

# ON THE REACTION OF BOTH THE IONS AND MOLECULES OF ACIDS, BASES AND SALTS<sup>1</sup>

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## I. On the Reaction of Sodium Ethylate and Methyl Iodide in Absolute Ethyl Alcohol at 0°

Until comparatively recently chemical transformations were thought by most chemists to be purely ionic. This was a natural consequence of the development of the theory of electrolytic dissociation by Arrhenius, especially since the earlier work on the hydrolysis of sugars, esters and amides by acids and the saponifications of esters by bases showed that these reactions are, in dilute solutions, nearly proportional to the concentration of the ions of the catalyzers. The natural conclusion was drawn that the reactions are brought about simply by the ions present. Notable among the opponents of this theory were Kahlenberg, Michael and Armstrong. Kahlenberg's work<sup>2</sup> was especially important as, besides other cases, he studied a number of very rapid reactions in nonaqueous solvents in which no appreciable ionization could be detected. As a result of this he came to the conclusion that the purely ionic theory of all chemical reactions was not established beyond question.

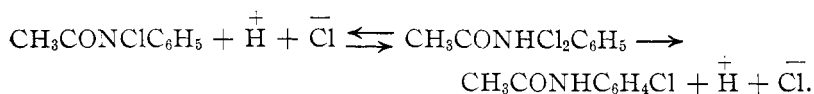
The work of Brunel<sup>3</sup> and Acree in 1905-6, of Johnson<sup>4</sup> and Acree in 1907 and the later work of Shadinger, Nirdlinger, Rogers, Chandler, Marshall, Robertson, Harrison, Shrader and Brown, brought out an entirely new principle in catalysis, namely, that acceleration may take place through the action of the nonionized acids, bases, and salts, as well as through the ions. In the case of the rearrangement of acetylchloraminobenzene, Johnson and Acree found that the reaction took place almost entirely through the nonionized salt according to the equation

<sup>1</sup> Contribution from the Chemical Laboratory of Johns Hopkins University.

<sup>2</sup> Jour. Phys. Chem., **5**, 339 (1901); **6**, 1 (1902) and other articles.

<sup>3</sup> Am. Chem. Jour., **43**, 505 (1910).

<sup>4</sup> Ibid., **38**, 259, 260 (1907).



This theory has now been adopted generally to explain the "deviations" from the ionic reaction, and in the case of the hydrolysis of cane sugar by hydrochloric acid, Worley<sup>1</sup> has shown that the molecular reaction is so great that its velocity is about twelve times that of the ionic reaction, as is shown in the following table:

Molecular proportions H <sub>2</sub> O:HCl	Molecular hydrolytic activity of acid	Degree of "ionization" $\mu_v, \mu_{00}$
30	385	0.725
40	323	0.778
50	290	0.813
60	269	0.837
80	243	0.859
100	229	0.871
2000	201	0.901

Dilutions (mols H <sub>2</sub> O)	$K_i$	$K_m$
30:60	100	1136
30:80	94	1154
30:100	91	1160
30:200	98	1143
40:80	104	1092
40:100	99	1110
40:200	103	1095
50:80	99	1121
50:100	92	1145
50:200	101	1112
60:100	77	1154
60:200	96	1159
80:100	79	1245
80:200	102	1102
100:200	109	1042
	Mean, 96	1138

The work which was taken up in this laboratory to prove this theory quantitatively was chiefly the reactions of ethylates

<sup>1</sup> Phil. Mag., (6) 27, 459 (1914).

and phenolates with alkyl halides. These substances were chosen because here we have a nonelectrolyte reacting with a univalent electrolyte whose ionization varies over a wide range. Then, too, in these cases, we are not hindered by troublesome side reactions, and the transformations are also easily controlled and easily and accurately determined.

In the present piece of work we took up the study of the reaction of sodium ethylate with methyl iodide at 0°, repeating the work of Miss B. M. Brown, to see if the same constants could be obtained by two independent workers.

If both the ethylate ions and the nonionized ethylate react we should have two reactions going on side by side, the velocity of one of which is proportional to the concentration of the ionized ethylate and the other proportional to the concentration of the nonionized ethylate, according to the equations



If we represent by  $K_i$  the velocity constant for the ionic reaction by  $K_m$  the velocity constant for the molecular reaction, and by  $K_N$  the total velocity constant, in solutions having unit concentrations, by  $x$  the change in concentration of the ethylate in time  $t$ , by  $C_{\text{ethylate}}$  the initial concentration of the ethylate in gram mols per liter, by  $C_{\text{alkyl halide}}$  the initial concentration of alkyl halide in gram mols per liter, we have the equation

$$\begin{aligned} dx/dt = K_i\alpha(C_{\text{ethylate}} - x)(C_{\text{alkyl halide}} - x) \\ + K_m(1 - \alpha)(C_{\text{ethylate}} - x)(C_{\text{alkyl halide}} - x). \end{aligned}$$

If we represent  $C_{\text{ethylate}}$  by  $A$  and  $C_{\text{alkyl halide}}$  by  $B$ , we obtain on integrating the above equation

$$K_N = K_i\alpha + K_m(1 - \alpha) = \frac{1}{At} \cdot \frac{x}{A - x} \text{ when } A = B$$

$$\text{and } K_N = K_i\alpha + K_m(1 - \alpha) = \frac{1}{(B - A)t} \ln \frac{A(B - x)}{B(A - x)}$$

when  $A >$  or  $<$   $B$ .

We know the values of A, B and  $t$  and can find  $x$  by titration. By substituting these values in the equation above we therefore obtain the values for  $K_N$ .

By measuring the reaction velocities  $K_N$  over a wide range of concentrations we obtain a series of simultaneous equations with different values of  $K_N$ ,  $\alpha$  and  $1 - \alpha$ , as follows:

$$\begin{aligned} K_N &= K_i\alpha + K_m(1 - \alpha) \\ K'_N &= K_i\alpha' + K_m(1 - \alpha'), \text{ etc.} \end{aligned}$$

By solving these equations for  $K_i$  and  $K_m$  we obtain the following values:

$$\begin{aligned} K_i &= \frac{K'_N(1 - \alpha) - K_N(1 - \alpha')}{\alpha' - \alpha} \\ \text{and } K_m &= \frac{K_N\alpha' - K'_N\alpha}{\alpha' - \alpha} \end{aligned}$$

Johnson and Acree<sup>1</sup> and Robertson and Acree<sup>2</sup> have given a full discussion of the derivation and application of these equations.

We find that by the use of these equations we obtain constant values for  $K_i$  and  $K_m$  for any given reaction. Furthermore, if this theory is correct, not only should we obtain constants for  $K_i$  and  $K_m$  for any given reaction, but  $K_i$  should be a constant for the reaction of a given alkyl halide with any ethylate; that is, the ionic velocity should be the same whether the ethylate ions come from sodium, potassium or lithium ethylates. On the other hand  $K_m$  may or may not be the same for different reactions. In fact we would expect the molecular velocities to be different in each case. The same, of course, would hold true with the phenolates as with all other analogous substances. That these relations do hold true is shown by the following tables of the values for  $K_i$  and  $K_m$  for given alkyl halides with different ethylates, phenolates, etc.:

<sup>1</sup> Am. Chem. Jour., **37**, 410; **38**, 258 (1907); **48**, 352 (1912).

<sup>2</sup> Ibid., **49**, 474 (1913).

## Temperature 0°

Reagents	$K_i$	$K_m$
Sodium ethylate and methyl iodide	0.004861	0.003033
Sodium ethylate and methyl iodide	0.004960	0.002940
Potassium ethylate and methyl iodide	0.005252	0.003369
Lithium ethylate and methyl iodide	0.005204	0.001974

## Temperature 25°

Sodium ethylate and ethyl bromide	0.00576	0.00233
Sodium ethylate and ethyl bromide	0.00543	0.00237
Potassium ethylate and ethyl bromide	0.00539	0.00296
Lithium ethylate and ethyl bromide	0.00574	0.00157
Sodium ethylate and ethyl iodide	0.0120	0.00427
Sodium ethylate and ethyl iodide	0.0122	0.00402
Potassium ethylate and ethyl iodide	0.0122	0.00457
Lithium ethylate and ethyl iodide	0.0122	0.00304
Sodium ethylate and methyl iodide	0.127	0.0594
Sodium ethylate and methyl iodide	0.129	0.0581
Potassium ethylate and methyl iodide	0.126	0.0687
Lithium ethylate and methyl iodide	0.137	0.0387
Sodium phenolate and methyl iodide	0.0282	0.00477
Potassium phenolate and methyl iodide	0.0283	0.00370
Lithium phenolate and methyl iodide	0.0287	0.00393
Sodium phenolate and ethyl iodide	0.00551	0.000987
Potassium phenolate and ethyl iodide	0.00518	0.001011
Lithium phenolate and ethyl iodide	0.00534	0.000910
Sodium thiourazole and ethyl iodide	0.435	0.170
Sodium thiourazole and ethyl iodide	0.463	0.158
Acetimidoethylester catalyzed by sodium ethylate	0.344	0.228
Benzimidoethylester catalyzed by sodium ethylate	0.1172	0.0976
<i>p</i> -Brombenzotrile and sodium ethylate	0.160	0.161
<i>p</i> -Brombenzotrile and potassium ethylate	0.163	0.144
<i>p</i> -Brombenzotrile and lithium ethylate	0.159	0.093

## Temperature 35°

Sodium phenolate and methyl iodide	0.0909	0.01310
Potassium phenolate and methyl iodide	0.1036	0.00983
Sodium phenolate and ethyl iodide	0.0183	0.00323
Potassium phenolate and ethyl iodide	0.0197	0.00270
Lithium phenolate and ethyl iodide	0.0174	0.00319

## REINTERPRETATION OF THE WORK OF OTHERS

## Work of Tubandt

Inversion of methone by sodium ethylate	0.41 at 20°, 0.41 at 20°	
	0.93 at 30°, 0.93 at 30°	

## Work of J. Stieglitz

Saponification of benzimidonium ethyl ester chloride at 25°	162.0 <sup>1</sup>	50.3 <sup>1</sup>
Saponification of benzimidonium ethyl ester bromide at 25°	163.8 <sup>1</sup>	46.5 <sup>1</sup>
Saponification of benzimidonium ethyl ester nitrate at 25°	163.2 <sup>1</sup>	48.2 <sup>1</sup>

## Work of Bredig and Stern

Change of benzaldehyde into benzoin by potassium cyanide	0.089	0.089
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## Work of Hecht, Conrad and Brückner

Sodium ethylate and methyl iodide at 0°	0.005799	0.002649
Sodium ethylate and methyl iodide at 12°	0.02896	0.01028
Sodium ethylate and methyl iodide at 18°	0.06305	0.02003
Sodium ethylate and methyl iodide at 24°	0.12877	0.04354
Sodium ethylate and methyl iodide at 36°	0.5606	0.1892
Sodium ethylate and ethyl iodide at 24°	0.0121	0.00294
Sodium ethylate and ethyl iodide at 36°	0.05282	0.01295
Sodium ethylate and propyl iodide at 36°	0.01025	0.001912
Sodium ethylate and cetyl iodide at 36°	0.01464	0.002541
Sodium ethylate and octyl iodide at 36°	0.01426	0.002407

## Work of Bruyn, Lulofs and Steger

Sodium methylate and 1,2,4-dinitrochlorbenzene in absolute methyl alcohol at 15°	1.299	0.724
Sodium methylate and 1,2,4-dinitrochlorbenzene in 90.3 percent methyl alcohol at 15°	1.376	0.759
Sodium ethylate and 1,2,4-dinitrobrombenzene in absolute ethyl alcohol at 15°	2.838	0.823
Sodium ethylate and 1,2,4-dinitrochlorbenzene in absolute ethyl alcohol at 15°	4.473	1.195
Sodium methylate and <i>o</i> -dinitrobenzene in absolute methyl alcohol at 45°	0.1458	0.1278
Sodium ethylate and <i>o</i> -dinitrobenzene in absolute ethyl alcohol at 45°	0.229	0.230

## Work of Segaller

Sodium phenolate and propyl iodide at 42.5°	0.0128	0.000753
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<sup>1</sup> These values are given in terms of Stieglitz's constants.

## Work of Ostwald

The inversion of cane sugar		
by hydrochloric acid at 25°	31.2	83.8
by hydrobromic acid at 25°	31.4	93.4
by nitric acid at 25°	31.4	73.1

## Work of Koelichen

The inversion of diacetone alcohol		
by sodium hydroxide	0.2315	0.2315
by barium hydroxide	0.232	0.150

## Salt Catalysis

It has been noted that the constants drop off slightly toward the end of the reaction in some cases but increase in others. Several theories have been proposed to explain this phenomenon, among which are a "salt effect," that is, (1) the catalytic effect of the salt formed in the reaction or of the ethylate ions or molecules themselves, and (2) the formation of olefines from the alkyl halides.

Arrhenius<sup>1</sup> and later Euler<sup>2</sup> and Stieglitz<sup>3</sup> thought that the "salt effect" was due to the change in activity or ionization of the water by the action of the salt. Acree<sup>4</sup> has shown that this explanation is untenable because in some cases it would call for a change in the ionization of water many times greater than could probably be caused in this way and also because the same salts in the same concentration sometimes exert a positive and sometimes a negative effect, and hence would have to increase the ionization of water in some cases and decrease it in others, an evident *reductio ad absurdum*. It has also been shown by Acree that in many cases the salt effect is entirely normal, that is, corresponding to the change in ionization of the reacting substances by the salt formed. In other cases an "abnormal salt effect" was observed, that is, a "salt effect" which was either too large or too small to correspond to the change in ionization of the reacting substances by the salt formed. Acree also showed that Stieglitz's own work proves

<sup>1</sup> Zeit. phys. Chem., 1, 110 (1887); 4, 226 (1889); 31, 197 (1899).

<sup>2</sup> Ibid., 32, 348 (1900).

<sup>3</sup> Am. Chem. Jour., 39, 29, 166, 402, 437, 586, 719 (1908); 32, 221 (1904).

<sup>4</sup> Ibid., 41, 475 (1909).

that the temperature coefficient of the hydrolysis of imido-ester salts is normal, whereas, on account of the increase in  $K_m$  with rise in temperature, the velocities at  $18^\circ$  and  $25^\circ$  would have to be 5 and 9 times, respectively, as large as those observed if the water caused hydrolysis through its ions alone. One side reaction, which may in part explain this decrease in reaction velocity, is the formation of olefines from the alkyl halide. This possibility was pointed out by Shadinger, Marshall, and especially by Robertson.

To check the accuracy of the values for "K<sub>N</sub> found" they were compared with the values of "K<sub>N</sub> calculated." The latter are found by substituting the proper values of  $K_i$ ,  $K_m$ ,  $\alpha$  and  $1 - \alpha$ , for the different concentrations of the ethylates in the equation

$$K_N = K_i\alpha + K_m(1 - \alpha).$$

From these two values, the calculated and found, the percent error is calculated by using the calculated value of  $K_N$  as the standard.

The percent of reaction due to the ions and to the molecules is found by dividing the values of  $K_i$ ,  $\alpha$  and  $K_m(1 - \alpha)$ , respectively, by the calculated values of  $K_N$  for the different concentrations of ethylate.

## EXPERIMENTAL

### Preparation of Absolute Ethyl Alcohol

The use of the purest alcohol obtainable was necessitated, since it has been shown by several workers<sup>1</sup> in this laboratory and also by Goldschmidt,<sup>2</sup> Lapworth,<sup>3</sup> Bredig and Fraenkel,<sup>4</sup> Kailan,<sup>5</sup> Gyr,<sup>6</sup> and others that reaction velocities are in many cases markedly affected by the presence of small quantities of

<sup>1</sup> Ber. deutsch. chem. Ges., **41**, 3227, 3228 (1908); Am. Chem. Jour., **41**, 457, 483 (1909); Ibid., **39**, 711 (1906); Zeit. phys. Chem., **60**, 728 (1907).

<sup>2</sup> Ber. deutsch. chem. Ges., **39**, 711 (1906); Zeit. phys. Chem., **60**, 728 (1907).

<sup>3</sup> Jour. Chem. Soc., **93**, 2163, 2187 (1908); Proc. Chem. Soc., **24**, 101, 152.

<sup>4</sup> Biochem. Zeit., **6**, 308; Zeit. phys. Chem., **60**, 202 (1907).

<sup>5</sup> Ber. deutsch. chem. Ges., **39**, 1053 (1906); Sitzungsber. Akad. Wiss., Wien, **116**, II, 155.

<sup>6</sup> Ber. deutsch. chem. Ges., **41**, 4322 (1908).



water. The method which has given best results is to boil up the alcohol with pure lime (400 grams of oxide to the liter) for several days, distill off the alcohol and then repeat the operation, using less oxide the second time. By this method it is easily possible to obtain alcohol containing less than 0.04 percent of water.

#### **Preparation of Standard Hydrochloric Acid**

The hydrochloric acid used in the titrations was made by the method of Hulett and Bonner,<sup>1</sup> by distilling a 20 percent solution of the acid and thus obtaining a solution of known concentration. This was collected in paraffin bottles which had been thoroughly soaked out and which were kept sealed after the distillation was finished. The acid was made up to the desired strength by weighing out the proper amounts of the constant boiling mixture and of water, and the concentration was checked by silver chloride determinations. The twenty liter bottle in which the acid was kept had been soaked out for several months with dilute acid.

#### **Preparation of the Sodium Ethylate Solution**

Sodium ethylate was prepared by dissolving pure sodium in absolute alcohol. As the sodium crust was cut off under kerosene the oil was first roughly removed by wiping the sodium with filter paper. To remove the last traces it was dipped into absolute alcohol before adding it to the alcohol used in making up the ethylate solution. The solution was standardized by drawing off measured quantities of the ethylate by means of a specially constructed pipette, to be described later, pouring it into water and titrating the sodium hydroxide formed against the standard acid. The flask containing the ethylate was placed in the 0° bath and alcohol was added to bring the mixture to the proper concentration. The ethylate solution was made up fresh each day, as it turns dark on standing. Shrader has found that this change in color does not materially affect the reaction velocity but that it interferes greatly in determining the end point in titrations.

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<sup>1</sup> Jour. Am. Chem. Soc., 31, 390 (1909).

### **Preparation of the Alkyl Halide Solution**

The alkyl halide solutions were made up by weighing the required amount of the alkyl halide into alcohol in a glass stoppered measuring flask and diluting to the mark with alcohol. Miss B. M. Brown found that 0.3 percent excess methyl iodide must be added to make up for the loss of the alkyl halide by vaporization.

### **The Bath**

The bath used for this work at 0° was made of copper and lined with tin. It was protected on all sides by pads of lamb's wool and felt. It was kept filled with finely crushed ice and water and was agitated by a specially arranged stirrer. The temperature was found to remain constant to within a few thousandths of a degree.

### **Machine Pipette**

Hecht, Conrad and Brückner, in carrying out their work on reaction velocities, mixed the solutions of ethylates and alkyl halides in one large flask and withdrew portions at definite time intervals for titration. By this method there is a great possibility for loss of alkyl halide on opening the flask, especially at higher temperatures. Therefore, in the work in this laboratory, small flasks of 20 cc or 40 cc capacity were used to contain the individual reaction mixtures.

For transferring the ethylate solution from the large flask in which the solution was made up to the small reaction flasks an ordinary pipette, surrounded by a jacket, which was filled with crushed ice and water, was used. The jacket was refilled once or twice while the solution was being transferred to the different flasks.

On account of the great volatility of methyl iodide, solutions of this substance cannot be transferred to the reaction flasks by means of the pipette described above, as much would be lost in the operation. To obviate this loss a machine which has been fully described by Robertson was used for measuring out the alkyl halide solution into the small flasks already containing the ethylate. A stream of water from the bath was kept running through the machine in order to keep the tem-

perature of the solution at 0°. Even then a small amount of alkyl halide was lost, but, as mentioned above, this was offset by adding 0.3 percent excess of methyl iodide when making up the solution. The small flasks were removed from the bath after definite time periods, the contents were poured into about 200 cc of cold water, and the sodium hydroxide formed from the remaining ethylate was titrated with the standard hydrochloric acid in order to determine the values of  $x$ . In these titrations 0.5 *N* acid was used with methyl orange as the indicator.

**On the Reactions of Sodium Ethylate and Methyl Iodide at 0°**

TABLE I

0.5 *N* Sodium Ethylate and 0.5 *N* Methyl Iodide at 0°

A = 10.00

$t$	$x$	$K_V$
150	2.070	0.001740
180	2.354	0.001709
210	2.647	0.001714
240	2.903	0.001704
Average,		0.001717
		$K_N = 0.003434$

TABLE II

0.5 *N* Sodium Ethylate and 0.5 *N* Methyl Iodide at 0°

A = 10.00

$t$	$x$	$K_V$
150	2.038	0.001706
180	2.323	0.001680
240	2.916	0.001715
264	3.110	0.001708
290	3.314	0.001694
Average,		0.001701
		$K_N = 0.003402$

TABLE III

0.25 *N* Sodium Ethylate and 0.25 *N* Methyl Iodide at 0°

A = 10.00

$t$	$x$	$K_V$
60	0.515	0.000905
120	0.967	0.000901
210	1.606	0.000911
270	1.980	0.000914
309	2.158	0.000891
397	2.700	0.000901
Average,		0.000904
		$K_N = 0.003616$

TABLE IV

0.25 *N* Sodium Ethylate and 0.25 *N* Methyl Iodide at 0°

A = 10.00

$t$	$x$	$K_V$
60	0.516	0.000906
120	0.976	0.000901
210	1.610	0.000913
270	1.972	0.000909
357	2.460	0.000913
384	2.592	0.000911
Average,		0.000909
		$K_N = 0.003636$

TABLE V  
0.25 *N* Sodium Ethylate and 0.25  
*N* Methyl Iodide at 0°  
A = 10.00

<i>t</i>	<i>x</i>	K <sub>V</sub>
118	0.958	0.000898
180	1.418	0.000918
240	1.788	0.000906
1277	5.287	0.000899
Average,		0.000905
K <sub>N</sub> =		0.003620

TABLE VI  
0.25 *N* Sodium Ethylate and 0.25  
*N* Methyl Iodide at 0°  
A = 10.00

<i>t</i>	<i>x</i>	K <sub>V</sub>
60	0.522	0.000918
120	0.982	0.000908
180	1.379	0.000899
240	1.772	0.000894
300	2.139	0.000903
360	2.448	0.000900
Average,		0.000902
K <sub>N</sub> =		0.003608

TABLE VII  
0.125 *N* Sodium Ethylate and  
0.125 *N* Methyl Iodide at 0°  
A = 10.00

<i>t</i>	<i>x</i>	K <sub>V</sub>
90	0.420	0.000487
150	0.652	0.000465
210	0.912	0.000478
330	1.344	0.000470
390	1.568	0.000476
Average,		0.000475
K <sub>N</sub> =		0.003800

TABLE VIII  
0.125 *N* Sodium Ethylate and  
0.125 *N* Methyl Iodide at 0°  
A = 10.00

<i>t</i>	<i>x</i>	K <sub>V</sub>
90	0.426	0.000494
150	0.670	0.000479
270	1.145	0.000479
330	1.352	0.000473
390	1.568	0.000476
Average,		0.000480
K <sub>N</sub> =		0.003840

### Summary of Sodium Ethylate and Methyl Iodide at 0°

TABLE IX—K<sub>N</sub> FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	K <sub>N</sub>	K <sub>N</sub> average
2	0.003434 0.003402	0.003418
4	0.003616 0.003636 0.003620 0.003608	0.003620
8	0.003800 0.003840	0.003820

TABLE X—THE IONIZATION OF SODIUM ETHYLATE AT 0°<sup>1</sup>

V	$\alpha$	1 - $\alpha$
1	0.136	0.864
2	0.237	0.763
4	0.335	0.665
8	0.435	0.565
16	0.531	0.469
32	0.633	0.367

TABLE XI— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	$K_i$	$K_m$
V = 2:V = 4	0.00499	0.00293
V = 2:V = 8	0.00496	0.00294
V = 4:V = 8	0.00495	0.00295
	Av., 0.00496	0.00294

TABLE XII— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	$K_N$ found	$K_N$ calculated	Error in percent
2	0.003418	0.003419	-0.03
4	0.003620	0.003616	+0.11
8	0.003820	0.003818	+0.05

TABLE XIII—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

V	Percent of reaction due to $\alpha K_i$	Percent of reaction due to $(1 - \alpha)K_m$
2	34.38	65.62
4	45.95	54.05
8	56.51	43.49

<sup>1</sup> Robertson and Acree: Diss., J. H. U., 1910; Am. Chem. Jour., 49, 474 (1913); Jour. Phys. Chem., 19, 406 (1915).

## II. Reinterpretation of the Work of Hecht, Conrad and Brückner on the Reaction of Alkyl Halides with Sodium Ethylate at Different Temperatures

As was mentioned above, some of the earliest work on the velocities of the reactions of alkyl halides with ethylates was done by Hecht, Conrad and Brückner,<sup>1</sup> but they did not interpret their results according to the ionic theory, as they considered these substances nonelectrolytes (nichtleitende Körper). Since we have shown by actual conductivity measurements that the ethylates are electrolytes, it was interesting to take their data and interpret<sup>2</sup> it on the basis of the reaction of both the ions and nonionized molecules of the sodium and potassium ethylates.

To test this theory we used our conductivity measurements at 0°, 25°, and 35° and calculated the ionization of the ethylate at the temperatures employed by Hecht, Conrad and Brückner. We then substituted these values for  $\alpha$  and those found for  $K_N$  by Hecht, Conrad and Brückner in the equations

$$(1) K_i = \frac{K'_N (1 - \alpha) - K_N (1 - \alpha')}{\alpha' - \alpha} \text{ and } (2) K_m = \frac{K_N \alpha' - K'_N \alpha}{\alpha' - \alpha}$$

and learned that we obtain constants for  $K_i$  and  $K_m$  which may be considered to check very well with the values found in this laboratory for the same reaction, if we remember the fact that this earlier work had so many sources of error which have since been eradicated.

From their data on the reaction of sodium ethylate and methyl iodide at 0° we obtain  $K_i = 0.005799$  and  $K_m = 0.002649$ , while, for the same reaction, the values found in this laboratory by Miss Brown<sup>3</sup> are  $K_i = 0.004861$  and  $K_m = 0.003033$  and the authors have found the values  $K_i = 0.004960$  and  $K_m = 0.002940$ . From their data on the reaction of sodium ethylate and methyl iodide at 24° we obtain  $K_i = 0.129$  and  $K_m = 0.0435$ , while for the same reaction at 25° the values found in this laboratory by Miss Brown are

<sup>1</sup> Zeit. phys. Chem., **5**, 289 (1890).

<sup>2</sup> Jour. Chem. Soc., **105**, 2582 (1914).

<sup>3</sup> Diss. J. H. U., 1913.

$K_i = 0.129$  and  $K_m = 0.0581$  and by Robertson  $K_i = 0.127$  and  $K_m = 0.0594$ . From their data on the reaction of sodium ethylate and ethyl iodide at  $24^\circ$  we obtain  $K_i = 0.0121$  and  $K_m = 0.00294$ , while the same reaction at  $25^\circ$ , the values found in this laboratory by Marshall,<sup>1</sup> are  $K_i = 0.0120$  and  $K_m = 0.00427$ , and by Shrader<sup>2</sup>  $K_i = 0.0122$  and  $K_m = 0.00402$ .

It is therefore seen that their work, which was not done from the standpoint of ionic reaction, can be explained very satisfactorily indeed by the theory that both the ions and molecules react side by side.

Hecht, Conrad and Brückner worked out their values for  $K_N$ , the reaction velocity, by the use of a purely empirical formula

$$(3) \quad \begin{aligned} K'_N &= K_N + a \log (V'/V) \\ K''_N &= K_N + a \log (V''/V) \\ K'''_N &= K_N + a \log (V'''/V) \end{aligned}$$

in which  $K'_N$  and  $K_N$  are the reaction velocities at any dilutions, "a" is an empirical constant, obtained by solving these simultaneous equations, and  $V'/V$  is the ratio of the volumes of the two solutions; that is, if we are comparing two solutions, say  $V = 10$  and  $V = 2$ , the  $V'/V$  used in the formula above would be the ratio of 10 to 2, which is 5.

As this formula is purely empirical we attempted to find the value of the Hecht, Conrad and Brückner factor "a" in terms of Acree's formula to see if we could find what this term "a" really means; for although their formula is empirical, it seems to hold in practice and it should be possible to give it some rational physical basis.

Representing by  $K'_N$  and  $K_N$  the reaction velocities of two substances at different dilutions we have by Acree's formula:

$$(4) \quad K_N = K_i\alpha + K_m(1 - \alpha)$$

$$(5) \quad \text{and } K'_N = K_i\alpha' + K_m(1 - \alpha')$$

Subtracting we have,

$$(6) \quad \begin{aligned} K'_N - K_N &= K_i(\alpha' - \alpha) - K_m(\alpha' - \alpha) \\ &= (K_i - K_m)(\alpha' - \alpha). \end{aligned}$$

<sup>1</sup> Jour. Phys. Chem., 19, 589 (1915).

<sup>2</sup> Diss. J. H. U., 1913.

According to Hecht, Conrad and Brückner,

$$\begin{aligned} K'_N &= K_N + a \log (V'/V) \\ \text{or } K'_N - K_N &= a \log (V'/V) \end{aligned}$$

Equating these two values for  $K'_N - K_N$  we get,

$$(7) \quad a \log V'/V = (K_i - K_m)(\alpha' - \alpha)$$

$$(8) \quad \text{and hence, } a = \frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)}$$

We then tested this equation (8) to see if we obtain a constant for "a" by substituting the proper values for  $K_i$ ,  $K_m$ ,  $\alpha$ ,  $\alpha'$  and  $V'/V$ . The tables on pages 372, 375, and elsewhere show that the values for "a" are really quite constant; since  $K_i - K_m$  is also a constant we see that in the work of Hecht, Conrad and Brückner and in the cases studied by us *the difference in ionization of two given solutions seems to be proportional to the logarithm of the ratio of their volumes*. This empirical relation seems to hold over a limited range, especially in the more concentrated solutions, both with those electrolytes which obey the Ostwald dilution law and those which do not. That it cannot hold over all ranges follows at once from the fact that

$$\frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)},$$

or "a," becomes gradually smaller and approaches zero for those solutions which are nearly completely ionized. We consider this to be a very important empirical relationship, which we shall develop for all of the cases where the reaction velocities and conductivities are available, whether the substances be organic or inorganic acids, bases and salts.

We then used Formula 3 for obtaining the calculated or theoretical values for  $K'_N$ ,  $K''_N$ ,  $K'''_N$ , etc., by taking any given value as  $K_N$  and using the average of the values of "a" found above. For uniformity we have called all these values of  $K'_N$ ,  $K''_N$ ,  $K'''_N$ , etc., simply "(1)  $K_N$  calculated" in the tables. It will be seen from the tables given on pages 372, 375 and elsewhere, that these values for  $K_N$  calculated are very close to those found experimentally. From the " $K_N$



found" and the "(1)  $K_N$  calculated," as explained above, the per cent error was determined, 0.00 error showing the value used as  $K_N$  in Equation 3.

Under the heading "(2)  $K_N$  calculated" we give the values of " $K_N$  calculated" for any given value of "V" by the use of the summation of the equations under (3). The sum assumes the form

$$K'_N + K''_N + K'''_N + K^a_N = nK_N + a \log \left\{ \frac{V'V''V'''V^a}{V^n} \right\}$$

in which  $n$  is the number of different concentrations studied and  $K_N$  is the reaction velocity,  $V \times K_V$ , calculated for any particular value of  $V$ . Under "(2) Error in per cent" is given the deviation of the " $K_N$  found" from the "(2)  $K_N$  calculated."

It is clearly recognized that all the values given in the tables below are not accurate beyond the second or third significant figure, even though four are sometimes given.

To test further the relations between the formula used by Hecht, Conrad and Brückner and that used by us, we used some of the work which was done in this laboratory, in which we have eliminated all sources of error as completely as possible, and obtained the values of " $a$ " from Equation 8, and of " $K_N$  calculated" from Equation 3. In our work on sodium ethylate and methyl iodide at 0° the values for " $a$ " and for " $K_N$  calculated," obtained from Equations 8 and 3, are given in the following tables:

TABLE XIV—"a" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

"a"	
V = 2:V = 4	0.000658
V = 2:V = 6	0.000664
V = 4:V = 8	0.000671
	<hr style="width: 50%; margin: auto;"/>
	Average, 0.000664

TABLE XV— $K_N$  FOUND, " $K_N$  CALCULATED," OBTAINED BY USING " $a$ " IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PERCENT

V	$K_N$ found	$K_N$ calculated	Error in percent
2	0.003418	0.003418	0.00
4	0.003620	0.003618	+0.06
8	0.003820	0.003818	+0.05

In the work of Shrader on sodium ethylate and ethyl iodide at 25° we find again this close agreement. The average value found for " $a$ " is 0.002297. We give in the following table the values for  $K_N$  calculated, the values for  $K_N$  found experimentally and the error in percent:

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.00521	0.00521	0.0
2	0.00595	0.00590	+0.8
4	0.00657	0.00659	-0.3
8	0.00723	0.00728	-0.7
16	0.00800	0.00797	+0.4
32	0.00865	0.00866	-0.1

It is seen that the values for " $a$ " are very constant and that the agreement between the values for  $K_N$  found and those calculated is excellent. These are only two of many cases which have been recalculated and in all we find this same excellent agreement.

We therefore find that the empirical formula

$$K'_N = K_N + a \text{ log } (V'/V)$$

used so successfully by Hecht, Conrad and Brückner can be transformed into our equations, which have as a rational basis the idea that both the anions and the molecules of the ethylates react with the alkyl halides. This is a beautiful example to illustrate the fact that all valid empirical formulas can be put on a rational basis by the proper study of the questions involved.

**On the Reactions of Sodium Ethylate and Methyl Iodide at 0°**

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

Conc. $\text{NaOC}_2\text{H}_5$ V	$K_N$ found
1	0.002958
2	0.003426
10	0.003996
20	0.004348

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 0°

V	$\alpha$	$1 - \alpha$
1	0.1362	0.8638
2	0.2372	0.7628
10	0.4587	0.5413
20	0.5766	0.4234

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

	$K_i$	$K_m$
V = 1:V = 2	0.006942	0.002324
V = 1:V = 10	0.005738	0.002518
V = 1:V = 20	0.005616	0.002528
V = 2:V = 10	0.005388	0.003120
V = 2:V = 20	0.005498	0.002780
V = 10:V = 20	0.005612	0.002626
	Av., 0.005799	0.002649

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.002958	0.003078	-4.05
2	0.003426	0.003395	+0.91
10	0.003996	0.004099	-2.57
20	0.004348	0.004465	-2.69

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

V	Percent of reaction due to $\alpha K_i$	Percent of reaction due to $(1 - \alpha)K_m$
1	25.66	74.34
2	40.51	59.49
10	64.89	35.11
20	74.88	25.12

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°

	"a"
V = 1:V = 2	0.001057
V = 1:V = 10	0.001016
V = 1:V = 20	0.001066
V = 2:V = 10	0.000998
V = 2:V = 20	0.001069
V = 10:V = 20	0.001233

Average, 0.001073

TABLE VII— $K_N$  FOUND,  $K_N$  CALCULATED BY USING "a" IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PER CENT

V	$K_N$ found	(1) $K_N$ calculated	Error in percent	(2) $K_N$ calculated	Error in percent
1	0.002958	0.002958	0.00	0.002981	-0.77
2	0.003426	0.003281	+4.42	0.003306	+3.63
10	0.003996	0.004031	-0.86	0.004379	-8.73
20	0.004346	0.004354	-0.15	0.004593	-5.38

## On the Reactions of Sodium Ethylate and Methyl Iodide at 12°

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 12°

Conc. $\text{NaOC}_2\text{H}_5$ V	$K_N$ found
2	0.01496
20	0.02014

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 12°

V	$\alpha$	1 - $\alpha$
2	0.2360	0.7640
20	0.5275	0.4725

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 12°

	$K_i$	$K_m$
V = 2:V = 20	0.02896	0.01028

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 12°

V	$K_N$ found	$K_N$ calculated	Error in percent
2	0.01469	0.01468	+0.07
20	0.02014	0.02012	+0.10

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	Percent of reaction due to $\alpha K_i$	Percent of reaction due to (1 - $\alpha$ ) $K_m$
2	46.55	53.45
20	75.92	24.08

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 12°

	"a"
V = 2:V = 20	0.005445

TABLE VII— $K_N$  FOUND,  $K_N$  CALCULATED BY USING "a" IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PERCENT

V	$K_N$ found	(1) $K_N$ calcu- lated	Error in per- cent	(2) $K_N$ calcu- lated	Error in per- cent
2	0.01469	0.01469	0.00	0.01469	+0.00
20	0.02014	0.02013	+0.05	0.02013	+0.05

**On the Reactions of Sodium Ethylate and Methyl Iodide  
at 18°**

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE  
AT 18°

Conc. $\text{NaOC}_2\text{H}_5$ V	$K_N$ found
2	0.03020
10	0.03844
20	0.04642

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 18°

V	$\alpha$	$1 - \alpha$
2	0.2382	0.7618
10	0.4190	0.5810
20	0.6190	0.3810

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND METHYL  
IODIDE AT 18°

	$K_i$	$K_m$
V = 2:V = 10	0.06490	0.01934
V = 2:V = 40	0.06264	0.02004
V = 10:V = 40	0.06162	0.02072
Av.,	0.06305	0.02003

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE  
AND METHYL IODIDE AT 18°

V	$K_N$ found	$K_N$ calculated	Error in percent
2	0.03020	0.03026	-0.19
10	0.03844	0.03804	+1.04
40	0.04642	0.04645	-0.06

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	Percent of reaction due to αK <sub>i</sub>	Percent of reaction due to (1 - α)K <sub>m</sub>
2	49.63	50.37
10	69.44	30.56
40	84.04	15.98

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 18°

"a"	
V = 2:V = 10	0.01113
V = 2:V = 40	0.01259
V = 10:V = 40	0.01429
Average, 0.01267	

TABLE VII—K<sub>N</sub> FOUND, K<sub>N</sub> CALCULATED BY USING "a" IN THE EQUATION K'<sub>N</sub> = K<sub>N</sub> + "a" LOG (V'/V) AND ERROR IN PERCENT

V	K <sub>N</sub> found	(1) K <sub>N</sub> calculated	Error in percent	(2) K <sub>N</sub> calculated	Error in percent
2	0.03020	0.02993	+0.9	0.02991	+0.97
10	0.03844	0.03879	-0.9	0.04639	-17.1
40	0.04642	0.04642	0.00	0.04721	-1.67

**On the Reaction of Sodium Ethylate and Methyl Iodide at 24°**

TABLE I—K<sub>N</sub> FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 24°

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	K <sub>N</sub>	Conc. NaOC <sub>2</sub> H <sub>5</sub> V	K <sub>N</sub>
1	0.05512	20	0.08696
2	0.06276	40	0.09448
5	0.07182	80	0.10226
10	0.07950	—	—

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 24°

V	$\alpha$	(1 - $\alpha$ )
1	0.1470	0.8530
2	0.2346	0.7654
5	0.3335	0.6665
10	0.4170	0.5830
20	0.5075	0.4925
40	0.6040	0.3960
80	0.7030	0.2970

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 24°

	$K_i$	$K_m$
V = 1:V = 2	0.1294	0.04230
V = 1:V = 5	0.1215	0.04194
V = 1:V = 10	0.1312	0.04184
V = 1:V = 20	0.1304	0.04212
V = 1:V = 40	0.1284	0.04244
V = 1:V = 80	0.1274	0.04264
V = 2:V = 5	0.1328	0.04126
V = 2:V = 10	0.1330	0.04122
V = 2:V = 20	0.1306	0.04194
V = 2:V = 40	0.1281	0.04260
V = 2:V = 80	0.1273	0.04296
V = 5:V = 10	0.1331	0.04114
V = 5:V = 20	0.1297	0.04280
V = 5:V = 40	0.1276	0.04386
V = 5:V = 80	0.1276	0.04434
V = 10:V = 20	0.1275	0.04510
V = 10:V = 40	0.1262	0.04608
V = 10:V = 80	0.1258	0.04630
V = 20:V = 40	0.1253	0.04740
V = 20:V = 80	0.1255	0.04726
V = 40:V = 80	0.1256	0.04700
Av.,	0.12877	0.04354



TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE  
AND METHYL IODIDE AT 24°

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.05512	0.05605	—1.68
2	0.06276	0.06352	—1.21
5	0.07182	0.07194	—0.16
10	0.07950	0.07905	+0.57
20	0.08696	0.08676	+0.23
40	0.09448	0.09498	—0.52
80	0.10226	0.10340	—1.17

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLE-  
CULES

Conc. $\text{NaOC}_2\text{H}_5$ V	Percent of reaction due to $\alpha K_i$	Percent of reaction due to $(1 - \alpha)K_m$
1	33.75	66.25
2	47.53	52.47
5	59.66	40.34
10	67.89	32.11
20	75.28	24.72
40	81.84	18.16
80	87.51	12.49

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND METHYLATE  
IODIDE AT 24°

	"a"		"a"
V = 1:V = 2	0.02478	V = 5:V = 10	0.02362
V = 1:V = 5	0.02272	V = 5:V = 20	0.02461
V = 1:V = 10	0.02299	V = 5:V = 40	0.02551
V = 1:V = 20	0.02359	V = 5:V = 80	0.02613
V = 1:V = 40	0.02429	V = 10:V = 20	0.02560
V = 1:V = 80	0.02488	V = 10:V = 40	0.02645
V = 2:V = 5	0.02116	V = 10:V = 80	0.02697
V = 2:V = 10	0.02222	V = 20:V = 40	0.02730
V = 2:V = 20	0.02324	V = 20:V = 80	0.02765
V = 2:V = 40	0.02416	V = 40:V = 80	0.02801
V = 2:V = 80	0.02489	Average,	0.02480

TABLE VII— $K_N$  FOUND,  $K_N$  CALCULATED BY USING "a" IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PERCENT

V	$K_N$ found	(1) $K_N$ calculated	Error in percent	(2) $K_N$ calculated	Error in percent
1	0.05512	0.05470	+0.77	0.05486	+0.47
2	0.06276	0.06216	+0.96	0.06233	+0.69
5	0.07182	0.07202	-0.28	0.07220	-0.52
10	0.07950	0.07949	0.00	0.08538	-6.89
20	0.08696	0.08696	0.00	0.09208	-5.56
40	0.09448	0.09442	+0.44	0.09879	-4.36
80	0.10220	0.10189	+0.30	0.10549	-3.12

**On the Reaction of Sodium Ethylate and Methyl Iodide  
at 36°**

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 36°

Conc. $\text{NaOC}_2\text{H}_5$ V	$K_N$ found	Conc. $\text{NaOC}_2\text{H}_5$ V	$K_N$ found
1	0.2344	20	0.3730
2	0.2663	40	0.4050
4	0.2984	80	0.4370
5	0.3088	160	0.4692
10	0.3408	1000	0.5540

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	$\alpha$	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3036	0.6964
5	0.3218	0.6782
10	0.3972	0.6028
20	0.4829	0.5171
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134
1000	0.9900	0.0100

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT  $36^\circ$

	$K_i$	$K_m$
V = 1:V = 2	0.5818	0.1710
V = 1:V = 4	0.5970	0.1656
V = 1:V = 5	0.6100	0.1659
V = 1:V = 10	0.5568	0.1668
V = 1:V = 20	0.5916	0.1693
V = 1:V = 40	0.5730	0.1725
V = 1:V = 80	0.5324	0.1754
V = 1:V = 160	0.5484	0.1771
V = 1:V = 1000	0.5602	0.1754
V = 2:V = 4	0.5968	0.1625
V = 2:V = 5	0.5626	0.1565
V = 2:V = 10	0.6126	0.1616
V = 2:V = 20	0.6068	0.1677
V = 2:V = 40	0.5724	0.1740
V = 2:V = 80	0.5562	0.1787
V = 2:V = 160	0.5620	0.1815
V = 2:V = 1000	0.5576	0.1775
V = 4:V = 5	0.6700	0.1247
V = 4:V = 10	0.6138	0.1609
V = 4:V = 20	0.5572	0.1722
V = 4:V = 40	0.5742	0.1813
V = 4:V = 80	0.5518	0.1878
V = 4:V = 160	0.5446	0.1911
V = 4:V = 1000	0.5574	0.1853
V = 5:V = 10	0.5968	0.1963
V = 5:V = 20	0.5754	0.1806
V = 5:V = 40	0.5614	0.1501
V = 5:V = 80	0.5486	0.1950
V = 5:V = 160	0.5434	0.1978
V = 5:V = 1000	0.5580	0.1907
V = 10:V = 20	0.5666	0.1916
V = 10:V = 40	0.5514	0.2014
V = 10:V = 80	0.5428	0.2076
V = 10:V = 160	0.5392	0.2098
V = 10:V = 1000	0.5576	0.1980
V = 20:V = 40	0.5432	0.2142
V = 20:V = 80	0.5376	0.2196
V = 20:V = 160	0.5302	0.2200
V = 20:V = 1000	0.5574	0.2248
V = 40:V = 80	0.5342	0.2267
V = 40:V = 160	0.5356	0.2247
V = 40:V = 1000	0.5578	0.2491
V = 80:V = 160	0.5362	0.2414
V = 80:V = 1000	0.5586	0.2234
V = 160:V = 1000	0.5584	0.1676
Average,	0.5606	0.1892

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT  $36^\circ$ 

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.2344	0.2464	-4.8
2	0.2664	0.2732	-2.4
4	0.2984	0.3020	-1.1
5	0.3088	0.3087	0.0
10	0.3408	0.3366	+1.2
20	0.3730	0.3686	+1.1
40	0.4050	0.4046	+0.1
80	0.4370	0.4434	-1.4
160	0.4692	0.4814	-2.5
1000	0.5540	0.5568	-0.5

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $\text{NaOC}_2\text{H}_5$ V	Percent of reaction due to $\alpha K_i$	Percent of reaction due to $(1 - \alpha)K_m$
1	35.11	64.89
2	47.64	52.36
4	56.36	43.64
5	58.42	41.58
10	60.20	39.80
20	73.48	26.51
40	80.41	19.59
80	87.00	13.00
160	91.22	8.78
1000	99.06	0.94

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 36°

		"a"			"a"
V = 1:V = 2	0.1064	V = 5:V = 10	0.1001		
V = 1:V = 4	0.1070	V = 5:V = 20	0.1054		
V = 1:V = 5	0.1066	V = 5:V = 40	0.1176		
V = 1:V = 10	0.0948	V = 5:V = 80	0.1068		
V = 1:V = 20	0.1064	V = 5:V = 160	0.1068		
V = 1:V = 40	0.1065	V = 5:V = 1000	0.1065		
V = 1:V = 80	0.0993	V = 10:V = 20	0.1065		
V = 1:V = 160	0.1066	V = 10:V = 40	0.1064		
V = 1:V = 1000	0.1070	V = 10:V = 80	0.1066		
V = 2:V = 4	0.1029	V = 10:V = 160	0.1064		
V = 2:V = 5	0.0914	V = 10:V = 1000	0.1064		
V = 2:V = 10	0.1064	V = 20:V = 40	0.1063		
V = 2:V = 20	0.1102	V = 20:V = 80	0.1062		
V = 2:V = 40	0.1064	V = 20:V = 160	0.1042		
V = 2:V = 80	0.1065	V = 20:V = 1000	0.0991		
V = 2:V = 160	0.1107	V = 40:V = 80	0.1064		
V = 2:V = 1000	0.1068	V = 40:V = 160	0.1066		
V = 4:V = 5	0.1025	V = 40:V = 1000	0.0905		
V = 4:V = 10	0.1064	V = 80:V = 160	0.1003		
V = 4:V = 20	0.0986	V = 80:V = 1000	0.0959		
V = 4:V = 40	0.1084	V = 160:V = 1000	0.0997		
V = 4:V = 80	0.1063				
V = 4:V = 160	0.1064				
V = 4:V = 1000	0.1064				Average, 0.1046

TABLE VII— $K_N$  FOUND,  $K_N$  CALCULATED BY USING "a" IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PERCENT

V	$K_N$ found	(1) $K_N$ calculated	Error in per-cent	(2) $K_N$ calculated	Error in per-cent
1	0.2344	0.2357	-0.56	0.2368	-1.01
2	0.2664	0.2672	-0.30	0.2683	-0.71
4	0.2984	0.2987	-0.11	0.2998	-0.46
5	0.3088	0.3088	0.00	0.3099	-0.35
10	0.3408	0.3403	+0.14	0.3414	-0.17
20	0.3730	0.3718	+0.32	0.3854	-3.22
40	0.4050	0.4033	+0.42	0.4167	-2.81
80	0.4370	0.4347	+0.52	0.4480	-2.45
160	0.4692	0.4662	+0.64	0.4793	-2.11
1000	0.5540	0.5495	+0.81	0.5634	-1.67

On the Reaction of Sodium Ethylate and Methyl Iodide  
at 24°

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE  
AT 24°

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	$K_N$	Conc. NaOC <sub>2</sub> H <sub>5</sub> V	$K_N$
1	0.004326	10	0.006842
2	0.004946	20	0.007624
5	0.006105		

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 24°

V	$\alpha$	1 - $\alpha$
1	0.148	0.852
2	0.235	0.765
5	0.336	0.864
10	0.422	0.578
20	0.512	0.488

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND ETHYL  
IODIDE AT 24°

	$K_i$	$K_m$
V = 1:V = 2	0.0104	0.00328
V = 1:V = 5	0.0124	0.00293
V = 1:V = 10	0.0121	0.00297
V = 1:V = 20	0.0120	0.00299
V = 2:V = 5	0.0137	0.00226
V = 2:V = 10	0.0127	0.00258
V = 2:V = 20	0.0123	0.00269
V = 5:V = 10	0.0117	0.00326
V = 5:V = 20	0.0118	0.00323
V = 10:V = 20	0.0118	0.00318
Average,	0.0121	0.00294

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT  $24^\circ$

V	$K_N$ found	$K_N$ calculated	Error in percent
I	0.004326	0.004294	+0.7
2	0.004946	0.005090	-2.8
5	0.006105	0.006014	+1.2
10	0.006842	0.006801	+0.6
20	0.007624	0.007625	0.0

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $\text{NaOC}_2\text{H}_5$ V	Percent of reaction due to $\alpha K_i$	Percent of reaction due to $(1 - \alpha)K_m$
I	41.70	58.30
2	55.86	44.14
5	67.60	32.40
10	75.08	24.92
20	81.25	18.75

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT  $24^\circ$

	"a"
V = 1:V = 2	0.002647
V = 1:V = 5	0.002464
V = 1:V = 10	0.002510
V = 1:V = 20	0.002563
V = 2:V = 5	0.002325
V = 2:V = 10	0.002451
V = 2:V = 20	0.002537
V = 5:V = 10	0.002616
V = 5:V = 20	0.002678
V = 10:V = 20	0.002738
Average,	0.002553

TABLE VII— $K_N$  FOUND,  $K_N$  CALCULATED BY USING "a" IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PERCENT

V	$K_N$ found	(1) $K_N$ calculated	Error in percent	(2) $K_N$ calculated	Error in percent
1	0.004326	0.004302	+0.5	0.004437	-2.50
2	0.004946	0.005071	-2.4	0.005206	-4.99
5	0.006105	0.006110	0.0	0.006534	-6.56
10	0.006842	0.006855	-0.2	0.007143	-4.21
20	0.007624	0.007624	0.0	0.008417	-9.42

### On the Reaction of Sodium Ethylate and Methyl Iodide at 36°

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 36°

Conc. $\text{NaOC}_2\text{H}_5$	$K_N$ found	Conc. $\text{NaOC}_2\text{H}_5$	$K_N$ found
1	0.01817	20	0.03234
2	0.02148	40	0.03594
4	0.02486	80	0.03926
5	0.02586	160	0.04258
10	0.02918	1000	0.05126

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	$\alpha$	$1 - \alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3036	0.6964
5	0.3218	0.6782
10	0.3972	0.6028
20	0.4829	0.5171
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134
1000	0.9900	0.0100



TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT  $36^\circ$

	$K_i$	$K_m$
V = 1:V = 2	0.05408	0.01162
V = 1:V = 4	0.05604	0.01126
V = 1:V = 5	0.05698	0.01109
V = 1:V = 10	0.05648	0.01118
V = 1:V = 20	0.05462	0.01152
V = 1:V = 40	0.05346	0.01173
V = 1:V = 80	0.05182	0.01203
V = 1:V = 160	0.05080	0.01221
V = 1:V = 1000	0.05164	0.01202
V = 2:V = 4	0.05782	0.01048
V = 2:V = 5	0.05900	0.01013
V = 2:V = 10	0.05730	0.01064
V = 2:V = 20	0.05474	0.01142
V = 2:V = 40	0.05338	0.01183
V = 2:V = 80	0.05168	0.01234
V = 2:V = 160	0.05070	0.01264
V = 2:V = 1000	0.05164	0.01235
V = 4:V = 5	0.06312	0.00818
V = 4:V = 10	0.05700	0.01084
V = 4:V = 20	0.05390	0.01219
V = 4:V = 40	0.05276	0.01273
V = 4:V = 80	0.05120	0.01337
V = 4:V = 160	0.05040	0.01372
V = 4:V = 1000	0.05164	0.01318
V = 5:V = 10	0.05572	0.01169
V = 5:V = 20	0.05312	0.01291
V = 5:V = 40	0.05230	0.01330
V = 5:V = 80	0.05092	0.01396
V = 5:V = 160	0.05024	0.01428
V = 5:V = 1000	0.05162	0.01362
V = 10:V = 20	0.05140	0.01453
V = 10:V = 40	0.05144	0.01449
V = 10:V = 80	0.05034	0.01522
V = 10:V = 160	0.04992	0.01551
V = 10:V = 1000	0.05162	0.01438
V = 20:V = 40	0.05148	0.01445
V = 20:V = 80	0.05010	0.01573
V = 20:V = 160	0.04976	0.01605
V = 20:V = 1000	0.05162	0.01432
V = 40:V = 80	0.04932	0.01744
V = 40:V = 160	0.04956	0.01732
V = 40:V = 1000	0.05162	0.01426
V = 80:V = 160	0.04948	0.01707
V = 80:V = 1000	0.05164	0.01241
V = 160:V = 1000	0.05168	0.00901
Average,	0.05282	0.01295

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT  $36^\circ$ 

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.01817	0.01910	-5.11
2	0.02148	0.02220	-3.34
4	0.02486	0.02505	-0.76
5	0.02586	0.02577	+0.35
10	0.02918	0.02878	+1.38
20	0.03234	0.03220	+0.13
40	0.03594	0.03607	-0.36
80	0.03926	0.04022	-2.44
160	0.04258	0.04431	-4.06
1000	0.05126	0.05358	-4.52

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. $\text{NaOC}_2\text{H}_5$ V	Percent of reaction due to $K_i$	Percent of reaction due to $(1 - \alpha)K_m$
1	42.67	57.33
2	55.24	44.76
4	64.01	35.99
5	65.95	34.05
10	72.89	27.11
20	78.59	21.41
40	84.94	15.06
80	89.85	10.15
160	93.76	6.24
1000	97.59	2.41

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND ETHYL IODIDE AT 36°

"a"		"a"	
V = 1:V = 2	0.01100	V = 5:V = 10	0.01101
V = 1:V = 4	0.01111	V = 5:V = 20	0.01074
V = 1:V = 5	0.01101	V = 5:V = 40	0.01115
V = 1:V = 10	0.01101	V = 5:V = 80	0.01116
V = 1:V = 20	0.01086	V = 5:V = 160	0.01111
V = 1:V = 40	0.01110	V = 5:V = 1000	0.01102
V = 1:V = 80	0.01106	V = 10:V = 20	0.01047
V = 1:V = 160	0.01079	V = 10:V = 40	0.01123
V = 1:V = 1000	0.01101	V = 10:V = 80	0.01117
V = 2:V = 4	0.01122	V = 10:V = 160	0.01111
V = 2:V = 5	0.01100	V = 10:V = 1000	0.01102
V = 2:V = 10	0.01101	V = 20:V = 40	0.01196
V = 2:V = 20	0.01087	V = 20:V = 80	0.01148
V = 2:V = 40	0.01109	V = 20:V = 160	0.01133
V = 2:V = 80	0.01109	V = 20:V = 1000	0.01112
V = 2:V = 160	0.01108	V = 40:V = 80	0.01103
V = 2:V = 1000	0.01104	V = 40:V = 160	0.01106
V = 4:V = 5	0.01033	V = 40:V = 1000	0.01095
V = 4:V = 10	0.01085	V = 80:V = 160	0.01102
V = 4:V = 20	0.01068	V = 80:V = 1000	0.01122
V = 4:V = 40	0.01105	V = 160:V = 1000	0.01088
V = 4:V = 80	0.01105		
V = 4:V = 160	0.01104	Average,	0.01103
V = 4:V = 1000	0.01100		

TABLE VII— $K_N$  FOUND,  $K_N$  CALCULATED BY USING "a" IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PERCENT

V	$K_N$ found	(1) $K_N$ calculated	Error in percent	(2) $K_N$ calculated	Error in percent
1	0.01817	0.01799	+1.00	0.01818	-0.05
2	0.02148	0.02131	+0.79	0.02150	-0.10
4	0.02486	0.02463	+0.93	0.02489	-0.12
5	0.02586	0.02570	+0.62	0.02589	-0.12
10	0.02918	0.02902	+0.55	0.02921	-0.10
20	0.03234	0.03234	0.00	0.03386	-4.49
40	0.03594	0.03566	+0.78	0.03716	-3.25
80	0.03926	0.03898	+0.71	0.04046	-2.96
160	0.04258	0.04230	+0.66	0.04375	-2.69
1000	0.05126	0.05109	+0.33	0.05262	-2.58

**On the Reaction of Sodium Ethylate and Propyl Iodide  
at 36°**

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE  
AT 36°

Conc. $\text{NaOC}_2\text{H}_5$ V	$K_N$	Conc. $\text{NaOC}_2\text{H}_5$ V	$K_N$
1	0.002977	40	0.006717
2	0.003670*	80	0.007420
4	0.004383*	160	0.008123
10	0.005312*		

\*Only experimental values found were V = 2 0.003696  
V = 4 0.004350  
V = 10 0.005330

+Values given for  $K_N$  above were calculated by the formula of Hecht, Conrad and Brückner.

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	$\alpha$	1 - $\alpha$
1	0.1543	0.8457
2	0.2322	0.7678
4	0.3033	0.6967
10	0.3972	0.6028
40	0.5801	0.4199
80	0.6842	0.3158
160	0.7866	0.2134

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE AT  $36^\circ$

	$K_i$	$K_m$
V = 1:V = 2	0.01050	0.001604
V = 1:V = 4	0.01096	0.001521
V = 1:V = 10	0.01111	0.001494
V = 1:V = 40	0.01040	0.001621
V = 1:V = 80	0.01007	0.001683
V = 1:V = 160	0.00986	0.001721
V = 2:V = 4	0.01137	0.001341
V = 2:V = 10	0.01131	0.001359
V = 2:V = 40	0.01039	0.001637
V = 2:V = 80	0.01004	0.001743
V = 2:V = 160	0.00984	0.001803
V = 4:V = 10	0.01127	0.001382
V = 4:V = 40	0.01025	0.001826
V = 4:V = 80	0.00994	0.001964
V = 4:V = 160	0.00997	0.002036
V = 10:V = 40	0.00994	0.002261
V = 10:V = 80	0.00974	0.002394
V = 10:V = 160	0.00966	0.002445
V = 40:V = 80	0.00955	0.002799
V = 40:V = 160	0.00957	0.002767
V = 80:V = 160	0.00959	0.002723
Average,	0.01025	0.001912

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE AT  $36^\circ$

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.002977	0.003205	-7.1
2	0.003670	0.003948	-7.1
4	0.004383	0.004455	-1.6
10	0.005312	0.005243	+1.3
40	0.006717	0.006777	-0.9
80	0.007420	0.007650	-3.0
160	0.008123	0.008509	-4.5

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	Percent of reaction due to $\alpha$ K <sub>i</sub>	Percent of reaction due to $(1 - \alpha)K_m$
1	49.59	50.51
2	60.58	39.42
4	70.12	29.88
10	78.03	21.97
40	88.16	11.84
80	92.12	7.88
160	95.22	4.78

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND PROPYL IODIDE  
AT 36°

	"a"		"a"
V = 1:V = 2	0.002154	V = 4:V = 10	0.001965
V = 1:V = 4	0.002063	V = 4:V = 40	0.002308
V = 1:V = 10	0.002025	V = 4:V = 80	0.002441
V = 1:V = 40	0.002216	V = 4:V = 160	0.001947
V = 1:V = 80	0.002321	V = 10:V = 40	0.001946
V = 1:V = 160	0.002392	V = 10:V = 80	0.001946
V = 2:V = 4	0.001969	V = 10:V = 160	0.001946
V = 2:V = 10	0.001968	V = 40:V = 80	0.002883*
V = 2:V = 40	0.002229	V = 40:V = 160	0.002859*
V = 2:V = 80	0.002352	V = 80:V = 160	0.002836*
V = 2:V = 160	0.002428		
		Average,	0.002247

\* Omitting marked values 0.002145.

TABLE VII—K<sub>N</sub> FOUND, K<sub>N</sub> CALCULATED BY USING "a" IN THE EQUATION  
K'<sub>N</sub> = K<sub>N</sub> + "a" LOG (V'/V) AND ERROR IN PERCENT

V	K <sub>N</sub> found	(1) K <sub>N</sub> calculated	Error in percent	(2) K <sub>N</sub> calculated	Error in percent
1	0.002977	0.003167	-5.9	0.003071	-3.06
2	0.003670	0.003823	-4.0	0.003747	-2.05
4	0.004383	0.004458	-1.6	0.004424	-0.92
10	0.005312	0.005312	0.0	0.005318	-0.10
40	0.006717	0.006603	+1.7	0.006926	-3.02
80	0.007420	0.007249	+2.3	0.007534	-1.51
160	0.008123	0.007894	+2.9	0.008142	-0.23

**On the Reaction of Sodium Ethylate and Cetyl Iodide at 36°**

TABLE I— $K_N$  FOUND FOR SODIUM ETHYLATE AND CETYL IODIDE AT 36°

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	$K_N$ found	Conc. NaOC <sub>2</sub> H <sub>5</sub> V	$K_N$ found
1	0.004220	80	0.010510
4	0.006212	1000	0.014140
10	0.007530		

TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	$\alpha$	1 - $\alpha$
1	0.1543	0.8457
4	0.3036	0.6964
10	0.3972	0.6028
80	0.6842	0.3158
1000	0.9900	0.0100

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND CETYL IODIDE AT 36°

	$K_i$	$K_m$
V = 1:V = 4	0.01550	0.002160
V = 1:V = 10	0.01574	0.002116
V = 1:V = 80	0.01427	0.002386
V = 1:V = 1000	0.01426	0.002386
V = 4:V = 10	0.01601	0.001936
V = 4:V = 80	0.01412	0.002776
V = 4:V = 1000	0.01426	0.002770
V = 10:V = 80	0.01380	0.003394
V = 10:V = 1000	0.01425	0.003094
V = 80:V = 1000	0.01426	0.002396
Average,	0.01464	0.002541

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND CETYL IODIDE AT 36°

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.004220	0.004406	-4.40
4	0.006212	0.006213	-0.01
10	0.007530	0.007346	+3.30
80	0.010510	0.010810	-2.85
1000	0.014140	0.014740	-4.24

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	Percent of reaction due to $\alpha$ K <sub>i</sub>	Percent of reaction due to $(1 - \alpha)K_m$
1	51.26	48.74
4	71.53	28.47
10	79.15	20.86
80	92.66	7.34
1000	98.32	1.68

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND CETYL IODIDE  
AT 36°

	"a"
V = 1:V = 4	0.003308
V = 1:V = 10	0.003309
V = 1:V = 80	0.003303
V = 1:V = 1000	0.003300
V = 4:V = 10	0.003306
V = 4:V = 80	0.003311
V = 4:V = 1000	0.003286
V = 10:V = 80	0.003310
V = 10:V = 1000	0.003303
V = 80:V = 1000	0.003392
Average,	0.003313

TABLE VII—K<sub>N</sub> FOUND, K<sub>N</sub> CALCULATED BY USING "a" IN THE EQUATION  
K'<sub>N</sub> = K<sub>N</sub> + "a" LOG (V'/V) AND ERROR IN PERCENT

V	K <sub>N</sub> found	(1) K <sub>N</sub> calculated	Error in percent	(2) K <sub>N</sub> calculated	Error in percent
4	0.006212	0.006217	-0.09	0.006205	+ 0.10
10	0.007530	0.007532	-0.03	0.007523	+ 0.10
80	0.010510	0.010524	-0.14	0.011994	-12.37
1000	0.014140	0.014154	-0.10	0.014986	-5.64

**On the Reaction of Sodium Ethylate and Octyl Iodide at 36°**TABLE I—K<sub>N</sub> FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE  
AT 36°

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	K <sub>N</sub> found	Conc. NaOC <sub>2</sub> H <sub>5</sub> V	K <sub>N</sub> found
1	0.003994	80	0.010190
4	0.006018	1000	0.013700
10	0.007294		



TABLE II—THE IONIZATION OF SODIUM ETHYLATE AT 36°

V	$\alpha$	$1 - \alpha$
1	0.1543	0.8457
4	0.3036	0.6964
10	0.3972	0.6028
80	0.6842	0.3158
1000	0.9900	0.0100

TABLE III— $K_i$  AND  $K_m$  FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

	$K_i$	$K_m$
V = 1:V = 4	0.01545	0.001902
V = 1:V = 10	0.01548	0.001997
V = 1:V = 80	0.01388	0.002188
V = 1:V = 1000	0.01382	0.002200
V = 4:V = 10	0.01551	0.001879
V = 4:V = 80	0.01365	0.002690
V = 4:V = 1000	0.01381	0.002616
V = 10:V = 80	0.01337	0.003286
V = 10:V = 1000	0.01381	0.002996
V = 80:V = 1000	0.01382	0.002322
Average,	0.01426	0.002407

TABLE IV— $K_N$  CALCULATED AND FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

V	$K_N$ found	$K_N$ calculated	Error in percent
1	0.003994	0.004235	-6.03
4	0.006018	0.006005	+0.22
10	0.007294	0.007114	+2.49
80	0.010190	0.010510	-3.14
1000	0.013700	0.014140	-3.21

TABLE V—PERCENT OF REACTION DUE TO IONS AND TO MOLECULES

Conc. NaOC <sub>2</sub> H <sub>5</sub> V	Percent of reaction due to $\alpha K_i$	Percent of reaction due to $(1 - \alpha)K_m$
1	51.95	48.05
4	72.09	27.91
10	79.61	20.39
80	92.83	7.17
1000	99.84	0.16

TABLE VI—"a" FOUND FOR SODIUM ETHYLATE AND OCTYL IODIDE AT 36°

	"a"
V = 1:V = 4	0.003360
V = 1:V = 10	0.003276
V = 1:V = 80	0.003250
V = 1:V = 1000	0.003230
V = 4:V = 10	0.003203
V = 4:V = 80	0.003200
V = 4:V = 1000	0.003200
V = 10:V = 80	0.003205
V = 10:V = 1000	0.003200
V = 80:V = 1000	0.003289
Average,	0.003241

TABLE VII— $K_N$  FOUND,  $K_N$  CALCULATED BY USING "a" IN THE EQUATION  $K'_N = K_N + "a" \text{ LOG } (V'/V)$  AND ERROR IN PERCENT

V	$K_N$ found	(1) $K_N$ calculated	Error in percent	(2) $K_N$ calculated	Error in percent
4	0.006018	0.005945	+1.22	0.005981	+ 0.62
10	0.007294	0.007271	+0.39	0.007271	+ 0.32
80	0.010190	0.010212	-0.32	0.011644	-12.55
1000	0.013700	0.013757	-0.42	0.014571	- 5.98

### Conclusions

1. The fact that chemical reactions may be accelerated through the action of the nonionized acids, bases and salts, as well as through the ions, is further proved by our work on sodium ethylate and methyl iodide at 0°.

2. The values found for  $K_i$  and  $K_m$  for the above reaction were:  $K_i = 0.004960$  and  $K_m = 0.002940$ , while the values found by Miss B. M. Brown for the same reaction were  $K_i = 0.004861$  and  $K_m = 0.003033$ . It will be seen that the two sets of values check very closely.

3. By a reinterpretation of the work of Hecht, Conrad and Brückner, from the standpoint that both ions and molecules react, it was found that we obtain constants for  $K_i$  and  $K_m$  which may be considered to check very well with the values

found in this laboratory for the same reaction, if we remember the fact that this earlier work had so many sources of error which have since been eradicated.

4. Hecht, Conrad and Brückner worked out their values for  $K_N$ , the reaction velocity, by the use of a purely empirical formula

$$\begin{aligned} K'_N &= K_N + a \log (V'/V) \\ K''_N &= K_N + a \log (V''/V) \text{ etc.,} \end{aligned}$$

in which  $K'_N$  and  $K_N$  are the reaction velocities at any dilutions, "a" is an empirical constant, obtained by solving these simultaneous equations, and V and V' are the volumes containing unit masses of the solutes. In terms of Acree's equation

$$"a" = \frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)}.$$

By substituting the values for  $K_i$ ,  $K_m$ ,  $\alpha'$ ,  $\alpha$ ,  $V'$  and V in the above equation it was found that the values for "a" are quite constant; since  $K_i - K_m$  is also a constant, we see that *the difference in ionization of two given solutions seems to be proportional to the logarithm of the ratio of their volumes.* This empirical relationship holds over a limited range, especially in the more concentrated solutions. That it cannot hold for more dilute solutions follows from the fact that

$$\frac{(K_i - K_m)(\alpha' - \alpha)}{\log (V'/V)}$$

or "a" becomes gradually smaller and approaches zero for those solutions which are nearly completely ionized.

5. It is seen that the empirical formula  $K'_N = K_N + a \log (V'/V)$  used by Hecht, Conrad and Brückner can be transformed into our equations, which have as a rational basis the idea that both the anions and molecules of the ethylate react with the alkyl halides.