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THE ACTION OF ALUMINUM ON HYDROCHLORIC ACID

AT DIFFERENT CONCENTRATIONS

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BY

GLADYS IONE ELMORE

A Thesis
Submitted to the Faculty of
the University of Mississippi
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in the Department of Chemistry

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PREFACE

It is hoped that future workers may profit by the information and experimental data assembled in this thesis.

It is a pleasure to acknowledge the consistent interest and help which has been given me by Dr. John N. Swan, Head of the Department of Chemistry of the University of Mississippi, under whose instruction this experimental work has been done.

I also wish to express my sincere thanks and appreciation to Dr. V. A. Coulter, Professor of Physical Chemistry, and to Mr. J. William Magee, Student of Physical Chemistry, for their assistance in keeping the apparatus in running condition.

GLADYS IONE ELMORE

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CHAPTER I

INTRODUCTION

It is a well known fact that metals are acted upon by acids when they are brought in contact with each other. Some metals are attacked more readily by acids than others, the activity depending upon the metal and upon the kind of acid, as well as upon the conditions under which they are acting.

"Ordinary zinc dissolves in all the common acids, usually with the evolution of hydrogen. In the case of nitric acid, however, the hydrogen acts upon the acid, reducing it to ammonia. The purer the zinc the less readily it is acted upon by sulphuric acid; pure zinc is scarcely acted upon at all by sulphuric acid."[1] By the addition of a few drops of platinum chloride, sulphuric acid can be made to act upon pure zinc. Dilute hydrochloric acid acts upon zinc.

Mercury is not attacked by hydrochloric acid; concentrated sulphuric acid acts very slowly at a low temperature; but when they are heated together mercuric sulphate, $HgSo_4$, sulphur dioxide and some mercury sulphide are produced. Concentrated nitric acid rapidly attacks mercury, forming mercuric nitrate and oxides of nitrogen. Dilute nitric acid acts slowly, giving another nitrate, mercurous nitrate, particularly if the metal is in excess.[2]

"Aluminum is resistant to the action of most acids except those of the halogen types as typified by hydrochloric acid."[3] In the case of inorganic acids, aluminum is more resistant to nitric acid, less resistant to sulphuric and is readily attacked by hydrochloric acid.[4] Thus it is seen that the order of action of the common acids on mercury, zinc and aluminum are as follows:

(1) Mercury; first nitric acid, second sulphuric acid, and third hydrochloric acid.

(2) Zinc; first nitric acid, second hydrochloric acid, and third sulphuric acid.

(3) Aluminum; first hydrochloric acid, second sulphuric acid, and third nitric acid.

It is the purpose of this thesis to work out the speed of action of aluminum on hydrochloric acid at different concentrations at a constant temperature.

CHAPTER II

ALUMINUM AND ITS PROPERTIES

"When a Buckeye boy in his teens poked a fellow classmate in the ribs with the remark, 'I'm going after that metal,' the real history of aluminum began."[5] This ambitious boy was none other than Charles M. Hall. While still a student in Oberlin College, Hall attacked the problem of making cheap aluminum and succeeded where the greatest scientists had failed.

"Behind the development of aluminum lies a story of the struggle, vicissitudes, and achievements of a modern industry about which little has been written other than along technical lines."[6]

Briefly, the early history of the metal is this: In 1825 the Danish Scientist, H. C. Oersted, first isolated aluminum in the form of minute metallic globules. Several decades later, aluminum was placed on the market at $90 a pound. About 1875 aluminum was used for a few expensive novelties, but the price of the metal was even then about $12 a pound; too high a cost to permit many uses of the new and interesting metal. These conditions continued until Charles M. Hall discovered his now famous process of obtaining aluminum by means of electricity instead of by chemical means. It was not until 1888 that this process had been perfected to the point where it might be said to be of commercial importance.[7] It is interesting to know that a few months after Hall's discovery a young Frenchman, Heroult, duplicated his process quite independently.[8] Since Hall and Heroult worked independently, the present day electrolytic process for the production of aluminum is commonly called the Hall-Heroult process. This process in a few words, consists in dissolving aluminum oxide in melting Cryolite in a carbon lined pot and passing an electric current through the mixture.[8] Aluminum is deposited in the bottom of the pot, while oxygen, liberated at the anode, combines with the carbon and escapes as carbon dioxide. Other materials are now used wholly or in part in place of the cryolite, but the principles used in the process are not changed.[9]

Aluminum stands today as the fifth metal in point of value produced and in use, following after iron, copper, lead and zinc. It stands fifth in the electromotive series: coming before aluminum in the order named are potassium, sodium, calcium and magnesium. Therefore, aluminum is a very active metal chemically as well as an important element for commercial purposes.

The pure metal, aluminum, is not over fifty years old and it is interesting to note the place it takes in the commercial world against the age-old metals like zinc, lead, copper, iron, etc. The commercial applications of aluminum were few up until 1888. The metal was used chiefly for watch fobs, inexpensive jewelry, novelties and trinkets, although, in 1886 Washington Monument was capped with a 100-ounce casting, "the largest piece of this metal ever cast in any country." On Thanksgiving Day, 1888, the Pittsburgh Reduction Company (since 1907 the Aluminum Company of America) began operating in the production of aluminum. Now the metal is used in the making of articles ranging all the way from cooking utensils to the frame works for large buildings like the Empire State Building in New York, where approximately 850,000 pounds of aluminum was used.

It is interesting to note just how, in the light of the basic policy, aluminum is fitting into the scheme of American life. In the point of volume, and in this order, these are the three largest present uses and fields served by aluminum:

(1) Transportation (air, land and water).

(2) The household (cooking utensils, parts of washing machines, phonographs, radio sets, etc.)

(3) Transmission of power and communication (about fifteen per cent of the entire volume of production domestically is used for this purpose, which is a market known to few people outside of the technical fields).

Aluminum for architectural utility promises to become a fourth major use, and may some day crowd its way into third place.[10]

The sources of aluminum are the most widely distributed of all the metals. It never occurs free, but nearly all rocks except sandstone and limestone contain aluminum compounds. Such silicates as feldspar, $K\ Al\ Si_3O_8$, and mica, $KAl\ Si\ O_4$, are common. Ordinary clay, $H_2Al_2\ (Si\ O_4)_2 \cdot 2H_2O$, cryolite, $Na_3Al\ F_6$, bauxite, $Al_2O_3 \cdot 2H_2O$, and corundum, Al_2O_3, are well known compounds of aluminum.[11] The principal bauxite producing districts in the order of their production are: Var, Southern France; Arkansas, United States; Dutch Guiana; Western Hungary; Jugoslavia; Herault, Southern France; and the Georgia-Alabama-Tennessee Field in the United States. The ore is generally mined by open-pit methods although there are some localities in which underground mining is necessary on account of the great depth of overburden or the character and attitude of the bauxite deposits.[12]

Aluminum resembles tin in appearance. Its density is 2.65, which is almost the same as glass, but only about one-third that of iron. It is ductile and malleable, especially at temperatures between 100° and 150°, when it can be hammered into very thin sheets. At higher temperatures, near its melting point, it is very brittle. It is hard and strong, being superior to most metals in these respects, although not equal to steel. It is an excellent conductor of heat and electricity.[13]

Aluminum is but slightly acted upon by water; moist air merely dims its luster. Further action is prevented in each case by the formation of oxide upon the surface of the metal. It combines with many of the non-metals, especially with the halogens and members of the sulphur family. It is an excellent reducing agent, combining with oxygen at a high temperature, with the liberation of much heat:

$$4\ Al + 3\ O_2 \longrightarrow 2\ Al_2O_3 + 2 \times 380,200\ \text{cal.}$$

Nitric acid and dilute sulphuric acid have but little action upon it; concentrated sulphuric acid dissolves it, forming the sulphate and liberating sulphur dioxide. Hydrochloric acid is its best solvent:

$$2\ Al + 6\ HCl \longrightarrow 2\ AlCl_3 + 3\ H_2$$

Aluminum resembles zinc in that it is readily dissolved in strong alkalies, forming aluminates and liberating hydrogen. It is also acted upon by sodium chloride, especially in the presence of oxygen and dilute acids such as acetic acid.[14] It is these outstanding properties of aluminum that make it of such great importance in the commercial world.

CHAPTER III

EXPERIMENTS

The experiments to be described were undertaken primarily in order to find out at what concentration hydrochloric acid is most active, especially upon aluminum. I have, therefore, undertaken the determination of the solubility of aluminum in hydrochloric acid at various concentrations at a constant temperature.

The temperature was kept at 30 C. or as near that as possible. A stop watch was used to determine the exact time of the samples, ranging within an hour's time of action. The percents of concentrations, ranging from one per cent to eight per cent and from thirty per cent to thirty-seven per cent which was the most concentrated, required a long period of time, and over night the temperature varied, therefore, this experiment deals only with the concentrations of acid from eight per cent to thirty per cent.

The description of the apparatus used in this experiment is as follows: Referring to Plate I, the outfit consists of a well insulated tank, tin-lined, of ten liters water capacity. The tank is equipped with a stirring device, S, operated by the electric motor, M. The use of the stirrer is necessary for close temperature regulation. The heating is effected by means of two heating coils, C_1 and C_2, which are connected to an outside current. The close temperature regulation which is obtained with this bath is made possible through the use of a sensitive polarized relay in conjunction with the mercury thermo-regulator, Th. When the temperature of the bath rises to the regulating point, the mercury in the capillary of the thermo-regulator rises and makes contact with a platinum point, thus operating the relay and disconnecting the heating units. This allows the bath to cool, and when the temperature has dropped slightly the mercury falls and allows the relay to connect the heaters again. The storage battery furnishes the power for operating the relay in this manner.

The aluminum and the acid are placed in the Erlenmeyer flask, F, which is suspended in the bath by a rod fastened to the stopper. This rod is connected in a set of pulleys which in turn is connected with another set of pulleys that is controlled by the water turbine, P. The water turbine is connected to the main waterline. By this set-up the speed of the rotating flask, F, can be controlled by the amount of water allowed to flow through the water turbine.

The materials used in this experiment were the best commercially obtainable. Sheet aluminum, a product of the Aluminum Company of America, 100 microns thick and 99.7 per cent pure was used. The acid was 37 per cent, specific gravity 1.1878, diluted with distilled water measured in graduated pipettes. The temperature at which this experiment was conducted was 30 C.

The aluminum was cut into one-half inch squares, cleaned and weighed, all pieces checking in weight to the fourth decimal place. The weight used was .2673 grams. Each time 15cc. of the concentrated acid was used. This gave sufficient acid to react completely with the aluminum and yet to have some acid left after the reaction ceased. It also produced enough solution in the 250cc. flask to come in contact easily with the aluminum. The method used to determine the amount of water to be added for exact per cent of concentration was as follows:

Problem: It is desired to add sufficient water to 15 cc. of hydrochloric acid, 37 per cent pure, to make a mixture 30 per cent pure. How many cc. of water are required?

Solution:

Let X = the number of cc. of water to add.

15 + X = number of cc. of solution after the addition of X cc. of water.

37% of 15 cc. = 5.55 cc. of pure acid already in 15 cc. of the concentrated acid.

The equation becomes:

$$.30(15 + X) = 5.55$$

$$450 + 30X = 555$$

$$30X = 105$$

$$X = 3.5$$ cc. of water to add in order to have a 30% solution.

It was found that the amount of water added for each per cent of concentration did not run in a constant ratio, therefore, this procedure was used, working out each per cent of concentration.

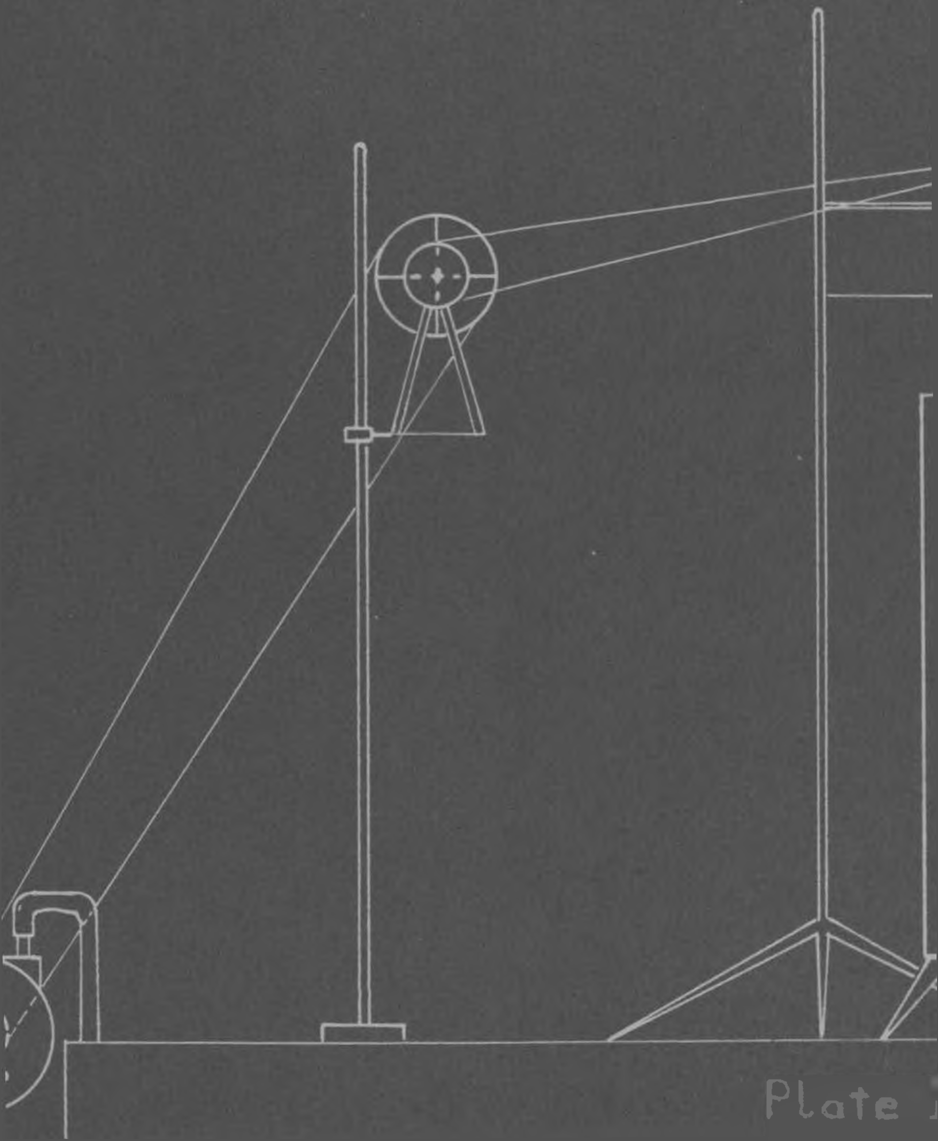
The experimental data obtained are set out in the data sheet and the corresponding graphical representation is shown in Figure I. Owing to the wide range of time and the size of the paper, Figure I represents the concentration of the acid from ten per cent to twenty-nine per cent only, and the time from fifteen minutes to 6.5 hours. From the data and the corresponding graph there seems to be some irregularity in the action of hydrochloric acid on aluminum between the concentrations twenty and twenty-two per cents. Since our chief interest lies in the irregularity of the curve, a second graph as shown in Figure II was constructed. This graph is drawn on a large scale using only the concentrations of the acid from percentages sixteen to twenty-nine. From the study of Figure II it will be shown that from twenty per cent to twenty-one per cent, there is an increase in the time of reaction, and at twenty-two per cent the time of reaction drops to its lowest point, which is fifteen minutes and thirty-two seconds. There must be some cause for this irregularity but just what the cause may be, I am not prepared to say and have not undertaken to determine the cause. It is known that the pure metals do not react with acids as rapidly as those that contain a high percentage of impurities. Some impurities act as catalytic agents and therefore speed up the reaction.

I noticed that after the aluminum was dropped in the acid the speed of reaction did not increase rapidly for the first several minutes. A gray precipitate which was aluminum chloride, $AlCl_3$, was formed and hydrogen was given off. The aluminum remained at the bottom of the flask until the precipitate became great and the aluminum was eaten away until it was lighter than the solution; then it rose to the top. In the more slowly acting percentages of acid the precipitate was dissolved as it formed, while in the most rapidly acting ones the precipitate was not dissolved until the reaction stopped and the solution was allowed to stand a few minutes.

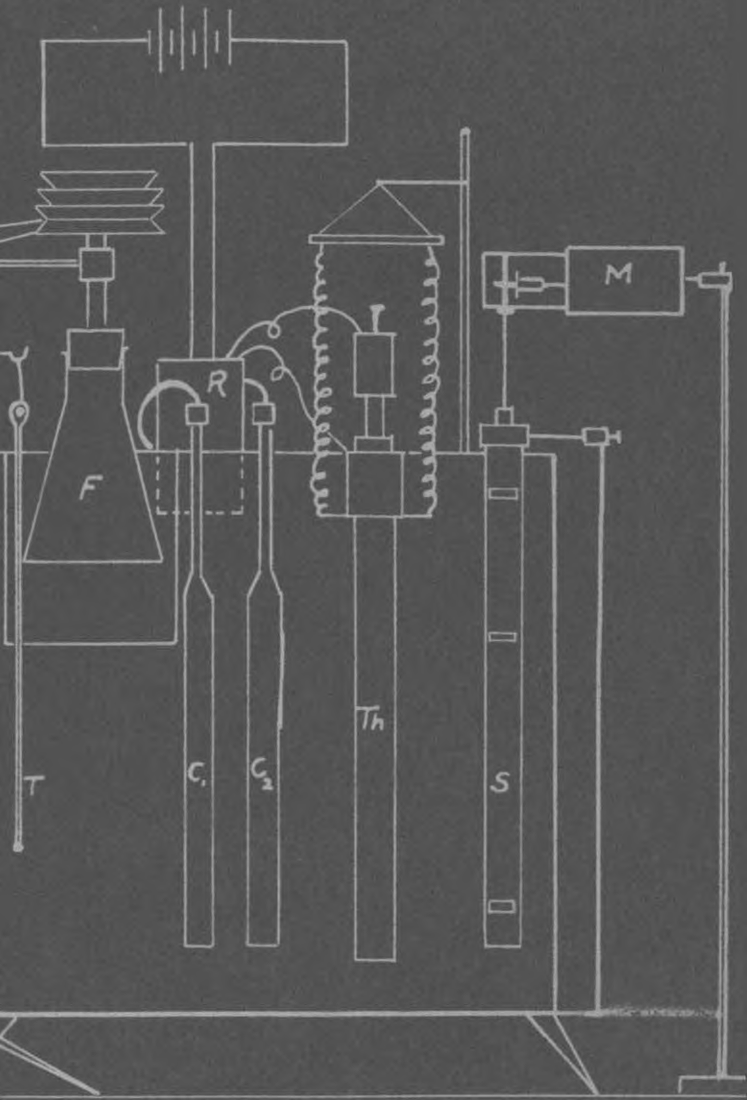
In summarizing the above experiments, the action of aluminum on hydrochloric acid at a constant temperature is not regular. There is a break in the regularity of the curve of activity; at twenty per cent concentration the time of reaction to completion is seventeen minutes, thirty seconds; at twenty-one per cent concentration the time increases again going up to nineteen minutes, forty-nine seconds; then at twenty-two per cent concentration the time of reaction reaches its minimum, which is fifteen minutes, thirty-two seconds. From eight per cent concentration to twelve per cent concentration the curve of increased activity was rapid. From twelve per cent to twenty per cent concentration the increased activity was almost constant; at twenty-one per cent concentration a sharp decrease in the rate of activity was indicated, for which I am unable to account. This temporary deviation was not observed between twenty-two per cent and twenty-nine per cent concentrations. The rapid increase in time required for complete reaction began at thirty per cent concentration, rising more rapidly than the rate of decrease of time which was utilized for the increasing concentrations of the acid used in the beginning of the experiment.

Experiments carried out at twenty-three different percentages of concentrates of the acid constitute the information upon which this thesis is based. Thirty experiments were run, but as the time required to dissolve the aluminum in the percentages of concentrations of the acid from thirty to thirty-seven percent was so great, and as the temperature varied a few degrees over a long period of time, the seven highest percentages of concentrations had to be discarded. In the twenty-three experiments used, the data obtained was verified by running the experiments several times under the same conditions until the time of speed of action was almost constant, or checked within a few seconds of each other. Particular emphasis was given to the experiments which constitute the break in the curve. Because of this break, the experiments at these percentages of concentrations of the acid were repeated until the conclusions were thoroughly verified. The number of accurately weighed pieces of aluminum used in obtaining the data for this thesis was about one hundred twenty-five: the number recorded was seventy-three.

CHARTS

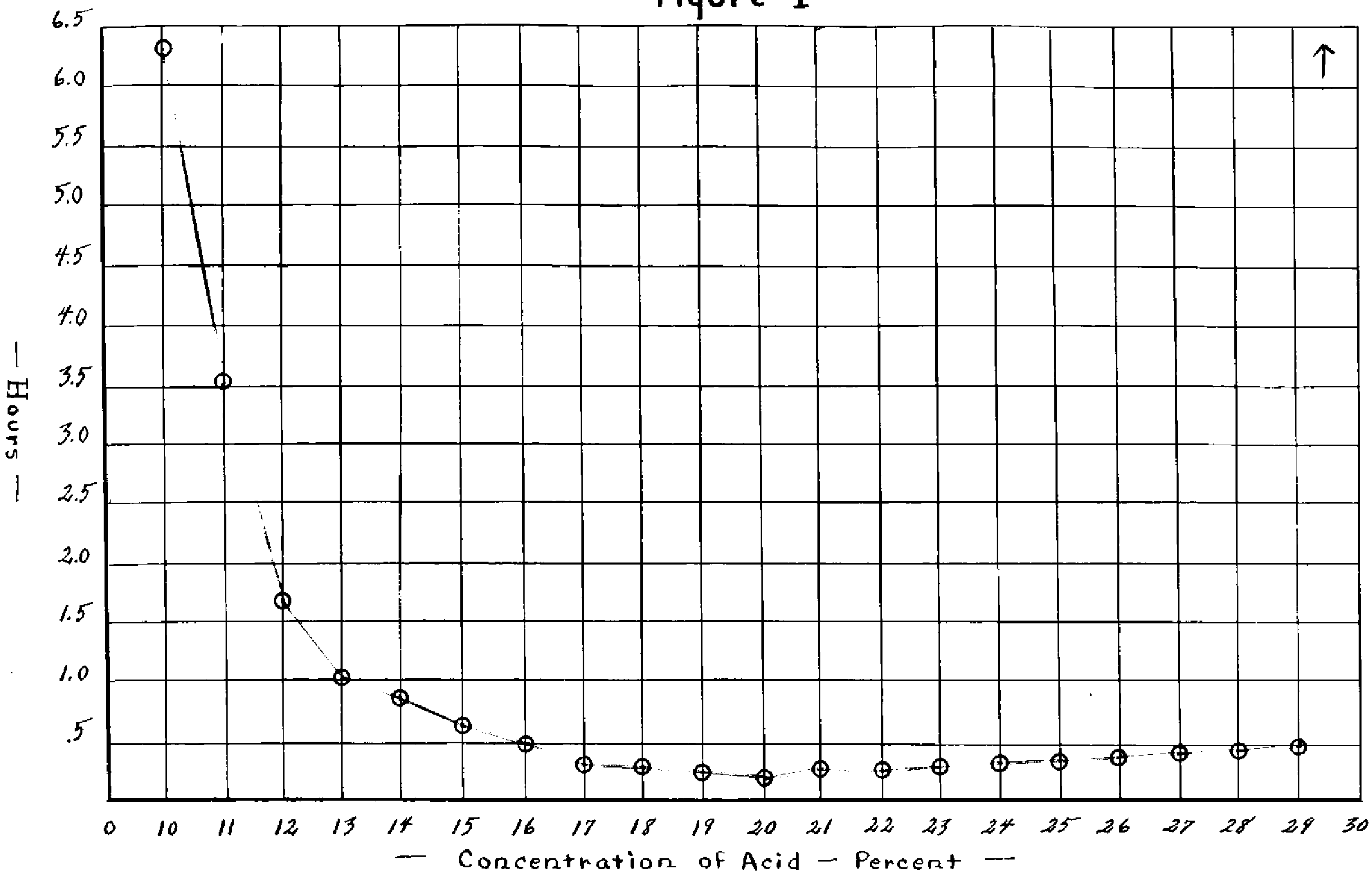


Plate



M
R
F
T
C_1
C_2
Th
S

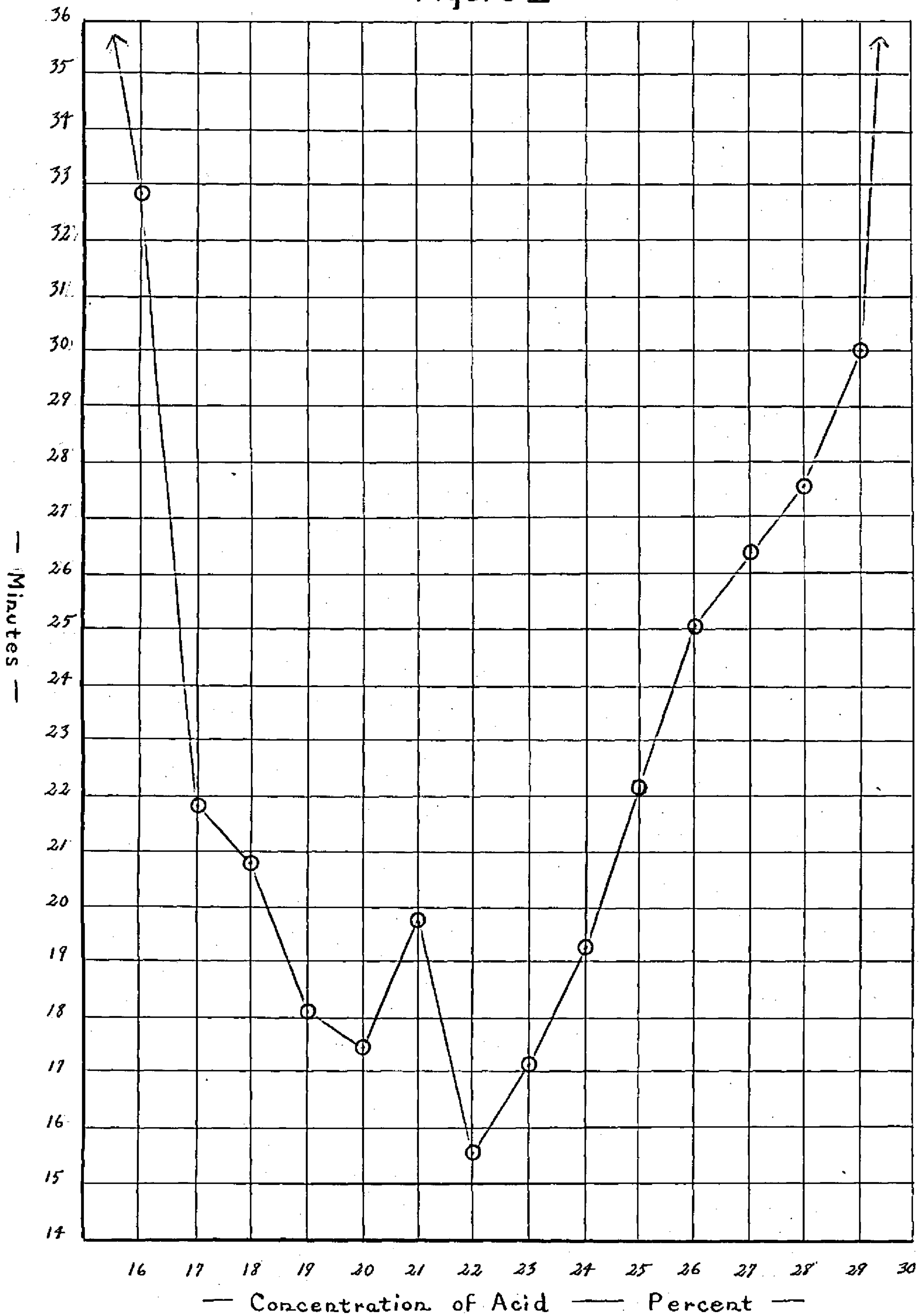
Figure I



Action of Aluminum on Hydrochloric Acid

1 CM. = 30 Minutes

Figure II



Action of Aluminum on Hydrochloric Acid

1 C.M. = 1 Minute

DATA SHEET

Concentration of acid percent	Water added	Time required to dissolve .2673 gr. of aluminum at 30°		
	CC.	HOURS	MINUTES	SECONDS
8	54.37	28	45	
9	46.66	15	30	
10	40.5	6	20	
11	35.45	3	5	
12	31.25	1	43	
13	27.69	1	3	42
14	24.64		53	29
15	22.		43	36
16	19.75		32	56
17	17.64		21	54
18	15.83		20	51
19	13.68		18	11
20	12.75		17	30
21	11.4		19	49
22	10.02		15	32
23	9.13		17	8
24	8.12		19	21
25	7.6		22	17
26	6.34		25	
27	5.9		26	22
28	4.82		27	30
29	4.13		30	
30	3.5	42		

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