Benzylsulfonaminopropionamide, (XVII).—The α-bromopropionbromide used in this experiment was prepared according to the directions of Zelinsky[1] and converted into the corresponding α-bromopropionamide by the method described by Bischoff.[2] Twenty-eight and two-tenths grams of benzylsulfonamide were converted into its potassium salt and the latter digested in alcohol with 25 g. of α-bromopropionamide for 6 hours. The liquor was still alkaline at the end of this time due to the presence of ammonia formed by hydrolysis. On cooling the propionamide deposited mixed with potassium bromide. This was washed with water and purified by recrystallization from hot water. It crystallized in prisms and melted at 167°. The compound is soluble in alcohol, water and acetic acid, and difficultly soluble in benzene and ether. The yield was 15 g.

Calc. for $C_{10}H_{14}O_3N_2S$: N, 11.57%. Found: N, 11.6, 11.56.

Benzylsulfonalanine, (XVIII).—The amide described above was hydrolyzed by boiling with a strong aqueous solution of barium hydroxide or until no ammonia was evolved. The barium was then exactly precipitated as barium sulfate and the filtrate evaporated to dryness. The acid remained as a crystalline residue and was purified by crystallization from boiling water. It separated in the form of plates which melted at 164–165°. A mixture of this with the unaltered amide melted at 155°.

Calc. for $C_{10}H_{13}O_4NS$: N, 5.75; S, 13.16. Found: N, 6.0, 5.8; S, 13.6.

Hydrolysis of Benzylsulfonalanine with Hydrochloric Acid. Alanine Hydrochloride, (XIX).—This change was accomplished by heating the sulfonamide with hydrochloric acid for 2 hours at 130°. After filtering the solution was evaporated to dryness and the alanine hydrochloride purified by crystallization.[3]

Calc. for $C_3H_7O_2N.HCl$: N, 11.2%. Found: N, 11.3.

New Haven, Conn.

[Contribution from the Chemical Laboratory of Johns Hopkins University.]

ON THE REACTION OF BOTH THE IONS AND THE NONIONIZED FORMS OF ACIDS, BASES AND SALTS: THE REACTION OF METHYL IODIDE WITH SODIUM, POTASSIUM AND LITHIUM ETHYLATES AT 0°.[4]

[TWENTY-FOURTH COMMUNICATION ON CATALYSIS.]

By Bessie M. Brown and S. F. Acree.

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A theory concerning chemical reactions was brought out by Brunel[5] and one of us in 1905–6, and Johnson[6] in 1907, when they showed by ex-

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[1] *Ber.*, 20, 2026 (1887).

[2] *Ibid.*, 30, 2312 (1897).

[3] Strecker, *Ann.*, **75,** 29 (1850).

[4] We are indebted to the Carnegie Institution of Washington for aid in this work.

[5] *Am. Chem. J.*, **43,** 505 (1910).

[6] *Ibid.*, **38,** 259, 260 (1907).

perimental evidence that, in some catalytic reactions, the acceleration may take place not only through the action of the ions, but also to a large extent through the nonionized portion of the salt.

The work of Shadinger,[1] and later, Nirdlinger and Rogers,[2] and Chandler,[3] showed that in absolute alcohol both the 1-phenyl-3-thiourazole anions and the nonionized sodium 1-phenyl-3-thiourazole react with alkyl halides.

In working with the phenolates, Robertson[4] found that both the phenolate ion and the nonionized sodium phenolate react with the alkyl halides, and Marshall,[5] Harrison,[6] and Myers[7] observed that both the ions and molecules of sodium, potassium and lithium ethylates are concerned in the catalytic effect of these compounds on the reversible addition of alcohol to acetonitrile, benzonitrile, *p*-bromobenzonitrile and others.

Other reactions studied, and which uphold this theory, are those of methyl iodide, ethyl iodide, and ethyl bromide with sodium, lithium, and potassium ethylates at 25°.

Any results which shed light upon the mechanism of organic reactions are of such extreme importance, that it was considered advisable to extend this study to other reactions, and to study some of the same reactions at *different temperatures*. Since at different temperatures the per cent. of ionization changes, it might be possible to decide whether the nonionized molecule or both ions together react, as we have pointed out in earlier articles,[8] and especially for the reactions of water.[9]

With this idea in view, the authors took up the study of the reactions of sodium, lithium, and potassium ethylates with methyl iodide at 0°, and also the effect of added sodium iodide on the reaction between sodium ethylate and methyl iodide at 25° which will appear in a later publication.

If both the ethylate ion and the nonionized ethylate salt react with the molecular alkyl halide, we have two reactions proceeding simultaneously, one proportional to the ionized part of the ethylate, α,[10] and the other proportional to the nonionized part, $1 - \alpha$. It follows that

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[1] *Am. Chem. J.*, **39**, 275 (1908).

[2] *Ibid.*, **49**, 116 (1913).

[3] Dissertation, Johns Hopkins University, 1912.

[4] Dissertation, Johns Hopkins University, 1910; *Am. Chem. J.*, **43**, 519; **49**, 474; THIS JOURNAL, **37**, 1902.

[5] *Am. Chem. J.*, **49**, 127, 369 (1913); *J. Phys. Chem.*, **19**, 589 (1915).

[6] Dissertation, Johns Hopkins University, 1912.

[7] *Am. Chem. J.*, **49**, 122, 132, 485 (1913).

[8] *Ibid.*, **48**, 374–377 (1912); **49**, 350–351, 378–382, 396, 403 (1913). Chandler, Chandler, Diss.

[9] *Am. Chem. J.*, **41**, 466–483 (1909); **48**, 369–372 (1912); *J. Phys. Chem.*, **19**, 594 (1915).

[10] These values were obtained by Dr. H. C. Robertson, *J. Phys. Chem.*, **19**, 381 (1915), to whom we are greatly indebted.

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

in which K_i is the velocity constant for the ionic reaction, and K_m is the constant for the molecular reaction in a normal solution, and x is the change in the concentration in the time t. If A represents C_{ethylate}, and B is substituted for $C_{\text{alkyl halide}}$ we obtain by integration the equation

$$(2)\ K_N = VK_V = K_i\alpha + K_m(1 - \alpha) = \frac{1}{At}\frac{x}{(A - x)} \text{ if } C_{\text{ethylate}} \text{ is equal to } C_{\text{alkyl halide}},$$

or

$$(3)\ K_N = VK_V = K_i\alpha + K_m(1 - \alpha) = \frac{1}{(B - A)t} \ln \frac{A(B - x)}{B(A - x)}$$

if C_{ethylate} is not equal to $C_{\text{alkyl halide}}$.

Substituting the data obtained for t, x, A, and B, we obtain a set of constants for K_V and K_N for each concentration of ethylate used. K_N represents the molecular velocity constant, or the velocity which that reaction would have if the concentration were normal, but the ionization corresponds to the concentration 1/V, when V is the number of liters containing one gram molecule. For each ethylate there are given two representative tables, I to VI, inclusive, showing the values of K_V for the different time periods and the average K_V and K_N for the particular value of V. In Tables VII, VIII and IX, are given the summaries for K_N for all of our 55 duplicate tables[1] corresponding to I to VI. To determine K_i and K_m for the separate ionic and molecular reactions, it is only necessary to substitute the proper values in the following simultaneous equations and solve for K_i and K_m:

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

Values for K_i and K_m are thereby obtained for every pair of concentrations, and the average of these is taken as the accepted value, and recorded in Table X. By substituting in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$, these values found for K_i and K_m and the values for α and $(1 - \alpha)$ corresponding to the different concentrations of the various ethylates, we obtain the theoretical values for K_N given in Tables VII, VIII and IX, under the heading "K_N calculated." These are compared with the corresponding values of "K_N found," and the experimental errors, called "Per cent. error," are thus obtained. The percentage of the reaction due to the ethylate ions is given under $K_i\alpha/K_N$ and the percentage due to the nonionized ethylate molecules is given under $K_m(1 - \alpha)/K_N$. For a complete mathematical and theoretical discussion of these equations,

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[1] See B. M. Brown, Dissertation, Johns Hopkins University, 1913.

see Johnson and Acree,[1] and the dissertations of Robertson, and of Harrison.

Robertson[2] and Marshall[3] discussed the possibility and probability of other reactions taking place simultaneously with those given above. We must consider, for example, the catalytic effect of the salt formed, or even of the ethylate itself, which we could designate as a "salt effect," and perhaps a side reaction, as well, in which olefines may be formed.

Since we obtain, however, from the equations used two constant values for K_i and K_m, we can state that we have either two reactions, or two or more sets of reactions, taking place, one being a function of the concentration of the ions, and the other of the nonionized portion.

If K_i represents the velocity constant of the reaction between the ethylate ion $C_2H_5O^-$, and methyl iodide, we would expect to find experimentally that the value for K_i is the same whether the methyl iodide is allowed to react with sodium, lithium, or potassium ethylates. Considering the greater difficulty in carrying out these reactions at 0° and the possibility of greater errors, there is quite satisfactory agreement between the values of K_i for the sodium, potassium, and lithium ethylates, namely, 0.00486, 0.00525, and 0.00524, respectively. Dr. W. A. Taylor[4] also obtained the value $K_i = 0.00496$ for sodium ethylate. The values for K_m would not necessarily be the same, and might be entirely different, because of the fact that the nonionized molecules of these three ethylates are different substances. In conformity with the theory we find the values 0.00303, 0.00337 and 0.00197 for K_m for sodium, potassium, and lithium ethylates, respectively, and Dr. W. A. Taylor's value 0.00294 for K_m for sodium ethylate agrees well with ours. The lower activity for the molecules of lithium ethylate has been observed in every one of a large number of other reactions.

Since viscosity may play an important part in the reaction velocities at 0°, especially in the more concentrated solutions, it will be extremely interesting, as well as important, to obtain all the necessary data, so that corrections can be made for the viscosity, and all other important physical factors.

To make the constants from the different concentrations of ethylate comparable, the reactions were allowed to run to about the same percentage completion, which was usually 50 to 60%, and an average value for the reaction velocity was obtained by taking the mean of the constants for the different time periods. When the last constants were low they were in some cases omitted and the remaining values averaged and starred.

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[1] *Am. Chem. J.*, **37**, 410 (1907); **38**, 258 (1907); **48**, 352 (1912).

[2] Dissertation, *loc. cit.*; THIS JOURNAL, **37**, 1903, 1908 (1915).

[3] *J. Phys. Chem.*, **19**, 594, 602, 607 (1915).

[4] Dissertation, Johns Hopkins University, 1914, p. 19. *J. Phys. Chem.*, **20**, 365 (1916).

It will be seen from the results that it makes very little difference in the calculated values for K_N when these starred values are used in place of the other values.

In the case of lithium ethylate the reaction was so much slower than in the other cases, that it was difficult to obtain the desired time periods, since it was, of course, impossible to titrate by artificial light. For this reason, in some of the more dilute solutions the reactions were 70 to 80% completed. But since the constants in these solutions did not decrease appreciably, there is practically no change introduced by using these values for the longer time periods.

It can be seen from the tables that there is very little difference between the values of K_N for the different concentrations of potassium ethylate, and that in some of the more dilute solutions, the values vary to such an extent that they nearly overlap for the different concentrations. The only remedy for this is to diminish the error as much as possible by taking the average of a large number of determinations. It was impossible to use solutions more concentrated than $N/4$ because the potassium iodide formed precipitated out almost immediately, and the ionization of the remaining potassium ethylate consequently changed. It was, therefore, thought advisable to find values for K_N for $3N/16$ and $3N/32$ potassium ethylate so as to give a few more calculated values for K_i and K_m and reduce the error.

It can be seen from the data given that the work at 0° is not quite as satisfactory as that at 25°. Although four significant figures are given in some of the tables, the experimental errors vary from 1 to 2%.

Experimental.

Preparation of Materials.—The method used in preparing the solutions and carrying out the reactions at 25° is described in detail by Robertson.[1]

The methyl iodide used was of special purity. To insure a large yield of a constant boiling material, two kilograms of the alkyl halide were shaken with dilute sodium carbonate solution to remove any traces of hydriodic acid, washed twice with water, and then shaken for a few minutes with anhydrous sodium sulfate, and filtered through glass wool. A considerable quantity of phosphorus pentoxide was added and allowed to remain overnight, after which the methyl iodide was distilled. This treatment with the phosphorus pentoxide was repeated, and the product thus obtained was fractionated. Special care was taken to have the condenser and all apparatus perfectly dry, and with these precautions, a product was obtained, the total quantity of which boiled within a few hundredths of a degree. A table is given below showing the boiling points of the different fractions, the barometric pressure and the boiling points at 760 millimeters after all the necessary corrections are made.

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[1] *Loc. cit.*

Observed b. p.	Barometer.	Corrected b. p.	Observed b. p.	Barometer.	Corrected b. p.
42.80–42.83	769.4 mm.	42.31–42.33°	42.91–42.86	770.6 mm.	42.35–42.35°
42.82–42.82	769.3	42.33–42.35	42.86–42.82	769.5	42.35–42.34
42.82–42.81	769.3	42.34–42.33	42.82–42.80	768.9	42.34–42.34
42.81–42.81	769.2	42.33–42.33	42.80–42.78	768.2	42.34–42.36
42.93–42.91	771.2	42.35–42.35	42.78–42.79	767.7	42.36–42.37

The rise in boiling point observed in the last fraction was probably due to superheating. No correction was necessary for the exposed stem, because the distilling flask with a long neck made especially for the purpose was used, which made it possible to surround the total column of mercury with the vapor of the alkyl halide. In correcting for the atmospheric pressure the value used was 0.03° per millimeter. The total amount of methyl iodide recovered in these ten fractions was 1,772 g. out of the 2,000 g. used. This is a very satisfactory yield for such a volatile substance. In order to decrease the loss due to the volatility of the methyl iodide, ice-water was continually run through the condenser by means of a fine lead coil of several turns surrounded by ice, and the receiving bottles cooled by ice-water and fairly tightly stoppered with cotton. Another sample purified in the same way boiled at 42.34–42.36°. A sample purified in the same way but distilled with the stem exposed and without special precautions boiled at 42.30–42.32°. A sample of good methyl iodide stood over summer and was then distilled once from phosphorus pentoxide. When fractionated it gave a large middle portion boiling at 42.34–42.36°. Another sample of methyl iodide made by the method used by Robertson boiled at 42.35–42.39°.

It would seem from the boiling points obtained that the methyl iodide used in the reactions was of especial purity. Nevertheless, it was not only a wise precaution but a point of great interest to determine the composition of such samples by analysis.

Satisfactory results were obtained by using small weighing tubes with ground glass stoppers which were especially made for the purpose and held about 2 cc. The alkyl halide could thus be weighed accurately and without loss. The weighing tube containing the alkyl halide was then placed in a regular Carius tube containing an excess of sodium ethylate, sealed, and heated a sufficient length of time in a water bath. It was necessary, of course, to mix the contents thoroughly before heating. The stopper in the little weighing tube was easily removed by warming the tube slightly and then shaking it gently. When the reaction was complete the contents of the tube were washed into a beaker, and then filtered into a calibrated flask, diluted to the mark and weighed. Each portion taken out for analysis was then weighed, since this procedure was much more accurate than the volume method.

In the following analyses Sample I and Sample II are taken from different samples of methyl iodide.

Sample I.

AgI obt. Air wt.	AgI calc. Vac. wt.	% error.
2.0346	2.0327	+0.12
2.0336	2.0339	+0.01
1.9956	1.9953	+0.04

Sample II. A.

AgI obt. Air wt.	AgI calc. Vac. wt.	% error.
1.5890	1.5889	+0.02
1.5886	1.5889	0.00
1.5894	1.5898	0.00

Sample II. B.

AgI obt. Air wt.	AgI calc. Vac. wt.	% error.
1.7232	1.7243	−0.03
1.7264	1.7280	−0.08
1.7271	1.7273	+0.01

Sample II. C.

AgI obt. Air wt.	AgI calc. Vac. wt.	% error.
1.5493	1.5500	−0.03
1.5489	1.5495	−0.02
1.5488	1.5499	−0.05

It is seen that we can easily make alkyl halides with a high degree of purity and that this method of analysis is very accurate. The percentage error is corrected to vacuum weights.

The Machine.—Since methyl iodide is so very volatile it would be impossible to transfer the solution to the reaction flasks by the use of an ordinary pipet, without losing a large amount of the alkyl halide. A special apparatus called the "machine" was devised to transfer these solutions with the least possible loss. This machine was described in detail by Robertson.

A large number of determinations were also carried out to see whether the 0.3% excess of methyl iodide ordinarily added was sufficient to make up for any loss of the alkyl halide during the preparation and transfer of the solution. While keeping the conditions the same as those used for studying the reactions, 10 cc. of the solution were run into a small reaction flask containing a 50% alcoholic solution of silver nitrate. The results obtained are given in the tables below. The calculated values given for the silver iodide include the excess added which is given in the parentheses under "Strength of solution."

At 0°.

AgI obt.	AgI calc.	Strength of soln.	% error.
1.1743[1]	1.1799	(100.5%)	−0.47
1.1729[1]	1.1799	(100.5%)	−0.60
1.1730[1]	1.1799	(100.5%)	−0.60
2.3584	2.3598	(100.5%)	−0.06
4.7279	4.7288	(100.7%)	−0.02
2.3576	2.3621	(100.6%)	−0.20
2.3583	2.3621	(100.6%)	−0.16
2.3542	2.3598	(100.5%)	−0.22
4.7057	4.7101	(100.3%)	−0.09
2.3495	2.3598	(100.5%)	−0.43
		Average,	−0.27

At 25°.

AgI obt.	AgI calc.	Strength of soln.	% error.
2.3535	2.3550	(100.1%)	−0.06
2.3500	2.3550	(100.1%)	−0.21
2.3424	2.3550	(100.1%)	−0.11
2.3570	2.3620	(100.6%)	−0.21
2.3533	2.3597	(100.5%)	−0.27
1.1727	1.1775	(100.3%)	−0.40
1.1712	1.1775	(100.3%)	−0.53
		Average,	−0.26

The average of the above analyses shows that the 0.3% excess of methyl iodide seems to be sufficient, although there is considerable variation in the results. However, in a number of reactions 0.5% excess was added.

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[1] Same solution.

Reaction Velocities at 0°.

For the study of the velocity of the reaction between methyl iodide, sodium, lithium, and potassium ethylates at 0° an ice bath was used which gave very satisfactory results. This consisted of a copper bath ten inches deep and fourteen inches in diameter which was tinned on the inside, and placed in a wooden box containing lamb's wool. The bottom was protected with a thick felt pad about one inch thick, and the top by a tightly fitting metal cover, over which were placed several pads of felt and wool. The metal cover was made in two pieces, one of which was removed when it was necessary to take out the flask, start the reaction, etc. Special attention is called to the stirring device. The motor is supported by an iron framework which is bolted firmly to the wall to prevent vibration. Motion is imparted to the propeller shaft by a friction pulley, by means of which the speed can be easily controlled.

TABLE I.—0.5 *N* SODIUM ETHYLATE AND 0.5 *N* METHYL IODIDE AT 0°.

A = 10.00.

t.	x.	K$_V$.
150	2.058	0.001728
180	2.342	0.001700
210	2.634	0.001703
240	2.896	0.001698
2728	8.200	0.001670
Average,		0.001700
K$_N$,		0.003400

TABLE II.—0.03125 *N* SODIUM ETHYLATE AND 0.25 *N* METHYL IODIDE AT 0°.

A = 10.01. B = 80.00.

t.	x.	K$_V$.
673	4.970	0.0001321
751	5.338	0.0001319
821	5.562	0.0001287
899	5.874	0.0001284
966	6.314	0.0001353
1095	6.714	0.0001337
Average,		0.0001317
K$_N$,		0.004212

TABLE III.—0.25 *N* POTASSIUM ETHYLATE AND 0.25 *N* METHYL IODIDE AT 0°.

A = 10.00.

t.	x.	K$_V$.
110	0.972	0.000980
190	1.600	0.001002
290	2.268	0.001015
350	2.604	0.001006
390	2.804	0.000997
1430	5.936	0.001021
1590	6.196	0.001024
Average,		0.001006
K$_N$,		0.004024

TABLE IV.—0.125 *N* POTASSIUM ETHYLATE AND 0.50 *N* METHYL IODIDE AT 0°.

A = 10.00. B = 40.00.

t.	x.	K$_V$.
190	3.192	0.0005285
240	3.832	0.0005311
290	4.376	0.0005282
330	4.792	0.0005299
360	5.064	0.0005280
390	5.360	0.0005331
460	5.880	0.0005271
Average,		0.0005294
K$_N$,		0.004235

TABLE V.—0.5 *N* LITHIUM ETHYLATE AND 0.5 *N* METHYL IODIDE AT 0°.

A = 9.98.

t.	x.	K$_V$.
180	1.782	0.001207
240	2.226	0.001196
300	2.643	0.001200
382	3.156	0.001210
1278	5.946	0.001153
1667	6.580	0.001161
Average,		0.001188
K$_N$,		0.002381
K$_N$,[1]		0.002411

TABLE VI.—0.03125 *N* LITHIUM ETHYLATE AND 0.25 *N* METHYL IODIDE AT 0°.

A = 10.00. B = 80.00.

t.	x.	K$_V$.
561	3.840	0.0001108
647	4.328	0.0001129
816	5.000	0.0001100
898	5.296	0.0001090
983	5.664	0.0001107
1053	5.928	0.0001114
2086	8.168	0.0001087
Average,		0.0001105
K$_N$,		0.003536

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[1] If last two values of K$_v$ are omitted.

TABLE VII.—K_N FOUND, K_N CALCULATED, α, $(1 - \alpha)$, ERROR IN PER CENT., AND PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES FOR SODIUM ETHYLATE AND METHYL IODIDE AT 0°.

V.	α.	$1 - \alpha$.	K_N found.	Av. K_N.	K_N calc.	% error.	Per cent. of reaction due to ions: $K_i\alpha/K_N$.	Per cent. of reaction due to molecules: $K_m(1-\alpha)/K_N$.
1	0.136	0.864	0.003299					
			0.003264	0.003281	0.003282	—0.03	0.21	0.79
2	0.237	0.763	0.003400					
			0.003420					
			0.003485	0.003435	0.003466	—0.90	0.34	0.66
4	0.335	0.665	0.003679					
			0.003621	0.003650	0.003645	+0.13	0.46	0.54
8	0.435	0.565	0.003825					
			0.003854	0.003840	0.003828	+0.31	0.57	0.43
16	0.531	0.469	0.003919					
			0.003985					
			0.004063					
			0.004077	0.004011	0.004004	+0.17	0.66	0.34
32	0.633	0.367	0.004212					
			0.004130					
			0.004165	0.004169	0.004190	—0.50	0.76	0.24

TABLE VIII.—K_N FOUND, K_N CALCULATED, α, $(1 - \alpha)$, ERROR IN PER CENT., AND PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES FOR POTASSIUM ETHYLATE AND METHYL IODIDE AT 0°.

V.	α.	$1 - \alpha$.	K_N found.	Av. K_N.	K_N calc.	% error.	Per cent. of reaction due to ions: $K_i\alpha/K_N$.	Per cent. of reaction due to molecules: $K_m(1-\alpha)/K_N$
4	0.365	0.635	0.004024					
			0.003982					
			0.004088	0.004031	0.004055	—0.62	0.47	0.53
16/3	0.401	0.599	0.004123					
			0.004124	0.004124	0.004123	+0.02	0.50	0.50
8	0.459	0.541	0.004224					
			0.004235					
			0.004258	0.004239	0.004233	+0.12	0.56	0.44
32/3	0.491	0.509	0.004347					
			0.004362					
			0.004329	0.004346	0.004292	+0.26	0.59	0.41
16	0.546	0.454	0.004480					
			0.004300					
			0.004424					
			0.004343					
			0.004405	0.004390	0.004397	—0.10	0.65	0.35
32	0.637	0.363	0.004466					
			0.004419					
			0.004582					
			0.004476					
			0.004556	0.004500	0.004568	—1.55	0.72	0.28

TABLE IX.—K_N FOUND, K_N CALCULATED, α, $(1 - \alpha)$, ERROR IN PER CENT., AND PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES FOR LITHIUM ETHYLATE AND METHYL IODIDE AT 0°.

V.	α	$1 - \alpha$.	K_N found.	Av. K_N.	K_N calc.	% error.	Per cent. of reaction due to ions: $K_i\alpha/K_N$.	Per cent. of reaction due to molecules: $K_m(1-\alpha)/K_N$
2	0.144	0.856	0.002420					
			0.002381					
			0.002411					
			0.002417					
			0.002425	0.002406	0.002440	—1.40	0.30	0.70
4	0.220	0.780	0.002728					
			0.002678					
			0.002663					
			0.002696	0.002690	0.002690	0.0	0.42	0.58
8	0.312	0.688	0.002971					
			0.002986	0.002978	0.002991	—0.43	0.53	0.47
16	0.409	0.591	0.003304					
			0.003423					
			0.003330					
			0.003231	0.003322	0.003310	+0.36	0.64	0.36
32	0.519	0.481	0.003665					
			0.003657					
			0.003536	0.003619	0.003668	—1.30	0.73	0.27

TABLE X.—K_i AND K_m FOR SODIUM, POTASSIUM, AND LITHIUM ETHYLATES AND METHYL IODIDE AT 0°.

Sodium Ethylate.			Potassium Ethylate.			Lithium Ethylate.		
V.	K_i.	K_m.	V.	K_i.	K_m.	V.	K_i.	K_m.
1 : 2	0.004598	0.003074	4 : 8	0.00543	0.00320	2 : 4	0.005590	0.001872
1 : 4	0.004883	0.003010	4 : 32/3	0.00562	0.00310	2 : 8	0.005317	0.001918
1 : 8	0.004896	0.003027	4 : 16	0.00528	0.00329	2 : 16	0.005360	0.001911
1 : 16	0.004878	0.003030	4 : 32	0.00513	0.00340	2 : 32	0.005174	0.001942
1 : 32	0.004824	0.003038	16/3 : 32/3	0.00564	0.00306	4 : 8	0.005134	0.002001
2 : 4	0.005109	0.002915	16/3 : 16	0.00522	0.00335	4 : 16	0.005297	0.001955
2 : 8	0.004995	0.002950	16/3 : 32	0.00508	0.00348	4 : 32	0.005115	0.002006
2 : 16	0.004930	0.002970	8 : 16	0.00517	0.00345	8 : 16	0.005411	0.001875
2 : 32	0.004849	0.002995	8 : 32	0.00502	0.00359	8 : 32	0.005109	0.002012
4 : 8	0.004914	0.003014	16 : 32	0.00493	0.00377	16 : 32	0.004922	0.002214
4 : 16	0.004874	0.003033						
4 : 32	0.004808	0.003066						
8 : 16	0.004846	0.003065						
8 : 32	0.004778	0.003116						
16 : 32	0.004737	0.003188						
Av.,	0.00486	0.00303		0.00525	0.00337		0.00524	0.00197
Dr. W. A. Taylor's Av.,	0.00496	0.00294						

Tests with a Beckmann thermometer showed that all parts of the bath remained within a few thousandths of a degree of zero. The ethylate solutions were made up at 0°, and transferred at this temperature into the reaction flasks by surrounding the pipet with a jacket containing cracked ice and water. Ice-water from the bath was run continuously through the jacket of the machine by means of a pump run by a small electric motor. Although the exposed circulation was made as short as possible, the temperature of the water returning to the bath had risen several degrees. Even when this current of water was returned to the bath in the vicinity of the thermometer, no change in the temperature could be detected unless the water played directly upon the thermometer. In that part of the bath which contained the reaction flasks, no change in temperature could be detected. The delivery tube of the machine and all exposed connecting tubes were protected by several layers of binding tape, and that liquid in the most exposed part of the delivery tip was discarded just before each 10 cc. portion was run out. The reaction flask containing the ethylate solution was lifted from the bath in a beaker containing cracked ice and water, and after the alkyl halide solution had been transferred to it, the flask was returned to the bath as rapidly as possible. Tests made with the thermometer showed that by this method the temperature was kept below 0.5°, and the zero point was quickly reached by shaking the flask two minutes in the bath. For the work with the $N/16$ and $N/32$ solutions 40 cc. portions were used instead of the usual 20 cc., and the solutions were mixed by inverting and shaking the flasks under the ice-water. The corks were protected by rubber fingers over the necks of the flasks. A rise in the temperature of even several tenths of a degree for one minute would have but little effect on the constants, especially those for the dilute solutions for which the time periods were so long.

Summary.

1. It was shown how to purify and analyze methyl iodide. A number of samples boiled at about 42.35° and contained not over 0.05% impurities.

2. Special apparatus and baths for work at 0° are described.

3. The rates of a large number of reactions between methyl iodide and sodium, potassium, and lithium ethylates at 0° were studied. The concentration of the ethylates ranged from $N/1$ to $N/32$.

4. When the reaction velocities K_N and the ionization α for the different concentrations for any given ethylate are substituted in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$ good constants are obtained for K_i and K_m.

5. The activity K_i of unit concentrations of the ethylate ion should be, and is, the same whether sodium, potassium, or lithium ethylate be employed, and averages about 0.0051 at 0°.

6. Since the nonionized molecules of sodium, potassium, or lithium ethylate are different substances, the values of K_m vary with the ethylate. For sodium ethylate it is about 0.0030, for potassium ethylate it is about 0.0034, and for lithium ethylate it is about 0.0020.

7. Since these solutions are concentrated and not ideal, the physical

constants such as viscosity, specific gravity, dielectric constant, refractive index, α, K_V, etc., are modified by the different substances present and corrections must be applied later to the data presented here. Only in this way can we obtain the final data freed from all normal and abnormal salt and solvent effects. It is believed from data obtained by adding some of these substances that these corrections will not be large enough to modify the general theory of the activity of both the ions and molecules of acids, bases, and salts.

JOHNS HOPKINS UNIVERSITY,
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[CHEMICAL SECTION, IOWA AGRICULTURAL EXPERIMENT STATION.]

A COMPARISON OF BARBITURIC ACID, THIOBARBITURIC ACID AND MALONYLGUANIDINE AS QUANTITATIVE PRECIPITANTS FOR FURFURAL.

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All of the methods for the quantitative determination of pentoses and pentosans in agricultural products are based upon the conversion of pentose into furfural by distillation with a mineral acid, preferably hydrochloric, and subsequent estimation of furfural in the distillate by means of a suitable reagent. Günther, Chalmot and Tollens[1] titrated the furfural with phenylhydrazine, using aniline acetate paper as an indicator. Stone[2] made use of the same reaction, but used Fehling's solution to determine the excess of phenylhydrazine. Later, Flint and Tollens[3] showed that this titration method was not accurate, on account of the levulinic acid resulting from the decomposition of hexoses, as well as the instability of the standard phenylhydrazine acetate reagent used. Jolles[4] titrated the furfural with potassium bisulfite and iodine. In the absence of other reducing substances, the furfural could be determined directly with Fehling's solution. Günther and Tollens[5] precipitated the furfural as hydrofurfuralimide by means of ammonia, while Chalmot and Tollens[6] used phenylhydrazine and weighed the resulting hydrazone. In both cases the condensation product was somewhat soluble.

Councilor[7] was the first to use phloroglucinol for the quantitative determination of furfural. This method was later studied and perfected by Tollens and his co-workers. The phloroglucinol method, although

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[1] *Ber.*, 24, 3577 (1891).
[2] *Ibid.*, 24, 3019 (1891).
[3] *Ibid.*, 25, 2912 (1892).
[4] *Ibid.*, 39, 96 (1906).
[5] *Ibid.*, 23, 1751 (1890).
[6] *Ibid.*, 24, 694 (1891).
[7] *Chem. Ztg.*, 17, 1743.