

THE CORROSION OF ALUMINUM BY HYDROCHLORIC
ACID VAPORS

by

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ABSTRACT

Aluminum has high resistance to attack in many environments but corrodes rapidly in most inorganic acids. The purpose of this investigation was to attempt to determine the rates and mechanism of the surface reactions for the corrosion of aluminum in hydrochloric acid vapors as a function of the vapor concentration, vapor composition, and temperature.

Corrosion tests were made by suspending aluminum foil samples, five centimeters by two centimeters, by a glass thread. The samples were located in the vapor over hydrochloric acid solutions. The glass thread with the sample was attached to the center of a glass rod. One end of the rod was fixed; the other was suspended from one end of the arm of an analytical balance, permitting periodic weighing of the corroding samples without removal from the flask.

The tests were conducted above hydrochloric acid solutions whose concentration varied from 2 to 32 weight per cent. Ten temperature levels, from zero to 48 °C, were employed so that the vapor pressures of the various acid concentrations overlapped. Weighings were made at 10 minute intervals for 200 minutes. The corrosion products were analyzed by standard x-ray diffraction techniques.

The rate of weight gain was found to be a linear function with respect to time and exponential with respect to hydrochloric acid concentration. The rate passed through a maximum at a hydrogen chloride partial pressure of 1.77 mm Hg. The decrease in rate above the maximum is due to the formation of a protective aluminum trichloride six hydrate ($\text{Al Cl}_3 \cdot 6 \text{ H}_2\text{O}$) film. Temperature increased the rate of weight gain at all hydrogen chloride partial pressures. Based on the analysis of the corrosion products the following mechanism is proposed for the corrosion of aluminum.

For hydrogen chloride partial pressures below 1.77 mm Hg., the hydrogen chloride acts as the electrolyte for the following electrochemical reaction



For hydrogen chloride partial pressures above 1.77 mm Hg., the hydrogen chloride enters into the reaction as follows



The energy of activation is approximately constant over the entire experimental range indicating that the same mechanism is controlling both proposed corrosion reactions. The controlling reactions would be the primary electrode reactions which are identical for both regions.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
Corrosion by Hydrochloric Acid	3
Effect of Purity	3
Acid Strength	4
Corrosion Periods	4
Aluminum Films	5
Natural Oxide Film	5
Types of Aluminum	6
Solubility of Oxide Films	8
Artificial Oxide Films	9
Aluminum Trichloride	12
Theory of Attack	14
Inhibitors	16
Mechanisms of Inhibition	16
Liquid Inhibitors	16
Chemical Treatments	17
Anodic Oxidation	20
Vapor Phase Inhibitors	21

	Page
Analysis of Corrosion Products	22
X-ray Diffraction	22
X-ray Fluorescence	22
Differential Thermal Analysis	22
Electrographic	23
Spectrographic	23
Microscopic	23
Qualitative	23
Quantitative	24
III. EXPERIMENTAL	25
Purpose of Investigation	25
Plan of Experimentation	25
Literature Review	25
Apparatus	26
Experimental Procedure	26
Analysis Procedure	26
Statistical Design	28
Materials	31
Apparatus	34
Method of Procedure	36
Preparation of Aluminum Sample	36
Preparation of Hydrochloric Acid Solutions	36

	Page
Construction of the Modified Analytical Balance System	37
Corrosion Reactor Components	37
Corrosion Test Procedure	38
Anhydrous Aluminum Trichloride Adsorption Test	39
X-Ray Analysis	39
Data and Results	40
Sample Calculations	62
IV. DISCUSSION	65
Rate of Weight Gain	65
X-Ray Analysis of Products	68
Adsorption by Anhydrous Aluminum Trichloride	69
Corrosion Mechanism	69
Statistical Analysis	72
Recommendations	73
Limitations	75
V. CONCLUSIONS	76
VI. SUMMARY	78
VII. BIBLIOGRAPHY	80
VIII. ACKNOWLEDGMENTS	84
IX. VITA	85

LIST OF TABLES

Table		Page
I.	Forms of Aluminum Oxide	7
II.	Solubility Products of Oxide Films	10
III.	Thickness of Oxide Coatings	11
IV.	Properties of Aluminum Trichloride	13
V.	Hydrochloric Acid Inhibitors for Aluminum	18
VI.	Statistical Design	29
VII.	Analysis of Hydrochloric Acid	32
VIII.	Corrosion Data For Aluminum Above Hydrochloric Acid Solutions	41
IX.	Activation Energy	58
X.	Water Adsorption by Anhydrous Aluminum Trichloride	60
XI.	X-Ray Analysis of Products	61

LIST OF FIGURES

Figure		Page
1.	Schematic Diagram of Vapor Phase Corrosion Reactor	27
2.	Change in Hydrogen Chloride Partial Pressure with Temperature	30
3.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 48 °C	42
4.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 44 °C	43
5.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 41 °C	44
6.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 35 °C	45
7.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 28 °C	46
8.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 17 °C	47
9.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 9 °C	48
10.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 7 °C	49
11.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 2 °C	50

Figure		Page
12.	Increase in Sample Weight With Time for Various Hydrochloric Acid Concentrations at 0 °C	51
13.	Change in Rate of Weight Gain With Hydrochloric Acid Vapor Pressure	52
14.	Variation of Rate of Weight Gain With Temperature	53
15.	Variation in Rate of Weight Gain With Hydrochloric Acid Concentration	54
16.	Change in Rate of Weight Gain With Ratio of Water to Hydrogen Chloride Partial Pressure	55
17.	Arrhenius Plot for Constant Hydrochloric Acid Vapor Pressure Tests Conducted in Air	56
18.	Change in Energy of Activation With Hydrochloric Acid Vapor Pressure	57

I. INTRODUCTION

Aluminum is one of the most widely used metals in the chemical and food industries. Aluminum and its alloys are favored because they are mechanically and physically satisfactory materials of construction and at the same time they are suitable from a corrosion standpoint. Some of the properties that make them desirable include good thermal conductivity, light weight, freedom from harmful physiological action, nonsparking, readily shapable, and resistant to corrosive attack by many commonly used materials.

Aluminum may not be used for most inorganic acids with the exception of concentrated nitric acid and dilute sulfuric acid. Hydrochloric acid is one of the most vigorous corrosive agents for aluminum. Hydrochloric acid vapors have also been found to corrode aluminum and its alloys where the vapors contact the metal. The removal of scale from heat exchanger tubes with hydrochloric acid cleaning solution is an example of where difficulty may occur.

Considerable work on the corrosion of aluminum in hydrochloric acid solutions has been done. There is a vast quantity of data available on corrosion of aluminum in liquid solutions on which to base corrosion theories and mechanisms. Very little work in

the field of vapor phase corrosion of aluminum has been done. With the increasing use of aluminum in industrial facilities, there is a need for studies to determine the effect of such quantities as temperature, acid concentration, water vapor concentration, and vapor composition on the rate of attack of acid vapors on aluminum.

The purpose of this investigation was to attempt to determine the rates and mechanism of the surface reactions for the corrosion of aluminum in hydrochloric acid vapors as a function of the vapor concentration, vapor composition and temperature.

II. LITERATURE REVIEW

The purpose of this section is to present a review of the important literature on the corrosion of aluminum in hydrochloric acid. The major topics discussed are: the corrosion by hydrochloric acid, aluminum films, aluminum tri-chloride, inhibitors and the methods of analysis of corrosion products.

Corrosion by Hydrochloric Acid

Aluminum suffers severe corrosion when in contact with hydrochloric acid. The corrosion may be intergranular (35), subgranular (30), pitting (40), uniform attack (1), or stress corrosion (24). In the vapor phase damp hydrogen chloride was found to cause rapid attack at 20 °C while the dry gas caused only slight attack (1).

Effects of Purity. The attack on the aluminum surface is highly dependent on the purity of the aluminum (7, 32, 33, 40). It was found that as little as 0.03 per cent impurities raised the relative corrosion rate in hydrochloric acid by a factor of 1000 and that 0.8 per cent raised the relative corrosion rate by 30,000 (40). The impurities or inclusions are cathodic to the oxide film (32) causing its decrease in resistance. This decrease in corrosion rate with purity is one of the disadvantages of

aluminum alloys. In ten per cent hydrochloric acid the loss of weight is 220 grams per square meter per day for 99.8 per cent pure aluminum, but only 5 grams per square meter per day for super pure aluminum (1).

Acid Strength. The rate of attack by hydrochloric acid solutions was found to increase with acid concentrations up to a maximum at 35 weight per cent (1) (Nine normal hydrochloric acid (2)). Above the maximum the rate decreases rapidly to approximately the same rate at 45 weight per cent as at 5 weight per cent (1). The decrease in rate above the maximum is attributed to the formation of a protective film of aluminum tri-chloride $AlCl_3$ (2).

Corrosion Periods. Aluminum corroding in hydrochloric acid was found to have three periods of corrosion (2, 33). There were

- a) An incubation period during which the aluminum does not dissolve.
- b) An induction period during which the reaction velocity increases rapidly.
- c) A reaction period during which the reaction velocity is constant or decreases slowly.

These periods are believed caused by the protective layer, the failure of the layer, and the access of the acid to the surface. The incubation and induction periods becomes shorter as the acid solution concentration is increased (33).

Aluminum Films

The corrosion resistance of aluminum in many environments is due to its natural oxide film or to some protective film formed in the environment.

Natural Oxide Film. There is a natural oxide film which forms on aluminum in dry air within 10 to 40 minutes after its exposure to air at room temperature. This film is on the order of 100 Angstrom in thickness and is thought of as being of the barrier-layer type (3, 19, 25). The barrier layer is an impermeable film which forms to a thickness just sufficient to prevent the transfer of ions from the surface of the metal to the oxide-air interface. The thickness of this layer is a function of the temperature. In the presence of water the oxide film will continue to grow. Increases in porosity or permeability to oxygen or water vapors resulting from absorption of water vapors and hydration of the film are believed responsible for the continued growth. It has been proposed by Mott (31) that the formation of thin protective films on aluminum can be explained based on two premises

1. Positive metal ions can leave the metal and diffuse through the oxide to combine with oxygen at the oxide-air interface to form new oxide provided electrons may pass from metal to free surface.

2. Electrons pass through the oxide layer by thermionic emission into the conduction levels of oxide or by quantum mechanical tunnel effect.

The passive film on aluminum has the effect of allowing current to flow to the metal but prevents the ions from flowing in the opposite direction⁽²⁹⁾. The film formed on aluminum may be thickened by heating. Aluminum alloys are age hardened at between 250 and 500 °F⁽¹⁶⁾. This heat treating increases the film on the metal to from 200 to 1000 Angstrom in thickness. These films are however subject to cracking.

Types of Aluminum. The oxide of aluminum or alumina (Al_2O_3) occur in various forms. The forms of the alumina and aluminum hydrates are shown in Table I^(10, 11, 22). The physical and chemical properties of aluminas are dependent in large measure on the temperature at which they are formed. The air formed film is generally amorphous alumina or sometimes gamma-alumina. When aluminum stands in water the corrosion product is usually beta-trihydrate but under some conditions alpha-trihydrate has been detected. When the water is between 80 and 100 °C the product is alpha-monohydrate^(6, 42). Bernard⁽³⁾ found for films formed between 80-100 °C hydrated aluminum oxide containing from 23 to 32 per cent water instead of the stoichiometric 15 per cent water was formed. The variation is believed due to the formation of a complex which

TABLE I

Forms of Aluminum Oxide

Alumina Form	Formula	Mineral Name	Crystal Structure
Alpha-alumina	α Al ₂ O ₃	Corundum	Rhombohedral
Beta-alumina	β Al ₂ O ₃	---	Hexagonal
Gamma-alumina	γ Al ₂ O ₃	---	Cubic
Sigma-alumina	δ Al ₂ O ₃	---	Rhombohedral
Alpha-monohydrate	α Al ₂ O ₃ · H ₂ O	Bohmite	Orthorhombic
Beta-monohydrate	β Al ₂ O ₃ · H ₂ O	Diaspore	Orthorhombic
Alpha-trihydrate	α Al ₂ O ₃ · 3H ₂ O	Gibbsite	Monoclinic
Beta-trihydrate	β Al ₂ O ₃ · 3H ₂ O	Bayerite	
X-hydrate	Al ₂ O ₃ · XH ₂ O	---	

Deltombe, E. and M. Pourbaix: The Electrochemical Behavior of Aluminum, Corrosion, 14, No. 11, pp. 16-20, (1960).

Edwards, J. D.: "The Aluminum Industry", pp. 164-168, McGraw-Hill Book Co., Inc., New York, N. Y., 1930.

Hodgman, C. D.: "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 41 ed.

on heating drives off the excess water or combines it with base metal to form the alpha monohydrate. Gamma-alumina is an intermediate form of oxide produced by heating amorphous alumina or one of the hydrates to a temperature between 500 and 900 °C (23, 42). Alpha-alumina or corundum, is only formed in air when the temperature is above 1000 °C. Hydrated aluminas, on being heated sufficiently to drive off combined water, form a porous structure which greatly increases their adsorptive capacity.

Solubility of Oxide Films. The corrosion behavior of aluminum is determined by the behavior of the oxide film with the solution concerned. It has been observed that the dissolution of the film is slower in acid than in alkaline solutions. Aluminum is a very basic metal and has a strong tendency to decompose water giving off hydrogen, and dissolving to form the aluminum cation (Al^{+++}). In the presence of alkaline solutions the aluminum has a strong tendency to decompose water giving off hydrogen and dissolving to form the aluminate ion (AlO_2^-). In noncomplexing solutions with pH between 2 and 14.6 the oxide film is formed. In salt solutions, aluminum always forms aluminum hydroxide ($Al(OH)_3$). When an aluminum film goes into solution it may form one of two possible ions depending on the pH of the solution. The colorless aluminum cation (Al^{+++}) forms in acid solution. The colorless aluminate anion (AlO_2^- or H_2AlO_3) is formed in basic solutions (10). The

solubility products for the various oxide in acid and basic solutions are tabulated in Table II (10, 23).

Artificial Oxide Films. Films very much thicker than natural oxide films may be produced by chemical or anodic treatment of aluminum and its alloys. The protective properties of artificial oxide films are widely different depending on their thickness, method of production, pretreatment and after-treatment. The structure of these films is different from the natural oxide films. Chemical treatments produce distinctly crystalline structures while anodic oxidation gives an amorphous film at ordinary temperature, which becomes crystalline, with very small grain size, upon increasing the temperature. The relative thickness of various artificial oxide coating on pure aluminum (99.5 per cent) are shown in Table III (42). The formation of these artificial films and their corrosion resistance is discussed under Inhibitors.

TABLE II

Solubility Products of Oxide Films

Oxide	In Acid $\ln (Al^{+++})(OH^-)$	In Base $\ln (H^+)(AlO_2^-)$
Al(OH) ₃	-32.3	-10.6
Al ₂ O ₃	-33.4	-11.8
Bohmite	-34.0	-12.4
Bayerite	-35.5	-13.8
Hydrargillite	-36.3	-14.6

Deltombe, E. and M. Pourbaix: The Electrochemical Behavior of Aluminum, Corrosion, 14, No. 11, pp. 16-20, (1960).

Hogness, T. R. and W. C. Johnson: "Ionic Equilibrium as Applied to Qualitative Analysis", Henry Holt and Co., New York, N. Y., (1954), 3 ed.

TABLE III

Thickness of Oxide Coatings

Type of Coating	Thickness of Oxide Coating (0.001 in.)
Natural oxide film	0.0002 - 0.006
Normal chemical coating	0.1 - 0.2
Normal anodising, sulphuric or oxalic acid	0.2 - 0.6
Normal anodising, chromic acid	0.1 - 0.2
Anodising, barrier coating	0.01 - 0.03
Anodising, hard coating	1 - 10

Wernick, S.: "Surface Treatment and Finishing of Aluminum and Its Alloys", Robert Draper Ltd., Middlesex, England, (1956).

Aluminum Trichloride

One of the corrosion products formed when aluminum dissolves in hydrochloric acid is aluminum trichloride (2, 39, 44, 45). It has been found that in aqueous solutions aluminum chloride forms the six hydrate. Electron diffraction photographs of the film structure and crystal size of the corrosion products of aluminum showed the aluminum trichloride six hydrate products were two dimensional crystals and fibers respectively as the hydrochloric acid increased from one normal to ten normal. Table IV (4, 22, 26, 41, 43) tabulates some of the physical properties of anhydrous aluminum chloride and aluminum trichloride six hydrate. The aluminum chloride film forming on the aluminum surface may act as a protective layer decreasing the rate of attack (2). The rate of dissolving of aluminum in hydrochloric acid is much slower than in hydrofluoric because of the aluminum chloride film (45). The surface condition of the metal is quite different in the two acids. The aluminum trifluoride forms a porous layer which does not have the protective properties of oxide layer or other protective films which form a tight adherent film and thereby inactivate the local cathods. The less negative potential (-0.577 volts in one normal hydrochloric acid) indicates that the aluminum trichloride film which is formed is less porous, less soluble in acid, and is more adherent to the surface than the aluminum trifluoride film.

TABLE IV

Properties of Aluminum Trichloride

Property	Anhydrous Al Cl ₃	Six Hydrate Al Cl ₃ • 6 H ₂ O
Crystal Structure	trigonal, isomorphous, triclinic, hexagonal, pseudo-rhombohedral	rhombic, orthorhombic
Color	white, yellow	colorless
Oder	hydrogen chloride	oderless
Deliquescent	very	some
Density	2.465	2.398 - .440
Boiling Point, °C	sublimes 177.8 - 185	decomposes
Solubility Hot Water	violently	very soluble evolves hydrogen chloride

Biltz, W.: Z. Anorg. Chem., 115, 241-252, (1921); J. Chem. Soc. Abs., 120 (II), 437 (21).

Hodgman, C. D.: "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 41 ed.

Kendall, J.: J. Amer. Chem. Soc., 45, pp. 963-996, (1923).

Thomas, C. A.: "Anhydrous Aluminum Chloride in Organic Chemistry", Reinhold Publishing Corp., New York, (1941).

Wooster, N.: Z. Krist. (A), 90, p. 562 (1935); C. A. Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry", Reinhold Publishing Corp., New York (1941).

When aluminum trichloride goes into solution a mixture of ions may occur. The three forms that occur are the aluminum ion (Al^{+++}), the aluminum mono-chloride ion ($AlCl^{++}$), and the aluminum di-chloride ion ($AlCl_2^+$) (10). These ions upon hydrolysis give respectively aluminum hydroxide ($Al(OH)_3$), aluminum chloride dihydroxide ($AlCl(OH)_2$), and aluminum di-chloride mono hydroxide ($AlCl_2OH$). The solubility product of aluminum trichloride in acid solutions has been quite difficult to measure because of the mixture of ions that may exist in solution. The solubility product of $(Al^{+++})(OH)^3$ has been calculated based on measurements of conductivities and electromotive forces in concentration cells of aluminum chloride and the value 1.06×10^{-33} or $10^{-32.97}$ has been obtained for very dilute solutions (10^{-4} M) (21). This value can be seen to be intermediate between those calculated for aluminum hydroxide ($Al(OH)_3$) and aluminum oxide (Al_2O_3).

Theory of Attack. The attack on aluminum in moist hydrochloric acid vapors is an electrochemical process (12, 13). A thin layer of water on the surface of the metal, believed a necessary condition for corrosion to occur (5), dissolves the acid vapors. The acid then attacks and removes the primary protective oxide film or penetrates through weak spots and reaches the metal surface. Ions can then leave the metal at these anodic areas and dissolve in the moisture layer. Hydrogen ions take up the electrons at the

cathodic points forming nascent hydrogen. The nascent hydrogen combines with the oxygen present in solution and forms the hydroxide ion. The proposed primary reactions are said to be:



The secondary reactions that follow these depend on the concentration of the oxide and the solubility of the products (12, 13, 37). The rate of attack is not proportional to the hydrogen ion concentration, but is related to the rate of diffusion of the acid through the corresponding film of corrosion products (27).

Inhibitors

This section deals with the various types of inhibitors which have been found effective in reducing the rate of attack on aluminum. The topics covered are mechanisms of inhibition, liquid inhibitors, chemical treatments, anodic oxidation, and vapor phase inhibitors.

Mechanisms of Inhibition. Inhibitors generally function in several ways: (12, 42)

1. Form insoluble corrosion products.
2. Reduce the open-circuit potential between local anodes and cathodes.
3. Increase the electrical resistance of the acid solution.
4. Increase local polarization of anodes, cathodes, or both.
5. Are strongly adsorbed on the surface of the metal and serve as a barrier.
6. Decrease rate at which metal goes into solution.

Liquid Inhibitors. Liquid inhibitors are the most effective method of inhibiting hydrochloric acid corrosion of aluminum. Cathodic inhibitors are the safest and most widely used type of inhibitor since they will decrease the corrosion rate in any concentration. Anodic inhibitors are quite dangerous since

insufficient inhibitor will cause an increase in the corrosion rate at the uninhibited areas. It has been proposed that the inhibitors work by:

1. The inhibitor being held to the metallic surface by electrochemical attractions.
2. The absorption theory which postulates the inhibitor being held to the surface by Van der Waals forces.
3. The actual effect is a combination of the first two.

There are many inhibitors for protecting aluminum against corrosion by hydrochloric acid. Table V shows the action of various inhibitors on hydrochloric acid on aluminum (1). Chromates are the only good anodic inhibitors but do not inhibit hydrochloric acid attack. Other inhibitors which have been found very effective for protection of aluminum include camphor, benzidine, urea, phenyl, nicotine sulfate, alkaloids, thiourea, iodine, amines, and nitrogen compounds which are usually effective in steel pickling (8, 12). The inhibited acid may be safely used for the cleaning of aluminum vessels and tanks.

Chemical Treatments. The most important coatings are of two types, based on thickening of the natural oxide present on aluminum surfaces and the production of phosphates, usually aluminum or zinc phosphates. A third type, which is used but is of minor importance, is the production of a chromate film. The oxide conversion coating

TABLE V

Hydrochloric Acid Inhibitors for Aluminum

Inhibitor	Inhibitor Concentration Per Cent	Acid Concentration Per Cent	Aluminum Purity	Reduction of Weight Loss (Per Cent)
Quinoline	1.1	5	Commercial	81
Quinoline	5.5	5	Commercial	99.5
Quinoline Ethiodide	1	5	Commercial	99
Quinoline Ethiodide	5	5	Commercial	99.6
2-Phenyl Quinoline	0.062	10	99.5	99.9
2-Phenyl Quinoline	0.0062	10	99.5	35
β Naphthoquinoline	0.054	10	99.5	98.5
β Naphthoquinoline	0.0054	10	99.5	52
Acridine	0.054	10	99.5	99
Acridine	0.0054	10	99.5	98
2-Phenyl Acridine	0.076	10	99.5	97
2-Phenyl Acridine	0.0076	10	99.5	94
Hexamethylene Tetramine	1	5	99.5	86
Gelatin	1	5	Commercial	98.5
Gelatin	5	5	Commercial	98.5
Dextrin	1	5	Commercial	96
Dextrin	5	5	Commercial	98

Aluminum In The Chemical and Food Industries, The British Aluminum
Co. Ltd., Salisbury House, London Wall, London EC2, No. 408, 1951.

can be used without further treatment but is usually used as an undercoating and a base for paint finishes. The oxidation reaction mechanism is believed to be the sodium carbonate present in the M.B.V. solution reacting with aluminum to form sodium aluminate:



the sodium aluminate then being partly hydrolysed:



The major oxidation processes in use are M.B.V. (Modifizierter Bauer-Vogel Process), E. W., and L. W., developed in Germany, the Pyllumin Process (England), and the Alrok Process (American). They all operate on approximately the same principle (38, 42).

In the phosphate processes, the aluminum reacts with the phosphoric acid, activated by the nitrate and fluosilicate or fluoborate, the solution becoming locally saturated at the interface and an acid phosphate being deposited (9). The "Bonderite 170" process is the chief method used. Phosphate coatings have good corrosion resistance but are more complicated and costly to produce. Neither chemical oxide or phosphate coatings provide useful protection against corrosion of aluminum and its alloys in hydrochloric acid.

Anodic Oxidation. The anodising coatings give a finer quality of finish and have a wider range of applications than chemical coatings. In anodising the aluminum piece is made an anode in an electrolytic solution. The anodic oxide film consists of two layers, the porous thick outer layer which grows on a thin, dense and dielectrically compact inner layer. The inner layer is formed first at high voltage and is a function of forming voltage and inversely with the dissolution velocity of the oxide film in the electrolyte. The theoretical maximum formed is a thickness of 14 Angstrom per volt (18). Once the layer has reached its limiting thickness, only a small leakage current can pass. The barrier layer allows the passage of nascent oxygen which is formed from water in the pores of the outer coating, and which acts continually on the aluminum to produce a new barrier layer. The pores are the result of anion attack. The oxygen formed in the pores prevents contact between the metal and the solution thus accounting for the protection of the barrier layer. The oxidation reaction is simple:



which takes place at the metal-oxide interface. The heat of formation of the oxide coating is approximately 14 BTU per square foot per each 0.1 mil of coating. If the piece is large and the coating is thick it is usually necessary to cool the solution since

the temperature must often be kept within ± 2 °C. These anodic finishes are extremely hard and adherent. They vary in thickness, and corrosive resistance depending on method of production, pretreatment, and after-treatment. The oxide film produced by anodizing aluminum is not protective against strong inorganic acids such as nitric or hydrochloric acid, and strong monobasic organic acids which dissolved the coating⁽¹⁾.

Vapor Phase Inhibitors. There are very few vapor phase inhibitors available. Vapor phase inhibitors are materials which volatilize at room temperatures. It has been found that formaldehyde, campher, benzidine, urea, and phenyl compounds offer some protection to aluminum exposed to volatile sulfur dioxide and chlorine⁽²⁸⁾. Vapor inhibitors in many situations are too costly and ineffective to warrant their use.

Analysis of Corrosion Products

The analysis of the corrosion products of aluminum is extremely important if the mechanism is to be understood. There are a number of physical techniques which can be used:

1. X-ray Diffraction. Most aluminum corrosion products are amorphous to x-rays and no definite patterns have been obtained. If the products are crystalline or if crystalline foreign matter is present it may be identified by this method. About a 10 mg sample is required⁽¹⁴⁾.
2. X-ray Fluorescence. The x-ray fluorescence technique is rather limited in use because the equipment is rather new. The method is non-destructive and the equipment is highly sensitive to many elements. It can not be used for determining the presence of elements below atomic number 12 (magnesium)⁽¹⁵⁾.
3. Differential Thermal Analysis. This method has been used to confirm that the corrosion products are generally amorphous. It has only limited use because there are a number of exothermic, irreversible reactions which occur at about 400-600 °C⁽¹⁵⁾.

4. Electrographic. This method may be used if there are deposited metals more noble than aluminum. The metals are dissolved anodically in contact with a gelatinized blotting paper to present a mirror image of the distribution of the original deposit. Chemical reagents can then be added to cause the coloration of the ions present⁽¹⁵⁾.

5. Spectrographic. The method uses Harvey's⁽¹⁷⁾ semi-quantitative analysis procedure. This method has been used to determine some 43 metallic elements. A 10 mg sample is required. A D.C. arc is struck to the products causing the radiation for the spectrograph.

6. Microscopic. This method may be used when there are only small amounts of the corrosion products and when only one type of product is present. A low power microscope is used to examine the nature of the products. The type of attack may also be determined by examination of the surface.

7. Qualitative. These tests are usually applied to the water soluble fraction of the corrosion products. It can be used for determining chlorides, sulfates, carbonates, nitrates, phosphates, copper, iron and calcium.

8. Quantitative. Quantitative tests have been developed for determining moisture content, loss on ignition, pH, chlorides, sulfates, carbonates, calcium, copper, iron, magnesium, silicon, total aluminum, and free aluminum in the corrosion. These tests are based on standard analytical procedures for aluminous materials.

III. EXPERIMENTAL

This section of the report contains the purpose of the investigation, experimental plan, a list of the materials and apparatus used, operational procedure, correlation of data and results, and sample calculations.

Purpose of Investigation

The purpose of this investigation was to attempt to determine the rates and mechanism of the surface reactions for the corrosion of aluminum in hydrochloric acid vapors as a function of the vapor concentration, vapor composition and temperature.

Plan of Experimentation

The method of approach used in this investigation is described below.

Literature Review. A search of the literature was made to obtain information concerning the principles of corrosion of aluminum, the kinetics of vapor-solid reactions, the method of correlating and analyzing experimental vapor-corrosion data, the chemical properties of the acid used in the vapor phase, and the published results of similar investigations.

Apparatus. The measuring system utilized in this investigation for continuously measuring the weight change of the corroding aluminum samples was a beam connected to a modified analytical balance similar to that used by W. H. Jago⁽²⁴⁾ for a related study in 1960. A schematic of the apparatus is shown in Figure 1. A glass reactor in which the vapor phase conditions can be controlled was used as the corrosion chamber for aluminum foil.

Experimental Procedure. For the experimental tests the vapor phase above the acid solutions was allowed to come to equilibrium inside the corrosion reactor before the aluminum sample was suspended inside the reactor. At equilibrium, the rate of weight change of the corroding specimen was determined for the particular set of operating conditions being investigated. The operating parameters and the range over which they were investigated was as follows:

(a) Acid concentrations in vapor and liquid phase were varied from two weight per cent acid to thirty-two weight per cent acid by two per cent increments.

(b) Temperature of the vapor phase was varied from 0 to 48 °C.

Analysis Procedure. In order to determine the mechanism of the corrosion reaction taking place on the surface of the aluminum sample, it was necessary to determine the chemical composition of the corrosion products formed. This was done by standard x-ray diffraction and analytical techniques.

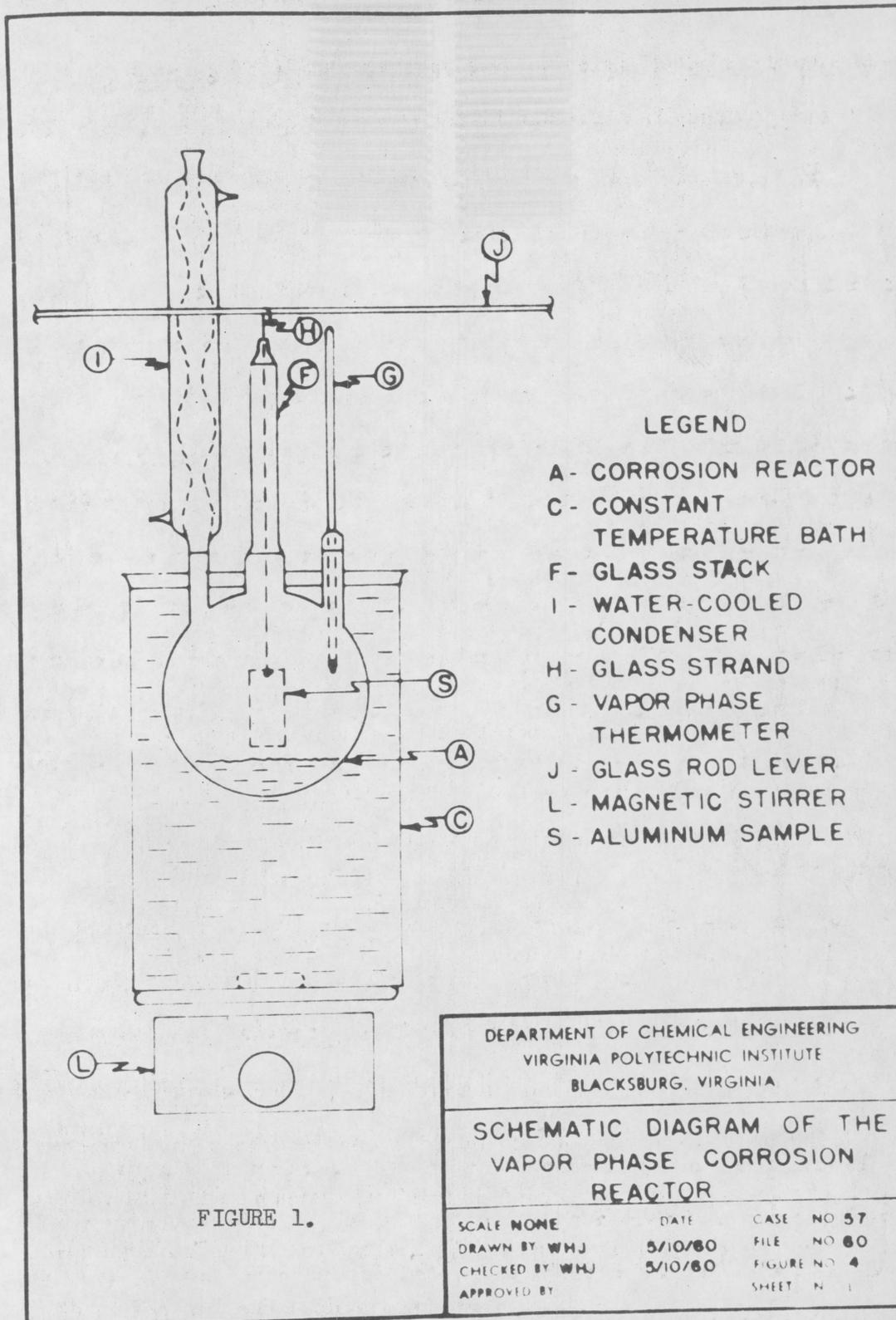


FIGURE 1.

Jago, W. H.: The Corrosion of Aluminum Over Nitric Acid Solutions, Unpublished Ph.D. Thesis, Library, Va. Poly. Inst., Blacksburg, Va., (1960).

Statistical Design. An experimental design, Table VI, was set up to minimize the number of tests required to determine the effects of temperature, concentration, and their interaction. The layout of the design is such that in most cases three tests may be run with the same acid solution. The data used in constructing the design is shown in Figure 2. Points were chosen from Figure 2 so as to give the same acid vapor pressure at various liquid concentrations and without excessive temperature levels.

TABLE VI

Statistical Design

Log HCl Partial Pressure mm Hg	<u>Temperature of Vapor Phase</u> <u>°C</u>									
	48	44	41	35	28	17	9	7	2	0
1.501	28	--	--	30	32	--	--	--	--	--
0.925	24	--	--	26	28	30	--	--	--	--
0.250	20	--	--	22	24	26	--	28	--	--
-0.520	--	16	--	18	20	22	--	24	--	--
-1.125	--	12	--	14	16	18	20	--	--	22
-1.825	--	--	8	10	12	14	16	--	--	18
-2.52	--	4	--	6	8	10	12	--	14	--
-3.250	--	--	2	--	4	6	8	--	10	--

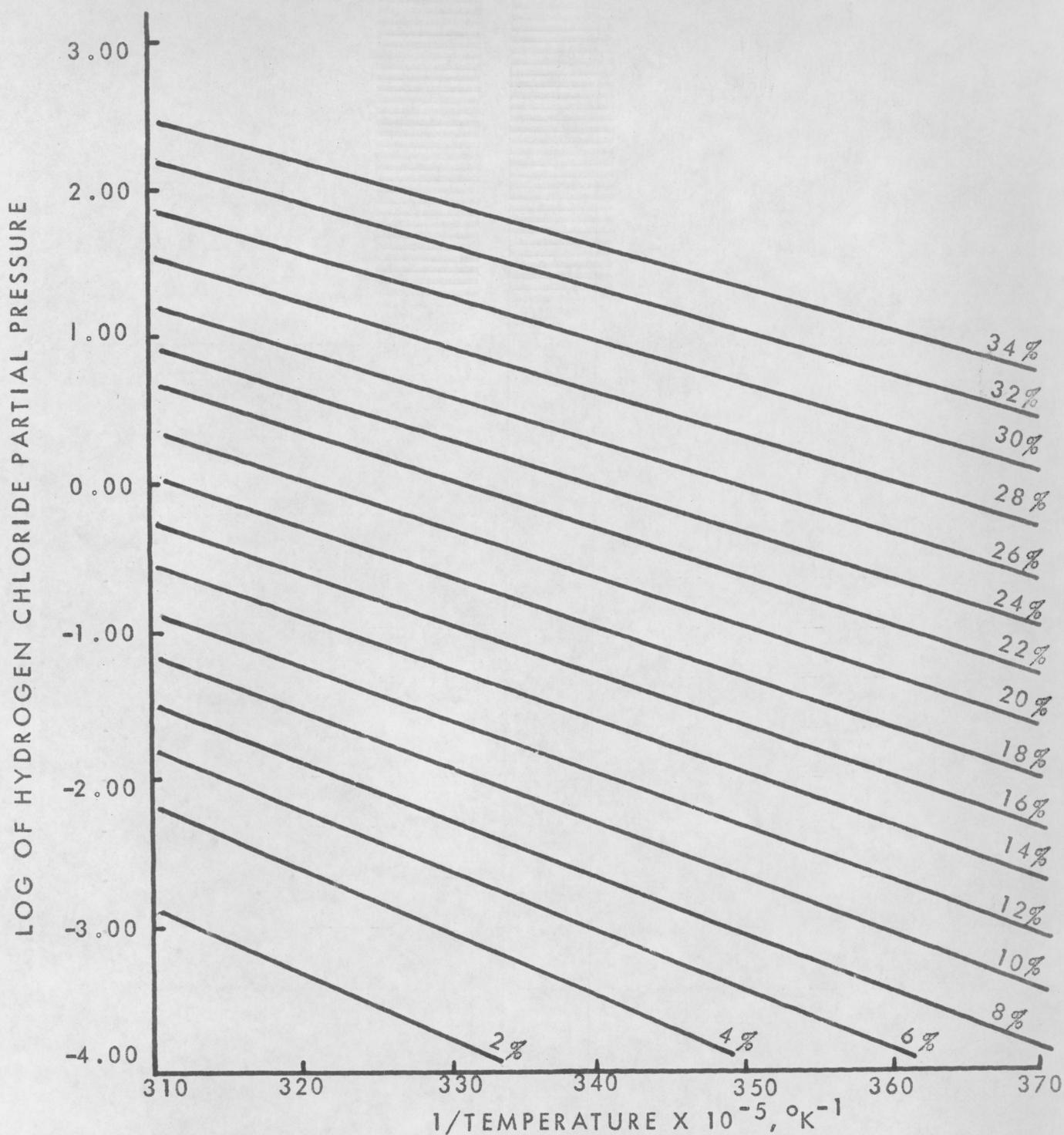


FIGURE 2. CHANGE IN HYDROGEN CHLORIDE PARTIAL PRESSURE WITH TEMPERATURE

Perry, J. H.: "Chem. Eng. Handbook", 3 ed., pp. 166-168, McGraw-Hill Book Co., New York, 1950.

Materials

The materials employed in this investigation are listed in the paragraphs following:

Aluminum. Commercial grade aluminum "Reynolds Wrap" foil, 99.9 aluminum⁽⁴⁶⁾. Manufactured by Reynold Metals Company, Richmond, Virginia. Used as the samples for the various corrosion tests.

Anhydrous Aluminum Trichloride. Cat No A-575, lot No 753856. Manufactured by Fisher Scientific Co., Fair Lawn, New Jersey. Used to determine the water uptake of aluminum trichloride in a desiccator.

Calcium Sulfate. Drierite, anhydrous, size 8-mesh. Manufactured by W. A. Hammond Drierite Co., Xenia, Ohio. Used to dry aluminum samples from reactor and maintain them in a moisture free environment.

Ether. Anhydrous, commercial grade, lot No 9483. Manufactured by J. T. Baker Chemical Co., Phillipsburg, New Jersey. Used to determine solubility of corrosion product.

Hydrochloric Acid. Reagent, C. P., code 1090, lot E 111005, analysis given in Table VII. Manufactured by General Chemical Division, Allied Chemical and Dye Corporation, New York, N. Y. Diluted solutions of acids used as the corroding media in the various tests.

TABLE VII

Analysis of Hydrochloric Acid

M.W. 36.46

Assay (HCl) 37-38 per cent

Sp. Gr. 1.188-1.192 per cent

Maximum Limits of Impurities

	<u>Per Cent</u>
Residue after Ignition	.0003
Sulfate (SO ₄)	.00008
Sulfite (SO ₃)	.0001
Free Chlorine (Cl)	.00005
Amonium (NH ₄)	.0003
Arsenic (As)	.0000008
Heavy Metals (as Pb)	.00008
Iron (Fe)	.00001
Meets ACS Specifications	

Obtained from General Chemical Division, Allied Chemical and Dye Corporation, New York, New York

Potassium Acid Phthalate. Reagent, crystal lot No K072.

Manufactured by General Chemical Division, Allied Chemical and Dye Corporation, New York, N. Y., U.S.A. Used to standardize the sodium hydroxide solution.

Sodium Hydroxide Pellets. Reagent, cat No S-318, lot 794564.

Manufactured by Fisher Scientific Co., Fair Lawn, New Jersey. Used to prepare standard sodium hydroxide solution.

Tri-ethylene Glycol. Technical grade, lot No S-7048 HH.

Manufactured by Carbide and Carbon Chemicals Corporation, South Charleston 3, West Virginia. Used as constant temperature medium in the constant temperature bath.

Water. Distilled. Obtained from the distillation of Virginia Polytechnic Institute tap water in a tin lined, steam heated, still unit in Randolph Hall, Virginia Polytechnic Institute, Blacksburg, Virginia. Used for diluting hydrochloric acid to the desired concentration.

Ice. Obtained from a Frigidaire ice machine located in Randolph Hall, Virginia Polytechnic Institute, Blacksburg, Virginia. Used to maintain temperature in constant temperature bath.

Tap Water. Obtained in Randolph Hall, Virginia Polytechnic Institute, Blacksburg, Virginia. Used as a constant temperature medium in the constant temperature bath for low temperature tests.

Apparatus

The apparatus utilized in this investigation was the following.

Balance. One, laboratory 200-gram analytical balance, model No 1-916. Obtained from Fisher Scientific Co., Silver Spring, Maryland, U.S.A. The balance was modified so as to allow continuous weighing of the corroding aluminum samples.

Barometer. One, mercury barometer, patent No 1,950,497. Obtained from W. M. Welsh Scientific Co., Chicago, U.S.A. Used for measuring atmospheric pressure.

Bath, Constant Temperature. Ethylene glycol or water, agitated, four liter, pyrex beaker, model No 1000. Obtained from the Corning Glass Works, Corning, New York. Used to maintain the corrosion reactor at constant temperature.

Condenser. One, pyrex glass spiral tube condenser. Obtained from the Corning Glass Works, Corning, New York. Used to condense hydrochloric acid vapors during the tests.

Flasks. Two, 500-milliliter, three-necked, ground glass joint, pyrex flasks. Obtained from Fisher Scientific Co., Silver Spring, Maryland, U.S.A. Used in construction of corrosion reactors.

Thermix-Stirring Hot-Plate. One, magnetic stirrer, hot plate, model No 11-493. Obtained from the Fisher Scientific Co., Silver Spring, Maryland, U.S.A. Used to maintain temperature in constant temperature bath.

Thermometers. Two, engraved stem mercury thermometers, type No. M-985, range -20 to 110 °C. Obtained from Fisher Scientific Co., Pittsburgh, Pennsylvania. Used to measure the vapor phase temperature and the constant bath temperature.

Watch. One, wrist watch with a sweep second hand. Manufactured by Waltham Watch Company, Waltham, Massachusetts. Used to measure time periods during corrosion tests.

Wire Thread. Chrome, 0.0063 inch in diameter. Obtained from the Driver-Harris Company, Harrison, New Jersey. Used to support the glass weighing level from the ring stand and the left-hand pan support of the modified analytical balance.

X-Ray Diffraction Machine. One, x-ray diffraction machine and components, type S300062, serial No. 277. Manufactured by the General Electric Company, Pittsburgh, Pennsylvania. Used to determine the composition of the corrosion products.

Miscellaneous. Beakers, desiccators, rubber tubing, ring stands, glass rods, pipets, burets, volumetric flasks, and general glassware. Used for making various acid solutions, hooked glass threads for supporting aluminum samples in vapor phase, and for other general laboratory uses.

Method of Procedure

This section of the report deals with the preparation of samples and materials, and with the operation of the equipment during the corrosion tests.

Preparation of Aluminum Samples. The aluminum samples were cut from a roll of "Reynolds Wrap" aluminum. The samples were five-by-two centimeters with a total area of 20 square centimeters. The samples were handled with tweezers at all times to allow as little grease, oil, or other foreign matter as possible from coming in contact with the surface. A darning needle was used to punch a hole in the aluminum samples one centimeter in from a two centimeter edge and one centimeter in from a five centimeter edge. The samples were suspended above the hydrochloric acid solution in the reactor on one end of a glass strand hooked through a hole in the sample.

Preparation of Hydrochloric Acid Solutions. The various hydrochloric acid solutions were prepared by diluting sufficient concentrated hydrochloric acid in distilled water to fill a 500-milliliter volumetric flask. A 5- to 25-milliliter sample was then pipeted and titrated against a standard one normal sodium hydroxide solution. One hundred milliliters of the standardized acid was then measured into the reactor for each test.

Construction of the Modified Analytical Balance System.

The left-side glass panel and the two weighing pans of an analytical balance were removed. A glass rod, 0.32 centimeter in diameter and 60 centimeters long, was notched in the center and one centimeter in from both ends. By means of a wire thread fastened at the end notches the glass rod was suspended from the left pan support and from a ring stand. A counterweight sufficiently large to zero the balance was suspended from the right hand pan support of the balance. The aluminum samples were suspended by a hooked glass thread from the notch in the center of the glass rod. The glass rod which acted as a second class lever was so arranged that a reading on the balance was equal to half the actual increase in sample weight.

Corrosion Reactor Components. A 500-milliliter, three-necked flask with ground-glass joints was used. A water cooled condenser was used in one of the narrow joints to condense any acid vapors. A thermometer, with standard taper joint and adapter, was used in the other narrow joint to measure the temperature of the vapor phase. In the center joint a glass stack was placed. The top of the stack had a four-millimeter opening through which the glass thread, suspending the test sample, passed. A schematic of the reactor system is shown in Figure 1, page 27.

Corrosion Test Procedure. One hundred milliliters of the hydrochloric acid solution was initially placed in the corrosion reactor. The magnetic stirrer was operated so as to maintain the desired vapor phase temperature. Water was circulated through the condenser and the temperature of the vapor phase in the reactor was allowed to come to equilibrium. For those tests conducted below room temperature a water-ice system with a siphon for level control was used to maintain the desired test temperature. After the system had reached thermal equilibrium the glass stopper, which had been placed in the center joint to prevent excessive condensation in the stack and on the glass thread, was removed. Using a pair of tweezers the test sample was suspended from one of the hooked ends of the glass strand. The glass stack and glass strand were then placed on the reactor. The aluminum sample was hung two centimeters above the hydrochloric acid solution, while the other end of the glass thread was placed in the center notch of the glass balance rod.

The rate of weight increase of the corroding specimens was then measured by readings on the balance. Readings of the weight increase were taken every ten minutes for two hundred minutes or until a sharp decrease in weight, caused by drops from the surface of the sample falling into the acid solution, occurred. The test was then halted and the stack, glass thread, and sample were removed. The sample was removed with a pair of tweezers, placed

in a stoppered glass bottle, and weighed. The weighed sample was placed in a desiccator with calcium sulfate and allowed to dry for 24 hours. The sample was reweighed after drying and stored in the desiccator.

The corrosion reactor, glass stack, and glass thread were disassembled, cleaned and reassembled after each test.

Anhydrous Aluminum Trichloride Adsorption Test. A sample of anhydrous aluminum trichloride (Al_2Cl_6) was placed in a shallow, wide-mouth weighing bottle, weighed and placed in a desiccator. The sample was removed from the desiccator, weighed and replaced at various times over a five-day interval.

X-Ray Analysis. The samples for analysis were stored in a desiccator before testing. The surface of the samples was sprayed with crylon clear plastic spray to prevent the oxidation of corrosion products. The crylon clear plastic spray was found to have no effect on the diffraction pattern of the aluminum or its corrosion products. The products were determined by standard x-ray diffraction methods. (14)

Data and Results

This section of the report presents the data and results obtained during the course of this investigation.

Vapor-Pressure Equilibrium Data for Hydrochloric Acid Solutions. The partial pressure of hydrochloric acid above its solutions was obtained from Perry's Handbook⁽³⁴⁾. The graphical representation of the data used in the experimental design is shown in Figure 2, page 30.

Corrosion Data. The data for the increase in weight of the aluminum samples above various hydrochloric acid solutions are tabulated in Table VIII. The graphical representation of the data is shown in Figures 3 through 12, and shows the increase in sample weight with time. These figures show a linear increase in sample weight with respect to time. Figures 13, 14, 15, and 16 show the variation of the rate of weight gain with hydrochloric acid partial pressure, vapor phase temperature, hydrochloric acid liquid concentration, and the ratio of the partial pressure of water to that of hydrochloric acid. An Arrhenis plot of the data is shown in Figure 17. The activation energies obtained from the slope of the Arrhenis plot are seen to be approximately constant in Figure 18. The calculated values for the activation energies are tabulated in Table IX. Note that the values are approximately constant at 7111 ± 908.9 calories per mole.

TABLE 8.

CORROSION DATA FOR ALUMINUM ABOVE HYDROCHLORIC ACID SOLUTIONS

TEST NO.	HYDROCHLORIC ACID CONC. WEIGHT %	TEMP. °C	BAROMETRIC PRESSURE mm Hg	VAPOR PRESSURE HYDROCHLORIC ACID mm Hg	WATER mm Hg	SAMPLE AREA cm ²	INITIAL SAMPLE WEIGHT mg	DRY SAMPLE WEIGHT mg	WEIGHT GAIN OF ALUMINUM SAMPLES mg																REACTION RATE mg/cm ² /min					
									10	20	30	40	50	60	70	80	90	100	110	120	130	140	150	160		170	180	190	200	
1	4	28	711.4	0.00562	28.3	20	47.3	49.5	0	0.4	1.0	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.4	1.6	1.8	1.8	1.8	2.0	2.0	2.2	0.0005			
2	4	44	704.7	0.00302	68.2	20	46.0	48.8	0.2	0.4	0.6	0.8	1.4	3.0	3.8	5.2	6.4	7.2	8.0	8.8	9.8	10.6	11.2	12.0	12.6	13.0	12.4	0.0015		
3	2	41	707.7	0.00562	58.3	20	46.6	47.7	1.0	1.6	2.8	3.0	3.0	3.2	3.2	3.4	3.4	3.6	3.6	3.8	4.0	4.4	4.6	5.0	6.2	—	—	0.0265		
4	20	28	691.6	0.316	17.5	20	46.0	68.1	4.4	8.4	15.2	20.0	25.2	31.0	35.4	41.2	46.2	51.4	56.8	62.4	68.4	73.8	79.2	84.6	91.2	—	—	0.1065		
5	20	44	709.7	1.77	51.1	20	46.1	—	13.8	36.4	59.2	81.8	10.68	128.4	103.4	122.4	142.2	92.8	—	—	—	—	—	—	—	—	—	0.0022		
6	6	35	—	0.00302	39.4	20	46.4	48.6	1.6	2.0	2.6	2.8	3.2	3.6	4.6	4.8	5.0	5.0	5.2	5.4	5.4	5.6	5.8	6.0	6.2	6.2	6.4	6.8	0.0235	
7	28	28	709.7	8.4	10.4	20	46.1	135.4	3.6	8.4	13.2	18.0	23.8	28.4	31.6	37.0	41.6	46.4	52.2	55.8	60.8	66.2	71.2	76.2	81.4	85.4	89.6	94.4	0.0245	
8	28	44	706.5	31.6	33.5	20	46.0	—	5.8	9.2	14.4	20.6	25.6	30.0	34.6	39.6	46.0	—	55.0	59.2	63.4	71.2	75.0	79.6	84.6	89.0	94.4	99.2	0.0068	
9	6	17	709.0	0.00562	12.6	20	46.1	46.6	0	0.2	0.2	0.4	0.6	0.8	1.2	1.2	1.4	1.8	2.0	2.0	2.2	2.4	2.6	2.8	2.8	2.8	2.8	3.4	0.005	
10	20	9	706.9	0.0749	5.2	20	46.6	53.5	0.2	0.8	1.6	2.6	3.6	4.6	5.4	6.6	7.6	8.6	9.4	10.6	11.4	—	—	—	—	—	—	—	0.016	
11	28	7	699.1	1.77	2.66	20	48.1	116.1	1.4	4.0	6.8	10.2	12.2	15.6	18.4	21.6	25.6	28.0	31.4	34.8	38.6	42.0	45.0	48.6	52.4	55.6	59.2	62.8	0.0085	
12	32	28	699.1	31.6	7.40	20	48.1	114.1	3.6	7.6	12.4	13.4	16.4	19.4	22.6	24.0	29.4	30.8	33.8	37.6	41.8	45.8	50.4	55.0	59.8	65.4	70.6	75.2	0.016	
13	18	17	705.6	0.0749	9.11	20	47.7	57.7	0.4	1.4	2.4	4.0	5.6	6.8	8.2	10.2	11.2	12.6	13.4	15.4	17.4	19.0	20.4	22.0	23.2	24.2	25.2	26.4	0.007	
14	24	7	710.0	0.316	3.62	20	47.3	67.2	0.2	1.0	2.8	3.8	5.2	6.0	8.2	10.4	12.0	13.8	15.8	18.0	19.8	22.2	25.0	27.0	29.2	31.6	34.4	36.4	0.0085	
15	24	28	710.0	1.77	14.1	20	48.0	205.5	4.0	12.8	24.4	36.2	48.2	60.2	72.0	84.6	96.6	108.8	120.6	133.8	148.6	156.8	168.8	180.4	192.2	204.0	215.4	225.4	0.060	
16	8	28	711.6	0.00302	25.0	20	45.7	46.8	0	0	0.2	0.2	0.2	0.2	0.4	0.4	0.6	0.6	0.6	0.6	0.8	0.8	0.8	0.8	0.8	1.0	1.0	1.0	0.004	
17	8	41	711.5	0.01492	51.5	20	46.3	51.1	1.6	4.4	5.0	5.6	7.0	8.0	9.0	10.2	10.8	11.6	12.6	14.0	15.4	16.6	17.2	17.6	18.4	19.0	20.4	22.4	0.0045	
18	24	48	711.7	8.4	41.6	20	46.2	293.4	8.0	26.4	44.2	62.2	79.0	91.4	106.8	119.0	136.2	151.8	166.0	181.0	194.2	208.0	221.0	235.2	249.8	262.4	278.0	294.2	0.078	
19	8	9	706.9	0.00562	7.5	20	46.0	46.0	0.2	0.2	0.2	0.2	0.2	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.004	
20	22	0	713.0	0.0749	2.33	20	46.6	52.7	1.4	1.6	1.8	2.0	2.4	3.0	3.6	4.8	5.6	7.2	7.6	8.4	9.2	10.2	10.8	11.8	12.6	13.4	13.8	15.2	0.016	
21	22	17	713.0	0.316	7.35	20	46.4	75.3	0.6	3.2	6.6	9.8	12.6	16.0	19.2	22.4	26.0	29.4	32.8	36.2	39.2	42.4	45.8	49.2	52.6	56.2	60.6	64.2	0.016	
22	18	0	710.6	0.01492	2.87	20	46.8	48.5	0.4	0.8	1.2	1.2	1.4	1.6	1.8	2.0	2.4	3.0	3.4	3.6	3.8	4.0	4.2	4.4	4.6	5.0	5.2	5.4	0.0012	
23	12	28	708.9	0.01492	22.4	20	46.3	51.0	0.2	1.0	1.6	2.4	2.6	3.2	3.8	4.0	4.6	5.2	5.6	5.8	6.4	6.6	7.0	7.4	7.8	8.2	8.8	9.2	0.0026	
24	12	9	706.0	0.00302	6.5	20	46.4	46.5	0	0.2	0.6	0.6	0.8	0.8	1.0	1.0	1.2	1.2	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.6	0.0046
25	22	35	706.1	1.77	22.8	20	46.1	—	5.0	17.4	33.0	47.0	62.0	79.0	94.2	109.0	123.2	137.4	151.2	169.2	184.8	192.2	208.4	226.4	244.4	262.4	278.0	294.2	0.075	
26	18	35	706.2	0.316	27.5	20	46.2	49.0	1.4	7.8	13.8	21.8	26.8	32.6	38.2	44.0	50.0	57.0	63.6	69.8	76.0	84.2	93.4	99.6	104.2	108.8	114.4	119.4	0.0425	
27	26	35	704.6	8.4	18.0	20	46.1	156.7	3.4	13.0	22.0	31.2	39.2	48.0	57.2	65.2	73.0	80.8	87.2	95.6	103.6	111.8	119.4	127.4	135.0	143.2	150.8	158.6	0.0425	
28	12	44	704.5	0.0749	51.7	20	47.1	71.0	5.0	8.4	12.8	15.2	17.0	18.2	20.4	22.8	25.4	28.2	31.4	33.4	35.8	38.2	40.2	42.0	44.2	46.4	48.6	50.6	0.0135	
29	16	44	704.7	0.316	41.6	20	46.2	78.5	6.0	13.6	20.2	26.6	33.2	40.0	46.6	53.0	58.8	64.2	70.6	77.0	83.8	89.8	96.0	102.6	108.6	114.0	119.2	125.0	0.0335	
30	10	35	705.4	0.01492	35.5	20	46.0	—	0.6	1.4	1.4	1.8	4.6	6.4	7.4	8.4	9.0	10.2	10.8	11.2	11.2	9.6	11.2	12.0	12.8	13.8	15.0	16.0	0.0096	
31	10	17	699.5	0.00302	12.2	20	46.4	46.6	0	0	0	0.2	0.4	0.4	0.6	0.6	0.6	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	1.0	1.0	1.0	0.0054	
32	26	17	699.5	1.77	5.82	20	46.3	147.3	3.4	7.8	11.8	17.8	23.8	29.8	35.4	40.0	46.2	52.2	57.6	63.2	69.4	75.4	81.2	87.0	92.8	98.4	104.4	0.028		
33	16	33	—	0.01492	5.86	20	46.5	48.0	0	0.2	0.4	0.6	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0	3.2	3.4	3.6	3.8	4.2	0.00105	
34	16	28	—	0.0749	18.5	20	46.0	58.5	2.4	4.6	6.2	7.0	8.4	10.4	12.0	14.0	15.4	16.6	18.2	19.4	21.0	22.4	23.4	25.4	27.6	29.0	30.8	—	0.0140	
35	30	35	698.1	31.6	13.7	20	45.8	109.4	2.8	6.0	8.8	12.4	15.2	18.0	20.4	22.4	25.0	28.2	30.8	33.8	38.0	41.8	45.0	48.4	51.8	55.8	60.4	—	0.0135	
36	30	17	701.9	8.4	4.35	20	46.1	87.3	1.0	3.2	5.2	7.8	10.6	13.4	16.6	19.2	21.6	22.6	2.58	28.0	29.4	31.6	33.6	36.2	38.0	39.6	41.8	—	0.0088	
37	14	—	—	0.01492	10.2	20	46.0	47.5	0.2	0.2	0.2	0.4	0.4	0.6	0.8	1.0	1.2	1.4	1.6	1.8	2.0	2.2	2.4	2.4	2.4	2.4	2.6	2.8	3.0	0.0004
38	14	2	—	0.00302	3.98	20	46.1	46.4	0	0	0	0	0.2	0.2	0.2	0.4	0.4	0.6	0.6	0.8	1.0	1.0	1.2	1.2	1.4	1.6	1.8	2.0	0.0004	
39	10	2	702.0	0.00562	4.45	20	46.3	46.4	0	0	0	0.2	0.2	0.4	—	1.0	—	—	—	—	—	—	—	—	—	—	—	—	0.0078	
40	14	35	702.0	0.0749	31.9	20	45.3	54.1	0.6	3.0	5.0	6.6	8.6	10.0	11.4	12.8	14.2	15.8	17.4	18.8	20.4	22.0	24.0	25.8	27.6	29.6	31.4	33.0	—	

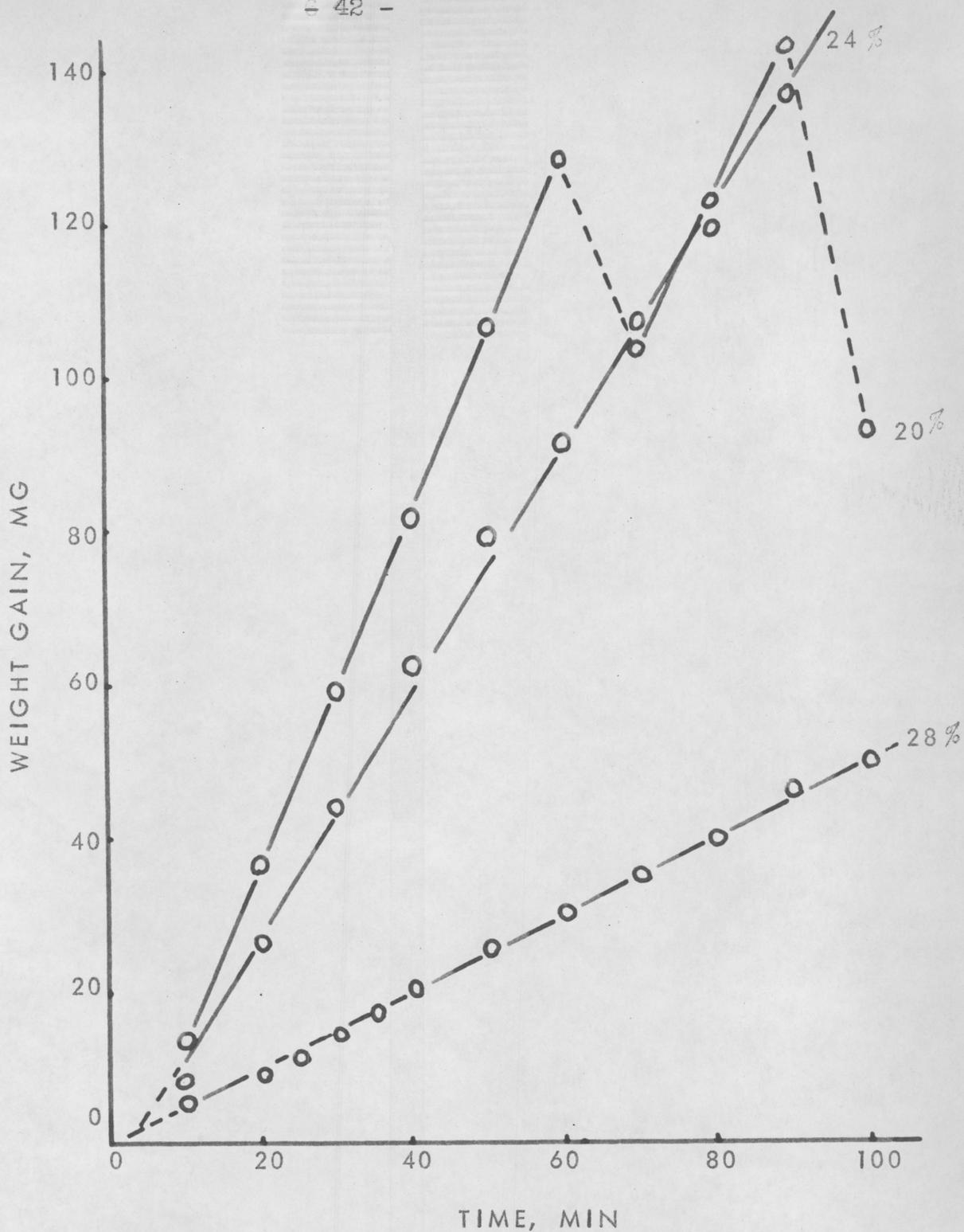


FIGURE 3. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 48°C

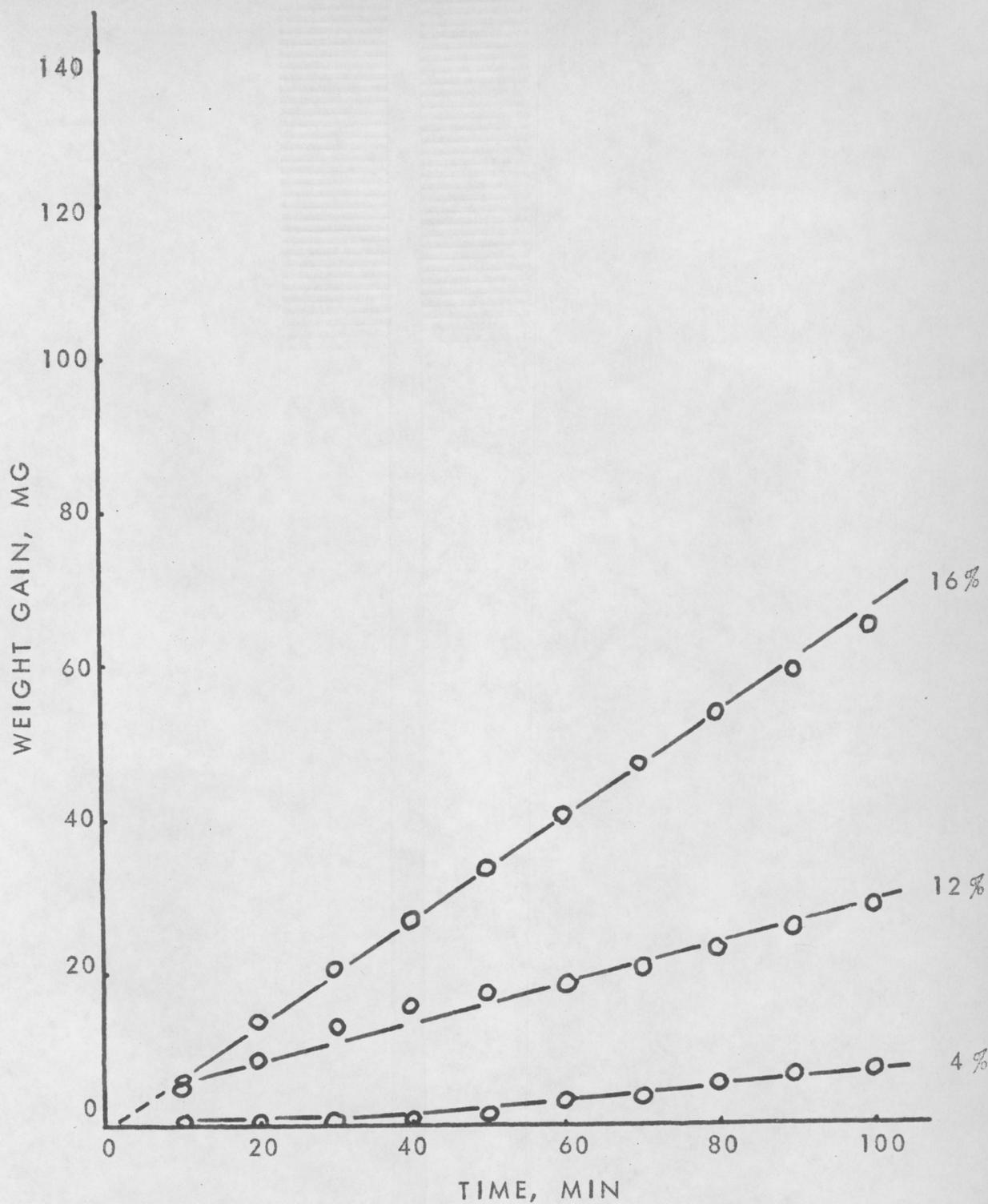


FIGURE 4. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 44°C

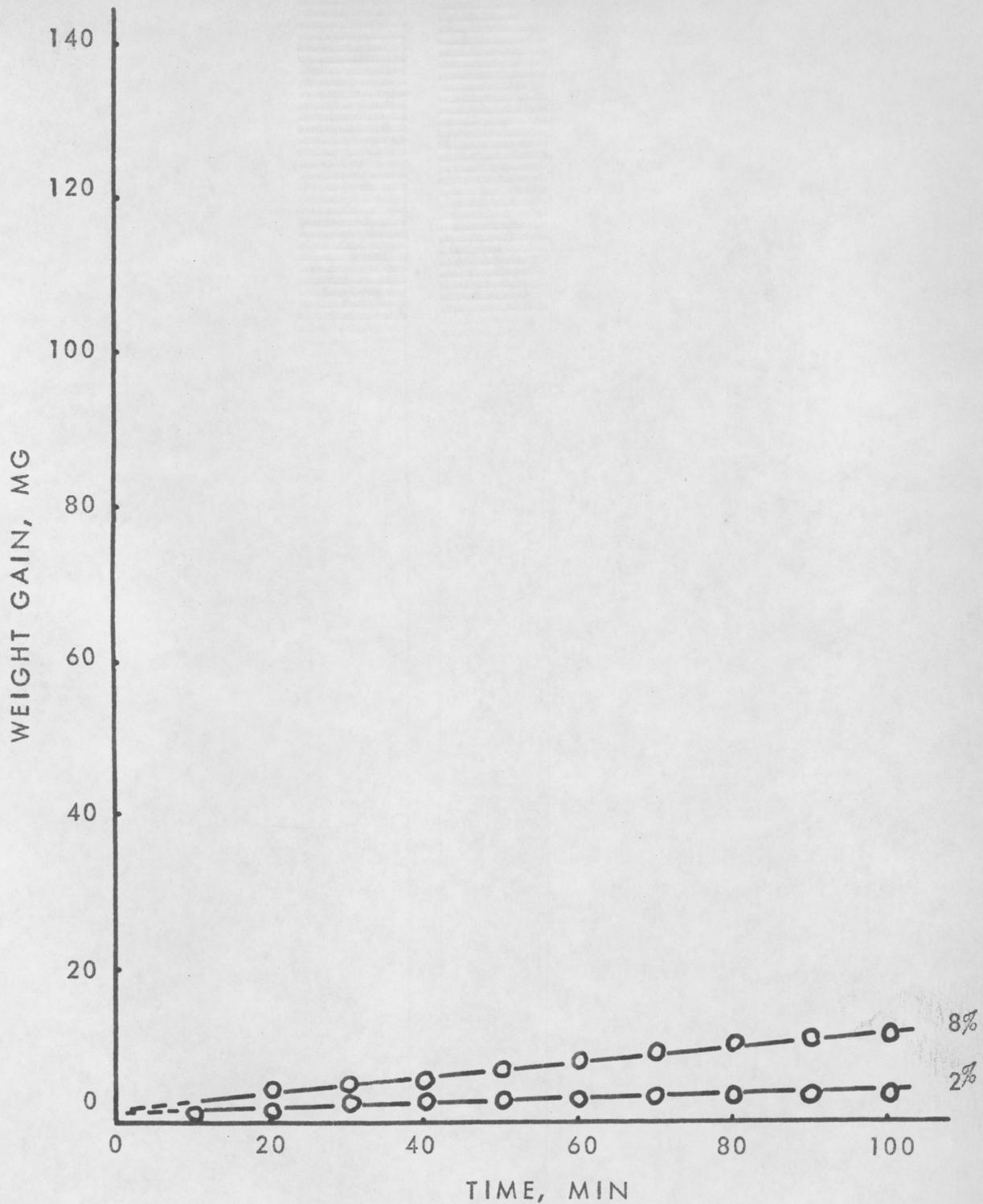


FIGURE 5. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 41°C

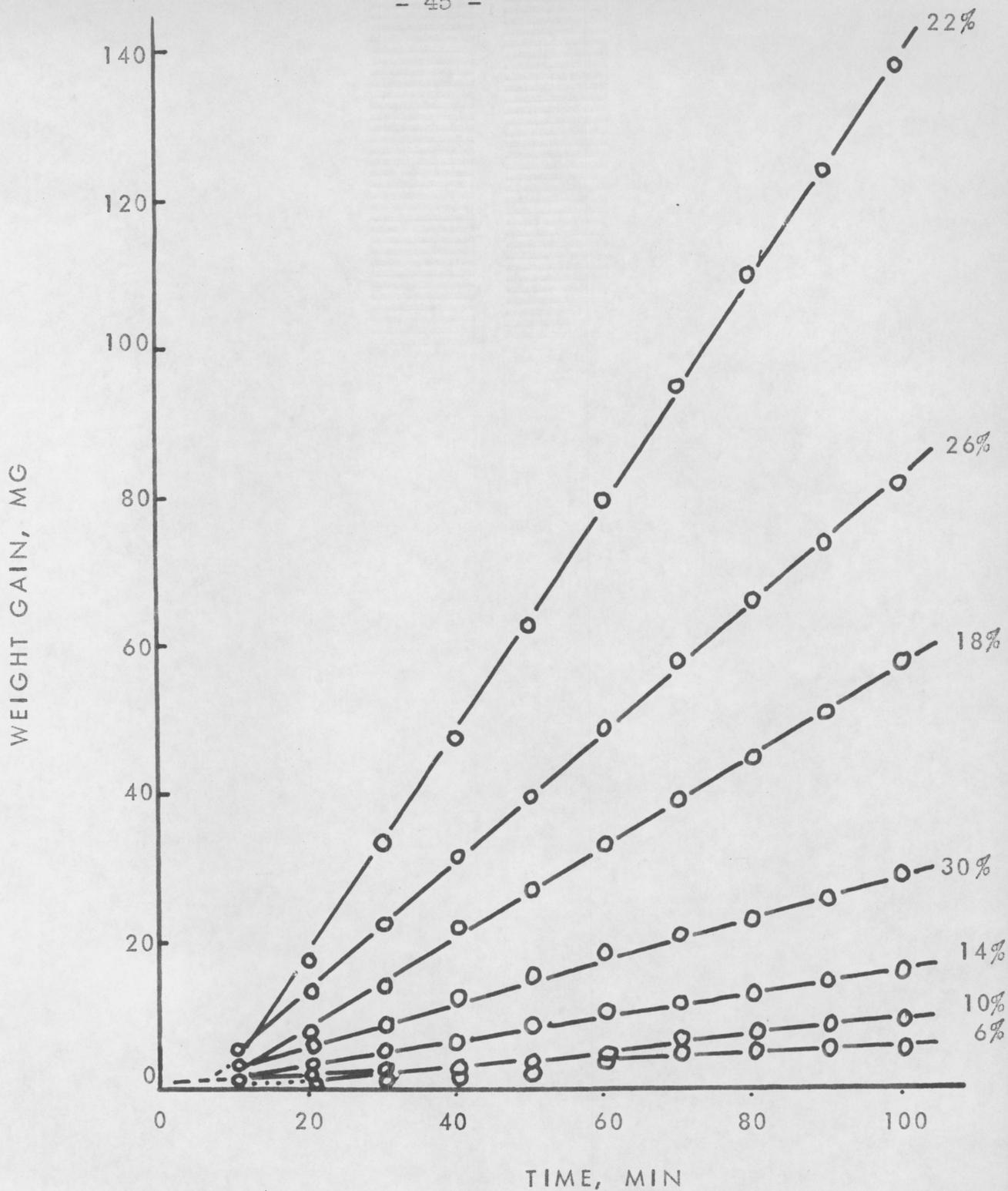


FIGURE 6. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 35 C

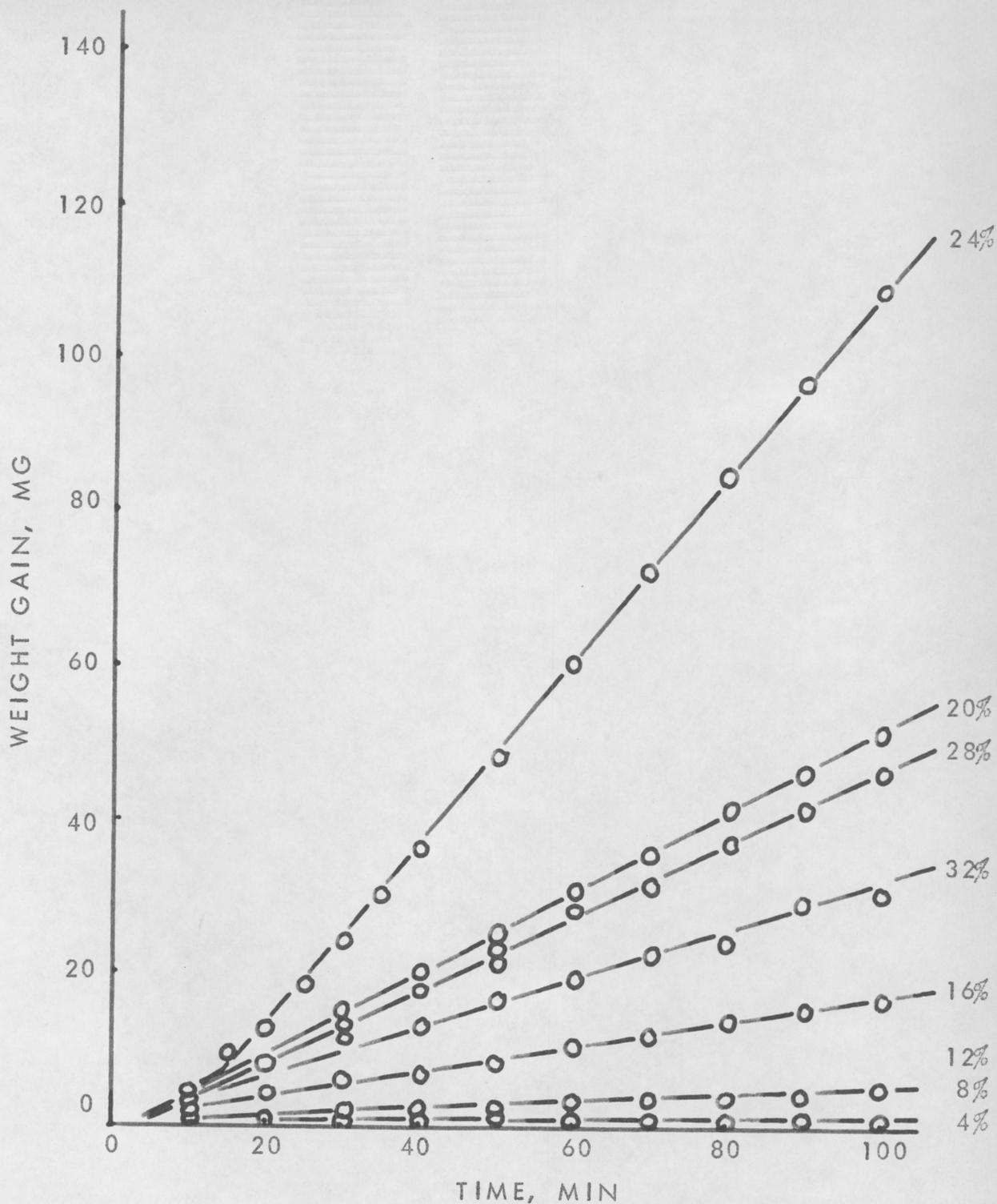


FIGURE 7 . INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 28°C

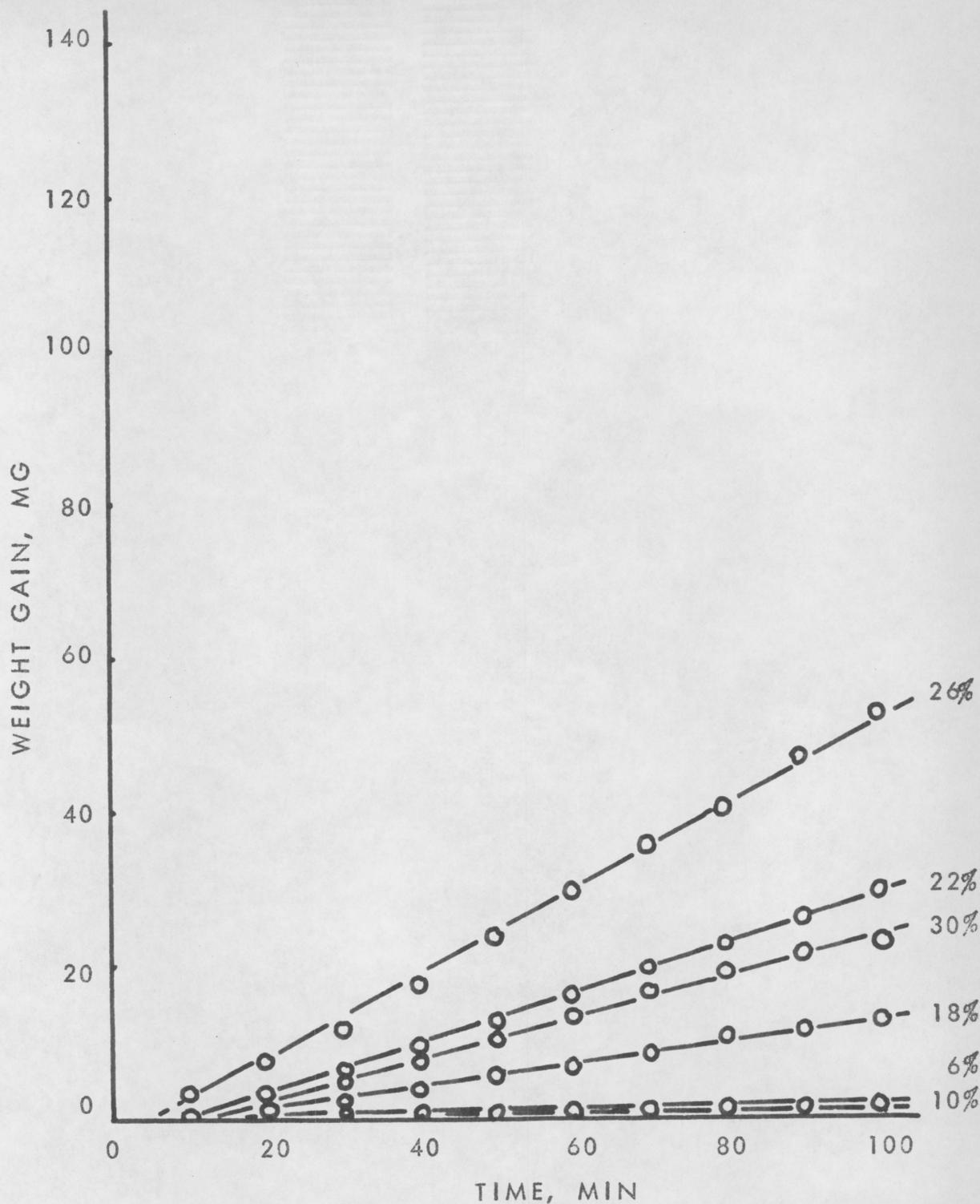


FIGURE 8 . INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 17°C

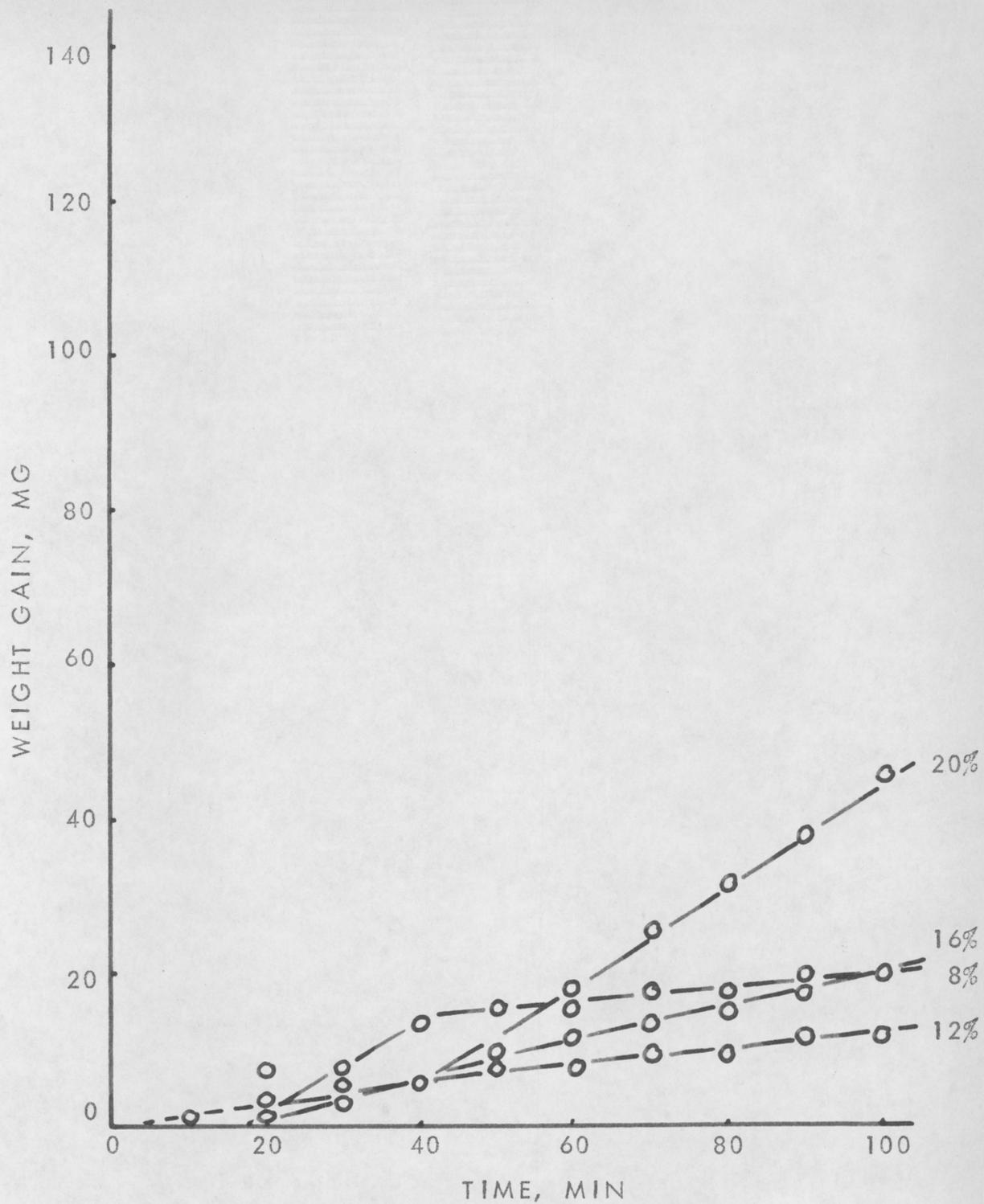


FIGURE 9. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 9°C

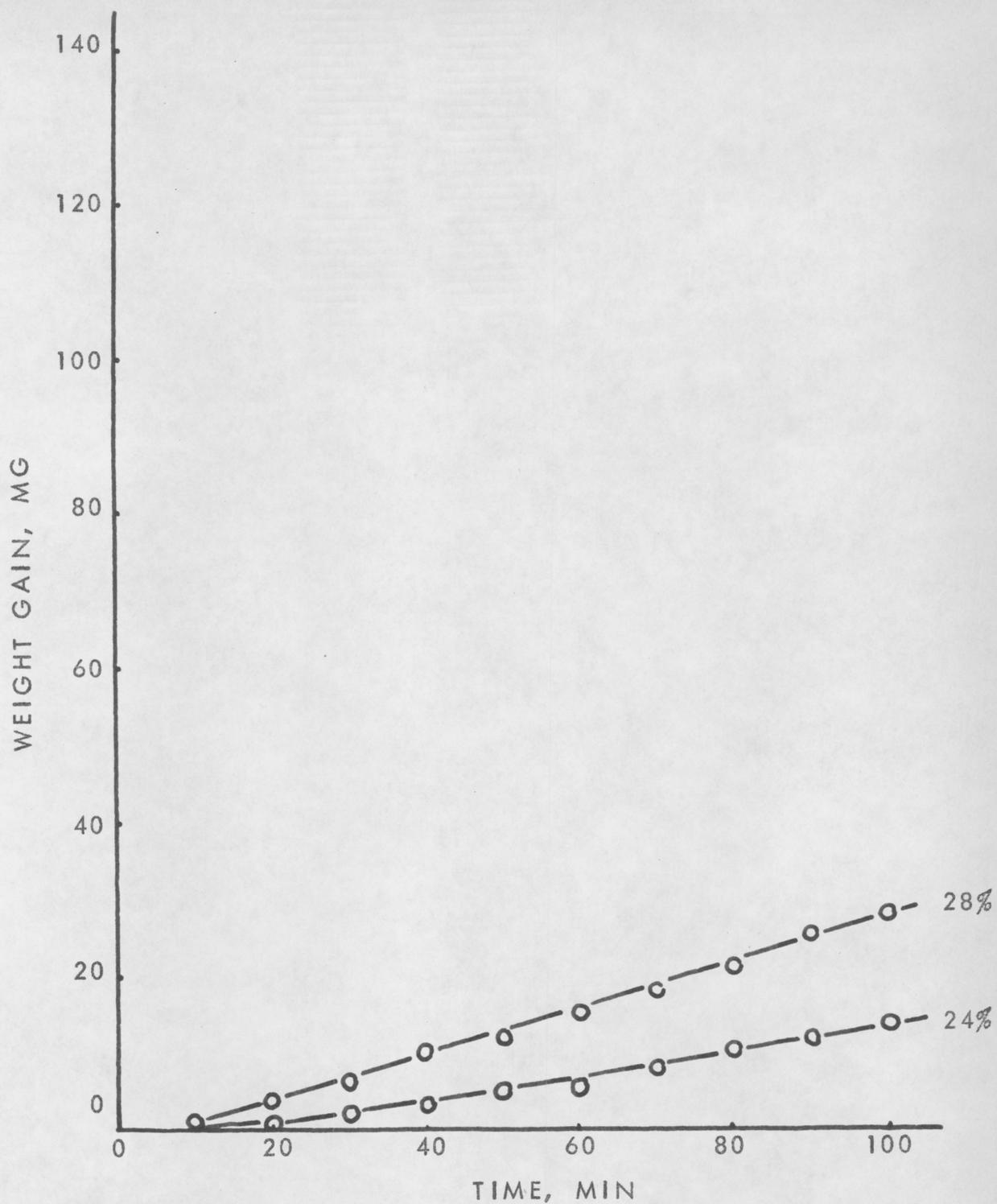


FIGURE 10. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 7°C

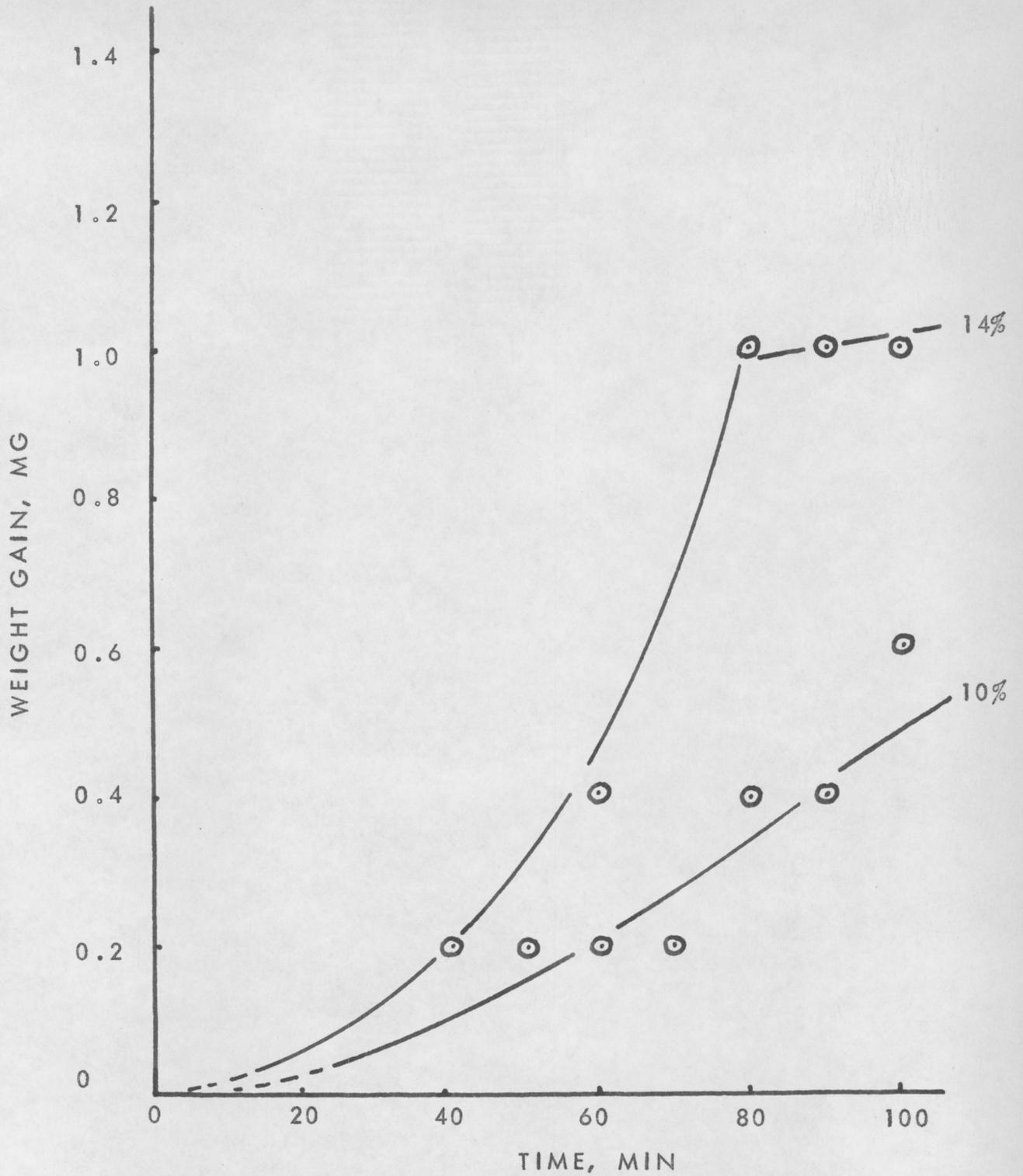


FIGURE 11. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 2 °C

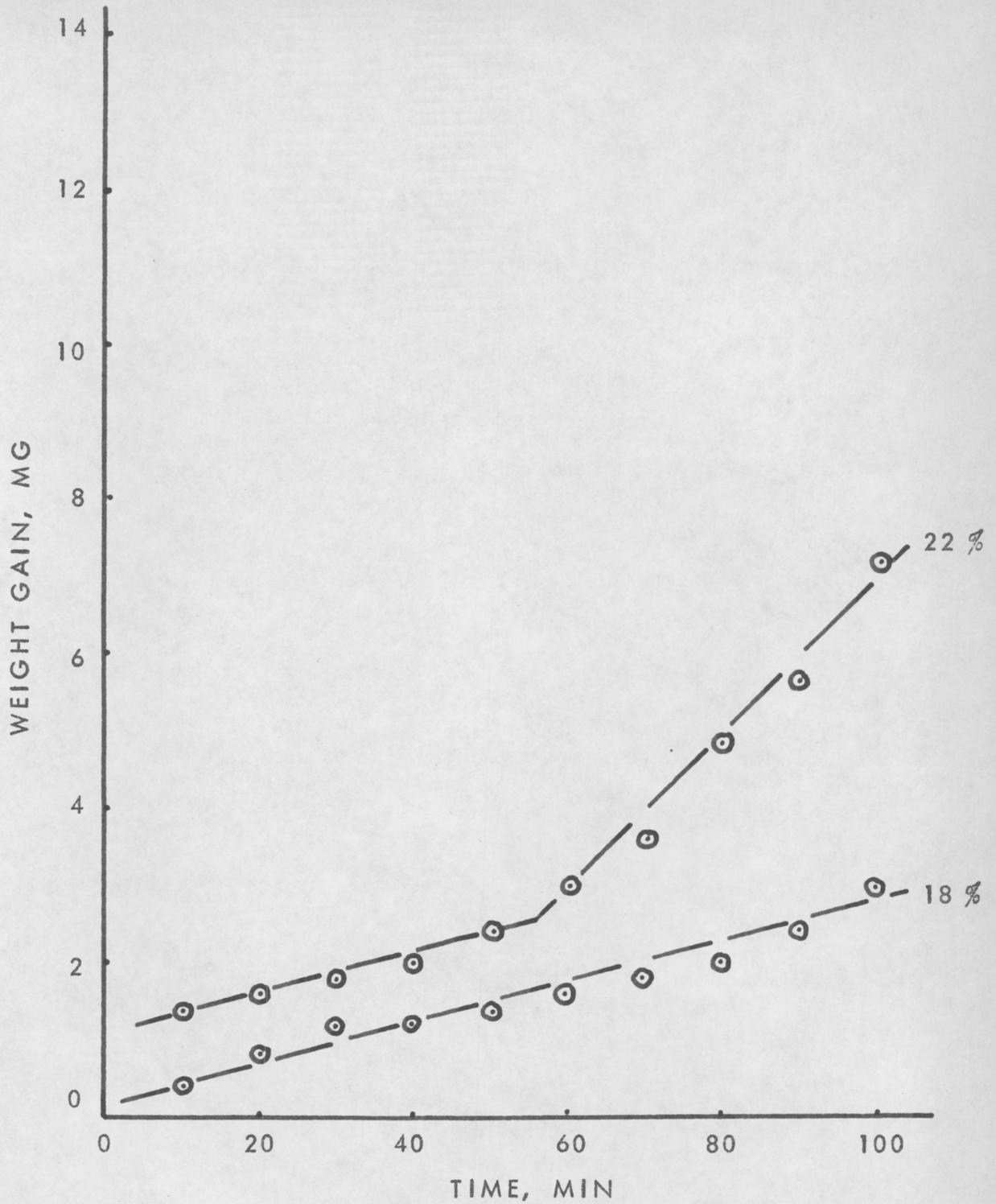
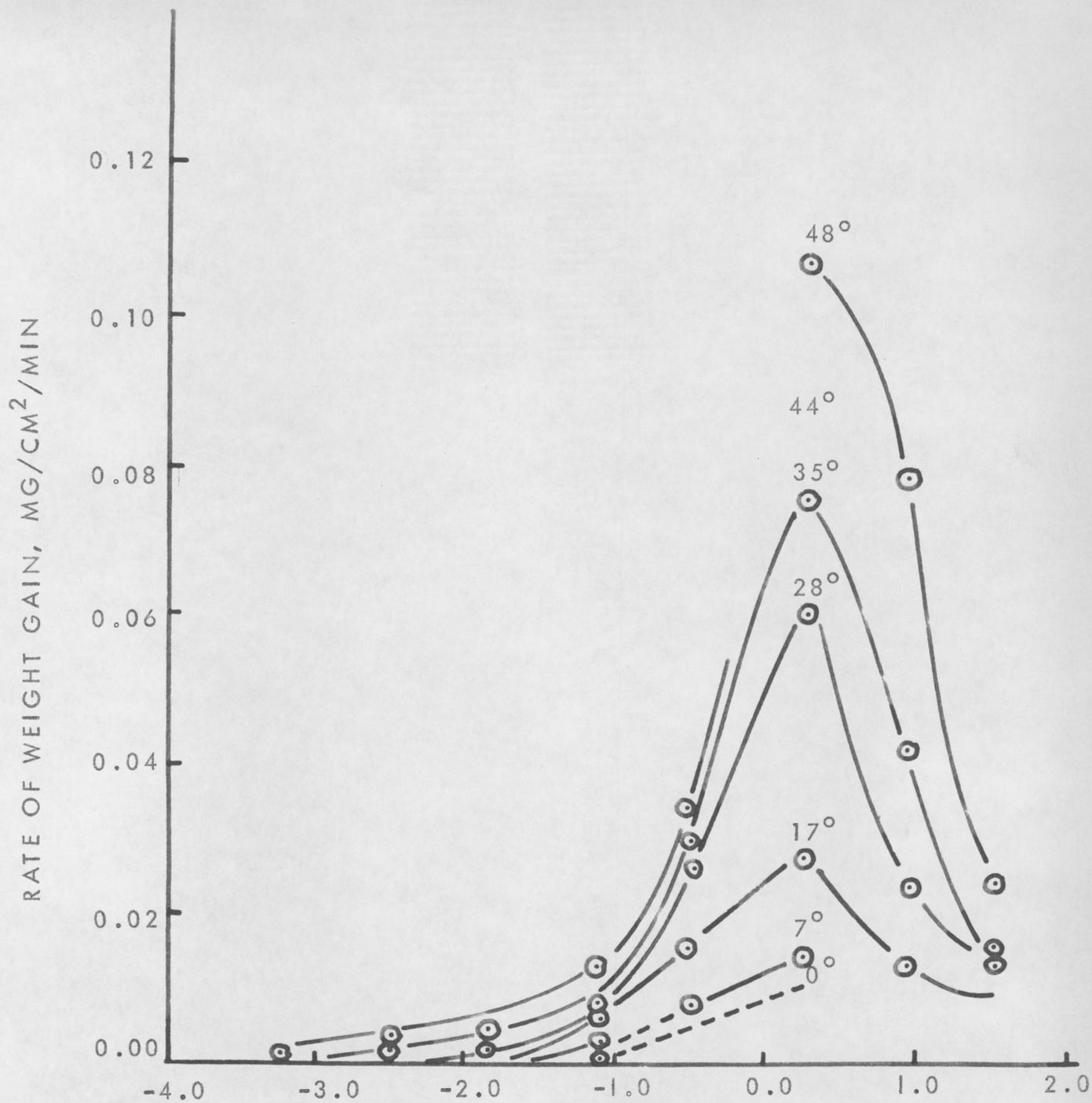


FIGURE 12. INCREASE IN SAMPLE WEIGHT WITH TIME FOR VARIOUS HYDROCHLORIC ACID CONCENTRATIONS AT 0°C



LOG OF HYDROCHLORIC ACID VAPOR PRESSURE
FIGURE 13. CHANGE IN RATE OF WEIGHT GAIN
WITH HYDROCHLORIC ACID VAPOR PRESSURE

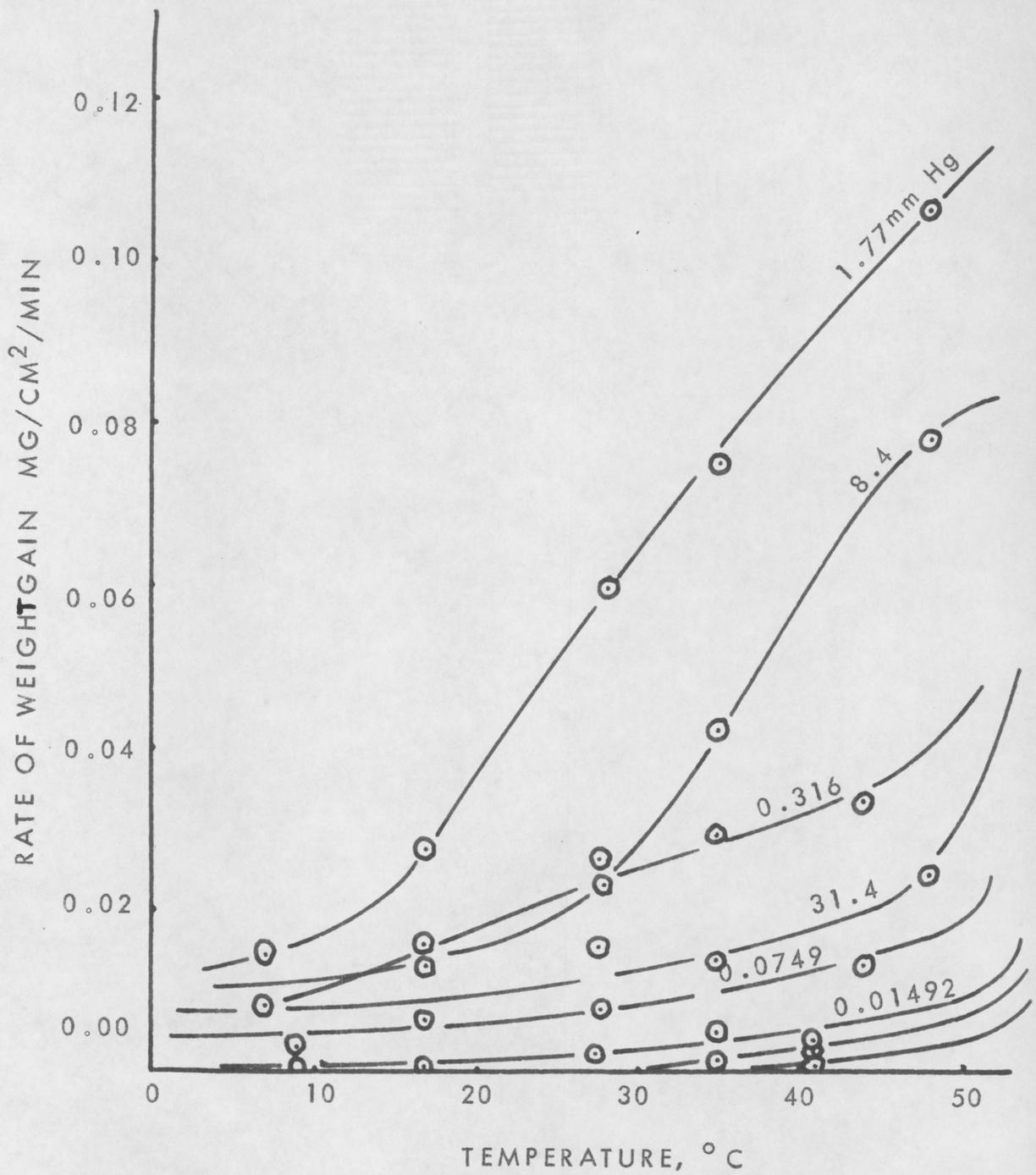
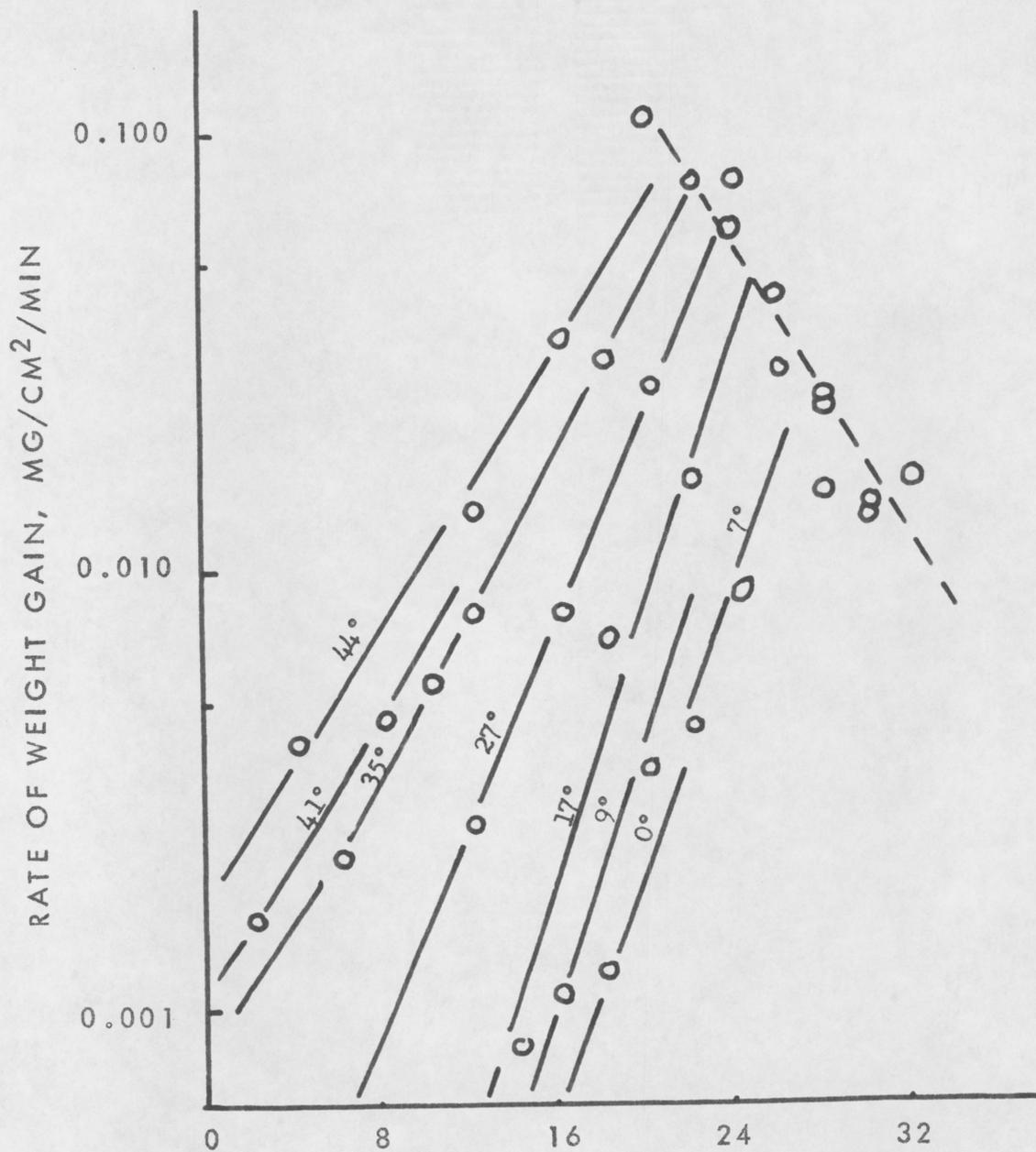


FIGURE 14. VARIATION OF RATE OF WEIGHT GAIN WITH TEMPERATURE



HYDROCHLORIC ACID CONCENTRATION, Wt. PER CENT

FIGURE 15. VARIATION IN RATE OF WEIGHT GAIN WITH HYDROCHLORIC ACID CONCENTRATION

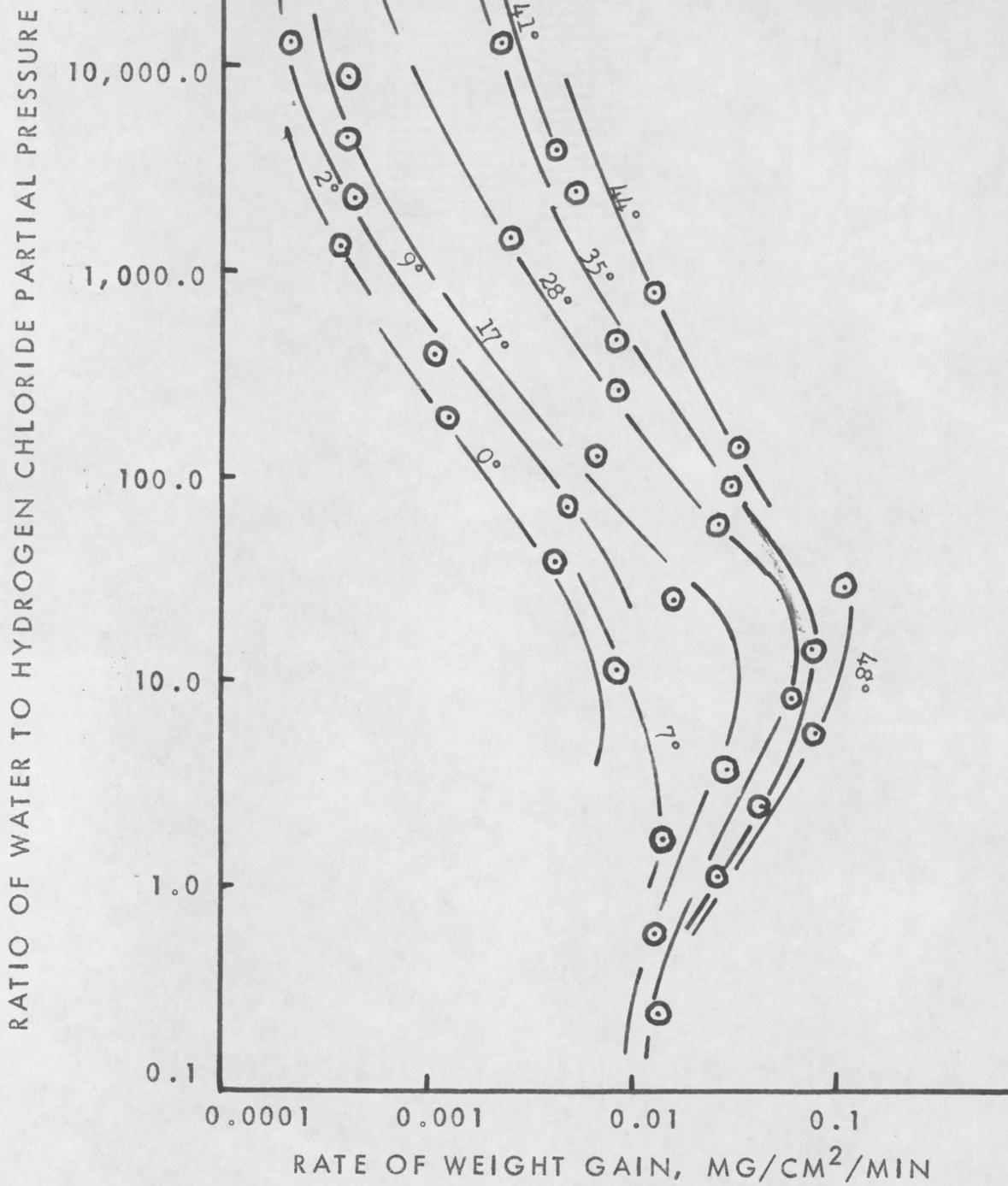


FIGURE 16. CHANGE IN RATE OF WEIGHT GAIN WITH RATIO OF WATER TO HYDROGEN CHLORIDE PARTIAL PRESSURE

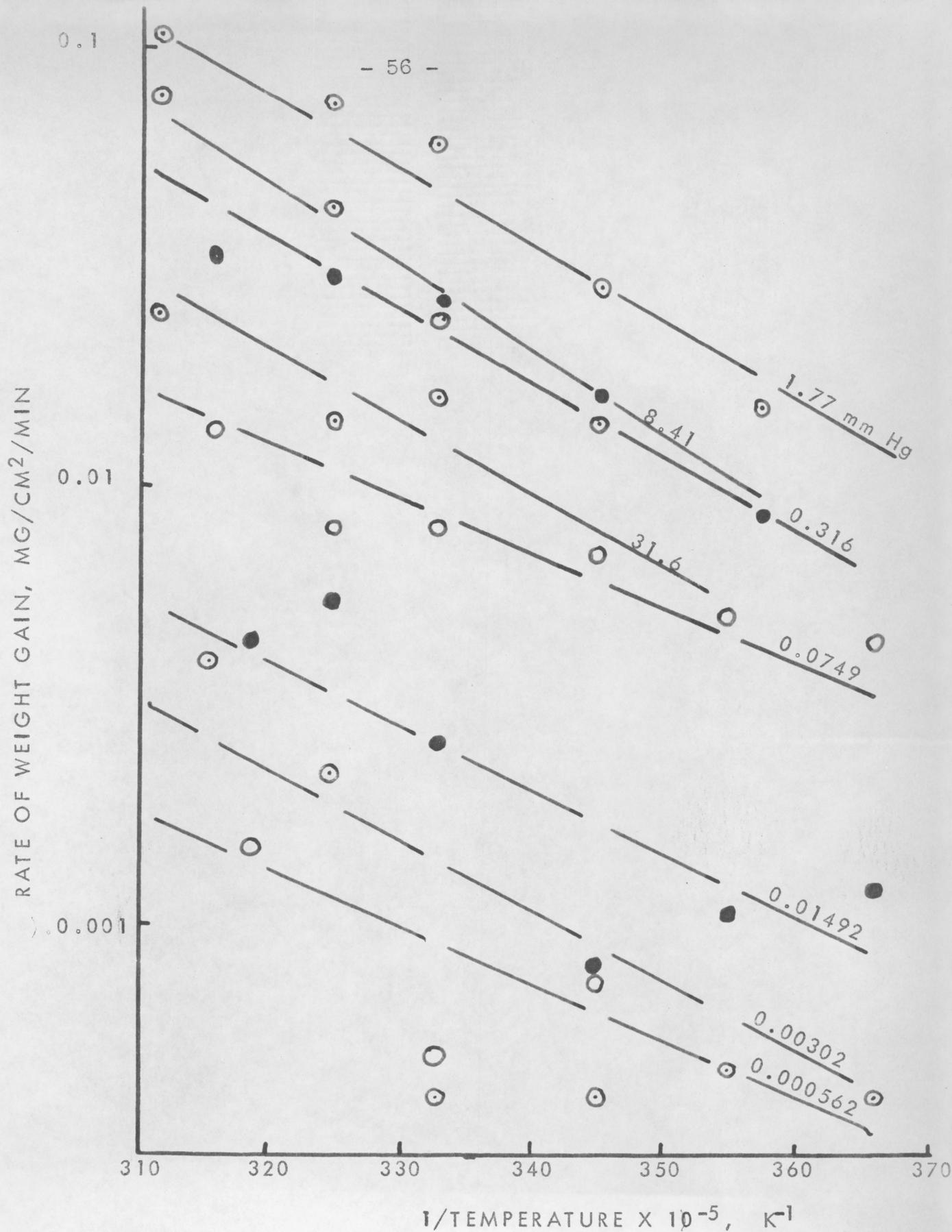
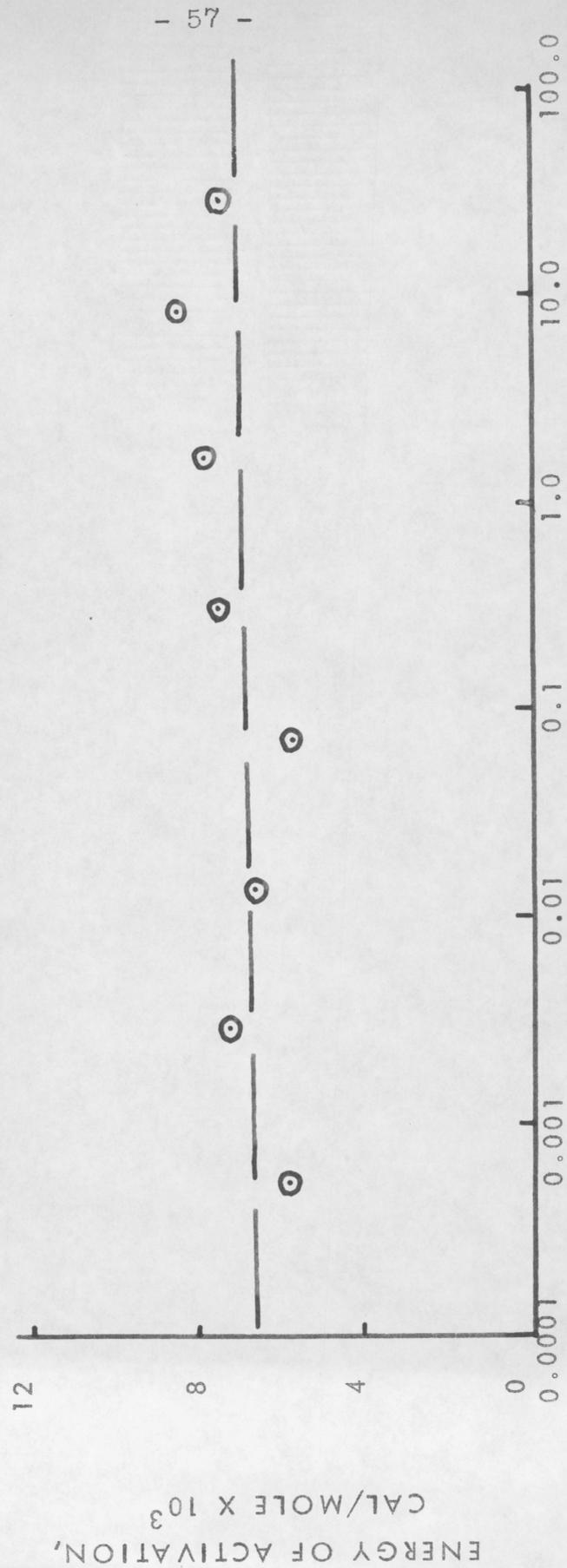


FIGURE 17. ARRHENIUS PLOT FOR CONSTANT HYDROCHLORIC ACID VAPOR PRESSURE TESTS CONDUCTED IN AIR



LOG OF HYDROCHLORIC ACID VAPOR PRESSURE

FIGURE 18. CHANGE IN ENERGY OF ACTIVATION
WITH HYDROCHLORIC VAPOR PRESSURE

TABLE IX

Activation Energy

Hydrochloric Acid Partial Pressure	Activation Energy
mm Hg	Cal/mole
31.6	7940
8.41	8660
1.77	7300
0.316	7550
0.0749	5690
0.01492	6610
0.00302	7300
0.000562	5840
Average	7111 ± 908.9

Data on Adsorption of Anhydrous Aluminum Trichloride. The data for the adsorption of water by anhydrous aluminum trichloride in a calcium sulfate desiccator are tabulated in Table I. It should be noted that aluminum trichloride does not take up water in the presence of drierite.

Analysis of Corrosion Products. X-ray diffraction analysis, used to determine the corrosion products, is tabulated in Table XI. The table shows the analysis of three samples of aluminum corroded above the maximum rate which occurred at a hydrochloric acid partial pressure of 1.77 mm Hg, and three samples from below this maximum rate.

TABLE X

Water Adsorption by Anhydrous Aluminum Trichloride

Time	Weight Gain	Per Cent Gain
Hours	MG	
0	0	0
0.5	-2.7	0.010
1.0	-3.6	0.013
18.0	-48.7	0.176
24.0	-52.2	0.189
41.0	-62.9	0.228
44.5	-64.1	0.232
67.5	-78.0	0.282
70.5	-76.5	0.277
73.7	-75.6	0.274
116.2	-97.4	0.352

TABLE XI

X-Ray Analysis of Products

Test Number	Sample Partial Pressure In Relationship to Partial Pressure At Maximum	Products
11	Above	Al ₃ AlCl ₃ · 6H ₂ O
26	Below	Al ₃ Al ₂ O ₃ x H ₂ O *
29	Below	Al ₃ Al ₂ O ₃ x H ₂ O *
30	Below	Al ₃ Al ₂ O ₃ x H ₂ O *
32	Above	Al ₃ AlCl ₃ · 6H ₂ O
36	Above	Al ₃ AlCl ₃ · 6H ₂ O

* Assume present but not observe due to small amount in relation to the aluminum. Its defraction band was covered by strong aluminum bands which occur at approximately the same wave lengths.

Sample Calculations

This section of the report contains samples of those calculations used in obtaining the rates of weight gain and activation energies, tabulated in Tables VIII and IX, pages 41 and 58, respectively.

Rate of Weight Gain. The rate of weight gain is the change of weight with respect to time. It is obtained by taking the slope of weight against time curves (Figures 3 to 12, pages 42 to 51).

The equation is:

$$r = \left(\frac{dw}{dt} \right) = \frac{w}{A \Delta t}$$

where:

r = rate of weight gain in mg/sq cm/min

w = weight gain of the corroding specimen, mg

A = total surface area of corroding specimen, sq cm

Δt = time interval, min

Substituting in values from Test 8, Figure 3, page 42.

$$r = \frac{39.5 - 15.0}{20(80 - 30)}$$

$$r = 0.0245 \text{ mg/sq cm/min}$$

Activation Energy. The activation energy for the reaction with hydrochloric acid vapors is obtained by taking the slope of the line on an Arrhenius plot at constant partial pressure of hydrochloric acid. The integrated Arrhenius equation is:

$$\ln k = -\frac{E}{RT} + C$$

where:

- k = reaction rate constant, sec^{-1}
- T = absolute Temperature, °F
- E = activation energy, cal/mole
- R = universal gas constant, cal/deg/mol
- C = integration constant

The reaction rate constant is related to the rate of weight gain by the equation:

$$r = kp$$

where:

- r = rate of weight gain, mg/sq cm/min
- p = hydrochloric acid partial pressure, atm.

Rearranging this equation and substituting into the integrated Arrhenius equation:

$$\ln r - \ln p = - \left(\frac{E}{R}\right) \frac{1}{T} + C$$

Simplifying:

$$\ln r = - \frac{1}{T} \left(\frac{E}{R}\right) + \ln p + C'$$

Rearranging and solving for the activation energy we obtain:

$$E = \frac{R \ln r}{(1/T)}$$

From the slope of the Arrhenius plot Figure 17, page 56, for a hydrochloric acid partial pressure of 1.77 mm Hg:

$$E = \frac{1.987 (\ln 0.076 - 0.023) 10^5}{(320 - 350)}$$

$$E = \frac{1.987 (1.19524)}{30}$$

$$E = 7940 \text{ cal/mol}$$

IV. DISCUSSION

This section of the report contains a discussion of the results of the investigation, the limitations, and recommendations.

Rate of Weight Gain. The rate of gain of corroding aluminum specimens was found to be a linear function with respect to time over the entire range of the statistical design. Figures 3 through 12, pages 42 to 51, show this linear relationship. The break in the 20 weight per cent plot, Figure 3, page 42, is due to the high rate at which the sample adsorbed water. As the corrosion products on the surface built-up, drops of solution fell from the sample into the acid solution. The nonuniformity of the curve for corrosion above the 14 weight per cent solution, as shown in Figure 11, page 50, is attributed to the sensitivity of the measuring system. The system has a sensitivity of approximately 0.2 of a milligram and at the low corrosion rates air currents made accurate readings difficult. The system should be modified to provide for longer runs at the lower corrosion rates. A continuous recorder of some type could be attached to the balance to eliminate the need for continual monitoring of the system. The two distinct linear portions of the corrosion curve above the 22 weight per cent solution, Figure 12, page 51, are attributed to changes in temperature of the sample. The sample at room temperature was placed into the 0 °C vapor phase.

Since the sample was hotter than the vapor phase, a water layer on the surface, which was necessary for corrosion, formed slowly as the sample cooled. Once the sample was at vapor phase temperature corrosion proceeded at its equilibrium rate. It was found that precooling the samples to the vapor phase temperature produced a more uniform rate of weight increase at the lower corrosion temperatures.

The rate of weight gain passed through a maximum at a hydrochloric acid partial pressure of 1.77 mm Hg. This is seen from Figure 13, page 52, where, up to 1.77 mm Hg partial pressure, the rate of weight gain increased to a maximum of 0.1065 mg/sq cm/min and above 1.77 mm Hg acid partial pressure the rate decreased. Below the maximum rate the hydrogen chloride vapors on the surface of the aluminum sample act as an electrolyte for the corrosion of the aluminum. Above the maximum the hydrogen chloride on the surface is of sufficient quantity to form an aluminum trichloride six hydrate ($\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$) which acts as a protective coating. It was found by Aronson⁽²⁾ that the rate of solution of aluminum in hydrochloric acid passed through a maximum in nine-normal acid and then decreased because of the formation of a protective aluminum trichloride film. W. H. Jago⁽²⁴⁾ also found that the rate of weight gain of aluminum in nitric acid vapors passed through a maximum; however, for nitric acid vapors this did not occur at a constant

acid vapor pressure but as a constant 40 weight per cent composition of nitric acid solution.

The experiment was designed to cover the entire corrosion range with a minimum number of tests and is therefore incomplete for some temperatures around the maximum. From Figure 15, page 54, it can be seen that the maximum shifts with temperature and hydrochloric acid solution composition. The data above the maximum are too close together to determine any variation because of temperature. No measurements were made at a temperature above 50 °C because it was found in preliminary runs that excessive water condenses on the neck of the glass stack causing the glass thread to stick to the wet side walls. A method of heating the sides of the glass stack would permit investigation at higher temperatures.

The effect of temperature on the rate of weight gain is seen in Figure 14, page 53. The rate increases with temperature for all acid concentrations. The change in rate of weight gain with the ratio of water to hydrogen chloride partial pressure is shown in Figure 16, page 55. It can be seen that as the temperature increases the maximum rate of weight gain shifts towards higher water content in the vapors with respect to hydrogen chloride.

The activation energy, used in the Arrhenius equation to predict the change in reaction rate with changes in temperature, is obtained by taking the slope of the lines of the log of rate against the reciprocal of the reaction temperature. The values of the activation energies, obtained from Figure 17, page 56, are tabulated in Table IX, page 58. Figure 18, page 57, shows a plot of activation energy against hydrogen chloride partial pressure. The activation energy is approximately constant at 7111 ± 908.9 calories per mole over the entire range of partial pressures, indicating that the same reaction mechanism is controlling on either side of the maximum.

X-Ray Analysis of Products. In order to determine what the mechanism of the reaction is it was necessary to know the products of corrosion. Table XI shows that below the maximum rate of corrosion, aluminum oxide is formed and that above the maximum aluminum trichloride six hydrate is formed. The diffraction peaks of aluminum and aluminum oxide are quite close to each other. Since the diffraction tests were made by bouncing the x-rays off of the corroded specimens, the aluminum base metal gave peaks which overshadowed the lesser aluminum oxide peaks, accounting for their nonappearance. Most of the oxides of aluminum formed at low temperatures are amorphous and therefore are not picked up by x-ray diffraction. A method which will determine what oxide

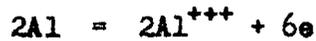
is formed should be used for samples below the maximum rate. The aluminum trichloride six hydrate peaks were easily distinguished from the background pattern. The aluminum trichloride six hydrate samples (those formed above the maximum) had a uniform coating on the surface of the aluminum and retained most of their weight on drying. The aluminum oxide samples (those formed below the maximum) adsorbed a layer of moisture on the surface which was dehydrated in the desiccator with Drierite. The aluminum oxide samples lost as much as 63 per cent (Test No. 17) of their increase in weight and the surface showed a high degree of pitting.

Adsorption by Anhydrous Aluminum Trichloride. A test was made to determine whether anhydrous aluminum trichloride, which is a highly deliquescent, would adsorb water when in a desiccator filled with calcium sulfate (Drierite). From Table X, page 60, it can be seen that the weight of the sample remained almost constant. The sample actually lost 0.5 per cent of its weight.

Corrosion Mechanism. Based on the x-ray diffraction analysis the following mechanism is proposed for the corrosion of aluminum: For hydrogen chloride vapors whose partial pressures is below 1.77 mm Hg., the hydrogen chloride on the surface acts as an electrolyte for the following electrochemical reaction.

Primary reactions occurring at the:

Anode



Cathode



Secondary reactions occurring at the:

Anode



Cathode



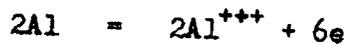
The overall corrosion reaction is:



For hydrogen chloride solution whose partial pressures is above 1.77 mm Hg., the hydrogen chloride enters into the reaction forming a protective film on the surface. The electrochemical reactions are:

Primary reactions are the same as before, occurring at the:

Anode

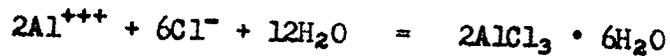


Cathode



Secondary reactions occurring at the:

Anode



Cathode



The overall corrosion reaction is:



From Figure 18, page 57, the value of the activation energy is seen to be approximately the same both above and below the maximum. A constant activation energy indicates that the same reaction is limiting the corrosion rate in both regions. The

limiting electrochemical reaction would therefore be one of the primary reactions

Anode



Cathode



which are common to both regions. Work with inhibitors to control these reactions should be investigated.

Statistical Analysis. A complete statistical analysis of the data will be made to determine the effects of temperature, hydrogen chloride and water partial pressures, hydrochloric acid concentration, and their interactions. A statistical corrosion model that best fits the data will also be developed. The analysis when completed will be published by Miss G. E. Foster of the statistics department.

Recommendations

The following recommendations are made for future study in the field of vapor phase corrosion:

1. A study of inhibitors be made to find an inexpensive inhibitor which could either be applied to the metal or added to the corroding fluid to reduce the corrosion attack.

2. That a more intensive preliminary investigation be made in order that more data around the maximum or minimum be obtained.

3. That the balance be modified so that the weight gain would be recorded continuously on a chart or drum of some type.

4. That the samples be preheated or cooled to the vapor phase temperature before being placed in the vapor environment so as to eliminate the initial condensation on the samples.

5. That a method be developed for heating the glass stack so as to reduce the tendency of the glass thread to stick to the wet side walls of the stack.

6. That a more accurate method of analysis be found for determining the presence of oxides in the corrosion products that are present.

Limitations

The following limitations prevailed during this investigation:

1. The accuracy of the weighing system was ± 0.2 milligram.
2. The temperature of the vapor phase varied from 0 to 48°C and was limited by the condensate in the glass stack.
3. The hydrochloric acid concentrations in the corrosion reactor varied from 2 to 32 weight per cent.
4. Atmosphere pressure was used in the corrosion reactor throughout the investigation.
5. The size of the aluminum foil corrosion samples used in this investigation was constant at 20 square centimeters.
6. Time of tests was constant at 200 minutes or until a loss in weight was recorded.
7. Analysis of the corrosion products was by standard x-ray diffraction.

V. CONCLUSIONS

Based on the results of an investigation of the rate of weight gain of corroding aluminum specimens, using a modified analytical balance system, for hydrochloric acid solution concentrations from 2 to 32 weight per cent and for vapor phase temperatures from 0 to 48 °C, the following conclusions were reached:

1. The rate of weight gain of aluminum in hydrogen chloride vapors is a linear function with respect to time.
2. A maximum rate of weight gain of aluminum in hydrogen chloride vapors occurs at a hydrogen chloride partial pressure of 1.77 mm Hg.
3. The rate of weight gain is an exponential function with respect to hydrochloric acid concentration.
4. The effect of increases in temperature is to increase the rate of weight gain for all hydrochloric acid concentrations tested.
5. Based on x-ray diffraction analysis of the corrosion products the decrease in corrosion rate above the maximum is due to the formation of a protective aluminum trichloride film.

6. For a partial pressure of hydrogen chloride below 1.77 mm Hg., the acid acts as an electrolyte for the following electrochemical corrosion reaction:



7. For a partial pressure of hydrogen chloride above 1.77 mm Hg., the acid reacts with the aluminum forming a protective aluminum trichloride film on the surface according to the reaction:



8. The energy of activation is approximately constant over the entire experimental range indicating that the same mechanism is controlling both reaction.

9. It is proposed that the limiting reactions are the primary electrode reactions occurring during the corrosion.

VI. SUMMARY

Aluminum has high resistance to attack in many environments but corrodes rapidly in most inorganic acids. The purpose of this investigation was to attempt to determine the rates and mechanism of the surface reactions for the corrosion of aluminum in hydrochloric acid vapors as a function of the vapor concentration, vapor composition, and temperature.

Corrosion tests were made by suspending aluminum foil samples, five centimeters by two centimeters, by a glass thread. The samples were located in the vapor over hydrochloric acid solutions. The glass thread with the sample was attached to the center of a glass rod. One end of the rod was fixed; the other was suspended from one end of the arm of an analytical balance, permitting periodic weighing of the corroding samples without removal from the flask.

The tests were conducted above hydrochloric acid solutions whose concentration varied from 2 to 32 weight per cent. Ten temperature levels, from zero to 48 °C, were employed so that the vapor pressures of the various acid concentrations overlapped. Weighings were made at 10 minute intervals for 200 minutes. The corrosion products were analyzed by standard x-ray diffraction techniques.

The rate of weight gain was found to be a linear function with respect to time and exponential with respect to hydrochloric acid concentration. The rate passed through a maximum at a hydrogen chloride partial pressure of 1.77 mm Hg. The decrease in rate above the maximum is due to the formation of a protective aluminum trichloride six hydrate ($\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$) film. Temperature increased the rate of weight gain at all hydrogen chloride partial pressures. Based on the analysis of the corrosion products the following mechanism is proposed for the corrosion of aluminum.

For hydrogen chloride partial pressures below 1.77 mm Hg., the hydrogen chloride acts as an electrolyte for the following electrochemical reaction



For hydrogen chloride partial pressures above 1.77 mm Hg., the hydrogen chloride enters into the reaction as follows



The energy of activation is approximately constant over the entire experimental range indicating that the same mechanism is controlling both proposed corrosion reactions. The controlling reactions would be the primary electrode reactions which are identical for both regions.

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Addenda

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