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THE CHANGE IN THE ORDER OF CATALYTIC ACTION  
OF LITHIUM CHLORIDE, SODIUM CHLORIDE,<sup>2997</sup>  
MAGNESIUM CHLORIDE, AND CALCIUM CHLORIDE<sup>23</sup>  
IN THE KETONIC SPLITTING OF  
ETHYL ACETOACETATE.

BY

RICHARD DWIGHT DUFF, B.S.

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A

THESIS

submitted to the faculty of the  
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI  
in partial fulfillment of the work required for the  
Degree of  
MASTER OF SCIENCE IN CHEMICAL ENGINEERING  
Rolla, Missouri  
1929

Approved by.....



Associate Professor of Chemistry

MSM  
HISTORICAL  
COLLECTION

## Preface

This investigation was undertaken at the suggestion of Dr. H. L. Dunlap and is a continuation of the work done by him on the neutral salt action in the ketonic splitting of ethyl acetoacetate.

The writer wishes to express his sincere thanks to Dr. H. L. Dunlap and to Professor E. A. Goodhue for helpful criticism and suggestions offered throughout the course of the work.

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The Change of Order in the Catalytic Action  
of the Neutral Salts Lithium Chloride,  
Sodium Chloride, Magnesium Chloride,  
and Calcium Chloride in the Ketonic  
Splitting of Ethyl Acetoacetate.

Introduction

The catalytic action of neutral salts on many reactions has been investigated under various conditions, and a large number of explanations have been put forward. In this work the catalytic action of normal solutions of lithium chloride, sodium chloride, magnesium chloride, and calcium chloride in the presence of .1 N. hydrochloric acid on the ketonic splitting of ethyl acetoacetate has been investigated at several temperatures between 80°C. and 95°C. An attempt has been made to explain the results obtained.

Historical Considerations

The name "catalytic force" was first applied by Berzelius<sup>1</sup> to the influence which certain

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1. Berzelius, Jahresber. fur Chem., 15, 237, (1836)

substances exert on reactions without being themselves changed.

There have been found a large number of reactions, such as the inversion of sucrose and the hydrolysis of esters, which are accelerated by the presence of an acid. Arrhenius<sup>2</sup> assigned the catalytic effect in such reactions entirely to the hydrogen ion. It had been previously found that equal concentrations of different acids showed different catalytic action, the more active mineral acids being the most effective. In working with the inversion of sugar in the presence of acetic acid, Arrhenius found that the reaction was greatly retarded by the addition of sodium acetate as would be expected from the law of mass action. This fact, in addition to his previous deductions concerning the dissociation of acids from conductivity data, led Arrhenius to believe that the catalytic effect of acids in such reactions was due to hydrogen ion.

Palmaer<sup>3</sup> later obtained results which did not support the explanation of catalytic effect as a

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2. Arrhenius, Z. physik. Chem., 5, 1, (1890)

3. Palmaer, Z. physik. Chem., 22, 492, (1894)

as a property of hydrogen ion. First, it was found that as the concentration of acid was increased the catalytic effect increased more rapidly than did the hydrogen ion concentration as shown by conductivity measurements, and second, it was found that the presence of certain neutral salts actually increased the catalytic action instead of decreasing it as would be required on the basis of the simple dissociation theory. This latter result, or neutral salt effect, has since been made the basis for numerous investigations, but no completely satisfactory and convincing explanation of it has yet been offered.<sup>4</sup>

Arrhenius<sup>5</sup> explained the anomalous neutral salt effect by assuming that the dissolved salts increased the degree of dissociation of the acid. Although this assumption seems to conflict with the usual ideas of dissociation, Arkadieu<sup>6</sup> and Åkerlöf<sup>7</sup> have found that the addition of neutral salts increases the hydrogen

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4. Rideal and Taylor, *Catalysis in Theory and Practice*, Macmillan, 1926, page 320.

5. Arrhenius, *Z. physik. Chem.*, 21, 1362, (1899)

6. Arkadieu, *Z. physik. Chem.*, 104, 192, (1923)

7. Åkerlöf, *Z. physik. Chem.*, 98, 260, (1921)

electrode potential and that this increase is proportional to the concentration of the salt. Among different salts, those which had the strongest tendency to form hydrates were found to have the greatest effect on the electrode potential.

Others explained neutral salt effect by assuming that the salt withdrew water from the solution, thus effecting a concentration of the acid. Numerous investigations<sup>8</sup> were carried out which seemed to support this theory.

Other investigators<sup>9</sup> obtained results which seemed to indicate that the undissociated acid molecule had catalytic effect as well as the

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8. Caldwell, Proc. Roy. Soc., 78 A, 272, (1906)  
Whympier, Proc. Roy. Soc., 79 A, 576, (1907)  
Armstrong and Watson, Proc. Roy. Soc., 79 A, 579, (1907)  
Worley, Proc. Roy. Soc., 87 A, 604, (1912)
9. Senter, J. Chem. Soc., 91, 460, (1907)  
Acree and Nirdlinger, Amer. Chem. Journ., 38, 489, (1907)  
Lapworth, J. Chem. Soc., 93, 2197, (1908)  
Goldschmidt, Amer. Chem. J., 48, 352, (1912)  
Taylor, J. Amer. Chem. Soc., 37, 551, (1915)  
Dawson and Reiman, J. Chem. Soc., 107, 857, (1915)



hydrogen ion. Snethlage<sup>10</sup> and Taylor<sup>11</sup> suggested that the greater the strength of the acid, the greater was the catalytic effect of the undissociated molecule compared to that of the ions.

Kendall<sup>12</sup> later amplified this dual theory of catalysis by assuming that there are a large number of catalytically active substances consisting of hydrates of the various ions and molecules present in a solution and that a number of complex equilibria are set up between these substances. These assumptions offer little aid in explaining neutral salt action as we have at present no means of determining the concentrations of the various possible substances.

There are in the literature a large number of references which, although they do not all bear directly on neutral salt effect, will be of value in explaining and interpreting the results obtained in this work. The more important of these will be cited.

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10. Snethlage, Z. Elektrochem., 18, 539, (1912)

Snethlage, Z. physik. Chem., 85, 211, (1913)

11. Taylor, Z. Elektrochem., 20, 202, (1914)

12. Kendall, Proc. Nat. Acad. Sci., 7, 56, (1921)

In a study of the effect of salts on ester hydrolysis, Holmes and Jones<sup>13</sup> found that salts with water of hydration had the greatest effect.

Manning<sup>14</sup> found that non-electrolytes exerted little influence on the rate of hydrolysis of esters, indicating that the hydration of the solute was not an effective factor in such reactions. He also found that the addition of potassium sulfate retarded the reaction while addition of the chlorides of the alkali and alkaline earth metals accelerated the reaction. Kellog<sup>15</sup> obtained similar results.

With the reaction between iodine and acetone, Rice and Lemkin<sup>16</sup> found that the addition of salts of strong acids with strong acids accelerated the reaction while addition of potassium sulfate to sulfuric acid retarded the reaction. They also found that the temperature coefficient was unaffected by addition of a salt of a strong acid to a strong acid but was affected by the addition of potassium sulfate to sulfuric acid.

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13. Holmes and Jones, *J. Amer. Chem. Soc.*, 38, 105, (1916)

14. Manning, *J. Chem. Soc.*, 119, 2079, (1921)

15. Kellog, *J. Amer. Chem. Soc.*, 31, 403, (1909)

Kellog, *J. Amer. Chem. Soc.*, 35, 396, (1913)

16. Rice and Lemkin, *J. Amer. Chem. Soc.*, 45, 1896, (1923)

Dahr<sup>17</sup> investigated the effect of neutral salts on the reaction between oxalic acid and chromic acid, sodium formate and iodine, sodium formate and mercuric chloride, and between sodium formate and silver nitrate. He found that the neutral salt effect was more pronounced in dilute solutions, that addition of neutral salts did not change the temperature coefficients of the reactions, and that the influence of sulfates was the opposite to that of chlorides.

Spohr<sup>18</sup> found that with the inversion of sucrose, additions of chlorides and bromides to hydrochloric and hydrobromic acids accelerated the reaction, while the addition of potassium sulfate to sulfuric acid retarded the reaction.

McBain and Kam<sup>19</sup> found that the effect of neutral salts on the partial vapor pressure of acetic acid solutions was independent of the concentration of the acid and that chlorides of the alkali metals raised

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17. Dahr, J. pract. Chem., 2, 32.

18. Spohr, Z. anorg. Chem., 128, 229, (1923)

19. McBain and Kam, J. Chem. Soc., 115, 1332, (1919)

the vapor pressure while sodium acetate and sodium sulfate lowered it.

Sziskovski<sup>20</sup> found that the alkali sulfates changed the color of dilute acid solutions of methyl orange to the alkaline side, while alkali halides and nitrates had the opposite effect.

Kiss and Bossanyi<sup>21</sup> investigated the effect of neutral salts on the reaction between iodides and persulfates. They found no change in the temperature coefficient of the reaction in the presence of neutral salts, and that the velocity of the reaction increased linearly with increasing neutral salt concentration.

Schmid and Olsen<sup>22</sup> investigated the action of neutral salts on the hydrolysis of cyanamide. They found that the specific action of neutral salts was independent of the temperature and were unable to explain their results on any dehydration theory.

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20. Sziskovski, Z. physik. Chem., 78, 426, (1912)

21. Kiss and Bossanyi, Rec. trav. chim., 47, 619, (1928)

Kiss and Bossanyi, Z. physik. Chem., 134, 26, (1928)

22. Schmid and Olsen, Z. physik. Chem., 124, 97, (1926)

Dawson<sup>23</sup> and his associates have investigated the action of neutral salts on a large number of catalytic reactions. Their treatment of the subject is largely mathematical and catalysis in the presence of neutral salts is explained as being due to the sum of the catalytic effects of hydrogen ion, acid anion, hydroxyl ion, and undissociated acid molecules.

Bowe<sup>24</sup> investigated the rate of hydrolysis of ethyl acetate and the inversion of sugar in the

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23. Dawson, J. Chem. Soc., 2282, (1926)  
 Dawson, J. Chem. Soc., 2872, (1926)  
 Dawson, J. Chem. Soc., 3166, (1926)  
 Dawson, J. Chem. Soc., 213, (1927)  
 Dawson, J. Chem. Soc., 756, (1927)  
 Dawson, J. Chem. Soc., 458, (1927)  
 Dawson, J. Chem. Soc., 1146, (1927)  
 Dawson, J. Chem. Soc., 1290, (1927)  
 Dawson, Hall, and Key, J. Chem. Soc., 2844, (1928)  
 Dawson, Chem. and Ind., 46, 897, (1927)  
 Dawson and Hoskins, Proc. Leeds Phil. Lit. Soc.  
 Sci. Sect. 1, 108, (1926)
24. Bowe, J. Phys. Chem., 31, 291, (1927)

presence of hydrochloric and hydrobromic acids and their neutral salts. He also investigated the hydrogen ion activity in these solutions and found a general agreement between these results and the rates of reaction he determined. He concluded that the observed effects of neutral salts were probably due to depolymerization of water in the solutions.

Kolthoff and Bosch<sup>25</sup> investigated the hydrogen ion activity of solutions containing neutral salts. They found that addition of neutral salts to a solution first decreased then increased the hydrogen ion activity as the salt concentration was increased. Przeborovskii, Fleissner, and Pofova<sup>26</sup> obtained similar results.

French<sup>27</sup> in working on the decomposition of hydrogen peroxide by iodide ion in the presence of neutral salts found wide variations between the

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25. Kolthoff and Bosch, Rec. trav. chim., 46, 430, (1927)

Kolthoff and Bosch, Rec. trav. chim., 47, 558, (1928)

26. Przeborovskii, Fleissner, and Pofova, Z. anorg. allgem. Chem., 167, 364, (1927)

x 27. French, J. Phys. Chem., 32, 401, (1928)

catalytic effects of different salts. He was unable to explain these variations except by assuming the presence of several different catalysts in the solution.

Numerous other investigations of the effect of neutral salts on the rate of reaction might be mentioned. The investigators agree on only one thing, the fact that there is no apparent generalization which will explain the effects of neutral salts in all cases. The explanations offered cover only small portions of data.

The work of several investigators indicates that addition of a neutral salt to a solution causes a change in the fundamental nature of the solution. Neutral salts have been found by Darmois<sup>28</sup> to affect the optical rotatory power of tartaric acid. Penneycuick<sup>29</sup> adduces good evidence for the hypothesis that in water the molecules are strongly associated and that such association is likely to be disturbed on addition of a salt. Leitner<sup>30</sup> has found that the specific heat of salt solutions varies widely with the temperature.

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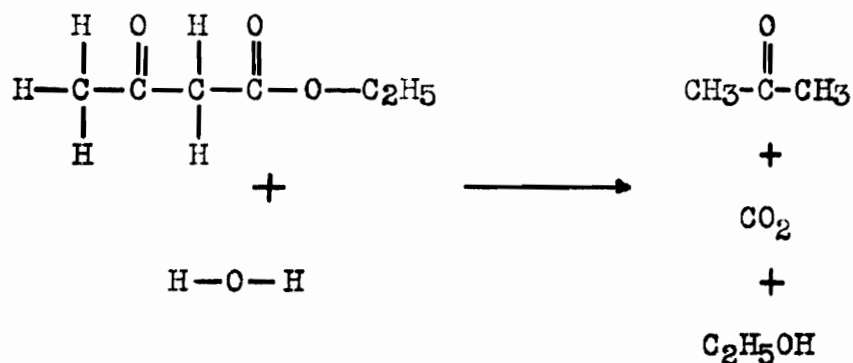
28. Darmois, Ann. phys., 10, 70, (1928)

29. Penneycuick, J. Phys. Chem., 32, 1681, (1928)

30. Leitner, Arch. Warmewirt, 9, 233, (1928)

In a determination of the extent of hydration of ions, Baborovsky and Velisek<sup>31</sup> found that in normal solution the degree of hydration of the lithium ion was 14 and that of the sodium ion was 9 as compared with 1 for hydrogen ion. Their determinations were based on conductivity and activity data.

Dunlap<sup>32</sup> used ethyl acetoacetate in studying the neutral salt effect of the alkali and alkaline earth chlorides on the hydrolysis of this ester by hydrochloric acid. Ethyl acetoacetate is decomposed thus in the presence of acids:




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31. Baborovsky and Velisek, Chem. Listy., 21, 227, (1927)

32. Dunlap, The Neutral Salt Effect of the Alkali and Alkaline Earth Chlorides upon Hydrochloric Acid in the Ketonic Splitting of Ethyl Acetoacetate. Unpublished dissertation presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Ohio State University, (1925).



Burki<sup>33</sup> found that the acetoacetic acid formed was completely decomposed at temperatures above 40°C. and Dunlap could find no indication of the presence of the free acid in his experiments. The ester thus possesses a distinct advantage for use in investigating neutral salt effect on the rate of hydrolysis, since the fraction of the ester decomposed can be determined by measuring the volume of carbon dioxide evolved in a known time. The rate of reaction can thus be determined more accurately than by the usual<sup>34</sup> method of removing a sample at intervals and determining the progress of the reaction by titrating the acid formed.

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33. Burki, *Helv. Chem. Acta.*, 1, 231, (1918)

34. Ostwald, *J. pract. Chem.*, 28, 449, (1893)

### Statement of the Problem

The object of this investigation has been to find the conditions of temperature at which the order of the catalytic action of the salts studied changes, and to determine whether there is an abrupt change in the catalytic action of any of the salts with temperature. The hydrolysis was carried out in a solution .1 N. in hydrochloric acid and normal with respect to the neutral salts. The salts used were lithium chloride, sodium chloride, magnesium chloride, and calcium chloride. The rate of reaction was investigated at 80°, 85°, 90°, and 95° for all the salts and at several intermediate temperatures for some of the salts.

The volume of carbon dioxide formed was measured at five minute intervals as a means of determining the rate of reaction. Since tests by Burki<sup>33</sup> and Dunlap<sup>32</sup> failed to reveal the presence of free acetoacetic acid, it can be safely assumed that this acid is immediately decomposed into acetone and carbon dioxide and therefore that the volume of carbon dioxide at any time will indicate the extent to which reaction has taken place.

### Experimental Part

#### Materials Used

The ethyl acetoacetate was obtained from the Eastman Kodak Company and was redistilled under reduced pressure, only the middle portion of the distillate being retained for use. The ester was stored in colored, glass stoppered bottles. Care was taken not to expose the ester to the action of air for too long a time before use.

The absolute ethyl alcohol used was dehydrated over lime and anhydrous copper sulfate in the usual manner and was stored in a glass stoppered bottle.

The lithium chloride, magnesium chloride, and calcium chloride were Baker's Analyzed Chemically Pure salts. The sodium chloride was an ordinary grade of salt purified by twice precipitating from water by means of hydrogen chloride, washing with water, and igniting at dull red heat. The salts were made up with distilled water into approximately 5 N. solutions. These solutions were allowed to stand for a few days and the slight amount of sediment formed was filtered off. The solutions were carefully tested for neutrality and were found to be neutral to litmus, basic to methyl orange and

acid to phenolphthalein. The normality of the salt solutions was determined gravimetrically by precipitating and weighing silver chloride. These values were later checked by titrating with a silver nitrate solution standardized against pure sodium chloride by Mohr's method. Aliquot portions of these solutions were used for making up the reaction mixture. The salt solutions were stored in glass stoppered bottles.

A sample of C.P. hydrochloric acid was tested and found to contain an inappreciable amount of non-volatile matter. This acid was made up with distilled water to an approximately normal solution and was standardized by precipitating and weighing silver chloride. This value was checked by titration against pure sodium carbonate using methyl orange indicator.

The distilled water was from the laboratory still and was tested to insure the absence of chlorides and sulfates.

#### Apparatus

The apparatus was essentially the same as that described by Goodhue and Dunlap<sup>35</sup> except for a few

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35. Goodhue and Dunlap, J. Amer. Chem. Soc., 50, 1916, (1928)

minor improvements. The thermostat was a galvanized iron tank surrounded by a wooden box containing asbestos insulation. The thermostat was heated by an electric hot plate placed beneath it and by two 500 watt immersion heaters and a 500 watt lamp immersed in the water in the thermostat. The lamp and hot plate were only used to bring the thermostat up to the desired temperature, the two immersion heaters being sufficient to maintain this temperature after it had once been reached. The immersion heaters were connected in a make and break circuit operated by a relay actuated by a mercury-xylene regulator. This device served to maintain the bath temperature constant within  $.1^{\circ}$  C. The water in the thermostat was covered with a layer of paraffin oil to cut down evaporation. The water in the thermostat was continuously circulated downward by a motor driven stirrer.

The flasks used for containing the reaction mixture were specially made of pyrex glass. They were of the flat bottomed type and had a capacity of about 200cc. The necks were approximately four and one half inches long and one inch in diameter. These flasks were connected with the condenser(as shown in Figure 1)

by a two hole rubber stopper into which was fitted the condenser tube and a glass rod which served to drop the vial of ester into the flask at the start of the reaction. The assembled flask and twelve inch condenser were firmly attached to a wooden frame by means of a stirrup, clamp, and rubber bands. This frame was suspended at the top (as shown in Figure 1) and the lower part connected to a pivoted arm from a pulley.<sup>36</sup> In operation this gave the flask motion about a circle three inches in diameter, serving to agitate the contents of the flask. About 50 grams of glass beads were placed in the flask. These aided in the agitation and prevented the vial from breaking the flask when it was dropped in. The condenser was necessary to prevent loss of alcohol and acetone from the flask during the reaction. The condensers had a side arm at the top provided with a stopcock. This served as a means for equalizing the pressure inside and outside the apparatus at the beginning of the reaction. The other opening at the top of the condenser was connected to the gas measuring apparatus by means of pure gum tubing and 1.5 millimeter glass tubing.

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36. Lueck, J. Amer. Chem. Soc., 44, 757, (1922)

The gas measuring apparatus (Figure 2) was a modified Blier-White chain of bulbs type.<sup>37</sup> The reaction flask was connected through the condenser, tubing, and a four way manifold to a 50cc. burette and two chains of ten bulbs each. The bulbs had capacities of approximately 50cc. each, and were carefully calibrated by weighing the water delivered. The proper corrections<sup>38</sup> for thermal expansion of glass and water and for air weighing were applied so that the capacity of each bulb represented the true volume contained at 20°C. For convenience in making readings, the top bulb of each chain was labeled with its own capacity, the second bulb with the capacity of the first plus the capacity of the second and so on. The bottom of each chain of bulbs and the burette were connected by rubber tubing to leveling bulbs. In the case of the chains of bulbs a stopcock was inserted between the leveling bulb and the chain of bulbs as shown in Figure 2. During the reaction, when 50cc. of gas had collected in the burette, it could be run over into one of the

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✓ 37. White's Fuel and Gas Analysis, page 376.

✓ 38. Bureau of Standards, Circular No. 19

chains of bulbs by properly adjusting the leveling bulbs and opening the stopcock. The volume of gas at any time during the reaction was equal to the volume contained in the chain of bulbs plus that contained in the burette. Thus an error in making any one reading had no effect on subsequent readings. The leveling liquid used was a five percent solution of sulfuric acid in water with a few drops of methyl orange added to facilitate reading. At the beginning of a reaction this liquid was saturated with carbon dioxide and the temperature of the gas measuring apparatus maintained constant within a degree or two during the reaction so that practically no gas would be dissolved or evolved by the leveling liquid. The apparatus contained duplicate sets of gas measuring apparatus and reaction flasks so that two determinations could be run simultaneously.

The bulbs and burette were inclosed in a box having two opposite plate glass sides. The temperature was maintained practically constant during a determination by circulating the water from the condensers through the box.



The vials used for introducing the ester were one dram homeopathic vials. These were loosely capped with the ends cut from similar vials to prevent contamination of the ester by distillate before the start of a reaction. Four glass rods approximately one millimeter in diameter were placed in the vial with the ester to aid in getting an immediate and uniform flow of liquid from the vial on starting the reaction.

Two determinations were run at the same time. The flasks, condensers, and gas measuring apparatus were as nearly alike as it was possible to make them. The pulleys to which the shaker arms were attached were the same diameter and were driven from the same shaft. The shaker arms were attached at the same distance from the center of the pulleys and the pivot posts for these arms were the same distance from the center of the pulleys. This arrangement gave each flask the same agitation. This is important as variations in shaking affect the rate of reaction.

#### Experimental Procedure

About 50 grams of carefully cleaned and dried glass beads were placed in the flask and enough of the standard salt and hydrochloric acid solutions

were run in from a burette to make 50cc. of solution .1 N. in hydrochloric acid and 1 N. in the salt. Sufficient water to make the volume of the solution 45.8 cc. was then run in from a burette. 1cc. of ethyl alcohol was added from a pipette. With the addition of 3.2 cc. of ester at the start of the reaction, the total volume of the solution was 50cc.

3.2527 grams of ethyl acetoacetate (one half molar in all determinations was weighed into one of the vials containing four glass rods. The vial was capped and placed on the trip rod in the neck of the flask and the stopper securely seated in the flask. The flask and condenser were then fastened to the frame as shown in Figure 1 by means of the stirrup, clamp, and rubber bands. Proper adjustment of flask, condenser, vial, and trip rod is necessary in order to get an accurately timed start. Obtaining a satisfactory adjustment requires considerable experience.

The temperature of the thermostat was adjusted to the desired point and the frames with attached flasks and condensers placed in position. Water connections were immediately made to the condensers.

and the agitating arms were fastened to the frames as shown in the diagram. Connections were made to the gas measuring apparatus and the apparatus tested for leaks. These operations required about fifteen minutes and care was taken not to prolong this time. Agitation of one of the flasks was then started and four minutes later the vial containing the ester was dropped into the solution and the stopcock on the side arm at the top of the condenser was simultaneously closed. The time of dropping the vial into the solution was noted and constituted the zero minute of the reaction from which all time intervals were measured. Readings of the volume of gas were made every five minutes during the reaction. The data was recorded under the headings reading number, time, volume of gas evolved, and temperature of the water surrounding the gas measuring bulbs. A fifth column was left vacant to be filled in later with the volume of gas corrected to standard conditions. The second flask was started two minutes after the first and the same procedure followed. Barometer readings were made at the start of the reaction and every hour thereafter. The observed pressure was corrected for temperature, latitude, and height

above sea level and this corrected value used in calculating the volume of gas at standard conditions. The correction for vapor pressure was obtained from vapor pressure tables for pure water. This was probably slightly different from the vapor pressure of the solution over which the gas was collected but the same corrections were made in all determinations.

#### Data

The following Tables (II to XXVII) show the volume of gas evolved at five minute intervals at various temperatures using normal salt and .1 N. hydrochloric acid. Table I for .1 N. hydrochloric acid alone at 90° is included for reference. Most of the values given were checked for at least two determinations. Where several runs were made, the values in the tables represent averages. All times are given in minutes and all volumes in cubic centimeters. Plates I and II represent the times plotted as abscissa and the volume of gas as ordinate. Several of the determinations at intermediate temperatures were omitted from the graphs for the sake of clearness. The values given in Tables II to XXVII were carefully plotted on a

large scale (four times that used in Plates II and II). The time taken to evolve 300, 350, 400, and 450cc. of gas was read off the large scale drawings for each of the salts at each temperature run. These values are shown in Tables XXVIII to XXXI. This data is shown graphically on Plate III, the time taken to produce a given volume of gas is plotted against the temperature for each salt used. Therefore the point at which two of these curves intersect corresponds to the temperature at which the two salts have the same catalytic effect.

TABLE I  
Effect of Various Catalysts on the Hydrolysis of  
Ethyl Acetoacetate at Different Temperatures

90°

.1 N. HCl (Alone)

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	444.7
2	5	28.9	21	100	454.1
3	10	66.2	22	105	465.7
4	15	102.0	23	110	476.4
5	20	137.3	24	115	484.2
6	25	167.9	25	120	494.1
7	30	196.9	26	125	504.3
8	35	225.6	27	130	514.0
9	40	250.8	28	135	521.2
10	45	275.8	29	140	527.8
11	50	296.8	30	145	532.8
12	55	320.8	31	150	536.6
13	60	338.1	32	155	540.8
14	65	356.2	33	160	544.0
15	70	372.9	34	165	548.0
16	75	390.7	35	170	551.0
17	80	408.3	36	175	554.0
18	85	421.3	37	180	556.0
19	90	433.0	38	185	557.7
			39	190	558.8

TABLE II

80°

1 N.LiCl

.1 N.HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	19	90	327.9
2	5	10.1	20	95	340.3
3	10	28.9	21	100	355.7
4	15	53.3	22	105	364.8
5	20	76.8	23	110	375.2
6	25	104.9	24	115	381.1
7	30	122.8	25	120	391.0
8	35	144.9	26	125	399.9
9	40	166.1	27	130	408.8
10	45	184.8	28	135	418.5
11	50	203.9	29	140	427.6
12	55	222.1	30	145	435.3
13	60	238.4	31	150	442.6
14	65	254.9	32	155	449.7
15	70	271.0	33	160	456.8
16	75	285.6	34	165	463.6
17	80	299.7	35	170	469.8
18	85	314.1	36	175	475.0

TABLE III

82°

1 N. LiCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	376.3
2	5	13.4	21	100	388.4
3	10	40.3	22	105	399.8
4	15	64.2	23	110	410.8
5	20	93.9	24	115	420.9
6	25	120.1	25	120	434.9
7	30	145.9	26	125	441.7
8	35	169.5	27	130	452.1
9	40	192.0	28	135	454.7
10	45	213.4	29	140	464.5
11	50	233.8	30	145	474.5
12	55	251.5	31	150	482.3
13	60	272.0	32	155	487.5
14	65	288.3	33	160	493.4
15	70	302.5	34	165	499.1
16	75	322.8	35	170	504.9
17	80	335.9	36	175	512.9
18	85	350.0	37	180	515.1
19	90	363.6			



TABLE IV

83°

1 N. LiCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	389.7
2	5	15.6	21	100	401.4
3	10	45.3	22	105	413.0
4	15	75.1	23	110	423.2
5	20	102.9	24	115	432.6
6	25	129.0	25	120	441.2
7	30	156.5	26	125	449.4
8	35	181.5	27	130	----
9	40	203.5	28	135	466.4
10	45	225.4	29	140	473.2
11	50	246.7	30	145	480.2
12	55	267.1	31	150	486.9
13	60	284.9	32	155	----
14	65	302.1	33	160	498.7
15	70	318.0	34	165	503.8
16	75	338.2	35	170	507.6
17	80	348.2	36	175	512.6
18	85	363.5	37	180	517.5
19	90	377.3			

TABLE V

83.5°

1 N. LiCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	17	80	354.7
2	5	15.2	18	85	369.3
3	10	41.8	19	90	382.0
4	15	73.0	20	95	394.3
5	20	103.0	21	100	405.7
6	25	131.1	22	105	418.9
7	30	157.1	23	110	429.3
8	35	181.6	24	115	438.4
9	40	205.6	25	120	449.2
10	45	228.2	26	125	458.0
11	50	248.8	27	130	466.1
12	55	268.9	28	135	474.0
13	60	288.2	29	140	481.5
14	65	305.9	30	145	488.4
15	70	324.0	31	150	495.3
16	75	339.4	32	155	500.9

TABLE VI

84°

1 N. LiCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	414.1
2	5	20.2	21	100	425.8
3	10	52.7	22	105	437.2
4	15	85.5	23	110	448.3
5	20	115.8	24	115	457.3
6	25	144.3	25	120	465.0
7	30	171.1	26	125	473.4
8	35	196.8	27	130	481.7
9	40	221.7	28	135	489.1
10	45	244.4	29	140	495.0
11	50	266.1	30	145	501.5
12	55	288.1	31	150	507.0
13	60	306.1	32	155	513.2
14	65	325.3	33	160	518.9
15	70	341.4	34	165	524.0
16	75	356.9	35	170	529.0
17	80	373.2	36	175	534.2
18	85	387.0	37	180	538.6
19	90	401.2			

TABLE VII

85°

1 N. LiCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	423.7
2	5	19.3	21	100	437.0
3	10	54.1	22	105	448.3
4	15	88.4	23	110	458.8
5	20	119.9	24	115	468.3
6	25	150.1	25	120	476.9
7	30	178.6	26	125	485.3
8	35	204.4	27	130	492.6
9	40	231.0	28	135	498.9
10	45	253.8	29	140	506.2
11	50	277.3	30	145	512.2
12	55	298.3	31	150	518.1
13	60	320.8	32	155	522.9
14	65	335.9	33	160	528.7
15	70	354.1	34	165	533.4
16	75	370.1	35	170	538.5
17	80	385.3	36	175	542.6
18	85	398.5	37	180	546.3
19	90	412.0			

TABLE VIII

90°

1 N. LiCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	17	80	463.3
2	5	38.0	18	85	477.6
3	10	86.0	19	90	490.4
4	15	128.0	20	95	500.5
5	20	165.2	21	100	509.9
6	25	205.7	22	105	518.0
7	30	242.0	23	110	527.1
8	35	274.0	24	115	534.5
9	40	301.0	25	120	541.3
10	45	330.9	26	125	546.1
11	50	353.4	27	130	551.9
12	55	376.4	28	135	556.9
13	60	396.0	29	140	564.0
14	65	415.0	30	145	566.2
15	70	432.8	31	150	569.6
16	75	448.5			

TABLE IX

94°

1 N. LiCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	14	65	457.2
2	5	51.5	15	70	472.3
3	10	110.5	16	75	485.6
4	15	163.8	17	80	494.9
5	20	211.8	18	85	505.2
6	25	254.2	19	90	514.9
7	30	291.7	20	95	523.3
8	35	323.9	21	100	530.7
9	40	353.8	22	105	537.5
10	45	379.7	23	110	542.3
11	50	402.8	24	115	547.6
12	55	423.2	25	120	552.5
13	60	441.5	26	125	556.3

TABLE X

80°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	19	90	331.9
2	5	12.7	20	95	344.4
3	10	33.6	21	100	356.8
4	15	59.3	22	105	368.1
5	20	80.6	23	110	378.6
6	25	107.0	24	115	385.8
7	30	128.7	25	120	395.5
8	35	150.7	26	125	405.2
9	40	170.8	27	130	414.3
10	45	190.8	28	135	422.8
11	50	209.5	29	140	431.8
12	55	227.5	30	145	439.2
13	60	244.3	31	150	449.5
14	65	260.6	32	155	453.9
15	70	276.0	33	160	460.8
16	75	294.3	34	165	468.1
17	80	305.0	35	170	474.3
18	85	319.1	36	175	482.1

TABLE XI

82°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	384.5
2	5	16.9	21	100	396.9
3	10	46.6	22	105	408.2
4	15	74.7	23	110	419.4
5	20	101.5	24	115	429.1
6	25	128.2	25	120	439.3
7	30	152.3	26	125	449.5
8	35	176.0	27	130	457.9
9	40	198.8	28	135	466.2
10	45	219.9	29	140	476.4
11	50	240.2	30	145	486.6
12	55	259.9	31	150	490.7
13	60	278.6	32	155	498.7
14	65	265.2	33	160	505.5
15	70	312.4	34	165	511.7
16	75	328.4	35	170	517.6
17	80	343.3	36	175	523.8
18	85	357.7	37	180	527.2
19	90	377.2			



TABLE XII

83°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	397.3
2	5	17.5	21	100	409.3
3	10	48.4	22	105	420.4
4	15	77.8	23	110	431.3
5	20	106.0	24	115	439.1
6	25	132.5	25	120	447.1
7	30	159.0	26	125	458.9
8	35	184.1	27	130	467.7
9	40	206.7	28	135	475.9
10	45	----	29	140	483.8
11	50	250.8	30	145	490.8
12	55	270.8	31	150	497.9
13	60	290.3	32	155	502.9
14	65	307.5	33	160	----
15	70	325.5	34	165	513.1
16	75	341.1	35	170	518.7
17	80	355.9	36	175	523.2
18	85	370.8	37	180	528.4
19	90	384.4			

TABLE XIII

83.5°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	17	80	358.2
2	5	15.6	18	85	372.3
3	10	45.6	19	90	385.5
4	15	75.0	20	95	397.9
5	20	104.2	21	100	409.6
6	25	131.6	22	105	422.0
7	30	158.8	23	110	433.1
8	35	185.4	24	115	443.7
9	40	208.4	25	120	453.0
10	45	231.1	26	125	462.2
11	50	252.4	27	130	470.8
12	55	273.1	28	135	479.5
13	60	291.5	29	140	487.1
14	65	308.8	30	145	494.1
15	70	327.4	31	150	501.0
16	75	342.9	32	155	506.6

TABLE XIV

84°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	412.3
2	5	19.8	21	100	423.8
3	10	52.5	22	105	436.1
4	15	82.8	23	110	447.0
5	20	114.7	24	115	456.8
6	25	143.7	25	120	466.0
7	30	170.3	26	125	474.7
8	35	196.8	27	130	482.8
9	40	219.9	28	135	489.7
10	45	243.4	29	140	497.0
11	50	265.9	30	145	503.0
12	55	285.5	31	150	509.3
13	60	305.0	32	155	515.1
14	65	323.8	33	160	521.2
15	70	340.4	34	165	526.4
16	75	355.6	35	170	533.7
17	80	371.2	36	175	536.7
18	85	385.7	37	180	540.9
19	90	399.0			

TABLE XV

85°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	426.1
2	5	21.0	21	100	438.1
3	10	56.7	22	105	448.5
4	15	91.3	23	110	459.5
5	20	122.7	24	115	469.4
6	25	152.6	25	120	478.1
7	30	181.2	26	125	486.8
8	35	206.7	27	130	495.5
9	40	233.2	28	135	500.9
10	45	255.9	29	140	507.6
11	50	279.0	30	145	514.3
12	55	299.1	31	150	519.4
13	60	318.0	32	155	526.5
14	65	337.7	33	160	532.0
15	70	355.4	34	165	536.5
16	75	370.6	35	170	541.0
17	80	385.4	36	175	545.2
18	85	399.5	37	180	549.2
19	90	413.0			

TABLE XVI

90°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	17	80	457.1
2	5	35.2	18	85	470.5
3	10	81.0	19	90	488.9
4	15	126.2	20	95	494.7
5	20	165.7	21	100	504.4
6	25	201.9	22	105	513.3
7	30	235.0	23	110	521.5
8	35	265.0	24	115	528.2
9	40	294.9	25	120	535.0
10	45	322.8	26	125	540.3
11	50	342.9	27	130	545.3
12	55	369.3	28	135	551.0
13	60	388.3	29	140	555.0
14	65	407.9	30	145	559.4
15	70	425.4	31	150	562.4
16	75	442.6			

TABLE XVII

94°

1 N. NaCl

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	14	65	445.0
2	5	43.6	15	70	460.3
3	10	99.6	16	75	474.2
4	15	149.8	17	80	486.7
5	20	193.9	18	85	496.1
6	25	236.0	19	90	505.8
7	30	274.3	20	95	514.8
8	35	397.2	21	100	522.7
9	40	329.4	22	105	529.6
10	45	364.4	23	110	535.3
11	50	388.2	24	115	541.4
12	55	408.7	25	120	546.8
13	60	427.6			

TABLE XVIII

80°

1 N. MgCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	354.1
2	5	12.6	21	100	367.2
3	10	36.2	22	105	377.9
4	15	62.8	23	110	389.5
5	20	85.8	24	115	399.4
6	25	110.5	25	120	409.3
7	30	132.6	26	125	419.3
8	35	153.9	27	130	428.8
9	40	174.9	28	135	437.3
10	45	195.4	29	140	445.6
11	50	214.2	30	145	454.0
12	55	232.7	31	150	460.6
13	60	249.4	32	155	469.6
14	65	266.5	33	160	475.8
15	70	281.9	34	165	482.0
16	75	296.9	35	170	488.1
17	80	312.5	36	175	492.7
18	85	328.3	37	180	496.7
19	90	341.3	38	185	501.8

TABLE XIX

85°

1 N. MgCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	439.3
2	5	23.1	21	100	450.5
3	10	58.9	22	105	462.6
4	15	95.6	23	110	472.0
5	20	128.6	24	115	481.9
6	25	159.4	25	120	490.4
7	30	189.4	26	125	498.4
8	35	215.7	27	130	504.3
9	40	241.8	28	135	512.1
10	45	266.3	29	140	517.6
11	50	289.1	30	145	525.1
12	55	309.7	31	150	530.8
13	60	330.4	32	155	535.8
14	65	348.9	33	160	540.2
15	70	366.9	34	165	545.3
16	75	382.3	35	170	549.5
17	80	398.4	36	175	554.0
18	85	415.1	37	180	557.4
19	90	427.3			



TABLE XX

90°

1 N. MgCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	19	90	500.5
2	5	40.0	20	95	510.8
3	10	92.4	21	100	519.4
4	15	137.0	22	105	528.4
5	20	178.5	23	110	535.7
6	25	217.5	24	115	542.9
7	30	252.8	25	120	548.7
8	35	285.6	26	125	554.4
9	40	313.3	27	130	559.3
10	45	340.6	28	135	562.3
11	50	367.1	29	140	564.5
12	55	388.3	30	145	568.0
13	60	409.6	31	150	571.6
14	65	428.4	32	155	574.2
15	70	448.4	33	160	576.6
16	75	461.9	34	165	579.1
17	80	476.9	35	170	581.9
18	85	489.5			

TABLE XXI

93°

1 N. MgCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	18	85	498.4
2	5	52.0	19	90	507.2
3	10	108.2	20	95	515.3
4	15	159.6	21	100	523.0
5	20	206.1	22	105	----
6	25	247.1	23	110	----
7	30	284.9	24	115	540.5
8	35	317.7	25	120	544.5
9	40	347.3	26	125	548.8
10	45	374.2	27	130	552.0
11	50	392.1	28	135	555.4
12	55	418.8	29	140	558.3
13	60	436.0	30	145	----
14	65	452.2	31	150	563.2
15	70	465.5	32	155	----
16	75	478.5	33	160	567.2
17	80	489.9			

TABLE XXII

95°

1 N. MgCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	15	70	473.3
2	5	56.8	16	75	487.5
3	10	118.2	17	80	495.4
4	15	173.6	18	85	505.8
5	20	221.8	19	90	514.5
6	25	262.9	20	95	522.5
7	30	301.0	21	100	529.2
8	35	332.1	22	105	534.9
9	40	360.8	23	110	539.9
10	45	390.5	24	115	544.9
11	50	407.9	25	120	548.7
12	55	427.7	26	125	551.6
13	60	444.9	27	130	555.0
14	65	460.0			

TABLE XXIII

80°

1 N. CaCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	344.2
2	5	11.3	21	100	355.6
3	10	34.1	22	105	367.5
4	15	59.4	23	110	378.7
5	20	83.4	24	115	389.0
6	25	105.7	25	120	400.0
7	30	127.4	26	125	409.5
8	35	148.1	27	130	418.1
9	40	168.1	28	135	427.3
10	45	188.7	29	140	435.8
11	50	207.1	30	145	444.2
12	55	225.1	31	150	452.0
13	60	242.3	32	155	459.6
14	65	259.2	33	160	466.7
15	70	273.5	34	165	473.5
16	75	288.5	35	170	480.0
17	80	304.0	36	175	485.3
18	85	318.0	37	180	490.3
19	90	332.3	38	185	494.0

TABLE XXIV

85°

1 N. CaCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	20	95	427.4
2	5	21.7	21	100	436.4
3	10	57.7	22	105	449.2
4	15	92.2	23	110	460.9
5	20	124.4	24	115	471.4
6	25	154.4	25	120	480.8
7	30	184.0	26	125	489.0
8	35	210.1	27	130	495.3
9	40	235.9	28	135	502.3
10	45	258.1	29	140	509.0
11	50	280.5	30	145	515.0
12	55	301.9	31	150	521.3
13	60	321.4	32	155	525.8
14	65	339.2	33	160	531.6
15	70	356.0	34	165	537.0
16	75	372.5	35	170	541.8
17	80	387.6	36	175	545.7
18	85	402.1	37	180	549.5
19	90	415.8			

TABLE XXV

90°

1 N. CaCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	19	90	489.5
2	5	36.2	20	95	500.0
3	10	84.4	21	100	509.6
4	15	129.2	22	105	518.2
5	20	169.1	23	110	528.7
6	25	206.9	24	115	533.7
7	30	241.2	25	120	539.8
8	35	273.4	26	125	544.5
9	40	302.3	27	130	551.0
10	45	328.9	28	135	556.9
11	50	354.1	29	140	561.1
12	55	377.7	30	145	565.0
13	60	396.8	31	150	568.8
14	65	417.2	32	155	571.0
15	70	433.8	33	160	573.1
16	75	449.6	34	165	574.7
17	80	462.8	35	170	577.6
18	85	477.2			

## TABLES XXVI

93°

1 N. CaCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	18	85	486.0
2	5	48.1	19	90	493.5
3	10	101.2	20	95	----
4	15	149.7	21	100	508.3
5	20	195.8	22	105	515.9
6	25	233.9	23	110	523.0
7	30	267.5	24	115	529.6
8	35	300.3	25	120	534.4
9	40	331.7	26	125	538.6
10	45	355.9	27	130	541.8
11	50	378.7	28	135	----
12	55	399.5	29	140	550.6
13	60	417.0	30	145	----
14	65	434.4	31	150	558.2
15	70	448.3	32	155	----
16	75	461.2	33	160	563.0
17	80	474.8			

TABLE XXVII

95°

1 N. CaCl<sub>2</sub>

.1 N. HCl

Reading Number	Time	Volume of Gas	Reading Number	Time	Volume of Gas
1	0	0.0	16	75	472.0
2	5	55.7	17	80	485.6
3	10	114.8	18	85	496.7
4	15	168.0	19	90	507.1
5	20	214.0	20	95	515.8
6	25	254.9	21	100	522.3
7	30	291.5	22	105	528.7
8	35	323.5	23	110	534.7
9	40	353.9	24	115	539.5
10	45	375.7	25	120	546.5
11	50	396.9	26	125	548.0
12	55	416.6	27	130	551.7
13	60	433.5	28	135	553.1
14	65	449.3	29	140	556.2
15	70	462.4	30	145	558.0



TABLE XXVIII  
Effect of Temperature on the Catalytic Action of  
Lithium Chloride

Temperature	Time to Produce 300cc.	Time to Produce 350cc.	Time to Produce 400cc.	Time to Produce 450cc.
80	80.00	99.58	124.17	155.83
82	68.54	85.00	105.00	130.00
83	64.90	80.83	99.80	123.33
84	57.92	72.71	89.58	111.04
85	55.63	69.17	85.63	105.83
90	39.17	48.75	60.02	74.36
94	31.25	38.96	49.17	62.50

**TABLE XXIX**  
**Effect of Temperature on the Catalytic Action of**  
**Sodium Chloride**

Temperature	Time to Produce 300cc.	Time to Produce 350cc.	Time to Produce 400cc.	Time to Produce 450cc.
80	77.71	97.50	121.67	152.29
82	66.45	82.08	101.04	125.83
83	62.92	78.13	96.67	120.63
84	58.33	72.92	90.21	112.08
85	54.79	68.54	84.79	105.63
90	41.04	51.04	62.92	77.50
94	33.96	42.29	52.71	66.46

TABLE XXX

Effect of Temperature on the Catalytic Action of  
Magnesium Chloride

Temperature	Time to Produce 300cc.	Time to Produce 350cc.	Time to Produce 400cc.	Time to Produce 450cc.
80	75.42	93.33	115.00	142.71
85	52.92	65.42	80.21	98.96
90	38.13	47.50	58.13	71.46
93	32.50	40.21	50.83	64.58
95	29.58	37.29	47.50	61.25

TABLE XXXI

Effect of Temperature on the Catalytic Action of  
Calcium Chloride

Temperature	Time to Produce 300cc.	Time to Produce 350cc.	Time to Produce 400cc.	Time to Produce 450cc.
80	78.54	97.29	119.80	148.13
85	54.58	67.92	83.75	104.17
<b>90</b>	<b>39.80</b>	<b>49.38</b>	<b>60.63</b>	<b>74.80</b>
<b>93</b>	<b>35.00</b>	<b>43.75</b>	<b>55.10</b>	<b>70.41</b>
95	31.04	39.38	50.42	65.63

### Hypothesis

Examination of the curves on Plate III shows that those for sodium chloride and magnesium chloride run almost parallel, magnesium chloride being the more active catalyst at all the temperatures investigated. The fact that these two curves are nearly parallel shows that for this reaction sodium chloride and magnesium chloride have practically the same temperature coefficients.

Considering the curves for sodium and calcium chlorides, we find that these curves intersect in the C and D sets of curves (on Plate III) but not in the A and B sets of curves. This fact shows that the catalytic activity of one or both of the salts, even at constant temperature, undergoes some change as the reaction proceeds. That is, if we use the time for producing 450cc. of gas as a basis for measuring catalytic activity, calcium chloride appears to be less active than sodium chloride at 95°. If we use the time taken to produce 350cc. of gas at the same temperature, sodium chloride appears to be the less active. Only one condition differs between the two sets of measurements, namely, the degree of completeness

of the reaction. The other conditions, temperature, concentration of acid and concentration of salt are identical insofar as it is possible to make them. This is a strong indication that some substance which is being formed or used up in the course of the reaction is affecting the catalytic activity of the salts. Of such substances there are several possibilities, namely carbon dioxide, water, ethyl acetoacetate, acetone, and alcohol. The concentration of carbon dioxide in the reaction mixture is constant since temperature and pressure remain the same and the solution is saturated at both times. The amount of water present is so large that the amount of it consumed in the reaction is almost negligible compared with the amount present. The amount of ester present certainly affects the rate of reaction, but it is difficult to see why a variation in the concentration of the ester should affect the activity of sodium and calcium chlorides to a different degree. This effect then must be due to the acetone and alcohol formed in the course of the reaction. The question arises, just what is the mechanism by which alcohol and acetone affect the rate of reaction.

To this question no definite answer can be given, but other evidence, particularly that put forward by Kendall<sup>12</sup>, indicates that there exist in the solution a number of complex equilibria between ions, salts, and acid molecules and their hydrates. These equilibria would certainly be disturbed by the introduction of inert solvents such as alcohol and acetone.

Considering now the four sets of curves A, B, C, and D as a whole, it is apparent that there are four points of intersection of the curves; that is points at which the catalytic effects of the salts involved are equal. On one side of such a point the salts have a certain order of catalytic effect. On the opposite side of the point the order of catalytic effect is reversed. For example, considering the D set of curves, the catalytic effect of lithium chloride is equal to that of sodium chloride at about 85.5°. Below this temperature, sodium chloride is the more effective catalyst, while above this temperature lithium chloride is the more effective. As previously mentioned, four such points were obtained: lithium chloride-sodium chloride between 85° and 86°; lithium chloride-calcium

chloride between 88° and 90°; lithium chloride-magnesium chloride between 94° and 95°; and calcium chloride-sodium chloride between 94° and 95°. The rather marked decrease in the catalytic effect of calcium chloride at the higher temperatures is probably affected by the interchange of water between some of the hydrates in the solution. The behavior of lithium chloride, which shows a constant increase in catalytic effect with temperature is probably due to a similar shifting of hydrate equilibria. It is unlikely that the shifting in the order of catalytic activity is due to hydrolysis of the salts. The hydrolysis of calcium chloride should increase the acid concentration and thereby effect an increase in the rate of reaction. It therefore seems probable that the shifting order of the salts is due to disturbance of equilibria between various hydrates. It is reasonable to believe that in this reaction, the actual hydrolysis of the ester is accomplished by water molecules and that the catalytic function of ions, notably hydrogen ion, is to act as a carrier for the water molecule or



to pull the water molecules away from neighboring ones. There is evidence for the belief that water molecules have a strong tendency to form polymers, due possibly to the unsymmetrical distribution of electrical charges in them. It seems probable that a molecule of water cannot react with the ester when it is attached to other water molecules or to an ion, but does become available for hydrolysis at the instant of its release from such a combination. The addition of a neutral salt, with the tendency of its molecules and ions to form hydrates, increases the amount of water capable of being transferred from one hydrate aggregate to another by the very active hydrogen ion. This increases the amount of "active" water in the solution and consequently the rate of reaction. The shifting in the catalytic effect of different salts with change of temperature can be explained on the basis of the corresponding change in the tendency of their molecules and ions to form hydrates. The fact that the curves obtained show no abrupt changes in catalytic effect indicates that there are a large number of hydrate equilibria in the solution. Were only one hydrate involved, its

formation or decomposition should give us a step like curve as is the general effect with hydrates. Probably, however, so many substances and their hydrates are involved, having overlapping and intermingling influences, that the general effect is a continuous change.

#### Summary and Suggestions

The catalytic activity of lithium, sodium, magnesium, and calcium chlorides in normal solution in the presence of .1 N. hydrochloric acid have been investigated over the temperature interval from 80° to 95°.

The catalytic activity of the above mentioned salts has been found to vary with the temperature and with the degree of completeness of the reaction. The variation of catalytic effect with temperature is apparently continuous and is different for each of the salts studied.

Four temperatures at which two of the salts have the same catalytic activity have been determined.

Further investigations of this reaction should

help to explain the action of neutral salts and perhaps the whole field of solutions. Investigations along the following lines should prove instructive:

(a) The effect of non-electrolytes such as alcohol and acetone on the reaction.

(b) The effect of the salts studied as well as other neutral salts over a wider range of temperature.

(c) The effect of bromides in the presence of hydrobromic acid, and if possible, the effect of iodides in the presence of hydroiodic acid.

(d) Determination of the activities of hydrogen ion and of lithium, sodium, magnesium, and calcium ions at the temperatures used in this work.

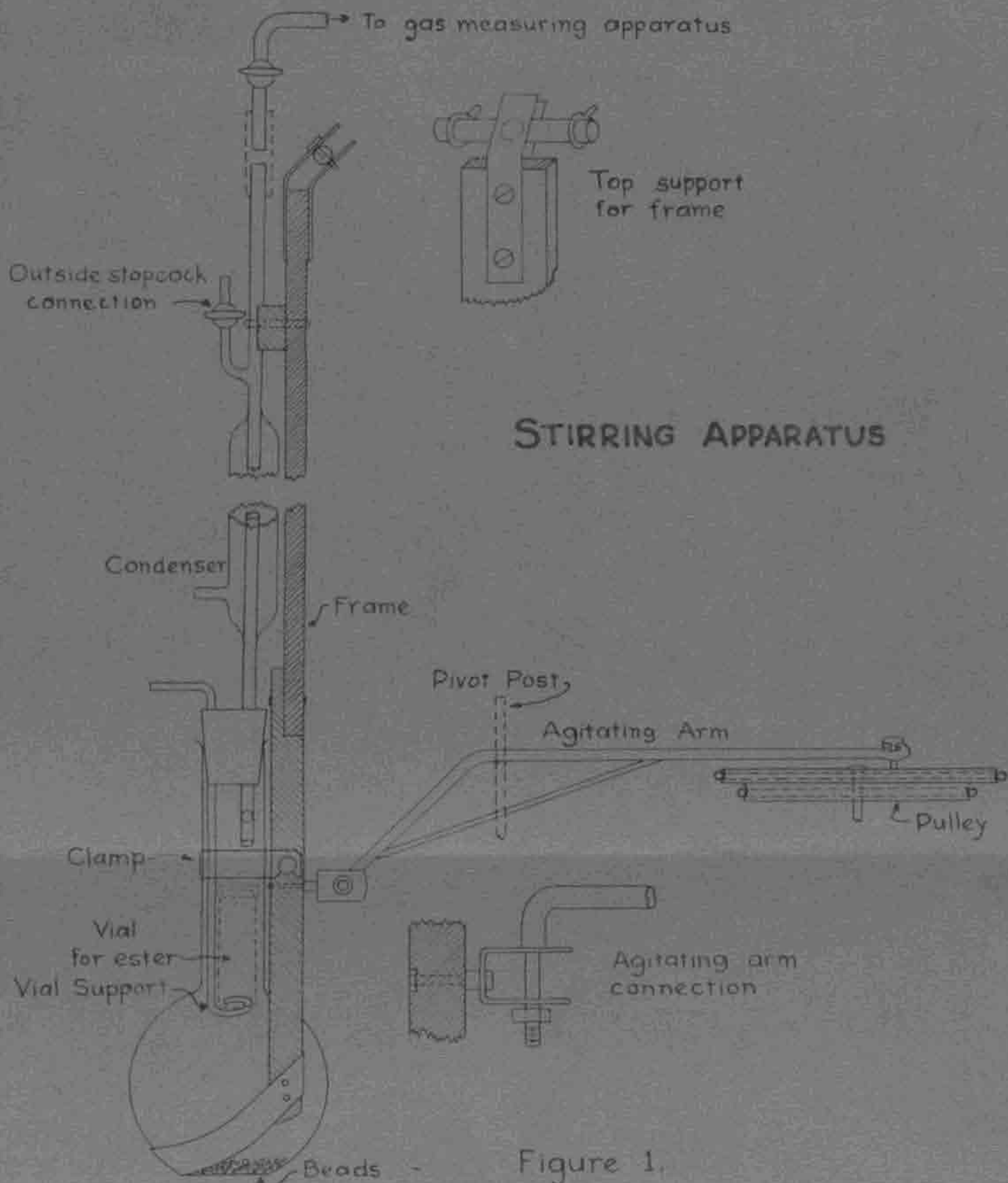


Figure 1.

# GAS MEASURING APPARATUS

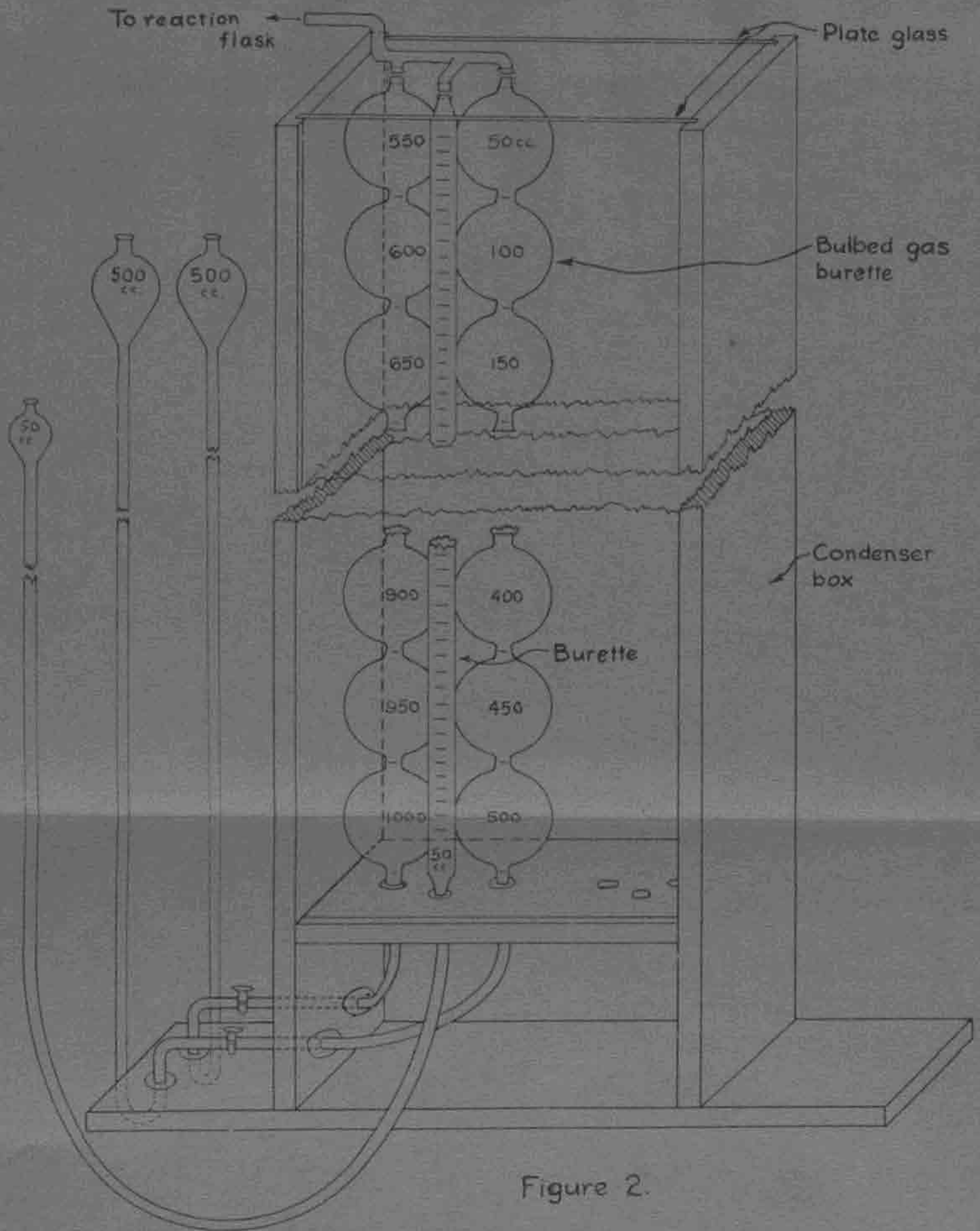


Figure 2.

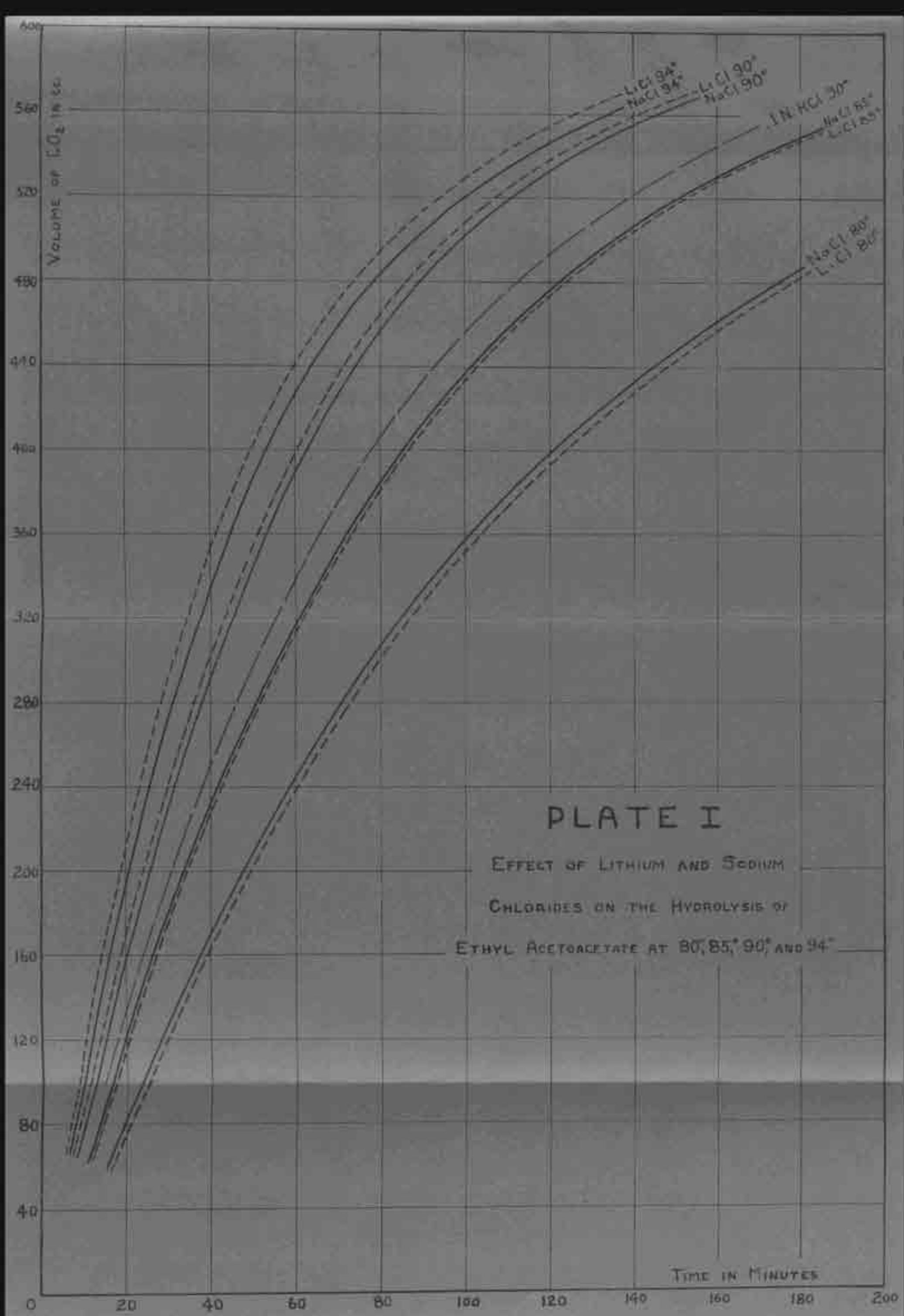


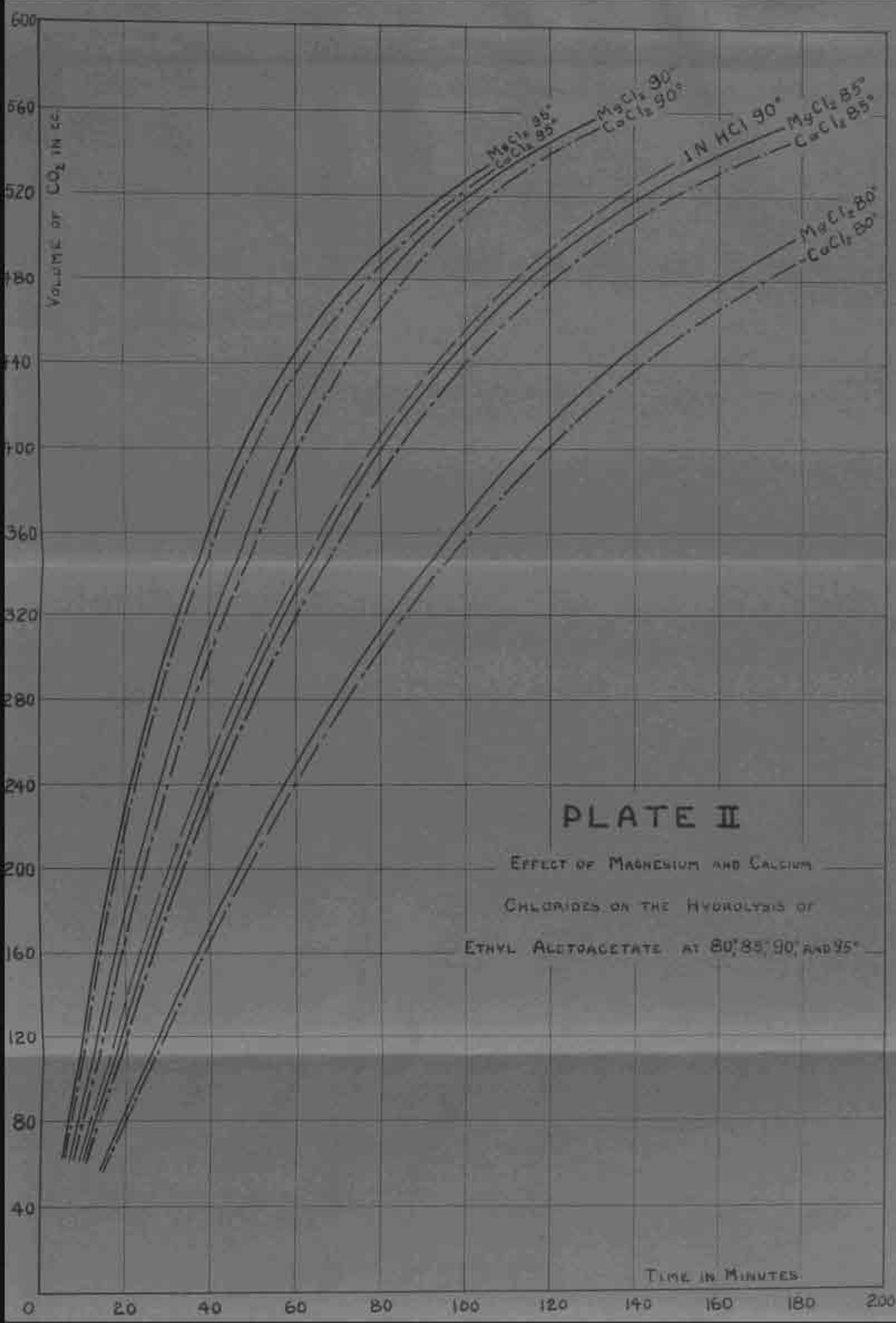
PLATE I

EFFECT OF LITHIUM AND SODIUM

CHLORIDES ON THE HYDROLYSIS OF

ETHYL ACETOACETATE AT 80°, 85°, 90°, AND 94°

TIME IN MINUTES



## PLATE II

EFFECT OF MAGNESIUM AND CALCIUM  
 CHLORIDES ON THE HYDROLYSIS OF  
 ETHYL ACETOACETATE AT 80°, 85°, 90°, AND 95°

TIME IN MINUTES

# PLATE III

## TEMPERATURE EFFECT ON THE CATALYTIC ACTIVITY OF LITHIUM, SODIUM, MAGNESIUM, AND CALCIUM CHLORIDES

