CONDUCTANCE, E.M.F., AND ACID–BASE CATALYSIS IN DEUTERIUM OXIDE

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An examination of the effects of deuterium substitution upon the properties of the oxide water discloses several interesting features. Those properties which are ordinarily classified as physical undergo as a rule less change on passing from the proto to the deutero form than do the properties which are classified as chemical. For example, the melting point of the waters is increased from 0° to 3.8°C., or +1.39 per cent on the absolute scale of temperature; the boiling point +0.39 per cent; the latent heat of fusion +6 per cent; and the latent heat of evaporation +2.5 per cent.

On the other hand, it is not unusual for equilibrium constants to be increased or decreased three- to four-fold; i.e., the substitution of D_2O for H_2O as the solvent for the reaction produces effects which are roughly one hundred fold greater than are the effects upon purely physical properties.

A noteworthy exception is the viscosity. Here we find a decrease of 23.2 per cent on passing from H_2O to D_2O. Since the mobilities of the ions are determined primarily by viscosity, it is to be expected that the conductance of electrolytes will be reduced in corresponding manner.

Aside from the viscosity, the dielectric constant plays the dominating rôle in influencing the behavior of electrolytes, since this property determines the electrical free energy of the ions. The recent measurements of Horst Muller (14) and of Abadie and Champetier (1) indicate that the dielectric constants of D_2O and H_2O agree within 1 per cent. The dipole moments of H_2O and D_2O are identical. This fortunate circumstance permits a variation in viscosity without the complication of having the dielectric constant vary at the same time. In deuterium and protium oxides, nature has given us two single-component isodielectric solvents which are free from the objection which complicates the use of two-component isodielectric solvents; namely, that one component by virtue of its greater polarizability will be attracted to the neighborhood of an ion and the second component will be repelled from that neighborhood.

Table 1 summarizes the effects of deuterium substitution upon the acidic

dissociation constants of weak acids. Particularly striking is the sixfold decrease in the ion product of the solvent. It is natural to expect, therefore, that the kinetics of acid–base catalyzed reactions should exhibit

TABLE 1

The effect of deuterium substitution on the acidic dissociation constants of weak acids

$K \times 10^z$	VALUE IN		K_H/K_D	OBSERVER*
	H_2O	D_2O		
$H_3O^+ \rightleftharpoons H_2O + H^+$	55.5	55.4	$\sim$1	Calculated
Chloroacetic acid $\times 10^3$	1.7	0.6	3.	S.
Salicylic acid $\times 10^3$	0.97	0.25	3.8	K.
Acetic acid $\times 10^5$	1.84	0.58	3.2	C.
$NH_4^+ \rightleftharpoons NH_3^0 + H^+ \times 10^0$	5.5	2.0	2.3	S.
Hydroquinone $\times 10^{11}$	2.6	0.68	3.8	K.
$(H^+)(OH^-)$ $\times 10^{14}$	1.00	0.16	6.2	A., B., and R.

* S. = Lewis and Schutz.
  K. = Korman and La Mer.
  C. = La Mer and Chittum.
  A., B., and R. = Abel, Bratu, and Redlich.

TABLE 2

Effect of the substitution of deuterium for protium on reaction kinetics

REACTION	CATALYST	k_H/k_D	OBSERVER*
Nitroethane neutralization	OH^-	6.0	W. J.
Sucrose inversion	H_3^+O	0.5	G. S. S.
Ester hydrolyses	H_3^+O	0.67	
	OH^-	0.75	W. J.
Nitramide decomposition	H_2O	5.2	V. K. L. and J. G.
Mutarotation of glucose	H_2O	3.86	W. H. H. and V. K. L.
	H_3O^+	1.32	W. H. H. and V. K. L.
	Ac^-	2.50	W. H. H. and V. K. L.
	$(Hac)^0$	2.2	W. H. H. and V. K. L.

* W. J. = Wynne-Jones.
  G. S. S. = Gross, Suess, and Steiner.
  J. G. = La Mer and Greenspan.
  W. H. H. = Hamill and La Mer.

pronounced effects. Table 2 shows that not only are the kinetic effects surprisingly large, but they may be either positive or negative.

The first reaction involves the rate of neutralization of the pseudo-acid nitroethane by hydroxyl ion and by deuteroxyl ion. The successive stages of this reaction were investigated by Wynne-Jones, using conductance

titrations. His results indicate that the rate at which a deuton in the nitroethane molecule is donated to a base, like OH^- or OD^-, is six times slower than the rate at which a proton is donated to the corresponding base.

On the other hand, for the inversion of cane sugar—a reaction catalyzed exclusively by hydrogen ion—the rate is twofold faster in D_2O than in H_2O.

The various H^+-catalyzed ester hydrolyses appear to give uniform values of 0.67; the alkaline hydrolyses give 0.75 for the ratio k_H/k_D. The solvent decomposition of nitramide exhibits a decrease of 5.2 fold on passing from H_2O to D_2O.
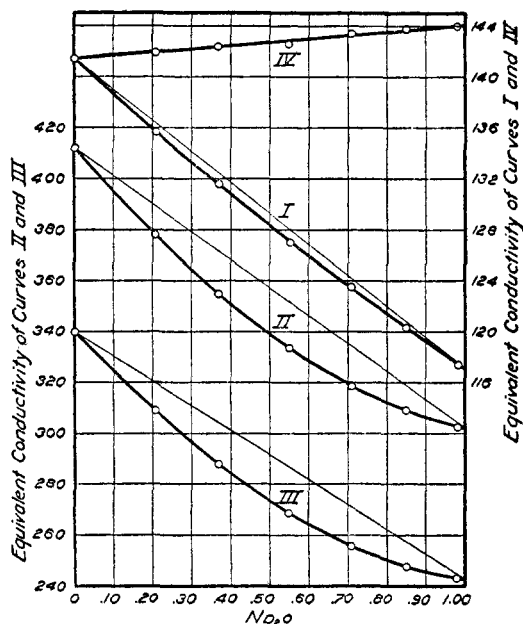
FIG. 1. Conductance data

The mutarotation of glucose is a reaction which is subject to multiple catalysis, but (by control of the pH and an accurate knowledge of the composition) it is possible to disentangle the effects of water, of H^+ ion, of basic ions (like acetate), and finally, even the catalysis due to the undissociated molecule of acetic acid, without ambiguity and with considerable precision, as shown recently (11) by Hamill and the author.

The interpretation of these acid–base catalyzed reactions requires an accurate knowledge of the dissociation constants of the acid–base systems involved. Since it is often impossible to obtain sufficiently large quantities of 100 per cent D_2O to carry out the kinetic measurements, it is necessary to resort to mixtures of D_2O and H_2O as the solvent.

An interesting question immediately arises. Are the kinetic and equilibrium constants sufficiently linear functions of the deuterium content of the solvent, so that it is safe to extrapolate data at intermediate concentrations to pure D_2O? The answer in many cases is emphatically "No!" Both the kinetic and equilibrium-constant data frequently exhibit curves with marked sags.

Figure 1 summarizes the conductance data of Weldon Baker (3). Curve I for potassium chloride indicates an almost linear decrease in equivalent conductance with increasing deuterium content of the solvent. Paul Walden has for many years advocated the rule that the mobility of ions in different solvents, when extrapolated to infinite dilution, should be inversely proportional to the viscosity of the solvent; i.e., $\Lambda_0\eta$ = constant. The Debye–Hückel–Onsager conductance equation yields the same result, provided that on passing from one solvent to another to vary the viscosity, the effective ionic carriers and their effective radii remain unchanged. H_2O and D_2O represent two ideal solvents for testing the Walden rule. Since their dielectric constants are identical, the ionic cloud effects should be identical at the same low concentration $(0.01\ M)$ in both solvents. Hence $\Lambda\eta$ should also be a constant at this concentration.

Curve IV shows that $\Lambda\eta$ for $0.01\ M$ potassium chloride is not exactly constant but rises steadily from 141.4 to 144.0, or 1.93 per cent. In more recent work Chittum (13) has shown that precisely the same small linear increase holds for potassium acetate.

The cause of the small deviation from linearity in curve I (exhibited also by potassium acetate) is not certain. Fuoss suggests that the inconstancy of $\Lambda\eta$ may arise from a difference in the times of molecular relaxation of the two solvents, which time of relaxation is not adequately taken into account in the electrophoretic term of the Onsager equation. From a practical point of view it appears that sufficiently accurate values of Λ for salts at intermediate concentrations of H_2O–D_2O can be computed by linear interpolation of $\Lambda\eta$.

The situation is entirely different when we investigate the conductance of acids. Curve II shows that $0.01\ M$ hydrochloric acid exhibits a very marked sag curve. A similar state of affairs holds for acetic acid, for the dissociation constant of acetic acid, and for the Walden product $\Lambda\eta$ for both acids (13).

A ready explanation (3) for the peculiar conductance of acids can be found in Born's theory (5) of hydrogen-ion conductance, which has recently been given a quantum-mechanical dress by Bernal and Fowler (4).
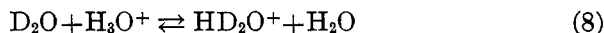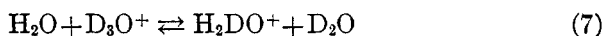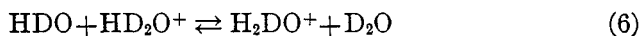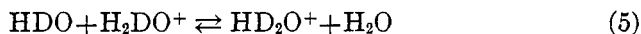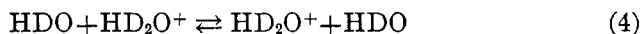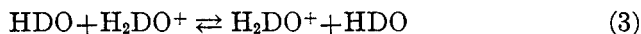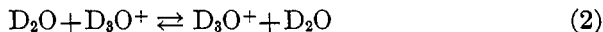
When an H_3O^+ ion is in sufficiently close contact with a water molecule, as in aqueous solutions, it need not retain its extra proton, since there is

another configuration of equal energy in which the extra proton has changed molecules, thus:

$$H_2O + H_3O^+ \rightleftharpoons H_3O^+ + H_2O \tag{1}$$
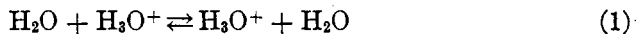
At any given time there is an equal probability of the proton being on either of the water molecules. However, if there is an applied field, F, the probability of the proton being found on one or the other of the water molecules is altered by an amount proportional to F, the migration of the proton being directed toward the region of lower potential energy.

The ions Cs^+, Rb^+, Th^+, K^+, NH_4^+, Cl^-, Br^-, and I^- have about the same mobility in aqueous solutions, which is the maximum mobility of any ions except H_3O^+ and OH^-. The ordinary mobility of ions of the same charge is *primarily* a function of their effective ionic volume and not of their mass. The conductance of H_3O^+ is about five times that of the ions just mentioned. If the mechanism of conduction of H_3O^+ were the same as that of other ions, the radius, calculated on the basis of Stokes' law, would be absurdly small (2.6×10^{-9} cm.). According to the present view, the conductance of H_3O^+ must be considered as composed of two parts, (1) ordinary conduction similar to that shown by other ions, and (2) proton exchanges leading to a Grotthus chain type of conduction. In H_2O–D_2O solutions, in addition to proton exchanges between H_2O molecules, several other types of proton and deuteron exchanges are possible.

$$D_2O + D_3O^+ \rightleftharpoons D_3O^+ + D_2O \tag{2}$$

$$HDO + H_2DO^+ \rightleftharpoons H_2DO^+ + HDO \tag{3}$$

$$HDO + HD_2O^+ \rightleftharpoons HD_2O^+ + HDO \tag{4}$$

$$HDO + H_2DO^+ \rightleftharpoons HD_2O^+ + H_2O \tag{5}$$

$$HDO + HD_2O^+ \rightleftharpoons H_2DO^+ + D_2O \tag{6}$$

$$H_2O + D_3O^+ \rightleftharpoons H_2DO^+ + D_2O \tag{7}$$

$$D_2O + H_3O^+ \rightleftharpoons HD_2O^+ + H_2O \tag{8}$$

The symmetrical exchanges represented by equations 2, 3, and 4 are similar to equation 1 in having the same energy after the proton or deuteron transfer as before. On the other hand the unsymmetrical exchanges represented by equations 5, 6, 7, or 8 require an absorption of energy from, or an evolution of energy to, the surrounding medium. The frequency of the exchanges illustrated by equations 1, 2, 3, and 4 is all of the same order of magnitude, while the frequency of those illustrated by equations 5, 6, 7, and 8 will be less because of the necessity of exchanging energy simul-

taneously with the surrounding medium. At a concentration of 50 per cent D_2O, we have the maximum probability that an acid ion will not be next to a water molecule with which its extra proton or deuteron can exchange readily. In addition to this classical explanation there are also quantum-mechanical reasons for a lowered rate of transfer in equations 5 to 8.

In table 3 Λ^* refers to the Grotthus chain contribution obtained by subtracting the normal mobilities from the observed mobility Λ. It will be noted that although the fundamental picture presented by Bernal and Fowler is undoubtedly correct, their quantitative predictions fall wide of the mark.
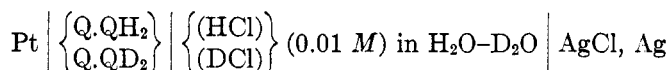
TABLE 3

|	OBSERVED BY BAKER AND LA MER	PREDICTED BY BERNAL AND FOWLER
$\Lambda_{H^*}/\Lambda^*_{D^+}$ =	268/182 = 1.48	20.
$\Lambda_{H^+}/\Lambda_{D^+}$ =	339.8/242.4 = 1.48	5.

E.M.F. IN D_2O

When hydroquinone, QH_2, is dissolved in D_2O the two phenolic protons[1] establish instantly an exchange equilibrium with the deutons of the solvent. It is only at high temperatures (100°C.) and in alkaline media that the protons attached to carbon undergo a slow exchange (15). The quinhydrone $(Q.QH_2)$ electrode by virtue of the rapidity of this exchange furnishes a means well adapted for studying exchange equilibria and the dissociation constants of acids in H_2O–D_2O mixtures.

Korman (12) has investigated the cell

$$\text{Pt} \left| \begin{Bmatrix} Q.QH_2 \\ Q.QD_2 \end{Bmatrix} \right| \begin{Bmatrix} (HCl) \\ (DCl) \end{Bmatrix} (0.01\ M) \text{ in } H_2O\text{–}D_2O \left| \text{AgCl, Ag} \right.$$

His results for $E \mid 0.01\ M$ HCl $\mid$ plotted against the deuterium content of the solvent are shown in figure 2. The E.M.F. in pure D_2O is 34.5 mv. higher than in H_2O. Most interesting is the appearance of a small but definite minimum value for 5 per cent D. Abel, Bratu, and Redlich (2) have investigated the cell

$$\text{Pt, } H_2\text{–}D_2 \text{ (g) } \mid \text{ HCl–DCl in } H_2O\text{–}D_2O \mid \text{AgCl, Ag}$$
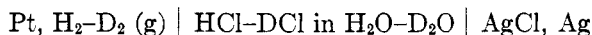
This cell also yields a minimum value for the E.M.F., but at about 40 mole per cent D. Table 4 gives a summary of the exchange equilibrium constants which may be calculated by combining both sets of measurements.

[1] Unpublished analyses by D. Price.

The exchange

$$2D^+ + H_2O \rightleftharpoons 2H^+ + D_2O$$
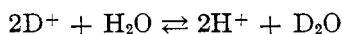
exhibits the surprisingly large value $K = 15.30$. This unequal distribution of the acid ions is of considerable importance in interpreting the
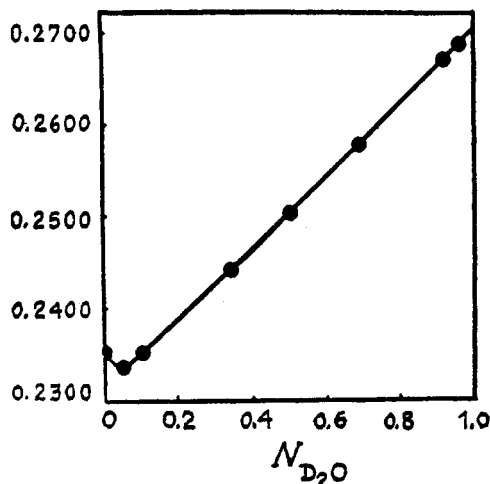

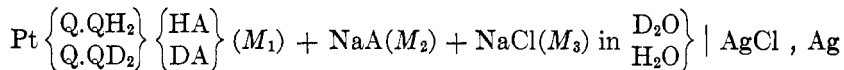FIG. 2. Quinhydrone electrode in heavy water. $E_{0.01MHCl}$

TABLE 4

Exchange equilibria in solution

NO.	PROCESS	$E^0 =$ $(0.059/n)$ $\log K$	K	OBSERVER
I	$2DCl + QH_2 = 2HCl + QD_2$	0.0345	14.64	L. and K.
II	$QH_2 + D_2O = QD_2 + H_2O$		0.96	H. and L.
III	$2DCl + H_2O = 2HCl + D_2O$		15.30	I-II
IV	$2DCl + H_2(g) = 2HCl + D_2(g)$	0.0034	1.30	A., B., and R.
V	$D_2(g) + H_2O = H_2(g) + D_2O$		11.80	III-IV
VI	$QH_2 + D_2(g) = QD_2 + H_2(g)$		11.26	I-IV
VII	$2H_2O + D_2(g) + 2NaOD = 2D_2O + H_2(g) +$ $2NaOH$	0.0431	28.58	A., B., and R.
VIII	$H_2O + 2NaOD = D_2O + 2NaOH$		2.42	VII-V
IX	$HCl + NaOD = DCl + NaOH$		0.40	½ (VIII-III)
X	$2NaOD + H_2(g) = 2NaOH + D_2(g)$		.21	VII-2V
XI	$D^+ + OD^- + H_2O = H^+ + OH^- + D_2O$	0.0233	6.13	½(VII + IV)

kinetic data of acid–base catalyzed reactions. K of reaction V, representing the exchange between the gases and the waters, is the square of the constant K'_3 employed by Farkas (7). Our E.M.F. value for $K'_3 = 3.44$ is

in excellent agreement with the averaged value of 3.36 obtained by previous investigators using analytical methods.

The E.M.F. of cells of the type

$$\text{Pt}\begin{Bmatrix} \text{Q.QH}_2 \\ \text{Q.QD}_2 \end{Bmatrix} \begin{Bmatrix} \text{HA} \\ \text{DA} \end{Bmatrix} (M_1) + \text{NaA}(M_2) + \text{NaCl}(M_3) \text{ in } \begin{Bmatrix} \text{D}_2\text{O} \\ \text{H}_2\text{O} \end{Bmatrix} \mid \text{AgCl} , \text{Ag}$$

where A refers to the anion of a weak acid, permits one to calculate the dissociation constants of the weak acid in the H_2O–D_2O mixtures. The results are in agreement with those obtained by conductance (table 1).

KINETICS

When the relative velocities of sucrose inversion, catalyzed by hydrogen and deuterium ions in mixtures of H_2O and D_2O, as compared to the veloc-
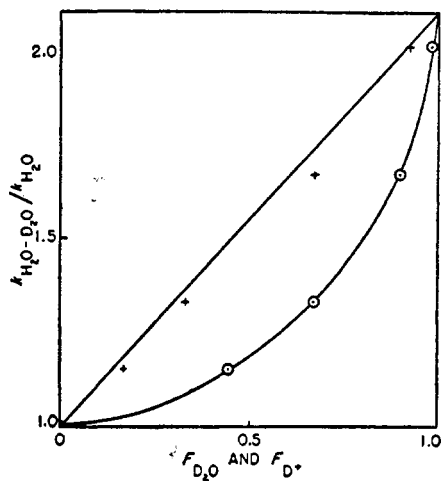
FIG. 3. Inversion of sucrose.   ⊙, F_{D_2O}; +, F_{D^+}

ity in pure water, are plotted against the fraction of D in the solvent, not only is a very marked sag curve obtained, but the rate is more rapid in D_2O (figure 3). Obviously the rate of this reaction is not proportional to the concentration of deuterium in the solvent; the explanation based upon the slower rate of proton as compared to deuteron transfer offered for the neutralization of nitroethane is inadequate. Wynne-Jones (16) therefore suggested that the greater rate in D_2O requires an equilibrium of the type:

Sucrose + Acid ⇌ (Sucrose H⁺ Complex) + Conjugate Base
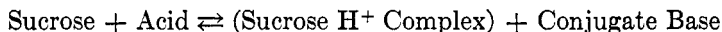
and a rate mechanism proportional to the dissociation of the sucrose ion.

It is possible to test this suggestion quantitatively (10) by assuming that the *relative rates will be proportional to the relative deuterium- and hydrogen-*

ion concentrations. In other words, a plot (crosses in figure 3) of the relative rate against the deuterium-ion concentration should yield a linear relation. The calculated value for the equilibrium constant for the reaction

$$H^+ + HDO = D^+ + H_2O$$
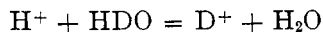
for each kinetic measurement in the mixed solvent yields

$$K = 0.11, 0.12, 0.10, 0.14$$

Korman (12) has measured this equilibrium independently by electromotive force methods, and found a value of 0.14. The constancy and the agreement between the kinetically assumed and the independently measured values of this equilibrium constant furnish evidence that our interpretation is correct (10).

When a similar explanation is advanced for the now abundant data on the solvent catalysis of glucose mutarotation, Hamill (11) found that the kinetically computed and the experimentally measured values for the exchange constant between light and heavy glucose were $K = 0.84$ and 0.69, respectively. The latter value refers to the geometric mean of the individual exchange constants of the five mobile hydrogens of glucose. It is to be expected that the kinetically determined values of K obtained from the equations

$$k_{obsd.} = k_{(H_2O)} - (k_{H_2O} - k_{D_2O})F_{DG}$$

$$(DG) / (HG) = F_{DG} / (I - F_{DG})$$

$$K = (DG)(HOH) / (HG)(HDO)$$

would involve only the kinetically active hydrogen on the aldehydic group. The exchange constant for tetramethylglucose, which possesses only this one exchangeable hydrogen on the aldehydic group, was found to be $K = 0.83$ (9). The significance of this agreement is demonstrated by the close adherence of the velocity constants to the linear relationship when they are plotted against the fraction of heavy glucose F_{DG} rather than F_D of the solvent (figure 4).

The experimental data for the acetate ion, the hydrogen ion, and the molecular acetic acid catalysis of mutarotation are necessarily of lower precision. They can be described as linear within the experimental error, in respect to either F_{DG} or F_{D_2O}.

The important rôle which the kinetics of the decomposition of nitramide, $H_2N_2O_2 \rightarrow N_2O + H_2O$, has played in the development of the modern concepts of acid–base catalysis, the remarkable obedience to a first-order rate equation, and the freedom from complicating side reactions—an ideal

behavior which is equally valid in heavy-water mixtures—make isotopic investigations of this reaction particularly significant. The reaction is not very sensitive to acid catalysis, but it is exceedingly sensitive to the presence of basic molecules. The catalytic minimum is broad. Between pH values of 2 to 5 it is flat. The substrate is a weak monobasic acid of dissociation constant 10^{-7}.

A semi-micro constant-volume gas evolution apparatus has been developed to investigate the reaction in D_2O (8). The results are as accurate (plus or minus 1 per cent) with 10 cc. of solvent as with the former macro apparatus, which required 100 cc. of solvent.

One is confronted with several possibilities for the mechanism of the reaction. The simplest assumption that only one form of substrate, pro-
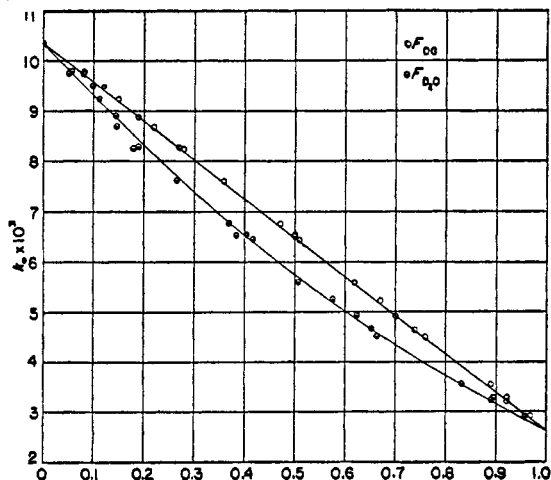

FIG. 4. Water catalysis in H_2O–D_2O at 24.97°C.

tonitramide, exists in the mixed waters and that this molecule undergoes a 5.2 fold slower rate of decomposition in D_2O than in H_2O can be eliminated on the grounds of the non-linear character of the curve and the acid properties of nitramide. A related mechanism extended to include the specific catalytic effects of HDO yields values of k_{HDO} which rise steadily. Hence this mechanism is improbable.

An equilibrium of the type

$$H_2N + D_2O = HDN + KDO;\ K_N$$
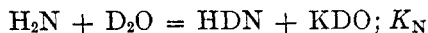
may be computed from the kinetic data in a manner analogous to that employed above for mutarotation. In terms of mechanism this scheme means that the velocity is determined entirely by the concentration of the

two forms of nitramide, the medium having no *direct* influence on the rate-determining step.   Table 5 shows that the kinetically calculated values of

TABLE 5

Solvent decomposition of nitramide

(Measurements by Joseph Greenspan)

PER CENT D IN SOLVENT	10^6k	K_N	K'_N
4.69	1176.0	3.37	33.46
28.10	861.1	2.91	3.97
45.83	661.8	3.07	2.00
77.91	384.4	3.39	0.56
95.40	271.7	3.32	0.10
98.67	250.7	3.55	
		3.27 ± 0.2	

$\bullet$ $100 \times \frac{\Delta\delta}{0.1079}$; $\blacklozenge$ $100 \times F_{CALC}$
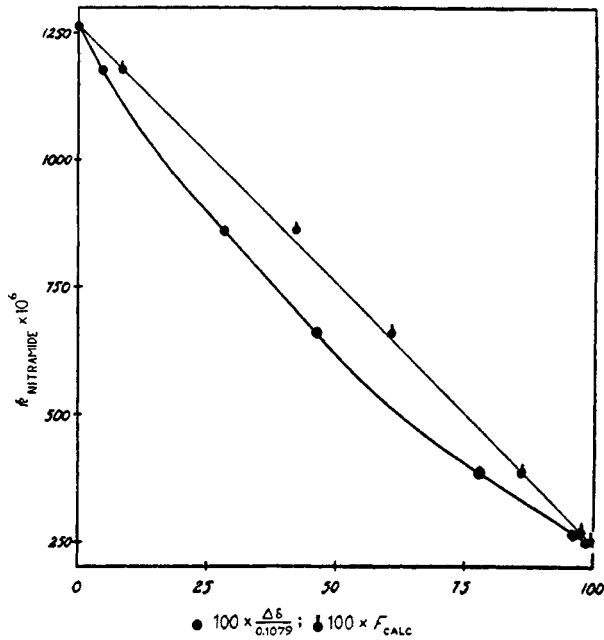
FIG. 5.

$\bullet$ k vs $100 \times \dfrac{\Delta\delta}{0.1079}$; $\blacklozenge$ k vs $100 \times F_{calcd}$.

K_N are remarkably constant over the range of 4 to 99 per cent D_2O.   The calculated value of the velocity constant, using the average value K_N

= 3.27, agrees with the observed values within experimental error as shown by the small deviations from the straight line in figure 5.   Unfortunately the instability of nitramide has thus far prevented a direct determination of the exchange constant.

We have also tested the possibility that two protons are exchanged. The resulting exchange (K'_N) constant drifts violently, which we take as evidence that the exchange of one, and not two protons, is kinetically important.   This result agrees with Pedersen's idea that the proton bound to nitrogen in the "aci" form is the one involved in the rate-determining step.

It appears from the data just cited that the displacement of the equilibrium of the isotopic exchange of the substrate or of the catalyst molecules with the solvent is an important factor in interpreting the kinetics in heavy-water mixtures.

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