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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MICHIGAN]

The Kinetics of the Thermal Decomposition of Pentachloroethane[1]

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The pyrolysis of C_2Cl_5H has been studied in a flow system between 407 and 438°. A cyclone-stirred flow reactor with helium as a carrier gas was used. Additional experiments in a packed tubular flow reactor with helium and nitrogen were also made. Contact time ranged from 6 to 35 seconds; initial concentrations ranged from 10^{-4} to 10^{-3} mole/liter. Major products were C_2Cl_4 and HCl; small amounts of C_2Cl_3H and Cl_2 were also formed. The ratio of HCl to Cl_2 had a nearly constant value of 470. Progress of the reaction was followed by titration of the HCl evolved. The data obtained in the cyclone-stirred reactor may be represented by the expression $\mathrm{d}x/\mathrm{d}t = k(a - x)(1 + bx)^{1/2}$, where the rate constant k and the acceleration constant b are: k (sec.$^{-1}$) $= 10^{13.0} \exp(-48{,}000/RT)$ and b (l./mole) $= 10^{-2.1} \exp(+23{,}000/RT)$ The integrated form of this rate expression fits the data from the tubular reactor. The rate of pyrolysis of pentachloroethane-*d* (91% D) was *ca.* 40% lower than that of C_2Cl_5H. Because of autocatalysis due to Cl_2 formation and inhibition by added propylene and CCl_3H, the pyrolysis appears to be a radical chain reaction with the initial step involving a C–Cl rupture. $D(C_2HCl_4–Cl)$ estimated from the present results is 72 kcal./mole.

Introduction

The pyrolysis of pentachloroethane was studied briefly by Barton[2] using a flow system with a clean-walled reactor. He reported that the kinetics were first order and that tetrachloroethylene and hydrogen chloride were the only products up to 450°. The present investigation, consisting of a more detailed study of the products and kinetics of the thermal decomposition of pentachloroethane and pentachloroethane-*d*, revealed a number of new features of the reaction and has suggested an auto-catalytic radical chain mechanism.

Experimental

The flow system was similar to that used in the study of the kinetics of pyrolysis of chloroform.[3] A known quantity (*ca.* 2 mmoles) of purified pentachloroethane[4] was introduced, at a constant known rate by a motor driven syringe, into a carrier stream of purified helium gas (1 atm.) and passed through a Vycor "cyclone-type" reaction chamber[5] which had been previously conditioned[6] (carbonized) by the equivalent of about one hundred pyrolysis runs.

The organic products in the exit gases were removed by a series of cold traps at −30° and −78°. Hydrogen chloride was trapped in a bubble tower, following the cold traps, containing an excess of sodium hydroxide solution and determined by back titration. The efficiency of the cold traps was proven in connection with the calibration of the syringe since the amount of pentachloroethane trapped was equal to the amount injected (±1%). The efficiency of the bubbler was demonstrated in two ways: (a) a second bubbler placed in series with the first during a run showed no chloride; (b) a known amount of hydrogen chloride was generated, passed through the reactor and trapped quantitatively.

The organic products from certain runs trapped at −195° were analyzed with a Perkin–Elmer Model 21 spectrophotometer (NaCl optics). The products were identified and assayed by comparing the spectrum of the products mixture with the spectra of known compounds at similar concentrations.

A large number of experiments were made under special conditions: (a) a tubular, packed Vycor reactor (surface area to volume ratio ten times greater than that in the "cyclone" reactor), conditioned as before, was used, (b) purified nitrogen was used as the carrier gas, (c) a series of compounds,[7] including all the observed products, were

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[1] From the Ph.D. dissertation of T. J. H., University of Michigan, 1957, available from University Microfilms, Ann Arbor, Mich.

[2] D. H. R. Barton, *J. Chem. Soc.*, 149 (1949).

[3] G. P. Semeluk and R. B. Bernstein, THIS JOURNAL, **76**, 3793 (1954); **79**, 46 (1957).

[4] The pentachloroethane ($n^{25}\mathrm{D}$ 1.5005) was prepared by the chlorination of trichloroethylene and purified by distillations at atmospheric and reduced pressure, then chromatographed through a silica gel column. Cryoscopic measurements indicated a purity >99.5 mole %.

[5] The reactor was constructed similar to a cyclone separator (volume equal to 64 ml.), designed to give complete mixing (C. B. Shepherd and C. E. Lapple, *Ind. Eng. Chem.*, **31**, 972 (1932)).

[6] The conditioning was necessary to eliminate the heterogeneous component of the reaction so that reproducible, homogeneous kinetics could be obtained (D. H. R. Barton and K. E. Howlett, *J. Chem. Soc.*, 155 (1949)).

[7] Dilute solutions of tetrachloroethylene, trichloroethylene and chloroform in pentachloroethane were made up and injected as usual. The tank gases (nitric oxide, propylene and hydrogen chloride) were mixed at known concentrations with the carrier gas during a normal injection of pentachloroethane. Oxygen, hydrogen and chlorine were generated by electrolysis (water and fused lead chloride, respectively), then mixed with the carrier gas.

added, (d) the pyrolysis of pentachloroethane-*d* was studied to determine the deuterium isotope effect.[8]

Results[9] and Discussion

A. Stoichiometry of Decomposition.—Infrared analysis of the organic products at nearly complete (97%) and intermediate decompositions (40 to 50%) showed tetrachloroethylene as the only major organic product formed, along with trace amounts of trichloroethylene (less than 1% of the tetrachloroethylene). Hydrogen chloride and small amounts of chlorine constituted the gaseous products. The amount of HCl produced (determined by titration) was within 1% of the loss of C_2Cl_5H (determined by infrared analysis).

Quantitative measurements of HCl and Cl_2 (Cl_2 was trapped in a KI solution which was then titrated with sodium thiosulfate) produced during decompositions at 427 and 437° gave a constant ratio $z \equiv [HCl]/[Cl_2]$ of 470 ± 40 for C_2Cl_5H; for C_2Cl_5D, z was 235, with a somewhat greater uncertainty.

These observations indicate that dehydrochlorination represents the essential feature of the stoichiometry: $C_2Cl_5H \rightarrow C_2Cl_4 + HCl$, and that the HCl produced is a reliable measure of the extent of decomposition.

B. Cyclone-stirred Flow Reactor.—By using a stirred reactor it was possible to study the kinetics of the reaction in more detail since the rate of reaction could be evaluated numerically[10]: rate $= x/t$, where x is the concentration (moles/liter) of HCl (or DCl) in the exit stream and t is the contact time. Figure 1 is typical of the kinetic data obtained. The data are expressed as the fraction of C_2Cl_5H decomposed, x/a *vs.* t (where a is the initial concentration of C_2Cl_5H). The solid lines are calculated lines based on eq. 1, 2 and 3 (below).

The reaction is not first order (since a plot of x/a *vs.* t would be independent of a) but appears to be autocatalytic. Sets of data at different values of a were obtained to determine the concentration dependence of the rate. The rate expression derived from the data is

$$\text{rate} = x/t = k(a - x)\,(1 + bx)^{1/2} \qquad (1)$$

where $(a - x)$ is the concentration of C_2Cl_5H or C_2Cl_5D in the exit stream, k is the initial rate constant and b is the acceleration constant. Plots of $[x/t(a - x)]^2$ *vs.* x are linear, the square root of the intercept equal to k and the ratio of slope to intercept equal to b. The results for C_2Cl_5H are summarized in Table I. The estimated uncertainties in k and b are ±10 and ±25%, respectively.

TABLE I

RATE CONSTANTS FOR THE PYROLYSIS OF PENTACHLOROETHANE

T (°K.)	$10^2\,k$ (sec.$^{-1}$) Obs.	$10^2\,k$ (sec.$^{-1}$) Calcd.[a]	$10^{-5}\,b$ (l./mole) Obs.	$10^{-5}\,b$ (l./mole) Calcd.[b]
680	0.386	0.372	1.55	1.55
691	0.626	0.654	1.19	1.20
700	1.093	1.053	0.89	0.97
710	1.670	1.740	0.94	0.77

[a] Calculated from the equation

$$k = 10^{13.0} \exp(-48{,}000/RT) \qquad (2)$$

determined by the method of least-squares from a plot of log k *vs.* $1/T$. [b] Calculated from the equation

$$b = 10^{-2.1} \exp(+23{,}000/RT) \qquad (3)$$

determined from a plot of log b *vs.* $1/T$.

The reproducibility of the data for C_2Cl_5D was not as good as that for C_2Cl_5H. The uncertainty in k and b (Table II) is therefore much larger than for C_2Cl_5H.

TABLE II

RATE CONSTANTS[a] AND ISOTOPIC RATE FACTORS[b] FOR PENTACHLOROETHANE-*d*

T (°K.)	$10^2\,k$ (sec.$^{-1}$)[a]	$10^{-5}\,b$ (l./mole)	(k_H/k_D)[b]
680	0.243	2.61	1.59
691	.426	1.99	1.47
700	.679	1.41	1.61
710	1.105	1.34	1.51
		Av.	1.54 ± 0.06

[a] Because of the scatter in the plots of $[x/t(a - x)]^2$ *vs.* x for C_2Cl_5D, it was not possible to obtain reliable values for the intercepts (k^2), although the slopes (k^2b) could be determined within about 10%. With the one assumption that the pre-exponential factor for k_D was the same as that for k_H the data were best represented by the equation

$$k_D = 10^{13.0} \exp(-48{,}600/RT) \qquad (4)$$

from this and the slopes the values of b were computed. [b] From the mean value of the isotope rate factor for the 91% D material one estimates the ratio $k_H/k_D = 1.59$ referred to pure C_2Cl_5D.

Figure 2 illustrates the dependence of the calculated results on the value of b. The solid and dashed curves are calculated for $b = 7.7 \times 10^4$ and 8.5×10^4 l./mole, respectively, holding k constant.

C. Tubular Flow Reactor.—Figure 3 illustrates the results of the experiments carried out in the packed tubular, flow reactor at 438°. The curves refer to initial concentration ranges of 1.6–5.9, 0.8–3.1 and 0.4–1.5 × 10^{-4} moles/l. C_2Cl_5H. The lines are theoretical curves calculated from the integrated form of the rate equation

$$kt = \frac{2.303}{(1 + ab)^{1/2}} \log \left\{ \frac{[(1 + ab)^{1/2} + (1 + bx)^{1/2}}{[(1 + ab)^{1/2} - (1 + bx)^{1/2}} \times \frac{(1 + ab)^{1/2} - 1]}{(1 + ab)^{1/2} + 1]} \right\} \qquad (5)$$

where a, t, x, b and k have the same significance as before. The values of the constants used in the calculation were $b = 7.5 \times 10^4$ l./mole (assumed the same as in the cyclone-stirred reactor) and $k = 1.33 \times 10^{-2}$ sec.$^{-1}$ (best fit to the data using eq. 5), which is in fair agreement with the data obtained in the stirred reactor.[11]

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(8) Pentachloroethane-*d* was prepared by the base-catalyzed exchange between trichloroethylene and deuterium oxide, followed by chlorination of the organic product (T. J. Houser, R. B. Bernstein, R. G. Miekka and J. C. Angus, THIS JOURNAL, **77**, 6201 (1955)). Purification was the same as for pentachloroethane; cryoscopic measurements showed a purity >99.9 mole %. The product was 91 ± 1% deuterated as determined by infrared and mass spectrometer analysis.

(9) A compilation of original data has been deposited as Document number 5545 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting $1.25 for photoprints or $1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

(10) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953.

(11) The surface area to volume ratio was 19 cm.$^{-1}$ in the packed, tubular reactor compared to 2 cm.$^{-1}$ in the stirred reactor. Assump-

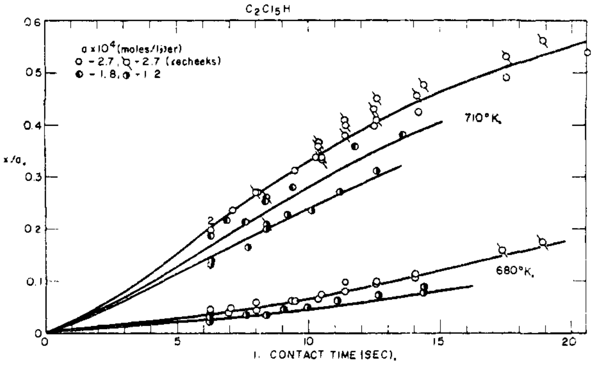

Fig. 1.—Stirred reactor. Fraction of HCl formed *vs.* contact time.

Some experiments in the tubular reactor were made using nitrogen as a carrier gas; the rate of decomposition was greater by about 25% relative to the rate with the He carrier. Several compounds were added[12] to the gas stream to determine their influence on the reaction and to establish radical chain nature of the reaction. Three of the products of the reaction, C_2Cl_4, C_2Cl_3H and HCl, as well as O_2 and NO, had no significant effect on the rate of HCl production. H_2, propylene and CCl_3H, however, reduced the rate significantly. Additions of Cl_2 at very low concentrations (comparable to those produced in the reaction, *ca.* 10^{-7} mole/l.) caused large increases in the rate, thus suggesting the origin of the autocatalytic nature of the reaction. The increases in the rate agree fairly well with those calculated from the increased Cl_2 concentrations, assuming $Z = 470$ and employing the rate equation 1.

D. Mechanism of Reaction.—The mechanism proposed to explain the observed rate law

$$-d[C_2Cl_5H]/dt = k[C_2Cl_5H]\{1 + b'[Cl_2]\}^{1/2} \quad (6)$$

where $b' = zb$, is

(1) $C_2Cl_5H \longrightarrow C_2Cl_4H\cdot + Cl\cdot$
(2) $Cl\cdot + C_2Cl_5H \longrightarrow C_2Cl_5\cdot + HCl$
(3) $C_2Cl_5\cdot \longrightarrow C_2Cl_4 + Cl\cdot$
(4) $C_2Cl_4H\cdot \longrightarrow C_2Cl_3H + Cl\cdot$
(5) $Cl\cdot + C_2Cl_5\cdot \longrightarrow C_2Cl_4 + Cl_2$
(6) $Cl_2 + C_2Cl_5H \longrightarrow C_2Cl_5\cdot + Cl\cdot + HCl$

Use of the steady-state assumption yields the above rate expression, eq. 6, with $k = (k_1k_2k_3/k_5)^{1/2}$ and $b' = k_6/k_1$.

The proposed mechanism indicates that $E_k = (E_1 + E_2 + E_3 - E_5)/2$ and $E_b = E_6 - E_1$. Using the experimental values of 48 and −23 kcal./mole for E_k and E_b, respectively, and assuming $E_2 = 3$, $E_3 = 21$ and $E_5 = 0$ kcal./mole, one obtains $E_1 = 72$ and $E_6 = 49$ kcal./mole.[13] The above value of $E_1 = 72$ kcal./mole appears reasonable for the C–Cl bond dissociation energy in pentachloroethane.

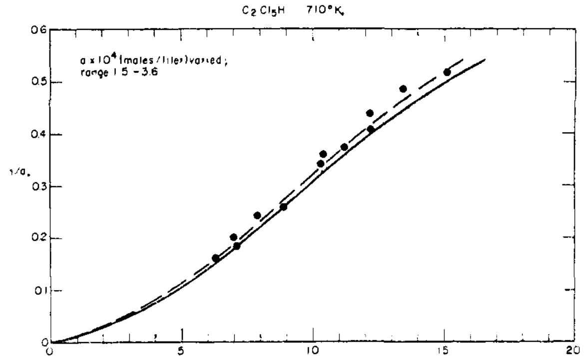

Fig. 2.—Stirred reactor. Fraction of HCl formed *vs.* contact time: ———, b = 7.7 × 10⁴ l./mole; - - - -, b = 8.5 × 10⁴ l./mole.

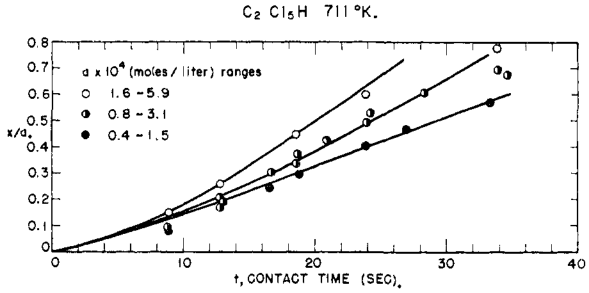

Fig. 3.—Tubular reactor. Fraction of HCl formed *vs.* contact time.

The isotope effect for the initial rate is $k_H/k_D = (k_{1H}k_{2H}/k_{1D}k_{2D})^{1/2}$. The ratios k_{1H}/k_{1D} and k_{2H}/k_{2D} may be estimated to be about 1.03 and 2.18, respectively, at 700°K. using the method of Bigeleisen,[14] with assumptions (a) the "rigid model" for the activated complex, and (b) the formation of the new D–Cl bond in mechanism step (2) has negligible influence on the isotope effect. Newton and Rollefson[15] measured the relative rates of photochlorination of CCl_3H and CCl_3D from 253–453°K. Extrapolation of their results to 700°K. gives $k_{2H}/k_{2D} = 2.35$, subject to considerable uncertainty. Using the value 2.18 the resulting calculated ratio is $k_H/k_D = 1.50$, to be compared with the experimental value of 1.59.[16] A complete discussion of the isotope effect in b and its relationship to k_{6H}/k_{6D} has been given elsewhere.[1]

The N_2 inert gas effect can be explained by modifying steps 1, 3 and 4 in the mechanism as[17]

$$M + C_2Cl_5H \longrightarrow C_2Cl_4H\cdot + Cl\cdot + M \quad (1')$$
$$M + C_2Cl_5\cdot \longrightarrow C_2Cl_4 + Cl\cdot + M \quad (3')$$
$$M + C_2Cl_4H\cdot \longrightarrow C_2Cl_3H + Cl\cdot + M \quad (4')$$

where M is the inert gas. Using the steady-state treatment as before, the rate law becomes

$$d[C_2Cl_5H]/dt = k[M][C_2Cl_5H]\{1 + b'[Cl_2]/[M]\}^{1/2}$$

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tions of no longitudinal mixing in the tubular reactor and complete mixing in the cyclone-stirred reactor are made in the kinetic treatment of the data.[10] The fit of the data to the rate expressions confirms the validity of these assumptions.

[12] Amounts added were in the following ranges, expressed as mole % relative to C_2Cl_5H: C_2Cl_4, 23–54; C_2Cl_3H, 0.7–1.3; HCl, 15–30; O_2, 25–60; NO, 21–24; H_2, 35–74; C_3H_6, 16–47; CCl_3H, 0.3–0.8; Cl_2, 0.01–0.03.

[13] These values for E_2 and E_3 are from J. Adam and P. Goldfinger, *Bull. soc. chim. Belg.*, **65**, 561 (1956). Using thermochemical data and bond dissociation energies (M. Szwarc, *Chem. Revs.*, **47**, 75 (1950)) one estimates a value for E_6 of 46 kcal./mole.

[14] J. Bigeleisen, *J. Chem. Phys.*, **17**, 675 (1949).

[15] T. W. Newton and G. K. Rollefson, *ibid.*, **17**, 718 (1949).

[16] Table II, footnote *b*.

[17] A similar treatment is made in the pyrolysis of CCl_3H, footnote (13) of reference (3b).

As the efficiency of the carrier gas for energy transfer to the substrate increases, the rate should increase.

A number of other mechanisms were considered; these included several radical mechanisms, some of which involved primary fission of the C–H or C–C bonds[18] or intramolecular elimination of HCl, but consideration of the observed rate expression, products, estimated bond dissociation energies, isotope effect and influence of radical chain inhibitors indicates that the proposed mechanism is the simplest to account for these features.

Acknowledgments.—Support of this work by the U. S. Atomic Energy Commission Contract No. AT(11-1)-321 and the Michigan Memorial-Phoenix Project is gratefully acknowledged.

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[18] The C–H bond dissociation energy in CCl_3H is estimated to exceed by some 20 kcal. the highest reasonable value for the C–Cl bond energy, 72 kcal./mole.[3] This is presumed to be the case for C_2Cl_5H as well.

Several other products would have been formed (CCl_4, CCl_3H, CCl_2H_2, etc.), if the C–C bond had ruptured.

[CONTRIBUTION FROM THE NAVAL MEDICAL RESEARCH INSTITUTE]

Transport Processes in Electrolyte Solutions[1]

BY R. J. PODOLSKY

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A lattice model that takes ion–solvent interaction into account is developed for aqueous electrolyte solutions. Application of absolute reaction rate theory to this model quantitatively correlates (a) the influence of an ion on the fluidity of a solution, (b) the influence of an ion on the self diffusion of the solvent, and (c) the limiting mobility of an ion. Also, the dependence of the limiting ionic mobility on temperature and on pressure is considered. Data for thirty-eight ionic species, with crystal radius less than or equal to 4 Å., are used to test the theory.

Although the theory for the change in rate of an ionic transport process with concentration is quite advanced,[2,3] the variation of rate with ionic species is only poorly understood. The hydrodynamic model, based on analogy with the motion of a macroscopic sphere through a viscous fluid, has serious shortcomings for ions of nearly the same size as the solvent molecule. This group includes most of the inorganic ions as well as the smaller organic ions. Since there is convincing evidence[4–6] that aqueous electrolyte solutions are highly structured, we thought it might be appropriate to use a lattice model for transport phenomena involving these ions. In the present paper fluidity, ionic mobility and solvent self diffusion are considered. The discussion is restricted to aqueous solutions of ions with crystal radius less than 4 Å.; however, because of their abnormal conduction mechanism,[4,7] the hydrogen and hydroxyl ions have been excluded.

Notation.—Since the connections between three different transport phenomena are considered, it is necessary to use an extensive list of symbols. For convenience, the definitions have been collected in Table I.

The Lattice Model for Transport Processes in Liquids.—The electronic distribution of the water molecule leads to formation of hydrogen bonds between adjacent molecules.[4,8] The most compelling evidence is the low density of ice and water compared with the density calculated on the basis of a close packed structure. This requires the strong directional forces that are characteristic of chemical bonds. Except at high temperatures, the liquid retains much of the crystalline character of the solid. With this high degree of coördination, the lattice model of the liquid state would be expected to be particularly relevant to water.

The lattice model has been used by Eyring and his collaborators[9] in the application of absolute reaction rate theory to transport processes in liquids. Brownian motion is considered to be a series of activated transitions between sites in a lattice structure. To make a transition a molecule must free itself of the "cage" formed by interaction with adjacent water molecules. The necessary energy is the activation energy for transition, ΔF^*_0. Transport results from superposition of a directional bias upon this random molecular motion.

In the case of self diffusion the directional bias stems from a concentration gradient of labeled molecules. It can be shown that the self diffusion coefficient D is related to the lattice spacing λ and the activation energy ΔF^*_0 by the expression[9]

$$D = \frac{RT}{Nh}\lambda^2 e^{-\Delta F^*_0/RT} \tag{1}$$

where R is the gas constant, T is the temperature, N is Avogadro's number and h is Planck's constant.

A velocity gradient generates the directional bias in the case of viscous flow. The relation between the fluidity ϕ and the lattice characteristics can be shown to be[9]

$$\phi = \frac{\lambda_2\lambda_3}{\lambda_1}\lambda^2 e^{-\Delta F^*_0/RT} \tag{2}$$

In this equation λ_1, λ_2 and λ_3 are parameters describing the lattice geometry; to a first approximation they can be set equal to λ.

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[1] The opinions expressed herein are those of the author and are not to be construed as official or reflecting the views of the Navy Department or the Naval service at large.

[2] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," Reinhold Publ. Corp., New York, N. Y., 1943.

[3] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Academic Press, New York, N. Y., 1955.

[4] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

[5] H. S. Frank and M. W. Evans, *ibid.*, **13**, 507 (1945).

[6] R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., New York, N. Y., 1953.

[7] E. Hückel, *Z. Elektrochem.*, **34**, 546 (1928).

[8] C. A. Coulson, *Research*, **10**, 149 (1957).

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