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DECOMPOSITION OF DIACETONE ALCOHOL IN ALKALI HYDROXIDE SOLUTIONS

By Gösta Åkerlöf

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I. Introduction

Higher velocities of catalyzed reactions in solutions of electrolytes have seldom been measured on account of rapidly increasing experimental difficulties. Using titration methods in some cases it may be possible to obtain relatively accurate results for reaction velocities with a half period as low as 150 seconds. This was shown by the measurements of Harned and Seltz[1] for the conversion of acetylchloro-aminobenzene to *p*-chloro-acetanilide in solutions of hydrochloric acid. A purely physical method for velocity measurements has therefore far greater possibilities because it eliminates the taking of samples, which necessarily involves a large waste of time. In the following will be given the results of some measurements of the decomposition of diacetone alcohol in concentrated alkali hydroxide solutions. It was found possible to obtain reasonably accurate results up to reaction velocities with a half period of about 35 seconds. For still higher velocities the difference between the calculated values and those obtained with the apparatus used increased rapidly with increasing alkali hydroxide concentration. This was because the temperature changes caused by the reaction could not be counteracted rapidly enough.

With the method for measuring these higher velocities worked out in detail, it was possible to study various questions of great theoretical interest. Electromotive-force measurements of Harned[2] for mixtures

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[1] Harned and Seltz, This Journal, **44**, 1475 (1922).

[2] (a) Harned, *ibid.*, **48**, 326 (1926); compare further (b) Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

of hydrochloric acid or the alkali hydroxides with the alkali chlorides at constant total molarity in aqueous solutions have shown that the logarithm of the activity coefficient of the acid or hydroxide varies directly as their respective concentrations. As Harned[2b,3] has also shown that a number of the ions of these electrolytes show a distinct additive behavior, it would seem to be most probable that this relationship is also valid for the single ions of the acid or the alkali hydroxides. It was found by Åkerlöf[4] that the decomposition velocity of diacetone alcohol in alkali hydroxide-alkali salt solutions is additive and always seemed to follow the activity of the hydroxyl ion as long as counteracting influences did not interfere. Therefore it was of considerable interest to measure the decomposition velocity in alkali hydroxide-salt solutions at constant total molarity over a wider concentration range. Just as for the electromotive-force measurements, here also a linear variation was found.

With varying constant total molarity a number of straight lines were obtained which seemed to be parallel within the experimental errors. The extension of these lines to zero salt concentration gave the logarithm for the pure hydroxide solution. Thus a method had been found of predicting experimentally with a certain degree of accuracy the decomposition velocity which would be expected for a pure hydroxide solution of a given concentration. It also was found that the thermodynamic activity of the alkali hydroxide present in the pure hydroxide solution was proportional to the reaction velocity. The values predicted from the activity function on the one hand and those from the constant molarity curves on the other agreed very well. Therefore it was possible to decide when the method used for the velocity measurements began to break down or at least when the accuracy of the results obtained might be suspected.

II. Experimental Methods

For reaction velocities up to $K = 0.1$ corresponding to a half period of three minutes, the experimental method used was in every detail the same as previously described. At higher velocities the trouble began. With increasing reaction velocities it was necessary to increase the amount of diacetone alcohol used in order to have enough left when the measurement could be started. However, at the same time it was found that the different values obtained for the velocity constant from a single run always showed a continuous decrease as the reaction proceeded toward its completion.

TABLE I

TEMPERATURE CHANGES DURING THE DECOMPOSITION OF DIACETONE ALCOHOL IN ALKALI HYDROXIDE SOLUTIONS

Time, min.	0.00	0.30	1.30	2.30	3.30	4.30	5.30	6.30	7.30	∞
Temperature	3.042	2.871	2.480	2.240	2.071	1.965	1.887	1.831	1.086	1.720
$K \times 10^5$ (sec.)	...	(201)	267	270	274	271	272	276	270	...

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[3] (a) Harned, THIS JOURNAL, 42, 1808 (1920); (b) *Z. physik. Chem.*, **117,** 1 (1917).

[4] Åkerlöf, THIS JOURNAL, **48,** 3046 (1926).

A detailed study of the heat of solution for the diacetone alcohol and the heat of reaction for its decomposition gave a clear conception of the difficulties encountered. When 5 cc. of diacetone alcohol at ordinary temperatures was dissolved in 100 g. of water, the temperature was found to increase 1.54 degrees. In an alkali hydroxide solution the heat of solution must be very nearly the same as in pure water and therefore in this case also an immediate increase was first observed. The temperature then began to drop, soon passed through the starting point and finally reached a value 0.19 degree lower. Table I gives a summary of some calorimetric measurements of the temperature changes using a Beckmann thermometer.

About 25 cc. of diacetone alcohol had been mixed with 520 g. of approximately 1 *N* sodium hydroxide in the silver foil solution vessel of the calorimeter. This was well heat-insulated and the temperature changes due to stirring amounted to about 0.005° in five or six minutes. Therefore only the end value has been given a slight correction. With increasing velocity the Beckmann thermometer is soon completely unable to follow the rapid temperature changes but it is possible that a method could be worked out with photographic registration of resistance changes for a thin wire or the electromotive-force changes for a set of thermocouples immersed in the solution.

With the apparatus available the following procedure was adopted for the measurement of higher reaction velocities. The reaction tube (Fig. 1) was evacuated for ten to fifteen minutes. In order to avoid temperature changes in the reaction tube at the start of the reaction due to temperature differences between the water pump belonging to the thermostat system and the water in the thermostat, this pump was started during the evacuation of the tube about five minutes before the diacetone alcohol was mixed with the solution to be used for the measurement. The running of the water pump usually caused a very slow temperature increase of 0.01 to 0.02° during the entire run of the measurement. The magnitude of the temperature change varied somewhat with the room temperature. The amount of water passed through the spiral in the reaction tube was approximately 1000 cc. a minute and the spiral had 30 complete windings on a total length of 15 inches.

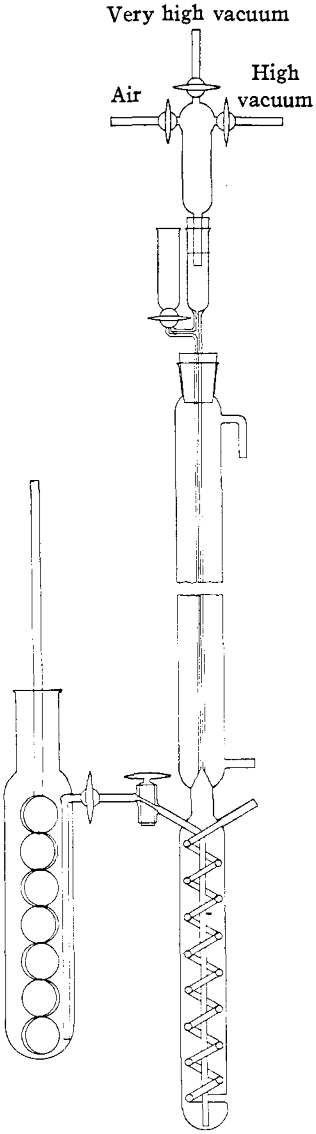

Fig. 1.—Apparatus used for the determination of higher velocities for the decomposition of diacetone alcohol in alkali hydroxide solutions.

The diacetone alcohol was carefully poured on top of the solution in the mixing vessel, then immediately mixed for a certain number of seconds with the alkali hydroxide solution with a very efficient high-speed stirrer. The filling of the reaction tube started the moment the stirrer stopped. After five seconds the tube was filled to eight or nine tenths. Then the filling was stopped in order to let some of the foam disappear. When a predetermined number of seconds had passed, the filling was completed, the stopcock to the vacuum line closed and a large drop of mercury drawn in from the supply tube at the top of the capillary. The entire length of the capillary was then kept filled with mercury (about 80 cm. pressure) for a few seconds in order to compress rapidly any tiny gas bubbles in the reaction tube. At last the mercury column was shortened to its usual length and the two stopcocks between reaction tube and mixing vessel were tightly closed. The measurement of the reaction velocity could be started a few seconds later.

After some training it was found that about five seconds were necessary for the setting of the cathetometer to any desired height with an error of less than 0.1 of one mm. The reader[5] of the stop watch obtained an accuracy of plus or minus one-fifth of one second, but this accuracy was usually unnecessary, when other possible errors are considered. The complete mixing of the diacetone alcohol with the solution could easily be accomplished in ten seconds. For the complete filling of the reaction tube a time of not less than thirty seconds was found to be desirable.

It is easy to understand that this method of measuring high reaction velocities has its difficulties. The solutions foamed violently during the filling of the reaction tube on account of the high vapor pressure of the acetone formed. It was impossible to wait until the greater part of the foam had disappeared and, therefore, a chance had always to be taken that a rapid compression would dissolve the remaining gas bubbles within a few seconds. The spiral in the reaction tube had a relatively large surface. In one way this was a decided disadvantage because it gave such good resting places for gas bubbles. On the other hand, the surface had to be large in order to insure a sufficiently constant temperature.

TABLE II

ATTAINABLE ACCURACY OF THE RESULTS

Solution with 2 *N* KOH			Solution with 1.8 *N* NaOH			Solution with 2.2 *N* LiOH		
Time in seconds	Cathetometer	$K \times 10^5$	Time in seconds	Cathetometer	$K \times 10^5$	Time in seconds	Cathetometer	$K \times 10^5$
0.0	8.00	...	0.0	10.00	...	0.0	10.00	...
24.4[a]	20.00	...	25.4[a]	20.00	...	25.2[a]	20.00	...
35.0	24.00	772	39.4	24.00	592	37.2	24.00	642
48.0	28.00	775	55.8	28.00	611	52.0	28.00	637
64.8	32.00	778	66.6	30.00	601	60.8	30.00	636
75.8	34.00	776	78.6	32.00	602	71.0	32.00	634
89.4	36.00	776	92.2	34.00	610	81.6	34.00	648
106.6	38.00	782	110.6	36.00	606	96.2	36.00	643
133.4	40.00	779	136.2	38.00	597	115.0	38.00	636
183.6	42.00	787	174.2	40.00	595	141.0	40.00	629
∞	43.3	...	∞	43.0	...	∞	44.6	...

[a] Used as starting time for the calculation.

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[5] The large number of very rapid, consecutive time readings required the utmost attention. The author is highly indebted to Dr. C. C. French, who made all the time readings for more than 150 high-velocity measurements. The author wishes also in this place to express his most sincere thanks to Dr. French.

The constancy of temperature could not be directly determined but the temperature changes during the measurement itself must naturally have been very small, as only the very last part of the reaction was measured. It was, however, another possible chance that had to be taken. It might then appear that the only way to test the possible value of the method and the efficiency of the apparatus used was to see whether constant and reproducible results could be obtained. Table II gives the summary of a few measurements.

The measurements given in Table II may seem to indicate a fairly high accuracy for the results obtained. However, it was found that at velocities with half periods of less than thirty seconds the deviation between measured and calculated velocities increased rapidly, although the measurements showed a high degree of constancy and were easily reproducible. Table III gives a summary of some measurements with 3, 3.5 and 4 *N* sodium hydroxide solutions.

Table III

Measurements of Very High Reaction Velocities

Solution with 3 *N* NaOH			Solution with 3.5 *N* NaOH			Solution with 4 *N* NaOH		
Time in seconds	Cathetometer	$K \times 10^4$	Time in seconds	Cathetometer	$K \times 10^4$	Time in seconds	Cathetometer	$K \times 10^4$
0.0	10.00	...	0.0	10.00	...	0.0	10.00	...
14[a]	20.00	...	11.0[a]	20.00	...	11.6	20.00	161
21	24.00	104	16.0	24.00	128	18.0	24.00	162
29	28.00	108	22.2	28.00	125	22.0	26.00	162
40	32.00	105	29.0	32.00	128	26.8	28.00	161
53	36.00	108	38.6	36.00	126	32.6	30.00	160
74	40.00	108	51.0	40.00	127	39.6	32.00	161
91	42.00	108	71.0	44.00	126	48.6	34.00	163
115	44.00	101	86.6	46.00	129	61.6	36.00	169
∞	45.8	...	∞	49.1	...	∞	38.6	...
K observed, 0.636			*K* observed, 0.761			*K* observed, 0.974		
K calculated, 0.69			*K* calculated, 0.85			*K* calculated, 1.09		

[a] Used as starting time for the calculation.

The measurements given in Table III were obtained with a larger reaction tube having two spirals. The water velocity was very high. The infinity values always decreased slowly after they had reached their highest point. This maximum point was used as infinity value. The differences between observed and calculated values increase rapidly with increasing concentration of the alkali hydroxide. This apparently must be due to the inefficiency of the apparatus used. The temperature changes of the solution due to the reaction follow the same formula that was used for the calculation of the reaction velocity. The velocity with which the temperature of the solution in the reaction vessel comes back to the temperature of the water in the thermostat also follows this formula (Newton's cooling law). As long as the velocity for this heat exchange between water and solution can follow the velocity for the temperature changes of the solution from the heat of reaction the observed expansion ought to give a true expression for the decomposition velocity of the diacetone alcohol. When this velocity increases beyond a certain limit, the velocity constants obtained must be too low, because the temperature decreased during the reaction.

III. Experimental Results with Aqueous Solutions of Potassium, Sodium and Lithium Hydroxide

A summary of the measurements with these solutions is given in Table IV. All concentrations are given in weight normality. For hydroxide concentrations of 0.8 and higher, the amount of diacetone alcohol used was about 5% of the total volume of the solution. The average error of the velocity constants is difficult to judge for the highest concentrations. Up to an hydroxide concentration of 1.6 *N* it may not exceed 2 or 3% unless there are unknown systematic errors. The velocity constants are given with the minute as the unit of time. In order to show how rapidly the experimental difficulties are increasing with increasing hydroxide concentration, the half period of reaction is given in seconds, *T*, for potassium hydroxide solutions.

TABLE IV

DECOMPOSITION VELOCITY FOR DIACETONE ALCOHOL IN SOLUTIONS OF POTASSIUM, SODIUM AND LITHIUM HYDROXIDE

Concn. in wt. norm.	KOH solutions			NaOH solutions		LiOH solutions	
N	*K*	*T*	*K/N*	*K*	*K/N*	*K*	*K/N*
0.1	0.0211[a]	851	0.211	0.0208[a]	0.208	0.0205	0.205
.2	.0402	449	.201	.0392	.196	.0384	.192
.4	.0790	229	.198	.0758	.189	.0732	.183
.6	.117	154	.195	.112	.187	.107	.178
.8	.154	117	.192	.149	.186	.139	.175
1.0	.196	92	.196	.186	.186	.174	.174
1.2	.246	74	.205	.227	.190	.210	.175
1.4	.293	62	.209	.268	.191	.245	.175
1.6	.347	52	.217	.314	.196	.280	.175
1.8	.402	45	.223	.362	.201	.313	.174
2.0	.468	39	.234	.412	.206	.346	.173
2.2	.542	33	.246	.469	.213	.380	.173

[a] These values are recently redetermined.

A graphical representation of the reaction velocity as a function of the alkali hydroxide concentration is given in Fig. 2. The figure shows that in solutions up to 1 *N* the velocity is approximately proportional to the hydroxide concentration. Fig. 3 has a much greater interest. Here the ratio between velocity constant and hydroxide concentration is plotted as a function of this concentration.

This ratio shows for lithium hydroxide solutions an almost continuous decrease, but for solutions of the other two hydroxides it passes through a minimum between 0.6 and 1 *N*, then increases, rapidly for potassium hydroxide but comparatively slowly for sodium hydroxide solutions. The comparison of the curves in Fig. 4 for the activity coefficients of the alkali

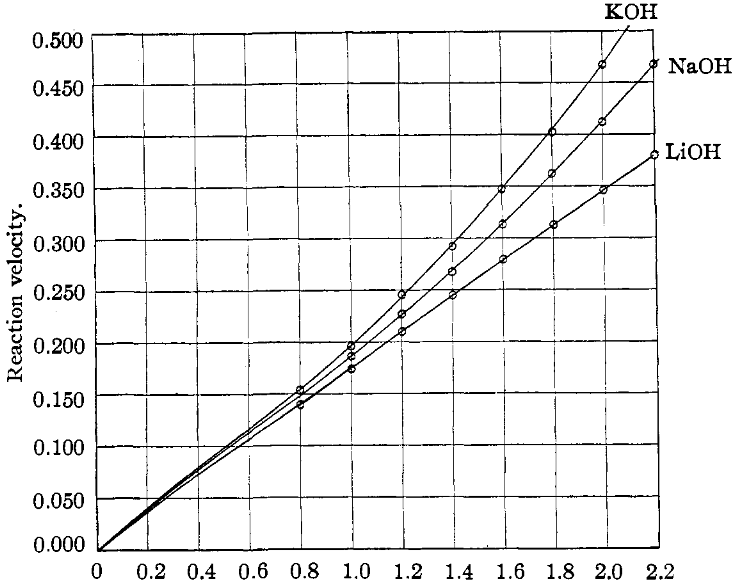

Fig. 2.—Curves for the decomposition velocity of diacetone alcohol in aqueous solutions of potassium, sodium and lithium hydroxide.

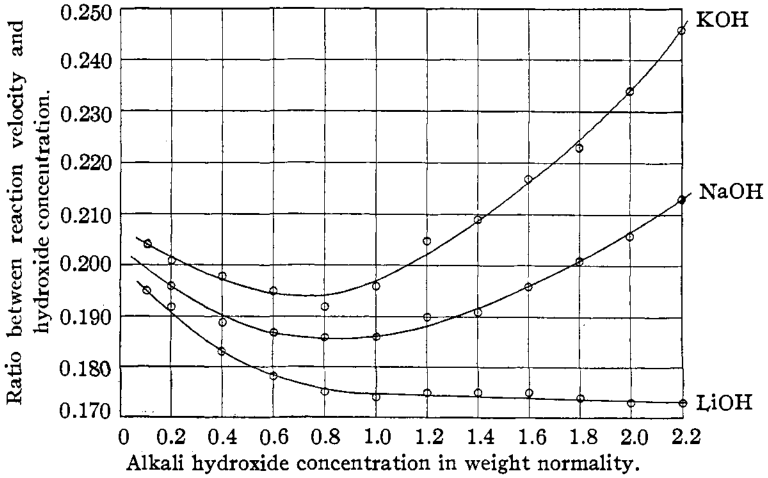

Fig. 3.—Curves for the ratio between concentration and decomposition velocity of diacetone alcohol in aqueous solutions of potassium, sodium and lithium hydroxide.

hydroxides as measured by Knobel,[6] Harned[7,3b] and Harned and Swindells,[8,2b] with the curves for the ratio between decomposition velocity and hydroxide concentration shows they are very similar to each other. For the two sets of curves the minima appear at about the same place and their distribution relative to each other is in both cases approximately the same. The close relationship between activity of the alkali hydroxide present and the decomposition velocity is still more clearly shown in Table V where the ratio between the activity of the alkali hydroxide and the velocity constant is given. The activity coefficients of the alkali hydroxides were calculated from the following equation

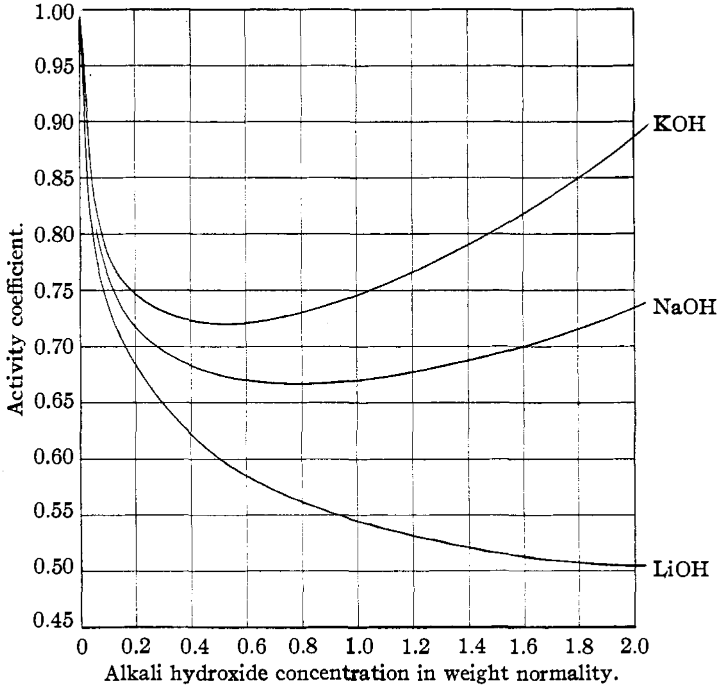

Fig. 4.—Curves for the activity coefficients of the alkali hydroxides in pure aqueous solutions.

$$\log \gamma_{\mathrm{MeOH}} = -\frac{0.354\sqrt{2m}}{1 + H\sqrt{2m}} + B\,2m - \log\left(1 + \frac{w \cdot 2m}{1000}\right)$$

where γ is the activity coefficient, A and B are empirical constants and w is the molecular weight of the solvent. The values of A and B are given in Table V. They were calculated by Harned and Åkerlöf.[2b]

The ratio between activity and velocity constant for potassium and

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[6] Knobel, This Journal, **45**, 70 (1923).

[7] Harned, *ibid.*, **47**, 676 (1925).

[8] Harned and Swindells, *ibid.*, **48**, 126 (1926).

Table V

Ratio Between Activity of the Hydroxide Present and the Decomposition Velocity of Diacetone Alcohol

Concn. in wt. norm.	KOH solutions		NaOH solutions		LiOH solutions	
N	γ	$\gamma N/K \cdot 10^2$	γ	$\gamma N/K \cdot 10^2$	γ	$\gamma N/K \cdot 10$
0.1	0.783	371	0.767	369	0.744	36
.2	.745	371	.716	366	.684	35
.4	.721	364	.685	362	.620	34
.6	.720	384	.669	358	.583	33
.8	.730	375	.666	358	.560	32
1.0	.745	380	.669	360	.542	31
1.2	.767	374	.677	356	.530	30
1.4	.791	378	.687	360	.520	30
1.6	.818	377	.700	357	.513	29
1.8	.849	381	.715	356	.507	29
2.0	.882	377	.732	355	.503	29
	$A = 0.777$		$A = 0.660$		$A = 0.500$	
	$B = .0632$		$B = .050$		$B = .0215$	

sodium hydroxide solutions is apparently a constant within the experimental errors. For lithium hydroxide solutions it varies slightly more and in a definite direction. However, the variations might easily be due to a combination of systematic errors in the velocity determinations and comparatively small errors of two or three millivolts in the electromotive-force measurements. Therefore it would seem to be proved with very little doubt that the decomposition velocity of diacetone alcohol in pure aqueous solutions of the alkali hydroxides is determined by the activity of the hydroxide present.

IV. Measurements at Constant Total Molarity with One Salt Present

The individual activity coefficients of the hydroxyl ion in pure alkali hydroxide solutions are unknown. It seems to be very probable that at a given concentration the activity coefficient of this ion is highest in potassium and lowest in lithium hydroxide solutions, which is the same order as for the ratio between activity of the hydroxide and the velocity constants. The activity coefficients of the cations of the alkali hydroxides change in the opposite order. Therefore it must be improbable that the activity of the hydroxyl ion is the only determining factor in the decomposition velocity of diacetone alcohol. This was also shown in the preceding paper. The compensating effect that must exist to keep the ratio between activity of the hydroxide and the decomposition velocity constant, may partly be caused by changes of the activity of the reacting substance due to the electrical field of the ions present. The presence of the hydroxyl ion is apparently necessary to get the reaction started. To account for the unknown effect it may therefore be assumed that after the start the cations participate to complete the process. In that case their activity must enter into the velocity function. However, this assumption might bring in another difficulty. The individual activity coefficient of the hydroxyl ion decreases when an alkali halide is added. At moderate salt concentrations this decrease seems to be of the same relative magnitude as the decrease in reaction velocity, although the activity of the cation increases rapidly.

On account of this unknown effect a simple relation between the activity of the hydroxide and the velocity cannot be expected when a salt is added. Harned[2a] and Harned and Åkerlöf[2b] have shown that the logarithm of the activity coefficient of hydrochloric acid or the alkali hydroxides in alkali chloride solutions at constant total molarity varies linearly with their concentration. Therefore it seemed that this case would offer the best possibilities for a theoretical interpretation of velocity measurements in alkali hydroxide-alkali salt solutions. A summary of the measurements is given in Table VI.

TABLE VI

VELOCITY MEASUREMENTS AT CONSTANT TOTAL MOLARITY OF 2

MeOH	KOH-KCl solutions		NaOH-NaCl solutions		LiOH-LiCl solutions	
N	K	Log K/N	K	Log K/N	K	Log K/N
0.1	0.0144[a]	−0.842	0.0123[a]	−0.910	0.0105	−0.979
.2	.0298	− .827	.0254	− .896	.0213	− .972
.4	.0619	− .810	.0539	− .871	.0454	− .945
.6	.0958	− .797	.0865	− .841	.0716	− .923
.8	.138	− .763	.121	− .820	.101	− .899
1.0	.177	− .752	.161	− .793	.135	− .870
1.2	.229	− .719	.202	− .774	.169	− .851
1.4	.281	− .697	.250	− .748	.211	− .822
1.6	.335	− .679	.293	− .737	.256	− .796
1.8	.392	− .662	.345	− .717	.301	− .777
2.0	.468	− .631	.412	− .686	.346	− .762

[a] Interpolated from results published in preceding paper.

A graphical representation of the values for log K/N given in Table VI is shown in Fig. 5 as a function of the alkali hydroxide concentration. In Fig. 6 are given the curves for the logarithm of the activity coefficients of the alkali hydroxides in solutions of the corresponding alkali chlorides at the constant total molarity of two. For the plotting of these last curves only two points could be obtained for each one of them but it has been shown by Harned and Åkerlöf that they must be straight lines.

As with the curves for the logarithm of the activity coefficients of the alkali hydroxides, those representing the velocity measurements are straight lines, but there is a great difference in the dispersion of the curves. In the former case they diverge at large angles but in the latter they seem to be very nearly parallel. This was partly to be expected. In Fig. 7 are given the electromotive-force changes for the hydroxyl ion in 0.1 N alkali hydroxide solutions at increasing concentrations of the corresponding alkali chlorides according to the calculations of Harned.[9] The electromotive force is proportional to the logarithm of the activity coefficient. Therefore the individual activity coefficients of the hydroxyl ion according to Fig. 7 must have quite different values for the three

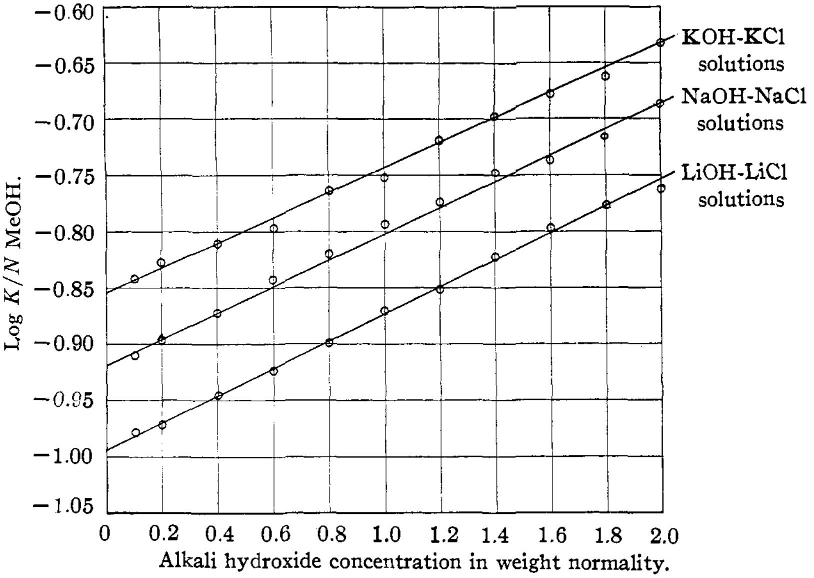

Fig. 5.—Curves for the logarithm of the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration in alkali hydroxide-alkali chloride solutions with the constant total molarity of 2.

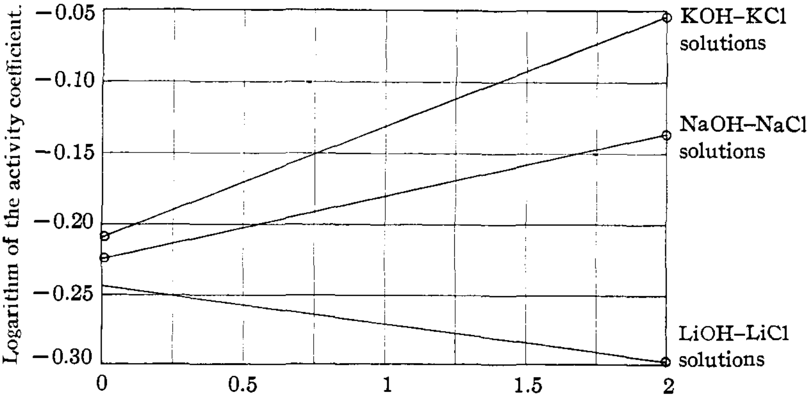

Fig. 6.—Curves for the logarithm of the activity coefficients of the alkali hydroxides in alkali hydroxide-alkali chloride solutions with the constant total molarity of 2.

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[9] Harned, *J. Phys. Chem.*, 30, 433 (1926).

alkali hydroxides at small hydroxide and high salt concentrations. To the electromotive-force differences shown in Fig. 7 should also be added the differences in the pure 0.1 N hydroxide solutions since the curves are all referred to the same starting point. This would draw them still further apart. With the simple assumption that the decomposition velocity of diacetone alcohol is proportional to the activity of the catalyzing ion, the difference in distribution for the two sets of curves in Figs. 5 and 6 would be easier to understand.

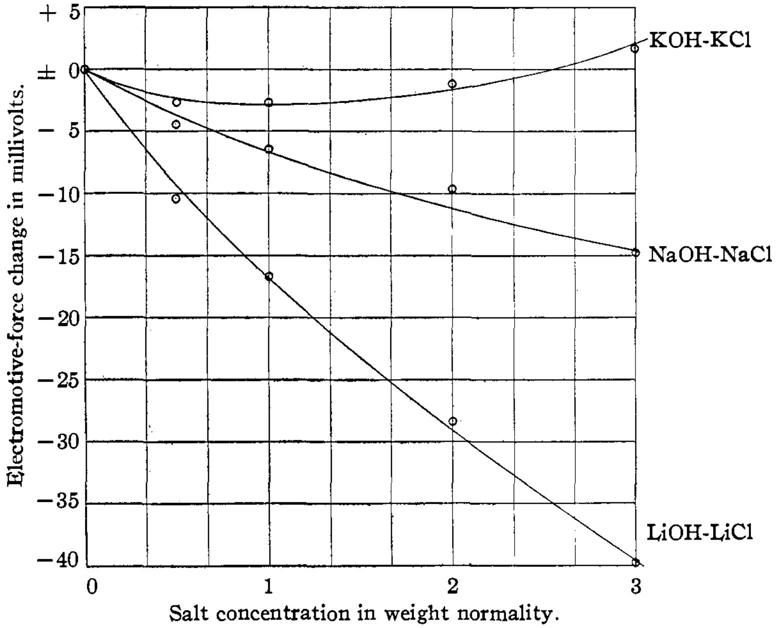

Fig. 7.—Curves for the approximate electromotive-force changes of the hydroxyl ion in 0.1 N alkali hydroxide solutions at increasing concentrations of the corresponding alkali chlorides.

However, at present the most important result of the velocity measurements at constant total molarity is that log K/N varies linearly with the hydroxide concentration. The concentration of the cations of the electrolytes present in these solutions is constant. According to the additivity principle of MacInnes[10] and Harned[3a,b] for the activity coefficients of strong electrolytes it may then be considered as approximately valid that the activity of the cations is constant. If this approaches the true conditions, the logarithm for the individual activity coefficient of the hydroxyl ion must vary linearly with the concentration of this ion. Since it was found that in addition to the activity of the catalyzing ion there was another factor, as yet unknown, on which the decomposition velocity

[10] MacInnes, This Journal, **41**, 1086 (1919); **43**, 1217 (1921).

of the diacetone alcohol was dependent, the variations in this factor in solutions of strong electrolytes must follow the same general formulas previously found for the activity coefficient of an ion from electromotive force measurements.

V. Measurements at Varying Constant Total Molarity with One Salt Present

Harned and Åkerlöf have found that the curves for the logarithm of the activity coefficients of the alkali hydroxides in solutions of their corresponding chlorides at varying constant total molarity as a function of the hydroxide concentration are represented by a series of parallel, straight lines. This is shown in Fig. 8 for potassium and sodium hydroxide solutions. A summary of the velocity measurements in sodium hydroxide-chloride solutions at varying constant total molarity is given in Table VII.

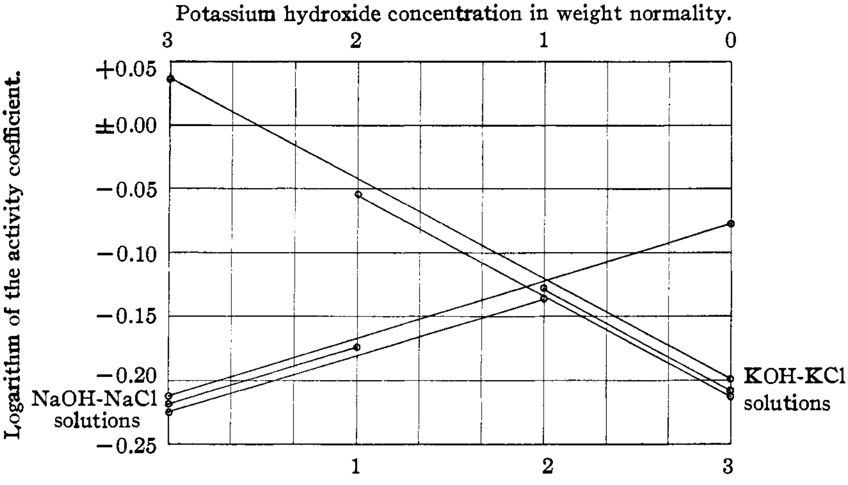

Fig. 8.—Curves for the logarithm of the activity coefficients of potassium and sodium hydroxide in solutions of the corresponding alkali chlorides at varying constant total molarity.

This table gives the values obtained for log K/N at the hydroxide concentrations 0.1, 1.0 and 2.0 N. A graphical representation of these measurements is shown in Fig. 9. The curves are drawn as straight lines, parallel to each other, except the line for the total molarity of one. The angle for this line with the others is, however, very slight. A comparison of these curves with those for sodium hydroxide-chloride solutions in Fig. 8 shows their relative distribution to be different, which was to be expected. The activity of the alkali hydroxide is determined by the product of the activities of cation and anion. As the function of the cation apparently

TABLE VII

VELOCITY MEASUREMENTS IN SODIUM HYDROXIDE-SODIUM CHLORIDE SOLUTIONS AT VARYING CONSTANT TOTAL MOLARITY

NaOH N	NaCl N	$K \times 10^4$	NaOH N	NaCl N	$K \times 10^4$	Log K/N
0.1	0.5	170[a]	...	...	...	.....
.1	1.0	149[a]	0.1	0.9	152[b]	−0.818
.1	2.0	121[a]	.1	1.9	123[b]	− .910
.1	3.0	101[a]	.1	2.9	102[b]	− .991
.1	4.0	91.8[a]	.1	3.9	92[b]	−1.036
.1	5.0	83.5[a]	.1	4.9	84[b]	−1.076
.1	6.0	78.1[a]	.1	5.9	78[b]	−1.108

NaOH	NaCl	$K \times 10^3$	Log K/N	NaOH	NaCl	$K \times 10^3$	Log K/N
1.0	0.0	186	−0.730	...	...	...	.....
1.0	1.0	158[b]	− .802	2.0	0.0	412	−0.686
1.0	2.0	133	− .876	2.0	1.0	342	− .767
1.0	3.0	119	− .924	2.0	2.0	301	− .823
1.0	4.0	109	− .963	2.0	3.0	280	− .854
1.0	5.0	98.8	−1.005	2.0	4.0	264	− .879

[a] Values given in preceding paper.

[b] Interpolated velocity measurements.

must be a little different from that of the hydroxyl ion, this must give a different distribution of the corresponding curves in the two cases.

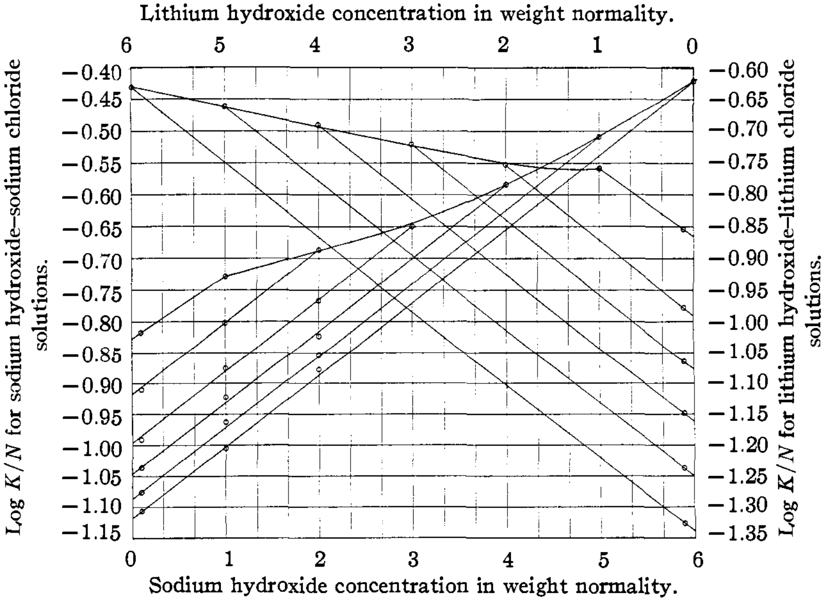

Fig. 9.—Curves for the logarithm of the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration in sodium and lithium hydroxide-chloride solutions with varying constant total molarity.

In Fig. 9 all lines are extended to zero salt concentration. This gives graphically the logarithm for the reaction velocity in the pure hydroxide solutions at higher concentrations. In Table V was shown $\gamma N/K = R$, where R is a constant. It would then be interesting to compare the values for the reaction velocities in pure hydroxide solutions on one side as calculated from the given activity coefficients of the alkali hydroxides and on the other as derived from the measurements at varying constant total molarity. Table VIII gives a summary of the calculations for potassium and sodium hydroxide solutions. To illustrate in a simple way the increasing speed of the reaction with rapidly growing alkali hydroxide concentration the half periods are given in seconds (T).

TABLE VIII

DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL IN SODIUM AND POTASSIUM HYDROXIDE SOLUTIONS AT HIGH CONCENTRATIONS

A. Potassium Hydroxide Solutions

K from activity			K from constant molarity		
N	γ_{MeOH}	K calcd.	Log K/N	K calcd.	T
2.0	0.882	(0.47)	−0.631	(0.47)	39
3.0	1.086	.86	− .558	.83	21
4.0	1.362	1.45	− .470	1.36	12
5.0	1.723	2.29	− .373[a]	2.12	7.9
6.0	2.194	3.49	− .252[a]	3.36	5.2
B. Sodium Hydroxide Solutions					
2.0	0.732	(0.41)	−0.686	(0.41)	44
3.0	.840	.69	− .646	.68	26
4.0	.982	1.09	− .580	1.05	17
5.0	1.162	1.61	− .505	1.57	11
6.0	1.387	2.30	− .418	2.29	7.9

[a] These values derived from measurements on potassium bromide solutions.

The values obtained by the two different methods for the decomposition velocity of diacetone alcohol in a hydroxide solution of a given concentration agree very well. This seems to indicate that the measurements on which these calculations are based must be consistent and have a fairly high degree of accuracy. It does not, however, exclude the possibility of certain systematic errors due to the experimental method used. The values calculated for hydroxide solutions with a higher concentration than 4 N are entirely hypothetical. There are a number of indications that these values may be approximately valid. It cannot be decided from the results given here whether the decomposition velocity with increasing hydroxide concentration finally reaches an upper limit which it does not exceed. If this were to be the case it seems that it should have been noticed long before this limit had been reached. Rather the contrary is observed, the reaction velocity accelerating with increasing hydroxide concentration.

To determine the decomposition velocity for lithium hydroxide solutions of higher concentrations than two, measurements were carried out with lithium chloride in 0.1 N hydroxide solutions. The solubility of lithium hydroxide decreases very rapidly with increasing lithium chloride concentration. Therefore no other measurements were made for salt solutions with higher hydroxide concentration than those given in Table VI. A summary of measurements and calculations is given in Table IX.

TABLE IX

DECOMPOSITION VELOCITY OF DIACETONE ALCOHOL IN LITHIUM HYDROXIDE SOLUTIONS AT VERY HIGH CONCENTRATIONS

LiOH	LiCl	LiCl			LiOH			
N	N	$K \times 10^4$	N	$K \times 10^4$	Log K/N	N	Log K/N	K
0.1	0.5	158	...	...	.....	...	.....	..
.1	1.0	136	0.9	140[a]	−0.854	...	.....	..
.1	1.5	118	...	...	.....	...	.....	..
.1	2.0	103	1.9	105[a]	−0.979	2.0	−0.762	(0.35)
.1	3.0	86.3	2.9	86[a]	−1.065	3.0	− .716	.58
.1	4.0	70.5	3.9	71[a]	−1.149	4.0	− .680	.84
.1	5.0	56.9	4.9	58[a]	−1.237	5.0	− .649	1.12
.1	6.0	46.9	5.9	47[a]	−1.328	6.0	− .621	(1.42)

[a] Interpolated values for the 0.1 N hydroxide solutions.

The velocity constants for concentrated, pure lithium hydroxide solutions calculated from the activity coefficients measured by Harned and Swindells agree fairly well with the values in Table IX. The agreement is, however, not as good as shown for potassium and sodium hydroxide solutions.

In Fig. 5 were shown the curves for log K/N for the three alkali hydroxide-chloride solutions at the constant total molarity of two. The most striking feature of these lines is that they seem to be very nearly parallel. If, instead of the alkali chlorides, the nitrates, bromides, iodides or thiocyanates had been used, apparently the same result would have been obtained. This is evident from a comparison with the velocity measurements given in the preceding paper and shown graphically in Fig. 10. The curves for the logarithm of the ratio between decomposition velocity and hydroxide concentration are given at the constant total molarity of 2 for potassium and sodium hydroxide solutions with the salts mentioned present. The curves for solutions where the salt present has the same anion seem to be parallel within the experimental errors. This also gives the reason why the velocity curves in various salt solutions with constant hydroxide concentration never cross each other, a point formerly stressed as important. With the constant total molarity curves for all salt hydroxide solutions of the same kind still assumed as straight, parallel lines different values would have been obtained for the velocity constant in a hydroxide solution of a given concentration if these curves crossed. This must, therefore, be impossible.

The activities of the chloride, bromide and iodide ions at the same concentration are probably quite different and the same must be true for the potassium, sodium and lithium ions. Still it was found that the direction of the curves in Fig. 5 was approximately independent of the nature of the cation and varied with the common anion of the salt present, which was shown in Fig. 10. Harned[3a,b,2b] has given the following postulate for the activity coefficients of the ions of strong electrolytes. In solutions of strong electrolytes of the same valence type and with a common ion, at constant temperature and concentration, the activity

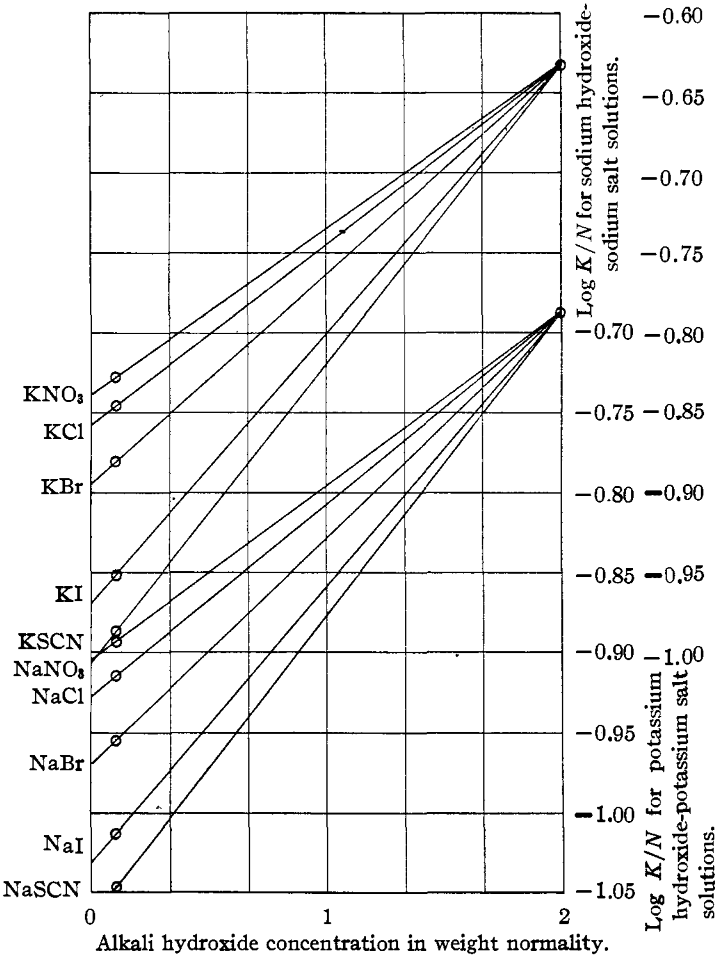

Fig. 10.—Curves for the logarithm of the ratio between decomposition velocity of diacetone alcohol and alkali hydroxide concentration in alkali hydroxide-alkali salt solutions of constant total molarity with varying anion of the salt present.

of this ion is a constant. In other words the logarithm of the activity coefficient of an ion is additive. At constant total molarity the concentration of the cation present is constant and thus its activity would be constant. This gives immediately the conclusion that the direction of the curves in Fig. 5 must be independent of the cation present, because when the activity of these ions is constant, then their influence on the reaction velocity may also be constant. The velocity changes would therefore be due solely to changes in the activity of the anions present. The halide ion may participate only indirectly in the reaction. The changes of the activity coefficient of the hydroxyl ion are then responsible for the variations of log K/N observed for potassium, sodium and lithium hydroxide-chloride solutions at constant total molarity.

VI. An Expression for the Reaction Velocity in Solutions with High Concentrations of the Electrolytes Present

Let us assume that we have an alkali hydroxide-alkali halide solution with only one salt present. The cation is common. At constant total molarity we have

$$\log \frac{K}{m_T - m_S} = B_s\,(m_T - m_S) + l \tag{1}$$

where m_T is the total concentration of the electrolytes present, m_S the salt concentration, B_s is a constant specific for the salt in the solution and l represents a function of the concentration. With decreasing salt concentration the following formulas are obtained for the pure hydroxide solution

$$\log \frac{K}{m_T} = B_s\, m_T + l \tag{2}$$

$$\frac{\gamma_{\mathrm{MeOH}(m_T)} \cdot m_T}{K} = R \tag{3}$$

where R is a constant, which may be called the reduction factor between thermodynamic activity of the alkali hydroxide and reaction velocity. Substitution of l with Equations (2) and (3) gives for (1)

$$\log \frac{K}{m_T - m_S} = \log \gamma_{\mathrm{MeOH}(m_T)} - \log R - B_s m_S \tag{4}$$

As mentioned before, $\log \gamma_{\mathrm{MeOH}}$ may be expressed by the formula

$$\log \gamma_{\mathrm{MeOH}} = -\frac{0.354\sqrt{2m}}{1 + A\sqrt{2m}} + B\,2m - \log\,(1 + 0.036\,m) \tag{5}$$

where A and B are empirical constants. This gives finally

$$\log \frac{K \cdot R}{m_T - m_S} = -\frac{0.354\sqrt{2m}}{1 + A\sqrt{2m}} + B\,2m_T - \log\,(1 + 0.036\,m_T) - B_s m_S \tag{6}$$

It might be of some interest that Equation (6) is of the same type as the simplified form of the general equation deduced by Hückel[11] for the activity coefficient of a strong electrolyte. Harned and Åkerlöf have

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[11] Hückel, *Physik. Z.*, **26**, 93 (1925).

shown that Hückel's general equation may be applied to the electromotive-force measurements for a large number of electrolytes in pure or mixed aqueous solutions. In Table X is given a comparison of observed reaction velocities and the values calculated from Equation (6). The observed values are interpolated from Table III in the preceding paper.

TABLE X

AGREEMENT BETWEEN OBSERVED REACTION VELOCITY AND THE VALUE CALCULATED FROM THE GENERAL EQUATION (6)

NaOH		NaCl solutions		NaBr solutions		NaI solutions	
$A = 0.660$		$B_s = 0.117$		$B_s = 0.139$		$B_s = 0.169$	
$B = 0.050$		$K \times 10^4$		$K \times 10^4$		$K \times 10^4$	
N	m_s	obs.	calcd.	obs.	calcd.	obs.	calcd.
0.1	0.9	152	146	146	139	134	131
.1	1.9	123	122	112	111	97	97
.1	2.9	102	106	93	92	74	75
.1	3.9	92	95	76	78	58	59
.1	4.9	84	86	63	67	46	48
.1	5.9	78	78	54	58	(39)	39

A better agreement between observed and calculated values could hardly be expected. It seems, however, as if the formula used might not be valid for solutions with small salt concentrations. It also cannot be used for hydroxide-salt solutions where the salt added increases the reaction velocity.

VII. Discussion

The measurements of relatively very high reaction velocities presented in this paper were not easy to carry out. The time required for every little detail had to be studied separately and shortened as far as possible or timed in such a way as to give the smallest possible error. The method is, therefore, not suitable for high precision measurements because it is too much hurried. It served to give fairly accurate and very important information in a so far completely unknown field. Its use might then be well justified. An attempt to work out an experimental method for measuring very high reaction velocities has been made by Hartridge and Roughton.[12] They give an excellent review of the theoretical possibilities and propose the use of rapidly flowing, continuously renewed solutions. For our purpose this would mean the use of very large quantities of highly concentrated alkali hydroxide solutions. A method using stationary solutions is, therefore, to be preferred if the desired sensitivity could be obtained.

In order to compare the results so far obtained from the study of the decomposition velocity of diacetone alcohol with results from investigations of other reactions, catalyzed by the same or other ions in solutions of strong electrolytes, we may first summarize the former.

[12] Hartridge and Roughton, *Proc. Roy. Soc.* (*London*), **104A,** 376 (1923).

1. At constant alkali hydroxide and varying salt concentration all velocity curves had the same general form independent of the salt present. From the measurements at varying constant total molarity this was confirmed as a logical conclusion.

2. At constant total molarity log K/N varies linearly with the hydroxide concentration. At varying constant total molarity log K/N gives a number of parallel, straight lines.

3. The influence of the salt added is additive and thus also the slope of the constant total molarity curves is additive. With increasing activity of the salt the salt action in general increases.

4. In pure hydroxide solutions the velocity is proportional to the thermodynamic activity of the hydroxide present.

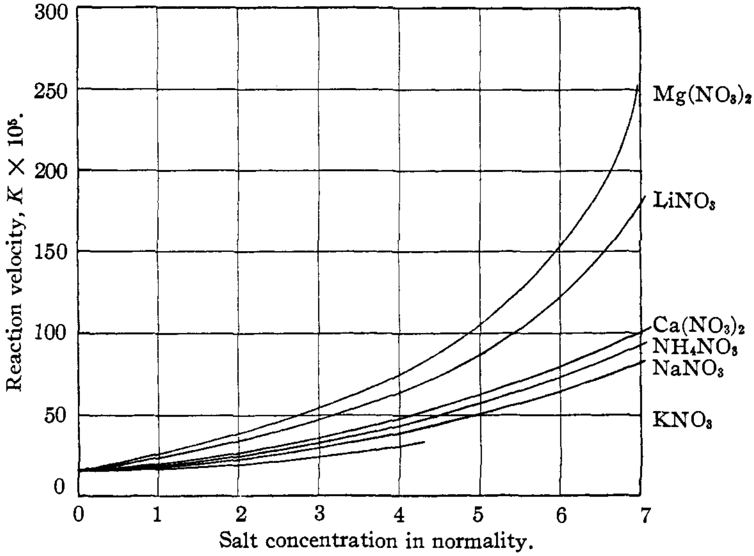

Fig. 11.—Curves for the velocity of hydrolysis of cyanamide in nitrate solutions of 0.25 N nitric acid.

Now we may compare these results with those for other reactions, and discuss what they have in common and where they differ. The first point seems to be valid for a large number of reactions. Harned[13] and Åkerlöf[14] have shown this for the hydrolysis of ethyl acetate, Grube and Schmid[15] for the hydrolysis of cyanamide, Rivett[16] for the conversion of acetylchloro-aminobenzene in acid-salt solutions. Harned[13] found it to

[13] Harned, This Journal, **40**, 1461 (1918).

[14] (a) Åkerlöf, *Medd. Vetenskapsakad. Nobelinst.*, **4**, 13 (1921); (b) *Z. physik. Chem.*, **98**, 260 (1921).

[15] Grube and Schmid, *Z. physik. Chem.*, 119, 19 (1926).

[16] Rivett, *ibid.*, **82**, 201 (1913); **85**, 113 (1913).

be valid for the decomposition of hydrogen peroxide by the catalytic action of the iodine ion in salt solutions. A graphical demonstration may be obtained from Figs. 2, 3 and 4 in the preceding paper and Fig. 11 in this paper. We may, therefore, be justified in assuming this to approach the true conditions for all monomolecular reactions catalyzed by ions of strong electrolytes, as the halide acids, the alkali and alkali earth hydroxides and iodides. Exceptions to this rule are as yet unknown, but it might also be said that only a few cases have been studied.

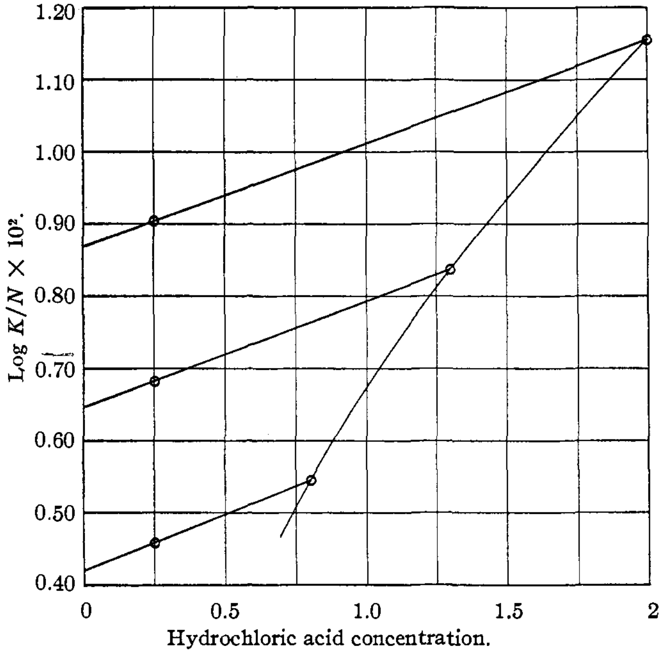

Fig. 12.—Curves for the logarithm of the ratio between conversion velocity of acetylchloro-aminobenzene and acid concentration in hydrochloric acid-sodium chloride solutions of varying constant total molarity.

The second point is far more difficult to investigate. In the literature there are no velocity measurements to be found for solutions with constant total molarity of the electrolytes present. However, this would not be any hindrance because the curves for varying constant total molarity were parallel. Thus, to study this case, only two points were necessary for each curve, one for a salt-catalyst, the other for the pure catalyst solution of the same total concentration. Measurements over a wider concentration range with solutions of the pure catalyst have seldom been carried out. Therefore a definite relationship between the thermodynamic properties of the catalyzing electrolyte and the reaction velocity generally cannot be proved. Nor is it possible to make an extrapolation of the reaction velocity for solutions of high concentrations. Often the probable experimental errors seem to be quite large. With a very limited concentration range it must then be rather difficult to arrive at a safe decision from some of the material available.

In the literature there is one case to be found where all the requirements necessary for a study of this point over a short concentration range are fulfilled. Harned and Seltz measured the conversion of acetylchloroaminobenzene to *p*-chloro-acetanilide in solutions of hydrochloric acid up to a concentration of 1.0 *M*. They found a definite relation between activity of the acid and the reaction velocity

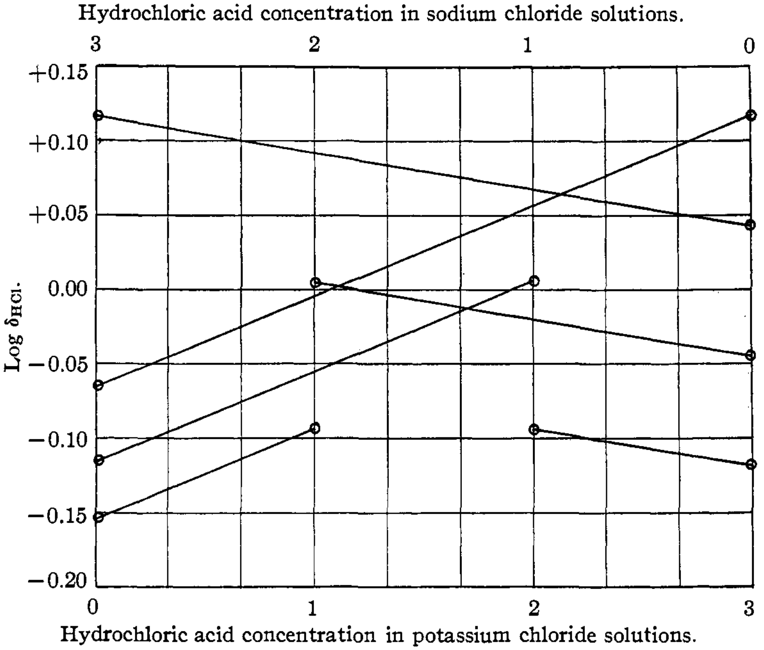

Fig. 13.—Curves for the logarithm of the activity coefficient of hydrochloric acid in potassium and sodium chloride solutions of varying constant total molarity.

$$K = R\gamma^2_{\mathrm{HCl}} \cdot n^2_{\mathrm{HCl}} \tag{7}$$

where R is the reduction factor between reaction velocity and activity of the acid. The activity coefficient of hydrochloric acid may be given by an equation similar to (5).[17,2a,b] In order to get the equation for the reaction velocity in acid-salt solutions, the measurements of Rivett for sodium chloride solutions in 0.25 N hydrochloric acid were interpolated. A few values of log K/N were plotted with these values for the pure

[17] Scatchard, THIS JOURNAL, **47**, 648 (1925).

acid solutions of the corresponding total concentrations. The curves obtained are given in Fig. 12. They must apparently be parallel, straight lines in analogy with the corresponding curves for the logarithm of the activity coefficient of hydrochloric acid in salt solutions at varying constant total molarity, which is shown graphically in Fig. 13 from the calculations of Harned and Åkerlöf. In regard to the calculations for the acetylchloro-aminobenzene reaction it may be noted that the concentration of the chlorine ion is constant at constant total molarity. Therefore log K is divided by the first power of the concentration of the acid, although the chlorine ion may participate in the catalysis.

In analogy with Equation (6) for the decomposition of diacetone alcohol, we, therefore, obtain the following formula for the conversion velocity in solutions with arbitrary acid-salt concentrations:

$$\log \frac{K \cdot R}{m_T - m_s} = -2 \left[\frac{0.354 \sqrt{2m_T}}{1 + A\sqrt{2m_T}} + B\, 2m_T + \log m_T - \log\,(1 + 0.036\, m_T) \right] - B_s m_s \tag{8}$$

where B_s is a constant characteristic for the salt present in the solution. In Table XI is given a comparison of observed and calculated reaction velocities. The observed values are interpolated from the measurements of Rivett.

Table XI

Agreement between Observed Reaction Velocities and the Values Calculated from the General Equation (8)

HCl $R = 13.8$ $A = 0.784$ $B = 0.0805$			KCl solutions $B_s = 0.181$ $K \times 10^4$		NaCl solutions $B_s = 0.162$ $K \times 10^4$		LiCl solutions $B_s = 0.107$ $K \times 10^4$	
m_T	$\gamma_{HCl}(m_T)$	m_s	obs.	calcd.	obs.	calcd.	obs.	calcd.
0.45	0.746	0.20	41.6	41.8	43.0	42.2	43.8	43.2
.65	.761	.40	58.2	57.8	60.7	59.0	63.1	62.0
.85	.786	.60	75.0	74.2	78.1	76.3	83.4	82.3
1.05	.818	.80	92.6	91.3	96.6	94.6	106	105
1.25	.855	1.00	111	110	116	114	129	130
1.45	.898	1.20	129	129	136	136	158	158
1.65	.944	1.40	148	149	157	159	...	...

The agreement between observed and calculated reaction velocity is very good. We have thus been able to show that also for the conversion of acetylchloro-aminobenzene the curves for log K/N at varying constant total molarity are represented by straight, parallel lines.

In the literature there are to be found measurements for two other reactions where this test could be applied as an indication that the reaction velocity is an activity function. These two reactions are the hydrolysis of ethyl acetate measured by Harned, Åkerlöf, Harned and Pfanstiel[18] and others and the hydrolysis of cyanamide, measured by Grube and Schmid. For neither of these two reactions has been found a definite

[18] Harned and Pfanstiel, This Journal, **44,** 2193 (1922).

relationship between activity of the catalyst and reaction velocity. However, Harned and Pfanstiel have shown it to be very probable that the velocity of hydrolysis for ethyl acetate may be proportional to the activity of the hydrogen ion. The ratio between velocity and acid concentration shows a minimum at the same place as the individual activity coefficient of this ion. A graphical representation of the values for log K/N of these two reactions in acid-salt solutions at varying constant total molarity is shown in Figs. 14 and 15. The data used for these figures, together with those for Fig. 12, are given in Table XII.

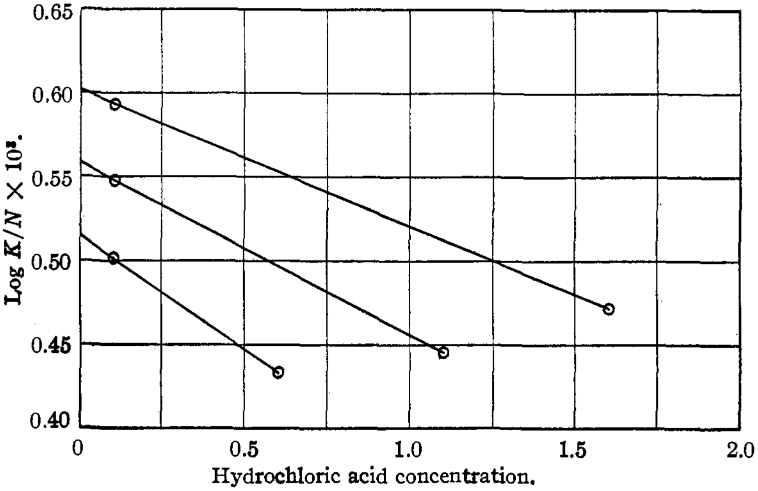

Fig. 14.—Curves for the logarithm of the ratio between velocity of hydrolysis for ethyl acetate and acid concentration in hydrochloric acid-sodium chloride solutions of varying constant total molarity.

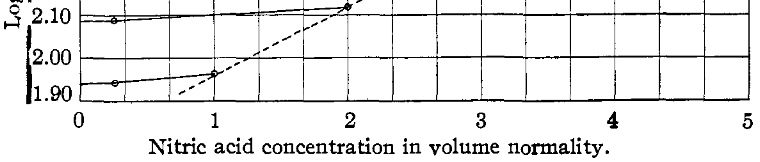

Fig. 15.—Curves for the logarithm of the velocity of hydrolysis for cyanimide in nitric acid-lithium nitrate solutions of varying constant total molarity.

TABLE XII

DATA FOR FIGS. 12, 14 AND 15

I. Conversion of Acetylchloro-aminobenzene
Measurements of Harned and Seltz and Rivett

HCl m	NaCl m_s	$K \times 10^4$	Log $K/m \times 10^2$	HCl m	$K \times 10^4$	Log $K/m \times 10^2$
0.25	0.55	72.0	0.459	0.8	280	0.544
.25	1.05	120	.681	1.3	896	.838
.25	1.75	200	.903	2.0	2860	1.155

II. Hydrolysis of Ethyl Acetate
Measurements of Harned and of Harned and Pfanstiel

HCl m	NaCl m_s	$K \times 10^5$	Log $K/m \times 10^3$	HCl m	$K \times 10^5$	Log $K/m \times 10^3$
0.1	0.5	31.7	0.501	0.6	163	0.434
.1	1.0	35.3	.548	1.1	307	.446
.1	1.5	39.3	.594	1.6	474	.471

III. Hydrolysis of Cyanamide
Measurements of Grube and Schmid

HNO_3 m	$LiNO_3$ m_s	$K \times 10^5$	Log $K/m \times 10^5$	HNO_3 m	$K \times 10^5$	Log $K/m \times 10^5$
0.25	0.75	21.8	1.941	1.0	91.7	1.962
.25	1.75	30.5	2.086	2.0	262	2.117
.25	2.75	42.7	2.232	3.0	555	2.267
.25	3.75	59.3	2.375	4.0	1065	2.425
.25	4.75	80.6	2.508	5.0	1950	2.591

The curves in Fig. 14 for the hydrolysis of ethyl acetate in hydrochloric acid-sodium chloride solutions appear to be only roughly parallel, with deviations in slope of about 5%. Certain facts may seem to indicate that these deviations could be within the experimental errors. Therefore we cannot safely decide whether these curves should be regarded as parallel or not. The curves in Fig. 15 represent a wide concentration range and they seem to be parallel within the experimental errors. The velocity of hydrolysis of cyanamide must, therefore, be regarded as a function of the activity of the electrolytes present.

Among other reactions where the velocity seems to be a function of the activity of the catalyst may be mentioned the inversion of cane sugar, although the data available are insufficient for a complete test. This reaction has been the subject for a very large number of small investigations. Each time only a few measurements were carried out. The sugar concentration used was usually rather high and varied considerably from one case to another. Therefore the measurements from different investigations cannot easily be compared with each other. However, Hantzsch and Weissberger[19] have shown that the ratio between inversion velocity and acid concentration is greatest for the acid with the highest activity coefficient.

[19] Hantzsch and Weissberger, *Z. physik. Chem.*, **125**, 251 (1927).

For the decomposition of diacetone alcohol in alkali hydroxide-salt solutions the influence of the salt added upon the reaction velocity was found to be additive. In these solutions almost any kind of an alkali salt could be used for a study of this point. In acid solutions the number of suitable salts is quite limited. Salts of acids which must be regarded as weak electrolytes cannot be used for this purpose and the same is true for bi- and polyvalent acids. It seems as though in this case the differences between reaction velocities in alkali and alkali earth chloride and bromide solutions of their respective acids should be the simplest and easiest to measure. There are, however, no measurements to be found in the literature for a study of a possible additivity of the salt action on other reactions. It seems to be very probable that this might be the case, because the salt action is in general proportional to the activity of the salt added.

In our discussion a first attempt has been made to trace a general formula that may be used to express the velocity changes of simple reactions in catalyst-salt solutions as a function of the thermodynamic activities of the electrolytes present. It may perhaps be possible to use such an equation for a discussion of the intrinsic mechanism of these reactions. A large literature has grown up on this subject but positive, general results have seldom been attained. We were able to show that there seem to be other factors as yet unknown, but which must be known before we can arrive at a clear understanding of these processes.

VIII. Summary

In this paper are described measurements of reaction velocities with half periods down to thirty seconds. Attempts to measure still higher velocities were made and were partly successful. The values obtained were probably too low due to increasing, unpreventable, systematic errors.

With the method given, the decomposition velocity of diacetone alcohol has been measured in pure aqueous solutions of potassium, sodium and lithium hydroxide up to a concentration of 2.2 N. The velocity was found to be proportional to the activity of the hydroxide present.

Velocity measurements were then carried out for alkali chloride-hydroxide solutions with constant total molarity of 2. Log K/N varied linearly as a function of the hydroxide concentration, which is analogous to the behavior of the logarithm for the activity coefficient of the hydroxide.

Measurements at varying constant total molarity gave a number of parallel lines, just as the curves for the logarithm of the activity coefficient of the hydroxides in the same solution are straight, parallel lines. These lines extended to zero salt concentration gave the velocity in hydroxide solutions at high concentrations. Values obtained from the activity function agreed very well.

At all concentrations, even in very dilute solutions, it seems to be valid that the decomposition velocity of diacetone alcohol is a function of the thermodynamic activities of the electrolytes present. A short discussion of the measurements for other reactions as compared with those presented in this paper is given.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND BOTANY OF THE UNIVERSITY OF WASHINGTON]

THE ACIDITY OF THE WATERS OF SOME PUGET SOUND BOGS[1]

BY THOMAS G. THOMPSON, JAMES R. LORAH AND GEORGE B. RIGG

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Introduction

This investigation was undertaken in order to ascertain the degree of acidity of certain bog waters and to study the relation of such acidity to the carbon dioxide content of the water, the color of the water and the stage of plant succession. It was thought that such data would be useful for interpreting the physiology of plants characteristic of bogs and also for explaining the rather marked corrosive action of such waters upon concrete and cement products.

Experimental

The waters studied were collected from four typical Puget Sound bogs. Two of the bogs, Esperance and Sunnydale, were characterized by the presence of methane dissolved in the waters and by the occurrence of a small pond which each bog surrounded. Bogs of this type have been designated as "wet bogs." The other two bogs, Ronald and White Center, experience a very great lowering of the water table in the summer months, evolve no methane and do not surround open bodies of water. Such bogs have been termed "dry bogs." A more detailed description of these bogs, their flora and the nature of the dissolved gases has been previously published.[2]

Effect of Dissolved Carbon Dioxide Upon Acidity

Samples of water were collected from at least two different points in each bog and the amounts of dissolved carbon dioxide carefully determined. This was accomplished by the complete removal of the dissolved gases by boiling the samples under diminished pressure for an hour.[2] Analyses of the liberated gases followed. Owing to the high dilution it was assumed that all of the carbon dioxide was present in the waters as carbonic acid,

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[1] Read before the Chemical Section of the Pacific Division of the American Association for the Advancement of Science, June, 1927.

[2] *Bot. Gaz.*, **84**, 264–278 (1927).