The only other vapor-pressure values at low temperatures for ethane or ethylene (aside from normal boiling points) are those of Maas and McIntosh,[1] who worked out values for ethane from —88.5° (the normal boiling point found by them) to —107.8°. At this temperature they found a pressure of 287 mm., or 2.3° from the value the authors found at 287 mm.

The normal boiling point of ethylene has been found by Olszeswki and by Ramsey and Travers to be 170.5° abs.[2] Travers believes both of these values to be about 1° too low and places greater faith in the value 169.5° abs. found by Wroblewski and Witkowski.[3] The authors of this paper found the normal boiling point to be 169.2° abs.

Thermometer and Manometer Corrections.

The thermometer measurements could be reproduced within 0.2° and pressure readings within 1 mm. Stem corrections on the thermometers were not necessary because they were calibrated with the same depth of immersion as during the vapor-pressure measurements. Corrections for the expansion of the mercury in the manometer and for the steel scale, all fell within the error of experimentation.

Summary.

Saturated vapor pressures for ethane and ethylene at low temperatures are shown. In the case of ethane the vapor pressures range from 760 mm. at —89.3° to 1 mm. at —159.8°. In the case of ethylene the vapor pressures range from 760 mm. at —103.9° to 4 mm. at —159.9°.

The authors' experience with a bath devised by Henning for maintaining constant low temperatures is described.

CHEMICAL LABORATORY, BUREAU OF MINES.
PITTSBURGH, PA.

ON THE REACTIONS OF BOTH THE IONS AND THE MOLE-CULES OF ACIDS, BASES AND SALTS.

THE REACTIONS OF SODIUM ETHYLATE WITH METHYL IODIDE IN ABSOLUTE ETHYL ALCOHOL AT 25°.[4]

[TWENTY-FIRST[5] COMMUNICATION ON CATALYSIS.]

BY H. C. ROBERTSON, JR., AND S. F. ACREE.

When Brunel and Acree began, in March, 1905, work on the theory that *both the ions and the nonionized form of acids, bases and salts must be considered*

[1] O. Maas and McIntosh, THIS JOURNAL, **36**, 737 (1914).
[2] M. W. Travers, "The Experimental Study of Gases," p. 243 (1901).
[3] *Loc. cit.*
[4] We are indebted to the Carnegie Institution of Washington for aid in this work.
[5] For references see *Am. Chem. J.*, **49**, 474 (1913).

chemically active, the reactions of alkyl halides with the urazole salts[1] and acids were chosen as a very important class of compounds with which to work out the above theory and our hypothesis of tautomeric[2] salts. It was seen that work with different[3] salts and different alkyl halides would be necessary in order to secure definite proof that the alkyl halide reacts with both the anion and the molecule of the electrolyte, and to learn the influence of different groups, and the position of the metal in the periodic system, on these reaction velocities. In every case studied since that time we have found both the anions and nonionized electrolytes taking part in the transformations according to the equation $K_n = [K_i\alpha + K_m(1 - \alpha)][1 + fC\ salt]$.

The most convincing argument in favor of the theory that both the ions and molecules react with the alkyl halides lies in the fact that the ethylate (phenolate) ion common to sodium, potassium and lithium ethylates (phenolates) should and does react with the *same*[4] velocity with the same alkyl halide, whereas the nonionized forms of these salts are *different* and react with *different* velocities with the same alkyl halide, in accordance with the theory. To illustrate, it was shown in the preceding article by Dr. E. K. Marshall that ethyl bromide and ethyl iodide react with both the anion and the nonionized form of sodium ethylate, and that potassium ethylate and lithium ethylate also react with these two alkyl halides in entire accordance with the theory.

In order to make the evidence for the theory as broad as possible we began in 1909 the present study of the action of methyl iodide on sodium ethylate at 25°. The work on methyl iodide and potassium and lithium ethylates at 25° was finished in 1912–13 by Dr. J. H. Shrader and Dr. Julia Peachy Harrison, and gave still further evidence for the usefulness of the hypothesis. Practically the *same* value for K_i was found for all three salts, but *different* values were obtained for K_m for the *different* nonionized forms of the salts, as is shown in the following table:

	K_i.	K_m.
Dr. H. C. Robertson: sodium ethylate and methyl iodide..........	0.127	0.0594
Dr. Bessie Marion Brown: the same.............................	0.1285	0.0581''
Dr. J. H. Shrader: lithium ethylate and methyl iodide............	0.1367	0.03871
Dr. Julia Peachy Harrison: potassium ethylate and methyl iodide..	0.1259	0.0687

Salt Catalysis.[5]

We recognize that the K_i and K_m calculated here may involve another reaction, called at present a "salt effect," for which a correction must be

[1] *Am. Chem. J.*, **37**, 71 (1907); **43**, 505 (1910); **44**, 219 (1910).

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

[3] *Ibid.*, **39**, 229 (1908).

[4] *Ibid.*, **48**, 356, 378 (1912); **49**, 484 (1913).

[5] For the literature on "salt catalysis" see *Ibid.*, **49**, 350, 485 (1913), and other recent papers.

made later. In order to learn the effect of such a "salt effect" on the values of K_i and K_m, we have assumed a case in which we have corrected, in Table XXIII, the observed values of K_N for a *positive* "salt catalysis" of 8% per gram molecule of electrolyte. It is seen in Table XXIV that this positive catalysis of 8% raises K_i from 0.127 to 0.136, about 7%, and lowers K_m from 0.0594 to 0.05538, a little less than 7%. It is evident from the harmony of our data with the results of Dr. Shrader and Dr. Harrison that we must conclude at present that the "salt effect," whether large or small, is nearly the same for the sodium, potassium and lithium ethylates. When we collect our final data we shall be able to discuss this subject much more fully.

Experimental.

The methods used have been described fully in earlier papers.[1] The values of A, B and x are given in terms of the number of cc. of acid necessary to neutralize 10 cc. of the original ethylate solution in the presence of methyl orange. The unit of time, t, is the minute. The constants

SODIUM ETHYLATE AND METHYL IODIDE AT 25°.

By H. C. ROBERTSON.

TABLE I.

0.5 N Sodium Ethylate and 0.5 N Methyl Iodide.

A = 10.02.

t.	x.	K_V.
20	4.34	0.0382
30	5.30	0.0374
42	6.14	0.0376
50	6.52	0.0373
60	6.87	0.0365
	Mean,	0.0374
	K_N,	0.0748

TABLE III.

0.25 N Sodium Ethylate and 0.5 N Methyl Iodide.

A = 10.00.   B = 20.00.

t.	x.	K_V.
10	3.15	0.0207
20	5.08	0.0208
30	6.32	0.0206
40	7.11	0.0200
50	7.70	0.0196
	Mean,	0.0203
	K_N,	0.0812

TABLE II.

0.5 N Sodium Ethylate and 0.25 N Methyl Iodide.

A = 20.00.   B = 10.00.

t.	x.	K_V.
10	2.98	0.0384
20	4.80	0.0380
30	6.01	0.0374
40	6.92	0.0376
50	7.49	0.0365
	Mean,	0.0376
	K_N,	0.0752

TABLE IV.

0.25 N Sodium Ethylate and 0.25 N Methyl Iodide.

A = 10.00.

t.	x.	K_V.
20	2.93	0.0207
30	3.80	0.0204
40	4.44	0.0200
50	4.98	0.0198
60	5.40	0.0196
	Mean,	0.0201
	K_N,	0.0804

[1] See especially *Am. Chem. J.*, 43, 505 (1910); 49, 116, 127, 369, 474 (1913).

TABLE V.

0.125 N Sodium Ethylate and 0.125 N Methyl Iodide.

A = 10.00.

t.	x.	K_V.
20	1.80	0.0109
30	2.42	0.0107
40	3.00	0.0107
50	3.53	0.0109
70	4.26	0.0106

Mean, 0.0107

K_N, 0.0856

TABLE VIII.

0.0625 N Sodium Ethylate and 0.125 N Methyl Iodide.

A = 20.00.   B = 40.00.

t.	x.	K_V.
20	3.93	0.00577
32	5.79	0.00580
40	6.88	0.00582
60	9.08	0.00579
75	10.33	0.00570

Mean, 0.00577

K_N, 0.0923

TABLE VI.

0.125 N Sodium Ethylate and 0.125 N Methyl Iodide.

A = 10.00.

t.	x.	K_V.
30	2.43	0.01070
40	3.02	0.01082
50	3.52	0.01086
60	3.90	0.01066
70	4.27	0.01065
80	4.60	0.01064

Mean, 0.01072

K_N, 0.0858

TABLE IX.

0.025 N Sodium Ethylate and 0.125 N Methyl Iodide.

A = 20.00.   B = 100.00.

t.	x.	K_V.
10	2.00	0.00213
20	4.38	0.00250
30	6.60	0.00258
40	7.84	0.00260
50	8.96	0.00250

Mean, 0.00255

K_N, 0.01020

TABLE VII.

0.0625 N Sodium Ethylate and 0.125 N Methyl Iodide.

A = 10.00.   B = 20.00.

t.	x.	K_V.
20	2.00	0.00587
30	2.78	0.00584
40	3.44	0.00580
50	3.99	0.00573
60	4.44	0.00560

Mean, 0.00577

K_N, 0.0923

TABLE X.

0.025 N Sodium Ethylate and 0.125 N Methyl Iodide.

A = 20.00.   B = 100.00.

t.	x.	K_V.
20	3.92	0.00223
30	5.84	0.00237
40	7.52	0.00243
50	9.00	0.00248
60	10.28	0.00250

Mean, 0.00244

K_N, 0.09760

TABLE XI.

0.125 N Sodium Ethylate and 0.125 N Methyl Iodide at 25° C. (1% Water added to the Alcohol used.)

$A = 10.00.$

$t.$	$x.$	$K_V.$
20	1.81	0.0110
30	2.50	0.0111
40	3.06	0.0110
50	3.58	0.0111
60	3.96	0.0109
	Mean,	0.0110
	K_N,	0.0880

TABLE XII.

0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 25° C. (In a soln. contg. 0.92 the mol. equiv. of Sodium Iodide and Ethyl Ether.)

$A = 10.00.$

$t.$	$x.$	$K_V.$
20	2.62	0.0178
30	3.46	0.0176
40	4.14	0.0176
60	5.13	0.0175
	Mean,	0.0176
	K_N,	0.0704

TABLE XIII.

0.125 N Sodium Ethylate and 0.125 N Methyl Iodide at 25° C. (In soln. contg. 1.14 the mol. equiv. of Sodium Iodide and Ethyl Ether.)

$A = 10.02.$

$t.$	$x.$	$K_V.$
20	1.60	0.0096
40	2.70	0.0092
50	3.18	0.0093
60	3.62	0.0094
	Mean,	0.0095
	K_N,	0.0760

TABLE XIV.

0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 25° C. (In a mixture of 90% Alcohol and 10% Ethyl Ether.)

$A = 9.98.$

$t.$	$x.$	$K_V.$
30	0.88	0.00322
40	1.153	0.00328
50	1.38	0.00321
60	1.59	0.00316
70	1.81	0.00316
	Mean,	0.00320
	K_N,	0.0640

TABLE XV.

0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 25° C. (Flasks coated with a thick layer of black paint so as to be opaque to light.)

$A = 10.00.$

$t.$	$x.$	$K_V.$
10	2.77	0.0383
20	4.30	0.0378
30	5.25	0.0368
40	5.90	0.0360
60	6.83	0.0359
	Mean,	0.0370
	K_N,	0.0740

TABLE XVI.

0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 25° C. (With 0.5 molecular equivalent of Sodium Iodide added.)

$A = 10.00.$

$t.$	$x.$	$K_V.$
20	2.64	0.0179
30	3.50	0.0179
40	4.16	0.0178
50	4.74	0.0180
60	5.16	0.0178
	Mean,	0.0179
	K_N,	0.0716

TABLE XVII.

0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 25° C. (With one molecular equivalent of Sodium Iodide added.)

A = 10.00.

t.	x.	K_V.
25	3.00	0.0171
30	3.38	0.0170
42	4.18	0.0171
70	5.40	0.0168
131	6.91	0.0170

	Mean,	0.0170
	K_N,	0.0680

TABLE XVIII.

K_N found for Sodium Ethylate and Methyl Iodide at 25°.

V.	K_N.	K_N average.
2	0.0748	
	0.0752	0.0750
4	0.0812	
	0.0804	0.0808
8	0.0856	
	0.0858	0.0857
16	0.0923	
	0.0923	0.0923
40	0.1020	
	0.0976	0.0998

TABLE XX.

K_i and K_m found for Sodium Ethylate and Methyl Iodide at 25°.

		K_i.	K_m.
$V = 2$:	$V = 4$	0.132	0.0577
$V = 2$:	$V = 8$	0.127*	0.0591*
$V = 2$:	$V = 16$	0.129*	0.0586*
$V = 2$:	$V = 40$	0.126*	0.0593*
$V = 4$:	$V = 8$	0.123	0.0616
$V = 4$:	$V = 16$	0.127*	0.0595*
$V = 4$:	$V = 40$	0.125*	0.0605*
$V = 8$:	$V = 16$	0.130	0.0567
$V = 8$:	$V = 40$	0.126*	0.0597*
$V = 16$:	$V = 40$	0.124	0.0632

	Average,	0.127	0.0596
Average of values,*		0.127	0.0594

TABLE XIX.

The Ionization of Sodium Ethylate at 25°.

V.	α.	$1 - \alpha$.
1	0.148	0.852
2	0.234	0.766
4	0.312	0.688
8	0.393	0.607
16	0.481	0.519
32	0.577	0.423
40	0.605	0.395

TABLE XXI.

K_N calculated and found for Sodium Ethylate and Methyl Iodide at 25°.

V. K_N found. K_N calculated. Error in %.

$K_i = 0.1270.$ $K_i = 0.1270.$
$K_m = 0.0596.$ $K_m = 0.0594.$

2	0.0750	0.0753	0.0752	+0.4	+0.3
4	0.0808	0.0807	0.0805	—0.1	—0.4
8	0.0857	0.0861	0.0860	+0.5	+0.4
16	0.0923	0.0920	0.0919	—0.3	—0.5
40	0.0998	0.1004	0.1002	+0.6	+0.4

			Average error,	+0.2	+0.4

TABLE XXII.—PER CENT. OF REACTION DUE TO IONS AND TO MOLECULES.

Concentration of NaOC$_2$H$_5$. V.	Per cent of reaction due to αK_i.	Per cent of reaction due to $(1 - \alpha)K_m$.
2	39.5	60.5
4	49.2	50.8
8	58.0	42.0
16	66.5	33.5
40	76.7	23.3

TABLE XXIII.—K$_N$ FOR SODIUM ETHYLATE AND METHYL IODIDE AT 25°, CORRECTED FOR A POSITIVE SALT CATALYSIS OF 8% PER GRAM MOLECULE OF SODIUM ETHYLATE.

V.	α.	$1 - \alpha$.	K_N calculated.	K_N corrected for salt catalysis.
2	0.234	0.766	0.0752	0.0722
4	0.312	0.688	0.0805	0.0789
8	0.393	0.607	0.0860	0.0851
16	0.481	0.519	0.0919	0.0914
40	0.605	0.395	0.1002	0.1000

TABLE XXIV.—K$_i$ AND K$_m$ FOUND FOR SODIUM ETHYLATE AND METHYL IODIDE AT 25°, CORRECTED FOR POSITIVE SALT CATALYSIS OF 8% PER GRAM MOLECULE OF SODIUM ETHYLATE.

	K_i.	K_m.
V = 2 : V = 4	0.1380	0.05210
V = 2 : V = 8	0.1343	0.05321
V = 2 : V = 16	0.1317	0.05401
V = 2 : V = 40	0.1296	0.05467
V = 4 : V = 8	0.1538	0.05502
V = 4 : V = 16	0.1298	0.05582
V = 4 : V = 40	0.1595	0.05646
V = 8 : V = 16	0.1285	0.05696
V = 8 : V = 40	0.1278	0.05748
V = 16 : V = 40	0.1274	0.05804
Average,	0.1360	0.05538

are independent of the laboratory units of concentration employed for the acid; hence K_i, K_m, K_N and K_V refer to the constants for one gram ion of ethylate ions per liter, one gram molecule of nonionized sodium ethylate per liter, etc., as explained in the preceding articles. The addition of considerable quantities of ether and sodium iodide to some of the reaction mixtures shows that the small amounts of these formed during the time periods measured have no great effect on the reaction velocities.

Conclusions.

1. The work presented by Dr. Robertson on the reaction of methyl iodide with sodium ethylate in absolute ethyl alcohol at 25° shows that the reaction is not purely ionic. The "deviation" is strictly proportional to the concentration of the *nonionized* sodium ethylate, and we may,

therefore, interpret the transformation as one involving the reaction of the methyl iodide with both the ethylate ions and the nonionized sodium ethylate.

2. The values $K_i = 0.127$ and $K_m = 0.0596$ agree well with those obtained for methyl iodide and potassium ethylate ($K_i = 0.126$ and $K_m = 0.0687$) by Dr. Julia Peachy Harrison, and for methyl iodide and lithium ethylate ($K_i = 0.1367$ and $K_m = 0.03871$) by Dr. J. H. Shrader. If the theory is correct the true values for K_i should be identical for all three ethylates and the same alkyl halide, and these studies and others, as a whole, confirm this conclusion.

3. The effect of an extra reaction, or "salt catalysis," on these reactions has been calculated.

4. A discussion of the reasons for working with various salts and alkyl halides shows that great care must be exercised in the final interpretation of these results. Chemical reactions are probably far more complex than we can realize with our present limited knowledge.

JOHNS HOPKINS UNIVERSITY,
BALTIMORE. MD.

ON THE REACTIONS OF BOTH THE IONS AND MOLECULES OF ACIDS, BASES AND SALTS.

A REINTERPRETATION OF THE REACTIONS OF SODIUM METHYLATE AND SODIUM ETHYLATE WITH 1,2-DINITROBENZENE, 1,2,4-DINITRO-CHLOROBENZENE AND 1,2,4-DINITROBROMOBENZENE.[1]

[TWENTY-SECOND[2] COMMUNICATION ON CATALYSIS.]

BY S. F. ACREE.

The very fine work of Hecht,[3] Conrad and Brückner on the action of sodium ethylate on alkyl halides, and that of Bruyn, Steger,[4] and Lulofs[5] on the reactions of sodium methylate and sodium ethylate with the nitro and halogen substitution products of benzene were not interpreted by them by the use of the ionization theory. Conrad[6] and his co-workers spoke of these substances as nonelectrolytes, or "nichtleitende Körper." Bruyn and his co-workers, while measuring the conductivities of the sodium methylate and sodium ethylate, recognized that they were dealing with peculiar cases that could not be explained on the ionization hypothesis alone. In a footnote[7] Bruyn suggested that his reactions may

---

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

[2] See especially Am. Chem. J., 48, 352 (1912); 49, 116, 127, 345, 369, 474 (1913).

[3] Z. physik. Chem., 5, 289 (1890). A similar reinterpretation of this excellent work will soon be published by Dr. W. A. Taylor.

[4] Ibid., 49, 329; 333, 336 (1904); Rec. trav. chim., 18, 13, 41.

[5] Z. physik. Chem., 49, 341 (1904); Rec. trav. chim., 20, 292.

[6] Z. physik. Chem., 5, 289 (1890).

[7] Rec. trav. chim., 18, 40; see also Z. physik. Chem., 49, 332 (1904).