THE EFFECT OF NEUTRAL SALTS ON HYDROLYSIS BY WATER.

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Received June 17, 1909.

Outline.—1. Historical. 2. Statement of Problem. 3. Description of Method (Apparatus, Thermostat, Tubes), Purification of Materials, Manipulation. 4. Results. 5. Conclusions.

Historical.—In the course of some experiments carried on in the spring of 1907,[1] it was found that the reaction between ethyl acetate and water,

$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH,$$

was greatly accelerated by the presence of potassium chloride. This was to be expected from a consideration of the work of Arrhenius,[2] Euler,[3] Spohr,[4] and many others. In their investigations of the so-called "salt-effect," *i. e.*, the acceleration of hydrolysis by acids due to the presence of a salt of the acid in question, they found that the effect of the salt was greater, the more dilute the acid. In the above-mentioned work with ethyl acetate in the presence of water and neutral potassium chloride, it was found that not only did the salt have an effect, but that this effect varied in no simple manner with the concentration of the salt. The acceleration was found to be greatest at a concentration somewhere between 1 per cent. and 20 per cent., and to become negative somewhere between 20 per cent. and saturation.

As no other work had been discovered along this line, save the work of W. A. Smith,[5] with sugar inversion in the presence of N/64 solutions of sodium succinate, sodium oxalate, sodium sulphate, potassium chloride and sodium carbonate, it was thought worth while to go into the subject more extensively than was possible at the time of the earlier work.

Statement of Problem.—The plan was to investigate, over a wide range of concentrations, the effect of:

1. The different salts of the same metal, having in mind chiefly the halides.
2. The same salt of the different metals, as the chlorides of potassium, sodium, barium, calcium, strontium, etc.
3. Changing the temperature.
4. Changing the concentration of the ester.

The work up to date has covered simply the effect of potassium chloride, potassium bromide, and potassium iodide at a fixed temperature and with a fixed concentration of the ester (0.4021 normal). The concentrations of the salts have been varied from 0.1 normal to 4.0 normal.

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[1] This Journal, **31**, 403 (1909).

[2] *Z. physik. Chem.*, 4, 237.

[3] *Ibid.*, **32**, 348.

[4] *J. prakt. Chem.*, **33**, 270.

[5] *Z. physik. Chem.*, **25**, 410.

Description of Method.—The general method of attacking the problem was that used in the first experiments, *i. e.*, sealing the materials in glass tubes, withdrawing a tube at intervals, and titrating the contents with caustic potash and phenolphthalein for the acetic acid formed. For the heating of the tubes, a thermostat was constructed, electrically heated from a 110 volt AC circuit, and regulated by the usual mercury bulb thermo-regulator. Perhaps a brief description of the thermostat and accessories will be of interest at this point. The inner vessel was a sheet-iron can, about 16 inches in diameter, and 16 inches deep. This was surrounded by a three-inch layer of corrugated asbestos, and the whole by another galvanized can. Heating was accomplished by two resistance coils, originally intended for fan-motor resistances, having resistances of about 110 ohms. between the ends and 55 ohms between the middle and each end. By various combinations of these coils, a very wide variation could readily be obtained in the amount of heat used. The current through the coils was adjusted by external resistance, until they kept the temperature a couple of degrees below the desired value. By means of a relay, the middle point of one coil was then short-circuited to one end of the same coil, thus halving the resistance and increasing the heat fourfold. When the temperature rose to the proper value, the thermo-regulator was so adjusted that it closed the auxiliary battery circuit and thereby opened the relay. Stirring was effected by means of a turbine stirrer, about 3 inches in diameter, driven by a 1/8 h. p. motor. This drew the melted paraffin from the bottom of the tank, past the heating coils, and threw it out of openings near the surface of the bath. Regulation, under favorable conditions, was within 0.15° of the desired temperature, although occasionally the relay or regulator would fail either to make or to break contact, letting the temperature rise or fall, as the case might be. As a result of these failures, several runs had to be discarded, but on the whole, the performance was satisfactory.

Previous experience had shown that in the matter of removing soluble matter from the glass of the vessels containing the reaction mixture, great care was necessary. Arrhenius, in his work on the salt-effect in the presence of acids,[1] found that with very great dilutions of the acid used, the results were very irregular. He ascribed this to alkali dissolved from the glass, and after using the flasks for three months with the more concentrated acids, he found, on repeating the work with dilute acid, that the results came with perfect regularity. In the author's previous experiments[2] the material was sealed in soft glass tubes. Although these had been boiled with acid and with water, they were a source of endless annoyance, as the glass dissolved to so great an extent as to

[1] *Z. physik. Chem.*, 4, 237.

[2] *Loc. cit.*

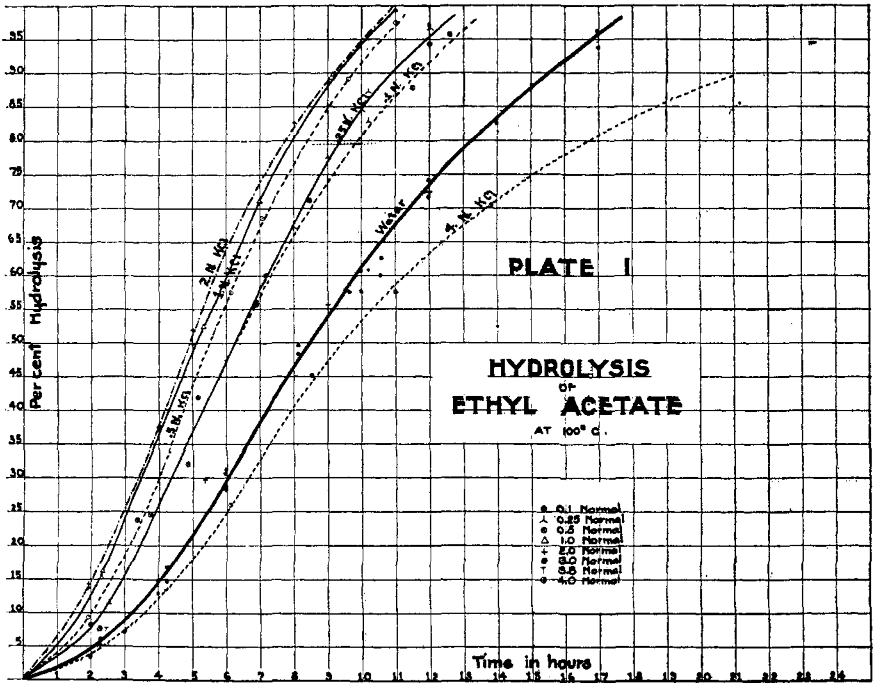
render the first runs made with them extremely irregular. For the present work, tubes of Jena glass were used. They were first filled with cleaning solution and heated for an hour or more in an actively boiling water bath, then rinsed three times with distilled water, then filled with distilled water and heated in the water bath for several hours. The regularity of the results, and the fact that no difference was observed between results obtained in tubes practically new, and in those which had been used at 100° for several hours, show that any soluble portions of the glass were completely removed by this treatment.

The ethyl acetate used was a good commercial grade, washed with 5 per cent. sodium carbonate solution and with water, and allowed to stand over calcium chloride over night before distillation. A Hempel column was used for the distillation. The boiling point was very constant throughout the larger part of the distillation, and, in fact, did not rise appreciably until the flask was almost empty. Only the middle portion of the distillate was used, the end portions being redistilled.

The potassium chloride and potassium bromide were both good commercial salts, purified by three crystallizations, and perfectly neutral. The potassium iodide was the source of much annoyance. Kahlbaum's best grade was used, the original package not being unsealed until needed for this work. The solutions were colored a faint yellow, while the crystals themselves showed a noticeable yellow tint. The salt was then recrystallized to form crystal meal, the small crystals spread out in a large crystallizing dish and dried for about a day on top of an oven heated to 160°. The lumpy, dried mass was then ground in an agate mortar, and again dried. This gave a very pretty, fine-grained product, which dissolved to form a perfectly clear solution. On heating the tenth-normal solution with the ester it turned a weak straw color and gave a starch test for iodine. The 0.25 and 0.5 normal solutions were colored a deep yellow and gave very strong starch tests. A 1.0 normal solution of the iodide sealed and heated *without* ester for 11.08 hours gave absolutely no coloration, but on acidifying and adding starch solution, the intense blue was at once produced. This, together with similar tests for iodate, showed very conclusively that it was present. All results obtained with this material were low. As potassium iodate reacts with an acid according to this reaction,

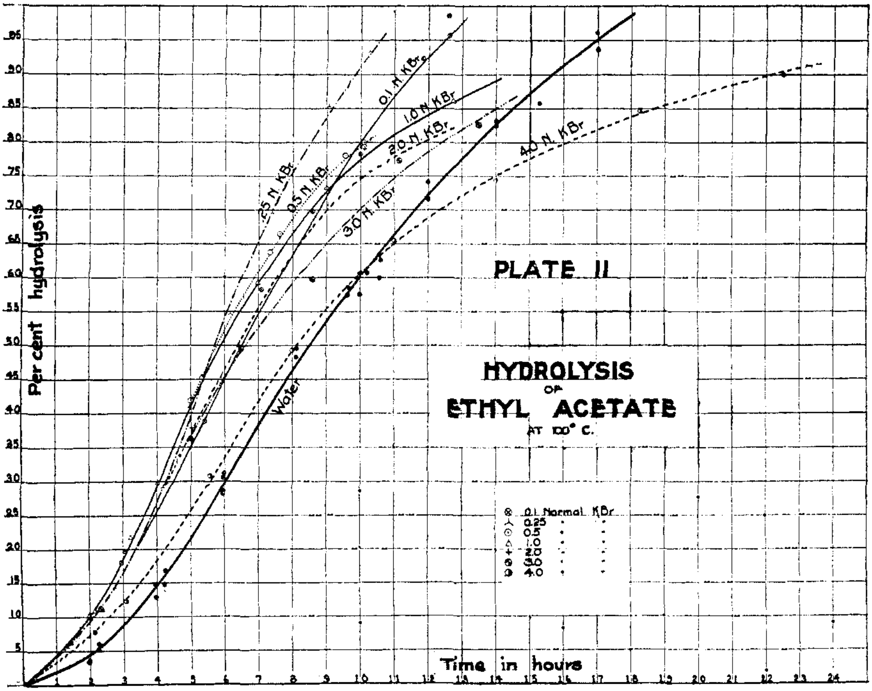
$$KIO_3 + 6KI + 6CH_3COOH = KI + 3I_2 + 6CH_3COOK + 3H_2O,$$

it is readily seen how a very small amount of iodate, present as an impurity, would neutralize a large amount of the acetic acid formed by the reaction between the ester and water, and so make the results appear low. The iodide was then heated to redness, in small batches, with carbon, the mass extracted with hot water, the solution filtered and evaporated down. This gave a product which, after drying, gave no test for iodate. Accordingly, the earlier work with 0.1 normal, 0.25 normal and 0.5 normal potassium iodide was repeated with this purified material, and the other results discarded. Although the solutions were free from iodate, they turned yellow on heating, and gave starch tests for free iodine. This was to be expected, as it is a matter of common experience that iodide solutions are unstable at even moderate temperatures. A few cubic centimeters of the unused 1.0 normal solution, on standing at room temperature a few days, showed a distinct yellowish tint. In view of the high coloring power of iodine, it is probable that the actual amount decomposed was so small that the potassium hydroxide formed would not neutralize an appreciable amount of the acetic acid from the ester. Since, however, the results were far below corresponding results for potassium chloride and potassium bromide, it seems fair to assume that the salt itself, or perhaps one or both of its decomposition products, has a very marked retarding effect on the reaction.



In order to know the extent of acceleration of the reaction by various concentrations of the salts, it was, of course, necessary to know the rate of the reaction when only the water and ester were present, and when the salts were used, to keep the amounts of water and of ester the same. Accordingly, the tubes were first charged with ethyl acetate (0.8847 g.)

and 25 cc. of water, making a solution 0.4012 normal with regard to the ester. The ester was pipetted into the tubes by means of a capillary funnel and the water, or salt solution, as the case might be, run in through the same funnel, washing down, in its course, all the ester. These were then sealed and placed in the thermostat at 100°. At intervals of two or three hours, two or three tubes were withdrawn, the time noted, and the tubes cooled by immersion in cold water. After the tubes had cooled to room temperature they were opened and the contents titrated in the tubes, with caustic potash and phenolphthalein. The results are shown

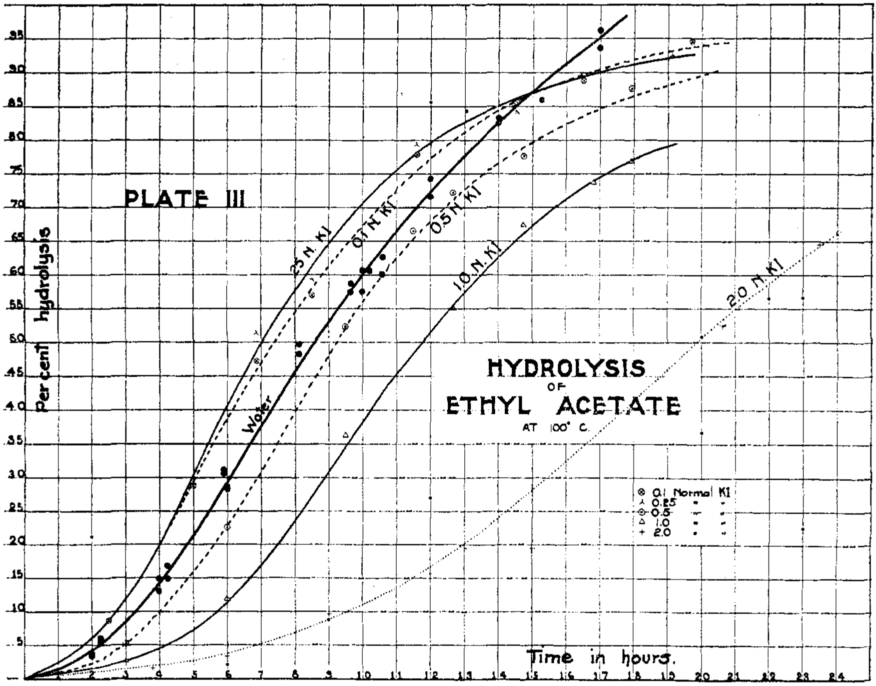


by the curve through the heavy black dots on Plates I, II and III. The consistency of these results is very gratifying, especially since many of them were obtained at widely different times, showing that the agreement of a few was not fortuitous.

The question arose, in the course of the work, whether the action went in the opposite direction after the tubes were cooled. To test this, tubes were often kept at room temperatures for several hours before titration. In no case did the results differ from the mean by more than the experimental error. It was also a matter of some importance to know what effect a moderate sized error in measuring the water would produce. To test this, the usual amount of ester was placed in tubes with 10, 15, 20, 25, 30 and 35 cc. of water, respectively, and heated for the times indicated. The results are given below:

Vol. of water. cc.	Time. Hrs.	Per cent. hydrolysis.		Time. Hrs.	Per cent. hydrolysis.		Mean.
10	10.59	65.9	....	9.5	54.3	50.2	52.3
15	10.59	65.9	....	9.5	52.7	51.0	51.8
20	10.59	62.7	....	9.5	50.2	49.1	49.9
25	10.59	62.7	60.1	9.5	49.9	48.8	49.3
30	10.59	61.4	....	9.5	46.1	46.1	46.1
35	10.59	54.3	....	9.5	47.6	44.6	46.1

While these results are not in the closest agreement, they show, particularly if plotted and a smooth curve drawn so as to average the points, that a change in the amount of water used, from 15 cc. less than the usual quantity, to 10 cc. more, affects the results at the most only 10 per cent.



This would mean that an error of 1 cc. in measuring the water was entirely admissible, causing an error in the result of only about 0.4 per cent. The actual error was probably never more than a couple of tenths of a cubic centimeter. The average accuracy of these results is about 2–3 per cent. deviation from the mean. While this seems large in comparison with ordinary analytical work, the reasons are not far to seek. First, the ester was pipetted (on account of the difficulty of weighing and transferring the large number of samples used). Second, the alkali used in titration had to be fairly strong (0.6648 normal in one case and 0.3799 normal in the other), so that the operation could be performed without transfer of the material from the tube to a flask. Both of these causes contribute to the inaccuracy of the results, but at the present time greater accuracy would not be of value commensurate with the labor involved.

In order to get amounts of the various salt solutions, which would contain the same amount of water as the blanks, the density of the salt solution was taken, its percentage water content figured, and the amount necessary to give 25 cc. of water calculated. At first it was thought necessary to exercise considerable care in measuring the salt solutions, a calibrated burette being used for the purpose. However, in the course of the work, at various times, amounts were used differing from the calculated quantity by from 0.2 cc. to 1 cc. In no case did such results vary from the mean by more than the experimental error. The results of the various "runs" are given in tabular form in the tables. As an example of the system used in recording results, a specimen record for the tenth-normal potassium chloride solution is given.

Solution, cc. H_2O.	Time, hrs.	Per cent. hydrolysis.	Serial No.
25	2.00	3.36	1
25	2.00	3.6	2
25	2.27	6.0	155
25	2.27	5.3	156
25	2.27	5.7	157
25	4.00	14.9	3
25	4.00	13.0	4
25	4.25	16.8	143
25	4.25	14.9	144
25	5.9	31.2	17
25	5.9	30.7	18
25	6.0	28.6	5
25	6.0	28.3	6
25	8.13	48.3	19
25	8.13	49.7	20
25	9.66	58.8	145
25	9.66	57.5	146
25	10.00	57.51	60
25	10.00	60.8	61
25	10.21	60.8	30
25	10.59	60.1	122
25	10.59	62.7	123
25	12.00	74.3	62
25	12.00	71.7	63
25	14.01	83.4	31
25	14.01	82.7	32
25	15.29	86.0	48
25	15.29	86.0	49
25	17.00	93.7	46
25	17.00	96.3	47

Solution, 25 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
0.1 *N* KCl	2.24	7.7	95
0.1 "	3.73	24.6	96
0.1 "	4.82	32.3	97
0.1 "	6.88	55.6	98
0.1 "	8.46	71.1	99
0.1 "	11.5	87.9	100
0.1 "	12.6	95.7	118

Solution, 25.2 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
0.5 *N* KCl	1.92	9.4	71
0.5 "	6.13	57.5	73
0.5 "	7.07	68.5	74
0.5 "	9.6	89.2	75
0.5 "	11.0	97.6	76

Solution, 25 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
0.25 *N* KCl	2.55	11.63	77
0.25 “	3.6	21.33	78
0.25 “	6.05	47.83	79
0.25 “	8.00	67.21	80
0.25 “	9.00	77.55	81
0.25 “	10.0	84.7	82
0.25 “	12.0	96.9	83
0.25 “	10.2	87.2	85
0.25 “	10.2	82.7	86

Solution, 25.75 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
1.0 *N* KCl	2.33	16.4	25
1.0 “	2.33	15.7	26
1.0 “	4.00	37.8	27
1.0 “	5.35	52.4	37
1.0 “	7.00	71.1	36
1.0 “	9.17	89.8	35
1.0 “	11.01	99.5	34

Solution, 26.6 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
2.0 *N* KCl	1.92	14.2	50
2.0 “	1.92	13.6	51
2.0 “	5.00	49.8	52
2.0 “	5.00	51.7	53
2.0 “	6.00	64.6	57
2.0 “	8.00	82.1	58
2.0 “	10.08	93.1	59

Solution, 29.25 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
4.0 *N* KCl	3.00	7.1	90
4.0 “	6.13	31.0	91
4.0 “	8.53	45.3	87
4.0 “	11.03	57.5	88
4.0 “	13.83	70.4	89

27.5 cc.			
3.0 *N* KCl	2.00	8.4	64
3.0 “	2.00	8.4	65
3.0 “	3.33	23.9	66
3.0 “	5.16	42.0	67
3.0 “	7.16	60.0	68
3.0 “	12.00	94.1	70

25 cc.			
0.1 *N* KBr	2.11	7.8	109
0.1 “	5.4	38.8	111
0.1 “	7.1	58.2	112
0.1 “	8.59	69.8	113
0.1 “	10.00	78.2	114
0.1 “	2.97	18.1	115
0.1 “	11.83	92.4	116
0.1 “	12.6	98.9	117
0.1 “	12.6	95.7	118

Solution, 28.5 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
3.8 *N* KCl	2.45	7.76	127
3.8 “	5.33	29.73	128
3.8 “	9.00	55.6	129
3.8 “	12.00	72.4	130

Solution, 25 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
0.25 *N* KBr	2.25	11.0	134
0.25 “	4.20	29.1	135
0.25 “	6.17	54.9	141
0.25 “	7.4	69.8	136
0.25 “	9.08	85.3	137
0.25 “	10.38	91.8	138
0.25 “	10.25	93.1	142

Solution, 26.7 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
1.0 *N* KBr	2.17	10.9	171
1.0 “	4.03	29.8	172
1.0 “	2.00	10.2	174
1.0 “	3.25	21.7	175
1.0 “	5.35	45.3	176
1.0 “	7.00	59.3	177
1.0 “	9.00	73.2	178
1.0 “	12.75	86.2	173

26.4 cc.			
0.5 *N* KBr	3.08	19.6	147
0.5 “	5.05	41.9	148
0.5 “	7.33	63.8	149
0.5 “	7.61	66.5	150
0.5 “	9.58	77.8	151
0.5 “	10.11	80.0	152
0.5 “	10.11	79.3	153

27.4 cc.			
2.0 *N* KBr	2.78	14.4	182
2.0 “	5.05	37.9	183
2.0 “	9.05	70.9	184
2.0 “	10.00	74.8	185
2.0 “	11.28	78.4	186

Solution, 29.39 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
3.0 N KBr	2.33	11.3	193
3.0 "	5.00	30.3	194
3.0 "	6.50	48.5	195
3.0 "	8.6	59.8	196
3.0 "	11.16	77.3	197
3.0 "	13.5	82.6	198

Solution, 30.25 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
4.0 N KBr	3.1	12.4	200
4.0 "	5.66	30.7	201
4.0 "	8.00	49.3	202
4.00 "	11.00	65.5	203
4.0 "	14.00	74.5	204
4.0 "	18.29	84.6	205
4.0 "	22.5	90.0	206
25 cc.			
0.1 N KI	2.5	8.6	239
0.1 "	5.0	28.7	238
0.1 "	6.85	47.1	240
0.1 "	8.5	57.0	241
0.1 "	11.6	73.0	242
0.1 "	14.5	85.7	250
0.1 "	16.5	88.8	251
0.1 "	19.7	94.6	252

Solution, 25 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
0.25 N KI	2.5	8.6	244
0.25 "	5.00	29.4	246
0.25 "	6.87	51.3	245
0.25 "	8.5	59.4	248
0.25 "	11.6	79.2	249
0.25 "	14.5	84.0	253
0.25 "	16.5	90.0	254
0.25 "	19.17	92.6	255
25.9 cc.			
0.5 N KI	3.0	5.2	256
0.5 "	6.0	22.6	257
0.5 "	9.5	52.4	258
0.5 "	11.5	66.6	259
0.5 "	12.66	72.3	264
0.5 "	14.75	77.6	265
0.5 "	17.92	87.6	266

Solution, 26.1 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
1.0 N KI	3.0	2.6	261
1.0 "	6.0	12.8	262
1.0 "	9.5	36.3	263
1.0 "	12.66	55.0	267
1.0 "	14.75	67.4	268
1.0 "	16.85	73.8	269
1.0 "	17.92	77.3	270

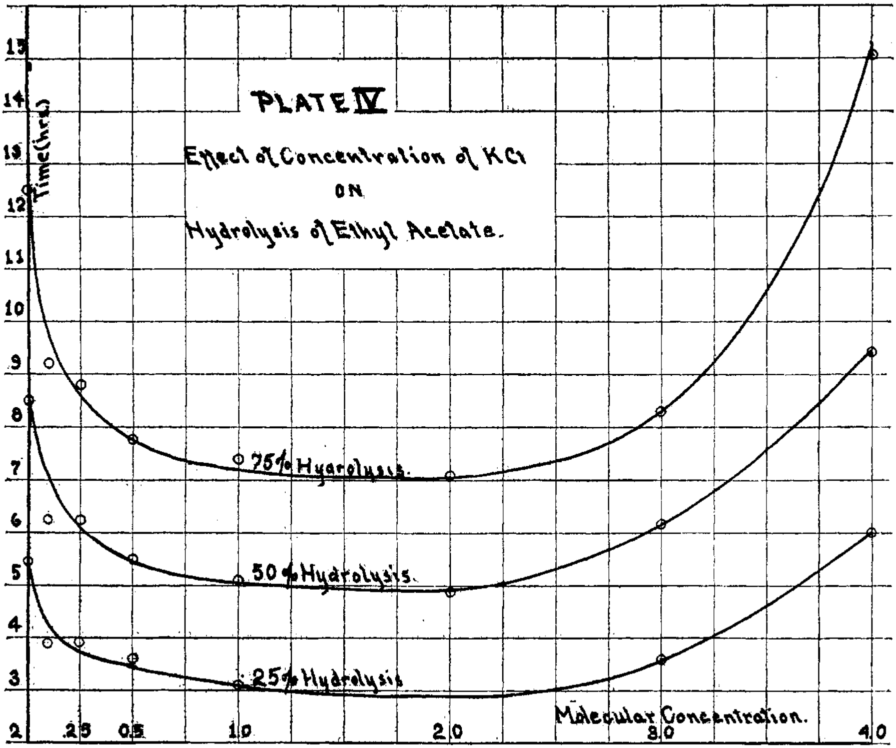
Solution, 27.1 cc.	Time, hrs.	Per cent. hydrolysis.	Serial No.
2.0 N KI	3.83	1.5	271
2.0 "	6.00	3.3	272
2.0 "	9.00	9.7	273
2.0 "	12.00	15.8	274
2.0 "	15.08	19.6	275
2.0 "	18.0	44.0	276
2.0 "	20.66	52.5	277
2.0 "	23.50	64.5	278

Results.—The accompanying curves show the course of the reaction for each concentration of the three salts studied, the curve for pure water being drawn for each plate. These curves give a much clearer idea of the effect of the different salts than do the tabulated results, since it was impossible, on account of the press of other work, to withdraw tubes at definite and fixed intervals. A comparison of the tabulated results would, as a result of the irregularity of intervals between successive withdrawals from the thermostat, be an exceedingly laborious matter, except in the graphical way. It will be seen from an inspection of the curves that the specific influence of the salts is greater in somewhat dilute solutions. As stronger and stronger solutions are used, the effect grows less and less, sinking to zero, and with further increase of concentration, becoming negative in character, so that the four times normal potassium chloride solution, for instance, hydrolyzes the ester more slowly than does the pure water.

In simple acid-inversion a velocity constant can be figured out from the equation:

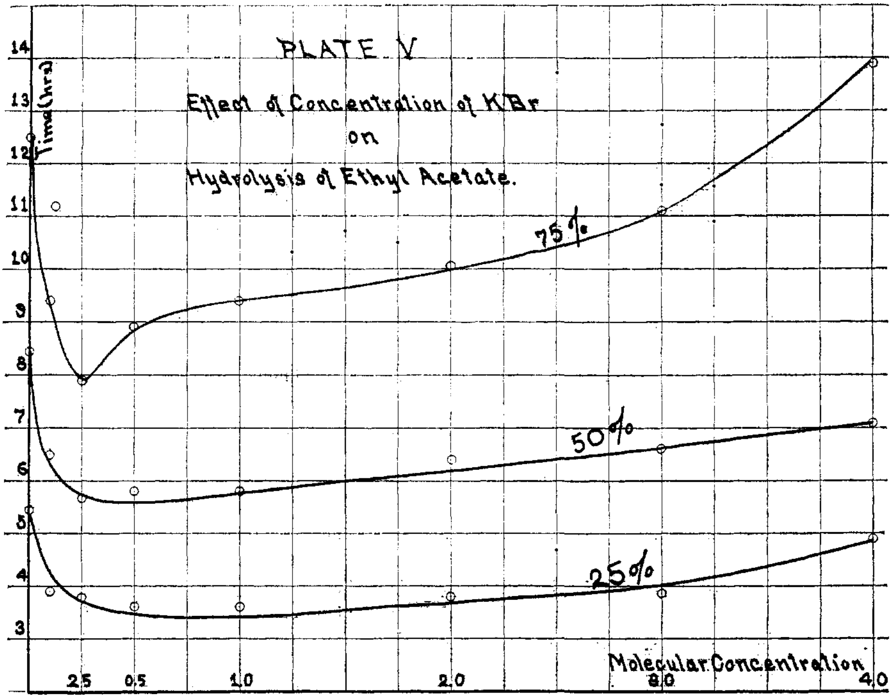
$1/t \log (a/a-x) = K$, where t is the time,
a is the original concentration,
x is the amount changed in time t.

It was thought that this might hold in the present case, but an inspection of the shape of the curves shows that no constant could be derived.

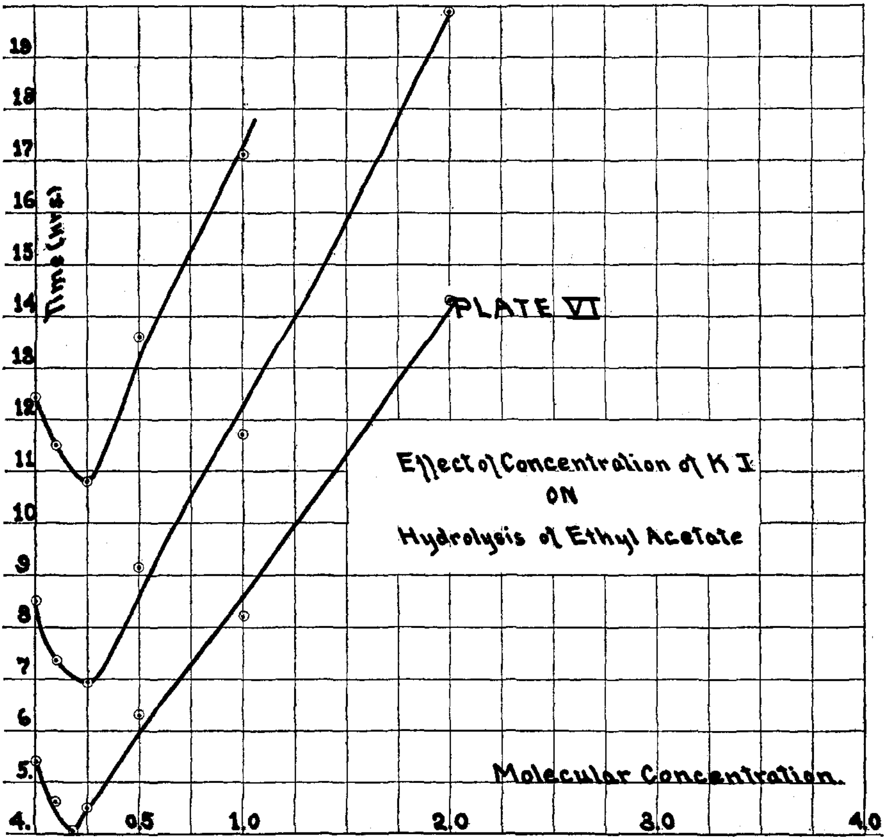


Substituting in the above formula the values derived from the 2.0 normal potassium chloride curve, we get as the values of K, 0.03539, 0.05116, 0.07504, 0.09442, 0.13010. An evaluation of the "constant" for the water reaction also gives a changing value. This might be expected in view of the fact that the acetic acid formed is sufficiently ionized to disturb considerably the conditions in the solution, while in the presence of strong acids, the ionization of the acetic acid is relatively of little importance.

Plates IV, V and VI are curves derived from Plates I, II and III, showing the relations between concentrations of the three salts used, and the time required to hydrolyze 25, 50 and 75 per cent. of the ester. They show very clearly the change in accelerating power with change in concentration. The minima of these curves evidently correspond to the solutions of greatest accelerating power. This maximum accelerating power evidently lies at about 1.8 normal for the potassium chloride and 0.5 normal for the potassium bromide and 0.25 normal for the potassium iodide. Plate IV indicates a velocity equal to that for pure water, or zero acceleration at the 50 per cent. mark, for a concentration of 3.8 normal potassium chloride. Such a solution was made up and used like the others, giving, as will be shown by the "T" on Plate I, a curve identical, throughout its central part, with that for water. For potassium bromide the effect is seen to be less than for corresponding concentrations of potassium chloride, although the curves are of the same general shape. There is, however, this much to be noticed, that while the potassium chloride curves are either entirely above or entirely below that for water, those for potassium bromide show a greater tendency during the latter half of the reaction to flatten out and *cross* the water curve.



The results for potassium iodide are, in general, far below those for corresponding strengths of potassium chloride and potassium bromide. This decrease of accelerating power from chloride to bromide, and from bromide to iodide, is, it will be noticed, in the inverse order of their stabilities. This may be of considerable significance, or it may be merely a matter of chance.



The "period of induction," in which the reaction is getting started, is very clearly shown in the flat portion of the curves for the first hour or two. After it has gotten well started, the velocity of the reaction is much greater than in the earlier stages. Again, near the close of the reaction, a very noticeable slowing up occurs.

Conclusions.

The mechanism of and reason for this acceleration is at present, it seems, beyond our reach. Why a material as stable and closely combined as potassium chloride should assist in such a remarkable way a reaction of this sort, is as incomprehensible as any one of the many other catalytic phenomena with which we deal. This investigation does seem to show, however, that the reaction is affected by the salt in two different ways. The first effect, which is predominant at small concentrations, is an accelerating one, while the other, which increases in magnitude with increase in concentration of the salt, and with decrease in the stability of the salt, is a retarding effect.

It may be that the two effects are functions of the ions, and that the potassium ion is responsible for the acceleration, and the halogen ion for the retardation. Although this would account for the difference in behavior between the three salts used, it would in no wise account for the difference between weak and concentrated solutions of the same salt. The work planned for next year, with different metals combined with a given halogen, may throw some light on this question.

Another guess, which, although it seems reasonable, is only a speculation, pure and simple, would make the accelerating effect due to the *ionized* salt, and the retardation to the undissociated part. This would explain the decreasing acceleration produced by more and more concentrated solutions of the salts, for as the concentration increases, the amount of ionized salt increases very slowly in proportion to the increase in the amount of undissociated salt. This hypothesis also seems to accord well with the experience of the earlier investigators, who worked with the accelerating effect of neutral salts in the presence of their respective acids. They universally found that the effect of the salt was greater the more dilute the acid. The greater the dilution of the acid, the fewer ions common to both the acid and salt, and hence the greater dissociation of the salt. As the concentration of the acid was increased, the dissociation of the salt would be forced back, and we should expect, according to this hypothesis, exactly what experience has proven to be the case, *i. e.*, a decrease in the accelerating effect of the neutral salt in question.

There have not been, so far as I have been able to find, any theories advanced for this phenomenon. The many conflicting theories as to the cause of the mechanism of the "salt-effect" in the case of acids do not, in general, apply here. However, a few of the theories, which might fit both cases, may be of interest. Euler[1] thinks that salts disturb the dissociation of the substances primarily concerned in the reaction, *i. e.*, increasing the ionization of the ester, water, or both.

Another suggestion made by Euler[2] is interesting. He assumes that the salt increases the reactive capacity of the water. This means that under the influence of neutral salts the per cent. of H and OH at any given instant is increased. "This sort of effect apparently comes,"

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[1] *Ber.*, **33**, 3202–3206 (1900).

[2] *Z. physik. Chem.*, **32**, 348–359.

says Euler, "under the already strongly supported theory that the ions of the neutral salt are combined with the solvent. The ions work after this in the capacity of H and OH carriers. It is necessary to accept that the water directly surrounding the charged ions is under extraordinarily high tension and, in consequence, it is strongly dissociated. In the immediate neighborhood of the neutral salt ions there is, therefore, a large number of the ions of water. This hypothesis explains many things which, without it, are mysteries. The fact that the effect of the neutral salt is greater with greater dilution of the acid is easily explained thus, for it is easily seen that the H and OH ions derived from the water come into greater prominence the smaller the H ions of the acid."

I have quoted this statement at some length, because it expresses the views of not only Euler himself but also of Spohr and Arrhenius. In the series of "Studies of Catalysis" by Stieglitz and his pupils, running through the *American Chemical Journal*, Stieglitz agrees[1] with these ideas. Euler also suggests the formation of intermediary compounds as one of the ways in which a catalyzer can act. Stieglitz and his pupils in the series just mentioned, have proven conclusively that in the case of imidoesters breaking down under the catalytic influence of acids, the intermediate compounds are formed.

H. E. Armstrong and his pupils[2] have worked out a theory to fit the case of inversion by acids and salts in combination. Their assumption is that the salt abstracts enough water from the solution to materially increase the concentration of both ester and acid. This theory of "Hydronation and Hydrolation" does not, it seems, fit the present case, although the advocates of it, who are opposed to the ionic hypothesis, use the theory with great freedom to explain the whole subject of the catalysis of esters and sugars. It is, however, difficult to imagine how a tenth of a gram molecule of salt per liter can hold in its grasp, so to speak, an amount of water large enough to materially affect the rate of reaction, especially at temperatures near the boiling point of the water. The results given on page 892 of this article show that a change of 1 cc. in the amount of water present would make a change in the extent of hydrolysis in a given time of only about 0.4 per cent. In order to increase the per cent. of hydrolysis for a given time by 30 per cent., which is reached in several instances, the water present would, on the theory of Armstrong, have to be decreased by about 75 cc., whereas the initial volume was only a third of this. This shows, it would seem, the futility of basing the explanation on any such idea as that of condensation of water by the salt.

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[1] *Am. Chem. J.*, **39**, 720.

[2] *Proc. Roy. Soc.*, Series A, Vol. **81**.

The old idea of Arrhenius might apply here. This was to the effect that in solution the ester existed in two forms, "active" and "inactive," the first being probably a single molecule, while the inactive form was a complex. Addition of a salt disturbs the equilibrium between these forms in favor of the active form. Later[1] on Arrhenius gives a little greater clearness to his idea by attributing the accelerating effect to an increase in osmotic pressure of the ester. He says: "Since foreign substances in general increase the osmotic pressure of a compound, they should, in general, accelerate the velocities or reaction, which is actually the case."

These appear to be the most logical of the many attempted explanations of the phenomenon. It should be noted, however, that not one of them really *explains* the facts, but simply seeks to express them in terms of other facts a trifle more familiar. The question as to which is the most reasonable of these various hypotheses, is difficult, or impossible, to answer. Each has its merits, and each at some point fails to explain all of the circumstances connected with the case. Fortunately, it is not at present necessary to accept as final any of the theories thus far proposed. It is hoped that the work already planned for the immediate future may throw some light on the subject.

In conclusion, I wish to thank Dr. W. E. Henderson, of the Chemical Department, and Dr. A. D. Cole, of the Physics Department, for kindly interest and advice during the course of the work, and for placing at my disposal every facility for its prosecution.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

AN ATTEMPT TO SEPARATE THE ALKALINE EARTH METALS IN THE ELECTROLYTIC WAY.

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Received May 1, 1909.

The electrolytic separation of the alkali metals[2] by strict attention to differences in decomposition potentials suggested the thought that the metals of the alkaline earths might be separated by an application of the same method. The halides of the latter metals had been analyzed by McCutcheon,[3] Lukens and Smith,[4] and separations of the alkalies from the alkaline earths, and of barium, strontium and calcium from magnesium were effected by the same chemists, but the separation of

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[1] *Z. physik. Chem.*, **28**, 317–335.

[2] THIS JOURNAL, **30**, 1705.

[3] *Ibid.*, **29**, 1445.

[4] *Ibid.*, **29**, 1455.