treatment at present; but insofar as interpretation is possible, the theory of compressible atoms seems to apply.

WOLCOTT GIBBS MEMORIAL LABORATORY,
HARVARD UNIVERSITY, CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE HYDROLYSIS OF ETHYL ACETATE BY NEUTRAL SALT SOLUTIONS.

BY WILLIAM E. HENDERSON AND DAVID R. KELLOGG.

Received January 28, 1913.

In the course of some previous work[1] one of us found that the reaction between ethyl acetate and water, represented in the equation,

$$CH_3COOC_2H_5 + H_2O = CH_3COOH + C_2H_5OH,$$

is greatly accelerated by potassium chloride, bromide, or iodide. The results obtained at that time seemed to be of sufficient interest to justify a further study of this neutral salt effect. Accordingly the investigation has been extended along two general lines, namely: (1) The catalytic effect of an additional number of salts has been studied at 100°. (2) Conductivity and viscosity data have been obtained for these salts at the concentrations and temperature employed in the hydrolysis experiments, and from these data the degree of ionization has been calculated.

Methods and Apparatus.

Measurement of Hydrolysis.—The velocity of hydrolysis was determined in the manner described in the earlier work, using the same apparatus but with the following changes: The sealing tubes were made with necks sufficiently wide to allow liquids to run in without the use of the capillary funnel. The ethyl acetate was measured with an automatic overflow pipet which added materially to the accuracy of the measurements. (At 25° this pipet delivered in three experiments, 1.2271 grams, 1.2283 grams, 1.2270 grams, or a mean of 1.2274 grams.)

The salts selected for study were the chlorides of sodium, lithium, calcium, strontium, barium, and cadmium, together with cadmium iodide. The halides of potassium were studied in the previous paper. Solutions of desired concentration were made by direct weighing of the dry salt except in the case of the chlorides of calcium and lithium. These were made up to approximately the concentration desired and their exact concentration determined by titration. The cadmium salts were crystallized several times, the others being taken from original packages of J. T. Baker's Analyzed Chemicals. Kahlbaum's ethyl acetate (1200 grams) was purified by washing with a 5% solution of sodium carbonate, no effervescence being noted. It was then washed three times with water,

---

[1] THIS JOURNAL, 31, 403, 886.

dried for some hours over calcium chloride with frequent shaking, and finally distilled. The portion distilling between 75.5° and 78°. (bar. 746) was retained for the work.

Methods of Analysis.—Until measurements on the cadmium salts were begun no difficulties in analysis appeared, as simple titration in the tubes is very easy. Owing to the insolubility of cadmium hydroxide, direct titration in the presence of cadmium salts is impracticable. Distillation *in vacuo* was resorted to, and after many failures the following procedure was adopted: The usual arrangement of apparatus was modified by inserting a rather long, vertical distilling tube between the distilling flask and the condenser, the purpose of which was to stop the spray of cadmium salt which persisted in going over into the receiver as the distillation proceeded to dryness. It was also necessary to insert a loose plug of absorbent cotton just below the exit of the distilling tube to render it entirely efficient. This tube was 35.0 cm. in length and 0.9 cm. in diameter, and was connected with a 100 cc., round-bottomed flask, air being admitted through a capillary extending the length of the distilling tube and almost to the bottom of the flask. The exit of the distilling tube was connected tightly with the condenser, and this in turn, by means of a long-stemmed adapter, with a 200 cc. plain cylinder. The latter contained an excess of standard alkali, and was closed by a two-holed stopper. The stem of the adapter passed through one hole and extended below the surface of the alkali; the second hole provided for a connection with the water pump. A tall beaker of boiling water was used to heat the flask, and condensation in the distilling tube was prevented by providing the latter with a steam jacket. Each sealed tube as it came from the thermostat was cooled, opened, emptied into the distilling flask, and rinsed once. The flask was then connected with the distilling tube and distillation carried to dryness by means of the water bath. The flask was then disconnected, the tube twice rinsed into it, and water added to bring the total to 30 or 40 cc. On again distilling to dryness all acetic acid was shown to be over.

Before this method was used in the analysis of samples of unknown composition, it was tested with known mixtures. A series of experiments showed: (1) that the acetic acid is quantitatively recovered; (2) that ethyl acetate is not appreciably hydrolyzed in the short time required by the operation; (3) that small quantities of hydrochloric acid come over with the acetic. At first the total acidity found was corrected by deduction of the hydrochloric acid as determined by titration, using potassium chromate as an indicator. Later this correction was discontinued, (*a*) because it was always smaller than the unavoidable errors of experiment, and (*b*) because it is uncertain how much of the correction is occasioned by hydrolysis of the cadmium salt, involving a real error, and what fraction is due to a partition effect between the competing hydrochloric and acetic acids, and not, therefore, to be counted as an error.

Measurement of Conductivity.—The problem which next presented itself was that of determining at 100° the conductivity of salt solutions such as had been used in the hydrolysis experiments. It was not thought desirable to attempt the measurement of this property in the presence of the ethyl acetate, as it was desired to find any peculiarities which might exist in the salt solution itself. A second reason for omitting the ethyl acetate is the fact that at 100° the hydrolysis of the ester would give enough acetic acid to continually change the conductivity.

The splendid work of A. A. Noyes on the electrical conductivity of aqueous solutions has shown that the conductivity of salt solutions can be determined with great accuracy at 100°, and affords conductivity data for potassium chloride at that temperature which may be used in determining the cell constant of any form of apparatus employed. Of course, without the elaborate apparatus devised by him it is impossible to obtain results of equal accuracy. For the present purpose this was not necessary for extreme accuracy would have no particular value in this work. It was hoped, however, that a relatively simple form of cell might be devised which would give, at this temperature, an accuracy about equal to that of ordinary laboratory measurements of this kind at room temperature. This was accomplished by the construction of the two cells which will now be described.

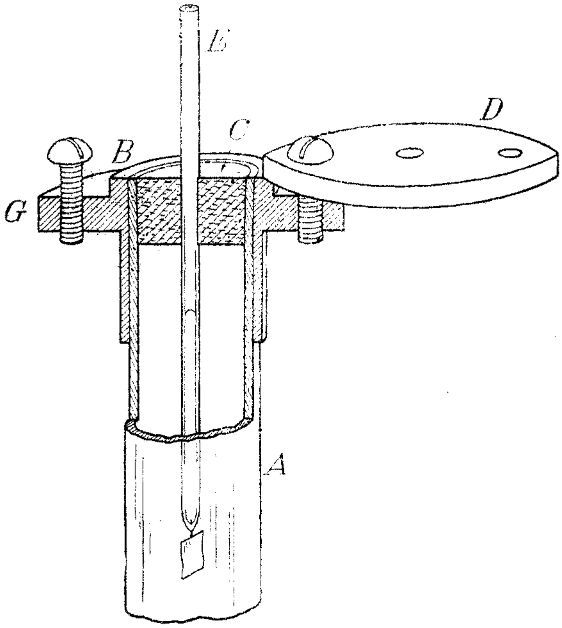

Fig. 1.

Conductivity Cells. — For the stronger solutions, tenth molar and upwards, a U-tube arranged as shown in Fig. 1 served admirably, a longitudinal section of one limb alone being represented. A loosely fitting brass collar, B, was set onto the glass tube A with plaster of Paris, after the end of the tube had been slightly flared. When the plaster of Paris had set, the projecting end of the tube A was ground off flush with B, using emery and water. The glass electrode tube E passes through a rubber stopper, C. The latter is forced into place by the screws through D threaded into G. A brass collar is set onto the electrode tube, flush with D, with plaster of Paris to make sure that the electrode is always held at the same height. D is always screwed entirely home so that the electrode is replaced in the same position after removing the stopper, electrode, and plate to fill the tube. About 1 cc. of air space was left above the liquid to provide for expansion. The cell was closed very tightly by the stopper, and loss of the solvent by volatilization was thus prevented. Upon long standing in the thermostat, drops of condensed solvent could be seen on the sides of the tube above the solution, but after mixing the solution again the same conductivity values were obtained as had been read at first.

For standardization of the cell, a 0.1 *N* solution of potassium chloride was used. According to Noyes[1] this has a specific conductance at 100° of 33.6^{-3} mhos. The cell constant, using this value for the specific conductance, was found to be 4.454. After the work had progressed somewhat it became necessary to change the position of the electrodes slightly. Redetermination of the constant gave the value 4.493, and a later adjustment gave 4.540. In these standardizations the deviations from the mean of successive bridge readings, after emptying and refilling the cell, were 0.20%, 0.27% and 0.27%, respectively. This apparatus gave great satisfaction, and proved to be an excellent instrument for securing conductivities at reasonably high temperatures. With the concentrated solutions no appreciable effect was produced by the solubility of the glass vessel. At greater dilutions, however, this became a very serious factor.

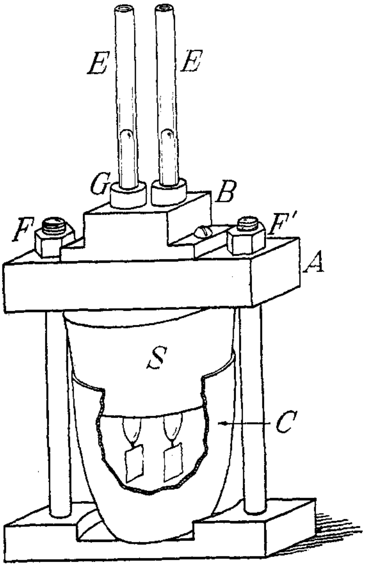

Fig. 2.

Accordingly for use with dilute solutions another type of cell was employed (Fig. 2). The vessel C is a platinum crucible. Electrode tubes E, E pass through the rubber stopper S. A brass plate, A, had two holes, slightly larger than the electrode tubes, drilled the same distance between centers as the holes in the stopper. A second piece of brass, B, had the same sized holes spaced a trifle farther apart, so that when it was screwed down on A it exerted a slight shearing stress and held the tubes firmly. Plaster of Paris was poured into the holes in B, and as an added precaution small guide

---

[1] "Electrical Conductivity of Aqueous Solutions." p. 47.

rings G were set on with it also. The rubber stopper was forced tightly into the crucible by screwing down the yoke A by means of the nuts F F′ on the threaded uprights. By this use of platinum most of the troubles from solution of foreign matter were eliminated, although very dilute solutions, upon long standing in this cell, did increase somewhat in conductivity, probably owing to material dissolved from the rubber stopper.

This cell was standardized with a 0.02 *N* solution of potassium chloride. Noyes gives the data for 0.01 *N* and for 0.08 *N* potassium chloride, and from this the conductivity of 0.02 *N* was calculated, both by graphical interpolation, and by use of the formula, $1/\Lambda = 1/\Lambda_0 + K(C\Lambda)^{n-1}$ in which $n = 1.4$. By the first method the value 7.346×10^{-3} was obtained and by the second the value 7.338×10^{-3}. The latter value was adopted. At various times in the work the electrodes were moved slightly, giving cell constants as follows: 0.2900, 0.2926, 0.2986. In these measurements the percentage accuracy was less than with the other cell, since the number by which the ratio is divided was so much smaller. Deviations from the mean of successive readings were 1.2%, 1.6% and 1.39% for the three values of cell constant given.

For all of the conductivity measurements a platinum-iridium bridge, calibrated according to Strouhal and Barus, was used. As the leads to the cell were rather long, their resistance was measured and an equal resistance was inserted in the other arm of the bridge.

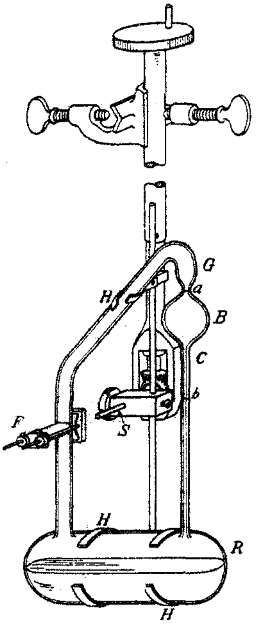

Fig. 3.

Measurement of Viscosity. — For use at 100°, where the vapor pressure of aqueous solutions is large, all types of open viscometers are unsuitable. A rotating disc might have been used, but both observations and calculation of results are extremely laborious with this type of instrument. Of the other forms, that of Thorpe and Roger as modified by Bingham and White seemed best suited to the requirements of the problem. This form of apparatus is complicated, however, and calls for a rather extensive set-up. In view of these facts an effort was made to design an instrument which would be both simple and accurate, and would at the same time form an entirely closed system. The results of these efforts is the viscometer represented in Fig. 3. The glass bulb B is connected at the lower end with the capillary C, and above joins the large tube G which connects with the reservoir R. The capillary also empties into R. The side tube F permits of easy filling. The glass part just described is held in the frame by the spring clips H, and is mounted on a shaft, S, at right angles to the plane of the glass part. The shaft carrying the viscometer is rotated by means of a bevel gear, actuated by the small head wheel at the top. The liquid whose viscosity is to be determined is run in at the side tube F, which may then be closed in any suitable manner. For the present work a rubber stopper was used, cut away so as to have a cylindrical piece to go inside F, and a square shoulder to rest on the end of F. This plug was held in place by a brass yoke that screwed down.

Having introduced a quantity of liquid sufficient to half fill the reservoir, paying no attention to the exact amount, the viscometer is closed and completely immersed in the thermostat. To get the liquid into the small bulb, the instrument is rotated so that it stands point downward. When the bulb and capillary have filled, rotation is continued until the capillary is again vertical. There is sufficient volume above the mark *a* to give plenty of time for setting the capillary vertical by coincidence with some previously determined reference line, and to snap the stop-watch as the meniscus passes the upper mark. It will be noted from Fig. 3 that the receiver R is very large in comparison with the bulb B. This makes it unnecessary to measure the liquid to be examined, as the capillary drains into what is virtually an open space. This eliminates back pressure, since the connecting tube is large also and has no liquid standing in it; hence the accuracy of the experiment is independent of the quantity of liquid present, provided it does not more than about two-thirds fill the receiver. Since the whole system is closed, there is no change in concentration by evaporation, and a given portion of liquid may be run through the capillary as many times as desired, each experiment requiring only a few minutes.

The Thermostat.—For viewing the passage of the liquid in the capillary tube it is necessary to have a thermostat regulated at 100° and large enough to permit of the rotation of the viscometer. It is very desirable to have a glass-sided thermostat, and one was obtained from Fritz Köhler which was well adapted in dimensions, but proved to be unable to stand the temperature without leaking. For a portion of the work a metal tank was used, illumined with a bung-hole lamp slipped within a long test tube and immersed in the tank. The socket was dispensed with, the wires being soldered directly to the base of the lamp. While the liquid in the capillary is invisible under such illumination, the air column which follows it is very bright and the readings are sharp. A large 880-watt "Quick-Hot" immersion heater was used as the main source of heat, supplemented by a smaller 440-watt heater on the relay. The former, being a special order, was not well designed and quickly burned out, and some of the measurements had to be made by placing the thermostat on a gas stove using the relay heater to maintain a constant temperature.

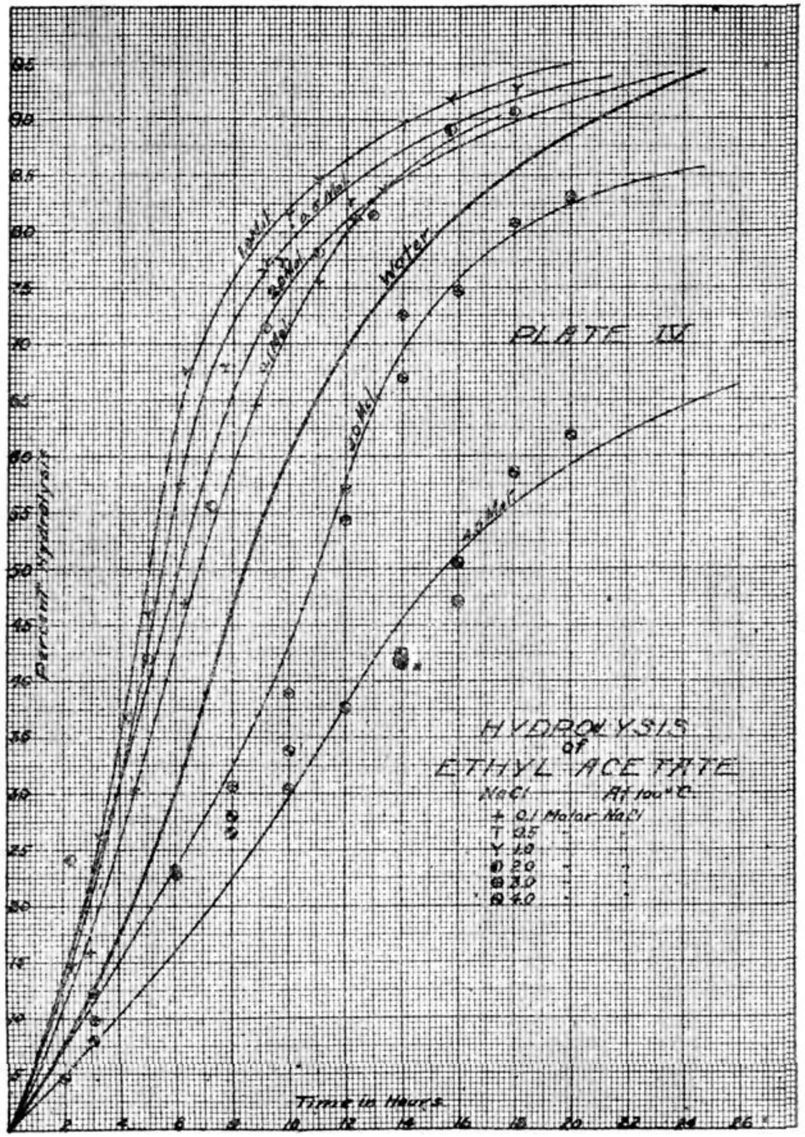
PLATE IV
HYDROLYSIS
of
ETHYL ACETATE
NaCl At 100° C.
+ 0.1 Molar NaCl
T 0.5
Y 1.0
● 2.0
⊕ 3.0
⊗ 4.0
Water
Percent Hydrolysis
Time in Hours
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
2
4
6
8
10
12
14
16
18
20
22
24
26

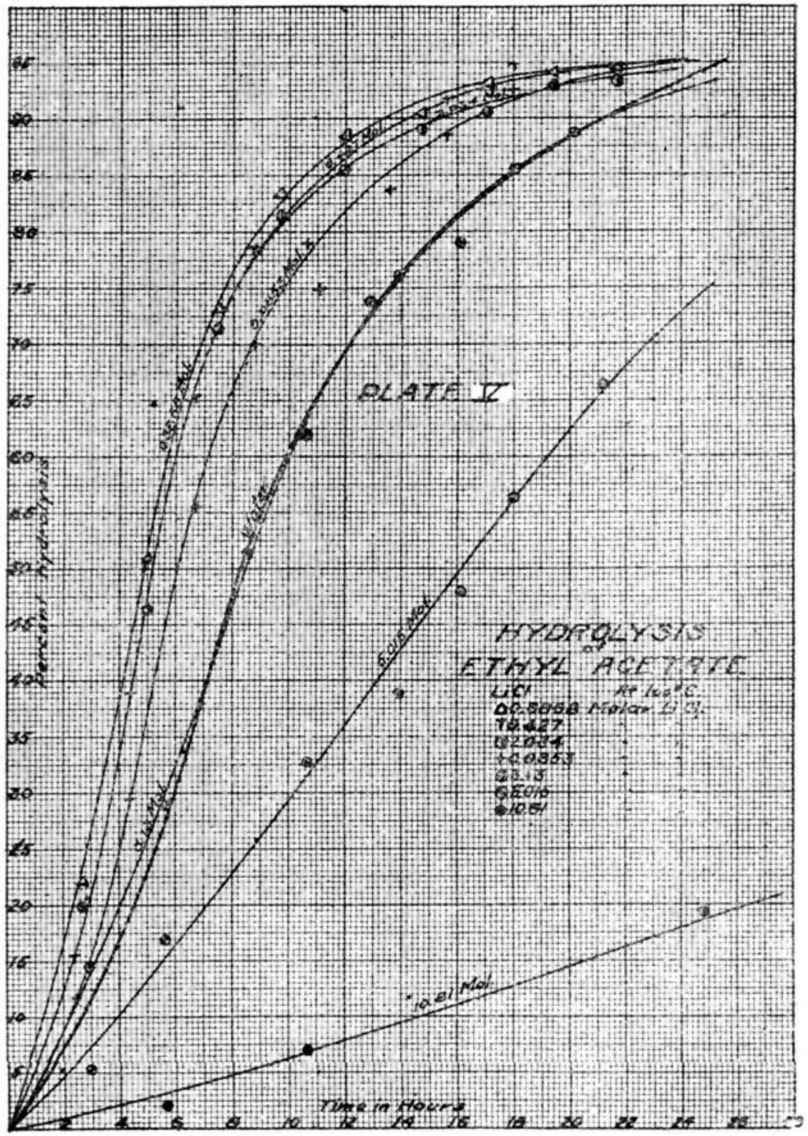
PLATE V
HYDROLYSIS
of
ETHYL ACETATE
LiCl At 100° C.
△ 0.5068 Molar LiCl
T 0.427
⊕ 2.034
+ 0.0353
⊗ 3.13
● 5.016
● 10.61
Water
5.016 Mol
10.61 Mol
Percent Hydrolysis
Time in Hours
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
2
4
6
8
10
12
14
16
18
20
22
24
26

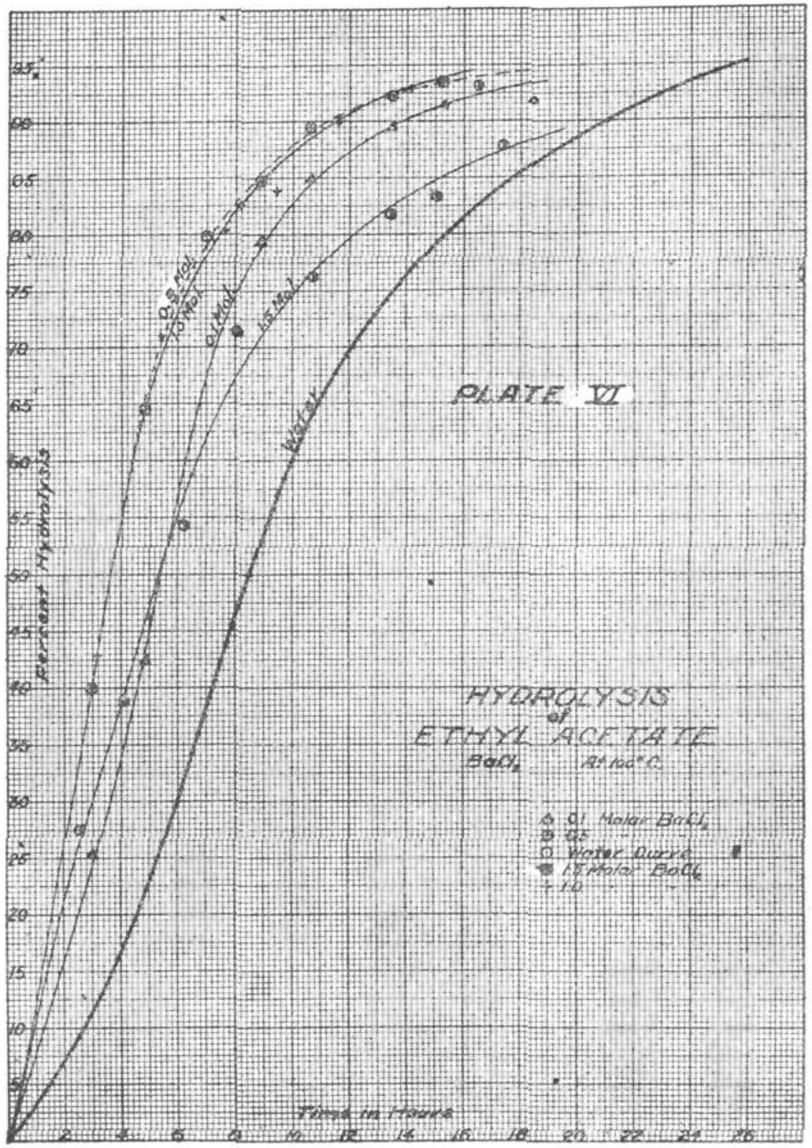

PLATE VI

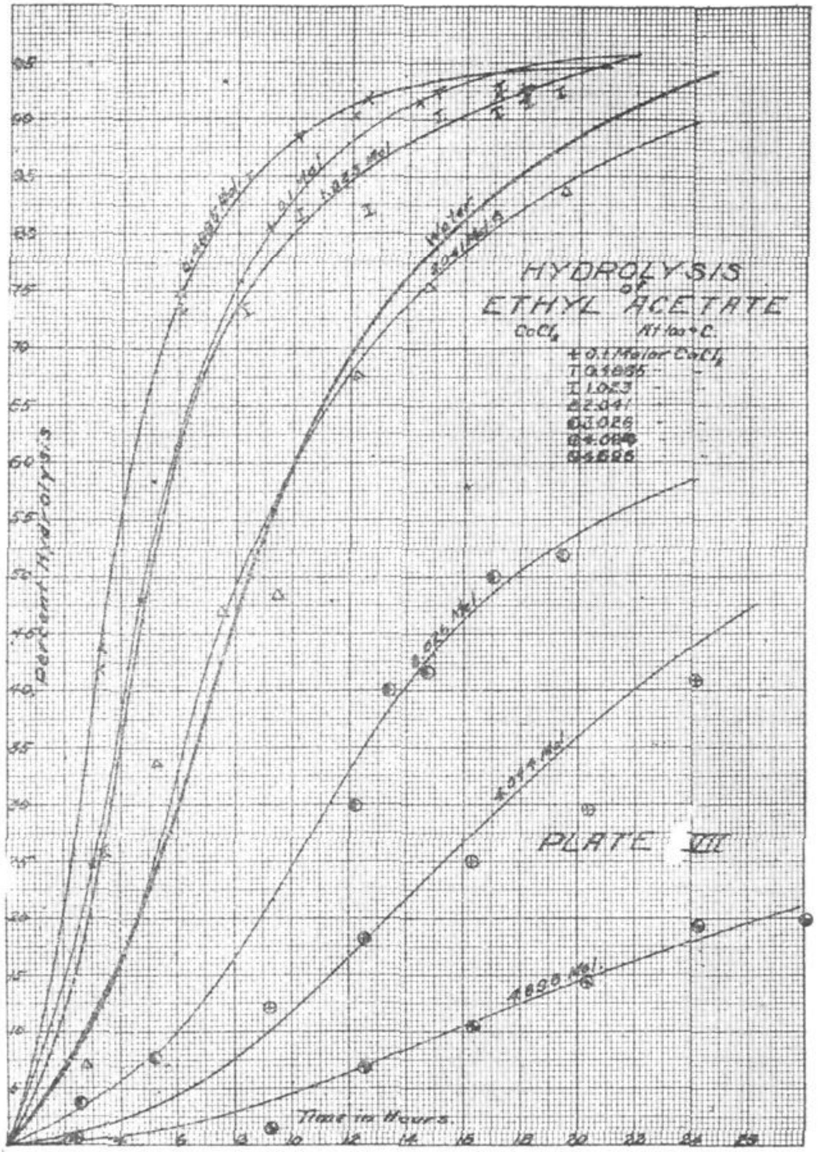

PLATE VII

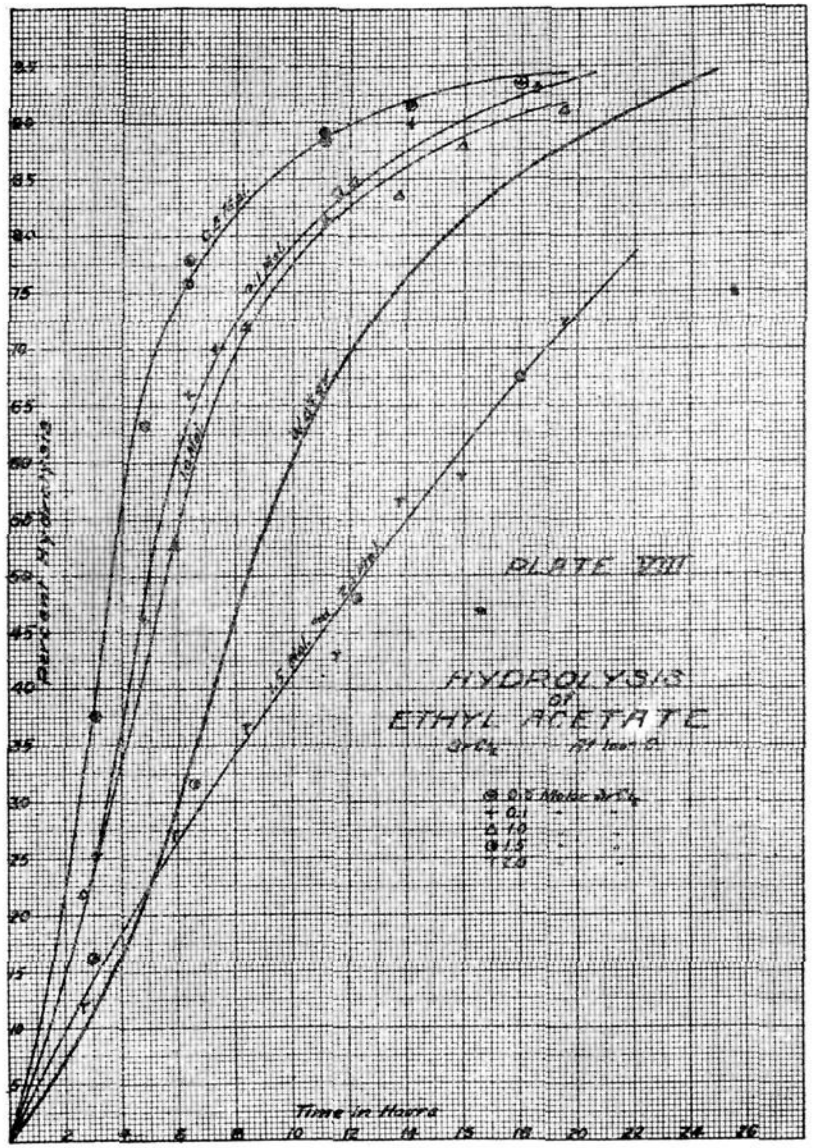
PLATE VIII
HYDROLYSIS
of
ETHYL ACETATE
SrCl₂ At 100° C.
⊗ 0.5 Molar SrCl₂
+ 0.1 " "
△ 1.0 " "
⊕ 1.5 " "
T 2.0 " "
0.5 Mol.
0.1 Mol.
1.0 Mol.
Water
1.5 Mol. and 2.0 Mol.
Percent Hydrolysis
Time in Hours
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
2 4 6 8 10 12 14 16 18 20 22 24 26

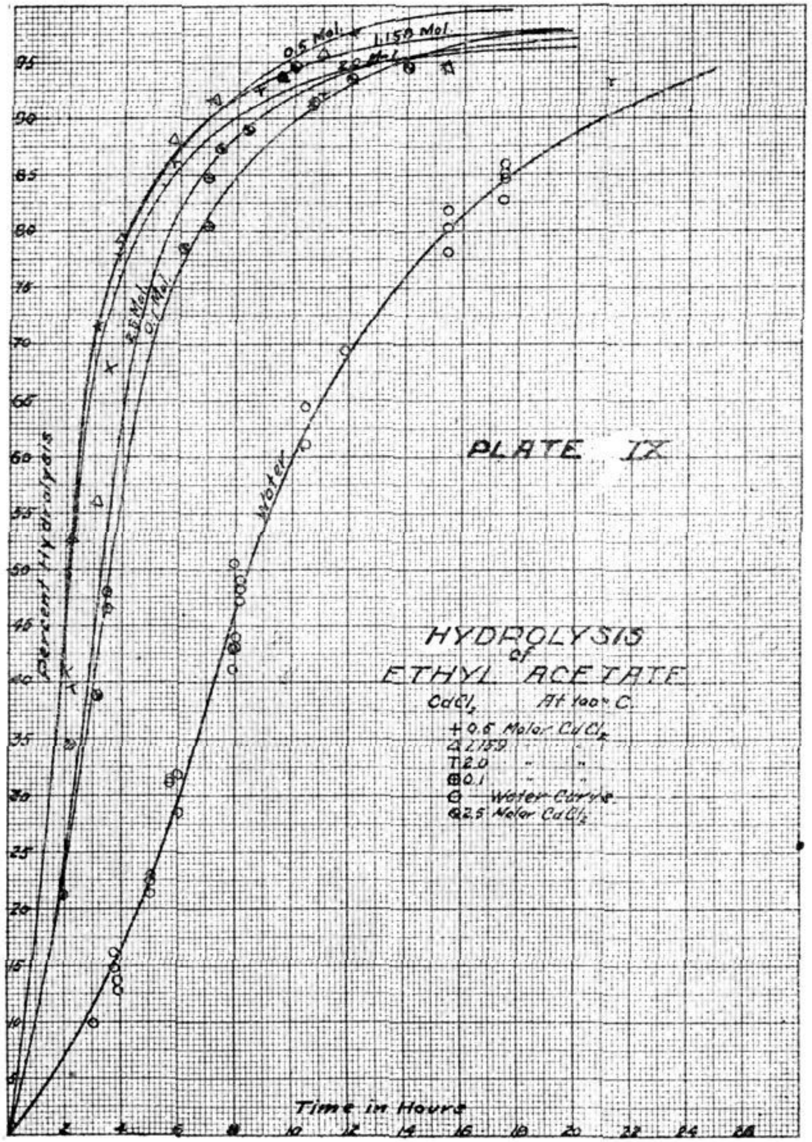
PLATE IX
HYDROLYSIS
of
ETHYL ACETATE
CdCl₂ At 100° C.
+ 0.5 Molar CdCl₂
△ 1.159 " "
T 2.0 " "
⊕ 0.1 " "
○ Water Curve
⊗ 2.5 Molar CdCl₂
0.5 Mol.
1.159 Mol.
2.0 Mol.
2.5 Mol.
0.1 Mol.
Water
Percent Hydrolysis
Time in Hours
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
2 4 6 8 10 12 14 16 18 20 22 24 26

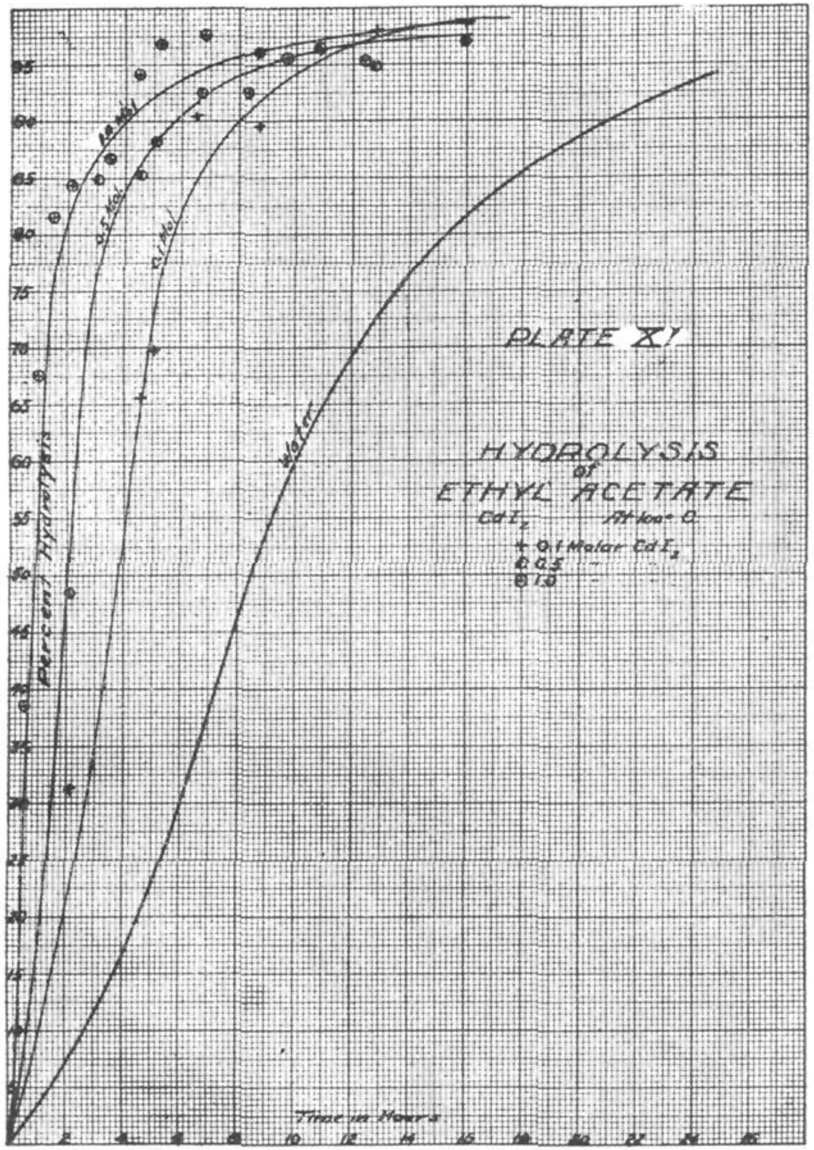
PLATE XI
HYDROLYSIS
of
ETHYL ACETATE
CdI_2 At 100° C.
+ 0.1 Molar CdI_2
⊙ 0.5
⊛ 1.0
1.0 Mol.
0.5 Mol.
0.1 Mol.
Water
Percent Hydrolysis
Time in Hours
2
4
6
8
10
12
14
16
18
20
22
24
26
95
90
85
80
75
70
65
60
55
50
45

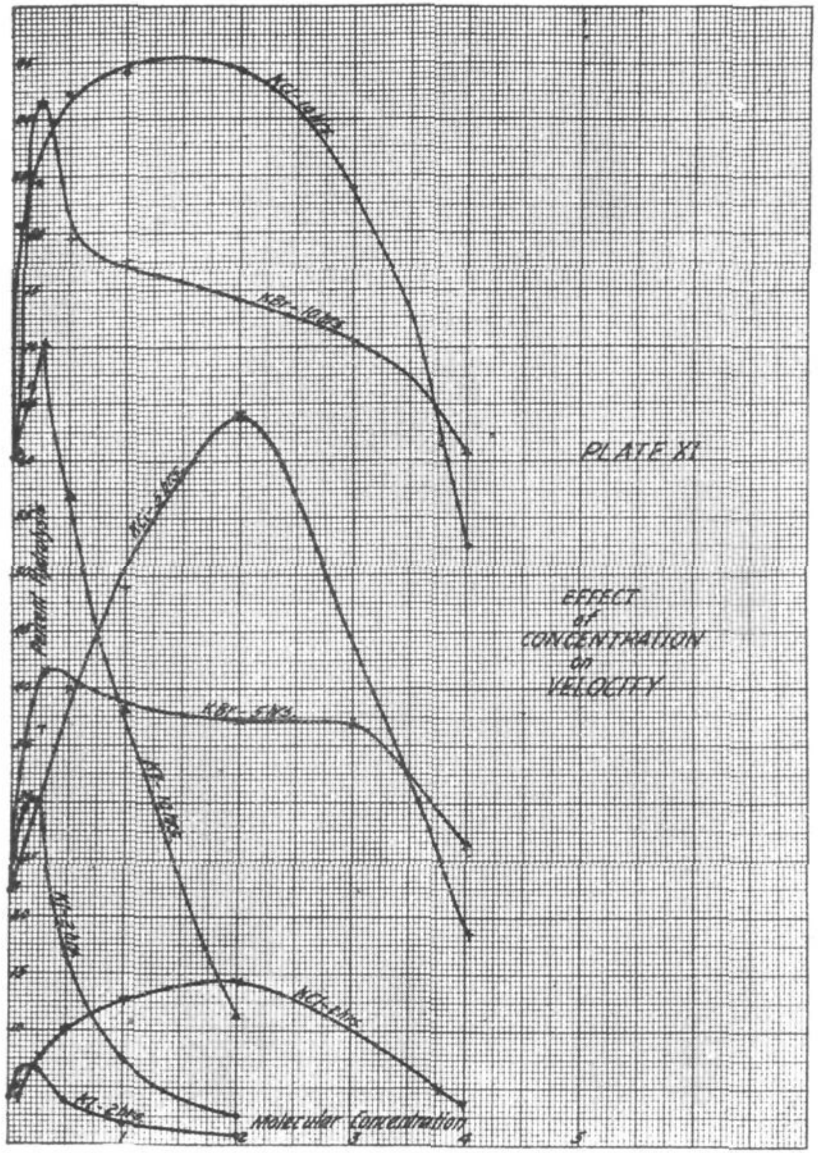
PLATE XI
EFFECT
of
CONCENTRATION
on
VELOCITY
KCl-10 hrs.
KBr-10 hrs.
KCl-5 hrs.
KBr-5 hrs.
KI-10 hrs.
KCl-2 hrs.
KI-2 hrs.
Percent Hydrolysis
Molecular Concentration
1
2
3
4
5

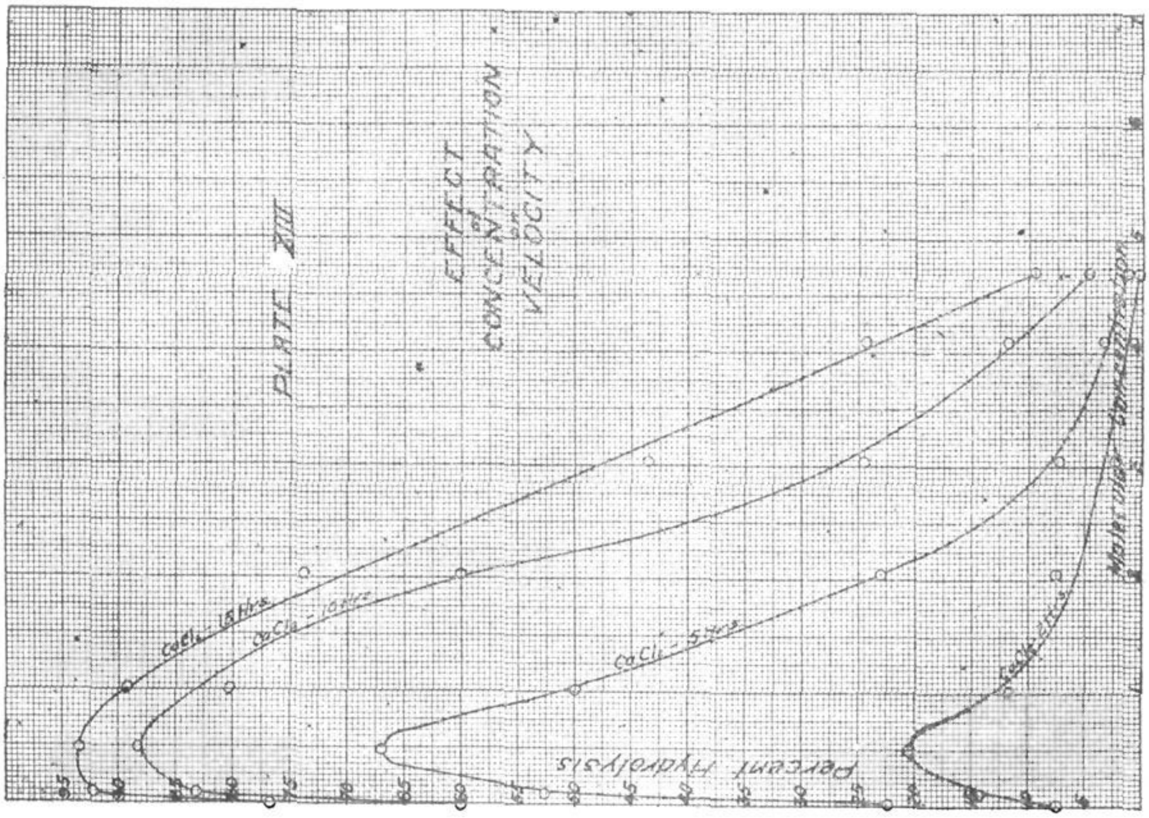
PLATE XIII
EFFECT of CONCENTRATION on VELOCITY
CoCl2 - 15 Hrs.
CoCl2 - 10 Hrs.
CoCl2 - 5 Hrs.
CoCl2 - 2 Hrs.
Percent Hydrolysis
Molecular Concentration
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
1 2 3 4 5 6 7

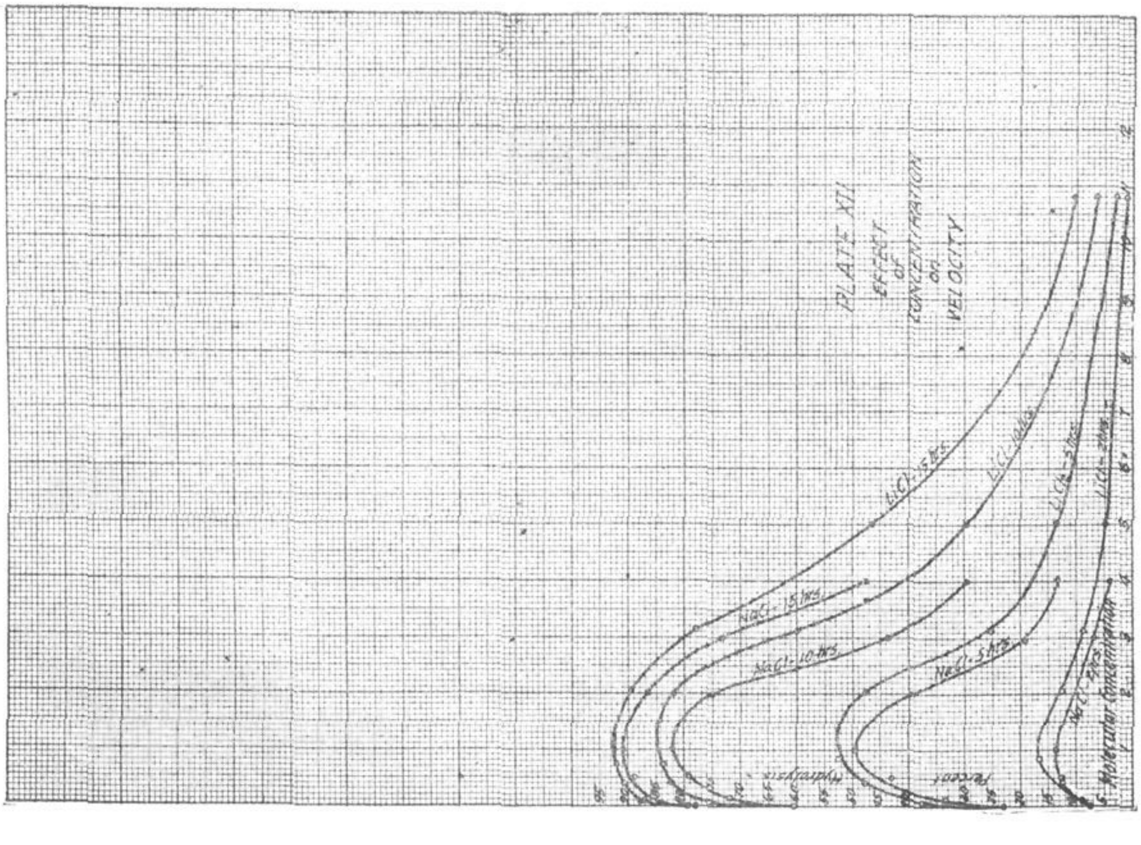
PLATE XII
EFFECT of CONCENTRATION on VELOCITY
NaCl - 15 Hrs.
NaCl - 10 Hrs.
NaCl - 5 Hrs.
NaCl - 2 Hrs.
LiCl - 5 Hrs.
LiCl - 10 Hrs.
LiCl - 5 Hrs.
LiCl - 2 Hrs.
Percent Hydrolysis
Molecular Concentration
5 10 15 20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95
1 2 3 4 5 6 7 8 9 10 11 12

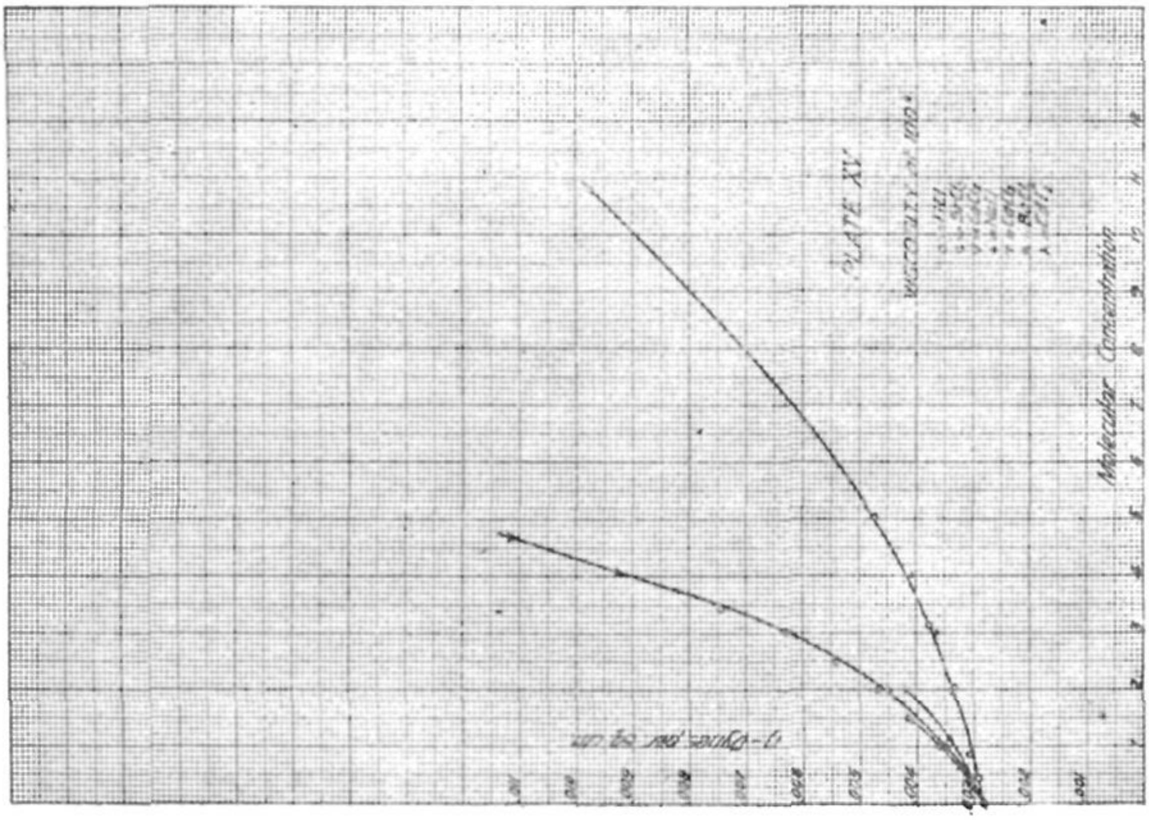
PLATE XV
VISCOSITY AT 100°
Molecular Concentration
η - Dynes per sq. cm.

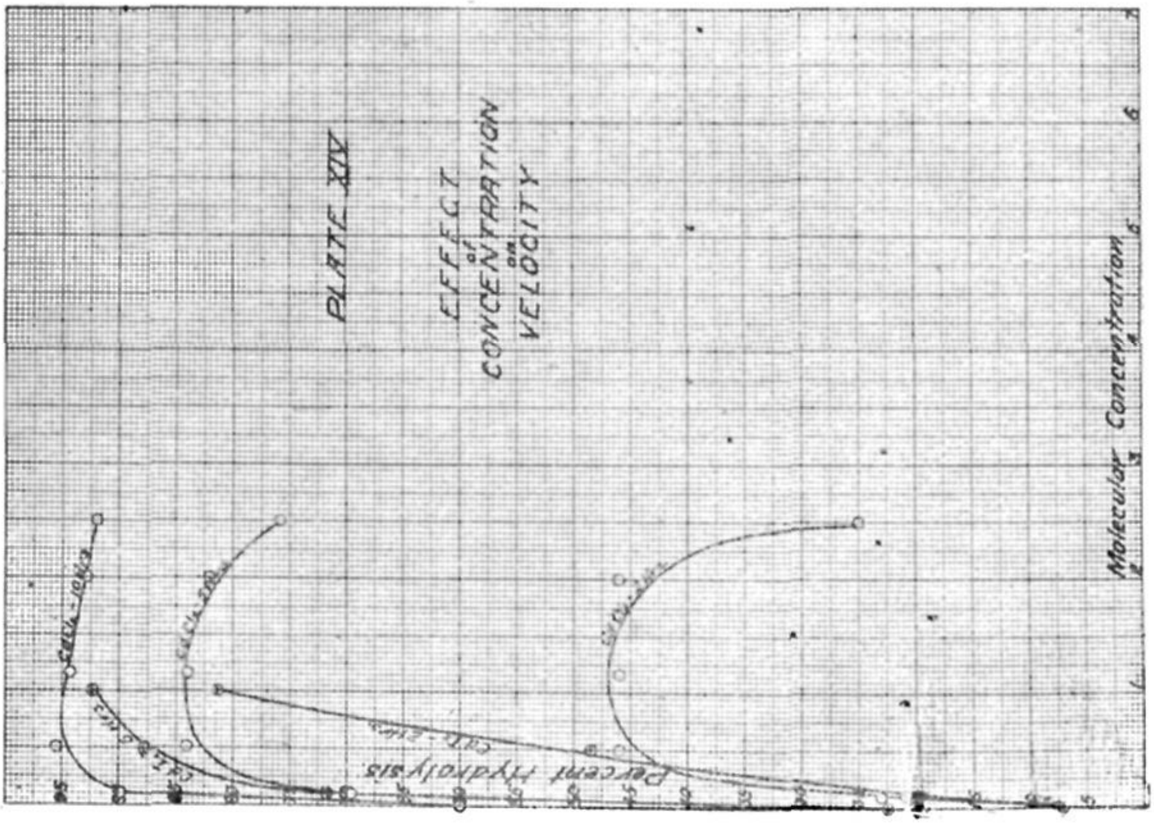
PLATE XIV
EFFECT of CONCENTRATION on VELOCITY
Molecular Concentration
Percent Hydrolysis

This arrangement was difficult to control, which accounts for the raggedness of some results. A new thermostat was designed and constructed which admirably meets the requirements of the case, but it was finished too late to be of use in this work. It was also found that with care a glass battery jar may be used, at least to temperatures approaching 100°.

For work at this temperature a solution of calcium chloride was employed within the thermostat. With continued use this becomes very turbid. As long as the turbidity was not too great, sharp readings could be made by using a square-ended glass tube (like a Nessler tube) as a submarine telescope. We are indebted to Mr. A. W. Davidson, A.M., for most of the measurements with this viscometer.

Density Determinations.—Density determinations were made by means of an ordinary Ostwald-Sprengel pyknometer, parallels being run in every case. These checked to a percentage accuracy as good as that of the stopwatch and usually better than that. With the dilute solutions 100° was very near the boiling point and these solutions boiled out of the pyknometer or were thrown out by small bubbles of air and vapor, so that the determination of their densities had to be abandoned. However, this was not a matter of any great moment, as interpolation on the viscosity curves gave results near enough to the true values. At small concentrations, viscosities differ from that of water by a very small amount, and hence a slight error in reading from the curves would occasion only a minimum error in the ratio.

Experimental Results.

Hydrolytic Effect of Alkali and Alkaline-Earth Chlorides.—The results of the experiments on the hydrolysis of ethyl acetate in the presence of the chlorides of the alkali and alkaline-earth metals are given in Tables I–VI and shown graphically on Plates IV–VIII. (For plates I–III, representing the effect of the halides of potassium, see previous article.) Table I gives the data for the hydrolytic effect of pure water upon the acetate at the concentration employed, and the curve derived from these data is traced as a heavy line on each of the plates for ready comparison. Tables VII and VIII, together with Plates IX and X, show the corresponding effect of the chloride and iodide of cadmium. These will be discussed more at length later on.

The most noticeable feature of these data is that all the salts employed, even at concentrations as low as 0.1 molar, increase to a large extent the rate of reaction. This increase is not, however, proportional to the concentration throughout a wide range: the ratio, acceleration ÷ molar concentration, grows steadily smaller passing through zero and becoming negative in all cases where the molar solubility is sufficiently high. This negative value is shown wherever a curve lies below the water curve.

Plates XI–XIV are derived curves, obtained by plotting as abscissas the molar concentration, and as ordinates the percentage of hydrolysis in 2 hours, 5 hours, and 10 hours. Plate XI shows the curves for the three halides of potassium, discussed in the former article. Plate XII shows the curve for sodium chloride and lithium chloride. It will be noted that the two sets of curves resemble one another very closely. Calcium, strontium, and barium chlorides gave results very nearly the same, and the curve for calcium chloride (Plate XIII) was drawn as typical of the group. It will be seen that these curves are much like those for the alkali chlorides, but show a somewhat larger effect.

TABLE I.—HYDROLYSIS OF ETHYL ACETATE BY PURE WATER.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. Cc. H_2O.	Time. Hrs.	% hydrolysis.	Serial No.
25	3.00	10.0	010
25	3.75	16.2	045
25	3.75	14.9	046
25	3.87	13.7	034
25	3.87	12.9	035
25	5.00	22.6	08
25	5.00	21.4	09
25	5.00	23.0	011
25	5.75	31.1	047
25	5.75	31.5	048
25	5.75	31.1	049
25	6.00	28.7	036
25	6.00	31.9	039
25	7.91	43.2	044
25	7.91	41.2	051
25	8.00	43.2	03
25	8.00	44.1	05
25	8.00	50.7	06
25	8.17	49.1	040
25	8.17	47.3	037
25	8.17	48.4	038
25	10.43	61.2	052
25	10.45	64.5	053
25	11.83	69.5	055
25	15.42	81.9	021
25	15.42	80.3	022
25	15.42	78.2	023
25	17.45	82.7	024
25	17.45	84.7	025
25	17.45	85.9	026
25	17.45	85.1	027

TABLE II.—HYDROLYSIS OF ETHYL ACETATE BY SODIUM CHLORIDE.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. 25 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.1 mol. NaCl	3.00	15.8	068
0.1 mol. NaCl	4.51	30.3	069
0.1 mol. NaCl	6.33	46.8	070
0.1 mol. NaCl	8.77	64.5	071
0.1 mol. NaCl	11.00	75.5	072
0.1 mol. NaCl	12.33	81.1	073
0.1 mol. NaCl	13.33	83.9	074
0.5 mol. NaCl	9.77	77.6	076
0.5 mol. NaCl	12.13	82.9	077
0.5 mol. NaCl	14.00	89.9	078
0.5 mol. NaCl	2.32	14.9	079
0.5 mol. NaCl	4.16	37.2	080
0.5 mol. NaCl	6.16	57.6	081
0.5 mol. NaCl	7.66	68.1	083
0.5 mol. NaCl	9.00	76.6	089
25.4 cc.			
1.0 mol. NaCl	3.25	26.2	085
1.0 mol. NaCl	5.00	46.0	086
1.0 mol. NaCl	6.27	67.7	087
1.0 mol. NaCl	9.18	77.4	088
1.0 mol. NaCl	11.00	84.7	089
1.0 mol. NaCl	9.93	81.5	090
1.0 mol. NaCl	15.68	91.9	092
1.0 mol. NaCl	18.00	92.6	093
26.0 cc.			
2.0 mol. NaCl	3.25	24.2	094
2.0 mol. NaCl	5.00	42.0	095
2.0 mol. NaCl	7.27	55.6	096
2.0 mol. NaCl	9.17	71.4	097
2.0 mol. NaCl	11.00	78.2	098

TABLE II (*continued*).

Solution. 26.0 cc.	Time. Hrs.	% hydrolysis.	Serial No.
2.0 mol. NaCl	12.93	81.5	0100
2.0 mol. NaCl	15.68	89.1	0101
2.0 mol. NaCl	18.00	90.7	0102
26.6 cc.			
3.0 mol. NaCl	3.06	12.36	0449
3.0 mol. NaCl	3.15	9.93	0450
3.0 mol. NaCl	6.02	23.23	0451
3.0 mol. NaCl	6.02	22.87	0452
3.0 mol. NaCl	8.00	30.55	0454
3.0 mol. NaCl	10.00	38.95	0456
3.0 mol. NaCl	12.00	54.31	0457
3.0 mol. NaCl	12.00	57.09	0458
3.0 mol. NaCl	14.00	67.00	0459
3.0 mol. NaCl	14.00	72.50	0460
3.0 mol. NaCl	16.00	74.61	0461
3.0 mol. NaCl	18.00	80.76	0462
3.0 mol. NaCl	20.00	83.08	0464
27.9 cc.			
4.0 mol. NaCl	20.00	61.82	0465
4.0 mol. NaCl	18.00	58.54	0466
4.0 mol. NaCl	16.00	50.56	0467
4.0 mol. NaCl	16.00	47.10	0468
4.0 mol. NaCl	14.00	41.81	0469
4.0 mol. NaCl	14.00	42.52	0470
4.0 mol. NaCl	12.00	37.70	0472
4.0 mol. NaCl	10.00	30.37	0473
4.0 mol. NaCl	10.00	33.77	0474
4.0 mol. NaCl	8.00	28.05	0475
4.0 mol. NaCl	8.00	26.50	0476
4.0 mol. NaCl	3.13	8.04	0479
4.0 mol. NaCl	2.00	4.64	0481

TABLE III.—HYDROLYSIS OF ETHYL ACETATE BY LITHIUM CHLORIDE.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. 25.0 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.0853 mol. LiCl	11.08	75.0	0299
0.0853 mol. LiCl	13.60	83.9	0300
0.0853 mol. LiCl	15.66	88.7	0301
0.0853 mol. LiCl	18.00	92.6	0302
0.0853 mol. LiCl	4.40	29.5	0303
0.0853 mol. LiCl	6.73	55.6	0304
0.0853 mol. LiCl	8.77	70.1	0305
0.0853 mol. LiCl	10.62	79.1	0306
0.0853 mol. LiCl	2.43	11.8	0307
0.427 mol. LiCl	11.08	96.6	0308
0.427 mol. LiCl	15.66	91.9	0310
0.427 mol. LiCl	18.00	94.7	0311
0.427 mol. LiCl	4.40	38.8	0312
0.427 mol. LiCl	6.73	65.3	0313
0.427 mol. LiCl	8.77	78.6	0314
0.427 mol. LiCl	10.62	94.6	0315
0.427 mol. LiCl	2.43	15.4	0316
0.8868 mol. LiCl	14.75	90.6	0317
0.8868 mol. LiCl	17.08	93.4	0318
0.8868 mol. LiCl	19.50	94.3	0319
0.8868 mol. LiCl	21.72	94.6	0320
0.8868 mol. LiCl	12.00	88.8	0321
0.8868 mol. LiCl	2.75	22.2	0322
0.8868 mol. LiCl	5.08	51.1	0323
0.8868 mol. LiCl	9.72	83.5	0324
0.8868 mol. LiCl	7.50	73.4	0325
2.034 mol. LiCl	14.75	89.1	0326
2.034 mol. LiCl	17.08	90.6	0327
2.034 mol. LiCl	19.50	93.1	0328
2.034 mol. LiCl	21.72	93.4	0329
2.034 mol. LiCl	12.00	85.5	0330
2.034 mol. LiCl	2.75	19.8	0331
2.034 mol. LiCl	5.08	46.4	0332
2.034 mol. LiCl	7.50	71.4	0333
2.034 mol. LiCl	9.72	81.5	0334
26.5 cc.			
3.13 mol. LiCl	3.00	14.5	0335
3.13 mol. LiCl	8.58	51.5	0336
3.13 mol. LiCl	10.75	62.0	0337
3.13 mol. LiCl	12.90	73.8	0338
3.13 mol. LiCl	5.72	29.1	0339
3.13 mol. LiCl	14.00	76.2	0340
3.13 mol. LiCl	16.20	79.1	0341
3.13 mol. LiCl	18.08	85.5	0342
3.13 mol. LiCl	21.20	88.7	0343
27.6 cc.			
5.015 mol. LiCl	3.00	5.2	0344
5.015 mol. LiCl	8.58	29.9	0345
5.015 mol. LiCl	10.75	32.6	0346
5.015 mol. LiCl	5.72	16.9	0348
5.015 mol. LiCl	14.00	38.8	0349
5.015 mol. LiCl	16.20	48.0	0350
5.015 mol. LiCl	18.08	56.4	0351
5.015 mol. LiCl	21.20	66.4	0352
33.1 cc.			
10.81 mol. LiCl	5.72	2.0	0353
10.81 mol. LiCl	10.75	6.9	0355
10.81 mol. LiCl	24.92	19.4	0356

TABLE IV.—HYDROLYSIS OF ETHYL ACETATE BY BARIUM CHLORIDE.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. 25.0 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.1 mol. BaCl$_2$	13.50	89.6	0121
0.1 mol. BaCl$_2$	15.33	91.6	0122
0.1 mol. BaCl$_2$	16.50	93.1	0123
0.1 mol. BaCl$_2$	18.45	91.9	0124
0.1 mol. BaCl$_2$	3.00	25.5	0125
0.1 mol. BaCl$_2$	4.88	42.6	0126
0.1 mol. BaCl$_2$	8.87	79.5	0128
0.1 mol. BaCl$_2$	10.63	85.1	0129
25.4 cc.			
0.5 mol. BaCl$_2$	13.50	92.3	0130
0.5 mol. BaCl$_2$	15.33	93.5	0131
0.5 mol. BaCl$_2$	16.50	93.1	0132
0.5 mol. BaCl$_2$	3.00	40.0	0134
0.5 mol. BaCl$_2$	4.88	64.5	0135
0.5 mol. BaCl$_2$	7.00	79.9	0136
0.5 mol. BaCl$_2$	8.87	84.7	0137
0.5 mol. BaCl$_2$	10.63	89.5	0138
25.6 cc.			
1.0 mol. BaCl$_2$	3.17	42.8	0139
1.0 mol. BaCl$_2$	5.42	71.0	0140
1.0 mol. BaCl$_2$	7.63	80.3	0141
1.0 mol. BaCl$_2$	8.20	82.7	0142
1.0 mol. BaCl$_2$	11.58	89.9	0143
1.0 mol. BaCl$_2$	11.58	90.3	0144
1.0 mol. BaCl$_2$	14.15	93.0	0145
1.0 mol. BaCl$_2$	9.42	83.9	0146
25.9 cc.			
1.5 mol. BaCl$_2$	2.57	27.5	0148
1.5 mol. BaCl$_2$	4.18	38.8	0149
1.5 mol. BaCl$_2$	6.22	54.3	0150
1.5 mol. BaCl$_2$	8.10	71.4	0151
1.5 mol. BaCl$_2$	10.78	76.3	0152
1.5 mol. BaCl$_2$	13.42	81.9	0154
1.5 mol. BaCl$_2$	15.07	83.4	0155
1.5 mol. BaCl$_2$	17.40	87.9	0156

TABLE V.—HYDROLYSIS OF ETHYL ACETATE BY CALCIUM CHLORIDE.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. 25.0 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.1 mol. CaCl$_2$	4.70	48.0	0237
0.1 mol. CaCl$_2$	6.63	67.3	0238
0.1 mol. CaCl$_2$	9.13	81.5	0239
0.1 mol. CalC$_2$	12.01	90.3	0240
0.1 mol. CaCl$_2$	3.00	24.6	0241
0.1 mol. CaCl$_2$	14.37	91.5	0242
0.1 mol. CaCl$_2$	17.10	92.3	0243
0.1 mol. CaCl$_2$	18.00	92.6	0244
0.489 mol. CaCl$_2$	3.27	43.7	0245
0.489 mol. CaCl$_2$	6.03	75.0	0246
0.489 mol. CaCl$_2$	8.32	85.1	0247
0.489 mol. CaCl$_2$	12.55	91.9	0248
0.489 mol. CaCl$_2$	13.27	42.0	0249
0.489 mol. CaCl$_2$	15.00	92.6	0250
0.489 mol. CaCl$_2$	18.10	92.6	0251
0.489 mol. CaCl$_2$	17.08	93.0	0252
0.489 mol. CaCl$_2$	10.15	88.7	0253
25.2 cc.			
1.023 mol. CaCl$_2$	3.43	25.8	0254
1.023 mol. CaCl$_2$	6.03	73.4	0255
1.023 mol. CaCl$_2$	8.32	73.4	0256
1.023 mol. CaCl$_2$	12.55	82.1	0257
1.023 mol. CaCl$_2$	15.00	90.3	0258
1.023 mol. CaCl$_2$	17.08	90.6	0259
1.023 mol. CaCl$_2$	19.25	92.3	0260
1.023 mol. CaCl$_2$	18.10	91.5	0261
1.023 mol. CaCl$_2$	10.15	81.7	0262
26.6 cc.			
2.041 mol. CaCl$_2$	2.58	7.1	0264
2.041 mol. CaCl$_2$	5.22	33.6	0265
2.041 mol. CaCl$_2$	7.52	46.8	0266
2.041 mol. CaCl$_2$	12.25	67.6	0267
2.041 mol. CaCl$_2$	14.72	75.3	0268
2.041 mol. CaCl$_2$	17.08	81.5	0269
2.041 mol. CaCl$_2$	19.48	83.7	0270
2.041 mol. CaCl$_2$	9.47	48.4	0271
27.6 cc.			
3.026 mol. CaCl$_2$	2.58	3.6	0272
3.026 mol. CaCl$_2$	5.22	7.7	0273
3.026 mol. CaCl$_2$	7.52	21.0	0274
3.026 mol. CaCl$_2$	12.25	29.9	0275
3.026 mol. CaCl$_2$	13.38	40.0	0276
3.026 mol. CaCl$_2$	14.72	41.6	0277
3.026 mol. CaCl$_2$	17.08	50.0	0278
3.026 mol. CaCl$_2$	19.48	51.9	0279
3.026 mol. CaCl$_2$	9.47	29.9	0280
28.8 cc.			
4.094 mol. CaCl$_2$	2.47	0.7	0281
4.094 mol. CaCl$_2$	9.27	12.1	0282
4.094 mol. CaCl$_2$	12.51	18.2	0283
4.094 mol. CaCl$_2$	16.38	25.0	0284
4.094 mol. CaCl$_2$	24.18	40.8	0285
4.094 mol. CaCl$_2$	27.95	55.6	0287
4.094 mol. CaCl$_2$	20.35	29.5	0288
4.094 mol. CaCl$_2$	5.69	1.5	0289

TABLE V (*continued*).

Solution. 29.2 cc.	Time. Hrs.	% hydrolysis.	Serial No.
4.696 mol. CaCl$_2$	2.47	0.7	0290
4.696 mol. CaCl$_2$	9.33	1.5	0291
4.696 mol. CaCl$_2$	12.57	6.8	0292
4.696 mol. CaCl$_2$	16.38	10.5	0293
4.696 mol. CaCl$_2$	20.35	14.3	0294
4.696 mol. CaCl$_2$	24.27	19.4	0295
4.696 mol. CaCl$_2$	28.07	19.8	0296
4.696 mol. CaCl$_2$	30.83	23.4	0297
4.696 mol. CaCl$_2$	5.73	1.1	0298

TABLE VI.—HYDROLYSIS OF ETHYL ACETATE BY STRONTIUM CHLORIDE.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. 25 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.1 mol. SrCl$_2$	3.07	25.4	0191
0.1 mol. SrCl$_2$	4.82	46.1	0192
0.1 mol. SrCl$_2$	6.35	66.1	0193
0.1 mol. SrCl$_2$	6.35	66.1	0194
0.1 mol. SrCl$_2$	7.26	70.1	0195
0.1 mol. SrCl$_2$	14.12	89.9	0196
0.1 mol. SrCl$_2$	11.15	81.3	0197
0.1 mol. SrCl$_2$	18.50	93.0	0198
25.3 cc.			
0.5 mol. SrCl$_2$	3.07	37.6	0199
0.5 mol. SrCl$_2$	4.82	63.3	0200
0.5 mol. SrCl$_2$	6.35	77.8	0201
0.5 mol. SrCl$_2$	6.35	75.8	0202
0.5 mol. SrCl$_2$	7.26	77.8	0203
0.5 mol. SrCl$_2$	11.15	88.3	0204
0.5 mol. SrCl$_2$	14.12	91.5	0205
0.5 mol. SrCl$_2$	11.15	89.1	0206
0.5 mol. SrCl$_2$	18.00	93.5	0207
25.4 cc.			
1.0 mol. SrCl$_2$	11.15	83.9	0208
1.0 mol. SrCl$_2$	13.75	83.5	0209
1.0 mol. SrCl$_2$	15.95	87.9	0210
1.0 mol. SrCl$_2$	19.50	91.1	0211
1.0 mol. SrCl$_2$	2.63	21.8	0212
1.0 mol. SrCl$_2$	5.83	52.7	0213
1.0 mol. SeCl$_2$	8.38	71.8	0214
1.0 mol. SrCl$_2$	12.13	84.8	0215
26.2 cc.			
1.0 mol. SrCl$_2$	11.50	43.2	0216
2.0 mol. SrCl$_2$	13.75	56.8	0217
2.0 mol. SrCl$_2$	15.95	58.8	0218
2.0 mol. SrCl$_2$	19.50	72.6	0219
2.0 mol. SrCl$_2$	2.63	12.1	0220
2.0 mol. SrCl$_2$	5.83	27.5	0221
2.0 mol. SrCl$_2$	8.38	36.8	0222

TABLE VI (*continued*).

Solution. 27.0 cc.	Time. Hrs.	% hydrolysis.	Serial No.
2.5 mol. SrCl$_2$	3.00	16.2	0228
2.5 mol. SrCl$_2$	6.63	31.5	0229
2.5 mol. SrCl$_2$	12.25	48.01	0230
2.5 mol. SrCl$_2$	18.00	67.5	0231

TABLE VII.—HYDROLYSIS OF ETHYL ACETATE BY CADMIUM CHLORIDE.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. 25.0 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.1 mol. CdCl$_2$	2.00	21.10	0375
0.1 mol. CdCl$_2$	3.47	46.50	0376
0.1 mol. CdCl$_2$	3.47	48.00	0377
0.1 mol. CdCl$_2$	7.00	80.40	0378
0.1 mol. CdCl$_2$	10.72	91.45	0380
0.1 mol. CdCl$_2$	10.72	91.06	0381
0.1 mol. CdCl$_2$	7.00	84.80	0382
25.3 cc.			
0.5 mol. CdCl$_2$	2.00	40.95	0385
0.5 mol. CdCl$_2$	3.50	67.80	0386
0.5 mol. CdCl$_2$	12.30	97.56	0387
0.5 mol. CdCl$_2$	8.70	92.50	0388
25.6 cc.			
1.159 mol. CdCl$_2$	2.20	52.64	0398
1.159 mol. CdCl$_2$	3.08	56.20	0399
1.159 mol. CdCl$_2$	5.75	88.20	0401
1.159 mol. CdCl$_2$	7.20	91.81	0402
1.159 mol. CdCl$_2$	11.00	95.08	0403
1.159 mol. CdCl$_2$	3.82	79.38	0404
1.159 mol. CdCl$_2$	15.32	94.50	0405
26.6 cc.			
2.0 mol. CdCl$_2$	2.20	39.69	0390
2.0 mol. CdCl$_2$	3.08	71.55	0391
2.0 mol. CdCl$_2$	3.82	78.06	0392
2.0 mol. CdCl$_2$	5.75	86.20	0393
2.0 mol. CdCl$_2$	7.20	91.67	0394
2.0 mol. CdCl$_2$	11.00	92.24	0395
2.0 mol. CdCl$_2$	15.32	94.83	0396
2.0 mol. CdCl$_2$	21.10	93.46	0397
27.1 cc.			
2.5 mol. CdCl$_2$	3.11	38.8	0412
2.5 mol. CdCl$_2$	2.17	34.5	0416
2.5 mol. CdCl$_2$	6.12	78.5	0483
2.5 mol. CdCl$_2$	7.42	87.3	0484
2.5 mol. CdCl$_2$	8.37	89.0	0486
2.5 mol. CdCl$_2$	10.00	94.6	0487
2.5 mol. CdCl$_2$	12.00	93.5	0488
2.5 mol. CdCl$_2$	14.00	94.5	0489

TABLE VIII.—HYDROLYSIS OF ETHYL ACETATE BY CADMIUM IODIDE.

1.2274 grams ethyl acetate. T = 100.0°.

Solution. 25.0 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.1 mol. CdI_2	2.13	31.30	0419
0.1 mol. CdI_2	4.58	65.68	0420
0.1 mol. CdI_2	5.07	69.86	0421
0.1 mol. CdI_2	8.67	89.51	0423
0.1 mol. CdI_2	10.82	96.30	0424
0.1 mol. CdI_2	12.82	98.09	0425
0.1 mol. CdI_2	15.98	98.59	0426
0.1 mol. CdI_2	6.48	90.50	0427
25.3 cc.			
0.5 mol. CdI_2	2.13	48.50	0428
0.5 mol. CdI_2	4.58	85.22	0429
0.5 mol. CdI_2	5.07	88.26	0430
0.5 mol. CdI_2	8.67	96.13	0431
0.5 mol. CdI_2	6.73	92.55	0432

TABLE VIII (*continued*).

Solution. 25.3 cc.	Time. Hrs.	% hydrolysis.	Serial No.
0.5 mol. CdI_2	10.82	96.66	0433
0.5 mol. CdI_2	12.82	94.80	0434
0.5 mol. CdI_2	15.98	97.09	0435
0.5 mol. CdI_2	3.03	84.94	0436
26.8 cc.			
1.0 mol. CdI_2	2.13	84.40	0437
1.0 mol. CdI_2	3.42	86.70	0438
1.0 mol. CdI_2	4.50	94.20	0439
1.0 mol. CdI_2	5.25	96.80	0440
1.0 mol. CdI_2	6.83	97.60	0441
1.0 mol. CdI_2	8.33	92.60	0442
1.0 mol. CdI_2	9.70	95.50	0444
1.0 mol. CdI_2	12.42	95.30	0445
1.0 mol. CdI_2	0.50	38.67	0446
1.0 mol. CdI_2	1.00	77.54	0447
1.0 mol. CdI_2	1.50	81.65	0448

Hydrolysis Effect Due to the Halides of Cadmium.—All the salts described up to this point are freely ionized, and it was thought that it would be of interest to determin the effect produced by a salt which is not noticeably ionized under the conditions of the experiment. The chloride and iodide of cadmium were selected as being the best adapted to this purpose.

As will be seen from Plates IX and XIV the accelerating effect of cadmium chloride, even at very small concentrations, is extremely large, while with increasing concentration the maximum effect is just passed at saturation. This large effect may possibly be due to a slight hydrolysis of the salt itself. In purifying cadmium chloride it was found that the solution still reacted faintly acid to litmus even after it had been boiled with a slight excess of cadmium hydroxide, changing blue litmus to a wine color. In apparent support of this view is the work of Long,[1] who put 500 grams of sugar and 42.958 grams of cadmium chloride in 250 cc. of water and found that "the rate of inversion is about as rapid as with 0.002 *N* hydrochloric acid at the same temperature and the same sugar concentration." Kahlenberg[2] has also noted the same thing. Obviously the work of Long does not prove that cadmium chloride is hydrolyzed, for its action is qualitatively the same as that of such salts as potassium and sodium chlorides, which are neutral in solution. It may be well to note at this point the fallacy of attempting to measure the hydrolysis of salts by means of their acceleration of sugar inversion or ester splitting, both of which reactions are accelerated by the simple salt effect of perfectly neutral, stable salts. Acceleration of these reactions by an

---

[1] THIS JOURNAL, **18**, 712.

[2] *Ibid.*, **21**, 15.

added salt may, therefore, mean either one of three things: (1) hydrolysis of the salt in question; (2) true salt effect; (3) some combination of the other two.

The extremely slight ionization of cadmium iodide renders this salt of particular interest. Plates X and XIV show that its accelerating effect is vastly greater than that of any other salt studied, though it is not possible to get a solution of sufficient concentration to even reach the maximum observed with all other salts. The behavior of cadmium iodide is also of interest in contrast with the fact that the iodide of potassium had a smaller accelerating effect than either the chloride or the bromide, and that it reaches its maximum at a smaller concentration than either of the latter salts.

Effect of Ionization on the Rate of Hydrolysis.—In order to determin whether the accelerating effect of the various salts bears any simple relation to their degree of ionization, the measurement of this latter property was undertaken.

For very dilute solutions the equation $\Lambda/\Lambda_0 = \alpha$ expresses the relationship with sufficient accuracy. It assumes, however, that the only factor producing a change in the value of Λ is the number of ions present, which involves the assumption that the viscosity remains unchanged upon dilution. Washburn has shown[1] that even as dilute solutions as 0.1 N may change in viscosity to such an extent as to introduce errors of as much as 8% in the value of α. As all of the solutions employed in the present study ranged from 0.1 molar to near saturation, a correction for the change in viscosity was obviously necessary. The viscosity measurements were made with the instrument described on an earlier page, and the degree of ionization as given by the ratio Λ/Λ_0 was multiplied by the relative viscosity V, the final expression being $\alpha = \Lambda/\Lambda_0 \times V$, in which α is the degree of ionization, Λ the equivalent conductivity at the dilution in question, Λ_0 the equivalent conductivity at infinit dilution, and V the viscosity relative to water at 100°. Conductivities were measured with the two cells already described.

The data secured have, of themselves, no particular interest, although their acquisition was accompanied by the usual difficulties of work at 100°. The accuracy attained was, of course, not of the same degree as that easily reached at room temperature, nor as that attained by Noyes at 100°. It was possible, however, to check successive readings within 1 or 2%—usually the former. The value of Λ_0 was obtained by extrapolation, using the equation $1/\Lambda = 1/\Lambda_0 + K(C\Lambda)^{n-1}$ in which K is a constant, C the equivalent concentration, and n a number not far from 1.5 in value, determined for each salt as described by Noyes.[2] Values

---

[1] THIS JOURNAL, 32, 1463.

[2] *Loc. cit.*, p. 50.

of Λ were obtained for three or four dilutions, at 0.05 molar, 0.01 molar, 0.005 molar, and 0.001 molar, and values of $1/\Lambda$ were plotted against $(C\Lambda)^{n-1}$, n being varied until it gave nearest a straight line. For the salts investigated n had the following values:

LiCl	1.3	$CaCl_2$	1.6	$BaCl_2$	1.5	CdI_2	1.53
NaCl	1.4	$SrCl_2$	1.4	$CdCl_2$	1.35	...	..

The final data will be found in Table X, which shows the conductivity data combined with the viscosity data given in Table IX. Plate XV shows the relations in graphical form. The viscometer was standardized at 100° by water, using Thorp and Roger's value of 28.3×10^{-4} dynes per cm.², and Matthiesen and Rosetti's value of 0.95863 for the density of water at that temperature. Time of flow of water was 24.8, 24.9, 24.9, 24.6, 24.8, 25.0, 24.9, 24.8, 24.9, 24.9. These readings give a mean of 24.86 with a deviation of 1.04%.

Since for any solution $\eta/\eta_{H_2O} = \dfrac{D \times T}{D_{H_2O} \times T_{H_2O}}$, the viscosity of any solution at this temperature and with this instrument will be $\eta = \dfrac{D \times T \times 28.3 \times 10^{-4}}{0.95863 \times 24.86} = D \times T \times 0.0001187$, in which the value 0.0001187 is the constant of the instrument. In the following tables, D is the density at 100°, obtained by the usual pyknometer method. The instrument was standardized at 25°, and by means of the coefficient of expansion of glass its volume at 100° was calculated. The value 25×10^{-6} was taken as the coefficient of cubical expansion of glass. T is the time of flow, η the viscosity in dynes per cm.², and η/η_{HO_2} the viscosity relative to water at 100°. An asterisk prefixed to a row denotes that the values in it were interpolated because of failure to determin the density.

The time recorded is the mean of from 5 to 10 readings, the smaller number being taken when temperature control was good and successive readings checked to within 0.2 or 0.3 second, while the larger number was taken when poor temperature regulation caused the readings to vary.

TABLE IX.—VISCOSITY OF SALT SOLUTIONS.

Solution. NaCl.	D.	T. (Secs.).	$\eta \times 10^4$.	$\eta/\eta_{H_2O} = V$.
4.0	1.1027	30.43	40.49	1.428
3.0	1.0678	28.84	36.57	1.291
2.0	1.0325	27.44	33.64	1.188
1.0	0.9959	26.25	31.04	1.095
*0.5	..	...	29.5	1.042
*0.1	..	...	28.66	1.914

TABLE IX (*continued*).

Solution.	D.	T. (Secs.).	$\eta \times 10^4$.	η/η_{H_2O} = V.
LiCl.				
0.0853	0.9584	25.09	28.55	1.006
0.427	0.9691	25.55	29.40	1.040
0.8867	0.9812	26.50	30.87	1.091
2.0337	1.0000	27.89	33.10	1.168
3.13	1.0355	30.82	37.89	1.338
5.015	1.0775	36.80	47.08	1.665
10.81	1.1787	69.36	97.07	3.420
$BaCl_2$.				
*0.1	..	...	28.80	1.180
*0.5	..	...	31.30	1.106
*1.0	..	...	36.00	1.271
1.5	1.2121	28.8	41.44	1.462
$CaCl_2$.				
*0.1	..	...	28.77	1.018
*0.5	..	...	31.30	1.106
1.008	1.0454	28.69	35.61	1.258
2.000	1.1220	33.51	44.64	1.575
3.026	1.2016	43.80	62.49	2.204
4.094	1.2781	60.36	91.53	3.230
4.696	1.3175	74.05	115.80	4.090
$SrCl_2$.				
*0.1	..	...	28.77	1.018
*0.5	..	...	31.30	1.106
1.0	1.0885	28.07	36.28	1.281
2.0	1.2137	32.40	46.69	1.647
2.5	1.2721	35.88	54.19	1.922
$CdCl_2$.				
*0.1	..	...	28.80	1.017
*0.5	..	...	30.50	1.077
1.159	1.1045	26.30	34.48	1.218
2.0	1.2448	28.61	42.29	1.429
CdI_2.				
*0.1	..	...	29.00	1.024
*0.5	..	...	32.00	1.103
1.0	1.2425	24.95	36.81	2.485

TABLE X.—DEGREE OF IONIZATION FROM COMBINED DATA OF CONDUCTIVITY AND VISCOSITY.

Solution.	Molar conc.	Λ.	Λ_0.	V.	α.
NaCl	4.0	151.3	362.0	1.428	59.6
	3.0	169.1	362.0	1.291	60.3
	2.0	193.7	362.0	1.188	63.3
	1.0	225.4	362.0	1.095	68.3
	0.5	248.9	362.0	1.042	73.6
	0.1	267.4	362.0	1.014	74.2

TABLE X (*continued*).

Solution.	Molar conc.	Λ.	Λ_0.	V.	α.
LiCl	10.81	39.06	396.0	3.42	33.8
	5.015	99.89	396.0	1.665	41.9
	3.13	127.9	386.0	1.338	43.1
	2.034	140.9	386.0	1.168	42.4
	0.887	203.2	396.0	1.091	56.0
	0.427	232.4	396.0	1.014	59.5
	0.0853	279.5	396.0	1.006	70.8
$BaCl_2$	1.5	137.5	416.0	1.462	48.3
	1.0	159.9	416.0	1.281	49.2
	0.5	192.0	416.0	1.106	51.0
	0.1	253.2	416.0	1.018	59.8
$SrCl_2$	2.5	99.0	388.0	1.922	49.0
	2.0	116.2	388.0	1.647	49.4
	1.0	155.1	388.0	1.281	51.3
	0.5	199.6	388.0	1.106	56.8
	0.1	260.9	388.0	1.018	66.2
$CaCl_2$	4.696	45.15	409.5	4.09	45.0
	4.094	55.4	409.5	3.23	43.6
	3.026	78.05	409.5	2.204	42.1
	2.000	117.5	409.5	1.575	45.2
	1.008	163.2	409.5	1.258	50.0
	0.5	196.4	409.5	1.106	53.1
	0.1	..	...	1.018	...
$CdCl_2$	2.0	20.15	325.5	1.494	9.25
	1.159	30.00	325.5	1.218	11.23
	0.5	52.90	325.5	1.103	17.93
	0.1	92.18	325.0	1.024	29.08
CdI_2	1.0	31.94	740.0	1.485	0.64
	0.5	40.50	740.0	1.103	0.60
	0.1	76.10	740.0	1.024	1.05

From the data of these tables several interesting relationships may be derived. The accelerating effect of lithium chloride is greater than that of sodium chloride (Plate XII); the degree of ionization is less. The chlorides of calcium, strontium, and barium all have a greater accelerating effect than either of the alkali chlorides; their degree of ionization is less. Cadmium chloride is the least ionized of any of the chlorides studied, yet it produces the greatest effect; while cadmium iodide, the least ionized of any of the salts investigated, produces the greatest effect of all.

Conclusions.

In the earlier article[1] a number of hypotheses were discussed which have been put forward to account for the effect produced by a neutral salt upon the velocity constant of various reactions. While it cannot be said that the data collected in this paper bring convincing evidence

---

[1] *Loc. cit.*, 897.

to the support of any one of these hypotheses, nevertheless the facts established demonstrate rather clearly that the final solution of the problem is to be sought in a specific effect of the non-ionized portion of the salt rather than in some function of the ions produced. To this extent our results are in accord with the recent work of A. A. Noyes, E. W. Washburn, J. Walker, and others, who attribute various abnormal effects of electrolytes to the non-ionized side of the equilibrium equation, rather than to the ions. In a recent contribution, published after this work was completed, Stieglitz[1] is inclined to take the same point of view as a basis for the discussion of the salt effect in hydrolysis phenomena among the imido ethers.

It is to be regretted that lack of time, as well as the inherent experimental difficulties, prevented any measurements of the concentration of the hydroxyl and hydrogen ions in the solutions employed and of the degree of hydrolysis of the salts present. Such measurement would have had an important bearing upon the problem, especially in connection with the hypothesis of Euler, namely, that at higher salt concentrations water is much more ionized than in dilute solutions, the increase in the concentrations of its ions increasing the velocity of hydrolysis.

If we admit that the hydrolysis of the ester is largely controlled by the concentration of the salt molecules, the cause of the maximum observed in these experiments finds an easy explanation. Not only does the concentration of the molecules increase as the total concentration rises, but the difficulty of meeting (*i. e.*, the viscosity) varies as well. Plate XV shows this very clearly. The observed maximum is, then, the resultant of two oppositly directed tendencies. On the one hand is the acceleration produced by the salt molecules which increases with concentration. On the other hand is the resistance offered to the meeting between the ester and the water with which it reacts; and when the viscosity becomes sufficiently great, the catalytic effect of the salt begins to diminish.

COLUMBUS, OHIO.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE RATE OF CONVERSION OF CINCHONINE TO CINCHOTOXINE.

(ON CATALYSES WITH WEAK ACIDS, IV.)[2]

BY H. C. BIDDLE AND LUDWIG ROSENSTEIN.

Received February 17, 1913.

Introduction.—The nature of the change of certain of the vegetable alkaloids to their toxic isomers has been the subject of recent investigations by Biddle[2] and later by Rabe.[3] It has been shown by the former that weak

---

[1] THIS JOURNAL, **34**, 1687.

[2] Biddle, *Science*, **32**, 486 (1910); *Ber.*, **45**, 526, 2832 (1912); THIS JOURNAL, **34**, 500 (1912); **35**, 273 (1913).

[3] Rabe, *Ber.*, **43**, 3300 (1910); **45**, 2927 (1912).