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The Acid-Base Catalysis of the Mutarotation of Glucose in Protium Oxide-Deuterium Oxide Mixtures

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The kinetics of the mutarotation of glucose has been studied in protium-deuterium oxide mixtures ($\text{H}_2\text{O}-\text{D}_2\text{O}$) to ascertain the effect of substituting deuterium for hydrogen upon catalysis by the aqueous solvent, by the acid ion, by an anion base and the conjugate molecular acid. The velocity of the water catalyzed reaction varies linearly with the fraction of heavy glucose and depends only indirectly upon the composition of the water. The velocity of the acid ion catalysis varies linearly with the $\text{H}_2\text{O}-\text{D}_2\text{O}$ content. For acetate ion catalysis the rate varies linearly with the fraction of D_2O or of DOAc . Measurements of the tempera-

ture coefficient show that the observed decrease in the rate of the water catalyzed reaction arises primarily from a decrease in the entropy of activation (B) and not from an increase in the energy of activation (E_{act}). A method has been devised for determining whether or not any property depends linearly upon the deuterio fraction of a substance which may assume two isotopic forms, HX and DX . For the available data on the inversion of sucrose, DX has been identified with D^+ . For the present work on the water catalyzed mutarotation of glucose, DX has been identified with heavy glucose.

INTRODUCTION

ACCORDING to present views, acid catalysis¹ depends upon the readiness with which a proton is donated by the catalyst and accepted by the substrate while the converse holds for a reaction catalyzed by bases. The discovery of deuterium permits the testing of these theories by correlating the effects of isotopic substitution upon the component rates with the changes of the acid dissociation constants of the catalyst and substrate. The isotopic effects upon the dissociation constants of acids and bases² indicate a still greater kinetic influence.

Hudson³ showed that the unimolecular rate constant for the mutarotation of α -glucose is

¹ Bronsted, *Chem. Rev.* **5**, 231 (1928).

² Lewis, *J. Am. Chem. Soc.* **56**, 1913 (1934); La Mer and co-workers, unpublished results.

³ Hudson and Dale, *J. Am. Chem. Soc.* **39**, 320 (1917).

identical with that for β -glucose, and that the observed velocity constant $k = k_\alpha + k_\beta$. Nelson and Beegle⁴ showed that for $p\text{H}$ between 4–6 the catalysis by H^+ and OH^- is negligible and that the specific rotations of α -glucose ($+111.2^\circ$), of β -glucose ($+17.5^\circ$) and of the equilibrium mixture ($+52.5^\circ$) are independent of temperature. Consequently, the ratio (α -glucose)/(β -glucose) $= k_\beta/k_\alpha = K$, is a constant independent of temperature. The observed velocity constant may be expressed $k_{\text{obs}} = k_\alpha + k_\beta = k_\alpha(1 + K)$; it is obvious that the energy of activation $E_{\text{obs}} = E_\alpha = E_\beta$. Since initial, final and equilibrium specific rotations of glucose are the same in light and heavy water it follows that for the ratio $k_\beta/k_\alpha = K$, the constant is independent of medium as well as of temperature. The over-all velocity constant may therefore be used in making comparisons of

⁴ Nelson and Beegle, *J. Am. Chem. Soc.* **41**, 559 (1919).

the catalytic efficiencies of light and heavy water since the change of catalyst does not alter the position of equilibrium.

Brönsted and Guggenheim⁵ showed that the rate constant k , for simultaneous multiple catalysis could be expressed in the form

$$k = k_{\text{H}_2\text{O}}C_{\text{H}_2\text{O}} + \Sigma k_A C_A + \Sigma k_B C_B$$

where $k_{\text{H}_2\text{O}}$, k_A and k_B are the specific rate constants of the medium (H_2O), of acids A and of bases B . Although the solvated hydrogen ion, H_3O^+ , is the most effective acid (proton donor) nevertheless (undissociated) molecular acids like HAc exhibited catalytic properties. Of the bases (proton acceptors), OH^- is the most effective, but any anion base, as Ac^- , is likewise catalytically effective. They employed the following empirical relations

$$k_A = GK_A^x \quad \text{and} \quad k_B = GK_B^y$$

to represent the dependence of catalytic rate upon the dissociation constant K ; G is a constant; x and y are 0.25 and 0.34.

TABLE I. Summary of some previous results for k and E_{act} with the catalysts H_2O , D_2O , H^+ and D^+ at 25°C .*

OBSERVERS	CATALYST	% D_2O	k	EXTRAPO- LATION FROM $t^\circ\text{C}$	E_{obs}	E FOR CALC.
K-K	H_2O	0	0.0110	—	17,600	
	H^+	0	0.333	—	19,300	
MH-K-B	H_2O	0	0.0111	various	17,500	17,500
	H^+	0	0.292	"	18,000	18,000
	D_2O	95	0.00350	"	17,800	17,800
	D^+	95	0.177	"	19,300	19,300
P	H_2O	0	0.0109	18		17,000
	D_2O	56	0.00580	18		17,000
	D_2O	95	0.00361	20		17,000
W-J	H_2O	0	0.0105	23.3		16,800
	H^+	0	0.29	23.3		20,000
	D_2O	98	0.0027	23.3		16,800
	D^+	98	0.22	23.3		20,000

K-K, Kilpatrick and Kilpatrick;⁶ MH-K-B, Moelwyn-Hughes, Klar, Bonhoeffer;⁷ P, Pacsu;⁸ W-J, Wynne-Jones.⁹

⁵ Brönsted and Guggenheim, J. Am. Chem. Soc. **49**, 2554 (1927).

* Throughout this paper, the symbols H^+ and D^+ will be used as abbreviated formulas for the solvated proton and deuterium.

⁶ Kilpatrick and Kilpatrick, J. Am. Chem. Soc. **53**, 3698 (1931).

⁷ Moelwyn-Hughes, Klar and Bonhoeffer, Zeits. f. physik. Chemie **A169**, 113 (1934); Moelwyn-Hughes, ibid. **B26**, 272 (1934).

⁸ Pacsu, J. Am. Chem. Soc. **55**, 5066 (1933); **56**, 745 (1934).

⁹ Wynne-Jones, J. Chem. Phys. **2**, 381 (1934).

PREVIOUS WORK IN $\text{H}_2\text{O}-\text{D}_2\text{O}$

Early reports of other investigations on the mutarotation of glucose in $\text{H}_2\text{O}-\text{D}_2\text{O}$ are presented in Table I for comparison below. These data, originally reported at various temperatures, have been calculated to 25°C for convenient comparison. The uncertainty involved in the extrapolation, where E_{act} has not been determined, is probably negligible.

MATERIALS AND PROCEDURE

Heavy water was recovered from glucose solution by distillation in vacuum and redistilled from alkaline permanganate. An Eimer and Amend C.P. grade of glucose, $[\alpha]_{\text{D}} = 109^\circ$, was employed.

The velocity was followed polarimetrically¹⁰ with an electric sodium vapor lamp and 200 mm water jacketed polarimeter tubes. For the earlier experiments¹¹ in 10–60 percent D_2O the polarimeter tube was of 14 cc capacity with a glass inner tube. For later experiments a similar tube of 2-cc capacity was used.

The effect of a difference in temperature between the room and the thermostat upon the temperature of the polarimeter tube was determined and the correction to be applied found to be 0.0076° per degree difference. The Beckmann thermometers in the thermostat were compared with B.S. calibrated thermometers to the nearest 0.01° . The temperature for parallel runs is reproducible to 0.02° .

For experiments with the 14-cc polarimeter tube the solutions were prepared volumetrically and with the 2-cc tube they were prepared gravimetrically, except for uncatalyzed runs when a trace of hydrochloric acid required to give a slightly acid solution (pH 4–5), was measured from a calibrated Beckmann capillary.

Solutions were made up by weight in a glass-stoppered weighing bottle and the reaction initiated by adding α -glucose. Solutions contained 0.10 g/cc of glucose.

At the conclusion of an experiment the density of the solution was determined with a calibrated 1-cc weight pipette and corrected for buoyancy.

¹⁰ A Goerz polarimeter with Lippich system, 0° to 360° in $\frac{1}{2}^\circ$, verniers to 0.01° diametrically opposed, was employed.

¹¹ Hamill and La Mer, J. Chem. Phys. **2**, 891 (1934).

The D₂O content of the medium was calculated on the basis of the specific gravity of the water, determined before the run, allowance being made for exchange and for dilution.

Generally 60 or 80 observations were made at regular intervals of 15, 30 or 60 seconds.

CALCULATIONS

The velocity constants were calculated analytically rather than graphically using the Guggenheim¹² method. Four observations are required for a single velocity constant and each observation is employed only once.

If the processes of isotopic exchange and mutarotation were coincident, or occurred independently at nearly equal rates, the proportion HG/DG would alter continuously and k_{obs} would drift. It is important, therefore, to examine the data critically for a possible drift of the velocity constants in heavy water. The slow velocity at 15°C in 93 percent D₂O yielded a large number of observations. The constants for different ranges, by three methods, appear in Table II. If any

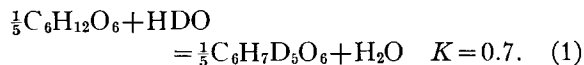
TABLE II. Velocity constants by different methods at 15.30°C in 93 percent D₂O.

METHOD	<i>t</i> (min)	No. Obs.	<i>k</i> (10) ^a
Guggenheim	13-46, 212-245; 77-110, 276-309	136	1165
Final observation	13....32 33....52 77...96 97....116	276...295 296...315 411...430 431...450	40 40 40 40
Repeated middle observation	77...116 13...52	276...315 212...251	475...514 411...450
		120 120	1167 1165

drift occurs it is less than 0.1 percent in k . We conclude, therefore, that exchange occurs much more rapidly than mutarotation.

ISOTOPIC EQUILIBRIA

Glucose should exhibit five exchangeable hydrogen atoms.⁷ Three experiments in 30 percent D₂O and one in 80 percent D₂O yielded an average value of 0.7 for the isotopic exchange equilibrium constant for the reaction (1).¹³



¹² Guggenheim, Phil. Mag. 2, 538 (1926).

¹³ It is important to remember that this constant is composite and is actually $(K_1K_2K_3K_4K_5)^{1/5}$, where subscripts refer to position in the molecule.

These experiments were followed by a general investigation of isotopic exchange with carbohydrates,¹⁴ in which the experimental technique and methods of calculation developed for the glucose exchange were employed and described. For tetramethylglucose which possesses only one exchangeable hydrogen atom, it was found that $K=K_1=0.83$.



This constant is important for the interpretation of the results of the present work.¹⁵

The isotopic equilibrium constants for several exchange reactions have been collected in Table III for later reference.

TABLE III. Isotopic equilibrium constants.

H ₂ O+D ₂ O=2HDO	$K_1=3.27$	(1) ¹⁶
2D ⁺ +H ₂ O=2H ⁺ +D ₂ O	$K_2=15.4$	(2) ¹⁷
D ⁺ +H ₂ O=H ⁺ +HDO	$K_3=(K_1K_2)^{1/2}=7.1$	(3)
HOAc=H ⁺ +OAc ⁻	K_4	(4)
DOAc=D ⁺ +OAc ⁻	$K_5; K_4/K_5=3.2$	(5) ^{17, 18}
H ₂ O=H ⁺ +OH ⁻	K_6	(6)
D ₂ O=D ⁺ +OD ⁻	$K_7; K_6/K_7=6$	(7) ¹⁹
HOAc+HDO=DOAc+H ₂ O	$K_8=K_4/K_5K_3=0.45$	(8)

EXPERIMENTAL RESULTS AND DISCUSSION

Water catalysis in H₂O-D₂O

The data for the spontaneous water reaction may be consistently accounted for either by attributing the change in velocity constant over the range H₂O-D₂O only to variation in basicity of the solvent (3) or alternately to variation in acidity of the substrate (4). Corresponding to these extreme views the following equations may be written:

$$k_{obs} = k_{H_2O}C_{H_2O} + k_{HDO}C_{HDO} + k_{D_2O}C_{D_2O}, \quad (3)$$

$$k_{obs} = k_{0H_2O} - (k_{0H_2O} - k_{0D_2O})F_{DG}. \quad (4)$$

The symbols have the significance: $k_{0H_2O} = 55k_{H_2O}$, $k_{0D_2O} = 55k_{D_2O}$, $F_{DG} = (DG)/\{(DG)+(HG)\}$. In order to test the former hypothesis it is only

¹⁴ Hamill and Freudenberg, J. Am. Chem. Soc. 57, 1427 (1935).

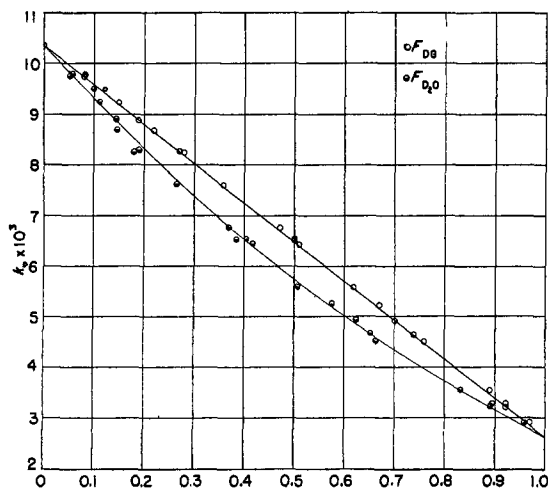
¹⁵ Hamill and La Mer, J. Chem. Phys. 4, 144 (1936).

¹⁶ Topley and Eyring, J. Chem. Phys. 2, 217 (1934).

¹⁷ La Mer and Korman, by e.m.f. measurements, unpublished.

¹⁸ La Mer and Chittum, conductance results, unpublished.

¹⁹ Abel, Bratu and Redlich, Zeits. f. physik. Chemie A173, 353 (1935).

FIG. 1. Water catalysis in $\text{H}_2\text{O}-\text{D}_2\text{O}$ at 24.97°C .

necessary to observe whether or not a constant value is obtained for k_{HDO} since all other quantities in (3) are known. To test the second hypothesis, (4) is employed to calculate F_{DG} and, since $(\text{DG})/(\text{HG}) = F_{\text{DG}}/(1 - F_{\text{DG}})$, from this to evaluate the isotopic equilibrium constant for Eq. (5).

$$K = (\text{DG})(\text{HOH})/(\text{HG})(\text{HOD}). \quad (5)$$

Both tests have been made and both k_{HDO} and K remain constant over the entire range of $\text{H}_2\text{O}-\text{D}_2\text{O}$ concentrations.^{11, 15}

Of these two hypotheses, that expressed by (4) is preferred for the following reasons. If the reaction rate depends only upon the basic strength of the catalyst, then according to the general relation $k_b = G(1/K_A)^2$ the molecules H_2O and D_2O should be equally effective catalysts since $K_B = 1/55$ for both. Also, the average value of the constant for (5) calculated from these data, $K = 0.84$, is confirmed by an earlier finding from isotopic exchange equilibrium measurements which gave, as the result of a single experiment, $K = 0.83$ for tetramethylglucose.¹⁴ It is to be expected that F_{DG} will be determined by the isotopic exchange constant for tetramethylglucose since the exchange constant for glucose is composite whereas that for tetramethylglucose refers to that hydrogen atom which is prototopically involved in mutarotation.

By substituting for F_{DG} in (4) its equivalent in (6)

$$\frac{0.84(\text{HOD})/(\text{HOH})}{1 + 0.84(\text{HOD})/(\text{HOH})} = F_{\text{DG}} \quad (6)$$

and for $k_{0\text{H}_2\text{O}}$ and $k_{0\text{D}_2\text{O}}$ the values 0.01040 and 0.00273, respectively, it is possible to obtain k_{calc} . The numerical data have been published¹⁵ and need not be repeated here. On the basis of k_{obs} the a.d. in k_{calc} is 1.2 percent. For twenty-three determinations of $k_{0\text{H}_2\text{O}}$ at 25°C the a.d. is 0.9 percent.

This comparison is expressed graphically in Fig. 1; the lower line gives the locus of points for k_{obs} vs. $\Delta s/0.1079$, where Δs is difference in specific gravity between heavy and normal water.

Acid catalysis

The experimental data for the acid catalyzed reaction, Table IV and Fig. 2, fit the equation $k = 0.311 - 0.084F_{\text{D}_2\text{O}}$, the a.d. being only 1.3 percent as compared to an a.d. from the mean of 1.6 percent for 17 determinations of k_{H^+} at 25°C .

It is unlikely that there is any real dependence of $k_{\text{H}^+ + \text{D}^+}$ upon the D_2O content of the medium. The system is complex, isotopically, since there are several isotopic varieties of substrate, of acid and perhaps of intermediate complex.

It is of interest to contrast with this reaction the acid catalyzed inversion of sucrose^{20, 21, 22} in $\text{H}_2\text{O}-\text{D}_2\text{O}$ for which the ratio of velocity constants $k_{\text{D}^+}/k_{\text{H}^+}$ is greater than two at 25°C and varies in a decidedly nonlinear manner with

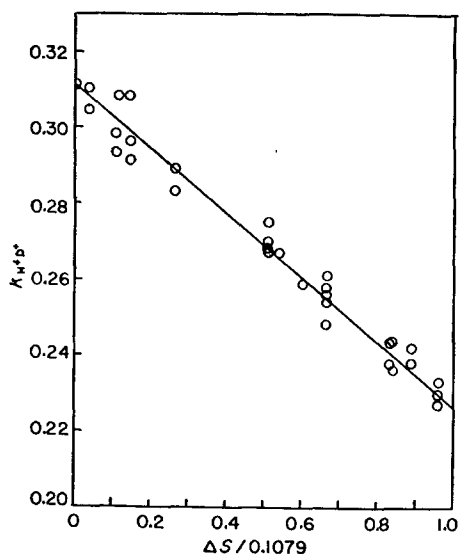
TABLE IV.

Δs 0.1079	No. Acid CONCENTRATIONS	$k_{\text{H}^+ + \text{D}^+}$	Δs 0.1079	No. Acid CONCENTRATIONS	$k_{\text{H}^+ + \text{D}^+}$
Hydrogen ion catalysis in $\text{H}_2\text{O}-\text{D}_2\text{O}$ at 24.97°C			Hydrogen ion catalysis in $\text{H}_2\text{O}-\text{D}_2\text{O}$ at 24.97°C		
0.000	17	0.311	0.840	2	0.241
0.035	2	0.307	0.890	2	0.240
0.108	3	0.300	0.960	3	0.230
0.145	3	0.298	1.000		(0.227)
0.265	2	0.286	Hydrogen ion catalysis in $\text{H}_2\text{O}-\text{D}_2\text{O}$ at 34.85°C		
0.507	3	0.271	0.831	3	0.723
0.51	1	0.267	0.840	2	0.680
0.54	1	0.267	0.890	1	0.709
0.60	1	0.259	0.960	3	0.660
0.663	5	0.256			
0.831	2	0.241			

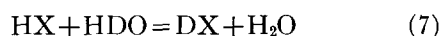
²⁰ Moelwyn-Hughes and Bonhoeffer, *Naturwiss.* **22**, 174 (1934).

²¹ Gross, Suess and Steiner, *Naturwiss.* **22**, 662 (1934).

²² Hamill and La Mer, *J. Chem. Phys.* **4**, 294 (1936).

FIG. 2. Hydrogen ion catalysis in H₂O-D₂O at 24.97°C.

change in D₂O content of the medium. If it be assumed, in analogy with the explanation successfully applied to the variation of k_0 in H₂O-D₂O, that the velocity constant varies linearly with the fraction of some substance which may be present in two isotopic forms, and that the following equilibrium exist

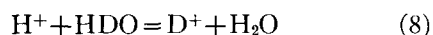


it is possible to calculate the isotopic equilibrium constant K_x for the assumed equilibrium. The data, together with the results of the calculation appear in Table V. The exchange constant for

TABLE V. Inversion of sucrose in H₂O-D₂O at 25°C.

$k_{\text{H}^+\text{D}^+}/k_{\text{H}^+}$	1.00	1.15	1.33	1.67	2.01	(2.10)
$F_{\text{D}_2\text{O}}$	0.000	0.444	0.671	0.90	0.981	1.000
K_x		0.11	0.12	0.10	0.14	

the reaction (8)



has been determined recently by La Mer and Korman as 0.14. (Table III.) For this reaction, therefore, the velocity constant varies nearly, if not quite, linearly with $(\text{D}^+)/(\text{H}^+ + \text{D}^+)$. This explanation, as a first approximation, indicates the comparative simplicity of a reaction catalyzed specifically by hydrogen ion as compared to a reversible prototropic reaction and deserves further study.

INFLUENCE OF TEMPERATURE

The integrated Arrhenius Eq. (9) where B and E_{act} are taken as constants independent of temperature,²³ accounts for the present results within the experimental error.

TABLE VI. E_{act} and B for the water catalyzed reaction in H₂O-D₂O.

$\frac{\Delta s}{0.1079}$	$t^\circ\text{C}$	$k_0(10)^5$	No. RUNS	E_{act}	B
0.000	15.30	401	2		
0.000	24.97	1040	23	16,860	10.36
0.000	34.85	2559	5	16,650	10.21
				16,710	10.25
0.831	24.97	356	1	16,650	9.74
0.831	34.85	876	1		
0.890	24.97	324	1	16,910	9.89
0.890	34.85	809	1		
0.929	15.29	116.5	2	17,090	10.00
0.929	34.85	769	2		
1.000	24.97	(273)		16,960	9.85

TABLE VII. E_{act} and B for the hydrogen ion catalyzed reaction in H₂O-D₂O.

$\frac{\Delta s}{0.1079}$	$t^\circ\text{C}$	$k_{\text{H}^+\text{D}^+}$	No. RUNS	E_{act}	B
0.000	16.84	0.126a	2		
0.000	24.98	0.313	2	19,230	13.6
0.000	24.97	0.311	16	19,450	13.7
0.000	34.85	0.891	10		
				19,400	13.7 ₀
0.831	24.97	0.240	2	20,370	14.3
0.831	34.85	0.722	3		
0.840	24.97	0.236a	3	18,900	13.2
0.840	34.85	0.862	3		
0.840	16.84	0.100a	3	19,300	13.5
0.840	34.85	0.703	3	19,560	13.7
0.840	24.97	0.244	1	20,000	14.0
0.890	24.97	0.240	2		
0.890	34.85	0.709	1	19,490	13.6
0.960	24.97	0.230	3		
0.960	34.85	0.660	3		
1.000	24.97	(0.227)		19,500	13.63

(a) A single portion of acidulated water was used for all runs in this group.

²³ See, however, V. K. La Mer, J. Chem. Phys. **1**, 289 (1933); J. Am. Chem. Soc. **55**, 1739 (1933).

$$\log k = B - E_{\text{act}}/2.3RT. \quad (9)$$

The observed difference of 250 calories in E_{act} for $k_{0\text{H}_2\text{O}}$ and $k_{0\text{D}_2\text{O}}$ may be due to experimental error. Although Moelwyn-Hughes finds a corresponding difference of 300 calories (see Table I) it may not be considered a confirmation of the difference reported here since his values of E_{act} are nearly 1000 cal. larger than ours. The observed difference for $k_{0\text{H}_2\text{O}}$ and $k_{0\text{D}_2\text{O}}$ is to be accounted for then, as due mainly to change in B , involving the entropy of activation, rather than in E_{act} .

The small difference in E_{act} for k_{H^+} and k_{D^+} is well within the experimental error whereas Moelwyn-Hughes found E_{act} for k_{D^+} to be the larger by 1300 cal. In general the results of the present work disagree with those of Moelwyn-Hughes and of Pacsu, but agree with those of Wynne-Jones.

Since the values found in the present work for E_{act} in H_2O and D_2O for both water and hydrogen ion catalysis (Tables VI and VII) are considerably lower than others which have been previously reported (Table I), it is important to decide between the two sets of values. As the simplest means for a comparison with previous work, velocity constants for the spontaneous water reaction at different temperatures are

TABLE VIII. Calculated values of B and E_{act} on the basis of recent determinations of water catalysis.

$t^\circ\text{C}$	k_0	E_{act}	B	OBSERVERS
A				
0.15	0.00078			N-B
15.29	0.00401	16,800	10.32	LM-H
18	0.00530	16,800	10.32	B-G
23.3	0.0089	16,900	10.40	W-J
24.97	0.01040	16,900	10.39	LM-H
25	0.0104	16,900	10.39	N-B
30	0.01634	16,700	10.23	LM-H
34.85	0.02559	16,900	10.39	LM-H
37	0.0301	16,700	10.24	N-B
		16,800	10.32	
B				
0.15	0.00078			N-B
18	0.00546	17,200	10.64	P
19.65	0.00646	17,200	10.64	M-K-B
20	0.00660	17,100	10.56	K-K
25	0.01098	17,200	10.64	K-K
29.74	0.01751	17,300	10.71	M-K-B
39.86	0.04533	17,400	10.79	M-K-B

B-G, Brønsted and Guggenheim;⁵ K-K, Kilpatrick and Kilpatrick;⁶ M-K-B, Moelwyn-Hughes, Klar and Bonhoeffer;⁷ LM-H, La Mer and Hamill, N-B, Nelson and Beegle;⁴ P, Pacsu;⁸ W-J, Wynne-Jones.⁹

collected in Tables VIIIA and VIIIB. E_{act} has been calculated for all on the basis of the 0.15°C value of Nelson and Beegle.⁴ The results are observed to fall into two groups; the selection of this point as a common basis for comparison is fair to all results since neither group of values for E_{act} shows a drift with temperature although there is a significant difference in values between members of the two groups. The present results are considered to be well confirmed by the others in Table VIIIA.

Neither Pacsu nor Moelwyn-Hughes, Klar and Bonhoeffer mention control of $p\text{H}$ within the limits of the catalytic minimum.⁴ We attribute their higher results to a failure to adequately control $p\text{H}$.^{11, 24}

Acetate ion catalysis

The individual k 's for acetate ion catalysis (Table IX, Fig. 3) agree, on the average, within

TABLE IX. Acetate ion catalysis and molecular acetic acid catalysis in $\text{H}_2\text{O}-\text{D}_2\text{O}$ at 24.97°C .

Δs 0.1079	No. Ac ⁻ CONCEN- TRATIONS	$k_{\text{Ac}}-(10)^4$	No. HAc CONCEN- TRATIONS	$k_{\text{HAcDAc}}(10)^4$
0.000	5	566	1	57
0.313	4	464	1	45
0.466	1	405		
0.43			2	36
0.652	4	355	2	33
0.919	2	255	2	25
1.000		(238)		(22)

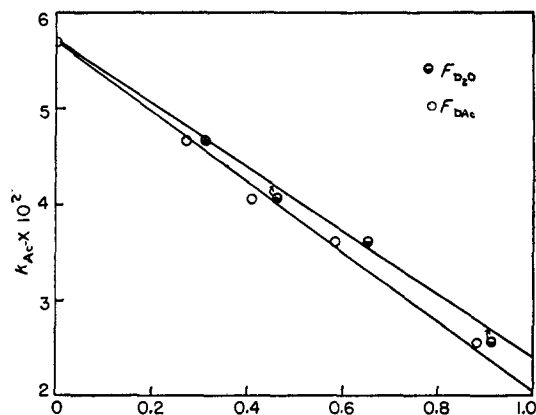


FIG. 3. Acetate ion catalysis in $\text{H}_2\text{O}-\text{D}_2\text{O}$ at 24.97°C .

²⁴ Wynne-Jones (Chem. Rev. 17, 115 (1935)) has also offered the same explanation.

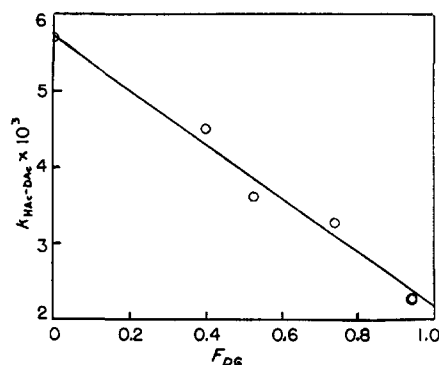


FIG. 4. Molecular acetic acid catalysis in H₂O-D₂O at 24.97°C.

2.5 percent of the values calculated from Eq. (10) and within 3.3 percent of the values calculated from Eq. (11).

$$k_{\text{Ac}^-} = 0.0567 - 0.0340F_{\text{D}_2\text{O}}, \quad (10)$$

$$k_{\text{Ac}^-} = 0.0567 - 0.0362F_{\text{DAc}}. \quad (11)$$

The precision of the experimental results alone is not sufficient to permit a choice between these equations.

Catalysis by molecular acetic acid

It may only be concluded that the ratio $k_{\text{Ac}^-}/k_{\text{HAc}}$ is roughly 10/1 in D₂O as well as in H₂O, and is in marked contrast with the ratio 1.37 for $k_{\text{H}^+}/k_{\text{D}^+}$. The results of these measurements are described by the equation $k = 0.0057 - 0.0034F_{\text{D}_2\text{O}}$ (see Fig. 4).

General acid-base catalysis

The isotope effect upon the Brönsted equations, $k_A = GK_A^x$ and $k_B = GK_B^y$, is summed up in Table X. Although two catalytic constants are insufficient to determine x or y with any considerable precision, they suffice for comparisons in H₂O and D₂O.

It is seen that x and y are not significantly affected by the media H₂O and D₂O and that as a result of this the ratio of the G 's is simply $G_{\text{H}_2\text{O}}/G_{\text{D}_2\text{O}} = k_{0\text{H}_2\text{O}}/k_{0\text{D}_2\text{O}}$ for base catalysis and $G_{\text{H}_2\text{O}}/G_{\text{D}_2\text{O}} = k_{\text{H}^+}/k_{\text{D}^+}$ for acid catalysis. We may write,

TABLE X. The influence of isotopes upon the constants of the equation $k = GK^x$.

k_B	B	K_B	G	y
0.01040 55	H ₂ O	1/55	8.7(10) ⁻⁴	0.384
0.0567 0.00273 55	Ac ⁻ (H ₂ O) D ₂ O	1/1.8(10) ⁻⁵ 1/55		
0.0238	Ac ⁻ (D ₂ O)	1/5.7(10) ⁻⁶	2.3(10) ⁻⁴	0.382
k_A	A	K_A	G	x
0.311	H ₃ O ⁺	55	0.11	0.27
0.0057 0.227	HAc D ₃ O ⁺	1.8(10) ⁻⁵ 55		
0.0022	DAc	5.7(10) ⁻⁶	0.07	0.29

$$\frac{k_{B, \text{H}_2\text{O}}}{k_{B, \text{D}_2\text{O}}} = 3.8 \left[\frac{K_{B, \text{H}_2\text{O}}}{K_{B, \text{D}_2\text{O}}} \right]^y = 3.8 \left[\frac{K_{A, \text{D}_2\text{O}}}{K_{A, \text{H}_2\text{O}}} \right]^y,$$

$$\frac{k_{A, \text{H}_2\text{O}}}{k_{A, \text{D}_2\text{O}}} = 1.37 \left[\frac{K_{A, \text{H}_2\text{O}}}{K_{A, \text{D}_2\text{O}}} \right]^x.$$

Since the ratio $K_{A, \text{D}_2\text{O}}/K_{A, \text{H}_2\text{O}}$ reaches a maximum of 1 for hydrogen ion, and a minimum of $\frac{1}{6}$ for H₂O (considering only the usual catalysts), other acids occupying intermediate positions in order of acid strength,²⁵ one infers that $k_{B, \text{H}_2\text{O}}/k_{B, \text{D}_2\text{O}}$ reaches its maximum for $B = \text{H}_2\text{O}, \text{D}_2\text{O}$ and that $k_{A, \text{H}_2\text{O}}/k_{A, \text{D}_2\text{O}}$ reaches its minimum for $A = \text{H}_3\text{O}^+, \text{D}_3\text{O}^+$. It will be of interest to observe whether or not similar results obtain for other reactions.

A SUMMARY OF RELATIONS ON ACID-BASE CATALYSIS IN H₂O-D₂O; THE EFFECT OF TEMPERATURE

H ₂ O-D ₂ O	$k = 0.01040 - 0.00767F_{\text{D}_2\text{O}}$
H ⁺ D ⁺	$k = 0.311 - 0.084F_{\text{D}_2\text{O}}$
	$k = 0.0567 - 0.0340F_{\text{D}_2\text{O}}$
Ac ⁻ (H ₂ O-D ₂ O)	$k = 0.0567 - 0.0362F_{\text{DAc}}$
HAc-DAc	$k = 0.0057 - 0.0034F_{\text{DG}}$
H ₂ O	$\log k = 10.25 - 16,710/2.3RT$
D ₂ O	$\log k = 9.85 - 16,960/2.3RT$
H ⁺	$\log k = 13.73 - 19,400/2.3RT$
D ⁺	$\log k = 13.66 - 19,500/2.3RT$

²⁵ Halpern, J. Chem. Phys. 3, 456 (1935), La Mer and Korman (unpublished).