are chiefly due to the formation of the ions from the elements, which are independent of the salts involved; at high concentrations because the molecules, being less hydrated and less compressible produce smaller contractions, and because the molecular volumes of the salts are very nearly additive.

5. The effect of rising temperature is found in general to diminish contraction or increase expansion owing to lessened hydration of all the substances concerned. Marked exceptions exist at ordinary temperatures in lithium chloride and bromide, and at high temperatures in potassium chloride also.

6. It is pointed out that no simple method exists for separating the effects due to ionized and un-ionized material because of the varying magnitude of the change for each ion or molecule with changing concentration.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF JOHNS HOPKINS UNIVERSITY.]

THE ACTION OF SALTS WITH WATER OF HYDRATION AND WITHOUT WATER OF HYDRATION ON THE VELOCITY OF SAPONIFICATION OF ESTERS.[1]

BY J. E. L. HOLMES AND HARRY C. JONES.

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Jones and Anderson,[2] in their work on the absorption spectra of solutions, studied the absorption spectra of neodymium chloride in water, in methyl alcohol and in mixtures of these two solvents. They found two sets of absorption spectra corresponding, the one to the aqueous solution and the other to the alcoholic.

In the mixture of these solvents both of these spectra were obtained. Similar results were obtained with neodymium nitrate and praseodymium chloride.

Jones and Strong[3] studied a fairly large number of salts in a large number of solvents, and found a large number of "solvent bands." This raised the question whether combined water has different power to absorb light from free water? This was answered by Jones and Guy,[4] by means of the radiomicrometer. They showed that *combined water* was *far more transparent than pure water.*

This conclusion was confirmed by the work of Jones, Shaeffer and Paulus.[5]

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[1] The results of this investigation are recorded in full in *Publ. Carnegie Inst. Wash.*, No. 230.

[2] *Publ. Carnegie Inst. Wash.*, No. 110; *Am. Chem. J.*, **41**, 163 (1909).

[3] *Ibid.*, No. 130 and 160; **43**, 37, 224 (1910); **45**, 1 (1910); **47**, 27 (1912); *Physik. Z.*, **10**, 449 (1909); *Phil. Mag.*, April, 1910; *J. chim. phys.*, **8**, 131 (1910).

[4] *Publ. Carnegie Inst. Wash.*, No. 190; *Ann. physik.*, **43**, 555 (1914).

[5] *Physik. Z.*, **15**, 447 (1914).

Having found the above physical difference between the action of free and of combined water, the question arose, is there a corresponding chemical difference between water in the combined and in the free state?

Reaction Chosen.

We decided to use the saponification of an ester in the study of the action of free and of combined water for the following reasons:

In the first place, as Berthelot and Saint Gilles[1] had shown, the speed of the reaction is dependent on the relative amounts of the substances used. By keeping the amount of the ester constant we could study the effect of the water in solutions of salts containing the same amounts of water.

Secondly, this reaction proceeds slowly and its velocity could therefore be easily measured.

Thirdly, the speed of the reaction is dependent on the temperature. However, as the temperature rises the hydrates become less complex. From the results obtained with the ester and pure water, as compared with those from solutions of the salts, we could study the effect of rise in temperature on the hydrated salts.

The hydrolysis of the various salts used in this work has been taken into account.

Statement of Problem.

The plan was to investigate the difference in the velocities with which free water and combined water saponified an ester under the following conditions:

(1) Time and concentration of the salts kept constant, temperature varying.

(2) Concentration of the salts and temperature constant, time varying.

(3) Time and temperature constant. Concentration of salts varying.

The conditions were so regulated that the percentage of ester saponified was always small; the $\overset{+}{H}$ ions of the acid formed being in relatively large numbers as compared with the $\overset{+}{H}$ ions from water, would in part suppress the ionization of water and effect the saponification themselves.

Experimental.

The reactions were allowed to take place in 100 cc. Jena bottles with ground glass stoppers. These bottles were suspended in constant temperature baths very similar to those employed by Davis and Putnam.[2]

A concentration was chosen arbitrarily, such that solutions of all the salts to be investigated could be obtained, *i. e.*, two normal. Later it

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[1] *Ann. chim. phys.*, **14**, 437 (1878); **15**, 220 (1878); **65**, 385 (1862); **66**, 5. 110 (1862); **68**, 225 (1865).

[2] *Publ. Carnegie Inst. Wash.*, No. **210**, 117 (1915).

was found to be necessary to change this concentration to normal, using also the more dilute solutions, half-normal and quarter-normal.

The ester first employed was ethyl acetate. After some preliminary work, this was discarded in favor of methyl acetate, since its solubility in some of the strong salt solutions was so slight as to give us a heterogeneous system. Methyl formate was also studied, to see if the results obtained with methyl acetate were of a *general character or specific to the ester in question.* The esters were fractionally distilled several times until they boiled at the proper temperature and their reaction was neutral to indicators. The methyl formate, on account of its apparent instability, had to be frequently redistilled.

The Base and the Indicator.

The finding of the proper base and indicator to be used in titrating the acid formed, gave us quite a little trouble. Sulfuric acid and sodium hydroxide from alcohol did not prove to be satisfactory with phenolphthalein as the indicator. This may have been due in part to the saponification of the ester by the strong base.

The result of an elaborate investigation of indicators, including phenolphthalein, methyl-orange and corallin, and of bases including ammonium, sodium and barium hydroxides, was to show that for our purpose the base to be used was dilute ammonium hydroxide, and the indicator corallin.

To test the accuracy of our method, 0.0733 g. of glacial acetic acid was weighed out and titrated with ammonia, corallin being used as the indicator. The amount of acetic acid calculated from the titration was 0.0730 g. We would then have an error of less than 0.5%. With other organic acids we found errors of less than 0.1%.

Data.

In the following tables of data, the methyl acetate per bottle is 4 cc. or 3.7028 g., the methyl formate, 2 cc. or 1.9402 g. It was found that calcium chloride and potassium nitrate on dilution increase, then decrease the velocity of the reaction. Duplicate measurements were therefore made with new solutions. It was at this point that we decided to study also methyl formate. The volumes of the solutions of the salts that contained 30 cc. of water were calculated, the water per cc. of the solution being the difference in weight between 1 cc. of the solution and the salt in 1 cc. The water used in preparing the solutions of the salts, bases, and acid, had been carefully purified and had a mean specific conductivity of 1.5 times 10^{-6} at 25°. This water was also used in recrystallizing the salts. In the tables of data the concentrations of the solutions of the salts are expressed as N, $N/2$, and $N/4$. Tables I, II, III, IV, and V give the percentages of the methyl acetate saponified, Tables VI, VII and VIII of the methyl formate. Duplicate measurements were made with fresh solutions of magnesium sulfate and strontium

TABLE I.—METHYL ACETATE.

	Solutions. N.	15°. 24 hours.	25°. 24 hours.	35°. 24 hours.	25°. 48 hours.	Solutions. *N*/2.	25°. 24 hours.	35°. 24 hours.	Solutions. *N*/4.	25°. 24 hours.
1	30 cc.	0.076	0.147	0.390	0.287	30 cc.	0.145	0.386	30 cc.	0.153
2	H_2O	0.076	0.145	0.392	0.289	H_2O	0.144	0.385	H_2O	0.152
3	30.87 cc.	0.100	0.224	0.720	0.516	30.48	0.206	0.669	30.27	0.196
4	KCl	0.100	0.222	0.722	0.513	KCl	0.206	0.666	KCl	0.198
5	31.23 cc.	0.099	0.194	0.611	0.431	30.66 cc.	0.201	0.612	30.48 cc.	0.177
6	KNO_3	0.097	0.196	0.614	0.431	KNO_3	0.201	0.613	KNO_3	0.177
7	30.84 cc.	0.119	0.387	1.68	1.03	30.39 cc.	0.400	1.35	30.24 cc.	0.278
8	$CaCl_2$	0.117	0.385	1.69	1.05	$CaCl_2$	0.398	1.36	$CaCl_2$	0.277
9	30.60 cc.	0.132	0.410	1.67	1.33	30.39 cc.	0.326	1.23	30.24 cc.	0.276
10	$MgCl_2$	0.134	0.411	1.67	1.30	$MgCl_2$	0.323	1.23	$MgCl_2$	0.276
11	30.87 cc.	0.130	0.378	1.41	0.992	30.45 cc.	0.297	1.12	30.27 cc.	0.236
12	$SrCl_2$	0.128	0.375	1.42	0.989	$SrCl_2$	0.297	1.12	$SrCl_2$	0.239

TABLE II.—METHYL ACETATE.

	Solutions. N.	15°. 24 hrs.	25°. 24 hrs.	35°. 24 hrs.	25°. 48 hrs.	Solutions. *N*/2.	25°. 24 hrs.	35°. 24 hrs.	Solutions. *N*/4.	25°. 24 hrs.
1	H_2O, 30 cc.	0.083	0.154	0.394	0.296	H_2O, 30 cc.	0.153	0.391	H_2O, 30 cc.	0.152
2	LiCl, 30.96 cc.	0.094	0.204	0.626	0.462	LiCl, 30.48 cc.	0.199	0.590	LiCl, 30.24 cc.	0.194
3	KNO_3, 31.29 cc.	0.099	0.215	0.631	0.457	KNO_3, 30.60 cc.	0.213	0.632	KNO_3. 30.39 cc.	0.212
4	NaCl, 30.57 cc.	0.109	0.247	0.808	0.590	NaCl, 30.30 cc.	0.241	0.746	NaCl, 30.21 cc.	0.222
5	$CaCl_2$, 30.87 cc.	0.129	0.393	1.72	1.15	$CaCl_2$, 30.39 cc.	0.306	1.35	$CaCl_2$, 30.27 cc.	0.285
6	$Ca(NO_3)_2$. 31.59 cc.	0.129	0.330	1.32	0.860	$Ca(NO_3)_2$, 30.69 cc.	0.310	1.12	$Ca(NO_3)_2$, 30.36 cc.	0.270

TABLE III.—METHYL ACETATE.

	Solutions. N.	15°. 24 hrs.	25°. 24 hrs.	35°. 24 hrs.	25°. 48 hrs.	Solutions. N/2.	25°. 24 hrs.	35°. 24 hrs.	Solutions. N/4.	25°. 24 hrs.
1	H_2O, 30 cc.	0.086	0.155	0.394	0.296	H_2O, 30 cc.	0.153	0.394	H_2O, 30 cc.	0.153
2	$NaNO_3$, 30.93 cc.	0.105	0.225	0.692	0.490	$NaNO_3$, 30.60 cc.	0.223	0.663	$NaNO_3$, 30.36 cc.	0.210
3	NaBr, 30.84 cc.	0.104	0.228	0.703	0.517	NaBr, 30.45 cc.	0.222	0.660	NaBr, 30.24 cc.	0.210
4	KBr, 31.11 cc.	0.107	0.230	0.690	0.507	KBr, 30.60 cc.	0.224	0.667	KBr, 30.39 cc.	0.216
5	$BaCl_2$, 30.93 cc.	0.142	0.377	1.38	0.967	$BaCl_2$, 30.48 cc.	0.315	1.09	$BaCl_2$, 30.24 cc.	0.267
6	$Mg(NO_3)_2$, 31.48 cc.	0.126	0.326	1.35	0.883	$Mg(NO_3)_2$, 30.66 cc.	0.285	1.13	$Mg(NO_3)_2$, 30.36 cc.	0.261

TABLE IV.—METHYL ACETATE.

1	H_2O, 30 cc.	0.086	0.155	0.395	0.296	H_2O, 30 cc.	0.155	0.395	H_2O, 30 cc.	0.155
2	KI, 31.53 cc.	0.030	0.038	0.057	0.048	KI, 30.78 cc.	0.073	0.172	KI, 30.42 cc.	0.136
3	NaI, 31.20 cc.	0.075	0.119	0.341	0.239	NaI, 30.57 cc.	0.171	0.498	NaI, 30.30 cc.	0.176
4	$CaBr_2$, 31.26 cc.	0.075	0.134	0.653	0.492	$CaBr_2$, 30.54 cc.	0.153	0.689	$CaBr_2$. 30.33 cc.	0.191
5	$MgSO_4$, 30.18 cc.	0.095	0.166	0.406	0.346	$MgSO_4$, 30.15 cc.	0.150	0.372	$MgSO_4$, 30.12 cc.	0.138
6	$Sr(NO_3)_2$, 31.56 cc.	0.139	0.297	1.09	0.711	$Sr(NO_3)_2$, 30.75 cc.	0.287	0.968	$Sr(NO_3)_2$. 30.36 cc.	0.260

TABLE V.—METHYL ACETATE.

1	H_2O, 30 cc.	0.087	0.153	0.392	0.297	H_2O, 30 cc.	0.153	0.392	H_2O, 30 cc.	0.153
2	LiBr, 30.81 cc.	0.033	0.053	0.128	0.100	LiBr, 30.45 cc.	0.105	0.307	LiBr, 30.21 cc.	0.161
3	Li_2SO_4, 30.75 cc.	0.103	0.153	0.306	0.278	Li_2SO_4, 30.36 cc.	0.149	0.297	Li_2SO_4, 30.18 cc.	0.139
4	$BaBr_2$, 31.47 cc.	0.081	0.179	0.705	0.445	$BaBr_2$, 30.75 cc.	0.223	0.813	$BaBr_2$, 30.39 cc.	0.241
5	$SrBr_2$, 31.47 cc.	0.075	0.096	0.250	0.190	$SrBr_2$, 30.72 cc.	0.130	0.387	$SrBr_2$, 30.39 cc.	0.164
6	$LiNO_3$, 31.02 cc.	0.086	0.167	0.508	0.370	$LiNO_3$, 30.54 cc.	0.182	0.555	$LiNO_3$, 30.33 cc.	0.201

TABLE VI.—METHYL FORMATE.

	Solutions. N.	15°. 4 hrs.	25°. 4 hrs.	15°. 8 hrs.	Solutions. *N*/2.	15°. 4 hrs.	Solutions. *N*/4.	15°. 4 hrs.
1	H_2O, 30 cc.	0.668	3.89	2.58	H_2O, 30 cc.	0.680	H_2O, 30 cc.	0.667
2	LiBr, 30.81 cc.	0.309	5.26	2.56	LiBr, 30.45 cc.	0.650	LiBr, 30.21 cc.	0.927
3	Li_2SO_4, 30.75 cc.	0.742	3.96	3.80	Li_2SO_4, 30.36 cc.	0.667	Li_2SO_4, 30.18 cc.	0.618
4	$BaBr_2$, 31.47 cc.	0.754	9.27	4.76	$BaBr_2$, 30.75 cc.	1.05	$BaBr_2$, 30.39 cc.	1.42
5	$SrBr_2$, 31.47 cc.	0.278	3.47	1.78	$SrBr_2$, 30.72 cc.	0.590	$SrBr_2$, 30.39 cc.	0.990
6	$LiNO_3$, 31.02 cc.	0.865	6.74	4.44	$LiNO_3$, 30.54 cc.	1.02	$LiNO_3$, 30.33 cc.	1.11

TABLE VII.—METHYL FORMATE.

1	H_2O, 30 cc.	0.661	3.87	2.58	H_2O, 30 cc.	0.680	H_2O, 30 cc.	0.680
2	NaBr, 30.87 cc.	1.05	7.00	4.25	NaBr, 30.42 cc.	0.988	NaBr, 30.21 cc.	0.927
3	KCl, 30.90 cc.	1.11	7.05	4.33	KCl, 30.45 cc.	1.11	KCl, 30.27 cc.	1.05
4	$BaCl_2$, 30.93 cc.	1.78	13.71	7.23	$BaCl_2$, 30.48 cc.	1.71	$BaCl_2$, 30.24 cc.	1.47
5	$Ca(NO_3)_2$, 31.59 cc.	1.24	9.86	5.25	$Ca(NO_3)_2$, 30.69 cc.	1.17	$Ca(NO_3)_2$, 30.36 cc.	1.11
6	$MgSO_4$, 30.18 cc.	1.36	8.50	5.92	$MgSO_4$, 30.15 cc.	1.10	$MgSO_4$, 30.12 cc.	0.926

TABLE VIII.—METHYL FORMATE.

1	H_2O, 30 cc.	0.670	3.89	2.60	H_2O, 30 cc.	0.661	H_2O, 30 cc.	0.680
2	KI, 31.56 cc.	0.192	2.14	1.09	KI, 30.81 cc.	0.494	KI, 30.42 cc.	0.667
3	$CaBr_2$, 31.26 cc.	0.618	8.59	4.73	$CaBr_2$, 30.54 cc.	0.982	$CaBr_2$, 30.33 cc.	1.03
4	$SrCl_2$, 30.87 cc.	2.55	17.44	10.69	$SrCl_2$, 30.45 cc.	1.98	$SrCl_2$, 30.27 cc.	1.64
5	$CaCl_2$. 30.87 cc.	2.97	19.86	12.74	$CaCl_2$, 30.39 cc.	2.18	$CaCl_2$, 30.27 cc.	1.85
6	$Mg(NO_3)_2$, 31.48 cc.	2.52	17.92	11.31	$Mg(NO_3)_2$, 30.66 cc.	2.02	$Mg(NO_3)_2$, 30.36 cc.	1.75

bromide, since the results obtained with these salts were very low as compared with the results from the other salts that contain a large amount of water of crystallization. The results found were, however, practically identical with those earlier obtained. In Table I duplicate results are given to show how concordant they were. Duplicate results were obtained in every case, but to economize space only one set is given.

Discussion of Results.

From Plates I and II, the salts which produce the greatest increase in velocity, and which have the largest temperature coefficients are magnesium chloride, calcium chloride, strontium chloride, barium chloride, magnesium nitrate, calcium nitrate, and strontium nitrate. All of these salts crystallize with water of crystallization, varying from six to two molecules each. Next come salts that do not have water of crystallization, as sodium chloride, sodium nitrate, potassium chloride and potassium bromide. Along with these salts we have some that have water of crystallization as sodium bromide, calcium bromide, lithium chloride, lithium bromide, lithium nitrate and magnesium sulfate, which seem to be exceptions in the light of the action of the other salts that crystallize with water.

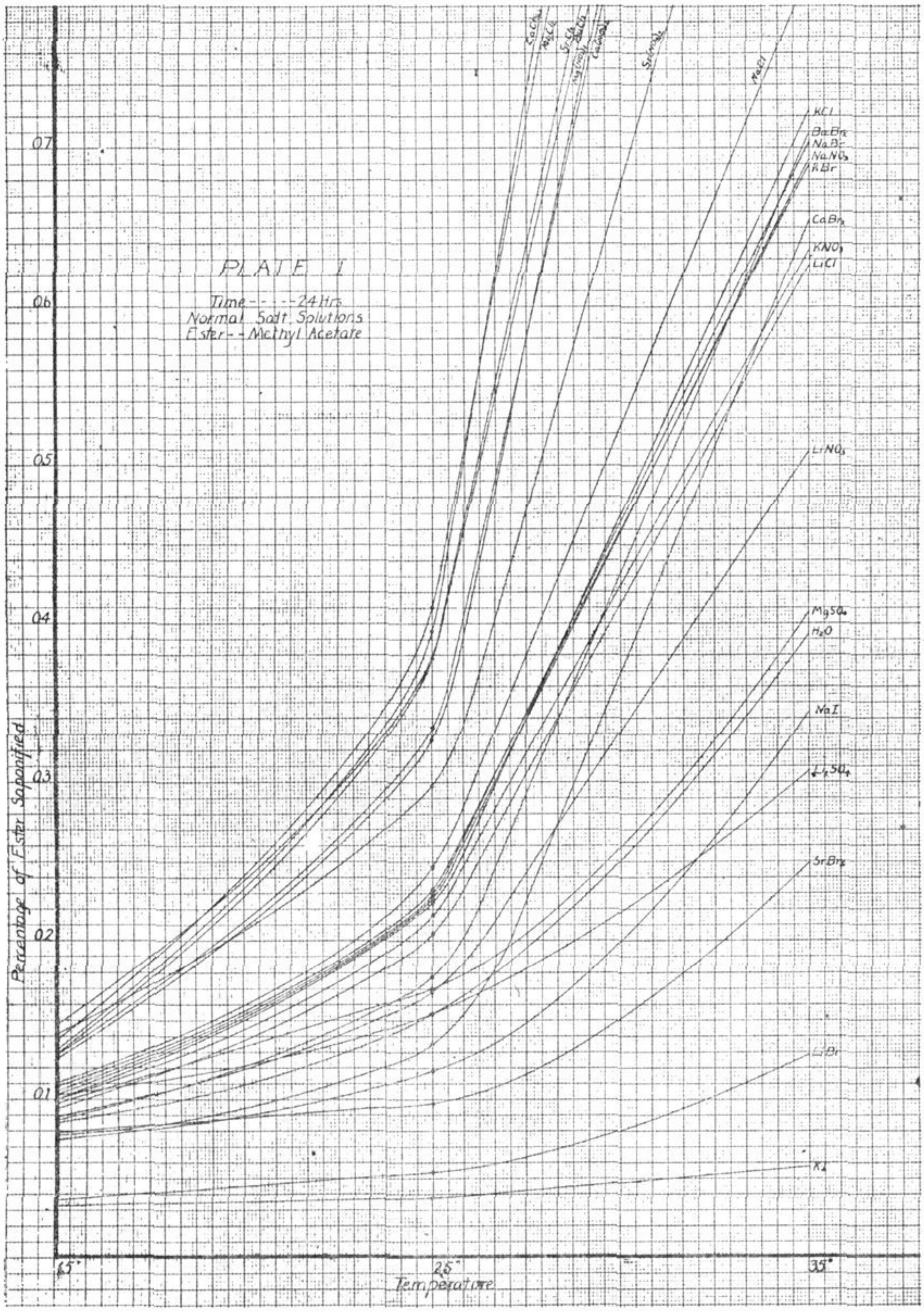
Still more inexplicable seem to be the curves for lithium sulfate, sodium iodide, strontium bromide, lithium bromide and potassium iodide, since these curves are below the curve for pure water.

Let us now consider Plate III. As the dilution is increased, salts such as magnesium chloride show a marked decrease in velocity, the salts with no water of crystallization showing a less decrease, while the apparent exceptions, such as calcium bromide, strontium bromide, etc., show a marked increase in velocity, most of their curves ending above the curve for water.

Let us now consider the salts of any one metal (Plates I and II), *e. g.*, calcium. The chloride increases the velocity more than the nitrate, the nitrate more than the bromide. With potassium and sodium, the chloride has more effect than the nitrate, the nitrate more than the bromide, the bromide more than the iodide. Of the salts studied, the sulfates seem to have least effect. There also seems to be a general relation between the metals themselves, as magnesium, calcium, strontium and barium, though in the series lithium, sodium and potassium, lithium seems to be an exception.

The curves for the methyl formate are of the same general character, the only difference being that the curves are more extended, more being above the curve for water, probably due to the larger amount of saponification. The curves for calcium bromide, barium bromide and magnesium sulfate with methyl formate do not seem to be exceptions, since they fall above the curves for salts with no water of crystallization.

Kellogg[1] found in the case of the halides of potassium, that the chloride increased the reaction most, the bromide less and the iodide least, normal potassium iodide actually decreasing the velocity. This seems to point to the fact that the anion plays an important part in the total effect of the



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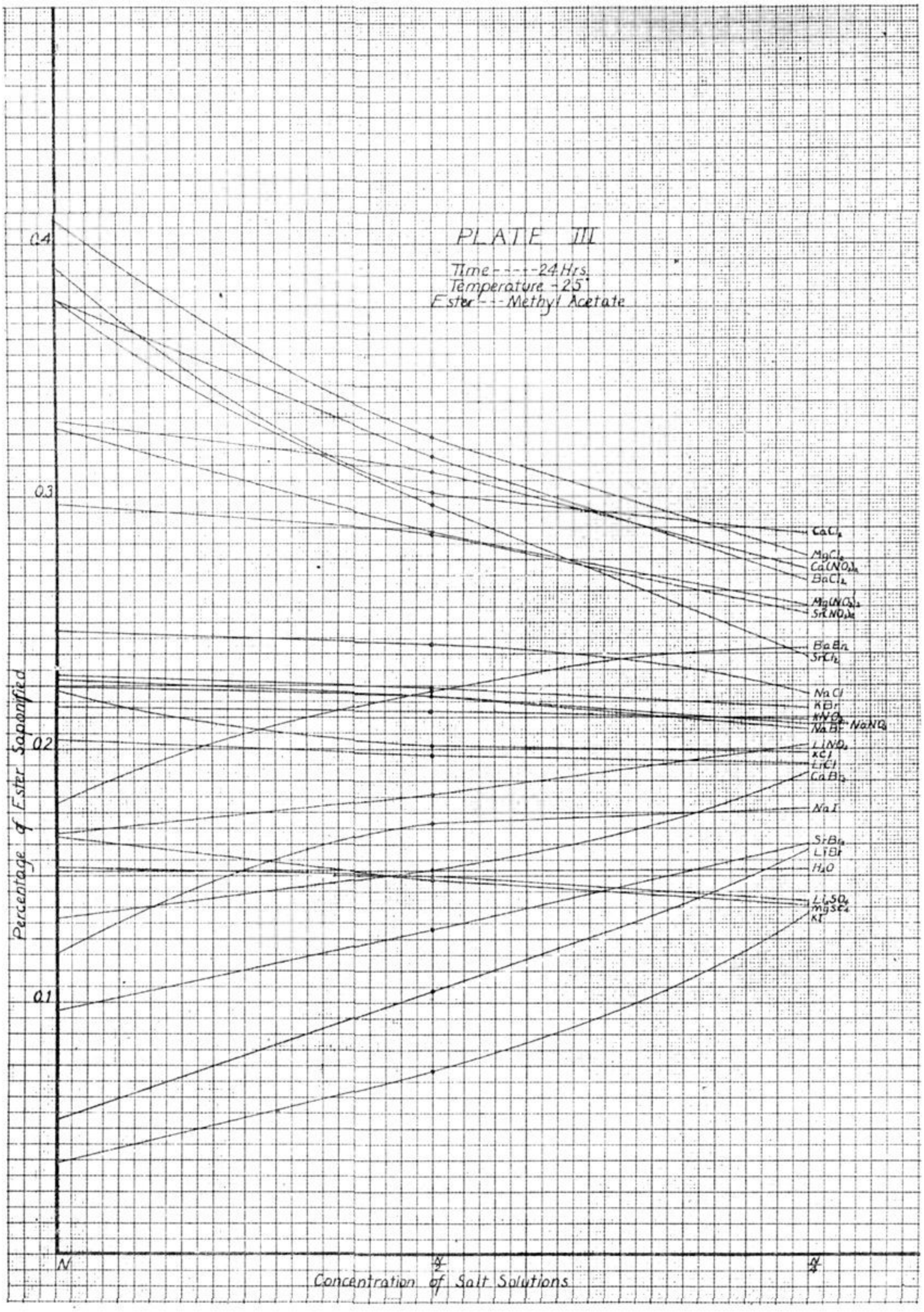
[1] This Journal, **31**, 886 (1909); **35**, 396 (1913).

salt on the reaction velocity. With more dilute solutions of potassium iodide (0.25 *N*) the velocity of the reaction is increased. Kellogg's

curves for strontium chloride, calcium chloride, and barium chloride show that the cation must also be taken into account. A possible explanation of the behavior of barium bromide, calcium bromide, etc., may be that the total effect, due to these salts, is due to a combination between a cation tending to increase the velocity and an anion tending to decrease it.



Kellogg[1] also finds that there is a concentration for each salt that will produce the greatest increase in the velocity of the reaction. Still further

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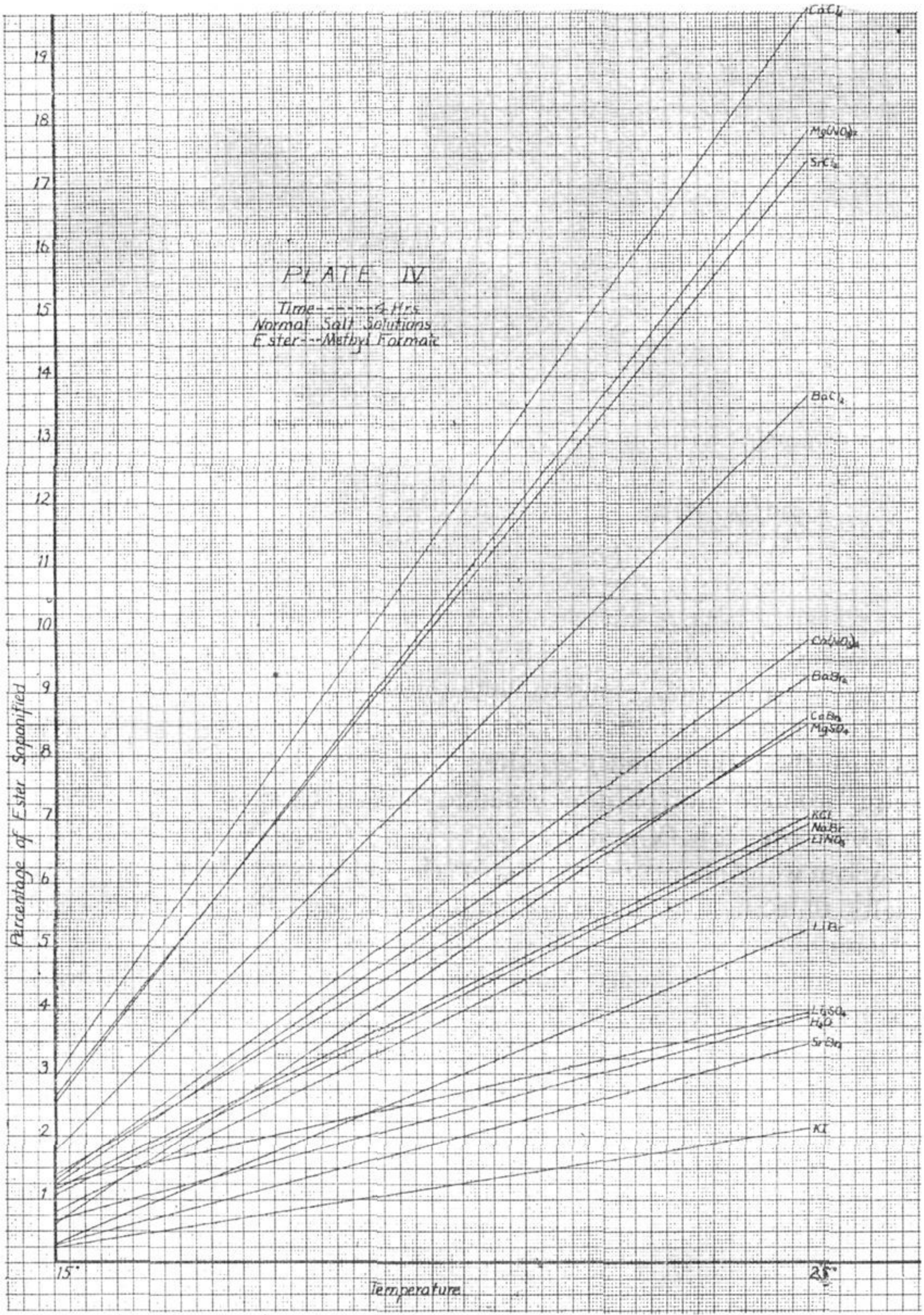
[1] *Loc. cit.*

increase or decrease of the concentration from this point, diminishes the velocity of the reaction.

The action of the apparent exceptions in the study of this problem, *i. e.*, lithium nitrate, lithium bromide, calcium bromide, etc., may be due to the concentration of maximum saponification not having been reached, since these salts all increase the velocity on dilution.



Altogether, it is probable that had the dilution been still farther increased, the apparent exceptions would have proved not to be exceptions at all. This seems to be all the more true in that the curves of Plate IV, where larger percentages of methyl formate are saponified, show that barium bromide, calcium bromide and magnesium sulfate have greater effect than potassium chloride and sodium bromide.

Therefore, it seems more than probable that with more dilute solutions, so as to reach the dilution of maximum saponification, and with a larger amount of ester saponified, most of the apparent exceptions on Plates I and II would no longer be exceptions, but we would have a general relation between salts with water of crystallization and salts without; the former increasing the velocity to a larger extent than the latter, having a larger temperature coefficient and decreasing more with dilution.

We are not satisfied with the results with strontium bromide, and hope in the near future to do more work with this salt.

The position of the curve for any salt seems then to be a function of its water of crystallization, supplemented by an effect due to the ions it forms; *e. g.*, water of crystallization would place the curve above the curves for salts that do not have water of crystallization, the anion Cl^- would place it above a salt with an anion NO_3^- or Br^-; and the cation Mg^{++} would place it above a salt with a cation Ca^{++}, Sr^{++} or Ba^{++}.

This general relation seems to hold among the salts that have no water of crystallization. On Plates I and II the lithium salts do not seem to fit in with the sodium and potassium salts, but what has been said about calcium bromide and barium bromide applies to these salts also, as is shown by Plates III, IV and V.

How can we explain this increase in the velocity of the reaction caused by salts that have water of crystallization, and the decrease in their effect on dilution?

Jones and Getman and Jones and Bassett[1] showed that the salts having large amounts of water of crystallization, are the ones that in solution are the most hydrated. Assuming that the effect of the salts with water of crystallization is due to their being hydrated, let us see what we should expect.

(1) According to Jones and Getman and Jones and Bassett, the chlorides, nitrates, etc., of such metals as magnesium, calcium, strontium and barium would increase the velocity of the reaction, with results that are very nearly the same, and much greater than the nonhydrated salts.

(2) As the concentration decreases, the effect would be lessened, since the total combined water would be less, the decrease being much more rapid than in the case of nonhydrated salts.

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[1] *Publ. Carnegie Inst. Wash.*, No. 60, 15.

(3) From the work of Jones and Pearce,[1] who showed that the hydrating power of a cation is an inverse function of its atomic volume, we

should expect the curves for the salts of magnesium, calcium, barium and strontium with a common anion, to be similar to those found by him,

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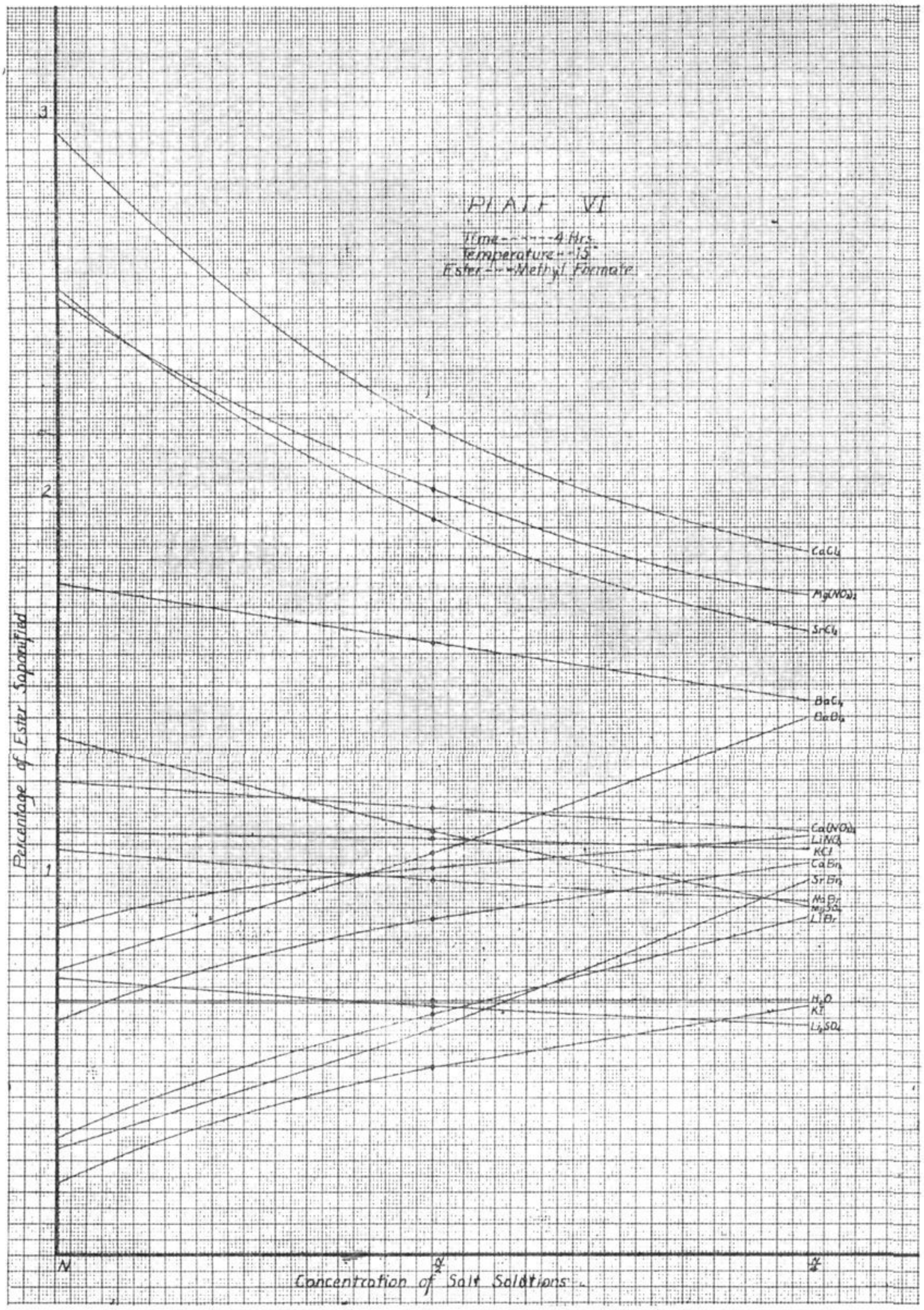
[1] *Publ. Carnegie Inst. Wash.*, No. 180, 57 (1913).

i. e., magnesium salts having the greatest effect, then calcium, strontium and barium.

Let us see if the experimental data confirm these conclusions, based



on the assumption that the difference in action between salts that have water of crystallization and salts that do not, is due primarily to the hydrates formed by the salts with water of crystallization.

Taking into consideration the facts brought out earlier, that the dilution of maximum saponification for the apparent exceptions had not been reached, and that larger percentages of ester saponified would also tend to make the apparent exceptions not real, we can draw from the curves the following conclusions:

(1) Salts with water of crystallization increase the velocity of the reaction much more than salts without water of crystallization.

(2) The effect of salts with water of crystallization decreases on dilution much more than that of salts without water of crystallization.

(3) Among the metals with common anions as magnesium, calcium, strontium and barium chlorides or nitrates, the curves arrange themselves in the order of the decreasing atomic weights of the cations.

We, therefore, conclude that the difference in action between salts with water of hydration and salts without, on the saponification of esters, is due primarily to the chemical difference between free and combined water.

As an explanation of this difference in action we venture the suggestion that the combined water[1] is more highly ionized than free water; and with hydrated salts, we have this effect added to the salt effect shown in the case of nonhydrated salts.

Pearce[2] shows that the cations are the ones that are hydrated; the anions, if hydrated at all, are only slightly so.

The curves for the halides of potassium show that in the saponification of esters, the anions play an important part. This is in line with what Kellogg[3] found.

Therefore, it seems probable that the anions are also hydrated to a certain extent.

But how can the larger temperature coefficient of reaction velocity of the hydrated salts be accounted for, since, with rise in temperature the hydrates become less complex? A study of Plates II and V shows that, temperature being constant, the amounts of ester saponified in the presence of the hydrated salts, as the time increases, is much greater than the amounts saponified in the presence of the nonhydrated salts.

This is probably due to the larger amount of acid formed by the saponification of the ester by combined water. With rise in temperature the larger amount of acid would give us a larger temperature coefficient. Another factor to be taken into consideration is the *hydrolysis* of the hydrated salts which, though small at low temperature, increases greatly as the temperature rises. The increased fluidity of the solution must also be taken into account, the hydrates becoming less complex with rise in temperature. These three factors would probably offset

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[1] Since this was written it has been confirmed by Palmaer and Melander, *Z. Elektrochem.*, 21, 418 (1915).

[2] *Publ. Carnegie Inst. Wash.*, No. 180, 57 (1913).

[3] *Loc. cit.*

the decomposition of the hydrates, giving less combined water, with the result that we would have a larger temperature coefficient of reaction velocity for the hydrated than for the nonhydrated salts.

From the standpoint of hydrates breaking down with rise in temperature, let us consider the effect of such rise in temperature on chemical reactions in general. The influence of temperature on the velocity of reactions is usually very great.

Berthelot[1] showed that the velocity with which an ester is formed is about twenty-two thousand times as great at 200° as at 7°.

Spohr[2] finds that cane sugar is inverted five times as rapidly at 55° as at 25°. Various attempts have been made to explain the effect of rise in temperature on the velocity of chemical reactions. A decrease in the viscosity of the medium with rise in temperature, allowing the ions to move more rapidly; a decrease in the mass of the ion with rise in temperature, and the increased kinetic energy of the molecules and ions, have been cited as the causes of the great increase, with rise in temperature, in reaction velocity. None of these theories seem sufficient to account for such an increase in the velocity of reactions as was noticed by Berthelot and others.

From the solvate theory of solution we see that ions and molecules attract to them molecules of the solvent. We would expect these ions to react more slowly, especially if the solvate were very complex, since the solvate would act as a protective covering around the ions and diminish the velocity with which they would react with one another. But suppose the temperature is raised, the solvate would become less and less complex, until finally the ions would not have any appreciable protective covering. In such a case, where the ions are in direct contact, we would expect the velocity of the reaction to be greatly increased.

We, therefore, suggest that this is one of the more important causes of the increase in the velocity of chemical reactions with rise in temperature.

In conclusion, we can say that the *chemical differences between free and combined water*, brought out in the study of this problem, are strictly analogous to the physical differences between free and combined water as shown by their power to absorb light, which led us to investigate this problem.

Summary.

The following conclusions have either been confirmed or brought out in this investigation:

(1) The reaction involving the decomposition of an ester proceeds slowly at ordinary temperatures and, therefore, can be readily and accurately studied.

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[1] *Essai de Mécanique Chimique*, 2, 93 (1879).

[2] *Z. physik. Chem.*, 2, 195 (1888).

(2) The hydrolysis of the chlorides and nitrates, etc., of calcium, magnesium, strontium and barium employed in the study of this problem, is so small that it alone cannot account for the results obtained.

(3) Salts with water of crystallization increase the velocity of the saponification of an ester to a greater extent than salts with no water of crystallization.

(4) On dilution, the effect with salts having water of crystallization decreases more rapidly than with salts without crystal water, which shows that the result cannot be due to hydrolysis alone.

(5) The curves for the saponification of methyl formate are very similar to those for methyl acetate.

(6) The large effect of salts with water of crystallization is probably due, in part, to their being hydrated, combined water being more highly ionized than free water.

(7) The amount of the saponification, and, therefore, the position of the curve seems to be due to the combined effect of both cation and anion.

(8) It is probable that anions as well as cations are somewhat hydrated.

(9) The hydration of cations is inversely proportional to their atomic volumes.

(10) There seems to be a dilution of maximum saponification for each salt.

(11) Hydrated salts show a large temperature coefficient, notwithstanding the decomposition of hydrates with rise in temperature, probably due in part to hydrolysis.

(12) Decomposition of hydrates may play an important role in the increased velocity of chemical reactions with rise in temperature.

(13) The chemical differences between free and combined water are analogous to the physical differences.

Further work is now in progress in this laboratory on this problem. Certain apparent discrepancies in this preliminary communication are being further investigated, and other lines of attack opened up.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE JOHNS HOPKINS UNIVERSITY.]

CONDUCTIVITIES OF CERTAIN ORGANIC ACIDS IN ABSOLUTE ETHYL ALCOHOL.

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During the past six years a fairly thorough and systematic study of the conductivity and dissociation of aqueous solutions of organic acids, as

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[1] The results of this investigation are recorded in full in *Publ. Carnegie Inst. Wash.*, No. 230 (1915).