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NOTES ON NEUTRAL SALT CATALYSIS.
I. THE ROLE OF THE SOLVENT IN NEUTRAL SALT CATALYSIS IN AQUEOUS SOLUTIONS.

BY HERBERT S. HARNED.

Introduction.

Owing to the abnormalities observed in the velocity constants in reactions between ethyl iodide and sodium, potassium, and lithium ethylates Acree[1] and his associates made the suggestion that both the ions and the undissociated molecules of these substances (e. g., the ethylates) were reactive. Thus:

$$C_2H_5I + OC_2H_5' \longrightarrow (C_2H_5)_2O + I^1$$
$$C_2H_5I + KOC_2H_5 \longrightarrow (C_2H_5)_2O + KI$$
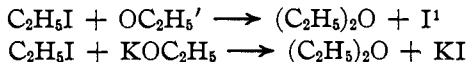
Let K_i be the velocity constant of the alkyl halide and ethylate ion, K_m the velocity constant of the alkyl halide and the undissociated sodium ethylate, then the observed velocity constant K will be given by

$$K = n_iK_i + n_mK_m$$

where n_i and n_m are the respective concentrations of the ion and the undissociated sodium ethylate molecule. In this same series of papers,

[1] Acree and Johnson, Am. Chem. J., **38**, 258 (1907); **48**, 352 (1912). These papers contain a bibliography of the work done up until 1912 on this type of reaction.

Acree employed the theory of the undissociated molecule to account for the abnormalities observed in catalytic reactions in aqueous solutions such as the conversion of chlorylacetanilide to p-chloroacetanilide catalyzed by hydrochloric acid, the hydrolysis of esters by acids and others.

More recently the suggestion that both the hydrogen ion and the undissociated acid molecule have catalytic activities has found supporters in Goldschmidt,[1] Bredig, Millar and Braune,[2] Snethlage,[3] and Taylor.[4] If K_m is the catalytic activity[5] of the undissociated molecule, n_m its concentration, K_H the catalytic activity of the hydrogen ion, n_H its concentration, then K, the observed reaction constant is given by

$$K = n_m K_m + n_H K_H.$$

The velocity constant in ester hydrolysis increases more rapidly than the hydrogen-ion concentration of the catalyzing acid. If the assumption be made that the undissociated acid molecule has a catalytic activity, then this increase in velocity constant can be explained. In the second place, this assumption will account for the abnormal behavior of neutral salts when added to the catalyzing acid solution. According to the law of mass action as applied without corrections for hydration and other effects to this equilibrium, the hydrogen-ion concentration of this solution should decrease, the concentration of the undissociated molecule should increase on the addition of neutral salts. The velocity constant increases and, therefore, in order to explain this anomaly, the undissociated molecule has been assumed catalytically active.

Two important objections can be made to the previous use of this theory when applied to neutral salt action with reactions of the catalytic type. In the first place, the values for the concentrations of the hydrogen ion at different salt concentrations and, consequently, the concentrations of the undissociated acid molecule have always been computed by means of the law of mass action in its classic forms. This is known not to give correct values in solutions at all concentrated. Direct measurement of these values have not been used. In the second place, not enough consideration has been given to the phenomena of solvation. Not until these two aspects of the problem have been better understood can the theory of the catalytic activity of the undissociated molecule receive confirmation in the domain of catalysis in liquid systems.

I—1.   **An Investigation of the Effects of Sodium, Potassium and Lithium Chlorides on the Velocity of Decomposition of Hydrogen**

[1] Z. physik. Chem., **70**, 627 (1910); **81**, 30 (1912).

[2] Z. Elektrochem., **18**, 535 (1912).

[3] Ibid., **18**, 539 (1912).

[4] Medd. K. Vetenskapsakad. Nobelinst., **2**, No. 35 (1913); **2**, No. 37 (1913); **3**, No. 1 (1914). THIS JOURNAL, **37**, 551 (1915); **39**, 422 (1917).

[5] The velocity constant is the measure of the catalytic activity.

Peroxide, Catalyzed by the Iodine Ion.—It is well known that the solutions of pure soluble acid-free iodides in a hydrogen peroxide solution effect its decomposition. All the peroxide oxygen is evolved and the concentration of the iodide or the iodine ion remains constant during the reaction. By a careful investigation of the effects of potassium and sodium iodides on the velocity of this decomposition, Walton[1] has shown that the reaction is complete in the direction of decomposition and is of the first order. Secondly, the velocity constant was found to be proportional to the iodine-ion concentration as calculated from conductance data using potassium iodide solution varying in strength from 0.00699 to 0.03684 N. The equation

$$v = \frac{dO_2}{dt} = KC_I C_{H_2O_2},$$

where v is the velocity or the differential coefficient of the oxygen evolved (O_2) in respect to time (t), C_I the concentration of the iodine ion, $C_{H_2O_2}$ the concentration of the hydrogen peroxide, and K the velocity constant, is a good expression for the behavior of this reaction using potassium iodide concentrations up to 0.04 N.

Walton has recorded one experimental result on the reaction velocity with each of the salts, potassium chloride, sodium chloride, sodium sulfate, sodium nitrate and potassium chlorate in a 0.0313 N potassium iodide solution. With the exception of the chlorate, all these increased the catalytic activity of the solution.

Walton explains the mechanism of this reaction by assuming the formation of the intermediate hypoiodite, which reacts with hydrogen peroxide, bringing about its decomposition and reforming the potassium iodide. This process may be represented as follows:

$$H_2O_2 + I' = H_2O + IO' \qquad (1)$$
$$\underline{H_2O_2 + IO' = H_2O + O_2I'} \qquad (2)$$
$$2H_2O = 2H_2O + O_2$$
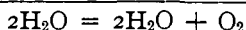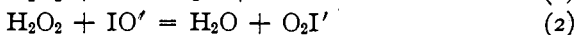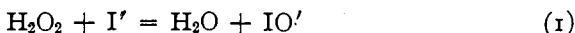
Reaction 1 is slow and measurable; (2) is extremely rapid. As a test of the validity of the above equations, the following distinct lines of direct and indirect evidence may be enumerated: (1) "The presence of iodine and free alkali in the solution[2] which must result in the cold in the formation of the hypoiodite ion;" (2) Walton showed that neither iodates nor periodates were formed as intermediate products; (3) from these assumptions in regard to the mechanism of the reaction, the kinetic law of the reaction may be deduced.

Further considerations of the conductance and freezing-point lowerings of these solutions led Walton to the conclusion that the hypoiodite ion

[1] *Z. physik. Chem.*, **47**, 185 (1904).

[2] Schöne, *Ann.*, **195**, 228 (1879).

was present in very small quantities. Brode[1] used the assumption of the formation of the intermediate hypoiodite ion to explain the reaction between hydrogen peroxide and potassium iodide in the presence of acids. Later, in a comprehensive and careful paper on the iodine catalysis of hydrogen peroxide, Abel[2] shows that this reaction takes place in two steps:

$$H_2O_2 + I_2 = 2H^+ + 2I^- + O_2 \qquad (1)$$
$$\underline{H_2O_2 + 2H^+ + 2I^- = 2H_2O + I_2} \qquad (2)$$
$$2H_2O_2 = 2H_2O + O_2$$
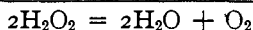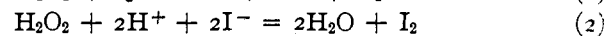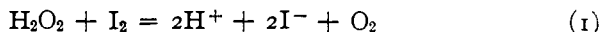
When the concentration of the iodine is such that Reaction 2 is taking place as fast as Reaction 1, there will be a pure hydrogen peroxide catalysis. Since all observers have noticed a slight separation of iodine from neutral solutions of potassium iodide and hydrogen peroxide, Walton's theory of this reaction must be considerably modified. However, the results of both Abel and Walton confirm the formulas

$$dO_2/dt = KC_{H_2O_2}C_I \quad \text{and} \quad 1.33 = K_1/C_I$$

as good expressions for the velocity of catalytic decomposition of hydrogen peroxide by iodine or the iodine ion at low iodine-ion concentrations. It is extremely important to note that C_{H_2O}, the water concentration, does not enter the equation which expresses the velocity of this reaction.

This reaction was selected for investigation because thereby neutral salt effects could be extended to ions other than the hydrogen ion and because the mechanism of the reaction had been so carefully studied. Enough results were obtained to follow the velocity constant—concentration of added salt plots up to $3 N$ concentrations. An effort was also made to improve the method of measurement.

Apparatus and Manipulation.

In determining the velocity of decomposition of hydrogen peroxide by measuring the volume of oxygen evolved at different time intervals, it is necessary to agitate the solution to such an extent that the gas is registered on the volume-measuring apparatus as soon as it is produced in the solution. Walton obtained sufficient agitation by the rapid shaking of the reaction vessel. In this series of measurements, the solution was agitated by a rapidly revolving glass stirrer sealed off from the outside by the well-known mercury seal method. Since the final apparatus employed differed from those previously used in a few important particulars and since by its use such excellent series of velocity constants were obtained, it is thought desirable to describe it in detail.

O (Fig. 1) is a wide-mouth thick glass bottle, in the neck of which the two-holed rubber stopper I is tightly held by means of a clamping device,

[1] Z. physik. Chem., **49**, 208 (1904).
[2] Z. Elektrochem., **14**, 598 (1908).

L, M, and N. L is a triangular metal plate, one-eighth of an inch in thickness, in the center of which a hole is cut wide enough to encircle the rubber stopper H and the tube K. At the 3 corners of the plate, small holes are drilled which permit the rods R R R to pass through. These rods are threaded and hold the nuts N N. By tightening the latter, the plate L can be pressed down on the stopper I, thus holding it in place. Through one hole in I the tube F passes which acts as a bearing to the glass shaft A. Through the other hole in I passes the tube K, which leads to the apparatus for measuring the gas volume. The latter was similar to that used by Walton and contained water. The gasometer was surrounded by a water jacket maintained at a temperature of 25.0° by pumping water from the thermostat through it. The tube F passes through the rubber stopper H which holds the tube G, which in turn serves to hold the mercury. The rubber stopper D is wired tightly on the shaft. The brass tube E is shoved half way up into D which is in turn wired tightly on to E. A metallic contact with the mercury is believed to make a tighter joint. It was found best to cover the stopper D and the upper part of E with marine glue. C is a metallic chuck held securely in position and in which the shaft A is free to rotate. B is a pulley which is securely fastened to metallic tube S which, in turn, is sealed on to the shaft A with marine glue. Since the stirrer is rotated between 1000 and 1500 revolutions per minute, these precautions were all necessary in order to prevent leakage. It is also extremely important to have the shaft well centered and slightly greased so that no glass is ground.

Fig. 1.

The glass cup J, sealed on to the shaft A, was used for introducing the potassium iodide.
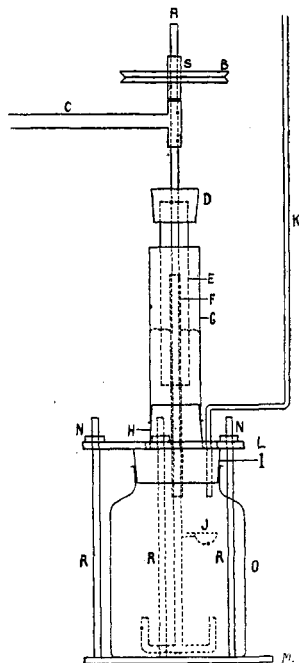
In making a determination, the following procedure was adopted: 5 cc. of an approximately 3% solution of hydrogen peroxide (purified by distillation) was introduced into the reaction bottle which had been previously steamed and carefully dried, and to this 20 cc. of water or a salt solution of known strength was added. Carefully calibrated pipets were employed. Solid potassium iodide was weighed out and rolled up in a small piece of quantitative filter paper. This was introduced into the cup J. The apparatus was then closed and clamped tight and then placed in a thermostat maintained at 25.00 ± 0.01°. When the solu-

tion had reached the temperature of the bath, the tube K was connected to the volume-measuring apparatus by a rubber tube tightly wired. As soon as the stirrer was rotated, the potassium iodide, along with the quantitative filter paper containing it, was thrown into the solution where the salt soon dissolved. Readings of the volume of oxygen evolved were taken at convenient, usually 5 minute, intervals. The zero reading was taken 5 minutes after starting, when an even state of gas evolution was assured.

Preliminary Measurements.

Since ground glass and sharp edges of glass cause the decomposition of hydrogen peroxide, preliminary experiments were made when hydrogen peroxide without the catalyst was stirred in the reaction vessel. It was also important to determine whether pure cellulose (quantitative filter paper) produced any evolution of gas. Finally, potassium and sodium chloride solutions were added to the hydrogen peroxide solution in order to find out whether these salts alone produced an appreciable decomposition in the absence of potassium iodide. Table I summarizes these observations:

TABLE I.

Decomposition in the Absence of Potassium Iodide.

Expt. No.	Substances in reaction vessel.	Time. (Hours).	Cc. of O_2 evolved.
1	5 cc. H_2O_2 (3%) + 20 cc. H_2O	1	0.00
		2	0.00
2	5 cc. H_2O_2 (3%) + filter paper + 20 cc. H_2O	1	0.00
		2	0.05
		3	0.05
3	5 cc. H_2O_2 (3%) + filter paper + 20 cc. H_2O	1	0.00
		2	0.05
		3	0.10
4	5 cc. H_2O_2 (3%) + 20 cc. (KCl (3 N))	1	0.00
		2	0.10
		3	0.20
5	5 cc. H_2O_2 (3%) + 20 cc. (NaCl (3 N))	1	0.10
		2	0.20
		3	0.35
6	5 cc. H_2O_2 + 20 cc. NaCl (3 N) + filter paper	1	0.10
		2	0.25
		3	0.40

The above results show conclusively that any decomposition caused by the apparatus, stirrer or the filter paper, is negligible. The presence of potassium and sodium chlorides do effect an extremely slow decomposition of the hydrogen peroxide. This confirms Engler and Nasse[1] and Schöne[2] who have reported that concentrated chloride and bromide solutions slowly

[1] Ann., 154, 231 (1870).
[2] Loc. cit.

decompose hydrogen peroxide.   In the next section, the magnitude of this error will be considered.

Final Measurements.

Five minutes after starting the initial or zero reading of the volume of oxygen was taken and then readings every 5 or 10 minutes until the decomposition was approximately 85% complete. After that, in every case, the reaction was allowed to proceed to completion and the final volume recorded. Since water was used in the volume-measuring apparatus, a correction was made for its vapor pressure. Readings of the volume were taken to within 0.05 cc. In Table II, two complete series of constants are given, calculated according to the equation of the first order, namely,

$$K = (1/t \log_e)(a/a - x) = (2.3026/t \log_{10})(a/a - x)$$

where K is the velocity constant, t the time in minutes, a the final volume of oxygen evolved, and x the volume of oxygen evolved in a time, t.

TABLE II.

Velocity of Decomposition of Hydrogen Peroxide Solutions.

5 cc. H_2O_2 (3.5% V), 20 cc. H_2O, 0.0830 g. KI (0.02 N).

Expt. No. 1.

$k = 1/t \log_{10}a/a - x.$
$k = 0.4343 K.$

$t.$		$x.$	$a - x.$	$k = 0.4343 K.$
5.00		7.50	50.40	0.01198
10.00		14.00	43.90	0.01199
15.00		19.65	36.25	0.01196
25.00		28.80	29.10	0.01194
35.00		35.80	22.10	0.01194
45.00		41.20	16.70	0.01197
55.00		45.20	12.70	0.01197
65.00		48.30	9.60	0.01198
75.00		50.60	7.30	0.01198
∞	a	57.90	. . .	. . .

Mean, 0.01197
$K = 0.0275$

5 cc. H_2O_2 (3.5% V), 20 cc. NaCl (3 N), 0.0830 g. KI.   KI (0.02 N) + NaCl (2.40 N).

Expt. No. 2.

$t.$		$x.$	$a - x.$	k
5.00		10.10	43.80	0.01795
10.00		18.20	35.70	0.01784
15.00		24.90	29.00	0.01788
20.00		30.30	23.60	0.01788
30.00		38.20	15.70	0.01784
40.00		43.60	10.30	0.01793
50.00		47.05	6.85	0.01792
60.00		49.40	4.50	0.01795
∞	a	53.90	. . .	. . .

Mean, 0.01790
$K = 0.0412$

These will suffice to show the constancy obtainable. The mean value of K was found to be reproducible in two completely different experiments to within 3 in the fourth place, an error of less than 1%.

Referring now to Table I, (5) and (6), it is seen that the hydrogen peroxide solution in the presence of 2.4 N sodium chloride evolves from 0.1 to 0.2 cc. of oxygen in one hour. If a correction is made for this in the last result (corresponding to $t = 60$) in Table II (2), 0.01768 is obtained which is 0.00022 below the mean, an error greater than that in reproducing the mean of one series of constants. This error becomes much less in the first readings ($t = 5$ to 30) and, if made for a complete series of constants, affects the general mean less than 0.0001, an error about equal to the reproducibility of the general mean. For this reason, this correction has been omitted. Table III contains the mean values of K.

TABLE III.

Velocity Constants.

$H_2O_2 = 0.70\%$ V.

Series 1. Conc. of KI (mols. per liter).	Conc. of chloride.	K.
0.02 N	0.000	0.0275
0.02 N	0.000	0.0275
0.02 N	1.600 N KCl	0.0285
0.02 N	1.200 N KCl	0.0295
0.02 N	1.800 N KCl	0.0309
0.02 N	2.400 N KCl	0.0316
0.02 N	2.400 N KCl	0.0318
0.02 N	0.600 N NaCl	0.0299
0.02 N	1.200 N NaCl	0.0326
0.02 N	1.200 N NaCl	0.0324
0.02 N	1.800 N NaCl	0.0368
0.02 N	2.400 N NaCl	0.0412
0.02 N	2.400 N NaCl	0.0409
0.02 N	0.437 N LiCl	0.0320
0.02 N	0.437 N LiCl	0.0315
0.02 N	0.875 N LiCl	0.0352
0.02 N	0.875 N LiCl	0.0357
0.02 N	1.312 N LiCl	0.0443
0.02 N	1.750 N LiCl	0.0544
0.02 N	1.750 N LiCl	0.0539

Series 2. Conc. of KI (mols. per liter).	Conc. of chloride.	K.
0.03 N	0.000 N	0.0418
0.03 N	0.000 N	0.0419
0.03 N	0.000 N	0.0417
0.03 N	0.600 N KCl	0.0435
0.03 N	0.600 N KCl	0.0435
0.03 N	1.200 N KCl	0.0448
0.03 N	1.800 N KCl	0.0462
0.03 N	2.400 N KCl	0.0485
0.03 N	0.600 N NaCl	0.0452
0.03 N	1.200 N NaCl	0.0497
0.03 N	1.800 N NaCl	0.0548
0.03 N	2.400 N NaCl	0.0610
0.03 N	2.800 N NaCl	0.0640

These results are plotted in Fig. 2. $K \times 10^3$ is plotted against salt concentration. Curves 2 and 4 correspond to potassium chloride in 0.02 N and 0.03 N potassium iodide solutions, respectively; Curves 1 and 3 to sodium chloride in 0.02 N and 0.03 N potassium iodide solutions, respectively; and 5 corre-sponds to lithium chloride in a 0.02 N potassium iodide solution.

The plots in Fig. 2 show that lithium chloride causes an increase in the velocity constant greater than sodium chloride which in turn causes a greater increase than po-tassium chloride. A glance at the best data obtainable on ionic hydration values will throw much light on the results.

In a series of measurements on the transference numbers of hydrochloric acid, lithium, sodium, potassium and cae-sium chlorides in the presence of raffinose as a reference substance, Washburn and his associates[1] have been able to compute the relative ionic hydration values of the cations of these salts. Table IV gives a summary of the results of these hydra-tion values relative to N_w^{Cl}, the hydration value of the chlorine ion.


Fig. 2.

TABLE IV.
Hydration Values.

$$N_w^{H} = 0.28 \pm 0.04 + 0.185 \ N_w^{Cl}$$
$$N_w^{Cs} = 0.67 \pm 0.1 + 1.03 \ N_w^{Cl}$$
$$N_w^{K} = 1.3 \pm 0.2 + 1.02 \ N_w^{Cl}$$
$$N_w^{Na} = 2.0 \pm 0.2 + 1.61 \ N_w^{Cl}$$
$$N_w^{Li} = 4.7 \pm 0.4 + 2.29 \ N_w^{Cl}$$

Also Remy,[2] from the measurements of the relative volume changes at the electrodes during the electrolysis of salt solutions while the middle portion of the solution was fixed with gelatine, has been able to compute values for the hydration of a number of ions referred to chlorine. A good agreement with the results of Washburn was obtained as shown by the

[1] THIS JOURNAL, **31**, 322 (1909); **35**, 751 (1913); **37**, 694 (1915).
[2] Z. physik. Chem., **89**, 529 (1915).
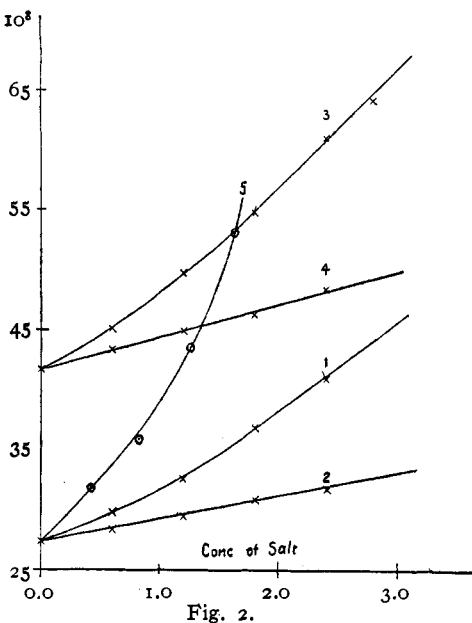
last two horizontal columns of Table V, which contains the molecules of water of hydration of a number of ions referred to the chlorine ion.

TABLE V.

Molecules of Water of Hydration Referred to the Chlorine Ion.

	N_w^{Cl}.	N_w^{H}.	N_w^{Cs}.	N_w^{K}.	N_w^{Na}.	N_w^{Li}.	N_w^{Ba}.	N_w^{Ca}.
Washburn......	0	0.28	0.7	1.3	2.0	4.7	...	...
	1	0.46	1.7	2.3	3.6	7.0	...	...
	2	0.65	2.7	3.3	5.2	9.3	...	...
	3	0.83	3.8	4.4	6.8	11.6	...	...
	4	1.0	4.7	5.4	8.4	14.0	...	...
Remy..........	4	..	...	5.4	8.4	12.6	1.5	6.3

Washburn's results were obtained with solutions from 1 to 1.2 N. Remy used solutions varying in strength from 0.5 to 1.5 N.

The lithium ion is the most highly hydrated of the alkali metal ions. The hydration value of the sodium ion lies between that of the lithium and the potassium ion. No numerical data are available on the hydration values of the undissociated molecules of these salts, although the lithium chloride molecule is probably hydrated to a considerable extent.

Comparing the above ionic hydration values at a salt concentration of 1.2 N with the neutral salt effects of sodium, potassium and lithium chlorides on the velocity of the reaction under consideration, the following rough but interesting relation is noticeable:

$$\frac{K_3 - K_2}{K_2 - K_1} = \frac{18}{7} (1.2\ N) \frac{N_w^{Li} - N_w^{Na}}{N_w^{Na} - N_w^{K}} = \frac{4.1^a}{1.9} = \frac{4.8^b}{2.4}$$
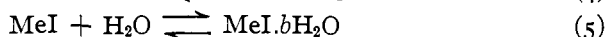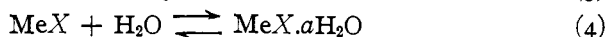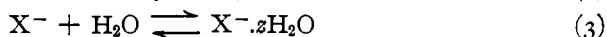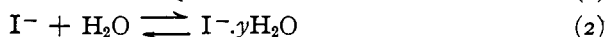
K_3, K_2, K_1 are the velocity constants corresponding to lithium, sodium and potassium chlorides, respectively, at 1.2 N concentrations. The undissociated lithium chloride molecule is probably highly hydrated which will increase the difference between the sodium and the lithium chloride plots.

Too much emphasis cannot be put on the above relationship, which demonstrates without a doubt that ionic hydration is to a large extent, if not entirely, responsible for the abnormalities observed. Since the anion of the salts used is the same, the neutral salt effect should be a function of the cations and the undissociated molecules. In this case, the ionic hydration far outweighs the influences of the undissociated molecules.

A mathematical deduction of the equilibrium relations in a system as complicated as this would at present, owing to the insufficiency of the data, be useless. The gross salt effect can be explained by considering the effect of hydration on the general equilibrium of the following reactions which represent the numerous equilibria possible in such a system:

^{a} Referred to $N_w^{Cl} = 2$.

^{b} Referred to $N_w^{Cl} = 3$.

$$Me^+ + H_2O \rightleftharpoons Me^+.xH_2O \tag{1}$$

$$I^- + H_2O \rightleftharpoons I^-.yH_2O \tag{2}$$

$$X^- + H_2O \rightleftharpoons X^-.zH_2O \tag{3}$$

$$MeX + H_2O \rightleftharpoons MeX.aH_2O \tag{4}$$

$$MeI + H_2O \rightleftharpoons MeI.bH_2O \tag{5}$$

$$Me^+ + I^- \rightleftharpoons MeI \tag{6}$$

$$Me^+ + X^- \rightleftharpoons MeX \tag{7}$$

Equations 1, 2, 5 and 6 represent the equilibrium before the salt is added. If the added salt is ionized and both the undissociated salt molecule and ions become hydrated according to (1), (3) and (4), there will be, of course, less free or uncombined water molecules present.

Using the Jones hydrate theory, there will be less active solvent or a contraction effect, and the activities of all the molecular and ionic species present will tend to increase except the solvent water molecules. This increase will cause all the equilibria to shift from left to right. Thus the total effect may be an increase in the concentrations and activities which will be greater, the greater the hydration values of the undissociated molecule and the ions of the added salt.

If the equation

$$K/C_I = 1.33$$

holds for the iodine ion catalysis of hydrogen peroxide, then an increase in velocity constant is to be expected on salt addition from a general consideration of the equilibrium involved, and, furthermore, the greater the hydration value of the added salt, the greater will be this increase. It is also an important result of the above complicated equilibria relations that the hydration effect will increase more rapidly than the increasing number of ions and molecules in the solution, so that it is necessary to compare the plots at salt concentrations at which the ionic hydration values have been determined.

I—2. **The Conversion of Chlorylacetanilide to p-Chloroacetanilide by Hydrochloric Acid—Neutral Salt Solutions.**[1]—Chlorylacetanilide liberates iodine from solutions of hydriodic acid, p-chloroacetanilide does not, and hence the chlorylacetanilide may be determined by adding a standard hydriodic acid solution and titrating the liberated iodine with sodium thiosulfate. It has been found that the reaction is of the first order and proceeds according to the equation

$$K = (2.3/t) \log (A_0/A_t)$$

where K is the velocity constant, t the time in minutes, A_0 the initial titer, and A_t the titer at the time t. K is found to be only approximately proportional to the square of the hydrogen-ion concentration. In the

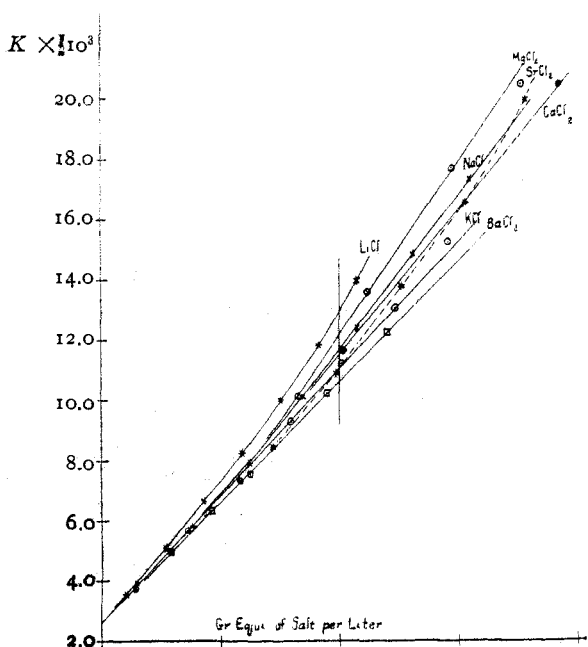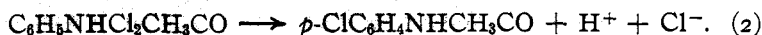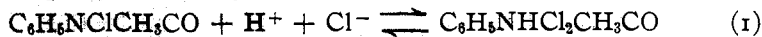[1] Rivett, Z. physik. Chem., **82**, 211 (1913); **85**, 113 (1913).

Fig. 3.

second paper, Rivett presents the results of the effects on this reaction of the chlorides of lithium, sodium, potassium, rubidium, caesium, magnesium, calcium, strontium and barium when dissolved in 0.2485 N hydrochloric acid. In all cases, the catalytic activity of the acid was increased. In Fig. 3 are given plots of most of these results. The velocity constant $K \times 10^3$ is plotted against added salt in gram equivalents per liter.

Acree and Johnson,[1] in a discussion of the mechanism of this reaction, have suggested the formation of an intermediate compound according to

$$C_6H_5NClCH_3CO + H^+ + Cl^- \rightleftharpoons C_6H_5NHCl_2CH_3CO \qquad (1)$$

$$C_6H_5NHCl_2CH_3CO \longrightarrow p\text{-}ClC_6H_4NHCH_3CO + H^+ + Cl^-. \qquad (2)$$

Reaction 1 is extremely rapid, Reaction 2 is slow and measureable. Hence

$$K = \frac{C_I}{C_C C_H C_{Cl}}$$

where C_I, C_C, C_H, C_{Cl} are the concentrations of the intermediate compound, the chlorylacetanilide, the hydrogen ion, and the chlorine ion, respectively. The velocity will be given by

$$v = kC_i$$

and hence

$$v = KC_C C_H C_{Cl} = KC_C C^2_H.$$

From the researches of Orton and Jones[2] on the action of chlorine on anilides,[3] Rivett concludes that the above is not a correct interpretation.

[1] Loc. cit.

[2] J. Chem. Soc., **95**, 1456 (1909).

[3] Solutions of chlorylacetanilide and hydrochloric acid give a test for chlorine, hence the reaction

$$C_6H_5NClCH_3CO + HCl \rightleftharpoons C_6H_5NHCH_3CO + Cl_2$$
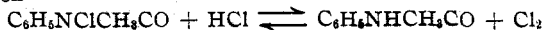
occurs. This will certainly affect the mechanism of the reaction under discussion.

It is important to note that the concentration of the water does not occur in the final velocity equation and it is difficult to see how it can because water does not in any way take part in the reaction.

A comparison of Rivett's results and the plots in Fig. 3 with the Washburn and Remy ionic hydration values offers much interest. It is found that, at the concentrations designated,

$$\frac{K_3 - K_2}{K_2 - K_1} = \frac{30}{15} \ (N) = \frac{32}{15} \ (1.2N),$$

a ratio which corresponds very closely with the ratios of the differences of the ionic hydration values given in the last section.[1] The same is roughly true throughout the series; the calcium chloride, caesium chloride (not included in the drawing since it falls so near the potassium chloride plot), and barium chloride plots fall in the expected positions.[2] (See Table V.) Also, it can be predicted with a fair degree of certainty that the hydration value of the magnesium ion will be approximately 10 referred to the chlorine ion as four. All this discussion tends to demonstrate that hydration has a most important influence in neutral salt catalysis and must by no means be neglected.

Rivett, near the end of his article, points out the similarity between the neutral salt action on the velocity of this reaction to the solubility of o-phthalic acid in the same salt solutions, and also to the deviations of the freezing-point lowerings of solutions of the same salts from the classic freezing-point law. Plots are given which clearly show this relationship. It is interesting, now, to note Rivett's own words of conclusion. "From these curves it is plain that a similar explanation for these quite different phenomena must be given. Whether this is to be found in the hydration of the dissolved substances or in a pure physical factor, or in both, is a leading question in the chemistry of solutions." It is obvious, at least, that the difference in these curves is a function of the differences in ionic hydration.

I—3. The Velocity of Hydrolysis of Ethyl Acetate Catalyzed by Hydrochloric Acid and Hydrochloric Acid-Neutral Salt Solutions.—Taylor[3] has carefully determined the velocity constants of hydrolysis of ethyl acetate at 25°, using 0.01 N, 0.025 N, 0.05 N, 0.1 N, 0.25 N and 0.479 N hydrochloric acid and also using the above strengths of acid in the presence of normal potassium chloride. This much only suffices to give two points on the velocity constant—salt concentration

---

[1] K_3, K_2, K_1 are the velocity constants in the presence of lithium, sodium and potassium chlorides, respectively, at the concentrations designated.

[2] Since only ionic hydration is here considered, and there may be large hydration effects produced by the undissociated molecules of these salts, too much accuracy must not be demanded in the position of these plots.

[3] *Medd. K. Vetenskapsakad. Nobelinst.*, **2**, No. 35 (1913).

plots which is not enough to determine their nature. Therefore, it was necessary to supplement Taylor's values by using a sufficient number of salt concentrations in acid of the same strength so as to be able to construct the velocity constant—salt concentration plots throughout an extended range of salt concentration. In Table VI are given the velocity constants at $25°$ obtained by using hydrochloric acid and hydrochloric acid salt mixtures. The technique possessed no originality and will not be described. Suffice it to say that the classic method of titrating the acetic acid formed at intervals during the course of the reaction with a $0.025\ N$ barium hydroxide solution was employed.

TABLE VI.

Velocity Constants.

HCl ($0.1\ N$). Temperature = $25.00 \pm 0.01°$.

$(K = 1/t \log_e t_\infty / t_\infty - t_x = (2.3/t \log_{10})(t_\infty / t_\infty) - t_x$ and
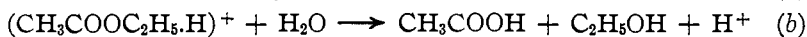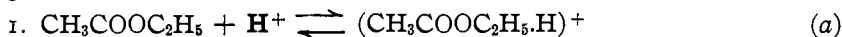
$k = 1/t \log_{10} t_\infty / t_\infty - t_x = 0.4343\ K.$

(t is the time in minutes, t_∞ is the final titer, t_x the titer at the time t.)

(1) Salt.		(2) Salt conc.	(3) $k \times 10^5$.	(4) Mean value of $k \times 10^5$.
KCl	(1)	0.000 (Taylor)	28.3	...
		0.000 (Taylor)	28.3	...
		0.000	28.8	...
		0.000	29.2	...
		0.000	28.8	...
		0.000	29.2	28.8
	(2)	0.500	31.5	...
		0.500	31.4	31.45
	(3)	1.000 (Taylor)	34.4	...
		1.000	34.2	34.3
	(4)	1.500	36.6	36.6
	(5)	2.000	39.2	39.2
	(6)	3.000	42.6	...
		3.000	43.0	42.8
NaCl,	(2)	0.500	31.7	...
		0.500	31.8	31.75
	(3)	1.000	35.9	...
		1.000	35.9	35.9
	(4)	1.500	39.3	39.3
	(5)	2.000	42.9	...
		2.000	42.8	42.85
	(6)	3.000	52.9	...
		3.000	51.7	52.3
LiCl	(2)	0.482	31.0	31.0
	(3)	0.964	33.0	33.0
	(4)	1.446	35.7	35.7
	(5)	2.409	39.5	39.5

Fig. 4 gives the plots of these results; $k \times 10^5$ is plotted against salt concentrations expressed in gram equivalents per liter.

The Mechanism of This Reaction and a Discussion of Hydration Effects.—Most investigators in this field are agreed that an intermediate

compound between the catalyzing acid and the ester is formed.[1] Two schemes of formulation of the intermediate compound have been suggested:

1. $CH_3COOC_2H_5 + H^+ \rightleftharpoons (CH_3COOC_2H_5.H)^+$ (a)

    $(CH_3COOC_2H_5.H)^+ + H_2O \longrightarrow CH_3COOH + C_2H_5OH + H^+$ (b)

The ester and the hydrogen ion react very rapidly to form the cation of the intermediate compound which in turn reacts with water and changes almost completely into acid and alcohol, regenerating the hydrogen ion. The first reaction is an equilibrium which can be expressed by
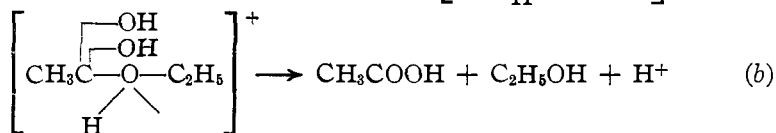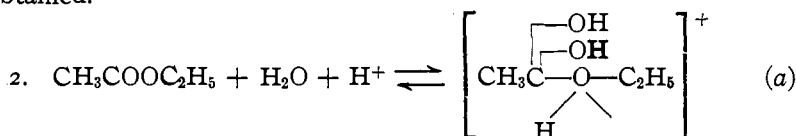
$$K = \frac{C_i}{C_e C_H}$$

where C_e, C_H and C_i are the concentrations of the ester, the hydrogen ion and the intermediate compound, respectively. The reaction velocity is given by

Fig. 4.

$$v = kC_iC_w$$

where C_w is the concentration of the water, v the reaction velocity and k the velocity constant. From these two equations,

$$v = KC_eC_HC_w$$

is obtained.

2. $CH_3COOC_2H_5 + H_2O + H^+ \rightleftharpoons \left[\begin{array}{c} {\scriptstyle -OH} \\ {\scriptstyle -OH} \\ CH_3C-O-C_2H_5 \\ H \end{array} \right]^+$ (a)

$\left[\begin{array}{c} {\scriptstyle -OH} \\ {\scriptstyle -OH} \\ CH_3C-O-C_2H_5 \\ H \end{array} \right]^+ \longrightarrow CH_3COOH + C_2H_5OH + H^+$ (b)

The equilibrium of reaction a will be given by

[1] Suggested by Stieglitz, *Congress of Arts and Sciences*, St. Louis, **4**, 276 (1904). (For literature references up to 1907, see Acree and Johnson (*Loc. cit.*).)
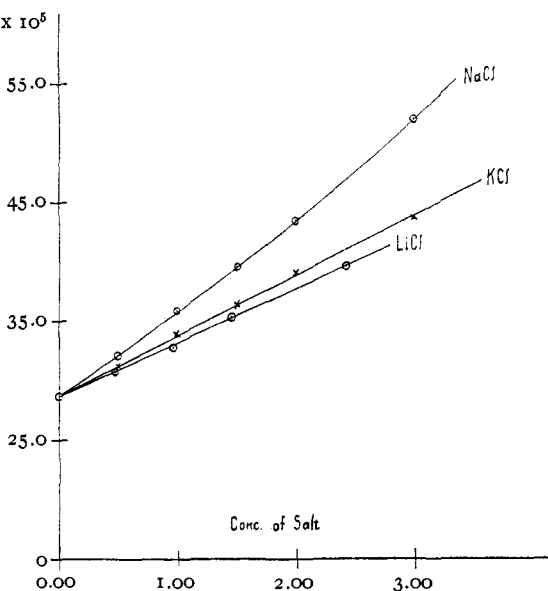
$$K = \frac{C_i}{C_e C_H C_w}.$$

The velocity of the reaction will be given by

$$v = kC_i.$$

Hence,

$$v = KC_e C_H C_w.$$

Both the above methods for expressing the mechanism of this reaction give identical expressions for the reaction velocity.

It is important to observe that in all cases the water concentration enters the final velocity equation, whereas, in the decomposition of hydrogen peroxide and the conversion of chlorylacetanilide, it plays no part. This will be seen to have an important bearing on the results in Table VI and the plots in Fig. 4.

Now, when a shifting of the equilibrium takes place on the addition of a salt to the catalyzing acid, the water concentration, C_w, and hence its activity, will decrease somewhat and the greater the hydration value of the added salt, the greater will be this increase. Scheme 2 for the mechanism of this reaction best expresses the results. Since the velocity is proportional to the concentration of the intermediate compound, the reaction will be of the first order. Secondly, this decrease in water concentration will shift the equilibrium of Reaction a so as to decrease the concentration of the intermediate compound and thus retard the reaction; such a retarding effect will be greater, the greater the hydration value of the salt. It is not, then, to be expected that the values of the velocity constants for the same concentrations of added salts will be proportional to the hydration values of the salts. On the other hand, referring to Fig. 4, it is seen that such a proportion is far from being the case and the retarding effect produced by the more hydrated lithium chloride is sufficient to cause it to increase the velocity constant less rapidly even than potassium chloride. The sodium chloride plot is also nearer the potassium chloride plot than would be the case if this retarding effect did not occur. This reaction, which, at first glance, seems to contradict the theory of hydration as applied to neutal salt catalysis, turns out to be good evidence of its validity. As a corollary of the above, it is necessary in studying pure neutral salt catalysis effects to use reactions which take place in aqueous solution without reacting with the water molecules present.

II. A RELATION BETWEEN THE INCREASE IN VELOCITY CONSTANTS CAUSED BY NEUTRAL SALTS AND THE ION ACTIVITIES OF THE SALT SOLUTIONS.

II—1. The Chlorine-Ion Activities of Solutions of Potassium and Sodium Chlorides Obtained from Measurements of the Cells, Hg | HgCl | MeCl (0.1 N) | MeCl(c) | HgCl | Hg.—In an article on "The Hydrogen- and

Chlorine-Ion Activities of Solutions of Potassium Chloride in 0.1 M Hydrochloric Acid," the author[1] has published a series of chlorine-ion activities in solutions of potassium chloride at different concentrations, calculated on the basis that the chlorine-ion activity of potassium chloride is 0.0730 at 0.1 N concentration. At that time, measurements were also made of the electromotive forces of the cells

$$Hg \mid HgCl \mid NaCl\ (0.1\ N) \mid NaCl\ (c) \mid HgCl \mid Hg.$$
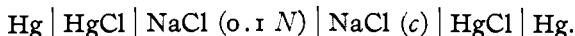
The results were not published then because the data available on the transference numbers of sodium chloride solutions at high concentrations which were needed in the calculations of the liquid potentials were considered insufficient to furnish the accuracy desired. These results are now published, and although no great accuracy is claimed, they are, at least, a good approximation.

A minute description of the technique of the measurements is not necessary. Lewis, Brighton and Sebastian[2] have found that by using dipping contacts at the liquid junctions, the liquid potentials after a minute or two were easily reproducible. A dipping method was also used by the author. One calomel electrode ended in a cup into which a capillary tube extending from the other electrode could be dipped. The solutions in both the cup and the capillary could be very easily renewed. On standing a minute or two these cells could be completely reproduced to within 0.1 of a millivolt. Table VII gives the results. E_t is the electromotive forces of the cells with transference, E_l the liquid potentials, $E_l + E_t$ the electromotive forces of the cells after elimination of the liquid potentials. In the last column are given the chlorine-ion activities of sodium chloride calculated on the assumption that the chlorine-ion activity of 0.1 N sodium chloride is 0.0730, the same as 0.1 N potassium chloride. If the activities of the 0.1 N solutions of the two salts are the same, then the absolute activities of the salts at this concentration are of little importance since activity ratios are used throughout. In calculating the liquid potentials, the formula

$$E_l = E_t \left(1 - \frac{1}{2n_c} \right)$$

was employed, where n_c is the cation transference number of sodium chloride.[3] The cation transference number of sodium chloride was taken to be 0.400 at 0.3 N concentration, 0.390 at 0.5 N, 0.380 at 1.0 N, and 0.370 from 1.5 to 3.0 N. Each result under E_t represents the mean of 3 determinations. The activities were computed by the formula

$$E_t + E_1 = 0.05915 \log 0.0730/a,$$

[1] This Journal, **38**, 1986 (1916).

[2] *Ibid.*, **39**, 2245 (1917).

[3] MacInnes, This Journal, **37**, 2301 (1915).

where a is the chlorine-ion activity of the solution designated. The temperature was maintained at $25.00 \doteq 0.01°$.

TABLE VII.

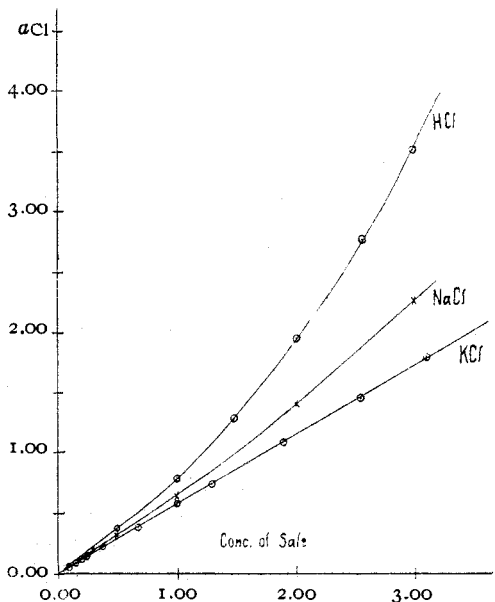| Conc. of salt. (c).	E_t	E_l	$E_t + E_l$	Activity of chlorine ion.
0.100	...	...	..	0.0730
0.300	—0.01991	—0.00498	—0.0249	0.192
0.500	—0.02912	—0.00821	—0.0373	0.312
1.000	—0.04202	—0.01328	—0.0553	0.628
2.000	—0.05611	—0.01972	—0.0758	1.397
3.000	—0.06530	—0.02293	—0.0882	2.261

Fig. 5.

Fig. 5 gives the plots of these results. The chlorine-ion activities of sodium and potassium chloride solutions are plotted against salt concentrations in gram equivalents per liter. As pointed out by Linhart,[1] the ion activities of hydrochloric acid calculated from the results of Ellis[2] are greater than those of potassium chloride. In Fig. 5, the square root of the ion-activity product of hydrochloric acid, computed from the results of Ellis, is plotted against the acid concentration. It is interesting to compare these curves with the data obtained by Forbes[3] on the solubility of silver chloride in these three reagents.

II—2. Comparison of the Velocity Constants in Neutral Salt Catalysis and the Ion Activities of the Added Salts.—If the plots in Fig. 5 are compared with those in Fig. 2, a striking similarity is noticeable. The chlorine-ion activities of solutions of sodium chloride are greater than those of potassium chloride of the same strength. Similarly, the increase in velocity constant due to the addition of sodium chloride to the potassium-iodide solution is greater than that due to the addition of potassium chloride in equivalent quantity. Secondly, the ion activity-potassium chloride concentration plot is a straight line. The velocity constant-potassium

[1] THIS JOURNAL, **39**, 2601 (1917).

[2] Ibid., **38**, 727 (1916).

[3] Ibid., **33**, 1937 (1911).

chloride concentration plots, for the decomposition of hydrogen peroxide by potassium iodide and potassium iodide-potassium chloride solutions (Fig. 2), and for the conversion of chlorylacetanilide (Fig. 3), for the hydrolysis of ethyl acetate (Fig. 4), both by hydrochloric acid and hydrochloric acid-potassium chloride solutions are straight lines. Euler[1] has given some results on the effect of potassium chloride on the velocity of inversion of cane sugar by hydrochloric acid. The plots of his results are straight lines. Taylor's results on the conversion of valerolactone to valeric acid[2] by 0.05 N hydrochloric acid and 0.05 N hydrochloric acid-potassium chloride solutions give a straight line when plotted similarly to the above. The same is true of the results of Trey on the neutral salt catalysis of methyl acetate.[3] The nature of these plots may, to a large extent, account for the success of the theory of the catalytic activity of the undissociated molecule in this field.[4]

All this points qualitatively to the conclusion that the increase in velocity constant by salt addition is a function of the chlorine-ion activities of the added salt solutions. Tables VIII and IX will clearly establish that the relation

$$K_1/K_2 = a_1/a_2$$

holds where K_1 and K_2 are the velocity constants corresponding to the same salt concentrations of potassium and sodium chlorides, respec-

TABLE VIII.

Velocity Constant and Activities.

(1) Conc. of KI = 0.03 N.

Conc. of KCl and NaCl.	$K_1 \times 10^2$ (KCl).	$K_2 \times 10^2$ (NaCl).	a_1 (KCl).	a_2 (NaCl).	$\dfrac{K_1 \times 10^2}{a_1}$	$\dfrac{K_2 \times 10^2}{a_2}$
0.000	4.18	4.18	...	...	...	...
0.500	4.31	4.45	0.305	0.311	13.14	14.20
1.000	4.45	4.79	0.584	0.628	7.63	7.65
1.500	4.57	5.20	0.860	1.000	5.32	5.40
2.000	4.70	5.64	1.150	1.397	4.08	4.04
2.500	4.85	6.12	1.433	1.815	3.38	3.32

(2) Conc. of KI = 0.02 N.

0.000	2.75	2.75	...	...	...	...
0.500	2.84	2.93	0.305	0.311	9.31	9.40
1.000	2.93	3.17	0.584	0.628	5.02	5.05
1.500	3.02	3.44	0.860	1.000	3.51	3.44
2.000	3.11	3.77	1.150	1.397	2.70	2.70
2.500	3.19	4.19	1.433	1.815	2.22	2.25

[1] Z. physik. Chem., **32**, 348 (1910).

[2] THIS JOURNAL, **39**, 422 (1917).

[3] J. prakt. Chem. N. F., **34**, 353 (1886).

[4] It is also interesting to note that the lowering of the vapor pressure of water caused by the addition of potassium chloride is directly proportional to the concentration of salt; in other words, the vapor pressure lowering-salt concentration plot is a straight line. (Lovelace, Frazer and Millar, THIS JOURNAL, **38**, 15 (1916).)

tively, and a_1 and a_2 are the chlorine-ion activity values of potassium and sodium chloride solutions of the same concentrations, respectively. (a_1 will also equal the potassium-ion activity of the potassium chloride solution, a_2 the sodium-ion activity of the sodium chloride solution.) Table VIII contains figures which show the relation between the velocity constants of decomposition of hydrogen peroxide and the activities of added salts.

There is certainly excellent agreement in the results of the last two columns throughout the entire range of salt concentrations employed. Table IX contains similar calculations from the results of Rivett on the conversion of chlorylacetanilide.

TABLE IX.
Velocity Constant and Activities.

Conc. of KCl and NaCl.	$K_1 \times 10^3$ (KCl).	$K_2 \times 10^3$ (NaCl).	a_1 (KCl).	a_2 (NaCl).	$\dfrac{K_1 \times 10^3}{a_1}$.	$\dfrac{K_2 \times 10^3}{a_2}$
0.50	6.83	6.92	0.305	0.311	22.4	22.2
0.60	7.65	7.80	0.365	0.380	20.9	20.5
0.80	9.30	9.65	0.480	0.505	19.3	19.1
1.00	11.10	11.75	0.585	0.630	19.0	18.7
1.20	12.8	13.6	0.700	0.750	18.3	18.1
1.50	15.3	16.9	0.875	0.980	17.5	17.3

Again, there is excellent agreement in the last two columns. The same relation does not hold for the hydrolysis of ethyl acetate for reasons previously stated.

In review, there are 3 relations reported in this communication which must prove of importance both to the field of neutral salt catalysis and to aqueous solution theory.

$$1. \qquad \frac{K_3 - K_2}{K_2 - K_1} = \frac{N_w{}^3 - N_w{}^2}{N_w{}^2 - N_w{}^1}.$$

This has been shown to be roughly true. It is positive evidence that the abnormalities observed in neutral salt catalysis are to a large extent, if not completely, due to hydration. Although this evidence does not necessarily disprove that undissociated molecules have catalytic activities, nevertheless, it demonstrates that the theory of the undissociated molecule has never been correctly applied in the domain of neutral salt catalysis.

$$2. \qquad \frac{K_1}{K_2} = \frac{a_1}{a_2}.$$

This relation holds quite rigidly for two reactions considered in this communication. In computing such equilibria, thermodynamic data are required.

3. From the two above expressions, the following may be deduced:

$$\frac{N_w{}^3 - N_w{}^2}{N_w{}^2 - N_w{}^1} = \frac{a_3 - a_2}{a_2 - a_1}$$

A number of interesting and important suggestions may be deduced from this relationship. In the first place it is thought that the thermodynamic degrees of dissociation are the correct ones and when more complete thermodynamic data are available, the calculation of equilibria in concentrated solutions will be rendered possible. Secondly, if, as above indicated, the thermodynamic degrees of dissociation or activities are a simple function of the ionic hydration values, the whole behavior of a concentrated solution of an electrolyte will become explicable.[1]

Summary.

1. Measurements of the accelerating effects of neutral salts on the iodine-ion catalysis of hydrogen peroxide and the hydrochloric acid catalysis of ethyl acetate have been presented.

2. The effects of different salts on the velocity constants have been shown to be grossly proportional to their ionic hydration values as determined by Washburn and his associates, both for the iodine-ion catalysis of hydrogen peroxide and the hydrochloric acid catalysis of chlorylacetanilide.

3. The reasons for the non-proportionality of the effects of different salts on the velocity constants of hydrolysis of ethyl acetate and the ionic hydration values have been explained.

4. The chlorine-ion activities of sodium chloride solution of concentrations up to $3.0\ N$, obtained by measurement of the cells

$$\text{Hg} \mid \text{HgCl} \mid \text{NaCl}\,(o.1\ N) \mid \text{NaCl}\,(c) \mid \text{HgCl} \mid \text{Hg},$$
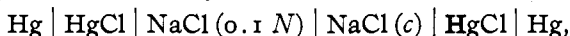
have been presented.

5. The relationship

$$\frac{K_1}{K_2} = \frac{a_1}{a_2}$$

holds rigorously where K_1 and K_2 are the velocity constants of decomposition of hydrogen peroxide on the presence of potassium iodide-potassium chloride solutions and potassium iodide-sodium chloride solutions of the same normality, respectively, and a_1 and a_2 are the chlorine-ion activities of the added potassium chloride and sodium chloride solutions, respectively.

6. This paper establishes in part some relationships between the hydration values of the ions of neutral salts, the effects of the same salts on reaction velocities in aqueous solutions, and the thermodynamic degrees of dissociation or activities of the salt solutions.

PHILADELPHIA, PA.

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[1] One important exception to this is hydrochloric acid. The square root of the ionic product of hydrochloric acid (Fig. 5) is greater than the chlorine-ion activity of sodium chloride, although the hydration value of the hydrogen ion is one and the hydration value of the sodium ion is 8.4.