measurements on the reaction kinetics by the flow method, and a determination of the adsorptions of the reacting gases. The principal results are as follows.

1. A quantitative method is developed for treating the results of kinetic measurements by the flow method.
2. The rate of the reaction is proportional to the pressure of hydrogen and independent of the oxygen pressure. The reaction is greatly retarded by the water formed. It is somewhat retarded by subjecting the catalyst to preliminary heating in oxygen. The average temperature coefficient is about 1.6.
3. The increase in the yield with increasing rate of passage of the gas mixture is satisfactorily accounted for by the lowering of the partial pressure of water vapor in the exit gases.
4. Hydrogen is not measurably adsorbed by active silver under the conditions obtaining in the catalysis. Oxygen, on the other hand, is strongly adsorbed, the amount taken up being nearly independent of pressure and temperature over the range in question.
5. The mechanism of the reaction is shown to depend on collisions of gaseous hydrogen molecules with adsorbed oxygen atoms which are free from adsorbed water. However, since under the conditions employed only about one such collision in a billion is effective, it is suggested that only those oxygen atoms react readily which are adjacent to bare spaces on the surface of the catalyst.

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DECOMPOSITION OF DIACETONE ALCOHOL IN ALKALI HYDROXIDE-ALKALI SALT SOLUTIONS

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Introduction

It has been shown in a number of investigations[1] that the velocity of reaction of compounds subject to catalytic decomposition in acid-salt solutions is nearly always directly parallel to the activity of the hydrogen

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[1] (a) Harned, This Journal, **40**, 1461 (1918). (b) Åkerlöf, *Medd. Vetenskapsakad., Nobelinst.*, **4**, 13 (1921); *Z. physik. Chem.*, **98**, 260 (1921). (c) Jones and Lewis, *J. Chem. Soc.*, **117**, 1120 (1920). (d) Harned and Pfanstiel, This Journal, **44**, 2193 (1922). (e) Harned and Seltz, *ibid.*, **44**, 1475 (1922). (f) Scatchard, *ibid.*, **43**, 2387 (1921); **45**, 1580 (1923). (g) Moran and Lewis, *J. Chem. Soc.*, **121**, 1613 (1922). (h) Fales and Morrell, This Journal, **44**, 2071 (1922). (i) Livingston and Bray, *ibid.*, **45**, 2048 (1923). Compare further the theoretical studies of (j) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922); **115**, 337 (1925). (k) Bjerrum, *ibid.*, **108**, 82 (1924); **118**, 251 (1925). (l) Christiansen, *ibid.*, **113**, 35 (1924).

ion, if that ion is present at moderate or high concentrations. Similar investigations in alkali-salt solutions have not been carried out, so that it appeared of interest to determine the rate of decomposition of some such substance as diacetone alcohol in solutions of potassium and sodium hydroxide containing various salts. The results obtained were somewhat remarkable in that they were always the opposite to those obtained in an acid-salt solution of corresponding concentration. Thus, the addition of sodium chloride to a solution of ethyl acetate catalyzed by hydrochloric acid increases the reaction rate but the addition of sodium chloride to a solution of diacetone alcohol catalyzed by sodium hydroxide diminishes the reaction velocity. The decrease in reaction rate caused by the alkali sulfates in acid catalysis is contrasted with the *increase* in reaction rate caused by the sulfates in the alkaline catalysis of diacetone alcohol.

These results are exactly parallel to the results of activity measurements; sodium chloride increases the activity coefficient of the hydrogen ion in hydrochloric acid but diminishes the activity coefficient of the hydroxyl ion in sodium hydroxide. In fact we may generalize the present state of our knowledge by stating that in an alkaline solution of a salt of a given valence type, the activity of the hydroxyl ion is always smallest where the salt present has the highest activity coefficient.[2] In conformity with this the rate of decomposition of diacetone alcohol seemed always to follow inversely the activity of the salt present. We may therefore make the following statement: the rate of decomposition of a compound by hydrogen and hydroxyl ions in salt solutions is always directly related to the activity coefficients of these ions. Increase of the activity coefficient increases the velocity; decrease of the activity coefficient decreases the velocity. This may be considered as one of the more important qualitative results of the investigation.

Experimental Methods

Materials.—All salts used were the best grade of analyzed chemicals that could be obtained. As long as there was no fear of decomposition upon heating, the salts were dried at a suitable temperature or melted and crushed. Thiosulfates and sulfocyanides were used in solution. These solutions were analyzed gravimetrically according to standard methods. The neutrality of the salts was tested carefully in all cases where possible. Because the alkali carbonates lose a little carbon dioxide when heated, the reaction velocities for their solutions were also measured with pure salt solutions in the absence of added hydroxide. The more complicated behavior of the alkali cyanide solutions will be mentioned later.

Standard 1.00 *N* hydroxide solutions were prepared with all necessary precautions and kept guarded against carbon dioxide in the air. They always contained slight traces of barium hydroxide. All salt-hydroxide solutions were made up with calculated amounts of salt, hydroxide and water. The water was twice distilled and air-free. All solutions except the cyanides were boiled in a high vacuum and then kept under a vacuum until they were needed for a measurement. It was found to be necessary to keep

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[2] Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

the solutions in the thermostat for at least two hours before the measurement. The best results were usually obtained with solutions which were kept in the thermostat overnight.

Thermostat.—The copper tank of the thermostat contained normally about 400 liters of water. The thermostat was provided with two large fan-blade stirrers, rotating with a speed of about 100 r.p.m. The thermoregulator had the shape of a well spread out heat radiator with a calculated surface of about 2200 sq. cm. The temperature was controlled with a Beckmann thermometer. Variation in the temperature could hardly be detected in periods of a week or more and during a measurement it was less than ±0.001°.

Reaction Tubes.—The decomposition of diacetone alcohol to acetone is followed by a small increase in volume. If this expansion is measured in a capillary at different times during the reaction, the velocity of the reaction may be calculated from the measurements. This method was employed by Koelichen,[3] who first discovered and carefully investigated the reaction.

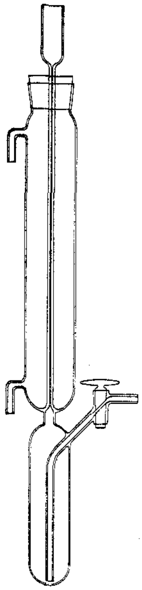

Fig. 1.—Apparatus used for the determination of the reaction velocity of the decomposition of diacetone alcohol to acetone in alkali hydroxide - alkali salt solutions.

The reaction tube is shown in Fig. 1. The reaction vessel used contained about 250 cc. of the solution. The solution was filled in through the tube leading to the bottom of this vessel. The glass wall of the vessel was rather thick in order to prevent very small continuous changes in inner volume during the measurement of the reaction due to the pressure from the mercury column in the capillary. The inner diameter of this capillary coming from the top of the reaction vessel was about 0.7–0.8 mm. The capillaries were selected with the greatest care from a very large number of tubes.[4] They were absolutely flawless in appearance and almost exactly straight. Only the middle part of a longer tube was used for the intended purpose. In order to support the capillary it was placed in the center line and at the lower end melted together with a wider glass tube. In order to prevent excessive strain in the capillary its upper end was held by a rubber stopper. The mantel tube was also carefully selected and of flawless glass.

The Measurement.—The reaction tube was first washed with water and alcohol, then dried in a stream of air. After it had been placed in the

[3] Koelichen, *Z. physik. Chem.*, **33**, 129 (1900).

[4] The capillaries were very kindly given to the author by Mr. Kimble of the Kimble Glass Co., N. J. A first selection of 16 kg. had been made with great care by Mr. Joseph Green of the same Company.

bath it was evacuated and kept under a vacuum until the filling was finished. In the meantime 4 to 5 cc. of diacetone alcohol had been added to the solution and well mixed with it. During the filling of the reaction tube the solution was first allowed to fill the greater part of the reaction vessel. After a few minutes' waiting to let the gas bubbles escape, the vessel was completely filled, the vacuum shut off, the tube put in its proper place and tightly clamped. The mantel around the capillary was then filled with water and a mercury drop placed in the opening of the capillary. The mercury drop was then brought down to the lower end of the capillary by letting out a little of the solution through the stopcock. This stopcock had to be carefully regreased for every measurement. The length of the mercury column in the capillary varied usually between 5 and 15 cm. A shorter column was to be avoided because several times it showed a tendency to split in smaller lengths and allow the solution to pass along the wall of the capillary.

After waiting for 5 to 15 minutes, which length of time varied with the reaction velocity, the measurement was started. The cathetometer was set on an even figure and the stop watch started when the lower end of the mercury column just passed the hair line. For every following reading of the time the cathetometer always was set on an even figure with differences of 2 to 4 cm. between two readings. The infinity value was finally obtained from three or four readings with suitable intervals of time. It was found that when the time readings were made, anything that might cause even the slightest variations in the temperature of the bath had to be avoided, as for instance putting in place another tube for measurement. This caused error of five to ten seconds for the subsequent readings. It was very inconvenient, therefore, to start several reactions at the same time and measure them simultaneously.

Accuracy and Calculation of the Results.—The reaction velocity is given by the formula: $K = (1/t)ln[l_\infty/(l_\infty - l_t)]$, where t is the time, l_t the length the mercury column has moved during this time and l_∞ the infinity value. For the total length the mercury column had moved from the starting point values were obtained, which generally varied between 40 and 60 cm. or on the average about 50 cm. The temperature coefficient for the expansion of the solutions is about 0.006 at 25°. A variation of 1 mm. in the infinity value may, therefore, be caused by a temperature change of 0.0003° as shown by the following calculation: $dT = (0.075/2)^2 \times 0.1 \times \pi/250 \times 0.006$.

The temperature variations in the bath were too small to be observed when everything was operating normally. If it is assumed that these variations were of the magnitude ± 0.001°, there might be an error of ± 0.3 cm. for the infinity value. Errors in the infinity value may also be caused in another way. Suppose a little air bubble remained in the solution after the measurement had been started and then slowly disappeared by dissolving. An air bubble with the volume of 0.001 cc. should cause a decrease in the infinity value of 0.22 cm. Tiny air bubbles were sometimes observed to adhere to small particles of stopcock grease. By frequently cleaning the reaction tubes with hot, concd. sulfuric acid, it was comparatively easy to avoid errors of this kind almost entirely.

On account of these evident difficulties in obtaining infinity values which could be considered safely as free from errors within certain small limits, the calculation of the velocity constant had to be carried out in such a way that the different values obtained showed as little change as possible in a certain direction. If, therefore, the two or three first K values showed increase (or very seldom decrease) to any considerable extent (about 5%) these values were discarded and the next measurement taken as a new starting point. The recalculation generally gave K values with a high degree of constancy. Sometimes, however, this was not the case even if the starting point was moved much higher up. The measurements were then repeated with freshly prepared solutions of the same concentrations. Examples of what could be accomplished in this way are given in Table I.

TABLE I

ATTAINABLE ACCURACY OF THE RESULTS

Solution with 4 N K_2CO_3			5.5 N $NaClO_3$			5.5 N NaSCN		
Time, seconds	Cathetometer	$K \times 10^7$	Time, seconds	Cathetometer	$K \times 10^7$	Time, seconds	Cathetometer	$K \times 10^7$
0	26.00	...	0	8.00	....	0	12.00	...
114	30.00	5719	128	10.00	1438	290	14.00	634
178	32.00	5722	262	12.00	1439	595	16.00	634
248	34.00	5720	403	14.00	1439	913	18.00	635
325	36.00	5725	551	16.00	1435	1244	20.00	635
411	38.00	5723	706	18.00	1435	1592	22.00	637
509	40.00	5710	870	20.00	1434	1960	24.00	635
619	42.00	5721	1043	22.00	1432	2350	26.00	638
750	44.00	5717	1230	24.00	1437	2761	28.00	638
913	46.00	5678	1420	26.00	1430	3200	30.00	636
1114	48.00	5670	1637	28.00	1434	3678	32.00	635
t_∞	54.7	..	t_∞	56.0	..	t_∞	60.0	..

These results seem to indicate, as previously found by Koelichen, that the volume changes of the solutions used were very nearly proportional to the changes in the concentrations of the diacetone alcohol and acetone, which had to be assumed for the use of the method.

Schmid[5] has recently given a thorough mathematical analysis of the methods for calculation of reaction velocities in order to get the best possible mean value from a given series of measurements. His excellent method could not be used to any advantage in the case of the present

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[5] Schmid, *Z. physik. Chem.*, **119**, 8 (1926). Compare further Moesveld, *ibid.*, **103**, 481 (1923). Wagner, *ibid.*, **115**, 130 (1925).

measurements because there was always a possibility of a larger error in the infinity values or a continuous change in the velocity constants.

Experimental Results

The velocity constants obtained with potassium hydroxide-potassium salt solutions are given in Table II; Table III contains the data for all sodium hydroxide-sodium salt solutions measured except those of the cyanide and carbonate solutions, which will be discussed separately. The amount of solvent used was in all experiments about 400 g. but all results are corrected to a round hydroxide concentration of 0.100 *N* for 1000 g. of solvent. All salt concentrations are given in weight normality. The amount of diacetone alcohol used was about 1% of the total volume of the solution. The average error of the results is probably about 1 to 2%. The velocity constants are given with the minute as unit of time.

TABLE II

SUMMARY OF THE RESULTS WITH POTASSIUM HYDROXIDE-POTASSIUM SALT SOLUTIONS. VALUES OF $K \times 10^4$

N	F	CrO_4	NO_2	NO_3	Cl	Br	I	SCN
0.00	204	204	204	204	204	204	204	204
0.50	207	195	187	185	183	178	168	162
1.00	209	191	176	171	166	158	141	133
1.50	214	183	164	158	153	143	122	115
2.00	221	179	156	148	142	130	108	100
2.50	229	174	148	139	133	120	96.5	89.3
3.00	237	172	140	134	126	112	88.3	82.1
3.50	250	170	137	131	123	106	81.8	73.9
4.00	262	168	135	129	121	102	76.0	68.5
4.50	271	167	130	...	119	101	71.0	62.1
5.00	277	...	...	...	...	98	65.8	51.4

TABLE III

SUMMARY OF THE RESULTS WITH SODIUM HYDROXIDE-SODIUM SALT SOLUTIONS. VALUES OF $K \times 10^4$

N	SO_4	CrO_4	NO_2	NO_3	ClO_3	Cl	Br	I	SCN
0.00	197	197	197	197	197	197	197	197	197
0.50	199	183	174	172	171	170	165	157	152
1.00	200	172	155	154	152	149	143	130	124
1.50	204	163	141	138	135	133	124	109	103
2.00	210	156	129	126	124	121	110	94.0	87.0
2.50	217	149	120	118	113	110	99.1	81.8	75.4
3.00	224	144	113	110	107	101	90.2	72.0	65.2
3.50	232	139	108	104	100	96.0	81.8	63.2	57.0
4.00	241	134	102	99.0	95.7	91.8	73.9	56.0	50.8
4.50	250	129	99	94.3	91.4	87.8	67.0	49.3	43.6
5.00	...	126	95	90.2	88.6	83.5	61.2	43.4	39.5
5.50	...	...	92	86.5	84.0	80.3	56.1	...	37.9
6.00	...	...	89	84.2	81.0	78.1	53.8	...	36.0

The graphical representation of the results with potassium salts in Fig. 2 and with sodium salts in Fig. 3 shows that all the curves given have the same general form. For salts with common cation they do not in any case cross each other. The relative position of all the curves for the potassium salts is always the same for the corresponding sodium salts except in one case. The curve for potassium cyanide solutions lies a little below that for potassium chloride solutions, whereas the curve for sodium cyanide solutions lies far above that for sodium chloride solutions. Normally, it should have come a little below this last curve.

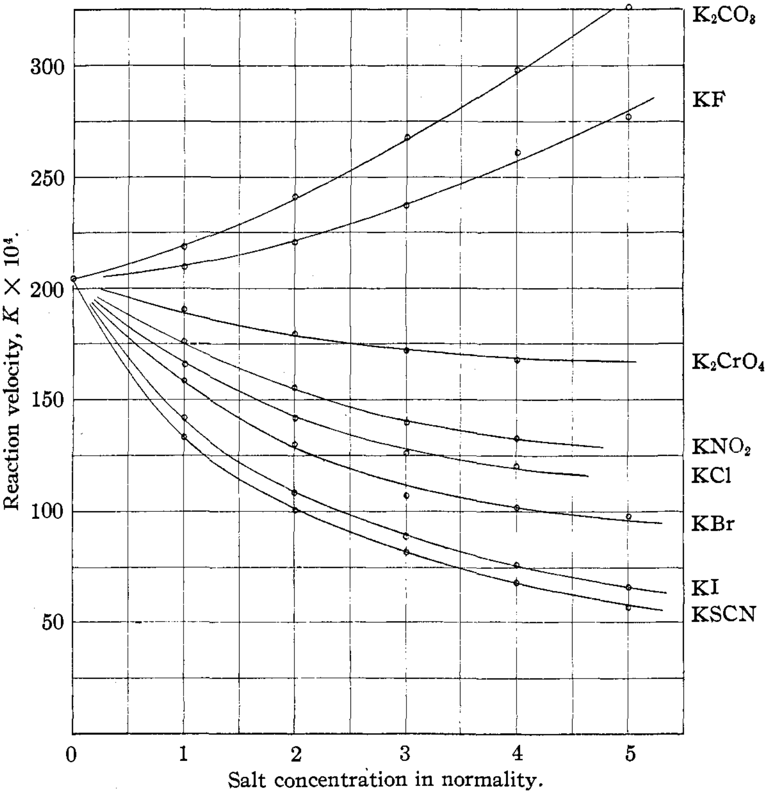

Fig. 2.—Curves for the reaction velocity of the decomposition of diacetone alcohol to acetone in alkaline solutions of different potassium salts at constant potassium hydroxide concentration of 0.1 *N* and increasing salt concentrations.

As already mentioned, all other curves in the two series of salt solutions always had the same relative positions. This is also shown in Table IV were the differences in reaction velocity for the corresponding potassium and sodium salt solutions are given. If these differences at corresponding concentrations are always the same, the influence of the salts upon the reaction velocity may be regarded as additive.

Table IV

Differences in Reaction Velocity, $\Delta K \times 10^4$, for the Two Solution Series with Common Anion

N	CO_3	CrO_4	NO_2	NO_3	Cl	Br	I	SCN	Mean
0.50	10	12	13	13	13	13	11	10	12
1.00	14	19	21	17	17	15	11	11	16
1.50	18	20	23	20	20	19	13	12	18
2.00	22	23	27	22	21	20	14	13	20
2.50	24	25	28	21	23	21	15	14	22
3.00	26	28	27	24	25	22	16	17	23
3.50	30	31	29	27	27	24	19	17	25
4.00	33	34	33	30	29	28	20	18	28
4.50	36	38	31	..	31	34	22	19	30
5.00	38	..	..	..	..	37	23	22	..

The differences obtained are in all cases of the same magnitude. For the two series of iodide and thiocyanate solutions they are a little smaller than the average for the others at the same concentration. This may

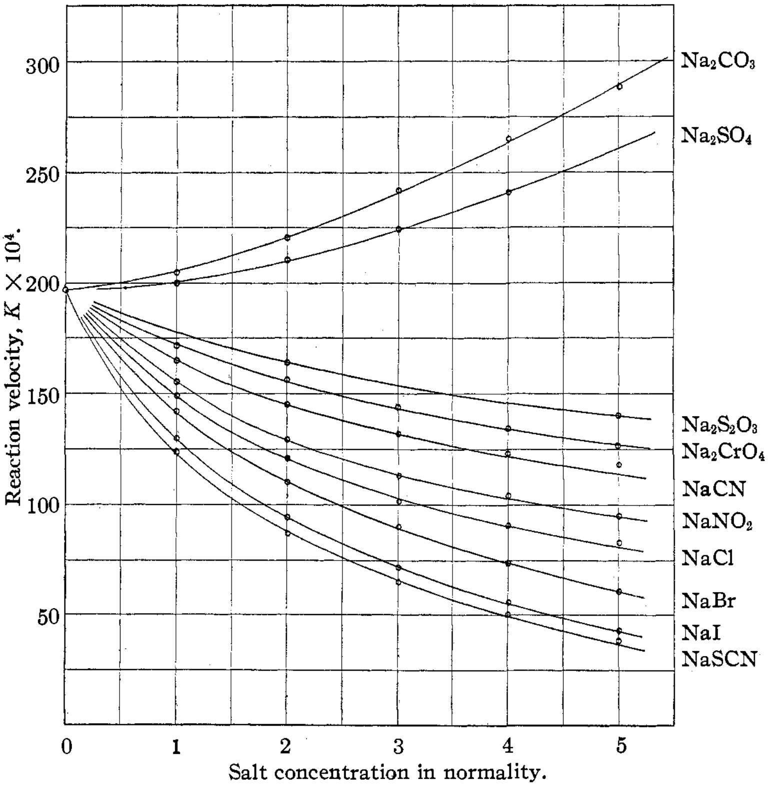

Fig. 3.—Curves for the reaction velocity of the decomposition of diacetone alcohol to acetone in alkaline solutions of different sodium salts at constant sodium hydroxide concentration of 0.1 N and increasing salt concentrations.

partly depend on experimental errors. The differences obtained for the cyanide solutions show, however, a very distinct deviation from these values.

Measurements with Alkaline Solutions of Potassium and Sodium Cyanide.—From the investigations of Knobel, Harned, and Harned and Swindells[6] it is known that the activity coefficients of the alkali metal hydroxides at the same concentration decrease in the order potassium, sodium, lithium. The activity coefficients of the alkali metal halides increase in the same order. As far as known, a similar reversal had not before been observed for any other simple electrolytes. Harned and Åkerlöf[2] attempted the explanation that this reversal for the alkali hydroxides was caused by the Stark effect of the electrical field of the cation on the asymmetrical hydroxyl ion. It is then evident that it would be of considerable interest to study the behavior of ions similar in structure to the hydroxyl ion. The cyanide ion like the hydroxyl ion consists of two atoms, and a reversal in behavior might therefore be expected for the activity coefficients of the alkali cyanides.

The measurements with potassium and sodium cyanide appeared to be a little complicated. A solution of these cyanides slowly condenses acetone to another compound. This reaction is also followed by a contraction of the solution. It was therefore impossible to obtain the right infinity value for the hydroxyl-ion reaction. The velocity of the diacetone alcohol decomposition was many times greater than for the above-mentioned condensation reaction of the cyanide ion, even in very concentrated solutions. An example of the constancy of the velocity values obtained is given in Table V. The accuracy of the values given in the summary of the measurements in Table VI is a little difficult to judge but it is most prob-

TABLE V

MEASUREMENTS WITH ALKALINE CYANIDE SOLUTIONS

Solution with 3 N KCN			Solution with 3 N NaCN		
Time, seconds	Cathetometer	$K \times 10^7$	Time, seconds	Cathetometer	$K \times 10^7$
0	14.00	..	0	14.00	..
82	16.00	2119	102	16.00	2187
170	18.00	2129	209	18.00	2192
262	20.00	2118	322	20.00	2192
358	22.00	2117	440	22.00	2204
459	24.00	2111	567	24.00	2204
564	26.00	2114	700	26.00	2212
677	28.00	2108	842	28.00	2222
796	30.00	2104	996	30.00	2228
∞	64.0 (calcd.)		∞	54.0 (calcd.)	

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[6] (a) Knobel, THIS JOURNAL, **45**, 70 (1923). (b) Harned, *ibid.*, **47**, 676 (1925); (c) *Z. physik. Chem.*, **117**, 1 (1925). (d) Harned and Swindells, THIS JOURNAL, **48**, 126 (1926).

able that all of them have the error in the same direction. The differences in velocity constants for the cyanide as well as for the bromide solutions are given in Table VI for the purpose of comparison.

Table VI

Summary of the Results with Alkaline Potassium and Sodium Cyanide Solutions

N	$K \times 10^4$ KCN	$K \times 10^4$ NaCN	$\Delta K \times 10^4$ CN	$\Delta K \times 10^4$ Br
0.00	204	197	...	..
0.50	181	179	2	13
1.00	163	165	−2	15
1.50	150	154	−4	19
2.00	139	145	−6	20
2.50	130	138	−8	21
3.00	123	132	−9	22
3.50	119	127	−8	24
4.00	117	123	−6	28
5.00	113	118	−5	37

The cyanide differences have reversed even the sign as compared with those for the bromide solutions. With the assumption that the reaction velocity always varies inversely as the activity coefficient of the salt present, potassium cyanide must have a higher activity coefficient than sodium cyanide at the same concentration. In other words, the alkali cyanides show a behavior similar to the alkali hydroxides. It should be noted that this reversal in behavior in contradistinction to the behavior of the halide ions has not yet been found for any other ions. All ions built up of more than two atoms seem to behave towards the alkali metal ions very similarly to the simple halide ions.

Measurements with Alkaline Solutions of Potassium and Sodium Carbonate.—The reaction velocity increased rapidly with increasing concentration of the salt. Pure carbonate solutions cause the reaction to take place slowly and it was found that the velocities in the pure solutions were very nearly proportional to the salt concentrations. Therefore, a correction which was proportional to the salt concentration was applied to the measured velocities for the alkali hydroxide-alkali carbonate solutions. A summary of the measurements with carbonate solutions is given in Table VII.

These two values may vary a little with the previous treatment of the salt for drying. Drying temperature was about 500°. The magnitude of the increase of the reaction velocity in the carbonate solutions is very surprising. If the carbonates were partly hydrolyzed in water, the addition of the alkali hydroxide must decrease the hydrolysis. The correction of the reaction velocities found for the pure carbonate solutions should then be smaller in the hydroxide-carbonate solutions; but even a correction of the measured values to the full extent for the velocity in the pure carbonate

TABLE VII

SUMMARY OF THE RESULTS WITH ALKALINE POTASSIUM AND SODIUM CARBONATE SOLUTIONS

N	$K \times 10^4$ K_2CO_3	$K \times 10^4$ Na_2CO_3	$\Delta K \times 10^4$ CO_3	$\Delta K \times 10^4$ Br
0.00	204	197	..	..
0.50	209	199	10	13
1.00	218	204	14	15
1.50	229	211	18	19
2.00	242	220	22	20
2.50	255	231	24	21
3.00	268	242	26	22
3.50	283	253	30	24
4.00	298	265	33	28
4.50	313	277	36	34
5.00	326	288	38	37

For the reaction velocity in pure carbonate solutions was obtained:

ΔK per g. equivalent of sodium carbonate = 4.2×10^{-4}

potassium carbonate = 8.9×10^{-4}

solutions gives an increase comparable with that which has been found for hydrogen-ion catalysis in acid solutions of the alkali chlorides. The alkali cyanides, which are salts of a very weak acid, decreased the reaction velocity. This is contrary to the classical explanation and not in line with that previously given for the behavior of the carbonates. Potassium and sodium sulfate, which are salts of a strong acid, gave an increase in reaction velocity of the same magnitude as the carbonates. The dissociation of an acid giving a certain salt may, therefore, not have anything to do with the specific influence of the salt upon the reaction velocity. It is very interesting to find that the differences in the decrease of the reaction velocity in solutions of potassium and sodium chloride or bromide at corresponding concentrations are very nearly the same as the differences in increase of the velocity in solutions of the two carbonates.

Discussion

The investigations of hydrogen-ion catalysis in pure acid and acid-salt solutions have shown that the reaction velocity always seems to be a function of the activity of the hydrogen ion, when this ion is present at comparatively high concentrations. The attempt of Åkerlöf[1b] to give an empirical relation between the reaction velocity for the hydrolysis of ethyl acetate and the hydrogen-ion activity led to a very simple equation. Recently, it has been shown by Grube and Schmid[7] that these results may be expressed better in a slightly different way. This does not change the main result of this investigation, that the velocity seems to be a definite function of the activity of the hydrogen ion. Further, it was also shown by Grube and Schmid that the hydrolysis of cyanamide in acid-salt solu-

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

tions and the decomposition of hydrogen peroxide with iodides in salt solution could both be expressed by the same general equation as that used for the ethyl acetate reaction. As shown by Åkerlöf from the measurements of Jones and W. C. McC. Lewis[1c] the relation between hydrogen-ion activity and reaction velocity for the cane sugar inversion follows the same formula as the ethyl acetate reaction. Since it must be possible to express the activity of the hydrogen ion in any one of these solutions by the same function, we may generalize the result of all of the investigations mentioned, in the following way: the velocity of a catalyzed reaction in acid-salt solutions is always a function of the activity of the ion acting as a catalyst. With increasing ion activity the reaction velocity also increases, if other factors which also influence the reaction, especially at high salt concentrations, do not counteract the increase.

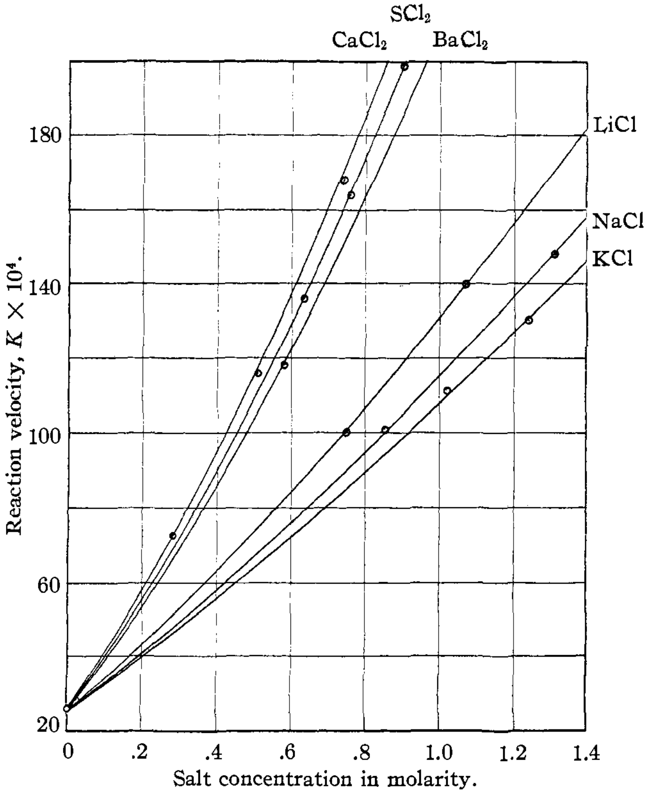

Fig. 4.—Curves for the reaction velocity of the conversion of acetylchloro-aminobenzene to *p*-chloro-acetanilide in some salt solutions of hydrochloric acid as determined by Rivett.

A graphical demonstration of this general result is given in Figs. 4 and 5. In Fig. 4 are plotted values of the reaction velocity for the conversion of acetyl chloro-aminobenzene to *p*-chloro-acetanilide as determined by Rivett.[8] In Fig. 5 are given the curves for the hydrogen-ion activities in the same acid-salt solutions that Rivett used. The comparison of the two figures indicates clearly that the reaction velocity always follows the hydrogen-ion activity. According to the investigations of Orton and Jones[9] and Harned and Seltz[1e] the velocity of this reaction is also a function of the chloride-ion activity. As this ion is common in all cases, the differences observed with the various salts are in a very great part due to changes in the activity of the hydrogen ions.

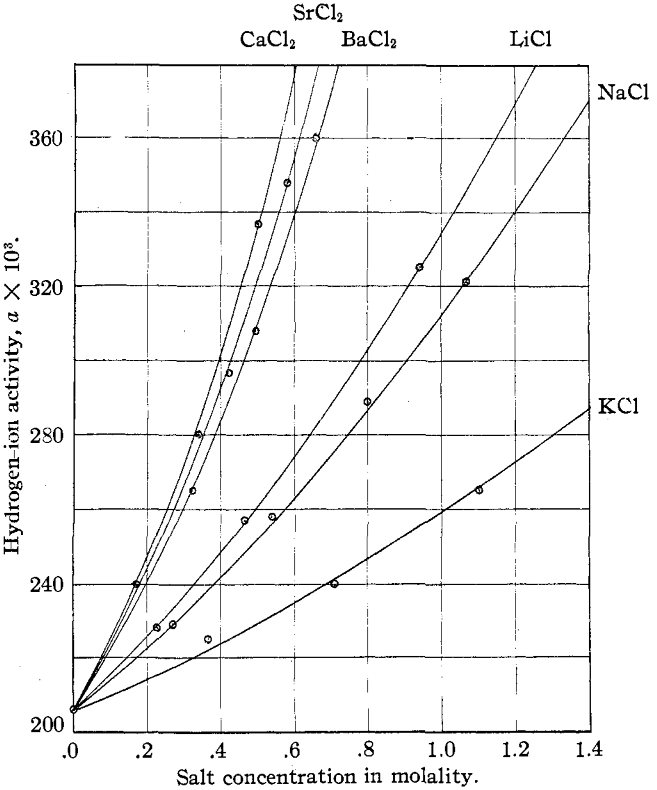

Fig. 5.—Curves for the approximate activities of the hydrogen ion in the same solutions that were used by Rivett for the determination of the conversion velocity of acetylchloro-aminobenzene to *p*-chloro-acetanilide.

Reactions in alkaline solutions have not yet been given as intensive a study as reactions in acid solutions. Koelichen had found that in alkali hydroxide solutions in diacetone alcohol or acetone, an equilibrium between

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[8] Rivett, *Z. physik. Chem.*, **82,** 201 (1913); **85,** 113 (1913).

[9] Orton and Jones, *Rept. Brit. Assoc. Adv. Sci.*, **1910,** p. 85.

these two compounds was formed. With increasing dilution the diacetone alcohol decomposed and the reaction was of the first order. At a diacetone alcohol concentration of 10% the velocity constants obtained showed a high degree of constancy. In the present investigation the execution of Koelichen's method has been greatly improved and, therefore, it was possible to decrease the initial concentration of the diacetone alcohol to about 1% of the volume of the solution.

The activity coefficient of the hydroxyl ion in the hydroxide-salt solutions used for measurements of the decomposition velocity of the diacetone alcohol is known approximately in only a few cases. The activity coefficients of potassium and sodium hydroxides in solutions of the alkali halides and sulfates have been determined by Harned,[10] Harned and James[11] and Åkerlöf.[12] At corresponding concentrations the activity was always found to be least when the salt present had the highest activity coefficient. The theory of Harned[6c] of the independent ion activity seems to be approximately valid for solutions of the salts mentioned. Therefore, the activity of the cation in salts of the same valence type and with common metal ion may be regarded as a constant at corresponding concentrations. As a conclusion it follows then that the activity of the hydroxyl ion decreases with increasing activity of the salt present. The change of the velocity constant for the decomposition of diacetone alcohol showed always the greatest decrease for the salt with the highest activity. The velocity constant and the hydroxyl-ion activity must, therefore, evidently follow each other or, in other words, the same rule that was found for the acid-salt solutions seems also to be valid for the alkaline salt solutions. A similar behavior has been found by Francis and Geake[13] for the decomposition of nitroso-triacetone-amine to nitrogen and phorone in alkaline salt solutions. This may indicate that the rule found has a general validity for alkaline salt solutions and is not specific for diacetone alcohol.

A similar demonstration of the experimental results for alkaline salt solutions as previously given for the acid-salt solutions is shown in Figs. 6 and 7. Fig. 6 gives the curves for the approximate potential changes of the hydroxyl ion in 0.1 *N* potassium hydroxide solutions of potassium chloride, bromide and iodide as obtained from the measurements of Harned, and Harned and James. The electromotive-force values are related to a reference state in 0.1 *N* pure potassium hydroxide solution. It could not be expected that these curves would follow the corresponding velocity curves given in Fig. 7 in their entire length. The volume concentration of the hydroxyl ion and the activity of the diacetone alcohol may also in-

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[10] Ref. 6 b, pp. 684, 689. Ref. 6 c.

[11] Harned and James, *J. Phys. Chem.*, **30**, 1060 (1926).

[12] (a) Åkerlöf, THIS JOURNAL, **48**, 1160 (1926). (b) Compare further, Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926).

[13] Francis and Geake, *J. Chem. Soc.*, **103**, 1722 (1913).

fluence the reaction velocity and they may change rapidly with increasing salt concentrations. A great similarity between the two sets of curves is, however, evident at moderate salt concentrations. As already mentioned, it is known only in a few cases that in the alkaline salt solutions hydroxyl-ion activity and salt activity follow each other inversely, but the probability of exceptions must be very small. It may therefore be considered as proved that the rule we have found is valid for both acid and alkaline salt solutions. This must be regarded as important and a great simplification for the coming theory in this field.

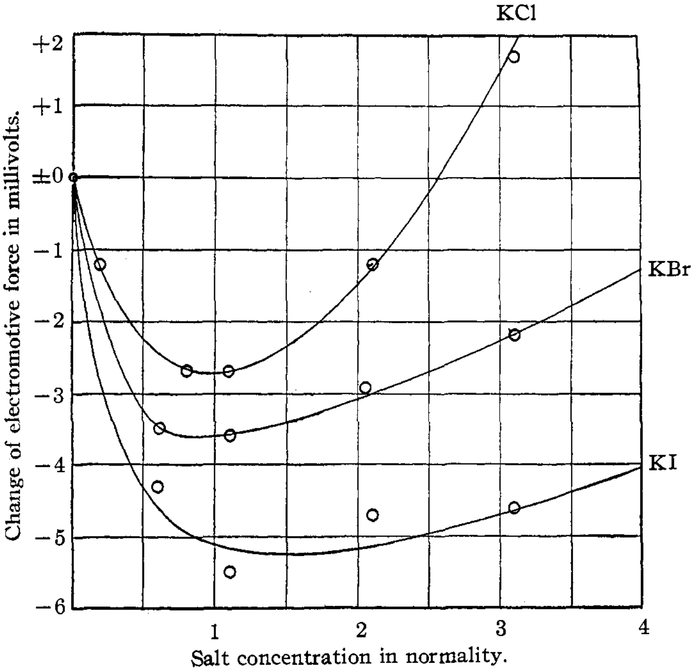

Fig. 6.—Curves for the approximate changes of the electromotive force of the hydroxyl ion in solutions of KCl, KBr and KI at constant potassium hydroxide concentration of 0.1 *N* and increasing salt concentrations.

A Relation between these Results and the Ionic Activity-Coefficient Product of Water.—When an increase in reaction velocity was found for acid-salt solutions, this generally corresponded with a decrease in velocity for the same alkaline salt solutions. It might then be suspected that these changes have some relation to each other. The equilibrium constant of water is given by the formula

$$K_{H_2O} = \frac{a_H \cdot a_{OH}}{a_{H_2O}} = \frac{\gamma_H \cdot \gamma_{OH} \cdot c_H \cdot c_{OH}}{a_{H_2O}} \qquad (1)$$

where a, γ and c denote activity, activity coefficients and concentrations, respectively. This formula must be valid at any concentration of the hydrogen or hydroxyl ions. If, then, the specific influence of the salt is to increase the activity coefficient of the hydrogen ion, the hydroxyl-ion activity must decrease, since there is no reason to believe that the concentrations of these ions change to any great extent at constant total concentration in a given salt solution. With the assumption of direct proportionality between ion activity and reaction velocity we should find

$$\left[\frac{k_{(s)}}{k_{(0.1)}}\right]_{\text{acid}} \times \left[\frac{k_{(s)}}{k_{(0.1)}}\right]_{\text{alk.}} = \frac{\gamma_{\text{H}(s)} \cdot \gamma_{\text{OH}(s)}}{\gamma_{\text{H}(0.1)} \cdot \gamma_{\text{OH}(0.1)}} \qquad (2)$$

where the index "s" refers to the salt solution and K is a reaction velocity. The product $\gamma_{\text{H}} \cdot \gamma_{\text{OH}} = \gamma^2_{\text{H}_2\text{O}}$ has been measured and calculated by

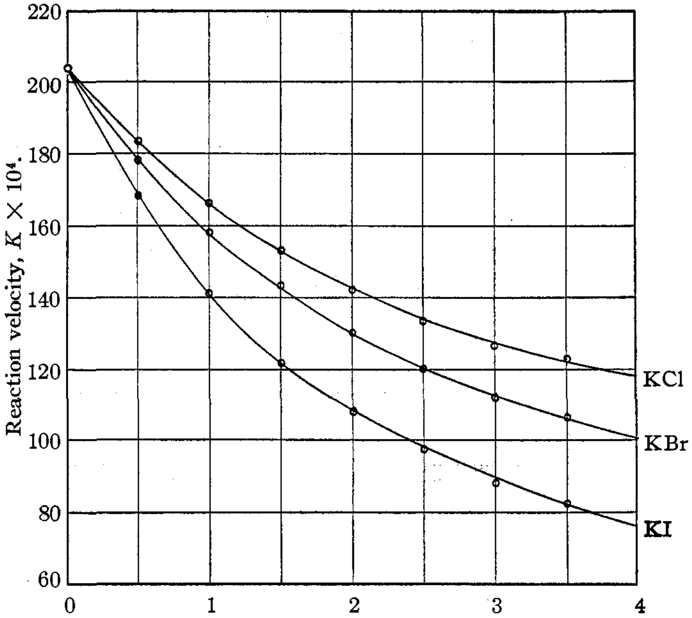

Fig. 7.—Curves for the reaction velocity of the decomposition of diacetone alcohol to acetone in alkaline solutions of KCl, KBr and KI at constant potassium hydroxide concentration of 0.1 N and increasing salt concentrations.

Harned,[14,6c] Harned and Swindells,[6d] Åkerlöf[12a] and Harned and James[11] for a number of different salt solutions.[12b] Table VIII gives the summary of a few calculations according to Formula 2. The velocity constants given for the acid side are measured by Harned[1a] for the hydrolysis of ethyl acetate in salt solutions of 0.1 N hydrochloric acid.

The values calculated from the velocity measurements are less for so-

[14] Harned, This Journal, **47**, 930 (1925).

Table VIII

Relation between Reaction Velocities in Acid and Alkaline Salt Solutions and the Ionic Activity Coefficient Product of Water

A. Calculations with potassium chloride solutions

N	$K \times 10^2$	$K \times 10^3$	$\left(\frac{k_s}{k_{0.1}}\right)_{\mathrm{acid}} \cdot \left(\frac{k_s}{k_{0.1}}\right)_{\mathrm{alk.}}$	$\frac{\gamma^2_{\mathrm{H_2O}(s)}}{\gamma^2_{\mathrm{B_2O}(0.1)}}$
0.00	28.8	20.4	..	..
.50	31.5	18.3	0.98	0.90
1.00	34.3	16.6	.97	1.01
1.50	36.6	15.3	.95	1.20
B. Calculations with sodium chloride solutions				
0.00	28.8	19.7	..	..
.50	31.8	17.0	0.95	0.91
1.00	35.9	14.9	.94	.98
1.50	39.3	13.3	.92	1.12

dium chloride than for potassium chloride solutions in agreement with the results from electromotive-force measurements. With alkali sulfate solutions, where the effects are reversed, similar results are obtained but the data available are partly at different concentrations and a comparison therefore is only approximate.

A better agreement could hardly be expected because changes in the reaction velocities caused by the increasing influence of other factors with the salt concentration have not been considered. The differences are, however, in the same direction as pointed out above for the relation between hydroxyl-ion activity and the velocity of the diacetone alcohol decomposition.

This investigation was made possible through a research fellowship given by the former President of the University, Dr. Charles C. Harrison. The author wishes to express his sincere thanks to Dr. Harrison.

Summary

The velocity of the decomposition of diacetone alcohol in a number of different salt solutions with constant hydroxide concentration has been measured at 25° with salt concentrations up to 6 N. The experimental method employed by Koelichen has been used in a greatly improved form.

The graphical representation of the experimental results showed that all the velocity curves obtained for the different salt solutions had very nearly the same general form independent of the nature of the anion of the salt present. For salts with common cation these curves did not in any case cross the curve for any other salt.

The measurements with potassium and sodium cyanide solutions seem to indicate a similar behavior for the cyanide ion as for the hydroxyl ion. This was expected in analogy to the explanation given by Harned and Åkerlöf for the behavior of the hydroxyl ions.

The results with alkaline solutions were compared with those for acid-salt solutions with regard to the activity of the ion acting as a catalyst. The same rule which was found to be valid for the relation between reaction velocity and activity in acid-salt solutions for a number of different reactions could also be applied to alkaline salt solutions. The reaction velocity follows always the activity of the ion causing the reaction, at least as long as counteracting factors do not cause an effect and the concentration of the catalyst is not very dilute.

A possible relation of the reaction velocities in acid and alkaline salt solutions to the water equilibrium in these solutions has been considered.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY, HARVARD UNIVERSITY]

FURTHER EVIDENCE CONCERNING THE MAGNITUDE OF INTERNAL PRESSURES, ESPECIALLY THAT OF MERCURY

BY THEODORE WILLIAM RICHARDS

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Internal pressures, dependent upon the attractive forces of chemical affinity and cohesion (which make possible the existence of compounds, solids and liquids) are among the most fundamental of the properties of matter. Even thermal internal pressures (calculated thermodynamically) are sometimes of the order of 20,000 atmospheres, yet they are obviously far less than the intrinsic cohesive and chemical pressures of compact solids. Coefficients of expansion and compression, as well as latent heats of evaporation and chemical action, indicate that these latter may often exceed 100,000 atmospheres.[1] Previous papers have sketched roughly a quantitative theory for the correlation of the data concerning these internal pressures. The present discussion corrects and amplifies the earlier work, and corroborates the previous provisional estimate of the order of magnitude and significance of intrinsic pressures by new evidence, thus strengthening the general principles of the theory, and providing a more definite outcome. The corrected values of the quantities in question are somewhat larger even than those suggested in previous papers.

1. Fundamental Equations

The present discussion is based upon the following fundamental equation of state for monatomic solids and liquids:[2]

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[1] Richards (a) THIS JOURNAL, **36**, 2417 (1914); (b) **46**, 1419 (1924); (c) **47**, 731 (1925); (d) *Chem. Rev.*, **2**, 315 (1925). This last historical paper contains many references to earlier work.

[2] Ref. 1 b, pp. 1423–1425. For a comparison of this equation with the somewhat similar, previously proposed equations of Mie and Grüneisen, see Ref. 1 d, pp. 327–329. These latter were essentially different in several important respects.