does not change the intercept greatly. The diffusion coefficients were then plotted vs. concentration of solute. The computations were made, except for several routine hand calculation checks, on either the UNIVAC I or the IBM 7090 at the Computation Center of the University of Chicago. The method used is straightforward except for the use of a polynomial approximation to the error function.[12]

Viscosity measurements were made in a 4-bulb dilution type Ubbelohde viscometer. The flow time for water was 115.4 sec. at the operating temperature of 25.00 ± 0.01°. The polymer solutions were filtered by suction through a fine sintered glass filter just prior to use.

III. Results and Discussion

The diffusion coefficients at infinite dilution of the various compounds studied are listed in Tables II, III, and V, and a few plots of D as a function of solute concentration are displayed in Fig. 1. As can be seen, there is essentially no concentration dependence (or only a small concentration dependence) of D in the range studied. It should be noted that our measurements cover a concentration range well above that for which typical dilute electrolyte "Debye–Hückel" effects can be seen. We shall analyze our findings under the three groupings of (a) uncharged molecules, (b) bolaform ions, and (c) fully charged ions.

A. **Uncharged Molecules.**—The behavior of uncharged linear macromolecules in dilute solution can be understood in terms of the properties of a model chain. The best example is the Kirkwood–Riseman theory[13] which represents the polymer molecule as a series of spherical beads connected at fixed bond angles. Because of the interaction of the flow field about one monomer bead with the flow fields due to other beads, the hydrodynamic resistance is very different from that characteristic of an equivalent number of independent beads. The result of Kirkwood and Riseman's treatment is that the frictional coefficient of a flexible chain molecule is equal to

$$\zeta = \frac{(3\pi^{1/2}/8)6\pi\eta_0\rho_G}{1 + (9\pi^{1/2}/2\eta_0\rho_G/4N\zeta_0)} \tag{1}$$

where ζ is the friction constant for the chain molecule containing N resisting centers each with friction constant ζ_0. The viscosity of the solvent is denoted η_0 and the radius of gyration of the chain molecule, ρ_G, is

(12) L. Kotin, L. Hook, and W. Davis, *Appl. Opt.*, **2**, 66 (1963).

(13) J. Riseman and J. G. Kirkwood, *J. Chem. Phys.*, **17**, 442 (1949).

related to the mean square end to end distance, $<h^2>$, by

$$\rho_G{}^2 = \frac{1}{6} <h^2> \qquad (2)$$

Equation 1 has been amply verified for the case of large N when due account is taken of the effect of excluded volume (ρ_G increases more rapidly than $N^{1/2}$). Equation 1 is, however, based on a mathematical approximation in which the molecule is represented as a random coil. For very short chains, the configurations characteristic of a random coil are not accurate representations of the real molecular configurations. The calculations of Kirkwood and Riseman cannot be easily extended to the description of nongaussian chains because of the complexity of the hydrodynamic interaction terms. A calculation based on the same model but with a simplification of the hydrodynamics has been proposed by Peterlin.[3] The simplification consists of replacing the exact hydrodynamic interaction, which varies from element to element, by the interaction averaged over all elements of the chain. Thus, it is assumed that the velocities of all the chain elements change by the same multiplicative factor. The error introduced by this approximation should be small for the case of diffusion (or sedimentation) where all elements move in the same direction; it will be more important in the case of viscosity where the elements of one half of the molecule move in the opposite sense to the elements of the other half. Peterlin's theory leads to a frictional coefficient of the same form as eq. 1 for the case of large N. The only difference between the exact result and Peterlin's formula is a small change in the numerical coefficient of the second term in the denominator of eq. 1. We shall therefore test the Peterlin theory in its original form.

For a chain of N spherical beads, each of radius a_0 and center to center separation b_0, the diffusion constant is found to be

$$D = \frac{kT}{N\zeta_0}\left(1 + \frac{a_0}{N}\sum_{p=1}^{N-1} g_p \frac{N-p}{R_p}\right) = \frac{kT}{N\zeta_0} f_D \qquad (3)$$

where the geometric term g_p is defined by

$$g_p = R_p <\frac{1}{r_p}> \qquad (4)$$

with R_p the root mean square separation of two elements p units apart and r_p the instantaneous distance separating the same elements p units apart. The factor g_p has the value $(6/\pi)^{1/2}$ for the case of a random chain and the value 1 for $p = 1$ and $p = 2$. Peterlin has calculated the term f_D for values of N up to 100 and presented the results in graphical form.

The hydrodynamic interference terms which contribute the term in parentheses in eq. 3 depend upon the valence bond angle, the hindrance to rotation, and the model parameters a_0 and b_0. The case of maximum hydrodynamic interaction occurs when $(a_0/b_0) = 0.5$ since then the monomer beads are in contact. Within the framework of this model, (a_0/b_0) cannot exceed 0.5. A brief examination of a table of bond lengths shows that the assignment of a_0 and b_0 is difficult in the case of the ethylenimines. Bond lengths along the chain are about 1.50 Å. (C–C, 1.54 Å.; C–N, 1.47 Å.) and the other bond lengths are about 1.0 Å. (C–H, 1.09 Å.; N–H, 1.01 Å.). If we regard the CH_2 and NH groups as the monomer beads, we should choose for a_0 a value close to 1.50 Å. since the covalent radius of hydrogen must be added to the figures quoted. But such a choice of a_0 would imply that b_0 was 3.0 Å., whereas b_0 cannot exceed 1.54 Å. The crux of the matter is, then, that nonoverlapping spheres with dimensions determined a priori from the

molecular geometry cannot be found for the molecules in question. It is best, then, to regard the Peterlin theory as a two-parameter theory, the parameters being ζ_0 and a_0/b_0. We shall choose to consider only the case $(a_0/b_0) = 0.5$ because this case corresponds to maximum hydrodynamic interaction between the beads, suggested by the discussion above, and also effectively reduces the theory to a one-parameter fit. From the experimental values of ζ_0, it is necessary that b_0 be given by

$$b_0 = \frac{\zeta_0}{3\pi\eta_0} \qquad (5)$$

since a_0, considered as a parameter, is determined from ζ_0, considered as a parameter, by the use of Stokes' law.

Having chosen $(a_0/b_0) = 0.5$, the values of the terms in parentheses will now depend only on the valence angle and barrier to rotation. For a randomly coiled molecule (N large)

$$<h^2> = Nl^2 \frac{1 + \cos\theta}{1 - \cos\theta} \cdot \frac{<1 + \cos\theta>}{<1 - \cos\theta>}$$
$$= Nl^2 \frac{1 + \alpha}{1 - \alpha} \qquad (6)$$

where l is the bond length, θ is the valence angle, and the term $<\cos\phi>$ is nonvanishing if there is a barrier to rotation which makes some of the values of the angle of rotation, ϕ, energetically favorable relative to other values of this angle. The variable α is defined by eq. 6. In terms of α, the hydrodynamic interaction term has the values displayed in Table VI.

TABLE VI

VALUES OF THE HYDRODYNAMIC INTERACTION TERM, f_D, IN EQ. 3 FOR $(a_0/b_0) = 0.50$

N	0	0.2	0.4	0.6	0.8	1.0
4	2.25	2.20	2.16	2.12	2.08	2.04
7	3.41	3.21	3.00	2.83	2.71	2.60
10	4.25	3.95	3.62	3.40	3.16	2.91
13	5.12	4.71	4.25	3.91	3.58	3.21

To test the validity of the Peterlin theory we calculate the friction constant of the monomer bead, ζ_0, and find that value of α which makes ζ_0 independent of N. The results of these calculations are displayed in Table VII, from which it is seen that the case $\alpha = 0$ best fits the experimental data.

TABLE VII

VALUES OF THE FRICTION CONSTANT, ζ_0, FOR VARIOUS VALUES[a] OF α

N	0	0.2	0.4	0.6	0.8	1.0
4	2.20	2.16	2.12	2.08	2.04	2.00
7	2.88	2.71	2.54	2.39	2.29	2.20
10	2.79	2.60	2.38	2.23	2.08	1.92
13	2.79	2.57	2.32	2.13	1.95	1.75

[a] All values quoted are in units of 10^{-9} g. sec.$^{-1}$.

The preceding result is superficially puzzling since it implies that $\cos\theta = <\cos\phi> = 0$. That this is not the correct interpretation is inherent in the choice $(a_0/b_0) = 0.5$ and eq. 5. From the experimentally determined value of ζ_0 we find $a_0 = 1.66$ Å., and therefore b_0 is required by the hydrodynamic treatment to be 3.32 Å. This value of b_0 greatly exceeds the bond length of 1.50 Å. If we assume that the root mean square end-to-end distance of the chain is accurately described in eq. 6, then with the known tetrahedral valence angle the term $(1 + \cos\theta) (1 - \cos\theta) = 2$.

In terms of the true bond length, l, and the enforced large value of b_0, eq. 6 should be written

$$<h^2> = 2 \left(\frac{b_0}{\sqrt{2l}}\right)^2 Nl^2 \frac{1 + \alpha'}{1 - \alpha'} \qquad (7)$$

where α' now accounts only for the residual barrier to rotation in excess of that value which makes $(1 + <\cos \phi>)/(1 - <\cos \phi>) = (b_0/\sqrt{2l})^2 = 2.45$. This corresponds to $<\cos \phi> = 0.42$, indicating a moderately large barrier to rotation, as expected from the known barrier in ethane. The value of $<\cos \phi>$ deduced is in substantial agreement with the value found by Rice[5] in applying the Peterlin theory to haloform ions. The apparent result that $\alpha' = 0$ is just a numerical accident since the correlation enforced by the hydrodynamic treatment just happens to account fully for the hindrance to rotation.

To complete the demonstration that eq. 3 accurately describes both short-chain behavior and the transition to long-chain behavior, it must be shown that with the value of ζ_0 determined for short chains, eq. 1, predicts the correct value of D for long chains. A combination of eq. 1, 2, and 7 shows that ζ depends on the ratio (a_0/b_0) but not on either independently. Taking $\zeta_0 = 2.80 \times 10^{-9}$ g. sec.$^{-1}$ then leads to the result (at 298°K.)

$$\begin{array}{ll} D_{47}\text{ (theory)} &= 4.25 \times 10^{-6} \\ D_{47}\text{ (exptl.)} &= 3.90 \times 10^{-6} \end{array} \Big\} \text{cm.}^2 \text{ sec.}^{-1}$$

$$\begin{array}{ll} D_{240}\text{ (theory)} &= 1.80 \times 10^{-6} \\ D_{240}\text{ (exptl.)} &= 1.60 \times 10^{-6} \end{array} \Big\} \text{cm.}^2 \text{ sec.}^{-1} \qquad (8)$$

Although not perfect, the agreement is satisfactory in view of the heterogeneity of the polymer samples.

We now consider the suitability of the same model of the polymer chain for the description of the intrinsic viscosity. Having already evaluated the friction constant ζ_0 and the parameters a_0 and b_0 we can make an *a priori* calculation of the intrinsic viscosity. We prefer, however, to proceed as before and to attempt to find a value of α for which ζ_0 is independent of N. Peterlin has shown[2] that the intrinsic viscosity, $[\eta]$, is given by

$$[\eta] = \frac{\zeta_0}{6NM_0}\left(\frac{S(j)}{1 + 0.2\left(\frac{a_0}{b_0}\right)\frac{S(j, p)}{S(j)}}\right)$$

$$S(j) = \sum_{j=1}^{N} R_j^2 \qquad (9)$$

$$S(j, p) = b_0 \sum_{p=1}^{n-1} \frac{g_p}{R_p} \sum_{j=l}^{N-p} <9r_j r_{j+p} - r_j^2>$$

where M_0 is the mass of the monomer bead. Equation 9 is less accurate than the equivalent relation describing diffusion because an average of a product has been replaced by the product of two averages. This mathematical approximation is not ordinarily good except for very unusual distributions. In addition, the assumption that the perturbation to the velocity of a bead is the same constant factor for all beads is less accurate for the description of the viscosity increment than for the description of the diffusion. In Table VIII we have displayed (except for a constant factor) the values of the hydrodynamic interaction term on the right-hand side of the first line of eq. 9. In terms of the table entries, denoted f_η, we have

$$[\eta] = \frac{b_0^2 \zeta_0}{36 M_0} f_\eta \qquad (10)$$

Using the value of b_0 determined by the diffusion measurements, we are led to the values of ζ_0 entered in Table IX.

It is readily seen that, as in the diffusion studies, the case $\alpha = 0$ best fits the data. However, the value of

TABLE VIII

VALUES OF THE HYDRODYNAMIC INTERACTION TERM, f_η, FOR VISCOSITY

$(a_0/b_0 = 0.50)$

N	α					
	0	0.2	0.4	0.6	0.8	1.0
4	4.2	4.9	5.5	6.2	6.8	7.5
7	6.2	7.5	9.2	10.8	13.3	16.2
10	7.5	9.6	12.1	15.4	20.8	27.9
13	8.3	11.2	14.2	19.6	28.3	42.0

TABLE IX

VALUES[a] OF THE FRICTION CONSTANT, ζ_0, FROM THE INTRINSIC VISCOSITY

N	α					
	0	0.2	0.4	0.6	0.8	1.0
4	6.79	5.81	5.19	4.60	4.19	3.80
7	5.48	4.52	3.69	3.14	2.55	2.09
10	4.93	3.85	3.06	2.40	1.78	1.33
13	4.94	3.66	2.89	2.09	1.45	0.98

[a] All values quoted are in units of 10^{-9} g. sec.$^{-1}$.

ζ_0 deduced from experiment using the theoretical formulas differs from that deduced from the diffusion measurements by approximately a factor of two. We have been unable to find any explanation for this discrepancy except that the Peterlin theory of viscosity is, because of the approximations made, inconsistent with the more nearly correct theory of diffusion. Since
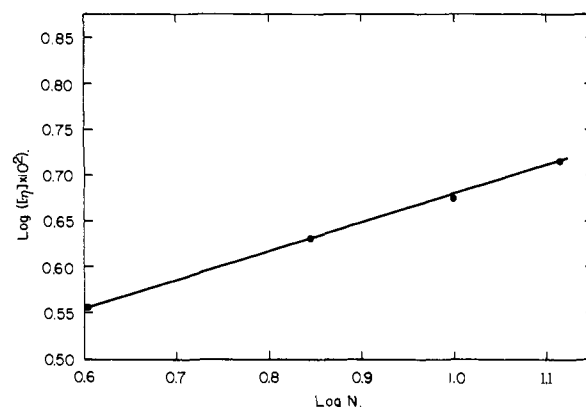

Fig. 2.—Dependence of limiting viscosity number on chain length for small N.

the theory does fit the experimental data with ζ_0 regarded as a parameter, we may ask if the theory makes proper predictions of the viscosities of long-chain molecules. To answer the preceding question we first examine the dependence of $[\eta]$ on N for small N. From the data in Table X we have constructed Fig. 2. It is seen that for the case of N small, the intrinsic viscosity is well represented by

$$[\eta] = 2.14 \times 10^{-2} N^{0.35} \qquad (11)$$

TABLE X

INTRINSIC VISCOSITIES OF VARIOUS AMINES

N	$[\eta]$ (100 cc./g.)
4	0.036
7	.043
10	.047
13	.052
PEI·(1)($N_{est} = 47$)	.099
PEI·(2)($N_{est} = 83$)	.131
PEI·(3)($N_{est} = 178$)	.192

For the case of large N, it is well known that the exponent of N cannot be less than 0.5. This conclusion depends, however, on the molecular configurations being representable as those of a Gaussian coil. That

the result quoted in eq. 11 is not spurious can be demonstrated by examination of other cases. For example, the viscosities of $Br[Me_3N(CH_2)_3NMe_3]Br$ and $Br[Me_3N(CH_2)_9NMe_3]Br$, measured by Goldberg and Fuoss,[14] correspond to a dependence of $N^{0.65}$ in water and only slightly higher in other solvents.

To proceed further we need values of N for the polymers available. It is expected that $[\eta] \propto N^{0.5}$ and this is found to be the case. Taking the transition from $[\eta] \propto N^{0.35}$ to $[\eta] \propto N^{0.5}$ to occur at the value of N characteristic of tetraethylenepentamine leads to $N_1 = 47$, $N_2 = 83$, and $N_3 = 178$, consistent with both the freezing point and diffusion measurements. If we accept the figures quoted and use the value of ζ_0 determined from the viscosities of the lower members of the series, the theory leads to

$$N = 50: \quad [\eta]_{calcd} = 10.5 \times 10^{-2}$$
$$[\eta]_{obsd} = 10.3 \times 10^{-2}$$
$$N = 90: \quad [\eta]_{calcd} = 13.1 \times 10^{-2} \qquad (12)$$
$$[\eta]_{obsd} = 13.8 \times 10^{-2}$$

where the observed values are taken from the line fitting the points on a plot of $\log [\eta]$ vs. $\log N$. It is difficult to make very accurate theoretical calculations of $[\eta]$ because the figures supplied in Peterlin's paper are difficult to read, and the calculations do not exceed $N = 90$. The agreement cited above may, therefore, be considered as a check for internal consistency.

The magnitude of the friction constant, ζ_0, is also of interest. Almost all studies of polymers dissolved in organic solvents lead to calculated monomer bead radii considerably smaller than expected.[15] Indeed, it is not uncommon for the effective Stokes' law radii to be a factor of five smaller than the known molecular radii. Similar but less marked effects have been noted in the case of the limiting conductances of monovalent ions in water. It is then of some interest that the value of a_0, deduced from the value of ζ_0, which fits the diffusion experiments, is 1.66 Å. This value is nearly the expected radius; it is close to the sum of the bond length (~1.05 Å.) and the covalent radius of hydrogen (~0.37 Å.). This observation can be rationalized as follows. The use of a hydrodynamic treatment implies that there is no slip between the (continuous) fluid solvent and the molecule. In the absence of specific forces, the molecular coarseness of a real fluid prevents this from being true on the scale of a molecular diameter. However, if specific forces exist, such as provided by hydrogen bonding, the classical hydrodynamic boundary condition of zero velocity at the boundary between the fluid medium and the solute molecule is likely to be satisfied. If this boundary condition is satisfied, classical hydrodynamics may be expected to hold even on the molecular scale. *Note that we are not implying that there is any bound solvent—only that hydrogen bonding tends to lead to zero differential velocity between the solute molecule and the first layer of solvent.*

We conclude, from the arguments presented, that the Peterlin theory of diffusion of short stiff chain molecules is an adequate characterization of real systems. However, mathematical approximations made lead to an inconsistency between the theory of diffusion and viscosity based on the same model.

B. Bolaform Ions.—We have examined two classes of bolaform electrolytes. The p,p'-polyphenyl disulfonates should be rigid and therefore describable by a hydrodynamic model very different from that suitable to the description of the (possibly) flexible ions

formed from the dihydrochlorides of ethylenediamine, ..., tetraethylenepentamine.

To examine the relationship between the frictional coefficients of the bolaform ions and its parent amine, the effect of K^+ or Cl^- on the diffusion constant must be removed from the raw data. We have already noted that the concentration dependence of the diffusion constant is very small. We therefore take as an approximation to D the relation[10]

$$D = \frac{RT}{\mathfrak{F}^2} \frac{(\nu_1 + \nu_2)}{\nu_1 |z_1|} \frac{\lambda_1^0 \lambda_2^0}{\lambda_1^0 + \lambda_2^0} \qquad (13)$$

where $\mathfrak{F}$ is the Faraday, ν_1 and ν_2 are the numbers of ions the electrolyte yields on dissociation, z_1, the valence of ion 1, and λ_1^0, λ_2^0 are the limiting conductances of the individual ions. Equation 13 which assumes independence of the ions arises from the breakdown

$$\zeta = \frac{\nu_1}{\nu_1 + \nu_2} \zeta_1 + \frac{\nu_2}{\nu_1 + \nu_2} \zeta_2 \qquad (14)$$

$$\zeta_i = |z_i| \mathfrak{F}^2 / \lambda_i^0 \qquad (15)$$

Since $\lambda^0_{Cl^-} = 76.35$ and $\lambda^0_{K^+} = 73.50$ at $25°$, we readily establish that $\zeta^0_{Cl^-} = 2.025 \times 10^{-9}$ g. sec.$^{-1}$ and $\zeta^0_{K^+} = 2.109 \times 10^{-9}$ g. sec.$^{-1}$. Using these values and eq. 14 the friction coefficients or diffusion constants of the bolaform ions may be computed. The values obtained are listed in Table IIIb. It is seen that the diffusion coefficient of a bolion decreases less rapidly with increasing N than does the value of D for the corresponding neutral molecule. We now consider whether the observed behavior is best described in terms of a flexible chain model or in terms of a rigid rod, since the presence of the repelling charges on the ends of the molecule may increase the end-to-end distance and stiffness so greatly that all chain flexibility is lost.

For a rodlike molecule, composed of successive spherical beads, the friction constant is given by[16]

$$\zeta = \frac{6\pi\eta_0 b_0 N}{\ln N - [1 - (6\pi\eta_0 b_0 / 2\zeta_0)]} \qquad (16)$$

It is this model molecule, and not the more familiar rigid ellipsoid, which we must consider as the limiting case in order to be consistent with our previous arguments. The friction constants of the constituent beads of a bolion will not all be the same because of the strong charge–solvent interaction. The use of a single friction constant is, therefore, an approximation. Nevertheless, it is readily seen that a plot of ND vs. $\ln N$ is linear as required by eq. 16. Previously, we found that ζ_0 was (fortuitously) close to $3\pi\eta_0 b_0$ and we may therefore anticipate that the second term in the denominator of eq. 16 plays little role in determining ζ. The experimental determination of ζ then requires the identification of $2\zeta_0$ with $6\pi\eta_0 b_0$; thus the slope of the plot mentioned will give ζ_0. By this method we find $\zeta_0 = 0.89 \times 10^{-9}$ g. sec.$^{-1}$. The accuracy of this determination is poor, and ζ_0 is subject to an uncertainty of a factor of two. Despite this uncertainty, it is worthwhile commenting that the average value of ζ_0 for the uncharged molecule is greater than that for the bolion. We shall comment further on this point in the last section of this paper.

To finish our comments on the diffusion coefficients of the bolions, it is pertinent to examine the behavior of the benzene disulfonates. We use, in this case, a rigid ellipsoid model for which[17]

$$\zeta = \frac{6\pi\eta_0(b^{*2} - a^{*2})^{1/2}}{\ln [(b^*/a^*) + ((b^*/a^*)^2 - 1)^{1/2}]} \xrightarrow{b^* >> a^*} \frac{6\pi\eta_0 b^*}{\ln (2b^*/a^*)}$$
$$(17)$$

(14) P. Goldberg and R. M. Fuoss, *Proc. Natl. Acad. Sci. U.S.*, **38**, 758 (1952).

(15) See, for example, C. Tanford, "Physical Chemistry of Macromolecules, John Wiley and Sons, Inc., New York, N. Y., 1961.

(16) J. G. Kirkwood and J. Riseman, *J. Chem. Phys.*, **18**, 512 (1950).

(17) F. Perrin, *J. Phys. Rad.*, **7**, 1 (1936).

with b^* and a^* the lengths of the semimajor and semiminor axes of the ellipsoid. A fit of the data is easily obtained, and it is found that the axial ratios and lengths of $TPDS^{-2}$, $BPDS^{-2}$, and BDS^{-2} are 7.00, 5.25, 3.00, and 21.6 Å., 16.2 Å., 9.3 Å., respectively. These dimensions agree moderately well with those obtained from molecular models: 8.02, 6.22, 4.43, and 19.40 Å., 15.06 Å., 10.72 Å.
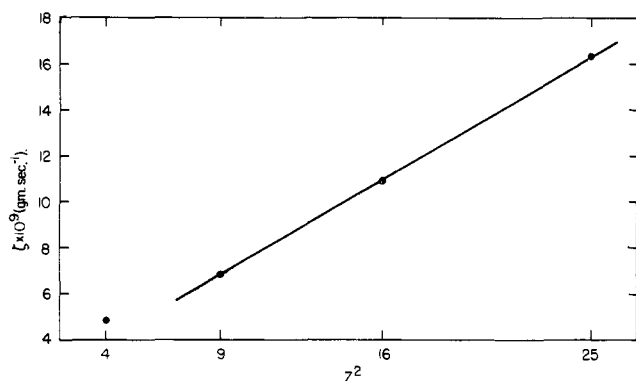

Fig. 3.—Dependence of friction constant on chain length for fixed number (2) of charges and on the number of charges.

We conclude, from the arguments presented, that the Kirkwood theory of diffusion of rod-shaped molecules is an adequate characterization of the behavior of the doubly charged amine ions. It appears that the friction constant per bead decreases even though the friction constant per ion increases (relative to the same quantities for the parent uncharged molecule) owing to increased hydrodynamic interaction between the monomer beads. The change in friction constant per bead will be related to changes in the solvent structure in the last section of this paper. Since the Kirkwood theory of diffusion of rod molecules is based on the same molecular model as the Peterlin (and Kirkwood) theory of diffusion of chain molecules, the fit obtained is a significant test of the internal consistency of the analysis. We may therefore regard with confidence the deduction that for the molecules ED, DT, TT, and TP, two charges at the ends of the molecule repel each other sufficiently to make dominant the completely stretched molecular configuration.

The limiting viscosity numbers of $ED \cdot 2HCl$, $DT \cdot 2HCl$, $TT \cdot 2HCl$, and $TP \cdot 2HCl$ are entered in Table IV. The Kirkwood theory[16] leads to the following expression for $[\eta]$

$$[\eta] = \frac{N \zeta_0 l^2}{3600 \eta_0 M_0} F(\lambda\delta) \qquad (18)$$

$\delta = 2/(N - 1)$, $\lambda = \zeta_0/6\pi\eta_0 b_0$, where l is the length of the molecule and $F(\lambda\delta)$ is a function varying between the limits 1.781 and 1 as N varies from zero to very large values. Also entered in Table IV are the values of $F(\lambda\delta)$ deduced from experiment. It is seen that asymptotic behavior is reached when $N = 13$, and that end effects dominate the behavior at small N, an observation in agreement with the interpretation of the diffusion measurements.

C. **Highly Charged Ions.**—We now turn to an examination of the behavior of highly charged ions. In view of the analysis of the preceding section, it is of particular interest to examine the change in friction constant with a change in the number of charges on the ion. The relevant data are summarized in Tables Va and Vb. As can be seen from Fig. 3, the friction constant is a smoothly increasing function of the number of charges on the ion. As might be expected, the friction constant increases in an extra linear man-
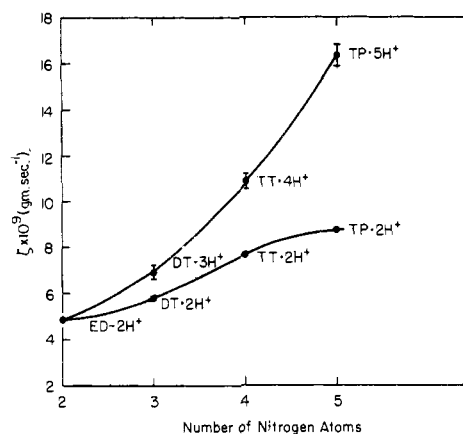

Fig. 4.—Dependence of friction constant on number of charges on the chain.

ner, indicating interaction between the density and flow patterns created by the superposed potential fields of the charges. This behavior is to be contrasted with that of the bolions, where ζ increases less than linearly between $N = 10$ and $N = 13$. Moreover, although the average value of ζ_0 decreased on going from the uncharged molecule to the bolion, it increases with each charge added after that. It is also clear from the data cited in Table IV and presented in Fig. 3 that the transition to polyion behavior has not yet been achieved for $TP \cdot 5H^+$ because of interactions caused by the flow fields about the charges, which interaction is larger than for the flow fields about uncharged beads. For, when the polymeric limit is reached, we expect that ζ will increase as $(N \ln N)$ or more slowly if the polyion is not fully stretched. Except for the point contributed by $ED \cdot 2H^+$, it is seen in Fig. 4 that the friction constant increases quadratically with the number of charges in the region of N examined. Our present studies are therefore in agreement with earlier equilibrium studies[11] of this system in establishing that the transition to polyion behavior requires more than five charges on a short-chain ion.

IV. Conclusions

One of the most interesting deductions which can be made from the data presented herein is that the average friction constant per bead drops on going from the neutral molecule to the bolion. We have already noted that if the solute molecule has hydrogen bonds to the solvent, the classical hydrodynamic boundary condition of zero slip is satisfied. Consider now the introduction of two charges on such a hydrogen-bonded molecule. Because of the orientation of solvent dipoles in the field of the charges, the hydrogen bond structure of the water is disrupted around an ion. Thus, the region of water between two charges, but far enough away from the charges that orientation effects are small, is robbed of its directional and structural bonds to the surrounding water molecules. Under these conditions, the effect of hydrogen bonding between the central portion of the solute bolion (say $TP \cdot 2H^+$) and the water is decreased, and the effective friction is thereby also decreased. If this decrease is large, the average friction constant can be less than that for the uncharged molecule. We believe this to be a possible explanation of the inferred behavior of ζ_0.

In conclusion, we have shown that the Peterlin theory of short chains provides an adequate description of the dependence of the friction constant on chain length. Peterlin's theory of viscosity is quantitatively inconsistent with experiment, but the qualitative de-

pendence of intrinsic viscosity on chain length is correctly described. Finally, the results described in this paper further confirm the observation that the transition from small ion to polyion behavior requires a rather large number of charges and a long chain.

Activation Energies from Bond Energies. I. Hydrogen Transfer Reactions

BY HAROLD S. JOHNSTON AND CHRISTOPHER PARR

A new procedure is proposed that uses bond energies and other properties of reactant molecules and no adjustable parameters from kinetic data to calculate activation energies and rate constants of elementary bimolecular hydrogen-transfer reactions. The new method is compared with theoretical treatments of this problem and with the semi-empirical approach of London, Eyring, Polanyi, and Sato. For all reactants of fairly well known bond energies, the method calculates activation energies within about 2 kcal. and rate constants within about an order of magnitude. The concepts used in this treatment are from ultra-simple valence-bond theory and ultra-simple activated-complex theory. The success of the method is regarded not to reflect validity on the assumptions used.

Introduction

The "activation energy" of a chemical reaction is the measure of how the specific rate k of the reaction changes with temperature

$$E = -R\, \partial \ln k / \partial (1/T) \qquad (1)$$

where R is the gas constant. Over a finite range of temperature the activation energy is usually regarded as if constant, and the specific rate expressed in the Arrhenius form

$$k = A e^{-E/RT} \qquad (2)$$

For many years chemists have been interested in calculating activation energies. These efforts can be classified as one of the following: I, theoretical; II, semi-empirical; III, 100% empirical, but the empiricism 100% *outside* the field of chemical kinetics.

The only chemical reaction for which serious attempts have been made to carry out a theoretical evaluation of activation energy is the hydrogen molecule–hydrogen atom exchange reaction, observable as para–ortho conversion of H_2, ortho–para conversion of D_2, or isotopic exchange between hydrogen and deuterium. These reactions are represented as

$$H + H\text{-}H \longrightarrow H\cdots H\cdots H \longrightarrow H\text{-}H + H \qquad (3)$$
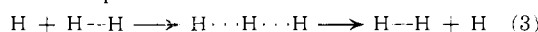
These calculations start with London,[1] in 1928, were pursued over the years by Eyring and co-workers,[2] and brought to the highest stage of development yet reported by Boys and Shavitt in Hirshfelder's group.[3,4] References to other workers in this area are given in the articles cited.[2-4] The calculations by Boys and Shavitt were much more refined and complete than previous ones, and only these calculations will be reviewed here. The potential energy surface for three hydrogen atoms was constructed by[4] "a linear variational calculation of the superposition of configuration type...6 1s-orbitals...66 configurations..." This major computation gave remarkably good agreement so far as absolute energy is concerned: the calculated binding energy of H_3 was 80.2 kcal./mole and the experimental value is about 102. The calculated binding energy for H_2 (using the same level of approximation) was 95.6 kcal./mole, and the experimental value is 109.32. The calculated potential energy of activation

was 15.4 kcal./mole, and the observed value is about 6 to 8. For the hydrogen molecule the H–H bond distance was calculated accurate to 1.4% and the force constant to 5.2%. The most stable form of the complex was found to be linear, in agreement with all earlier theoretical work on this case. The potential energy surface when plotted against the two bond lengths of the H_3 complex gave a smooth, single, symmetrical saddle point. From the location of the saddle point and from curvatures evaluated at the saddle point, Shavitt[4] used activated complex theory to calculate the specific rate or rate constant k for reaction 3. This 100% theoretical calculation of the rate constant is shown as the dashed line in Fig. 1, along with the experimental data[5-7] on the para–ortho H_2 conversion. The theoretical line lies below the experimental points by about a factor of 10^2 at 1000°K. and 10^4 at 300°K. A chemical kineticist is not satisfied with the accuracy of this theoretical calculation, yet one certainly agrees with Shavitt[4] that "it is not expected that this situation will be much improved except by a calculation that is some orders of magnitude greater than that of Boys and Shavitt." The qualitative aspects of these theoretical studies (linear, symmetrical complex, and the general nature of the potential energy surface) are of great value to the kineticist, who is forced to seek a chemist's solution to a chemical problem in going beyond the H_3 reaction.

The "semi-empirical" approach to evaluating potential energy surfaces was developed by Polanyi and Eyring[8,9] from the theoretical work of London.[1] The simplest quantum mechanical theory of the hydrogen molecule is that of Heitler and London,[10] and the theoretical expressions for stable singlet and unstable triplet hydrogen molecule are

$$W_{\mathrm{S}} = (A + \alpha)/(1 + \Delta), \quad W_{\mathrm{T}} = (A - \alpha)/(1 - \Delta) \qquad (4)$$

where A, α, and Δ are definite integrals defined in the Heitler–London theory (sometimes named, respectively, the Coulomb, exchange, and overlap integrals). The Heitler–London theory gives the dissociation

(1) F. London, "Probleme der modernen Physik, Sommerfeld Festschrift." S. Hirzel, Leipzig, 1928, p. 104; Z. Elektrochem., **35**, 552 (1929).

(2) R. S. Barker, R. L. Snow, and H. Eyring, J. Chem. Phys., **23**, 1686 (1955).

(3) S. F. Boys and I. Shavitt, University of Wisconsin Naval Research Laboratory Technical Report WIS-AF-13 (1959).

(4) I. Shavitt, J. Chem. Phys., **31**, 1359 (1959).

(5) A. Farkas, Z. physik. Chem., **B10**, 419 (1930); Table 2 (factor of 4 error in this table was corrected).

(6) M. van Meerssche, Bull. soc. chim. Belges, **60**, 99 (1951); Table 111.

(7) K. H. Geib and P. Harteck, Z. physik. Chem. Bodenstein-Festband, 849 (1931), experiments 9-13.

(8) H. Eyring, Naturwissenschaften, **18**, 914 (1930); H. Eyring and M. Polanyi, Z. physik. Chem., **12B**, 279 (1931); H. Eyring, J. Am. Chem. Soc., **53**, 2537 (1931).

(9) S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(10) Any textbook on quantum chemistry.