

THE DESIGN, CONSTRUCTION, AND OPERATION OF A PILOT PLANT  
FOR THE PRODUCTION OF TRICHLOROACETIC ACID  
FROM ACETIC ACID AND CHLORINE

by

William V. Brown

A Thesis Submitted for Partial  
Fulfillment of the Requirements  
for the  
Degree of Master of Science  
in  
CHEMICAL ENGINEERING

Approved:

In Charge of Investigation

Head of Major Department

Dean of Engineering

Director of Graduate Studies

Virginia Polytechnic Institute

Blacksburg, Virginia

1951

## TABLE OF CONTENTS

	Page
I. INTRODUCTION . . . . .	1
II. LITERATURE REVIEW . . . . .	3
III. EXPERIMENTAL . . . . .	55
Purpose of Investigation . . . . .	55
Plant of Experimentation . . . . .	55
Materials . . . . .	56
Apparatus . . . . .	60
Method of Procedure . . . . .	61
Data and Results . . . . .	76
Sample Calculations . . . . .	98
IV. DISCUSSION . . . . .	105
Discussion of Results . . . . .	105
Plant Design for Sodium Trichloroacetate . . . . .	131
Recommendations . . . . .	198
Limitations . . . . .	200
V. CONCLUSIONS . . . . .	201
VI. SUMMARY . . . . .	203
VII. BIBLIOGRAPHY . . . . .	205
VIII. ACKNOWLEDGEMENTS . . . . .	214
IX. VITA . . . . .	215

TABLE OF TABLES

	Page
I. Development Laboratory Data on The Production of MCA from Acetic Acid . . . . .	10
II. Density of Trichloroacetic Acid at Various Temperatures and Variation in Boiling Point at Different Pressures .	25
III. Physical Properties of Chemicals Involved in the Production of TCA . . . . .	26
IV. Solubility of Chlorine and Hydrogen Chloride in 100 Grams of Water at 760 mm Absolute Pressure . . . . .	27
V. Materials of Construction for Use With Chemicals Involved in the Production of TCA . . . . .	36
VI. Effect of Quantity of Reagents Used on Dichloroacetic Acid Results . . . . .	44
VII. Melting and Boiling Points of Derivatives of the Chloroacetic Acids . . . . .	48
VIII. Results of The Chlorination of Acetic Acid to Trichloroacetic Acid, in The Presence of Red Phosphorus, at Atmospheric Pressures, and Between The Temperatures of 68 to 320°F . . . . .	73
IX. Degree of Chlorination of The Various TCA Products Produced in Pilot Work . . . . .	89
X. Results of Chromatographic Analysis of Mixtures of Chlorinated Acetic Acids for TCA . . . . .	91

	Page
XI. Direct Volumetric Analysis of Mixtures of Chlorinated Acetic Acids for TCA . . . . .	92
XII. Indirect Volumetric Analysis of Mixtures of Chlorinated Acetic Acids for TCA . . . . .	93
XIII. Pyridine Test For Trichloroacetic Acid . . . . .	94
XIV. Pyridine Test For Monochloroacetic Acid . . . . .	95
XV. Analysis of Viscous Material Remaining After Chlorination of Acetic Acid to TCA . . . . .	96
XVI. Approximate Densities of Different Mixtures of Chlorinated Acetic Acids at 295° F . . . . .	97
XVII. Results of Preliminary Calculations for Equipment Capacity . . . . .	151
XVIII. Cost of Equipment for TCA Plant . . . . .	192
XIX. Labor and Supervision Costs For TCA Plant . . . . .	193

TABLE OF FIGURES

	Page
1. Price of Hydrochloric Acid From 1925 to 1949 . . . . .	12
2. Price of Chlorine From 1920 to 1948 . . . . .	14
3. Price of Acetic Acid From 1923 to 1949 . . . . .	15
4. Price of Chloral Hydrate From 1925 to 1949. . . . .	17
5. Price of Sodium Chlorate From 1925 to 1949. . . . .	18
6. Price of Ethyl Alcohol From 1930 to 1949. . . . .	19
7. Mutual Solubility of TCA and Acetic Acid. . . . .	28
8. Mutual Solubility of DCA and Acetic Acid. . . . .	29
9. Mutual Solubility of MCA and Acetic Acid. . . . .	30
10. Mutual Solubility of MCA and TCA. . . . .	31
11. Mutual Solubility of MCA and DCA. . . . .	32
12. Mutual Solubility of DCA and TCA. . . . .	33
13. Quantitative Flow Sheet of Process for Producing TCA . .	40
14. Calibration Curve for Chlorine Flow Meter . . . . .	77
15. Rate of Chlorine Absorption by Glacial Acetic Acid, Chlorine Feed Rate, and Reaction Temperature, Test Five .	79
16. Absorption of Chlorine by Glacial Acetic Acid, Test Five .	80
17. Rate of Chlorine Absorption by Glacial Acetic Acid, Chlorine Feed Rate, and Reaction Temperature, Test Six .	81
18. Absorption of Chlorine by Glacial Acetic Acid, Test Six. .	82
19. Rate of Chlorine Absorption by Glacial Acetic Acid, Chlorine Feed Rate, and Reaction Temperature, Test Seven. . . . .	83

	Page
20. Absorption of Chlorine by Glacial Acetic Acid, Test Seven .	84
21. Rate of Chlorine Absorption by Glacial Acetic Acid, Chlorine Feed Rate, and Reaction Temperature, Test Eight . . . . .	85
22. Absorption of Chlorine by Glacial Acetic Acid, Test Eight .	86
23. Concentration and Yield of TCA in Relation to Reaction Time, Test Eight . . . . .	87
24. Degree of Chlorination of Product Eight at Various Reaction Times . . . . .	90
25. Estimated Unit Cost, Capital Investment, and Net Income Versus Concentration of TCA in Final Product . . . . .	133
26. Concentration and Yield of TCA, and The Degree of Chlorination of the Reacting Mass Versus Reaction Time. . . . .	135
27. Flow Diagram for Sodium Trichloroacetate. . . . .	140
28. Gas Manifold System for Chlorinators. . . . .	175
29. Liquid Manifold System for Chlorinators . . . . .	176
30. Chlorinator Section . . . . .	177
31. Neutralization-Packaging Section. . . . .	178
32. Absorption Section . . . . .	179
33. Storage Section. . . . .	180
34. Building and Grounds Section. . . . .	181

## I. INTRODUCTION

Man has long been hampered in his efforts to grow food plants, raise animals, and carry on other activities of an advancing civilization by obnoxious plants or weeds. Weeds add greatly to man's labors and resist his efforts of control because they can often survive frost, high temperatures and drought, can grow under widely varying soil and climatic conditions, and produce enormous amounts of seeds that will survive for years.

The control of weeds is rapidly becoming of increasing importance throughout all agricultural areas and is playing a part in the broad conservation program. Tillage operations are both time consuming and expensive, often representing from one tenth to one third of the total value of the crops produced. Weeds compete with crops for water, nutrients, and light; they help spread diseases; some are poisonous to animals; some disrupt water distribution and flow along waterways and spread their seeds to irrigated land; and they are hazardous and bothersome to train movements when growth covers the rails.

The methods of weed control are many and varied. Among the most common methods of weed control are hand, mechanical, biological, burning, and chemical methods. It has been said that even if the cost of application of chemicals is as high as 15 to 20 dollars per acre, it is cheaper than the older hand or mechanical methods.

There is no one chemical that will give control of all weeds without undue hazards, and therefore, the use of selective weed killers has

become essential. Annual and perennial grasses, such as quack, Johnson, and Bermuda, are among the most obnoxious of the weeds. Sodium trichloroacetate, arsenical compounds, and chlorates are the only commercial weed killers that will control noxious grasses; since the arsenicals are poisonous and chlorates flammable, sodium trichloroacetate is expected to supplement them in grass control. The demand for this compound is expected to exceed the supply for the next few years.

It is the purpose of this investigation to design, construct, and operate a pilot plant for the production of sodium trichloroacetate from acetic acid and chlorine, and further, to study the compounding of chloral hydrate and sodium chlorate to give a desirable grass killer formulation.



## II. LITERATURE REVIEW

A search of the chemical and chemical engineering literature was made to find and integrate the previous work done on the many problems encountered in the development of a process for producing trichloroacetic acid (TCA) and a subsequent plant design. Many duplicating references were omitted for the sake of brevity. However, it is felt that the review is as complete as time and means allowed.

### History

The importance of weed control is becoming more apparent every day. Among the noxious weeds to the railroads of the eastern United States in maintaining the right-of-way, are Johnson and Bermuda grasses. Recently, it was discovered that salts (sodium and ammonium) of trichloroacetic acid were exceptionally good for control of these grasses, especially Bermuda. Thus, the first large use of TCA has become apparent. However, little is known about the manufacture of TCA even though it was first prepared in 1838. Solution to the problems of producing TCA would help answer the needs of railroads in the eastern United States for a herbicide and might also help the social and economic problems that have arisen in rural areas in many parts of the country.

Importance of Chemical Weed Control. Of the some half-million known species of plants inhabiting the earth, relatively few (50) have proven to be obnoxious to man. However, these few plants,

called weeds, have so hampered man's efforts that he has spent a great deal of time and labor in attempting to eradicate or control their growth.

One of the most important factors that caused high cost of weed control, in the past, was the method of control used. The newer chemical methods<sup>(43)</sup> are usually the cheapest.

Necessity of TCA Production. A few of the annual and perennial grasses have become very obnoxious to man. The use of a TCA - sodium chlorate formulation<sup>(63)</sup> has proven to be an answer to the control of these grasses. However, the production of TCA has been restricted to the past two years (1948-49), and at the present time, is being manufactured by only two companies in the United States. The 1949 price of TCA was about 37 cents per pound (for a 90 per cent product); the marketing of this weed killer may be hindered by the present high price.

TCA Plant as Small Industry. There is a need for small industries to carry on seasonal operations in many rural areas of the nation. These industries would help solve the social problems arising from the seasonal nature of farm labor. It is believed that a process for the production of TCA could fulfill the requirements for such an industry. Also, a company could provide year around employment by producing a weed-killer formulation during the winter and applying the formulation during the growing seasons.

History of TCA. Trichloroacetic acid was prepared by Dumas<sup>(34)</sup> in 1838 by the chlorination of acetic acid in the presence of sunlight. The knowledge of the strong acidic properties of TCA led to its application as a wart remover. Later it was used as a chemical intermediate in

the preparation of other organic chemicals in the laboratory. It has been used as a catalyst in some organic reactions. However, its power to kill grasses was not observed until about 1946; a patent for its application as a herbicide received by du Pont<sup>(8)</sup> in that year.

Costs of Weed Control. It has been reported<sup>(62)</sup> that control of weeds along railroads is one of the major items of expense in maintaining the right-of-way. Also, the annual cost to farmers, from weeds, in the United States has been estimated to be three billion dollars.

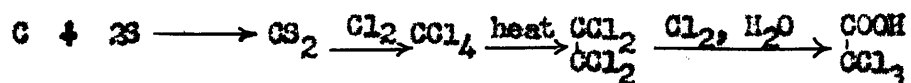
TCA as a Herbicide for Railroads. It was found<sup>(64)</sup> that the application of a formulation of TCA (100 pounds of 60 per cent TCA) and sodium chlorate (200 pounds) per mile of railroad track, on a 29 foot width, and at a rate of about four to five miles per hour, was the most economical herbicide of 31 tested along railroad right-of-ways. The estimated cost of materials was \$38.05 per mile of track (1950). The kill resulting from an application of this formulation was from 80 to 90 per cent, one month after application, on Johnson and Bermuda grasses and other weeds in 12 tests made.

#### Preparation and Manufacture of Tri-, Di-, and Mono- Chloroacetic Acids

The following information concerning the preparation and manufacture of TCA, DCA, and MCA was presented in a Plant Design for the Production of Trichloroacetic Acid as designed and compiled by members of the Graduate Chemical Engineering Plant Design class, of 1949-1950, at the Virginia Polytechnic Institute, Blacksburg, Virginia. This information, to which several references have been added, constitutes a review of the literature on the subject.

Preparation and Manufacture of TCA. There are several sources of methods of preparation and manufacturing conditions for TCA.

Methods of Preparation of TCA. The following methods have been given<sup>(2,7,34)</sup> for the preparation of TCA: from chloral or chloral hydrate by oxidation with fuming nitric acid, nitrous acid, with  $\text{NO}_2$  at 40 to 60°C, (70 per cent yield), with aqueous chlorates plus catalyst, with potassium permanganate, potassium chlorate, and with  $\text{CaO}_2\text{Cl}_2$ ; by chlorination of acetic acid in the presence of sunlight; from tetrachlorethylene chloroformate by standing in water in the presence of light for four months; from pentachloroethyl chloroformate with water on heating (yield is small owing to other modes of reaction); from pentachloroethyl trichloroacetate with water; and by synthesis from its elements as follows:



Conditions of TCA Manufacture. Groggins<sup>(30)</sup> reported that TCA may be manufactured by passing the requisite quantity of chlorine into 200 pounds of acetic acid, five pounds of red phosphorus, one pound of iodine, and five pounds of phosphorus pentachloride, at 160°C. Similar quantities of these catalysts are proposed by Gatterman<sup>(23)</sup> who also gives purification methods for TCA in the presence of catalysts.

Patent for Manufacture of TCA from Acetic Acid. Strossacker<sup>(61)</sup>, in a patent issued in 1930, stated that the chlorination of acetic acid is effected in the presence of chlorinating catalysts such as sulfur chloride, sulfur, phosphorus, or acetic anhydride to form TCA.

The chlorination is continued at higher temperatures (suitably up to 160°C) to form TCA.

Patent for Manufacture of TCA from Acetyls. Theobald<sup>(65)</sup>, in a patent issued in 1944, described methods of producing chloroacetyl chlorides which on hydrolysis yield the corresponding acid. The reactions involve heating an anhydrous mixture of carbon monoxide and a polyhalomethane in the presence of anhydrous Friedel-Crafts type of catalyst at 70 - 400°C, under superatmospheric pressures.

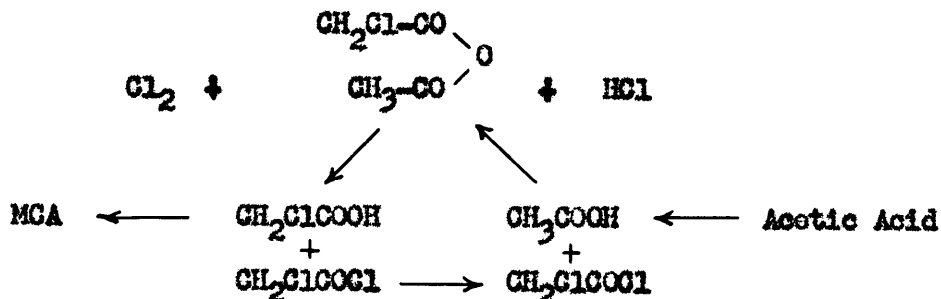
Manufacture of MCA and DCA. Conditions for the manufacture of mono- and dichloroacetic acids (MCA and DCA) are more abundant than for TCA. The following paragraphs contain that information which applies to this investigation.

Manufacture of MCA from Acetic Acid. In the course of correspondence with Mr. P. H. Groggins of the Department of Agriculture, Washington, the Fabricacion De Productos Quimicos Organicos of Barcelona, Spain, revealed that their efforts to further chlorinate dichloroacetic acid to trichloroacetic acid had proven unsatisfactory as of May, 1949. The company was at that time studying the possibility of using the mother liquors from MCA manufacture to produce DCA and perhaps TCA. They reported that from 100 pounds of acetic acid, their plant produced 125 to 130 pounds of MCA and from 15 to 20 pounds of residual acids with the following composition:

CH <sub>3</sub> COOH	32.7 per cent
CH <sub>2</sub> ClCOOH	42.2
CHCl <sub>2</sub> COOH	18.1
CCl <sub>3</sub> COOH	6.8

The company reported that the residual acids had been chlorinated into DCA (90 per cent yield), using a mixture of  $\text{Cl}_2\text{S}_2$  and iodine as catalysts, but the yield of TCA from the reaction could not be increased due to pyrogenation when the temperature reached  $180^\circ\text{C}$ . The use of phosphorus and iodine as catalysts for the reaction was also studied, however, pyrogenation still occurred.

Manufacture of MCA from Acetic Acid Using Acetic Anhydride and Sulfur as Catalysts. A research report, supplied upon inquiry by Mr. P. H. Groggins, revealed that MCA may be produced from acetic acid and chlorine using three per cent acetic anhydride and 0.7 per cent sulfur as catalysts at  $100^\circ\text{C}$ . A product containing 93 per cent MCA, 6.5 per cent DCA, and 0.5 per cent TCA was obtained after 70 hours of chlorination. The role of acetyl chloride in the reaction was hypothesized as follows:



The reaction takes place under liquidous conditions at atmospheric pressure.

Conditions of MCA Manufacture from Acetic Acid. Groggins<sup>(31)</sup> has given the following conditions for the manufacture of MCA. MCA is prepared by passing chlorine through glacial acetic acid at  $100^\circ\text{C}$ . The ratio of chemicals used is 365 pounds of acetic acid to 14 pounds

of red phosphorus. Chlorine is admitted to the reactor at a rate of 20 pounds per hour for the first hour, 40 pounds per hour for a second period of one hour, and at a rate of 60 pounds per hour for the remainder of the seven to ten hour period. Results of eight tests on the production of MCA, including reaction time and yields, have been tabulated in Table I.

Manufacture of MCA in Vapor Phase. Spence(58), in a patent issued in 1945, claimed that monochlorinated aliphatic acids and esters are produced by the vapor phase reaction of chlorine and excess acid or ester in the absence of catalysts and at a temperature of 250 to 500°C.

Effect of Catalysts on the Chlorination of Acetic Acid. Bruckner(10) reported that the velocity of chlorination of acetic acid in the presence of iodine, phosphorus, and sulfur increases with the amount of catalysts used, but not in direct proportion to the three catalysts. Iodine gives the best results alone, but more effective chlorination is obtained with mixtures of the three catalysts. Chlorination in the presence of iodine, phosphorus, and phosphorus pentachloride mixtures are more rapid than with sulfur, phosphorus, and phosphorus pentachloride mixtures. Binary mixtures of catalysts are less effective than ternary. Sulfur and phosphorus appear to react by accelerating the formation of acetyl chloride, and iodine by the dispersion of chlorine through the reaction mixture by the formation of iodine monochloride and trichloride.

TABLE I  
Development Laboratory Data on The  
Production of MCA from Acetic Acid

Test Number	Reaction Time hours	Acetic Acid Used lb	Chlorine Used lb	Average Chlorine Rate lb/hr	MCA Concentration in Product %	Yield MCA <sup>a</sup> %
1	12.25	350	485	39.6	100	93.0
2	9.0	350	480	53.4	100	91.1
3	8.0	350	485	60.6	100	88.5
4	11.0	350	425	38.6	100	85.7
5	8.0	350	425	53.1	100	84.0
6	7.0	350	435	62.1	100	83.5
7	7.75	350	430	55.5	100	81.5
8	8.33	350	425	51.1	100	81.5

<sup>a</sup> Yield in per cent of theoretical based on acetic acid.

Groggins, P. H.: "Unit Processes in Organic Synthesis", pp. 242-3.

McGraw-Hill Book Co., Inc., New York, N. Y., 1947, 3d ed.



### Commodity Survey

A commodity survey of the raw materials, used in the preparation of TCA by the more common methods, is presented in this section. This survey is a prerequisite to an estimation of the cost of producing TCA and thus the selection of the more economical process from this point of view.

Hydrochloric Acid. There are at present (1949), 74 plants producing hydrochloric acid at a combined rate of 1,440 tons per day. The current methods<sup>(3)</sup> of production are the Mannheim process, Hargreaves process, the burning process, and processes in which HCl is formed as a by-product.

Aside from the growing use of HCl in the petroleum fields, there has been no increase in demand for some time. In many areas, more by-product acid is produced than the locale will absorb. Generally speaking, transportation charges for long distant shipments are not economical.

There are four grades of HCl available. In the technical grade, both 18 and 20 deg Be are available, also, 20 deg Be technical pure, and 22 deg Be chemical pure.

Figure 1, shows graphically the variation in the price of HCl for the period 1925 to 1949.

Chlorine. The most important source<sup>(12)</sup> of chlorine in the U. S. is from the electrolysis of sodium chloride. The annual production of chlorine is 1,767,000 tons (1949), and there are now (1950) a total of 45 manufacturers. The consumption of chlorine has been generally upward in the past 10 years. In fact, the chlorine produced from the electrolytic process is often considered more important than the caustic soda. This

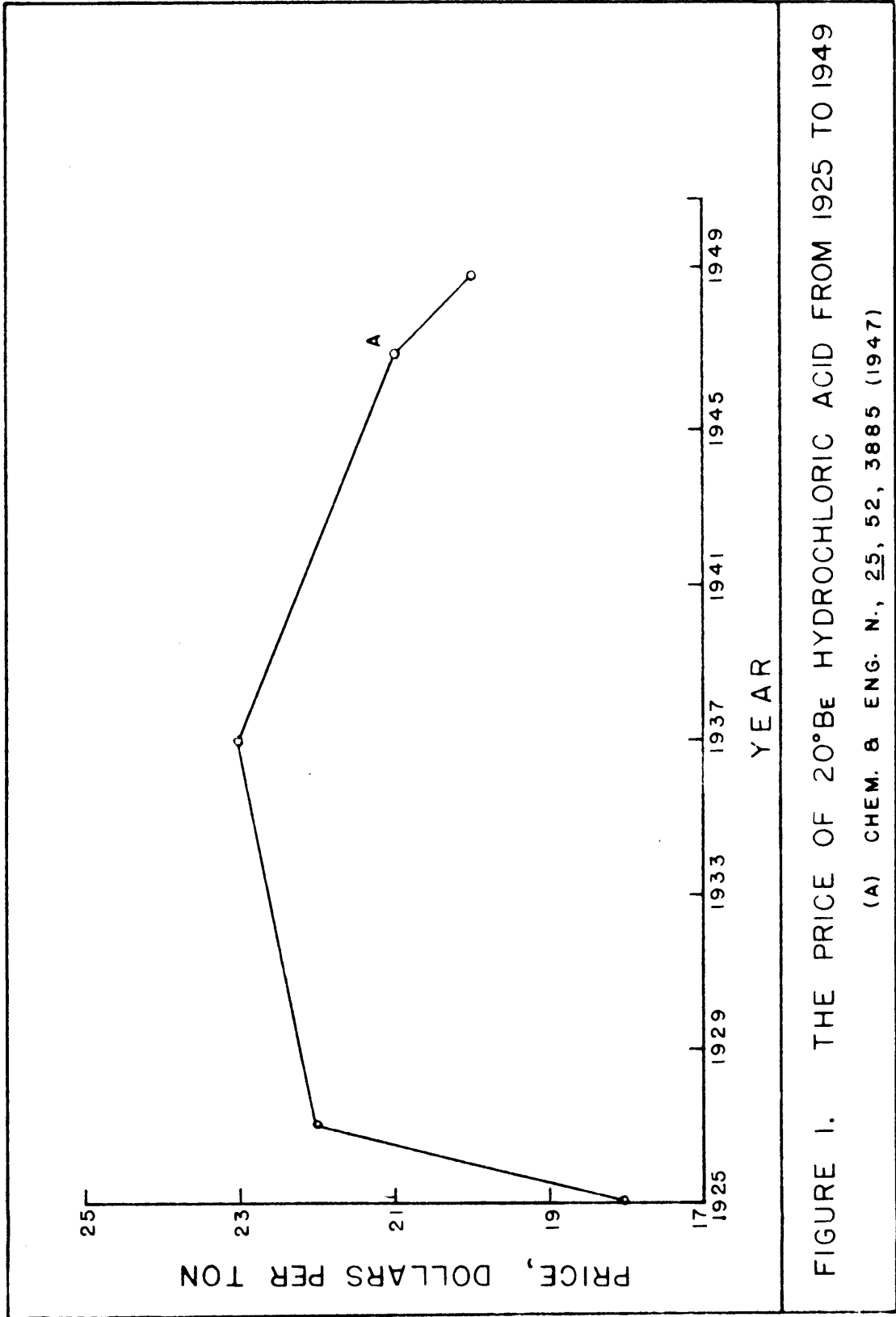


FIGURE 1. THE PRICE OF 20°Be HYDROCHLORIC ACID FROM 1925 TO 1949

(A) CHEM. & ENG. N., 25, 52, 3885 (1947)

upward trend is due to the growing use of chlorinated hydrocarbons.

The price trend of chlorine for the years 1920 to 1948 is shown in Figure 2.

Acetic Acid. Acetic acid is being produced by the following methods<sup>(55)</sup>: wood pyrolysis, fermentation process, the carbide process, and as a by-product in many industries such as the cellulose acetate industry. There were 1,267,518,000 pounds of acetic acid produced in 1945, and the present (1949) number of manufacturers is 72. It is used in the preparation of many products in the process industries, such as acetic anhydride, sodium acetate, cellulose acetate, ethyl acetate, butyl acetate, white lead, and for dyeing. Synthetic acetic acid has replaced the natural product to a considerable extent, and as a result, the price has fallen. By-product acetic acid will continue to be produced at much the same level - if not a higher level. The rise in price from 1942 to 1947 is indicative of a price readjustment. Figure 3, shows graphically the price trend of acetic acid from 1923 to 1949.

Chloral Hydrate. There are seven major producers of chloral hydrate at the present time. The major use<sup>(11)</sup> of the compound is as an intermediate in the production of DDT. Production was 1,558 tons in 1945. Two grades are available, technical and U.S.P. The uptrend in price of chloral hydrate is probably due to the higher costs of raw materials as well as increased demand. The manufacture of DDT will probably not increase significantly for sometime. Present methods of producing chloral hydrate do not seem to be too efficient. It is believed that the price trend for the next five years will be stable to

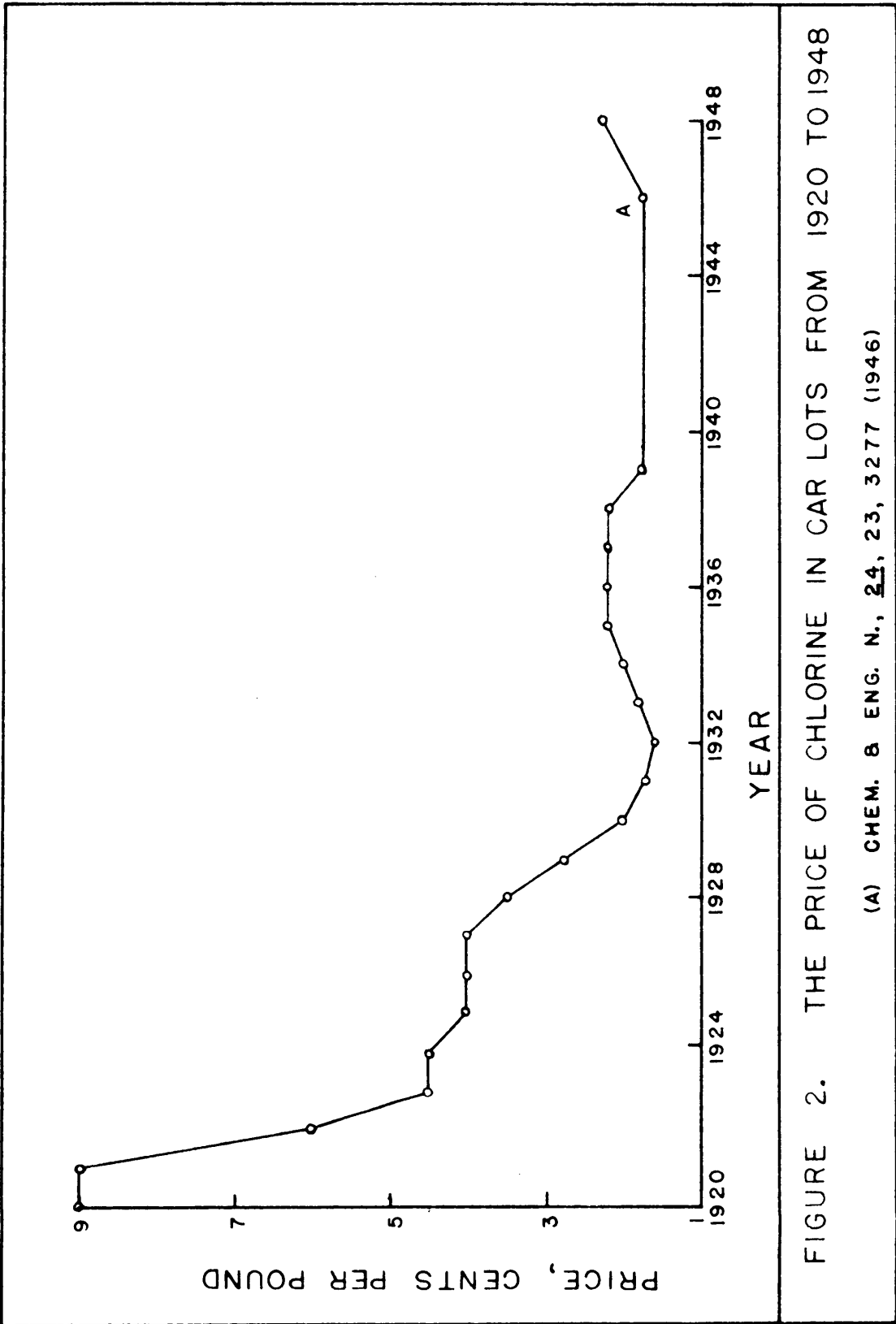
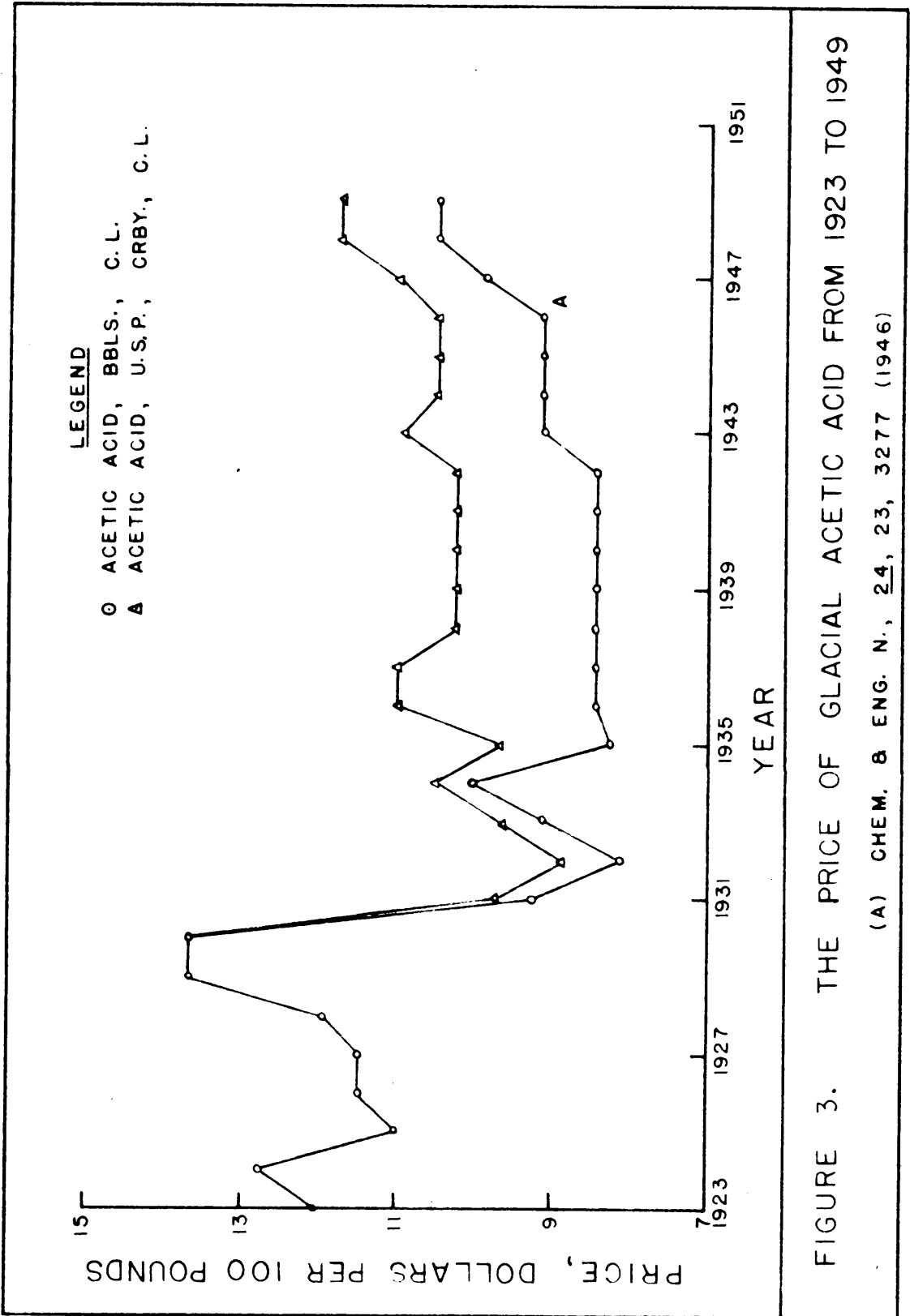


FIGURE 2. THE PRICE OF CHLORINE IN CAR LOTS FROM 1920 TO 1948

(A) CHEM. & ENG. N., 24, 23, 3277 (1946)



declining. The price of chloral hydrate for the years 1925 to 1949 is depicted in Figure 4.

Sodium Chlorate. Sodium chlorate is produced mainly by the electrolytical process(32). The current production of this compound is not known, but over 12,000 tons per year were recently used for weed killing - its largest use. It is currently being produced by five main chemical manufacturers. The Federal government is interested in weed control and has indicated that it will subsidize sodium chlorate to the extent of four cents per pound for use on farms and grazing land. All attempts to lower the price to four cents have failed, however, and there are no prospects of the price lowering in the near future. The price trend of sodium chlorate for the past 25 years is shown in Figure 5.

Ethyl Alcohol. Ethyl alcohol(57) is produced by the fermentation of molasses and grain and by synthetic processes. Slightly more than 600 million gallons were produced last year (1948) by 17 manufacturers. Production capacity was almost twice the production. Synthetic alcohol sales were almost half the total sales. In the future, synthetic alcohol seems sure to capture the market - thus the price will stay down. The price of ethyl alcohol is shown in Figure 6.

Monochloroacetic Acid. Monochloroacetic acid is produced(31) by the direct chlorination of acetic acid. Its use is in manufacturing intermediates, dyes, in organic synthesis, and in medicine. The annual production of this compound by some five manufacturers is unknown. The following is a list of the price of MCA for the years 1935 to 1948.

1935-6	\$0.18 per pound
1937	0.16 - 0.17
1938	0.15 - 0.16
1945	0.17
1946	0.165
1947-8	0.175

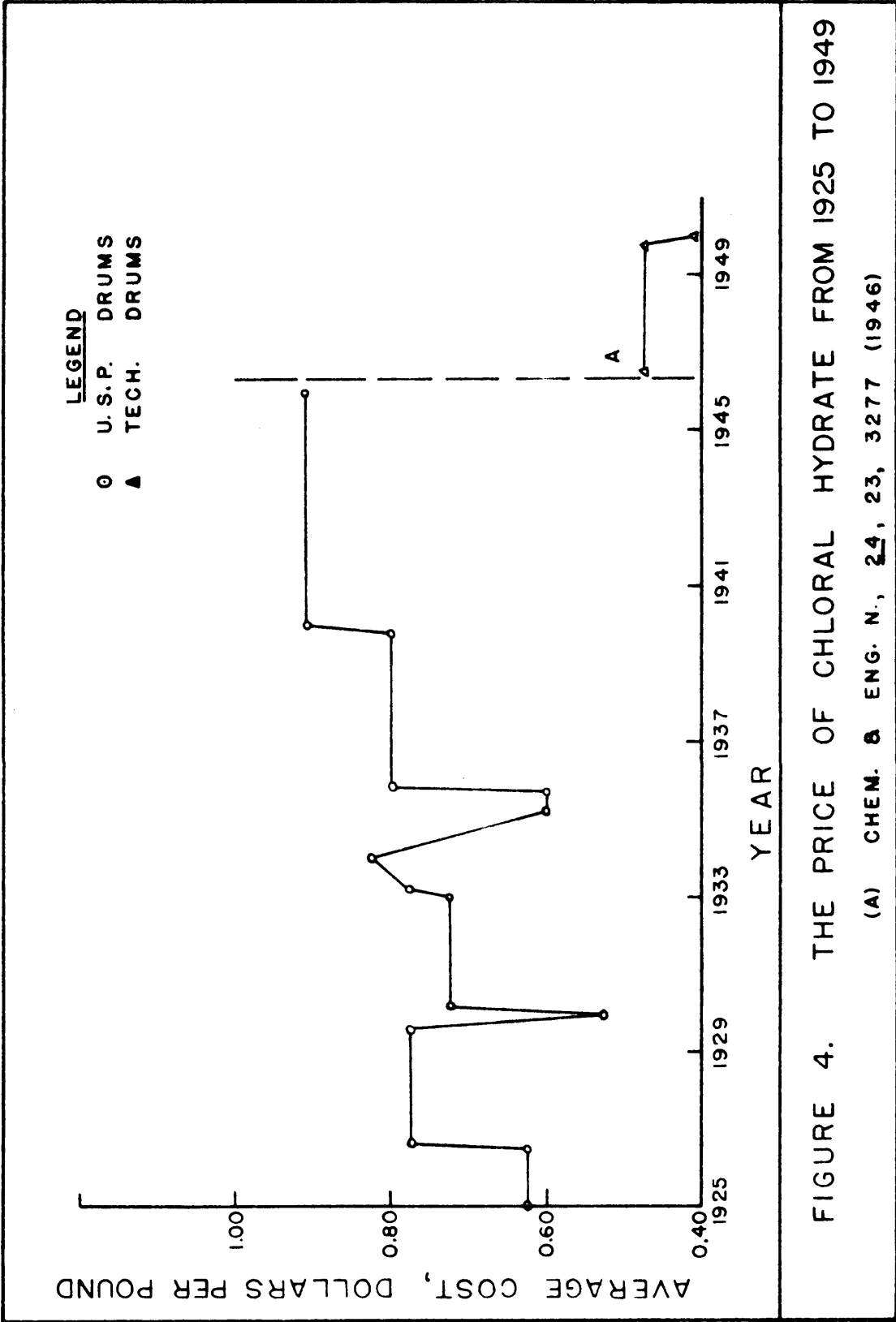
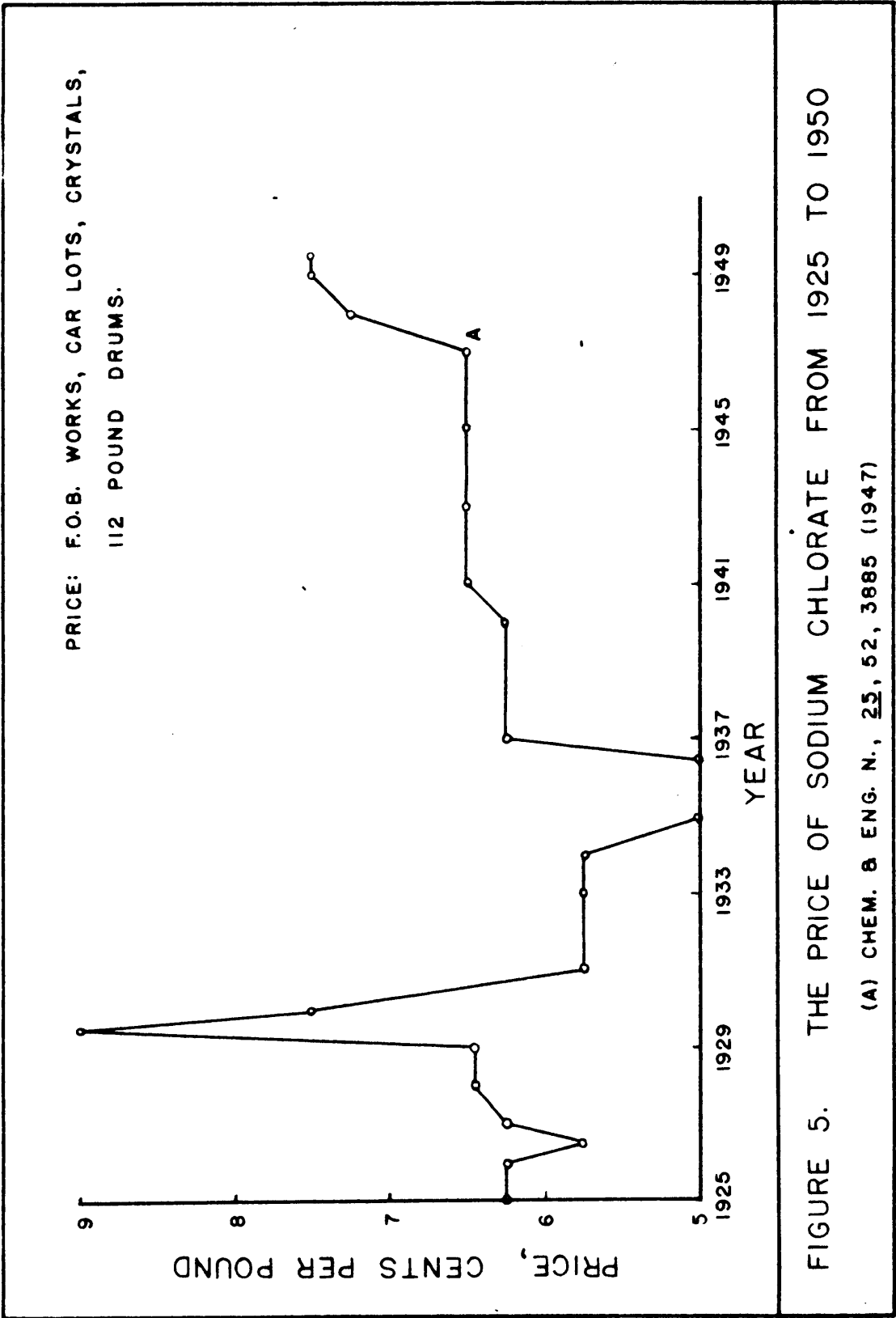


FIGURE 4. THE PRICE OF CHLORAL HYDRATE FROM 1925 TO 1949

(A) CHEM. & ENG. N., 24, 23, 3277 (1946)





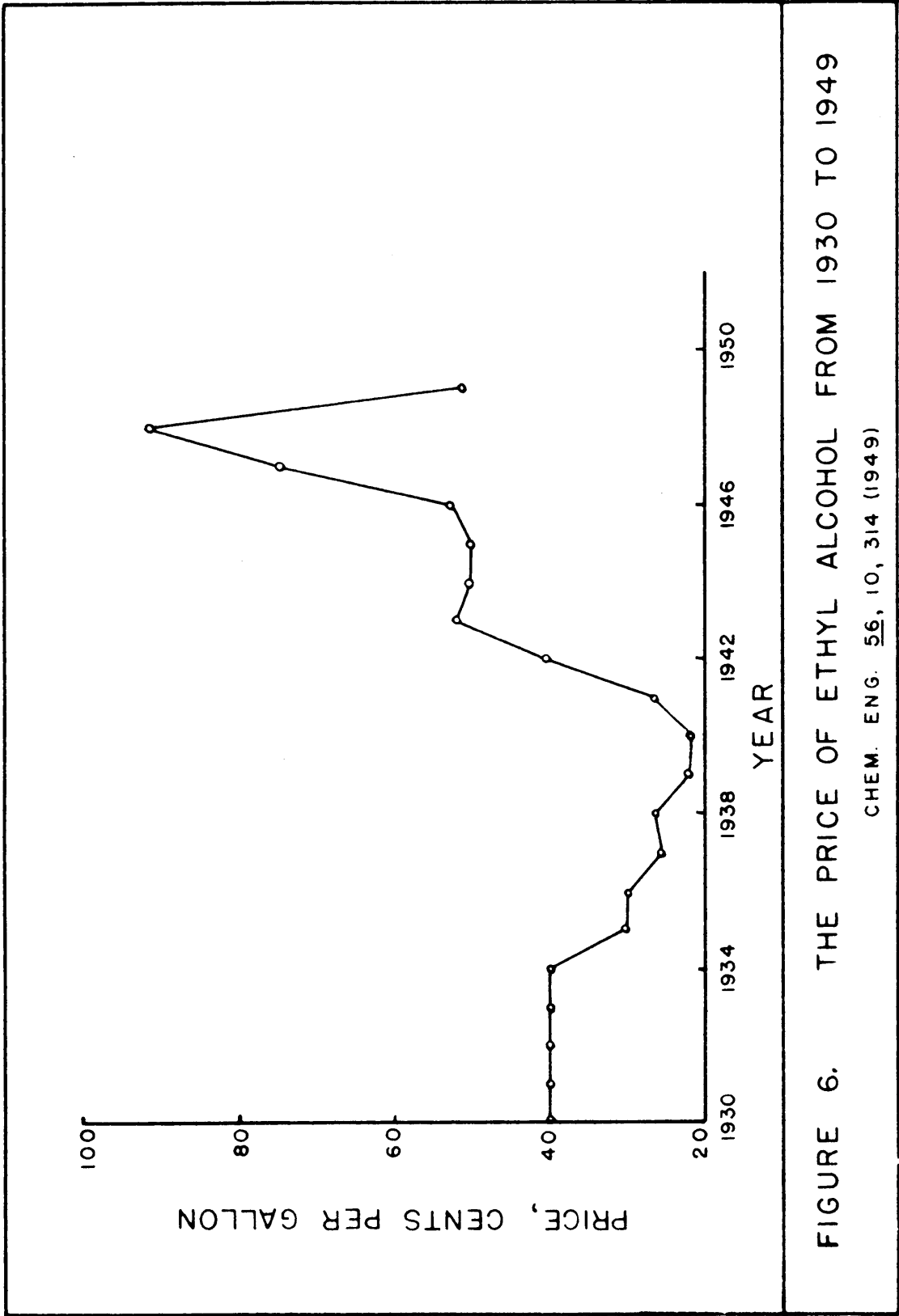


FIGURE 6. THE PRICE OF ETHYL ALCOHOL FROM 1930 TO 1949

CHEM. ENG. 56, 10, 314 (1949)

Dichloroacetic Acid. Dichloroacetic acid is produced by the chlorination of acetic acid or mother liquor from MCA production. Its uses are as intermediates and pharmaceuticals. The price from 1935 to 1937 was \$1.00 per pound. Dow Chemical Co. is the only supplier in the U. S. at the present time (1949).

Raw Material Cost Estimate Summary

Costs of producing TGA by several methods were computed by the Graduate Plant Design Class, based on prices of raw materials arrived at by a study of the commodity surveys. The following is a summary of the costs of producing sodium trichloroacetate, 100 per cent yield, the sodium salt of the acid obtained by neutralization with soda ash.

<u>Method of Preparation</u>	<u>Cost, per lb</u>
Acetic acid + chlorine	\$0.060
Chloral hydrate + sodium chlorate	0.489
Alcohol + chlorine + sodium chlorate	0.101
Carbon tetrachloride + formaldehyde + sodium chlorate	0.779
Carbon tetrachloride + aqueous chlorine + sodium carbonate	0.127
Chloral hydrate + nitric acid	0.499

Prices of raw materials, on which the above cost estimates were based, are as follows:

<u>Material</u>	<u>Cost, per lb</u>
Acetic acid, glacial	\$0.11
Carbon tetrachloride	0.08
Chloral hydrate	0.50
Chlorine, liquid	0.02
Ethyl alcohol, 95 per cent	0.065
Formaldehyde	0.037
Hydrochloric acid	0.005
Nitric acid (concentrated)	0.05
Sodium carbonate, technical	0.0145
Sodium chlorate	0.075
Sulphonyl chloride	0.91
Phosphorus (red)	0.35

The design class concluded that the chlorination of glacial acetic acid was the most promising method for the manufacture of TCA on the basis of the above raw material cost estimate and consideration of the methods of preparation.

### Halogenation

Groggins<sup>(28,29)</sup> has given the mechanism and rules of halogenation. Halogenation may involve reactions of addition, substitution (of hydrogen), replacement (of groups such as hydroxyl or sulfonic acid groups). Each type of reaction involves a specific halogenating agent and a suitable catalyst. The catalysts, with exception of carbon and light, are characterized by the fact that they are halogen carriers, (iron, antimony, and phosphorus). Iodine and bromine which are capable of forming mixed halogens with chlorine are also used as catalysts.

### Methods and Rules of Chlorination

The following methods and rules of chlorination have been given by Groggins and are useful as guides to evaluating chlorinating reactions.

Methods of Chlorination. The methods<sup>(28)</sup> of chlorination are: direct action of chlorine gas; with HCl; with sodium hypochlorite; with phosgene; with sulfuryl chloride; with phosphorus chlorides; by Sandmeyer and Gattermann reactions; and by electrochemical methods.

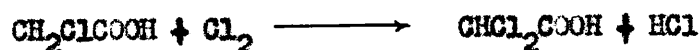
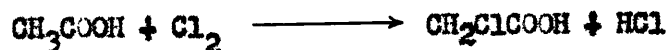
Rules of Chlorination. In chlorination<sup>(29)</sup>, the general tendency is for substitution; no polymerization or skeleton rearrangement will

occur. The order of substitution (with reference to chemical bonds) in primary is less than secondary is less than tertiary. Excessive temperatures and/or time results in appreciable pyrolysis of the chlorides. With an excess of hydrocarbon, chlorination conditions remaining constant, the ratio of monochloride over polychloride products is directly proportional to the ratio of hydrocarbon over chlorine. Therefore, to increase polychloride products, an excess of chlorine is required. Dichlorination proceeds by two mechanisms, (a) loss of HCl followed by the addition of chlorine to the resulting olefin, and (b) progressive substitution. In vapor phase chlorination, the presence of a chlorine atom on a carbon atom tends to hinder further reaction upon that carbon atom. In vapor phase chlorination, increased pressure increases the relative rates of primary substitution.

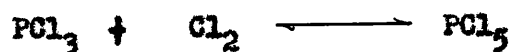
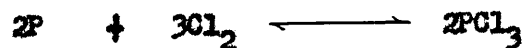
#### Reactions in the Chlorination of Acetic Acid

The following chemical reactions occur or probably occur during the chlorination of acetic acid to produce trichloroacetic acid.

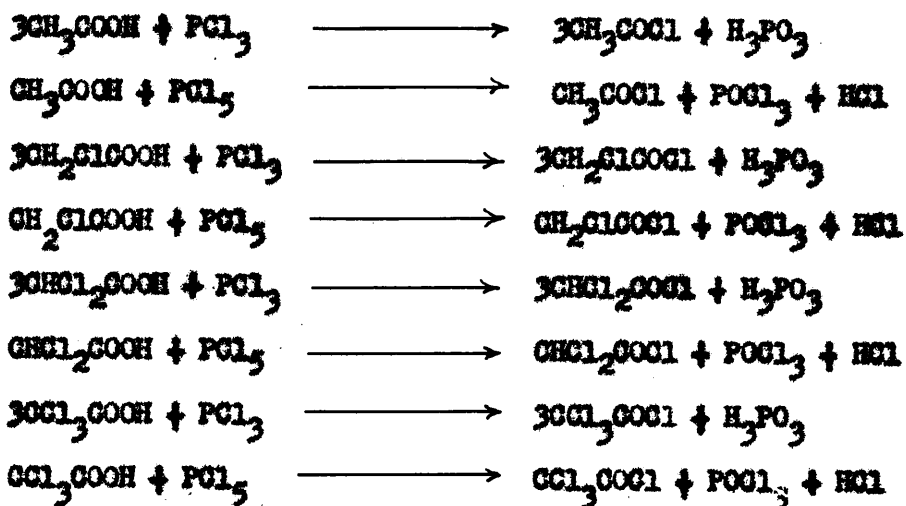
##### Main Reactions.



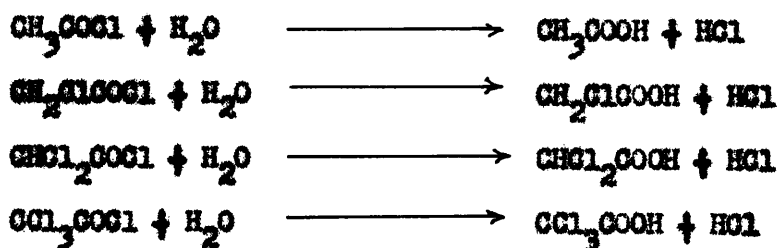
##### Reactions Between Catalysts and Chlorine.



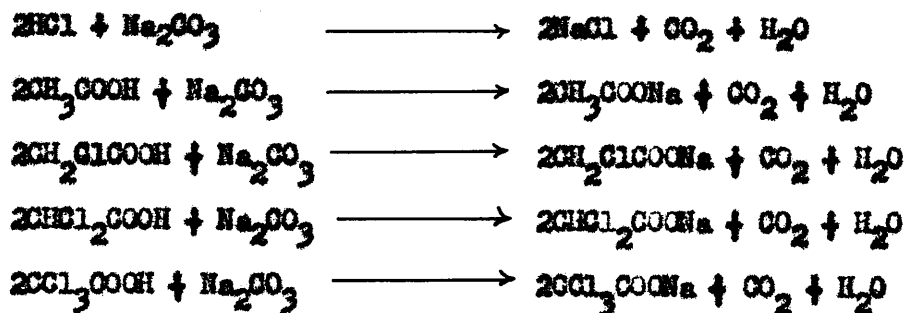
Other Side Reactions.



Reactions of Chlorinated Products in Water.



Reactions of Aqueous Acid Solution with Soda Ash.



Physical Properties of Compounds Involved  
in the Production of TGA

This section is devoted to the presentation of those physical properties of the substances, used in the production of TGA from acetic acid, that may be of importance to this investigation.

Table II contains data on the density of TCA at various temperatures, and the variation in boiling point of TCA at different pressures.

In Table III are listed the more common physical properties of the substances involved in the production of TCA.

The solubility - temperature relationships of hydrochloric acid and chlorine in water are given in Table IV.

Figures 7, 8, 9, 10, 11, and 12 show graphically the solubility relationships of binary mixtures of acetic acid, MCA, DCA, and TCA.

Solubilities of MCA, DCA, and TCA in sulfuric acid have been given by Kendall<sup>(39)</sup>, and in water by Pickering<sup>(45)</sup>.

Measurements of vapor pressure curves of solutions of MCA, DCA, and TCA in acetone, methyl ether, methyl-ethyl ether, and ethyl ether have been given by Weissenberger<sup>(76)</sup>.

The densities of pure components and aqueous solutions<sup>(78,79,80,81,82)</sup>, electrical conductivities<sup>(95,96,97)</sup>, heats of fusion<sup>(89,93)</sup>, heats of solution in water<sup>(91,92)</sup>, heats of vaporization<sup>(90)</sup>, ionization constants<sup>(103)</sup>, refractive indices<sup>(98,99,100,101)</sup>, specific heats<sup>(84,85,86,87,88)</sup>, thermal conductivities<sup>(94)</sup>, and volume changes on melting<sup>(83)</sup> of MCA, DCA, and TCA are given in the International Critical Tables.

#### Chemical Properties of TCA

The following chemical properties have been cited because of their bearing upon subsequent work in the course of this investigation.

TABLE II

Density of Trichloroacetic Acid at Various Temperatures  
and Variation in Boiling Point at Different Pressures

Temperature	Density of TCA	Boiling Point TCA	Pressure (abs)
°C	gm/ml	°C	lb/sq in.
25	1.62	107	21
61	1.603	115	22
75	1.583	141	25
100	1.545	197.5	760
125	1.508	-	-

West, C. J. (Compiler): "International Critical Tables", p. 28.

McGraw-Hill Book Co., Inc., New York, N. Y., 1933. Vol. 3.

TABLE III

**Physical Properties of Chemicals Involved  
In The Production of Trichloroacetic Acid**

Name and Formula	Mol. Weight	Sp. Gr. (compared to water at 40°C)	Melting Point °C	Boiling Point °C	Solubility in 25°C Water gm/100 gm solution
Acetic Acid $\text{CH}_3\text{COOH}$ (a)	60.0	1.0492 (20°C)	16.6	118.5	-
Chloroacetic Acid $\text{CH}_2\text{ClCOOH}$ (a)	94.5	1.398 (65°/65°)	69.1 (oc)	189	86 (30°C)
Dichloroacetic Acid $\text{CHCl}_2\text{COOH}$ (a)	128.95	1.551 (25°C)	32.5, -4.0	193	8.63
Trichloroacetic Acid $\text{CCl}_3\text{COOH}$ (a)	163.4	1.6298 (61°C)	57.3	197.5	120 (25°C)
Chlorine $\text{Cl}_2$ (a)	70.91	1.468 (0°C)	-	-34.5	-
Acetyl Chloride $\text{CH}_3\text{COCl}$ (a)	78.5	1.1051 (20°C)	-112.0	51.8	decomposes
Chloroacetyl Chloride $\text{CH}_2\text{ClCOCl}$ (a)	112.9	1.495 (0°C)	-	105	decomposes
Dichloroacetyl Chloride $\text{CHCl}_2\text{COCl}$ (b)	147.4	-	-	108	decomposes
Trichloroacetyl Chloride $\text{CCl}_3\text{COCl}$ (c)	181.8	1.6564 (0°C)	-	117.9	decomposes
Phosphorus (red) P (a)	124.8	2.20 (20°C)	590 43 atm	ignites 200	-
Phosphorous Acid $\text{H}_3\text{PO}_3$ (a)	82.0	1.651	74	decomp. 200	-
Phosphoric Acid $\text{H}_3\text{PO}_4$ (a)	98.0	1.834 (18°C)	42.3	$\frac{1}{2} \text{H}_2\text{O}$ 213	2340 (26°C)
Phosphorus Oxychloride $\text{POCl}_3$ (a)	153.4	1.675	2.0	107.2	decomposes
Phosphorus Trichloride $\text{PCl}_3$ (a)	137.5	1.574 (20°C)	-111.8	76.0	decomposes
Phosphorus Pentachloride $\text{PCl}_5$ (a)	208.3	1.60	148 subl. pressure	under 160	decomposes
Sodium Carbonate $\text{Na}_2\text{CO}_3$ (a)	106.0	2.509 (0°C)	851	decomp.	-

(a) Perry, J. H. et al: Physical and Chemical Data, "Chemical Engineers' Handbook" (J. H. Perry, Editor), pp. 271-367. McGraw-Hill Book Co., Inc., New York, N.Y., 1941. 2d ed.

(b) Huntress, E. H.: "Organic Chlorine Compounds", p. 3:5290. John Wiley and Sons, New York, N. Y., 1948.

(c) Huntress, E. H.: "Organic Chlorine Compounds", p. 3:5420. John Wiley and Sons, New York, N. Y., 1948.



TABLE IV

Solubility of Chlorine and Hydrogen Chloride in 100  
Grams of Water at 760 mm Absolute Pressure

Temperature °C	Chlorine grams	Hydrogen Chloride grams
0	1.46	82.31
12	0.88	76.30
18	-	73.41
20	0.716	67.3
30	0.562	63.3
40	0.451	59.6
50	0.386	56.1
60	0.324	-
70	0.274	-
80	0.219	-
90	0.125	-
100	0.0	-

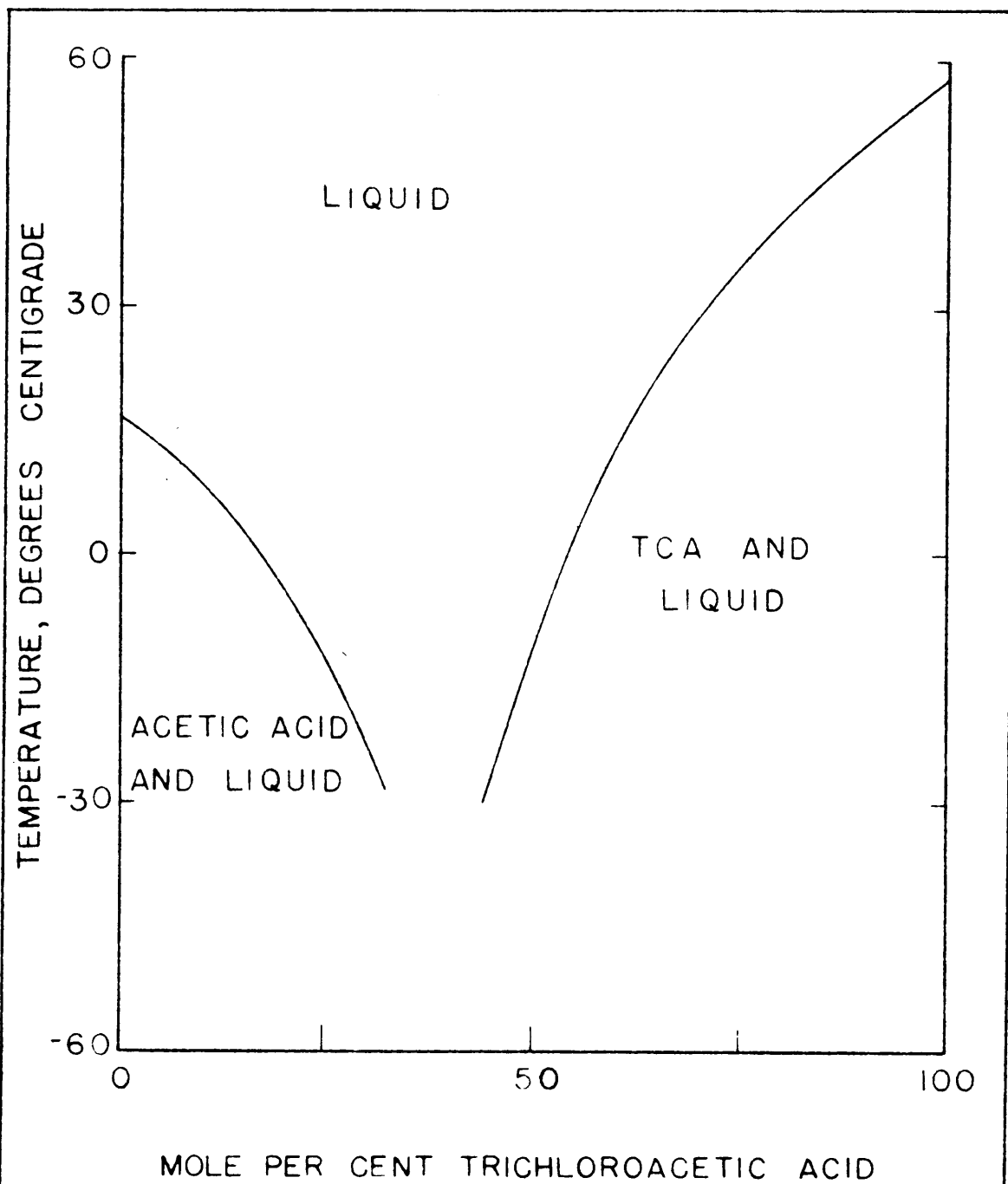


FIGURE 7. SOLUBILITY-TEMPERATURE DIAGRAM FOR ACETIC ACID AND TRICHLOROACETIC ACID

KENDALL, J.: J. AM. CHEM. SOC., 36, 1722 (1914)

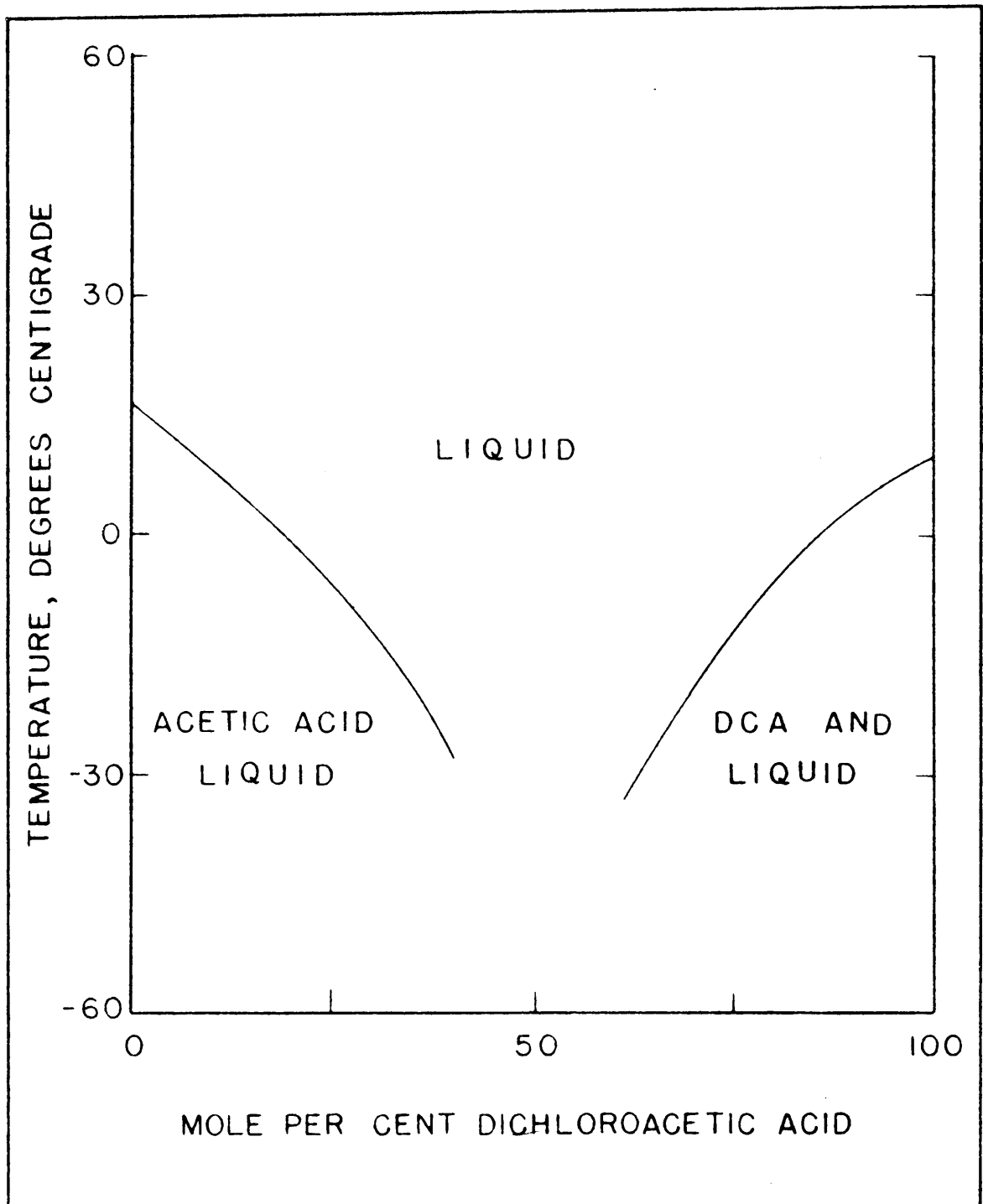


FIGURE 8. SOLUBILITY-TEMPERATURE DIAGRAM FOR ACETIC ACID AND DICHLOROACETIC ACID

KENDALL, J.: J. AM. CHEM. SOC., 36, 1722 (1914)

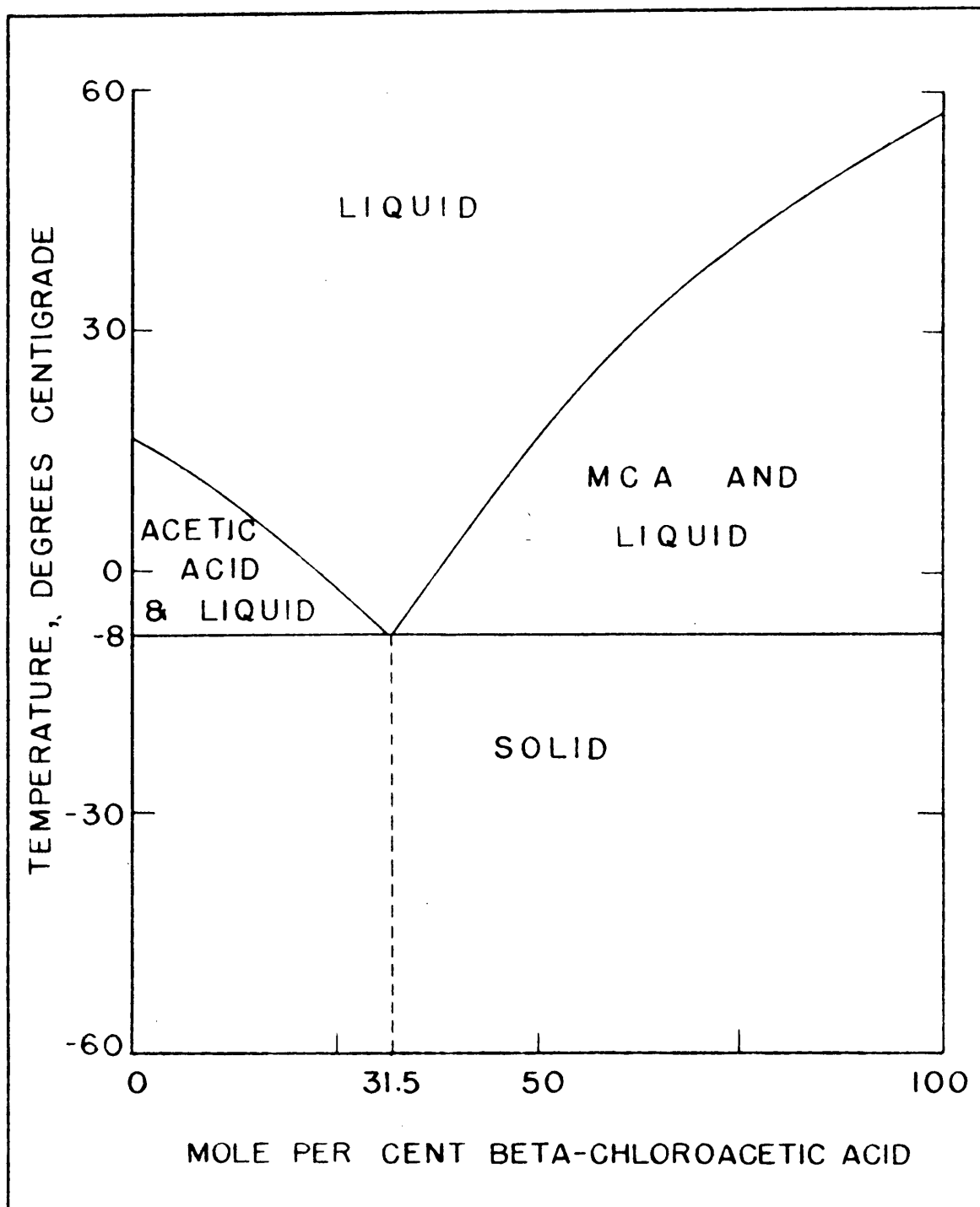


FIGURE 9. SOLUBILITY-TEMPERATURE DIAGRAM FOR ACETIC ACID AND MONOCHLOROACETIC ACID

KENDALL, J.: J. AM. CHEM. SOC., 36, 1722 (1914)

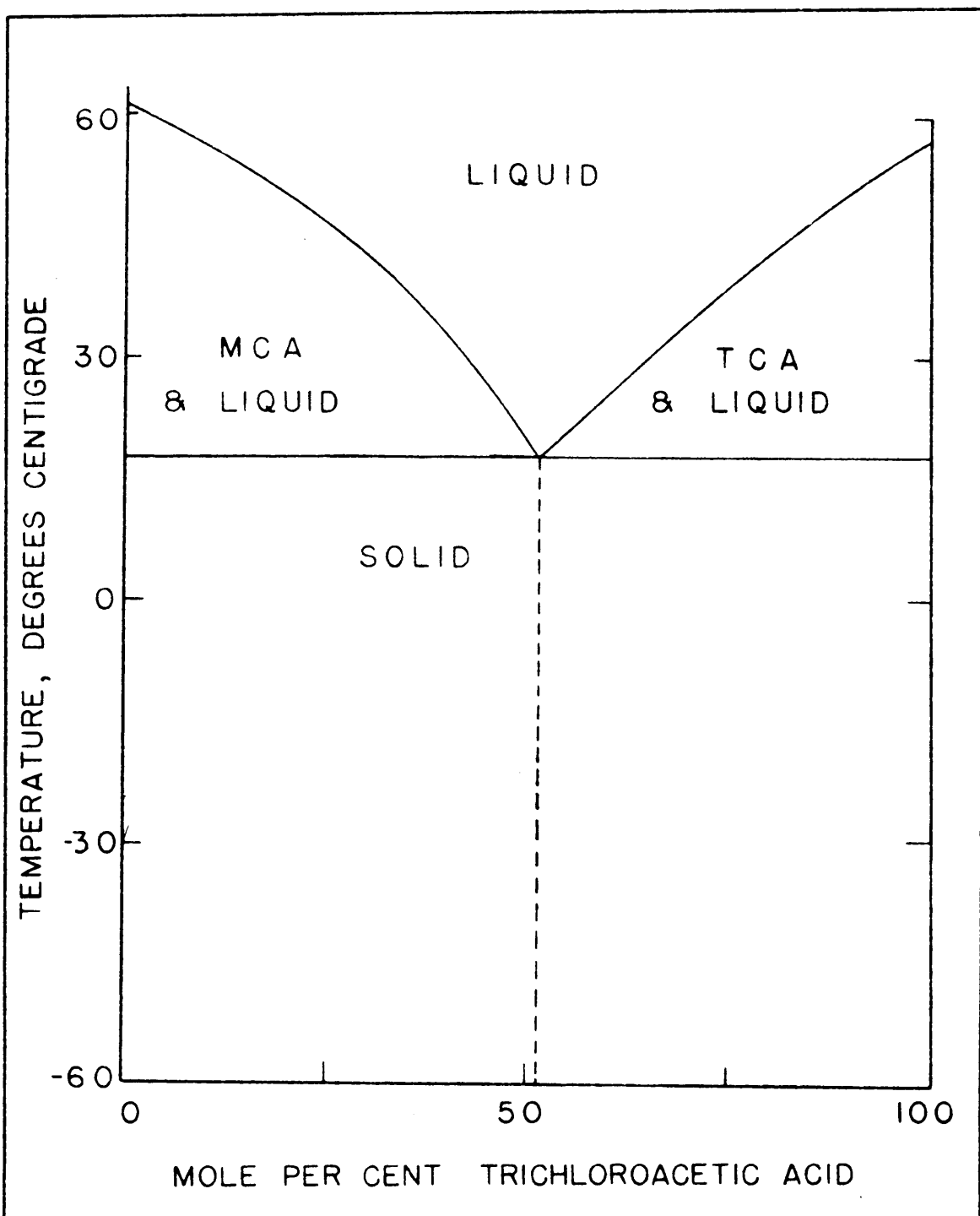


FIGURE 10. SOLUBILITY-TEMPERATURE DIAGRAM FOR MONO- AND TRICHLOROACETIC ACIDS

KENDALL, J.: J. AM. CHEM. SOC., 36, 1722 (1914)

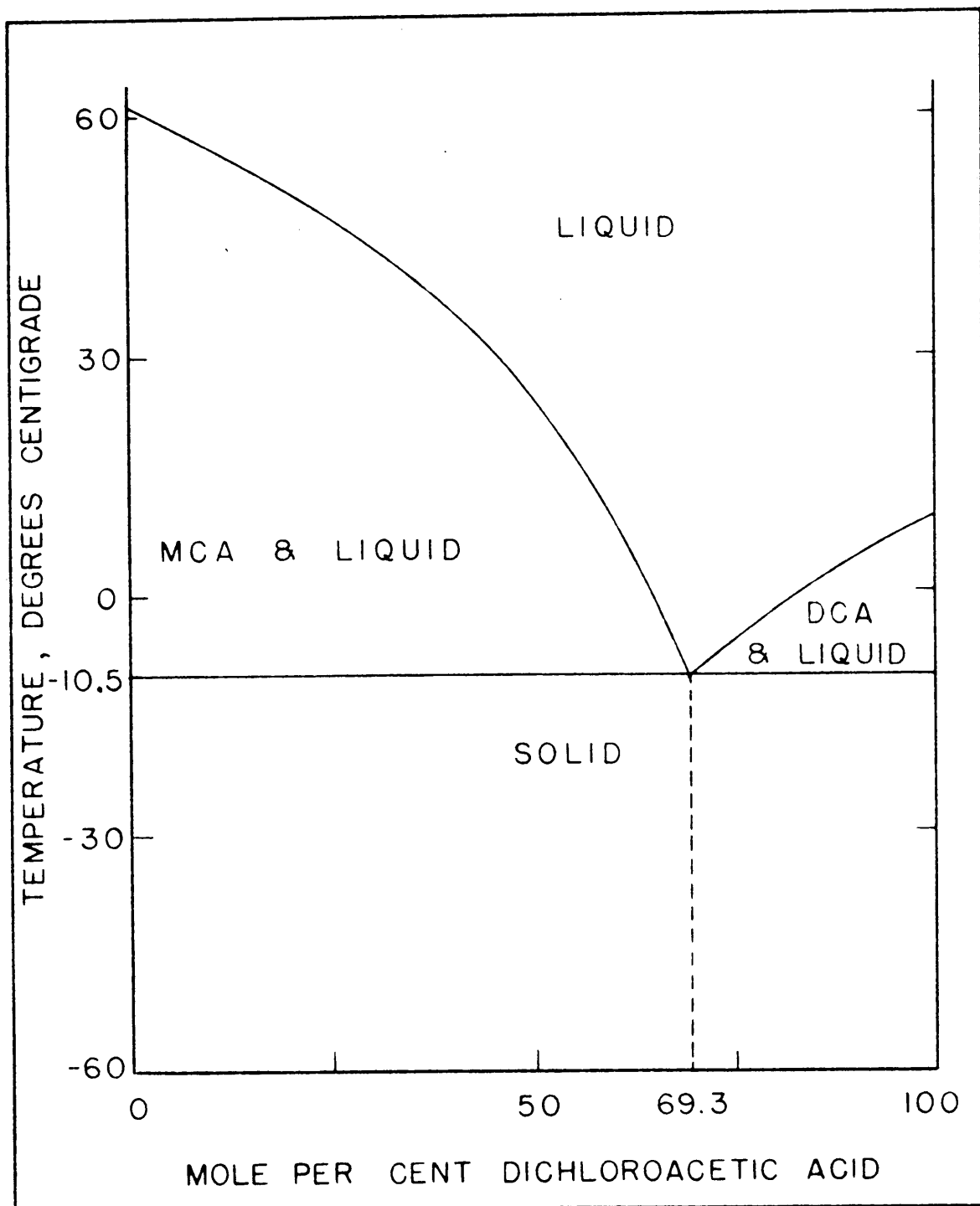


FIGURE II. SOLUBILITY-TEMPERATURE DIAGRAM FOR MONO- AND DICHLOROACETIC ACIDS  
KENDALL, J.: J. AM. CHEM. SOC., 36, 1722 (1914)

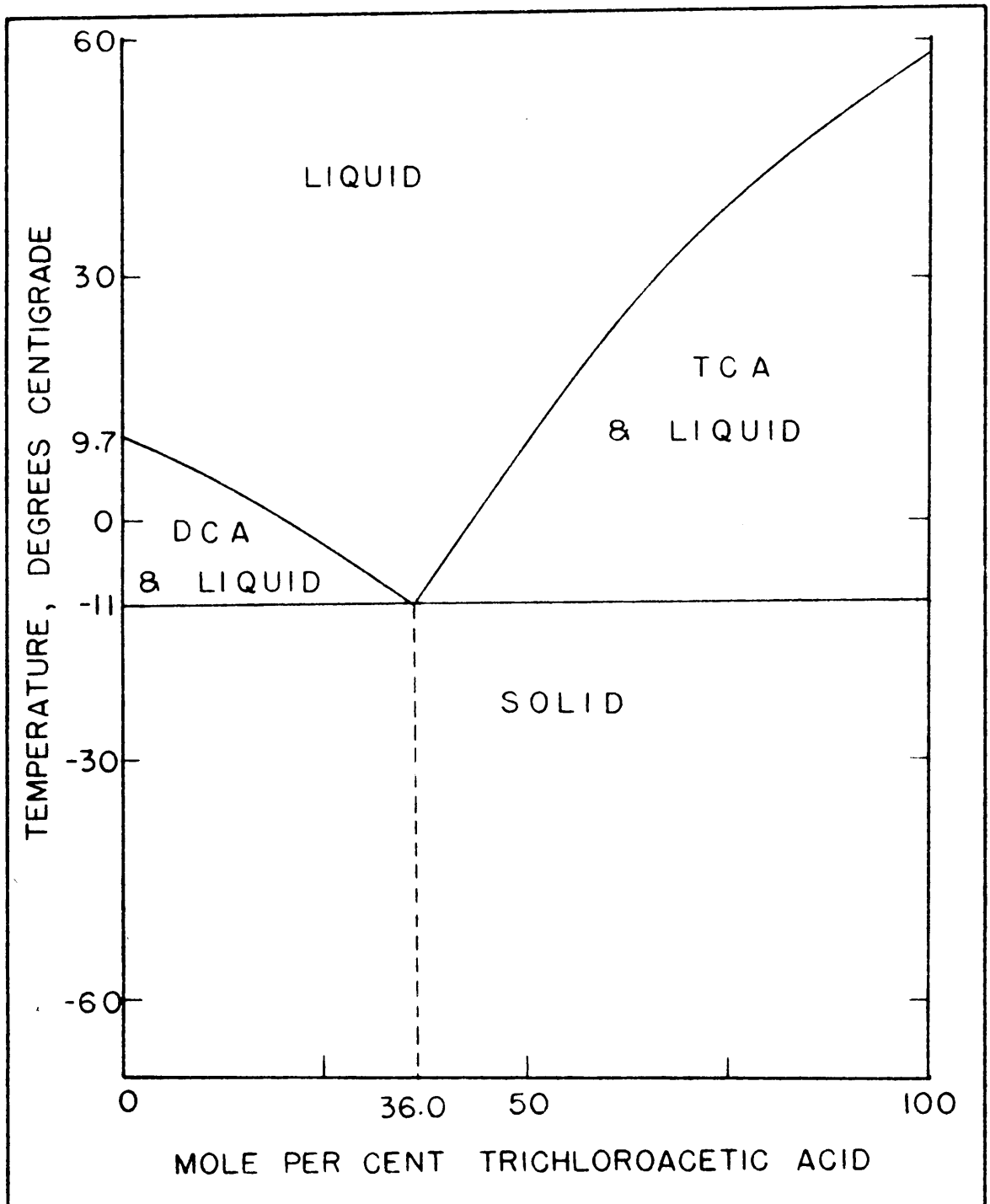


FIGURE 12. SOLUBILITY-TEMPERATURE DIAGRAM FOR DI- AND TRICHLOROACETIC ACIDS  
KENDALL, J.: J. AM. CHEM. SOC., 36, 1722 (1914)

TCA decomposes<sup>(43,46)</sup> in hot alkaline or strong alkaline solutions to form chloroform and carbon dioxide. The velocity of decomposition of TCA to  $\text{CHCl}_3$  and  $\text{CO}_2$  was determined for its solutions in water, aniline, and in binary mixtures of aniline and  $\text{CHCl}_3$  and toluene by Pearce and Nelson<sup>(43)</sup>. They found that the reaction proceeds more rapidly in light than in dark regardless of the nature of the solvent.

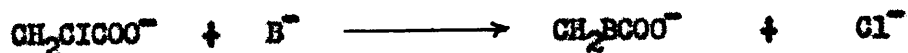
Verhoek<sup>(68)</sup> reported that TCA decomposes in water, aniline, and related solvents but not in non-basic solvents such as benzene, carbon disulfide, carbon tetrachloride, ether, acetone, nitrobenzene, ethyl benzoate, toluene, chloroform, amyl alcohol, ethyl acetate, acetic acid, or 6 N sulfuric acid. The velocity of decomposition of sodium trichloroacetate (NTA) in water at temperatures from  $50^\circ$  to  $90^\circ\text{C}$  and at a 0.1 molar concentration were given. Verhoek concludes that the decomposition of the acid and salts of TCA in water follow the first order law; that the reaction velocity is dependent upon the concentration of trichloroacetate ion; that the stability of the ion is determined by the extent of solvation and the nature of the solvating substance; and that the formation of the chloride ion in aqueous solutions of trichloroacetates is the result of an oxidation of the chloroform (to  $\text{CO}_2$  and  $\text{HCl}$ ) which results from the decomposition of the trichloroacetate.

Jaeger and Berger<sup>(36)</sup> have noticed that TCA, with less than one equivalent of ferric hydroxide, decomposes rapidly under diffuse sunlight or ultraviolet light from a mercury arc. Carbon dioxide and



$C_2Cl_6$  are formed. If excess ferric hydroxide is present, the photochemical reaction is replaced by the reaction of thermal decomposition to form  $CHCl_3$  and  $CO_2$ .

The rate of the reaction



in which  $B^-$  is a basic anion, was followed by determining the  $Cl^-$  by Dawson<sup>(14)</sup>. The velocity coefficient increases with increase in the basic strength of the participating base.

Lamborn<sup>(41)</sup>, in a patent issued in 1948, stated that a crystalline halogenated fatty acid having two to four carbon atoms in the molecule was mixed dry with an alkali or alkaline earth carbonate or bicarbonate to form salts. An example was given - MCA (294 parts) and dry  $Na_2CO_3$  (167 parts) were mixed for 0.75 hours. The reaction proceeded substantially to completion with little evolution of heat to yield sodium monochloroacetate in dry powdery state.

#### Materials of Construction

Table V gives the safe materials<sup>(18,24,69)</sup> of construction for use with various chemicals involved in the production of TCA. The materials of construction selected by the plant design class for the various pieces of equipment have been noted on the flow sheet on page 40. In the case of the reactors (chlorinators), the final choice was between monel and glass-lined equipment. Selection of monel was based on its wearability.

TABLE V

Materials of Construction For Use With  
Involved in The Production of Trichloro

Material Chemical	Carbon and Graphite	Alumina Alloys (1)	Durimet and Chloromet	Glass Lined Steel	Silver (1)	Tantalum	Chemical Porcelain	Hastelloy	Chemical Stoneware	Nickel and (1) Nickel Alloys	Harveg 60	Stainless Steel (1)	Rubber Lined Steel Tanks	Brasses (1)	Gold
Acetic Acid (2)	X	X	X	X	X	X	X	X	X	X	X	X			
Hydrochloric Acid (3)	X		X	X	X	X				X			X	X	X
Chlorine, Dry (2)										X	X	X			
Chlorine, Wet (2)	X			X		X	X	X	X				X		
Chloroacetic Acid (2)						X		X		X	X			X	
Acetyl Chloride												X			

- (1) Vilbrandt, F. C.: "Chemical Engineering Plant Design", pp McGraw-Hill Book Co., Inc., New York, N. Y., 1949. 3d e
- (2) Equipment and Construction Materials, Chem. Eng. 55, 11-9
- (3) Gaylord, W. M.: Hydrochloric Acid Versus Construction Mat Chem. Eng. 56, 1-231 (1949).

### Estimation of Desired Capacity of Plant

The following was decided by the graduate design class for estimation of the desired plant capacity. There would be an eight hour day, and a five day week. The weed growing period, for the southern states, during which the weed killer would be applied was estimated to be 20 weeks. The time required for putting the equipment into shape - two weeks. The time required for storing the equipment and preparing to start production - two weeks. The vacation for employees was set at four weeks, with an additional week for Christmas and two days for Thanksgiving. Thus, the total time excluded from production was 29 weeks and two days. The time left for production was 21 weeks, or 105 days, or 840 hours.

It was decided that the plant would probably require ten employees plus two clerks. The ten men would be split up into pairs for applying the weed killer, therefore five spraying units would be used by the company. Two additional men for each spraying unit would be hired for the spraying season only.

One spray unit can cover 100 miles of railroad track per day. The quantity of TCA required per mile of track is 200 pounds. Therefore, one spraying unit could spray 20,000 pounds or ten tons of TCA per day. Five units would consume 50 tons per day. The spraying season was fixed at 20 weeks, or 100 days (5-day week). Production was then placed at 5,000 tons annually (per 21 weeks), or 13,600 pounds of trichloroacetic acid per hour (seven-hour day).

Assumptions Made for Plant Design

The Graduate Chemical Engineering Plant Design class (1949-1950) of Virginia Polytechnic Institute, arrived at the following assumptions as a basis for making a design for a plant to produce TCA from acetic acid and chlorine.

1. Chlorination can be carried out stepwise (multibatch), with different conditions for chlorination in each stage.
2. Chlorination will take place under liquidous conditions.
3. Recycle of residual liquors will assist in control of the reaction.
4. Acetic acid charged into the first reactor will be converted 100 per cent to TCA.
5. Four stages or steps will be required for the chlorination.
6. No acetic acid leaves reactor number four.
7. Countercurrent chlorine (and HCl) flow will be used.
8. The time of reaction in each stage will be seven hours.
9. The temperature will be varied between 100 and 160 °C, being 100, 120, 140, and 160 °C in each reactor respectively.
10. No acetic acid will be required for carrying the catalyst.
11. Phosphorus (red) will be used as the catalyst.
12. Water entering the first and fourth reactors will be absorbed by the HCl and thus will not react.
13. Acetic acid used will be 99.5 per cent  $\text{CH}_3\text{COOH}$  and 0.5 per cent  $\text{H}_2\text{O}$ .
14. The chlorine and HCl dissolved in the liquid of the first reactor goes through the process.

15. Polymers will form in the fourth reactor alone.

16. The reaction mass from the fourth reactor will be sent directly to neutralization, drying, size reduction, and packing, this being because the mass from the fourth reactor contains 89 per cent TGA and recycle is not required.

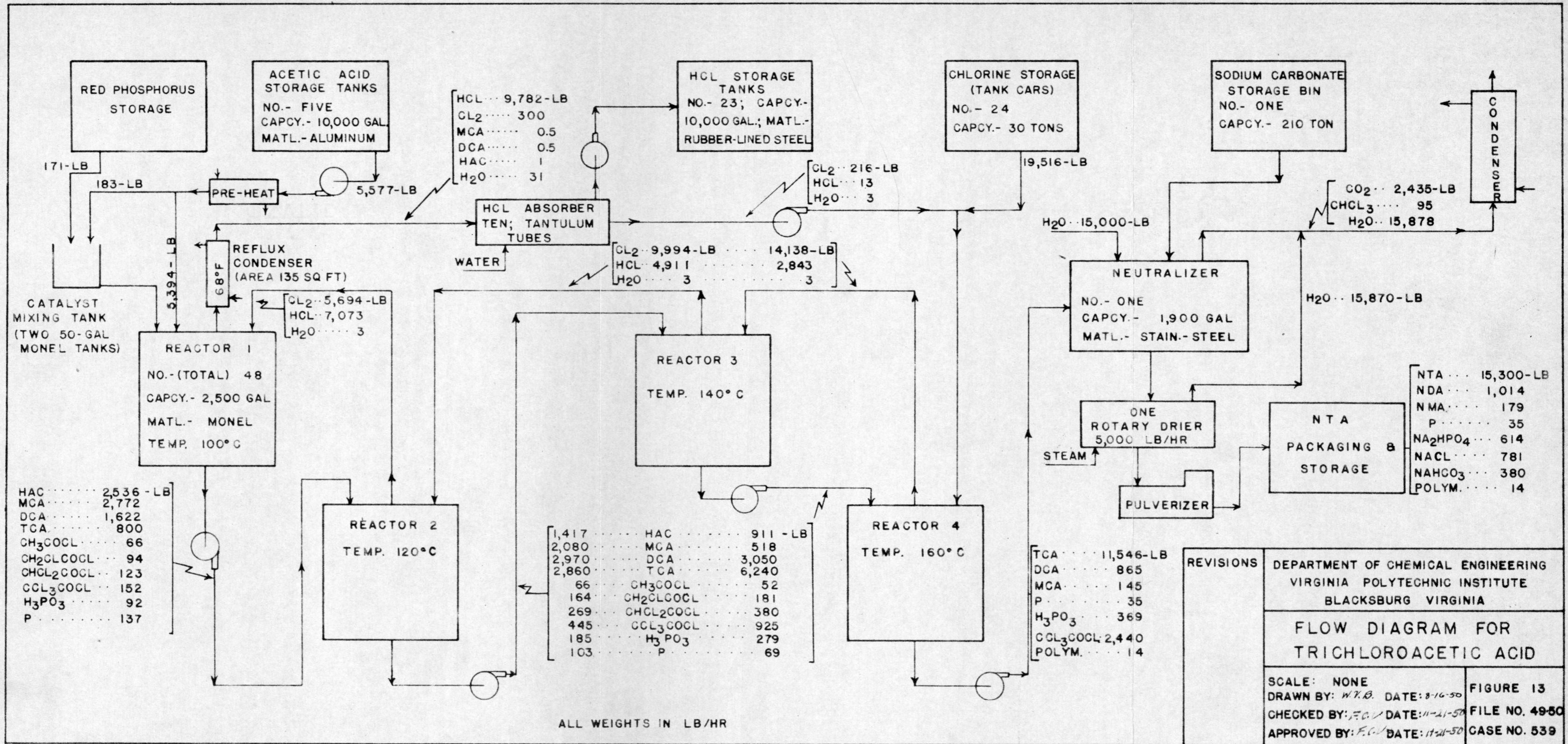
17. The same catalyst will be used in each reactor, and 80 per cent of the phosphorus will be used up in the four steps of the reaction, phosphorus trichloride being formed with subsequent formation of acetyl chlorides and phosphorus acid; one-fourth of the reacting phosphorus will react in each reactor.

18. There are negligible amounts of the chlorinated derivatives of acetic acid in the gases leaving the second, third, and fourth reactors.

19. All acetyl chlorides formed will leave in the liquid form from the fourth reactor as trichloroacetyl chloride.

Quantitative Flow Sheet for The Production  
of Trichloroacetic Acid

Figure 13 is the quantitative flow sheet of the process for producing TGA as drawn by the Graduate Chemical Engineering Plant Design Class of 1949-50.



Conclusions of Graduate Plant Design Class on  
Feasibility of Producing TCA

The Graduate Plant Design Class (1949-1950) of the Virginia Polytechnic Institute, decided that it was feasible to produce sodium trichloroacetate in the amount of 5,770 tons per annum when the production was based on 21 weeks of operation, an eight-hour day, and a 5-day week.

The capital investment required, embracing the building and real estate, equipment costs, and working capital, was estimated to be \$3,624,579. The gross income of the plant was estimated to be \$4,585,810; the annual costs \$2,314,010; thus, the net income would be \$2,271,800 at a selling price of \$0.41 per pound of sodium trichloroacetate, in containers, and at a depreciation rate of ten per cent of the total plant cost.

Raw material costs including costs for water, power, steam, and packaging were estimated to be \$970,066; building and real estate costs \$418,980; and total equipment costs \$2,251,892.

The annual cost for 25 laborers, including a plant manager, was estimated to be \$39,858 (for an operation period of 21 weeks plus one week vacation).

Estimation of the unit cost of sodium trichloroacetate was \$0.18 per pound. The market value of sodium trichloroacetate at the time of the plant design was \$0.41 per pound.

### Analysis of Mixtures of Chlorinated Acids

It has been foreseen that an analysis of a mixture of chloroacetic acids will be indeed difficult by normal means. This, of course, is due to the similarity of the properties of the three acids and their derivatives (simple derivatives). Possible means of analysis are ordinary volumetric analysis, separation of individual components and their subsequent identification, microscopic analysis, conductrimetric analysis, and chromatographic analysis. The following paragraphs present a review of the literature on the methods of analysis as applied or applicable to the acid mixtures.

Volumetric Analysis. Pool(46) has given the following method for estimating the quantities of acetic, chloroacetic, dichloroacetic, and trichloroacetic acids in a mixture of these acids.

Total Acid. A known volume of the solution is titrated with a normal solution of KOH. Let "a" equal the volume of normal KOH required;  $M_a$ ,  $M_m$ ,  $M_d$ , and  $M_t$  the molecular weights, and "p", "q", "r", and "s" the weights of acetic acid, MCA, DCA, and TCA in the mixture respectively. Then it follows that-

$$a = \frac{1000p}{M_a} + \frac{1000q}{M_m} + \frac{1000r}{M_d} + \frac{1000s}{M_t} \quad (1)$$

Estimation of TCA. An equal volume of the mixture of acids is boiled with excess KOH solution, the TCA decomposing to form  $K_2CO_3$ . The TCA is then estimated by precipitating the carbonate as barium carbonate and titrating with a normal acid. The value of "s" in equation (1) may then be calculated.



Estimation of DCA. An equal volume of the acid mixture is boiled with an excess of lime water. The dichloroacetic acid decomposes forming calcium oxalate (insoluble in acetic acid and water) and calcium glycollate. The calcium salts are then separated by means of acetic acid and the oxalate calcined to form calcium carbonate. The carbonate is determined and the value of "r" in equation(1) calculated.

Estimation of Total Chloride. Finally, an equal volume of the acid solution is boiled with KOH solution in a reflux apparatus and the chlorides thus released (as HCl) precipitated by silver nitrate. If "d" equals the weight of silver chloride formed, then -

$$d = 143.38 \left( \frac{1000q}{Mn} + \frac{2000r}{Md} + \frac{3000s}{Mt} \right) \quad (2)$$

and "p" and "q" may then be calculated from this equation and equation (1).

Modification of Pool's Method. Dalin<sup>(13)</sup> claims that the determination of DCA in MCA is made accurate to one to two per cent by a modification of the standard method. The acetic acid in the chloroacetic acid is determined by addition of an inert substance boiling at about 150° C, such as methyl amyl ketone, and distilling. The acetic acid comes over in the first portion of distillate, and is determined by titration with alkali hydroxide. The older Army method of analysis, based on Pool's work (page 45), is invariably low by a factor of 15 to 85 per cent. Use of too much water and reagents is believed to cause the discrepancy. The reliability of the results of the revised method of analysis is shown in Table VI.

TABLE VI

Effect of Quantity of Reagents Used on Dichloroacetic Acid

Results

Quantity of Reagents	Number of Replications	Dichloroacetic Acid Concentration	
		Known %	Found %
1	6	2.40	2.38 ± 0.02
1	4	2.06	2.09 ± 0.04
1	5	100 (a)	102 ± 1 (a)
1	5	2.4	2.30 ± 0.02
1	4	2.05	2.05 ± 0.02
1	3	3.50	3.48 ± 0.02
4.5	4	2.05	1.76 ± 0.04
4.5	5	3.00	2.52 ± 0.13
5	2	2.06	0.72 ± 0.04
4 (b)	3	3.50	0.5

- (a) Analysis of recrystallized dichloroacetic acid.
- (b) Results obtained in another laboratory.

Dalin, G. A. and J. W. Hainsohn: Analysis of Chloroacetic Acid, Anal. Chem. 20,

470-2 (1948).

Estimation of TCA by Direct Titration. It has been reported<sup>(67)</sup> that acetyl chloride and TCA can be titrated with sodium acetate in acetic anhydride solution with methyl orange or with dimethyl yellow as indicators. With tropeolin OO, the color change takes place before the true endpoint is reached. The reaction of TCA and sodium acetate is instantaneous. No indication is given that sodium acetate and DCA or MCA do or do not react.

Estimation of MCA by Direct Titration. Frankis<sup>(21)</sup> has given this method of analyzing for MCA. Twenty milliliters of standard 0.1 normal thioglycolic acid, 0.5-gm  $\text{Na}_2\text{CO}_3$ , five milliliters of ten normal NaOH, and 20 milliliters of a solution containing approximately 1.0 to 1.5 millimoles of sodium chloroacetate are put in a flask. The mixture is heated to the boiling point in one minute, cooled, and five milliliters of concentrated HCl are added. The excess thioglycolic acid is titrated with 0.1 normal iodine solution. One mol of thioglycolic acid is equivalent to one mol of sodium chloroacetate and also one mol of iodine.

Pyridine Test for TCA. A qualitative test for compounds containing  $\text{CCl}_3$  groups has been reported by Fujiwara<sup>(22)</sup>. Some of the liquid, containing the compound to be tested, is mixed with three milliliters of ten per cent sodium hydroxide solution and two milliliters of pyridine. The mixture is then heated to the boiling point. A red coloration appearing is reported to be a positive test for  $\text{CCl}_3$  groups. Brain<sup>(9)</sup> has given a modification of the Fujiwara reaction for testing trichloroethylene. Brain used a 40 per cent sodium hydroxide solution and pyridine in the same ratio as given by Fujiwara.

Analysis by Separation of Addition Compounds. Analysis of the chloroacetic acids by the quantitative separation of one or more of the acids through the formation of an addition compound has received attention.

Phenol - TCA Addition Compound. Alphen<sup>(1)</sup> reports that phenols react with TCA and alkali in the same way as with chloroform and alkali in the Reimer and Tiemann reaction, hydroxy aldehydes being formed. The reaction proceeds more quickly than with chloroform but yields are poor due to side reactions. The phenol - TCA addition product is a white crystalline material with a melting point of 37.6°C, and is unstable.

Pyridine - MCA Addition Compound. Ramsey<sup>(48)</sup> reports that a qualitative test for MCA proposed depends on the precipitation of a well defined crystalline mass when MCA is heated with excess pyridine in a water bath at 60°C. If desired, confirmation may be obtained by preparing pyridine betaine picrate which melts sharply at 142-3°C. The qualitative procedure is quantitatively carried out under controlled conditions; the crude product is purified, dried and weighed. If the reaction mixture contains 20 per cent or more water, no precipitate may appear even if MCA is present; but the precipitate will appear when the pyridine is evaporated and will not dissolve when pyridine is again added. Ramsey also reports that TCA and DCA give negative results to this test.

Other Addition Compounds of The Chlorinated Acids. Shriner and Fuson<sup>(56)</sup> have suggested that the anilide, p-toluide, or the p-nitro benzil ester of the chlorinated acids be used for their

identification. However, it is doubtful that suitable separation of any one compound, from a mixture, may be effected by the formation of these derivatives. Table VII gives the melting and boiling points of previously mentioned derivatives.

Solubility of the Chlorinated Acids. The chlorinated acetic acids are soluble to much the same extent in organic and inorganic solvents; the only exceptions being those solvents that may aid decomposition of one or more of the acids. Solvents for the acids (known systems) have been given by Seidall<sup>(53)</sup>.

Microscopic Analysis. The method of analysis given by Pool (page 45) has obvious disadvantages. It is long and involved, and the reactions upon which the method is based are not strictly quantitative. Direct estimation by microscopic methods would be quite advantageous.

Barium Salts. The use of microscopic analysis for determining chlorinated acids, both individually and in mixtures, has received considerable attention of investigators. Wilson and Keenan<sup>(104)</sup> report a method for the microscopic analysis for MCA by use of the barium salt. They report that the monohydrated barium salt occurs in plates, frequently in overlapped layers, many of hexagonal habit. Eisenberg<sup>(16)</sup> has also done work on the identification of MCA as the barium salt. Wilson states that DCA yields a barium compound that produces a vitreous, hygroscopic residue. TCA gives a crystalline barium salt that has so far not been found suitable for microscopic identification, although it crystallized in a habit distinctly different from that of the MCA salt.

TABLE VII

Melting and Boiling Points of Derivatives of  
the Chloroacetic Acids

Derivative Acid	Boiling Point °C	Melting Point °C	Anilide °C	p-Toluide °C	p-Nitro benzil ester °C
Chloroacetic acid	-	63° (MP)	134° (MP)	120° (MP)	-
Dichloroacetic acid	1890	-	118° (BP)	-	-
Trichloroacetic acid	-	57°	94° (MP)	141° (MP)	80° (MP)

Shriner, R. L. and R. C. Fuson: "The Systematic  
Identification of Organic Compounds",  
p. 98. John Wiley and Sons, Inc.,  
New York, N. Y., 1935.

Ammonium Salts. The ammonium salts of the chloroacetic acids are quite stable and may be suitable for microscopic analysis. Bateman<sup>(4,5)</sup> reports that ammonium DCA forms lustrous pearly leaflets which are non-deliquescent, but does not mention the crystalline habits of the mono and tri-chloroacetates other than to state that they are white crystalline compounds.

Copper Salts. Bateman<sup>(4,5)</sup> has given some properties of the copper salts of MCA, DCA, and TCA and hydrates of each of these salts. While there seems to be a slight difference in color, Bateman gives no indication of visible difference in crystalline form or marked differences in solubilities in several solvents.

Use of the Microscope. The use of the microscope<sup>(26)</sup> in chemical analysis requires the specimens to be prepared for microscopic examination, the particles counted, and the depth and length of the particles be estimated.

Preparation for Microscopic Examination. Small particles may be observed at low magnification without preparation whatsoever, but for magnifications over 100X, the specimens should be mounted in some suitable medium and covered with a cover glass.

Particle Counts. To count the number of particles in a given volume of liquid, it is necessary to take a minute sample of known volume, spread it over a known area, and count the number of particles in a known portion of this area. An originally unknown volume may be computed from measurement of the depth and area of the containing cell.

Measurement of Length. By use of a stage micrometer scale, the ratio of the ocular to the stage scale may be determined. From this ratio, the value of the divisions on the ocular scale in terms of actual lengths on the stage may be found.

Measurement of Depth. A calibrated fine adjustment serves as a micrometer screw which enables the microscopist, by focusing first on the top and then on the bottom of an object, to measure height or depth.

Conductrimetric Titration of Chloroacetic Acids. There has been work done on conductrimetric titration of individual chloroacetic acids. Ismailov<sup>(35)</sup> reports that aliphatic acids can be titrated with sufficient accuracy in acetone solutions. The salt of TCA in 85 per cent acetone solution has been titrated with HCl with a quinhydrone electrode. Results have been shown by Ruehle<sup>(52)</sup> of a potentiometric titration of TCA using  $\text{CH}_2\text{OHCH}_2\text{OCH}_3$  as a solvent. Rabinovich<sup>(47)</sup> has indicated that in the titration of MCA or TCA by  $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$  in benzene solution containing quinhydrone, the potential rises to a maximum and then falls. The addition of MCA to TCA, both in benzene, leads to a more negative potential owing to a reaction. Addition of TCA to MCA raises the positive potential. Maryott<sup>(42)</sup> has reported conductrimetric titrations of acids, including TCA, in benzene and dioxane. Electrimetric titration curves have been shown<sup>(6)</sup> for the copper salt of TCA using a quinhydrone electrode.

The electrical conductivity of MCA, DCA, and TCA at 30°C and various concentrations has been reported<sup>(33,42,54,95,96,97)</sup>.



Chromatographic Analysis. Chromatography was first observed in 1906 by the Russian botanist M. Tswett, who employed the chromatographic method to investigate plant and animal pigments. Chromatographic analysis has been tentatively defined by Eliel<sup>(17)</sup> as the differential adsorption of two or more substances by an adsorbent material.

Theoretical Aspects. Chromatographic adsorption<sup>(17,25,75,105)</sup>, like any other adsorption, is produced by forces which act between the molecules of the adsorbent and the adsorbate. These forces depend on the nature of the adsorbent and on the molecular arrangement of the substances being adsorbed. However, variation of the adsorption sequence, particularly among compounds of the same class, seems to indicate<sup>(60)</sup> that the relationship between adsorbability and chemical structure is more complex than at first supposed.

Adsorbents. In using the chromatographic method, much depends upon the choice of adsorbent. The adsorbents are limited to those materials which are inert to the solvents, eluents, and solutes. Also, the adsorbents should not be strongly acidic or basic. Alumina, magnesium oxide, calcium hydroxide, magnesium carbonate, calcium phosphate, calcium carbonate, talc, inulin, and sucrose (in this order of decreasing activity), as well as gypsum, fuller's earth, kieselguhr, silica gel, charcoal, permutit, and Brockmann aluminum oxide are some of the commonly used adsorbents.

Solvents and Eluents. In chromatography, the solvent is a liquid used to dissolve the material to be adsorbed and to introduce this material into the adsorbent bed. Elution<sup>(17)</sup> is the process

of separating an adsorbate from an adsorbent by means of a liquid, an eluent. Eluents used in chromatography (in order of decreasing strength) are acids, alcohols, ketones, esters, ethers, unsaturated hydrocarbons, aromatic hydrocarbons, and saturated aliphatic hydrocarbons. These may also be used as solvents and are in order of increasing strength as solvents. In short, of the list of compounds given, the acids are most strongly adsorbed on most adsorbents, the alcohols less strongly adsorbed, and so on.

Apparatus and Technique. Chromatographic equipment may range in size from those that use less than one gram of adsorbent up to those which use several pounds. The adsorption columns<sup>(27)</sup> are usually glass tubes having a tapered end. The column may or may not have a compressed air connection at the top for forcing the eluent through the adsorbent bed. Technique in use of the column depends upon whether the adsorbates are colored or colorless.

Adsorption of Solutes. The substances to be separated should be introduced into the column in dilute solution. Petroleum ether is the usual solvent. Ether possesses little eluent power (favors adsorption). The solvent used should be the same as that used in preparing the column.

Liquid Chromatogram. This method<sup>(17,27)</sup> is used to separate colorless substances. After the solution containing the adsorbate has passed through the column (by virtue of its own weight is desirable), more solvent is passed through the column and tests made to determine when the substances adsorbed first appear in the

elute. Thereafter, fractions are collected until elution ceases. Development is then continued by use of stronger eluents until essentially all of the adsorbate is removed. Identification of fractions may be by various methods (as crystal form) after evaporation of the eluent.

Sequence of Adsorption. The sequence of adsorption<sup>(60)</sup> (of two or more substances) is not the same under all circumstances; it varies with column conditions, the solvent and adsorbent, and with the kinds of adsorbates. Slight changes in column conditions may spell the difference between success and failure of the attempted separation. Thus, care must be used in the purification of solvents and in the preparation of adsorbents.

Absence of Theoretical Approach. The resolving power of an adsorption column depends<sup>(60)</sup> upon the properties of the adsorbent, solvent, and adsorbates. Also, it depends upon the relative concentration of the adsorbates, the amount of solution added to the column, and on the temperature. As stated before, the interrelationship of these properties and conditions is quite complex. This fact and the tendency of many adsorbents to combine irreversibly with the adsorbates is so common that the approach to the problem of resolving unknown mixtures remains largely a matter of trial and error.

Adsorption of Chloroacetic Acids. It has been reported by Ermolenko<sup>(19)</sup> that adsorption by wood charcoal from non-aqueous solvents increases in the series acetic acid, mono-, di-, and trichloroacetic acid. However, Ferrandis<sup>(20)</sup> states that in general

there is competition between solubility and adsorbability in the adsorption of mono-, di-, and trichloroacetic acids from non-aqueous solutions by charcoal.

#### Purification of Hydrochloric Acid

Large quantities of hydrochloric acid are produced during the process of manufacturing TCA, and therefore, its disposal must be considered. The proposed method of disposal of HCl is its purification and sale. Purification of HCl gas is usually effected<sup>(3)</sup> by cooling, passing the gas through a coke tower to remove suspended foreign materials and absorbing the HCl in water in a silica absorber.

### III. EXPERIMENTAL

The experimental work of this investigation was carried out with definite purpose and plan. A description of the materials and equipment used, experimental procedure, and sample calculations of the results has been given in this section to clarify and augment the data and results of the pilot work.

#### Purpose of Investigation

It was the purpose of this investigation to design, construct, and operate a pilot plant for the production of trichloroacetic acid from acetic acid and chlorine.

#### Plan of Experimentation

The following plan of experimentation was deviated from as the actual work progressed in order that the more important phases of the problem be considered as they became evident.

Design of Pilot Plant. The design of the pilot plant was based on information available on the production of monochloroacetic acid and a plant design for the production of TCA worked out by the Graduate Chemical Engineering Plant Design Class (1949-50) of the Virginia Polytechnic Institute. The design was for the process of producing TCA by the chlorination of glacial acetic acid in the presence of red

phosphorus between the temperatures of 212° and 320°F. The reaction was to take place at atmospheric pressures in the liquid phase.

Operation of The Pilot Plant. The operational procedure was patterned after that suggested by the graduate design class. The operation of the pilot plant was to be such that the validity of the assumptions, made by the class for design, could be ascertained.

### Materials

A list of the materials used in this investigation, their source and description, follows.

Acetone. Lot No 15389. Obtained from Carbide and Carbon Chemicals Corp., New York, N. Y. Used as a solvent and eluent in chromatographic analysis.

Acid, Acetic. Glacial, lot No 1-402043-C. Manufactured by General Chemical Co., New York, N. Y. Used as a raw material in the production of trichloroacetic acid.

Acid, Hydrochloric. CP, 35-37 per cent, lot No. E 407014. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in analysis for dichloroacetic acid.

Acid, Nitric. CP, reagent, 70 per cent, sp gr 1.42, lot No E 403005. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in chloride analysis.

Acid, Silicic. CP, precipitated, lot No 451269. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as an adsorbent in chromatographic analysis.

Acid. Sulfuric. CP, 95-96 per cent, lot No E 406026. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in analysis for dichloroacetic acid.

Alumina. Activated, 14-20 mesh. Manufactured by the Aluminum Ore Company, Pittsburgh, Pa. Used as an adsorbent in chromatographic analysis.

Ammonium Chloride. CP, granular, lot No 123047. Obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in analysis for trichloroacetic acid.

Ammonium Hydroxide. CP, 28 per cent, lot No E 212003. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in analysis for dichloroacetic acid.

Ammonium Thiocyanate. CP, crystalline, lot No D 113. Manufactured by the General Chemical Co., New York, N. Y. Used in analysis for chlorides.

Asbestos. Medium fibre, gooch grade, lot No E 264. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in analysis for dichloroacetic acid.

Barium Chloride. Reagent, crystalline, lot No D 320. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in analysis for trichloroacetic acid.

Calcium Carbonate. CP, lot No 72946. Obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in preparation of calcium acetate.

Carbon (Cliffchar). Activated, R-10x30 granular. Manufactured by the Cliffs-Dow Chemical Co., Marquette, Mich. Used as an adsorbent in chromatographic analysis.

Chloral Hydrate. USP, crystal, lot No 8645. Obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. Used to prepare trichloroacetic acid.

Chlorine. Liquid, 105 pound (net) cylinder. Obtained from the Pennsylvania Salt Manufacturing Co., Wyandotte, Mich. Used to chlorinate acetic acid.

Ether, Diethyl. USP, code 1701. Obtained from Eimer and Amend, New York, N. Y. Used as a solvent and eluent in chromatographic analysis.

Ethyl Acetate. CP, absolute, lot No 52246. Obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. Used as a solvent in chromatographic analysis.

Ferric Ammonium Sulfate. USP, lot No 2406. Obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. Used as Volhard indicator in chloride analysis.

Filter Paper. Qualitative, No 516. Manufactured by the Filter Paper Co., Chicago, Ill. Used in analytical work.

Manganous Sulfate. Monohydrate, powder, lot No 0156. Manufactured by the General Chemical Co., New York, N. Y. Used in analysis of calcium oxalate.

Nitrobenzene. Mono, liquid, lot No 1845. Obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J. Used in chloride analysis.

Phosphorus, Red. Amorphous, lot No 490623. Obtained from Fisher Scientific Co., Pittsburgh, Pa. Used as a catalyst in the chlorination of acetic acid.



Potassium Hydroxide. Reagent, pellets, lot No D 306.

Manufactured by the General Chemical Co., New York, N. Y. Used in analysis of chlorides and dichloroacetic acid.

Potassium Permanganate. Reagent, crystal, lot No D 235.

Manufactured by the General Chemical Co., New York, N. Y. Used in analysis for dichloroacetic acid.

Pyridine. Purified, code 2165, lot No 96. Manufactured by the General Chemical Co., New York, N. Y. Used in analysis for mono- and trichloroacetic acids.

Silver Nitrate. Reagent, lot No D 183. Manufactured by the General Chemical Co., New York, N. Y. Used in chloride analysis.

Sodium Carbonate. USP, monohydrate. Obtained from the M. J. Weber and Co., Chicago, Ill. Used in standardizing acid solutions and neutralizing TGA products.

Sodium Chloride. USP, granular. Manufactured and distributed by Merck and Co., Inc., Rahway, N. J. Used in analysis for trichloroacetic acid.

Sodium Oxalate. Reagent, powder, lot No D 191. Obtained from the General Chemical Division, Allied Chemical and Dye Corp., New York, N. Y. Used in standardizing permanganate solutions.

Sucrose. Domino cane sugar, contains three per cent corn-starch, confectioners XXX. Manufactured by the American Sugar Refining Co., New York, N. Y. Used as an adsorbent in chromatographic analysis.

Water. Distilled. Obtained from the Department of Chemical Engineering, Virginia Polytechnic Institute, Blacksburg, Virginia. Used in analytical work.

### Apparatus

A list of the equipment used in this investigation, with identifying information for each piece, follows.

Balance. Chainomatic, type-DLB, No 15345. Manufactured by William Ainsworth and Sons, Inc., Denver, Colo. Used to weigh fractions of chlorinated acids collected during chromatographic analysis.

Weights. One to 50 grams. Manufactured by Fisher Scientific Co., Pittsburgh, Pa. Used with chainomatic balance.

Balance. Pan, 610-gram capacity. Manufactured by Ohaus, Newark, N. J. Used in weighing samples of chlorinated acids removed from the chlorinators at various times for analysis.

Balance. Pan, 9,000-gram capacity. Manufactured by Ohaus, Newark, N. J. Used in weighing the reactors at various times.

Glassware. Pipets, erlenmeyer flasks, volumetric flasks, burets, beakers, graduated cylinders, funnels, and distilling flasks were used in the different analyses.

Heating Mantle. Glas-Col, size 1,000-milliliter, 110-volt, cat No A 42-494. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to heat the chlorinators.

Powerstat. Type 116, primary volt 115, 50-60 cycle, max output 7.5 amp, cat No A 42-584. Obtained from Phipps and Bird, Inc., Richmond, Va. Used to regulate power input to heating mantle.

Thermometers. Glass, mercury filled, range 30°-400°F, subdivisions 2°, cat No 14-990. Obtained from the Fisher Scientific Co., Pittsburgh, Pa. Used to measure reaction temperature during chlorination of acetic acid.

Oven. Cenco-De Khotinsky constant temperature apparatus, regulated temperature range 50° to 200°C, cat No 95050A, ser No 745, watts 400, 230-volt, ac. Manufactured by Central Scientific Co., Chicago, Ill. Used for drying adsorbent used in chromatographic analysis.

Microscope. Ser No WM 1728, 5X to 97X oculars. Manufactured by Bausch and Lomb Optical Co., Rochester 2, N. Y.

### Method of Procedure

Those methods of procedure used in this investigation have been outlined in the following paragraphs. In the case of standard analyses, references have been made to the literature rather than describing the procedure in detail.

Microscopic Identification of MCA, DCA, and TCA. Identification of MCA, DCA, and TCA was attempted by microscopic examination of ammonium and sodium salts of the acids. The salts were prepared for examination in the following manner. About a 50 per cent aqueous solution of the acids to be examined was neutralized with ammonium hydroxide (to excess) or with sodium hydroxide (to phenolphthalein). More dilute solutions were prepared by addition of distilled water to a portion of the solution of salts just described. The slides for microscopic examination were prepared by placing a drop of the salt solution on a slide and allowing it to dry in air at about 70 to 80°F.

Separation and Identification of TCA by Phenol Addition Compound. Ten grams of a mixture containing TCA (60 per cent by weight) were added to ten grams phenol (redistilled) at 50°C (122°F), and the solution

thoroughly stirred. The solution was cooled (in air at 85 to 90°F) until crystallization took place. The temperature and the extent of crystallization of the mixture was observed at this time. Separation of TCA depended upon crystallization of a TCA-phenol addition compound only. Identification and an estimate of the amount TCA present depended<sup>(1)</sup> upon the freezing point of the addition compound; the freezing point relationship for the system TCA-phenol being known.

Analysis of the Viscous Material After Chlorination. About five or six grams of the viscous material was weighed to the 0.001 gram and 25 milliliters distilled water added. After stirring, the solution was titrated with one normal sodium hydroxide to the methyl orange end point, the amount of sodium hydroxide required recorded, and titration continued to the phenolphthalein end point. This procedure has been given by Treadwell and Hall<sup>(66)</sup> for analysis of phosphoric acid.

Pyridine Test for TCA. About one gram of purified TCA (prepared in the manner described by Wertheim<sup>(77)</sup>) was weighed to the 0.01 gram in a 100-milliliter pyrex beaker, and 10 to 15 milliliters of a aqueous, 40 per cent KOH solution added by means of a 50-milliliter buret. Three or four milliliters of purified pyridine were added to the caustic solution and the mixture heated to about 160°F. The hot mixture was then titrated with 40 per cent KOH solution (maintaining temperature 150 to 170°F) until a faint pink coloration appeared in the pyridine layer.

Pyridine Test for MCA. From three to five grams of MCA were weighed to the 0.001 gram in a 100-milliliter beaker and 30 milliliters purified pyridine added. The mixture was stirred until the MCA had dissolved, and then heated in a water bath at 140 to 160°F for one hour with occasional stirring. The precipitate formed was filtered off on qualitative filter paper and transferred to a weighed watch glass. After drying in air at 85 to 95°F for two hours, the precipitate was placed in an oven at 150°C (302°F) until constant weight was reached.

Direct Volumetric Analysis for TCA. The procedure used in the direct analysis for TCA in the presence of MCA and DCA was set up on the basis of Pool's method<sup>(46)</sup> of analysis of chlorinated acetic acids.

Preparation of Solution A. About five grams of the acid mixture to be analyzed were weighed to the 0.001 gram and dissolved in 100 milliliters distilled water. The acid solution was poured into a liter round-bottomed flask fitted with a liebig condenser. A caustic solution, made from 150 milliliters distilled water and 40 grams NaOH, was added to the flask and the resulting solution refluxed for one and one-half hours. After cooling to about 20°C, the solution was made to 500 milliliters in a volumetric flask. This solution was termed "solution A".

Preparation of Carbonate for Titration. A 200-milliliter portion of solution A was pipeted into a 600-milliliter beaker and 20 grams barium chloride added in the form of a saturated aqueous solution. The beaker was filled with distilled water and the mixture stirred for five minutes. The liquid was decanted from the precipitate and filtered, using a buchner funnel. The

precipitate was subsequently washed with one liter of distilled water, in 200-milliliter portions, decanting and filtering the first four portions. After the last washing, the precipitate was also transferred to the filter. The filtrate was made to one gallon with tap water, stirred for five minutes, and filtered. The precipitate was washed with 200 milliliters concentrated ammonium chloride solution (aqueous), to remove the oxalates, and then with 100 milliliters distilled water.

Titration of Carbonate. The precipitate was transferred to a beaker and titrated with normal HCl until five to ten milliliters in excess of the methyl orange end point. The excess HCl was titrated with normal KOH to methyl orange.

Blank Determination. A blank determination was made using the same procedure and quantities of materials, omitting the acid sample.

Volumetric Analysis for Chlorinated Acetic Acids. Since the direct analysis for TCA based on Pool's work<sup>(46)</sup> was reported and observed to be in error by as much as 85 per cent, the following procedure was adapted from Dalin's work<sup>(13)</sup> on analysis of chlorinated acetic acids. TCA was estimated indirectly by first determining the DCA, total chloride, and inorganic chloride. The total chloride was adjusted for inorganic chloride and chloride due to DCA, and the remaining chloride proportioned between MCA and TCA assuming no acetic acid present.

Preparation of Solution A. A four to five-gram sample of the acid mixture to be analyzed was weighed to the 0.001 gram and dissolved in 100 milliliters distilled water. The acid solution

was poured into a liter round-bottomed flask fitted with a liebig condenser, and 200 milliliters of a 40 weight per cent KOH solution added. The mixture was then refluxed one hour. After cooling to 20°C, the mixture was made to 500 milliliters in a volumetric flask. This solution was termed "solution A".

Determination of Total Chloride. Total chloride was determined by neutralizing 50 milliliters solution A with concentrated nitric acid (to litmus) and adding ten milliliters excess acid. Tenth-normal silver nitrate was added to ten to 20-milliliter excess and the mixture boiled to coagulate the silver chloride. The silver chloride was filtered off, washed with ten to 15 milliliters of 15 per cent nitric acid, and the excess silver nitrate in the filtrate titrated with tenth-normal ammonium thiocyanate, using two milliliters Volhard indicator and two milliliters nitrobenzene.

Determination of DCA. DCA was determined by first neutralizing 100 milliliters solution A with concentrated HCl (to litmus), and adding 20 milliliters excess acid. The excess HCl was then neutralized with 28 per cent ammonium hydroxide, ten milliliters excess being added. The resulting solution was evaporated to saturation and 20 milliliters 28 per cent ammonium hydroxide and 50 milliliters five per cent calcium acetate were added. The mixture was stirred for two or three minutes and allowed to stand for six hours (at 70 to 90°F). The mixture was then filtered through organic free asbestos (gooch grade) utilizing a buchner funnel, and the precipitate washed with 100 milliliters two per cent ammonium hydroxide, 50 milliliters one per cent calcium

acetate solution, and 50 milliliters distilled water. The precipitate and asbestos were transferred to a 600-milliliter beaker, 200 milliliters distilled water and 25 milliliters of 98 per cent sulfuric acid added, the mixture heated to 60 to 100°C, two milliliters manganous sulfate added, and the mixture titrated with tenth-normal potassium permanganate solution until a pink color persisted for at least 30 seconds.

Determination of Inorganic Chloride. Inorganic chloride was determined by first weighing a four to six-gram sample of the acid mixture to the 0.001 gram, dissolving it in 100 milliliters distilled water, and adding ten milliliters concentrated nitric acid. Tenth-normal silver nitrate was added to ten or 20-milliliter excess, two milliliters Volhard indicator and two milliliters nitrobenzene added, and the mixture shaken well. The excess silver nitrate was then titrated with tenth-normal ammonium thiocyanate.

Chromatographic Analysis. The chromatographic method of procedure presented is that finally used with four different mixtures of chlorinated acetic acids. It applies, for the most part, to the different combinations of eluents and adsorbents tested chromatographically in this investigation.

Apparatus. The apparatus for chromatographic analysis consisted of an adsorption column, a rubber stopper and hose connection to a compressed air source, and twenty 100-milliliter beakers which served as elute receivers. The adsorption column was a one-inch inner diameter pyrex tube, tapered at one end. The column was 21 inches in length to the point of taper. It tapered to a six-



millimeter inner diameter pyrex tube, one and one-fourth inches in length. The overall length of the column was 23.5 inches. The rubber hose, for connecting a compressed air source to the top of the column, fitted loosely on a glass tube in a one-hole rubber stopper. The other end of the hose was attached to a one-eighth inch bronze needle valve in a 50 pound per square inch (gage) air line. The loose fitting of rubber hose on glass tube allowed air to escape slowly, so that the air pressure on the column could be controlled by means of the needle valve. The column was mounted vertically, tapered end down.

Chromatographic Procedure. Thirty grams activated carbon were weighed out and pulverized with a mortar and pestle. The carbon was then heated for 12 hours at 150°C (302°F), and after cooling, was suspended in 120 milliliters acetone. A piece of glass wool was pushed to the bottom of the adsorption column to act as a porous plug. The carbon-acetone suspension was poured into the column and about 30 milliliters additional acetone used to wash the carbon down the sides of the column. The excess acetone was gently blown through the column at five to ten milliliters per minute. Thirty milliliters acetone were poured slowly (to prevent disturbing the adsorbent bed) into the column, and gently blown into the adsorbent. About four grams of the acid mixture to be analyzed was weighed to the 0.001 gram, dissolved in 15 milliliters acetone, and slowly poured into the column. Ten milliliters acetone were used to wash out the sample container, and this added to the column. The acid solution was blown gently

into the adsorbent bed at a rate of about one-fourth milliliter per minute. The acetone displaced by the sample was discarded. After the sample had been blown into the adsorbent, 150 milliliters acetone were poured into the column and elution begun. The rate of elution was one-fourth to one-half milliliter per minute until 50 milliliters elute had been collected; the rate was then increased to one-half to one milliliter per minute for the succeeding 20 to 30 milliliters elute, and to two or three milliliters per minute for the remainder of the elution. The first 50 milliliters of elute were collected in three-milliliter fractions, the next 20 to 30 milliliters elute in five milliliter fractions, and the remaining elute in ten to 15-milliliter portions. All fractions were collected in weighed 100-milliliter beakers. The fractions were dried by placing them in the path of 90°F air being circulated by an electric fan. The weight and physical characteristics (liquid, solid, or both) were observed after one or two hours drying, and also after the fractions had dried completely.

Four-Stage Chlorination of Acetic Acid. The procedure used in the operation of the pilot plant for four-stage chlorination of acetic acid was based on the procedure outlined by the graduate design class of the Virginia Polytechnic Institute for their plant designed to produce TCA.

Apparatus. The pilot plant consisted of four reactors, a chlorine meter and distribution line, and a waste gas absorber. With the exception of the absorber and chlorine meter, the pilot plant was constructed using standard glassware. A description of the components of the pilot plant follow.

Reactors: The reactors were liter, three-neck distilling flasks, each fitted with a 12-inch liebig condenser mounted for reflux in the left side flask opening. The right side flask opening was fitted with a draw-off tube (six millimeters inner diameter pyrex) leading to the bottom of the flask, and closed off at the top by use of a short section of sealed glass tubing and tygon tubing. The central flask opening was fitted with a three-hole stopper through which a glass mercury thermometer ( $30^{\circ}$  to  $400^{\circ}$ F), a vent tube, and a chlorine distributor tube protruded. The vent tube (four millimeters inner diameter pyrex, three inches long) was closed off in the same fashion as was the draw-off tube.

Chlorine Distributor: The chlorine distributor was constructed of six-millimeter pyrex tubing. The distributor end consisted of four prongs, emerging symmetrically out and down from the central down-take tube. The central down-take tube was nine inches long, to the beginning of the prongs. Each prong was 1.5 inches long, with its gas outlet tip drawn out to about a 0.5-millimeter diameter opening. In cross-section, the prongs fell symmetrically on a one inch diameter circle, the center of which was the down-take tube.

Chlorine Meter: The chlorine flow meter consisted of of an 18-inch length of 1/16-inch inner diameter copper tubing, bent in the form of a loop, and connected in the chlorine distribution line through glass tees on either end. The pressure drop across the tube was measured by means of a 22-inch, chlorinated-water filled manometer. The meter was calibrated by means of compressed air,

the air rate being varied from 100 to 2,500 milliliters per minute (at 60°F and one atmosphere). The calibration curve for air was corrected for use with chlorine by means of the general orifice equation.

Waste Gas Absorption Column: The waste gas absorption column consisted of a vertical pyrex tube, 1-11/16-inch inner diameter and 20 inches long, filled with half-inch diameter glass marbles. Each end was fitted with a two-hole rubber stopper. The top end was provided with a vent tube, to the atmosphere, and a water inlet. The bottom end was fitted with a water outlet and a gas inlet. The gas inlet projected up into the column about six inches and was bent over so that water could not enter the tube. All fittings were constructed of six-millimeter pyrex tubing.

Interconnection of Equipment: The reactors were connected for series gas flow, nine inches from center to center. Chlorine entered the reactor on the right and waste gas left the reactor on the extreme left to pass on to the absorber. The gas lines leading from reactor to reactor, connected the reflux condenser of one reactor to the chlorine distributor of the reactor on its left.

The chlorine feed rate was adjusted by means of a manual needle valve attached to the chlorine cylinder. Chlorine gas distribution lines and waste gas exit lines were constructed of six-millimeter pyrex tubing. Glass tubing was interconnected in all cases by tygon tubing. All stoppers used were rubber. The reactors were heated with hemispherical Glass-Col heating mantles with powerstats to regulate heat output.

Procedure for Bringing Pilot Plant in Stress. The procedure for bringing the pilot plant into stress may be divided into four parts, corresponding to the four stages of chlorination.

First Stage: The first reactor (on the right) was charged with 534 grams glacial acetic acid. (This quantity of acid would yield one liter TGA on a 100 per cent yield basis.) Red phosphorus, 20.8 grams, was added to the reactor. Chlorine was fed to the reactor at a rate of 25 grams per hour for the first hour. The chlorine feed rate was then increased to 50 grams per hour for the second hour, and to 78 grams per hour for the remaining five hours of the seven-hour reaction period. The initial temperature was 70 to 80°F. The heat of reaction brought the temperature up to about 150 to 160°F, after which heat was applied to raise the temperature to 212°F. The temperature was maintained at 212°F throughout the remainder of the first stage. The path of gas flow was from the chlorine cylinder to the chlorine meter, and then to the distribution line leading to the first reactor. The waste gases passed up through the reflux condenser to the waste gas manifold, through a liquid trap (125-milliliter orien-meyer flask), and then to the absorber.

Second Stage: The second reactor (from the right) was charged with acetic acid and phosphorus, as before, and connected in series with the first reactor, so that the gases leaving reactor one passed through reactor two. The temperature of reactor one was raised to 248°F (120°C) and the temperature of reactor two to 212°F in the same manner as during the first stage. Again, these

temperatures were maintained constant throughout the second stage of chlorination. Chlorine was admitted to reactor one at a rate of 103 grams per hour for the first hour, at 123 grams for the second hour, and at 156 grams per hour for the remaining five hours of the second stage.

Third Stage: The third reactor (from the right) was charged with acetic acid and phosphorus and connected in series with reactors one and two. The path of gas flow was from the chlorine source to the meter, to reactor one, through reactor two to reactor three, and thence to the gas absorber. The temperature of reactor one was 234°F (110°C), that of reactor two was 248°F, and that of reactor three was 212°F; these temperatures being maintained constant during this stage. Chlorine was fed to reactor one at a rate of 181 grams per hour for the first hour, at 206 grams for the second hour, and at 234 grams per hour for the remaining five hours.

Fourth Stage: The fourth reactor was charged with acetic acid and phosphorus, and connected in series with the other three reactors. Thus, the gases leaving reactor three passed into reactor four and from there to the absorber. At this point, the pilot plant was in stream.

In-Stream Operation. The temperatures of the reactors for in-stream operation were as follows: reactor one, 320°F (160°C); reactor two, 234°F (110°C); reactor three, 248°F (120°C); and reactor four, 212°F (100°C). These temperatures were maintained constant within five degrees Fahrenheit for all in-stream operations.

Chlorine was fed to the first reactor at a rate of 259 grams per hour for the first hour, at 234 grams for the second hour, and at 212 grams per hour for the remaining five hours of the fourth-stage reaction period. At the completion of the fourth-stage of chlorination (total chlorination time reactor one was 26 hours at this point), reactor one was removed from the line and all other reactors shifted one position to the right. Thus, reactor two became reactor one, reactor three became reactor two, and so forth. Another reactor was charged with acetic acid and phosphorus, and placed in line on the extreme left. The procedure as given in this paragraph was then repeated. Thus, every seven hours, a reactor was removed from the line with a finished product.

Observations. Observations of temperatures within the reactors and the chlorine feed rate were made every 15 minutes. The chlorination operation was interrupted every hour in order to weigh the reactors and their contents, thus a running log of the weight of the various reaction masses was kept.

Post Fourth Stage Chlorination. During the course of the investigation, it became necessary to chlorinate beyond the fourth-stage (26 hours). This was done by maintaining fourth-stage conditions in the reactor (320°F and 78 gram per hour chlorine feed rate) for the additional time desired. When operated in conjunction with other reactors, the time cycle of the other reactors were not changed, but remained as given in the previous paragraphs.

Single-Stage Chlorination. After operation of the four-stage pilot plant, it was evident that stage operation (temperature variation in steps between 212° and 320°F) was not desirable. Therefore, a pilot plant for single stage chlorination of acetic acid was designed and constructed. The operational procedure used with this pilot plant has been described in the following paragraphs.

Pilot Plant Equipment. The apparatus used in the construction of the single-stage plant was standard glassware as in the four-stage plant. The chlorine meter, waste gas absorption column, and the reactor design and construction was identical with that used in the previous plant. However, only one reactor was used. A return condenser and condensate collector were used in conjunction with the reactor. The return condenser was a 12-inch liebig condenser, connected to the gas exit end of the reflux condenser, and mounted at 30 degrees with the horizontal, pointed downward in the direction of gas flow. An air lift was used to circulate cold water between an ice and water reservoir and the return condenser. The lower end of the return condenser was fitted with an adapter which led to within one inch of the bottom of the condensate receiver (a liter, round-bottomed flask). The waste gases left the receiver through a six-millimeter pyrex tube to the gas absorber. The condensate receiver was immersed up to its neck in a water and ice or water bath, depending upon the period of chlorination as explained in the procedure following. Thus, the gas flow path was from the chlorine cylinder through the chlorine meter and



distributing line to the reactor, through the reflux condenser, the return condenser, condensate receiver, waste gas exit line, liquid trap, and to the waste gas absorber. All fittings and joints were sealed with tygon paint.

Procedure for Single Stage-Chlorination. The reactor was charged with 534 grams glacial acetic acid and 20.8 grams red phosphorus. The temperature of the acetic acid was recorded. Without prior heating, chlorination was begun; chlorine being fed to the reactor at a rate of 59 grams per hour. The temperature of the reaction mass and the chlorine feed rate were observed and recorded every 15 minutes. After the first hour, the chlorination was interrupted in order to weigh the reactor and contents. During the next 15 hours, the reaction mass was weighed every two hours; during the chlorination period from 16 hours to 50 hours, the weight was observed every five hours; and during the remaining period (50 to 90 hours) the weight was observed every ten hours.

The temperature of the reaction mass was raised gradually to 320°F within the first ten hours of chlorination.

For the first six hours, the chlorine feed rate was 59 grams per hour. The chlorine feed rate for the period six to 16-hours was 47 grams per hour; for the period 17 to 70-hours, 30 grams; and for the period 70 to 90 hours, the feed rate was about 47 grams per hour. More detailed information concerning chlorine feed rate variation may be found in Table VIII, page 78.

During the first 16 hours of chlorination, water at about 40°F was used as a coolant for the return condenser and the condensate receiver. Thereafter, water at approximately 16°C (61°F) was used as a coolant. The coolant for the reflux condenser was, at all times, water at about 16°C.

Ten to 15-gram samples of the reaction mass were removed for analysis after 30, 35, 40, 45, 50, 60, 70, 80, and 90 hours of chlorination respectively. Condensate collected in the condensate receiver was transferred to the reactor whenever the reaction mass was weighed.

#### Data and Results

The data and results of this investigation have been tabulated or depicted graphically on the pages following. Observations of supplementary value only have been presented in the discussion of results.

The calibration curve for the chlorine flow meter has been given in Figure 14. The curve for air was modified as shown in the sample calculations, page 98, resulting in the curve for use with chlorine.

The data and results of the chlorination of acetic acid have been presented in Table VIII. The rates of chlorine absorption of acetic acid, chlorine feed rates, and reaction temperatures have been graphically treated in Figures 15, 17, 19, and 21. Figures 16, 18, 20, and 22 show graphically the cumulative weights of the various reaction masses in relation to the reaction time. Figure 23 summarizes graphically the concentration and yield of TCA with respect to reaction time in

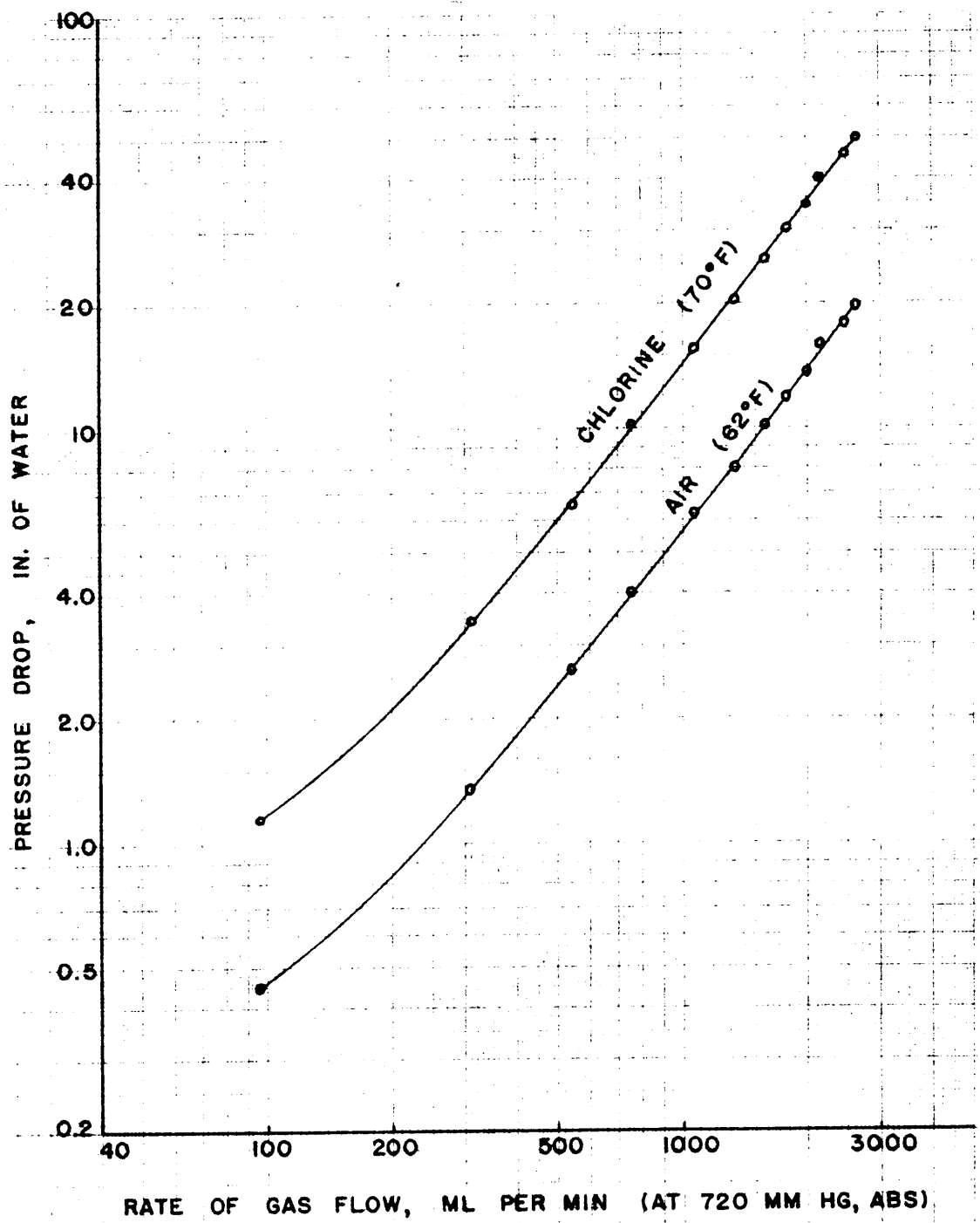


FIGURE 14. CALIBRATION CURVE FOR CHLORINE FLOW METER



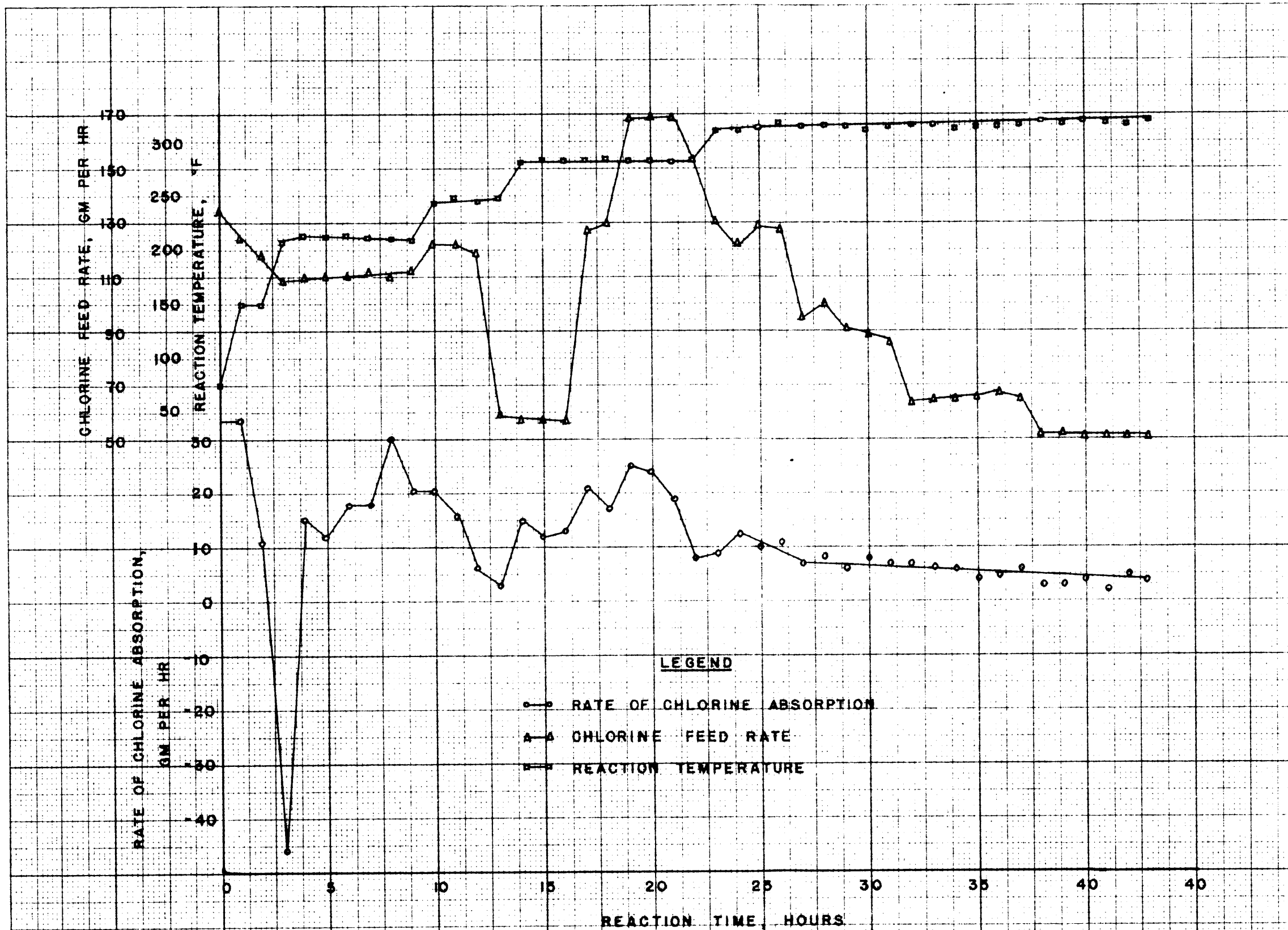


FIGURE 15. RATE OF CHLORINE ABSORPTION BY GLACIAL ACETIC ACID, CHLORINE FEED RATE, AND REACTION TEMPERATURE, TEST FIVE

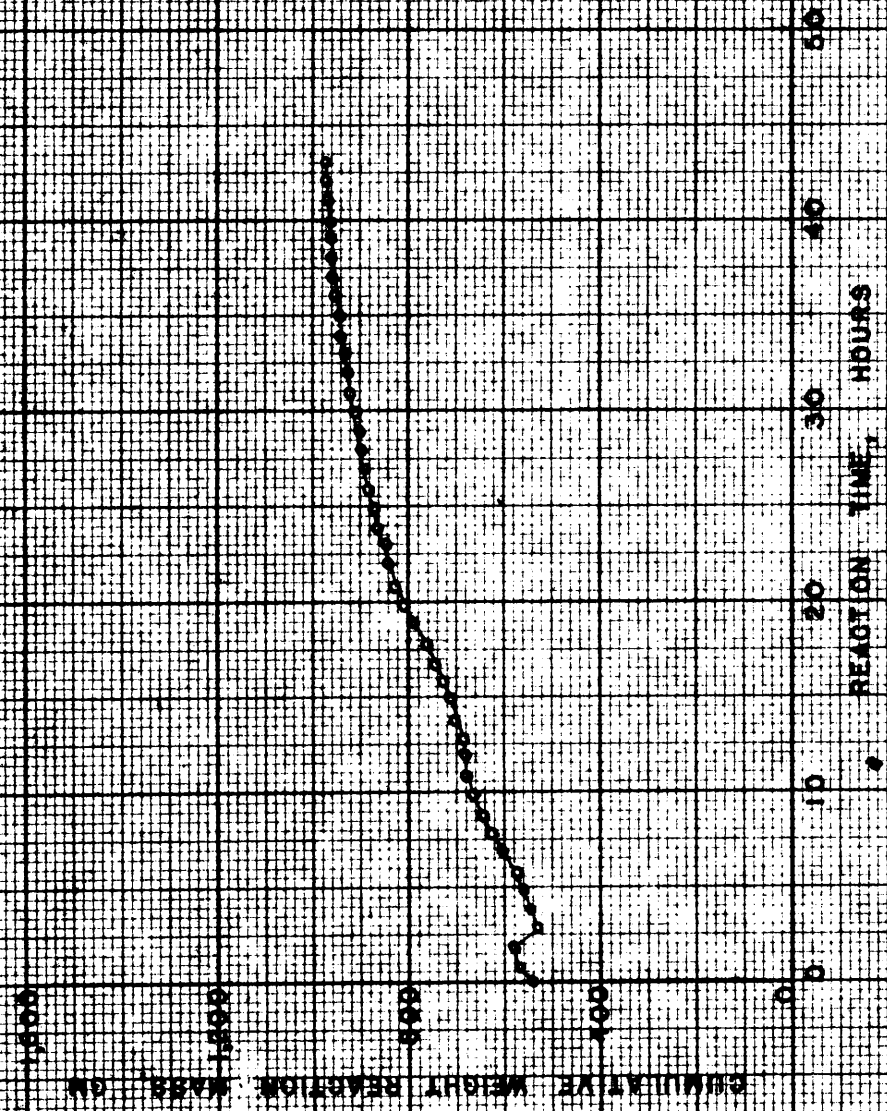


FIGURE 15. ABSORPTION OF CHLORINE BY  
GLACIAL ACETIC ACID, TEST FIVE

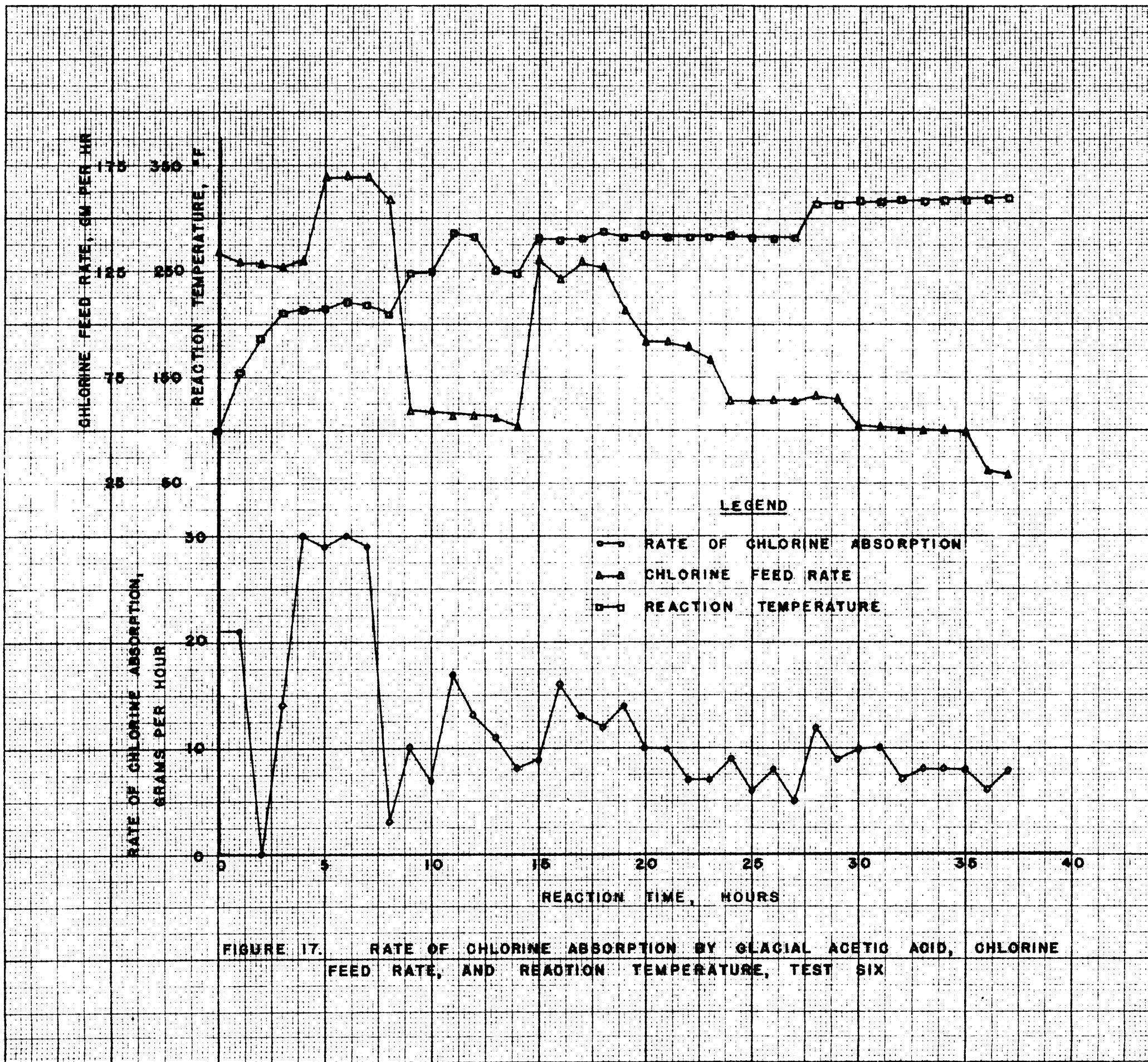


FIGURE 17. RATE OF CHLORINE ABSORPTION BY GLACIAL ACETIC ACID, CHLORINE FEED RATE, AND REACTION TEMPERATURE, TEST SIX

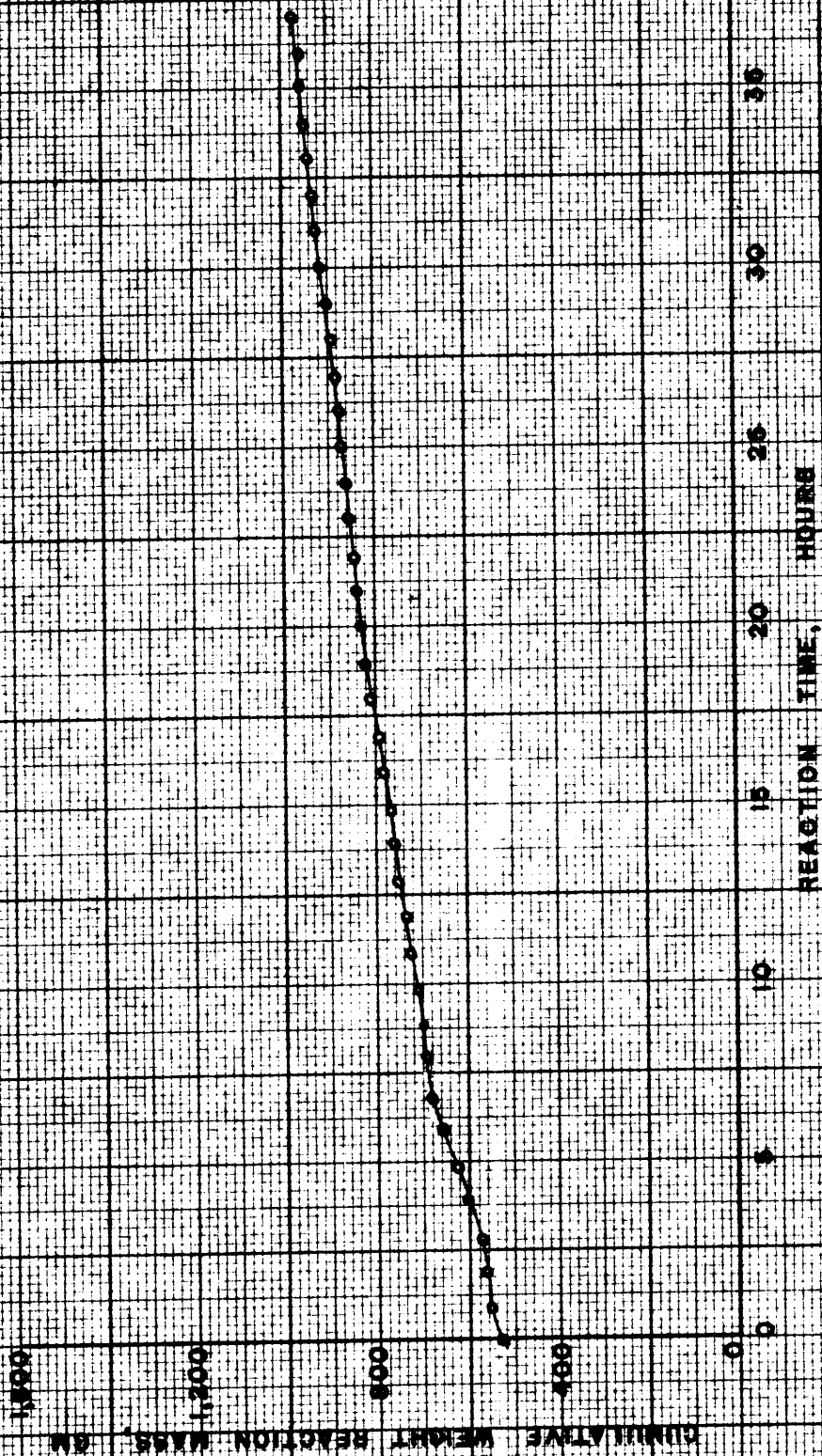


FIGURE IV. ABSORPTION OF CHLORINE BY GLACIAL ACETIC ACID, TEST SIX



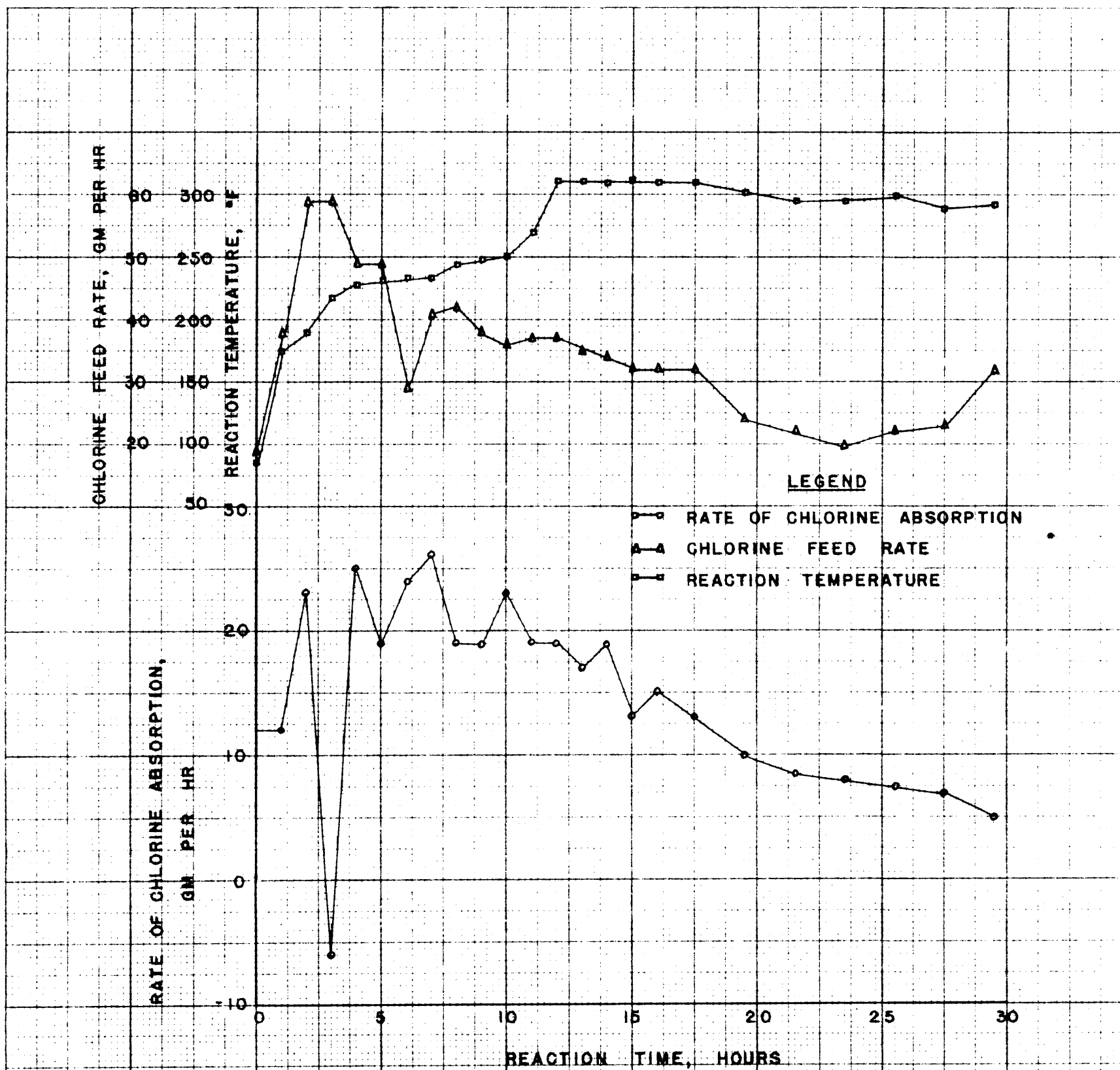


FIGURE 19. RATE OF CHLORINE ABSORPTION BY GLACIAL ACETIC ACID, CHLORINE FEED RATE, REACTION TEMPERATURE, TEST SEVEN

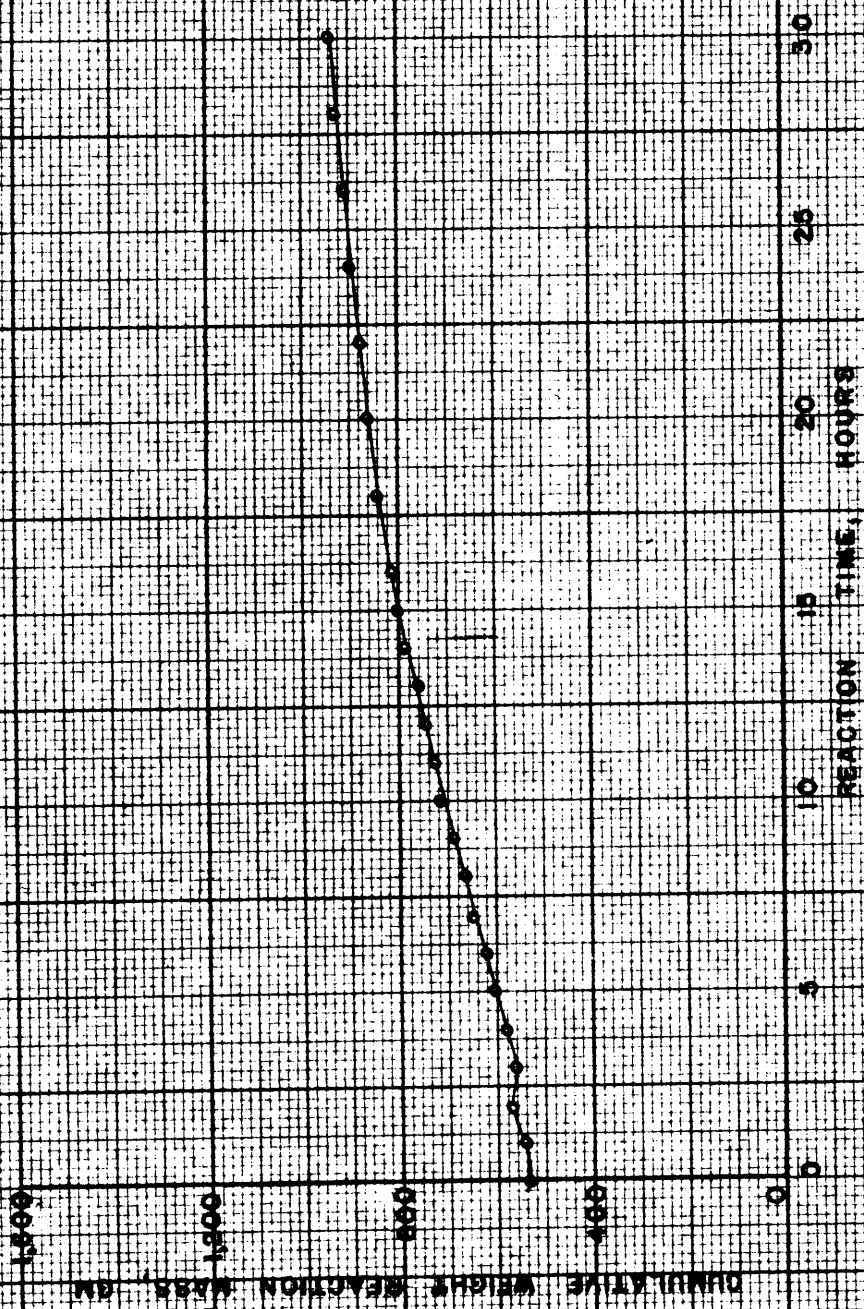


FIGURE 20. ABSORPTION OF CHLORINE BY GLACIAL ACETIC ACID, TEST SEVEN

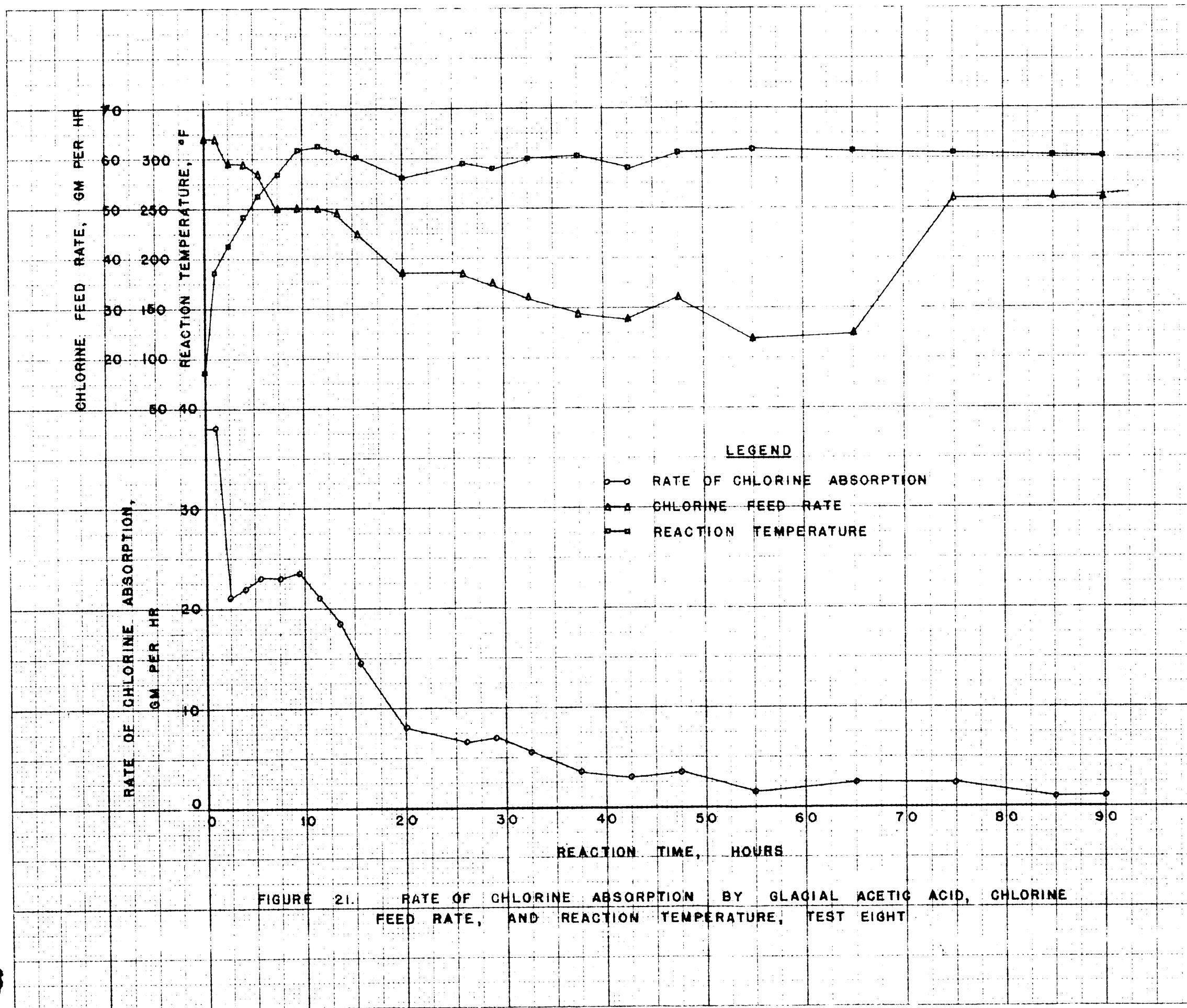


FIGURE 21. RATE OF CHLORINE ABSORPTION BY GLACIAL ACETIC ACID, CHLORINE FEED RATE, AND REACTION TEMPERATURE, TEST EIGHT

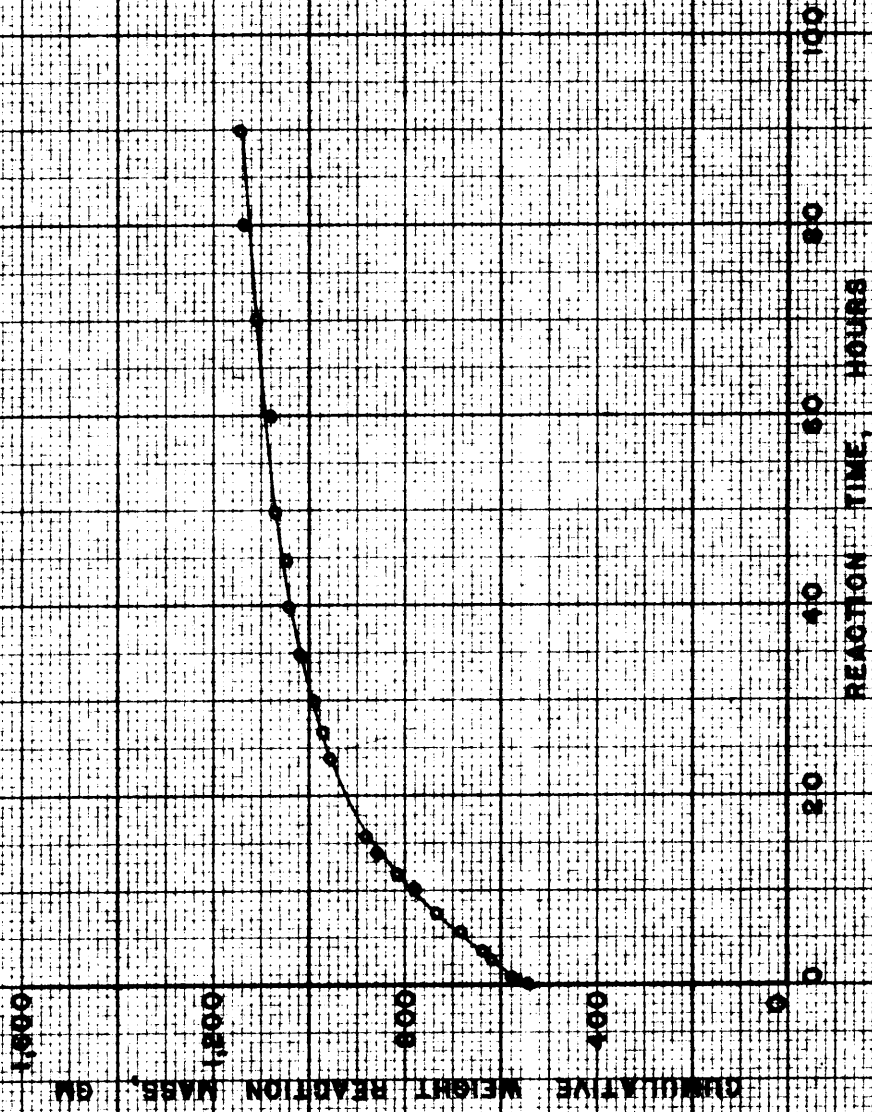


FIGURE 22. ABSORPTION OF GHEORINE BY  
GLACIAL ACETIC ACID, TEST EIGHT

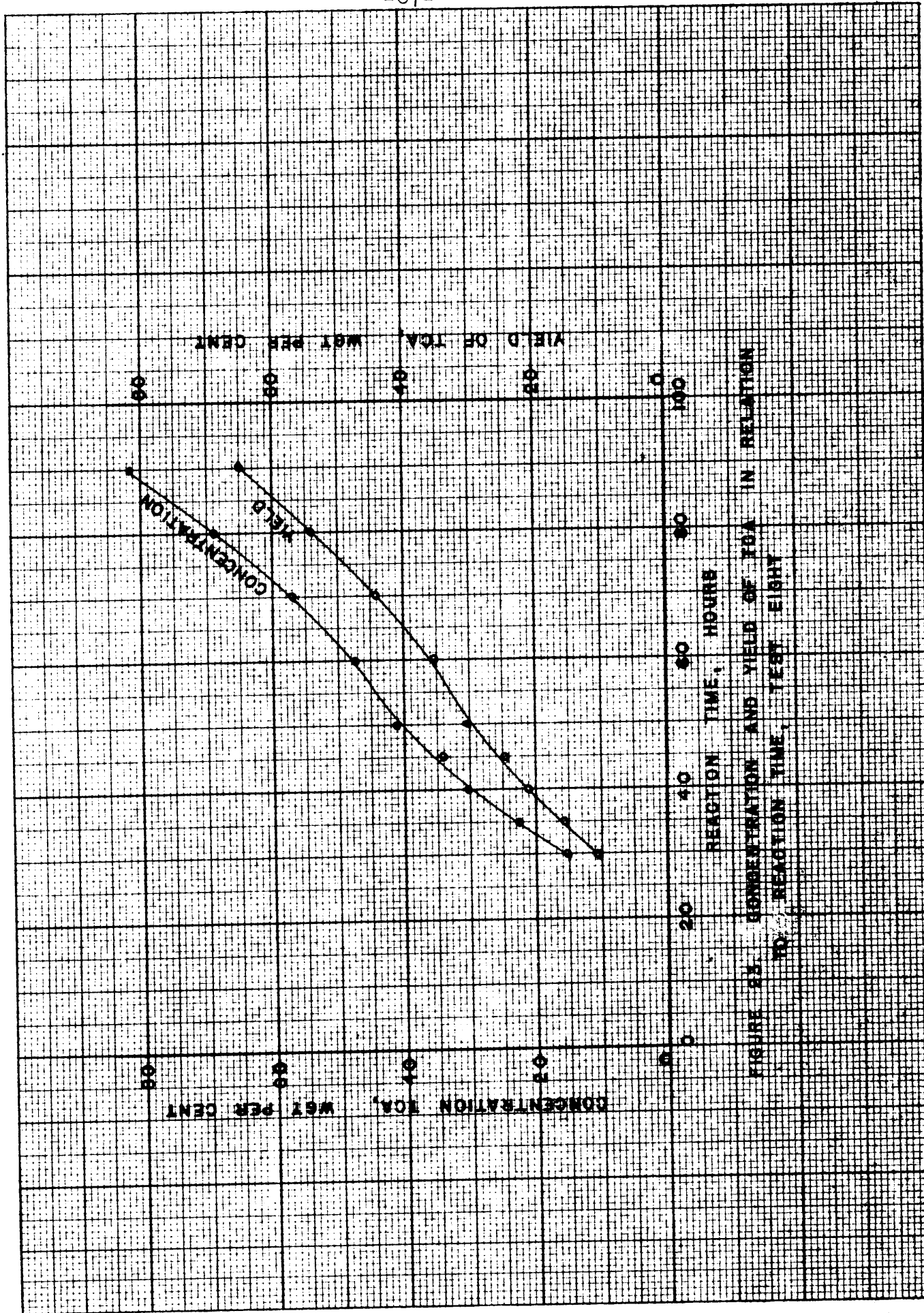


FIGURE 23. CONCENTRATION AND YIELD OF TOA IN RELATION TO REACTION TIME, TEST EIGHT

single-stage chlorination of acetic acid. The degree of chlorination (or degree of completion of the reaction) of product eight at various reaction times has been tabulated in Table IX and treated graphically in Figure 24.

Results of chromatographic analysis of mixtures of chlorinated acetic acids for TCA, utilizing carbon and acetone as adsorbent and eluent, have been given in Table X. Tables XI and XII contain the results of direct and indirect volumetric analyses for TCA. The results of pyridine tests for TCA and MCA have been tabulated in Tables XIII and XIV.

The results of analysis of the catalyst material after completion of chlorination, have been listed in Table XV.

The approximate densities of different mixtures of the chlorinated acetic acids at 296°F have been tabulated in Table XVI.

TABLE IX

Degree of Chlorination of The Various TCA Products

Produced in Pilot Work

Product Number	Reaction Time hours	Weight Reaction Mass gm	Yield TCA %	Chlorine Content of Acid		Degree of Chlorination %
				gm/gm	gm	
1	45	681	24.6	0.601	410	43.3
3	49	898	21.6	0.578	519	54.7
4	63	915	37.6	0.599	548	57.8
5	43	978	34.1	0.594	580	61.2
6	37	968	24.4	0.575	556	59.8
7	30	937	0.0	0.509	476	50.3
8	30	993	10.5	0.527	524	55.2
8	35	1021	16.0	0.557	569	60.0
8	40	1039	21.8	0.568	589	62.1
8	45	1053	24.8	0.570	610	64.4
8	50	1071	30.5	0.591	634	67.9
8	60	1086	35.6	0.598	649	68.4
8	70	1112	44.5	0.608	676	71.4
8	80	1136	54.3	0.621	706	74.5
8	90	1146	63.5	0.634	725	76.5
Theoretical	-	1454	100.0	0.651	948	100.0

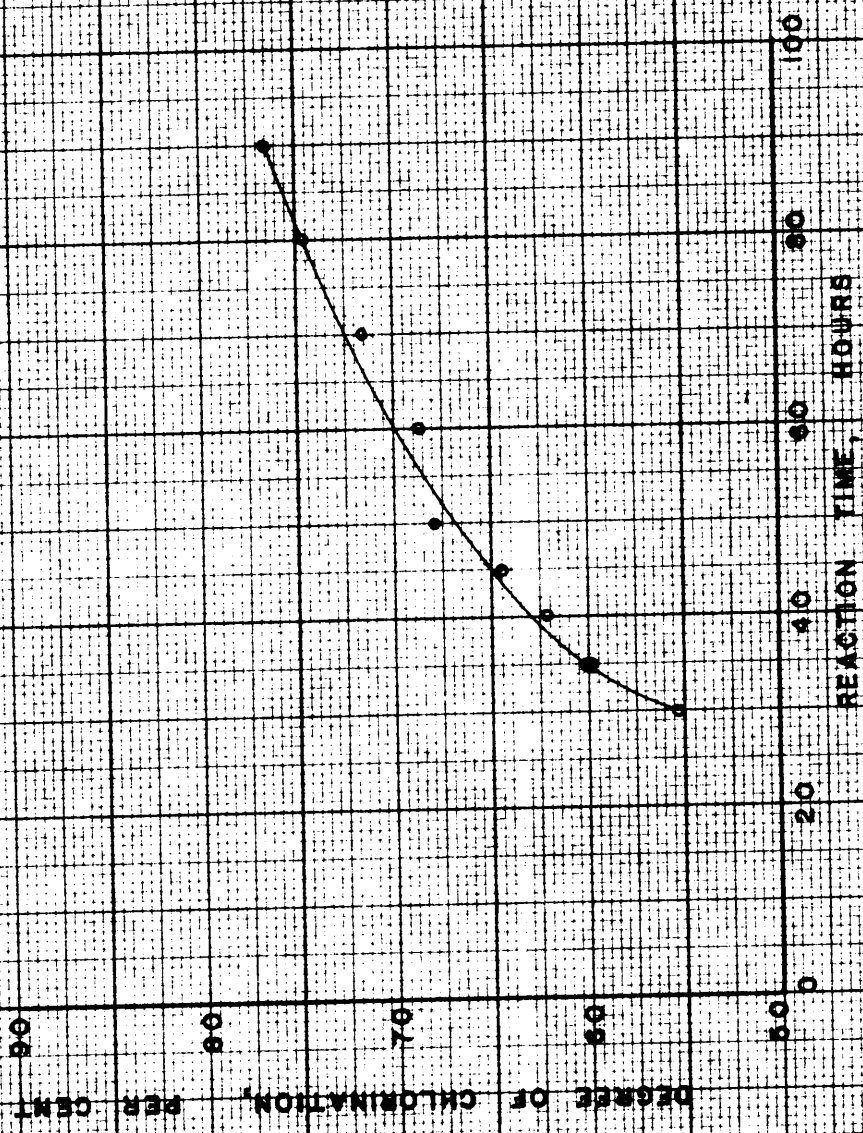


FIGURE 24. DEGREE OF CHLORINATION OF PRODUCT EIGHT AT VARIOUS REACTION TIMES



TABLE X  
 Chromatographic Analysis of Four Mixtures of Chlorinated  
 Acetic Acids, Utilizing Activated Carbon as Adsorbent and Acetone as Eluent

Product Number	Analysis of Products %		Crystalline Material Recovered % (by weight of original)	Weight of Sample for Analysis gms	Ratio of Crystalline Material Recovered (Per Cent)- %	
	MCA	(by weight) DCA TCA			TCA	TCA Plus MCA
1	0.0	49.7 50.3	36.5	5.251	0.725	0.725
4	6.7	33.0 60.2	38.4	5.018	0.638	0.574
5	6.0	43.5 50.5	35.6	5.100	0.705	0.630
6	6.9	56.8 36.5	22.3	4.866	0.612	0.515

TABLE XI  
Direct Volumetric Analysis of Mixtures of Chlorinated Acetic Acids For TCA

Product Number	Analysis of Products (Weight Basis) %		Weight of Sample for Analysis gm	Titration of Sample with 0.99% N HCl ml	Titration of Excess HCl with 0.836 N KOH ml	TCA Found %	Error Between Samples % of mean
	MCA	DCA					
1 <sup>a</sup>	0.0	49.7	4.936	37.1	1.1	37.3	68.4
1 <sup>a</sup>	0.0	49.7	4.936	45.6	0.5	75.5	
4 <sup>a</sup>	6.7	33.0	5.019	41.6	1.0	56.5	13.4
4 <sup>a</sup>	6.7	33.0	5.019	43.3	0.5	64.5	
5 <sup>a</sup>	6.0	43.5	5.298	33.0	0	24.5	13.4
5 <sup>a</sup>	6.0	43.5	5.298	59.7	0	126	
NTA <sup>a</sup>	-	-	5.00	54.5	1.5	107 <sup>c</sup>	14.8
NTA <sup>a</sup>	-	-	5.00	48.4	1.1	83.5 <sup>c</sup>	
Blank A	-	-	-	27.7	1.0	-	-
6 <sup>b</sup>	6.9	56.8	5.333	26.1	0	79.0	6.1
6 <sup>b</sup>	6.9	56.8	5.333	27.3	0	84.0	
Blank B	-	-	-	4.3	0	-	-

a. Use Blank A.  
 b. Use Blank B.  
 c. Per cent sodium trichloroacetic acid.

TABLE XII

Volumetric Analysis of Mixtures of Chlorinated Acetic Acids

Test No.	Reaction Time	Sample Weight <sup>b</sup>	Titration of Oxalate With 0.097 N $KMnO_4$	Titration of Total Chloride (0.100 N $AgNO_3$ )	Titration Excess $AgNO_3$ with 0.107 N $NH_4CNS$	Sample Weight <sup>c</sup>	Titration Inorganic Chloride (0.100 N $AgNO_3$ )	Titration Excess $AgNO_3$ (0.107 N $NH_4CNS$ )	Analysis of Products (Weight Basis)		
									MCA %	DCA %	TCA %
	hours	gm	ml	ml	ml	gm	ml	ml			
1	45	4.112	32.7	84.9	14.2	1.659	6.7	6.2	0.0	49.7	50.3
3	49	4.216	39.6	84.8	14.9	-	-	-	4.3	58.7	36.9
4	63	4.159	22.0	82.9	11.9	-	-	-	6.7	33.0	60.2
4	63	4.159	22.0	84.9	13.5	-	-	-	7.2	33.0	59.8
4	63	4.370	23.1	78.8	5.0	-	-	-	8.0	33.0	59.0
5	43	4.132	28.7	85.8	16.1	-	-	-	6.0	43.5	50.5
6	37	4.392	79.6 <sup>a</sup>	75.8	4.3	2.197	8.15	7.45	6.9	56.8	36.5
6	37	4.392	40.0	84.2	12.2	-	-	-	7.1	57.0	35.9
6	37	4.386	39.3	83.2	11.4	-	-	-	7.2	56.1	36.7
7	30	4.242	50.3	90.0	24.4	4.085	20.8	16.5	24.1	75.9	0.0
8	30	4.121	44.8	80.4	16.6	4.685	19.7	15.4	24.7	68.0	7.3
8	35	5.132	55.7	96.5	14.5	4.877	24.6	19.2	18.9	68.0	13.2
8	40	4.886	48.7	99.3	19.5	5.742	13.7	12.2	7.8	62.5	29.7
8	45	4.320	43.5	100.0	27.4	7.126	16.0	13.8	5.1	63.0	32.0
8	50	4.678	42.7	100.0	20.9	6.193	12.1	10.5	3.2	57.1	39.5
8	60	4.662	39.0	99.6	19.3	4.736	17.6	15.8	0.8	52.4	46.8
8	70	4.647	31.9	100.0	17.9	-	-	-	0.0	43.0	57.0
8	80	5.019	27.3	100.0	11.6	-	-	-	0.0	34.0	66.0
8	90	5.026	29.1	105.0	14.2	-	-	-	0.0	14.4	85.6
8	90	8.530	48.0	100.0	22.4	-	-	-	0.0	17.7	82.3

<sup>a</sup> Two-fifths of sample weight used for DCA analysis.

<sup>b</sup> For DCA and total chloride analysis.

<sup>c</sup> For inorganic chloride analysis.

TABLE XIII

Pyridine Test For Trichloroacetic Acid

Test Number	Sample Weight TCA	Titration of TCA with 40 Per Cent KOH	Weight KOH Solution Added	TCA in Solution at Color Change	Sample Error
	gm	ml	gm	%	%
1	0.93	44.1	61.8	1.50	+ 3.5
2	0.85	42.9	60.0	1.40	- 3.5
3	0.75	43.6	61.1	1.21	-16.5
4	0.90	42.1	59.0	1.50	+ 3.5
5	0.85	38.6	54.0	1.55	+ 7.0
6	1.05	36.7	51.4	2.00	+38
7	0.85	34.5	48.3	1.73	+19.5
8	1.20	24.6	34.4	3.38	+95.2
9	0.90	55.5	77.6	1.15	-20.7
10	1.00	63.2	88.5	1.12	-22.7
11	0.80	58.1	81.4	0.974	-33.1
12	0.85	62.0	86.7	0.970	-33.1
13	0.85	60.0	84.0	1.00	-31.0
14	0.75	63.5	88.9	0.836	-42.7
Total				20.32	
Mean				1.45	
15 <sup>a</sup>	0.548	15.2	21.3	2.5	-
16 <sup>a</sup>	0.961	11.6	16.2	7.9	-
17 <sup>a</sup>	0.688	12.0	16.8	3.93	-
18 <sup>a</sup>	0.773	56.3	78.8	0.970	-
19 <sup>a</sup>	0.625	56.4	78.9	0.786	-
20	0.777	46.2	64.6	1.19	-
21	0.725	63.5	88.9	0.809	-
22	0.451	38.9	54.4	0.824	-

<sup>a</sup> Temperature controlled between 170° - 180°F.

TABLE XIV

Pyridine Test For Monochloroacetic Acid

Test No	Sample Weight MCA	Weight Pyridine Added	Weight of Addition Compound	Ratio of Addition Compound to MCA Sample
	gm	gm	gm	gm/gm
1	1.103	49	0.568	0.515
2	4.323	49	3.722	0.862
3	3.273	49	1.984	0.607
4	3.056	29	4.319	1.415
5	3.822	29	4.509	1.181
6	2.607	29	2.935	1.125

TABLE IV

Analysis of Viscous Material

Remaining After Chlorination of Acetic Acid to TCA

Sample Number	Sample Weight gm	Titration of Sample with 1.01 N NaOH to-			Calculation to				
		Methyl Orange ml	Phenolphthalein ml		$H_3PO_4$ gm	$PCl_5$ gm	$POCl_3$ gm	$H_3PO_3$ gm	
One	5.828	63.30	62.30		6.22	13.23	9.73	5.203	
Two	6.349	70.50	63.10		6.55	13.93	10.25	5.478	

TABLE XVI

Approximate Densities of Different Mixtures  
of Chlorinated Acetic Acids at 295°F

Product Number	Analysis of Products (Weight Basis)			Yield of TCA	Chloride Contained in Products	Density of Mixtures at 295°C
	%			%	gm/gm	gm per ml
	MCA	DCA	TCA			
1	0.0	49.7	50.3	24.6	0.601	1.48
3	4.3	58.7	36.9	21.6	0.578	1.44
4	6.7	33.0	60.2	37.6	0.599	1.50
5	6.0	43.5	50.5	34.1	0.594	1.47
6	6.9	56.8	36.5	24.4	0.575	1.47
8	0.0	17.7	82.3	63.5	0.634	1.51

Sample Calculations

The following paragraphs contain samples of the calculations used in determining the results reported in this investigation.

Calibration of Chlorine Meter. The conversion of the calibration data using air to data applicable to chlorine is depicted in the following example. The general orifice equation(15) for gases involving flow rate is:

$$Q = K \frac{(d_m) (P)}{(d_g) (T)} (h) \quad (1)$$

where

- Q = rate of gas flow
- K = constant, including discharge coefficient
- d<sub>m</sub> = density of manometer fluid
- d<sub>g</sub> = density of gas flowing
- h = pressure drop across meter
- P = absolute pressure of gas
- T = absolute temperature of gas

Thus, setting Q (air) equal to Q(chlorine); and since d<sub>m</sub>, K, and P were the same for air and chlorine, there results:

$$\frac{h_1}{(d_{g1}) (T_1)} = \frac{h_2}{(d_{g2}) (T_2)} \quad (2)$$

or

$$h_1 = \frac{(d_{g1}) (T_1)}{(d_{g2}) (T_2)} (h_2)$$

where Q<sub>1</sub> = Q<sub>2</sub> = 1,069 ml per minute  
d<sub>g1</sub> = 0.2011 lb/cu ft (at T<sub>1</sub> and P<sub>1</sub>), (chlorine)  
d<sub>g2</sub> = 0.0808 lb/cu ft (at T<sub>2</sub> and P<sub>2</sub>), (air)  
T<sub>1</sub> = 530°R (chlorine)  
T<sub>2</sub> = 522°R (air)  
h<sub>2</sub> = 6.20 in. water (air)

then

$$h_1 = \frac{(0.2011) \times (530)}{(0.0808) \times (522)} \times (6.20) = 15.6 \text{ in. water}$$



Setting  $h_1$  equal to  $h_2$  will result in an error of about 30 per cent, due to the variation of  $K$  with pressure drop.

Yield of TCA in Products. The yields of TCA (percentage) of theoretical) in the various products of the pilot work were determined as shown in the following example.

$$\% \text{ yield TCA} = \frac{\text{weight TCA in product}}{\text{theoretical weight TCA}} \times (100) \quad (3)$$

where	weight TCA theoretical producible in each reactor	1,454.0 gm
	weight of product one	681.0 gm
	percentage TCA in product one	50.3 %

Then, the yield of TCA in product one is:

$$\frac{(681) \times (0.503) \times (100)}{(1,454)} = 24.6\%$$

Degree of Chlorination. The degree of chlorination as used in this investigation may be defined as the ratio of the weight of combined chlorine in the product in question to that in a theoretical product of 100 per cent TCA in a 100 per cent yield based on acetic acid.

The chlorine content of the theoretical product was determined as follows:

$$\text{wt Cl}_2 = \left( \frac{\text{wt HAc}}{\text{MW HAc}} \right) \times \left( \frac{\text{MW TCA}}{\text{MW TCA}} \right) \times (\text{At wt Cl}_2) \times (3) \quad (4)$$

where	wt HAc = weight of acetic acid charged to reactor	534.0 gm
	MW HAc = mol weight acetic acid	60.0
	MW TCA = mol weight TCA	163.5
	At wt Cl <sub>2</sub> = atomic weight of chlorine	35.5

Then, the theoretical chlorine content is:

$$\frac{(534) \times (163.5)}{(60.0) \times (163.5)} \times (35.5) \times (3) = 948 \text{ gm}$$

The chlorine content of product eight was determined as follows:

$$\text{wt Cl}_2 = \frac{(\text{wt Cl by analysis})}{(\text{wt of sample})} \times (\text{wt product}) \quad (5)$$

where	weight chloride in product eight by analysis	5.40 gm
	weight of sample product eight for analysis	8.53 gm
	total weight product eight	1,146.0 gm

Then, the chlorine content of product eight is:

$$\frac{(5.40)}{(8.53)} \times (1146) = 725 \text{ gm}$$

The degree of chlorination in product eight was determined in the following manner:

$$\begin{aligned} \text{deg chlorination} &= \frac{(\text{wt Cl in product})}{(\text{theoretical wt Cl})} \times (100) \quad (6) \\ &= \frac{(725)}{(948)} \times (100) = 76.5\% \end{aligned}$$

Direct Volumetric Analysis for TGA. The amount of TGA present in a mixture of chlorinated acetic acids, as determined by a modification of Pool's method<sup>(46)</sup>, was calculated as shown in the following example.

$$\%TGA = \frac{((\text{ml N HCl}) - (\text{ml N KOH}) - \text{ml blank}) \times \left( \frac{\text{MW TGA}}{2,000} \right) \left( \frac{500}{200} \right) (100)}{\text{wt. original acid sample}} \quad (7)$$

where	HCl (0.994 N)	=	26.1 ml
	KOH (0.835 N)	=	0.0 ml
	HCl blank	=	4.3 ml
	MW TGA	=	169.5
	weight original acid sample product six	=	5.393 gm

The milli-equivalent of TGA is its molecular weight over 2,000 since each mol of TGA produces one mol carbonate with an equivalent of two when titrated with acid to methyl orange. The ratio of 500/200 appear-

ing in equation (7), corrects for a 200-milliliter portion, out of a 500-milliliter solution of the sample, used for analysis. Then, the amount of TCA in product six is:

$$\frac{((26.1) \times (0.994)) - (4.3) \times \left(\frac{163.5}{3000}\right) \times \left(\frac{500}{200}\right) \times (100)}{5.333} =$$

TCA = 79.0%

Volumetric Analysis for Chlorinated Acetic Acids. The amounts of

MCA, DCA, and TCA present in the various products were calculated from the experimental data in the following manner:

weight original sample product eight at 50 hours, used for DCA and total chloride analysis	4.678 gm
KMnO <sub>4</sub> (0.097 N) equivalent to oxalate in DCA analysis	42.7 ml
AgNO <sub>3</sub> (0.100 N) titrated total chloride to excess	100.0 ml
NH <sub>4</sub> CNS (0.107 N) titrated excess AgNO <sub>3</sub>	20.9 ml
weight sample product weight at 50 hours used for inorganic chloride analysis	6.193 gm
AgNO <sub>3</sub> (0.100 N) titrated inorganic chloride to excess	12.1 ml
NH <sub>4</sub> CNS (0.107 N) titrated excess AgNO <sub>3</sub>	10.5 ml
mol weight MCA	94.5
mol weight DCA	129.0
mol weight TCA	163.5

Per cent DCA:

$$\%DCA = \left[ \frac{(\text{ml KMnO}_4) \times (N) \times \left(\frac{\text{MW DCA}}{1000}\right)}{(\text{sample wt}) \times \left(\frac{100}{500}\right)} \right] \times (100) \quad (8)$$

$$= \left[ \frac{(42.7) \times (0.097) \times \left(\frac{129}{1000}\right)}{(4.678) \times \left(\frac{100}{500}\right)} \right] \times (100) = 57.1\%$$

Total Chloride:

gm chloride =

$$((\text{ml N AgNO}_3) - (\text{ml N NH}_4\text{CNS})) \times \left(\frac{\text{EW Cl}}{1000}\right) \times \left(\frac{500}{50}\right) \quad (9)$$

$$= |((100) \times (0.100)) - ((20.9) \times (0.107))| \times \frac{(35.5)}{1000} \times \frac{(500)}{90}$$

$$= 2.755 \text{ gm}$$

Inorganic Chloride:

gm chloride =

$$((\text{ml N AgNO}_3) - (\text{ml N NH}_4\text{CNS})) \times \frac{(\text{At wt Cl})}{1000} \times \left( \frac{\text{wt sample for total chloride}}{\text{wt sample for inorg. chloride}} \right) \quad (10)$$

$$= [((12.1) \times (0.100)) - ((10.5) \times (0.107))] \times \frac{(35.5)}{1000} \times \frac{(4.678)}{6.193}$$

$$= 0.0024 \text{ gm}$$

Chloride as DCA:

gm chloride =

$$\left( \frac{\text{DCA}}{100} \times (\text{sample wt}) \right) \times \frac{(\text{At wt Cl}) \times (2)}{\text{MW DCA}}$$

$$= (0.571) \times (4.678) \times \frac{(35.5) \times (2)}{129} = 1.472 \text{ gm}$$

Chloride as MCA plus TCA:

gm chloride =

$$(\text{total Cl}) - (\text{Cl as DCA} + \text{inorg. Cl}) \quad (12)$$

$$= (2.755) - (1.472 + 0.0024) = 1.30 \text{ gm}$$

Weight Original Sample as MCA plus TCA:

$$\text{wt MCA} + \text{TCA} = (\text{wt orig. sample}) - (\text{wt DCA in sample}) \quad (13)$$

$$= (4.678) - ((0.571) \times (4.678)) = 2.002 \text{ gm}$$

Calculation of Percentage MCA and TCA: Assuming that there is no acetic acid present in the product, calculation of the percentage MCA and TCA depends upon the distribution of chlorine between MCA and TCA. The weight of MCA plus TCA was known and also the chloride attributable to the two acids. Therefore, two equations result:

$$\text{wt Cl as (MCA} + \text{TCA)} = \left( \frac{\text{wt MCA}}{\text{MW MCA}} \times (\text{At wt Cl}) \right) + \left( \frac{\text{wt TCA}}{\text{MW TCA}} \times (\text{At wt Cl}) \times (3) \right) \quad (14)$$

$$\text{wt (HGA + TGA)} = (\text{wt HGA}) + (\text{wt TGA}) \quad (15)$$

$$\begin{aligned} \text{let } a &= \text{wt HGA} \\ b &= \text{wt TGA} \end{aligned}$$

$$\text{then } 1.30 = \left(\frac{a}{94.5}\right) \times (35.5) + \left(\frac{b}{103.5}\right) \times (35.5) \times (3)$$

$$\text{or } 1.30 = 0.376a + 0.751b \quad (14)$$

$$2.002 = a + b \quad (15)$$

Solving equations (14) and (15) simultaneously:

$$a = 0.02$$

$$b = 1.98$$

$$\text{and } \% \text{HGA} = \left(\frac{a}{\text{sample wt}}\right) \times (100) = \left(\frac{0.02}{4.678}\right) \times (100) = 0.43$$

#### IV. DISCUSSION

This section provides the reader with a discussion of the results and limitations of the investigation, and recommendations for future study.

##### A. Discussion of Results

The following discussion presents the investigator's analysis, criticism, interpretation, and evaluation of the results of this investigation. Experimental observations, not reported in the preceding section, have been presented in the discussion.

Calibration of Chlorine Flow Meter. The usefulness of the frictional resistance type gas flow meter for measurement of low rates of flow cannot be overemphasized. It is simple, economical, and easily constructed. However, calibration may be a drawback if not made with the gas to be measured. Conversion of calibration data obtained with one gas to that for use with another may reduce accuracy beyond desirable limits.

Utilization of the general orifice equation, for the conversion of calibration data obtained with air to that for use with chlorine, was found to be accurate within two per cent, by one test; this one test was not considered conclusive. However, it did serve to indicate the proper use of the orifice equation for conversion. Converting by use of the orifice equation (see page <sup>98</sup>), it was found that

the constant K varied with either pressure drop or with the gas flow rate. The one test made indicated that K varied with pressure drop rather than with flow rate. Thus, an error of about 30 per cent was averted.

The purposes of chlorine metering were reproducibility with the pilot plant, comparable feed rate data, and an approximate measurement of the actual flow rate so that a check could be had on the amount of excess chlorine used.

Chlorination of Acetic Acid. The results of chlorinating acetic acid are of primary importance in this investigation. Both four-stage and single-stage pilot work are discussed in the following paragraphs under the same headings so that the factors influencing the chlorination need not appear twice in this section.

The investigation has shown that TCA can be produced in 82 per cent concentrations, at a 63.5 per cent yield, by chlorinating glacial acetic acid in the presence of red phosphorus for 90 hours, between 70 and 320°F and at atmospheric pressures. The question of commercial application of the process will depend upon the time required for the reaction and the yield of TCA. Therefore, the discussion will deal mainly with those factors affecting the rate of reaction and the yield.

Deviations from Procedure. The deviations from the established procedure were as follows:

1. Crystallization of MCA in gas exit lines during second-stage chlorination caused pressure to be built up in the system. The cause of the crystallization was entrainment of MCA in the exit gases; the reflux condenser being operated at 16°C (melt-

ing point of MCA is 57°C). To alleviate the situation, the second stage of chlorination was carried out with only one reactor in line. This resulted in low gas rates (300 to 360 ml per minute), thus leading to reduced crystallization of MCA in exit lines.

2. Preliminary investigation indicated that the time required for each stage was not necessarily seven hours as assumed by the plant design class. Thus, it became imperative to obtain information pertinent to estimating optimum stage time. The procedure was changed so that chlorination was continued at each stage until the rate of absorption dropped from the initial peak of from 12 to 33 grams per hour and began to level off at rates of from five to seven grams per hour. Chlorination, under conditions of the next stage, was then initiated.

Rates of Reaction. The rates of reaction were followed during the various tests of the pilot work by keeping a running log of the weight of the reaction masses (see Table VIII). The factors affecting the rate of reaction have been discussed in the following paragraphs.

Temperature: It is evident from the rate of chlorine absorption curves (Figures 15, 17, 19, and 21) that in general, increases in temperature caused increases in the rate of reaction. Referring to Figure 17, at a reaction time of six hours, the temperature was increased from 208 to 248°F causing the reaction rate to increase from three grams to ten grams. Also, at reaction times of 10, 13, and 27 hours, increases in temperature of 40°F about doubled the reaction rate.



After noting the stepwise effect of temperature on the reaction rate under four-stage conditions, the logic of single-stage chlorination, in which the temperature is raised to the maximum allowable (320°F) within the first seven to nine hours of the 28 to 30-hour reaction period becomes more evident. The effect of single-stage chlorination is to smooth out the stepwise effect of the rate of reaction curve, thus utilizing the reaction time more efficiently.

A correlation of reaction rate with temperature cannot be made utilizing the data from this investigation because of fluctuations in other operating conditions. The data and results serve to indicate what may be expected by varying the reaction temperature.

Concentration: Concentration affects both the point of reaction equilibrium and the rate of reaction. The net rate of reaction decreases as the point of equilibrium is approached. However, excess chlorine of from 40 to 90 per cent was present during the pilot work of this investigation. This removes from discussion the effect of equilibrium on the rate of reaction, since the point of equilibrium was stabilized. There remains for discussion the effect of concentration on the reaction rate, and how the rate may be increased by increasing concentration of chlorine.

The concentration of chlorine in the reaction mass depended upon the chlorine feed rate and the rate of chlorine absorption. The rate of chlorine absorption depended upon the area of liquid-gas contact, the time of contact, the concentration

difference between gas and liquid, and catalysis. These factors, influencing chlorine concentration, were affected by chlorine feed rate and distribution. Thus, the question of the effect of chlorine concentration on reaction rate reduces to a discussion of chlorine dispersion in the reaction mass.

Groggins<sup>(29)</sup> stated, in presenting rules for chlorination, that high concentrations of chlorine promote the formation of polychlorinated compounds. It was for this reason that excess chlorine was used in the pilot work. After the first two hours of chlorination in the various tests, the chlorine feed rate to the four-stage reactors was never less than 40 per cent in excess of that required for the observed rate of gain in weight by the reaction masses. During single stage chlorination, the chlorine feed rate was at all times 68 per cent in excess (or greater) of that required.

The data and results give no indication that increase in reaction rate accompanied any increases in chlorine feed rate of from 25 to 100 per cent after the first two hours of reaction. Of course, fluctuations in other variables and operating conditions could have obscured any relationship that existed. However, during single-stage chlorination (test 8) the feed rate was increased from 25 to 52 grams per hour at 65 hours, without causing an increase in the rate of chlorine absorption. A similar experience was had with test 7 (single-stage chlorination) during the reaction times of 25 to 30 hours. These observations indicate that increased feed rates of from 25 to 100 per cent, during the tests

conducted in the pilot work, would not have resulted in increased rates of reaction.

Although the results show that increased chlorine feed rates would have had no appreciable effect, better chlorine distribution would have increased the rate of reaction. The importance of chlorine distribution was observed at one point in the investigation. At 31 hours for test 3 and at 22 hours for test 4 (both four-stage tests), four-prong chlorine distributors were installed in the pilot plant in place of single downspout distributors. The rate of chlorine absorption of product #3 increased from four to five and eight grams per hour. The rate of absorption of product #4 increased from eight to 22, 13, and 14 grams per hour. Thus, the effect was to increase the rate of chlorine absorption about two to 2.75 times the original value.

The foregoing discussion reveals the importance of efficient chlorine distribution. No agitation, other than that caused by evolution of chlorine from the distributor, was utilized in pilot work. Thus, the use of an agitator for increasing the rate of reaction is indicated.

Catalysis: The investigation was limited to the use of red phosphorus as a catalyst. During the reaction, phosphorus was chlorinated to tri- and pentachlorides. Therefore, the catalytic effect of these two compounds must be considered. Two questions that arise must be answered before considering the effect of the catalysts on reaction rate. First, how do these three compounds promote chlorination? And second, was there evidence that one of these compounds was the main catalytic agent?

Groggins<sup>(28)</sup> reports that phosphorus acts as a catalyst in the chlorination of acetic acid by promoting the formation of acetyls. However, it is known that  $\text{PCl}_3$  and  $\text{PCl}_5$  react with acetic acid, MCA, DCA, and TCA to form the corresponding acetyl chloride. Therefore, it is not clear whether Groggins was inferring that the element phosphorus promoted the formation of acetyls, or that it promoted the reactions through its chlorides. The latter action is not catalytic, but rather a side reaction, since phosphorus acid and/or phosphorus oxychloride are formed.

Phosphorus pentachloride is a strong chlorinating agent, approaching the strength of gaseous chlorine at elevated temperatures ( $300^\circ\text{C}$ ). Either phosphorus trichloride or pentachloride may be considered as the catalyst in promoting chlorination. Phosphorus pentachloride decomposes into chlorine and phosphorus trichloride, thus providing chlorine for the reaction. The trichloride is rechlorinated by gaseous chlorine to the pentachloride. The catalyst cycle may be imagined to start and end with either of the chlorides.

During pilot work, it was observed that about half (ten grams) of the red phosphorus disappeared in producing MCA in about 80 to 90 per cent concentrations. But, after the temperature had reached about  $140^\circ\text{C}$  ( $284^\circ\text{F}$ ) and about half the reaction time (15 hours) had lapsed, all the phosphorus had disappeared and a heavy, viscous layer had formed on the bottom of the reactor. This viscous material, at first believed to be phosphorus pentachloride, was determined to be a mixture of phosphoric and phosphorous

acids. A qualitative analysis of the material indicated the presence of the phosphate ion. The presence of the phosphite ion was not observed, but it may have been obscured. No inorganic chloride was present, indicating the absence of  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{PCl}_3$ ,  $\text{POCl}_3$ , and acetyls. The source of phosphorous acid was, of course, from the side reaction of  $\text{PCl}_3$  and acids to form acetyls. The phosphoric acid evidently was formed by the action of water on  $\text{PCl}_5$  and/or  $\text{POCl}_3$ . The origin of the water may have been from the acetic acid, chlorine, atmosphere, and/or contamination during sampling.

Any catalyst ( $\text{PCl}_3$  or  $\text{PCl}_5$ ) remaining during the latter portion of the reaction period must have been dissolved in the TCA-DCA phase. But, an analysis of product #8 (single-stage chlorination) at 70, 80, and 90 hours indicated negligible amounts of inorganic chloride present. Therefore, it is doubtful whether there was any significant catalytic action during the latter phases of the reaction period. More complete condensation and condensate return would help alleviate this situation, since the viscous material accounts for less than 60 per cent of the phosphorus originally present.

Groggins<sup>(31)</sup> has reported that in the production of MCA from acetic acid, only three-fourths of the original phosphorus used in the initial batch is required for make up in succeeding batches. No indication was given of the form of the remaining catalyst, although it was evidently the element. Thus, it appears that during the first half of the reaction period in producing TCA,

phosphorus, phosphorus trichloride and pentachloride are the catalytic agents, and during the latter half of the reaction period phosphorus pentachloride is the main catalyst.

In reactions involving catalysts, the rate of reaction may be increased by increasing the concentration of the catalysts. The effect of increasing the amount of catalyst was observed in the pilot work by addition of ten grams red phosphorus in test 1 during the fourth stage of chlorination. Product #3 at 36 hours was second in line in the pilot plant at the time of the catalyst addition. During the three hours following, product #1 lost 23, 22, and eight grams per hour in succession. The losses may be attributed to the vaporization of acetyls and phosphorus chlorides formed; formation of acetyls being promoted by additional catalyst. During the same three hour period, product #3 gained 45, 23, and 24 grams per hour respectively. This is evidence of loss of products from product #1 by vaporization and entrainment. The rate of gain in weight (chlorine absorption) of product #1 did not rise above two grams per hour during the next five hours of reaction. The effect of increasing the amount of phosphorus in the reaction mass appears to be the formation of acetyls with subsequent loss of these products due to their low boiling points (50 to 118°C) and no increase in actual rates of reaction leading to the formation of TCA. However, the results of increased catalyst concentration may have been obscured by operating conditions. It was hypothesized (page 8) that chloroacetyl chloride is a catalyst in the formation of MCA by the chlorination of acetic acid. Then possibly di- and

trichloroacetyl chlorides are catalysts in the formation of DCA and TCA. Thus, loss of acetyls after the addition of red phosphorus to product #1 may have nullified the possible effect of increased phosphorus concentration on the rate of reaction. The role of acetyls as catalysts in producing TCA deserves further investigation.

It is seen that this investigation is of little value as a quantitative guide to the effect of reaction conditions on the reaction rate in the production of TCA. However, the work does point the way for future investigation.

Yield of TCA. The concentrations and yields of TCA obtained in the various tests of this investigation have been presented in Table VIII and in Figure 23. Two factors affect the yield of TCA in the final product. They are reaction time and loss of products. Given enough time, no matter what the reaction rate may be, a product of desired concentration may be produced, provided the point of equilibrium is favorable and loss of the final product does not occur to excess. Reaction time affects yield in the same manner, but if loss of products is high, this latter factor dominates.

Effect of Reaction Time: The effect of reaction time on the concentration and yield of the products produced during pilot work cannot be determined quantitatively because of the fluctuations in temperature, concentration, and operation that occurred. Some qualitative observations may be of value, however.

Yields of TCA in product #5 and #6 appear to have been greater than in products #3 and #4 at comparable reaction times (all four products of four-stage reaction). The reasons may be noted in the larger cumulative weights of the reaction masses of products #5 and #6 (as much as 30 per cent greater) and their higher concentrations of TCA (about 10 per cent greater). Evidently, operation was more efficient during tests 5 and 6.

A further comparison of yields reveals that in only one test out of four, four-stage chlorination produced a product (product #5) containing higher concentrations of TCA (17 per cent greater) at comparable reaction times than that produced by single-stage chlorination (product #8). The question arises as to whether or not this is evidence of more efficient chlorination with four-stage than with single-stage chlorination. The answer may be found by comparison of the cumulative weights of the products in question. The four-stage product weighed some 65 grams less than the single-stage product at a comparable time. The answer is more evident by comparison of the degrees of chlorination. (The degree of chlorination is a quantitative expression for the degree of completion of the reaction on a theoretical basis.) The four-stage product had a degree chlorination of 61.2 per cent, and the single-stage, 63 per cent (see Table IX). Thus it can be concluded that four-stage chlorination was not as efficient as single-stage in producing a high yield of TCA.

But what of the effect of reaction time on TCA yield? Groggins<sup>(31)</sup> has given production data for MCA. The highest yield



(93.0 per cent) occurred at the highest reaction time (12.25 hours), but there seems to be no definite correlation between reaction time and yield. At 45 hours, the concentration of TCA in product #8 (single-stage chlorination product, this investigation) was 34.2 per cent, the yield was 24.8 per cent, and the degree of chlorination was 64.4 per cent. At 90 hours, or double the previous reaction period, product #8 contained TCA in 82 per cent concentration, 63.5 per cent yield, and the degree of chlorination was 76.5 per cent. Both concentration and yield more than doubled during the last 45 hours of the reaction period, but the degree of chlorination only increased about 20 per cent. The low gain in the degree of chlorination is evidence of low rate of reaction (1.0 to 3.5 grams per hour) during the latter half of the reaction period, but never-the-less producing an increase in yield. Thus, the results reported in the literature and in this investigation indicate that reaction time affects yield mainly by allowing operational inefficiencies to progress.

Effect of Product Losses: As far as the yield of TCA is concerned, loss of products may be a result of side reactions, decomposition, leaks, and losses incurred by passage of gases through the reaction mass - that is vaporization and entrainment. There are no side reactions; all products of chlorination (except HCl,  $\text{POCl}_3$ , and  $\text{H}_3\text{PO}_3$ ) can be classified as intermediate or final products. No leaks occurred during pilot work. Thus, loss of products during pilot work was attributable to pyrogenation, vaporization, and entrainment.

Losses of material were 15 to 30 per cent lower during single-stage work than during four-stage work. In general, losses were particularly noticeable during the initial four to seven hours of the chlorination, negative rates of chlorine absorption (of six to 46 grams per hour) occurring on three different occasions. During four-stage chlorination, material entrained in gases leaving one reactor was collected in the following reactor and therefore did not leave the system. Only entrainment from the last reactor in line resulted in loss of material. Losses due to vaporization of products depended upon temperature, pressure, and gas flow rate. The pressure remained constant (at one atmosphere) for all practical purposes during the pilot work. Temperatures were higher by 40 to 120° (F) for longer periods of time (ten to 15 hours) during single-stage than during four-stage work. Gas flow rates were about the same, per unit weight of reaction material, in both types of reaction. However, condensation was better provided for in single-stage work. This seems to have more than made up for the longer periods during which high temperatures were used.

Analysis of losses occurring during single-stage reaction reveals the need for more condensation. If the single-stage product, (#8) had been further chlorinated from 82 to 100 per cent TCA, without further losses, the final product would have weighed 1,201 grams. The amount of glacial acetic acid charged to each reactor would theoretically result in 1,454 grams of TCA. Thus, the product of 1,201 grams TCA would have represented a yield of 82.6 per cent. The yield indicates that substantial losses occurred. The total

losses that occurred during the production of product #8 were 244 grams; calculated as the difference in the weight of a theoretical product (of same concentration as product #8 but that would product 1,454 grams TCA on further chlorination to 100 per cent TCA) and the weight of product #8. During the first thirty hours of chlorination, 123 grams of material were lost. Thus, half of the total losses took place during the first third of the reaction period when lower boiling components were present. The insertion of a return condenser and condensate receiver caused the recovery and return of 187 grams of products to the reactor during the 90-hours of reaction. The size and character of these losses show, without a doubt, that if sufficient condensation had been provided, losses may have been greatly reduced.

In view of the high losses (244 gm) that occurred, it would seem that pyrogenation took place during the reaction. Groggins<sup>(29)</sup> reports that excessive temperatures and/or time of reaction may result in pyrogenation of chlorinated hydrocarbons. Both Groggins<sup>(30)</sup> and Strosacker<sup>(61)</sup> have reported that 160°C (320°F) is the maximum temperature practical for chlorinating acetic acid to TCA in the liquid phase. No doubt this limit was fixed because higher temperatures resulted in pyrogenation. But, Groggins<sup>(29)</sup> also reports that pyrolysis is almost completely eliminated by use of the liquid phase in chlorination. Since temperatures of less than 160°C (320°F) and the liquid phase were used during the pilot work, the argument of pyrolysis must shift from consideration of temperature to reaction time.

Groggins<sup>(31)</sup> has given development data on the production of MCA by chlorinating acetic acid (see Table I). He reports yields of MCA ranging from 81.5 to 93.0 per cent (at 100 per cent MCA concentrations) of the theoretical based on acetic acid, with chlorine usages of 1.21 to 1.39 parts per part of original acetic acid and reaction periods of from seven to 12.75 hours. It would appear from this data that higher yields of MCA are the result of liberal chlorine usages and long reaction periods, but not a result of low chlorine usage and long reaction periods. On further analysis, variation in reaction time of about 30 per cent seems to have no uniform effect on yield. Evidently then, pyrogenation was not a factor in causing variation in yield, because if it had been, the effect of reaction time on yield would have tended to be uniform (reaction time being the sole cause of pyrogenation left in the argument). Applying this reasoning to the losses reported on the pilot work of this investigation, it can be concluded that the effect of reaction time on yield is not due to progressive pyrogenation but rather to vaporization and entrainment.

The discussion of yield narrows at this point to losses. It may be safely concluded that the variation in yield of MCA reported by Groggins, and of TCA reported in this investigation, are due largely to fluctuations in operating efficiency - mainly condensation.

Comparison of Pilot Work With Reported Work. The previous discussion led to the conclusions that the time required for the

production of TCA and the yield of TCA were dependent on the efficiency of operation - that is adequate chlorine distribution and condensation. A comparison of the results of this investigation with results reported in the literature where a commercial type chlorinator was used, would provide an estimate of the operational efficiency of the pilot plant chlorinator in respect to commercial type chlorinators. Such an estimate would be valuable as a basis for a plant design using the data of this investigation.

Table I presents development data on the production of MCA as reported by Groggins<sup>(31)</sup>. Eight tests were conducted using a commercial type chlorinator, initially charged with 350 pounds of acetic acid. Average values of the results reported in Table I will be used for comparison. The average values indicate that using the type chlorinator described by Groggins, MCA in 100 per cent concentrations can be produced in 86 per cent yields in nine-hours at 100°C and atmospheric pressures, using 1.28 parts chlorine per part of original acetic acid. The reaction took place in liquidous phase and utilized red phosphorus as a catalyst.

In test 6 of this investigation (four-stage chlorination), MCA in about an 80 to 85 per cent concentration was produced in a 73 per cent yield in eight hours at 85 to 212°F, using 2.0 parts chlorine per part of original acetic acid.

The pilot work required 1.56 times as much chlorine to produce a product of only 85 per cent the yield of MCA as that reported by Groggins; reaction time, temperature, and catalysis being comparable. Thus, correcting for the difference in yield, the pilot work was only

54 per cent (85/1.56) as efficient as the reported work in dispersing chlorine. It was previously shown that increased chlorine dispersion resulted in increased rate of reaction. Therefore, utilizing equipment similar to that described by Groggins, either 54 per cent of the chlorine used in the pilot work may be used to produce a comparable TCA product, or the same amount of chlorine may be used - resulting in a shorter reaction period.

Suppose equipment similar to that used in obtaining the data reported by Groggins were utilized to produce TCA under the conditions of temperature, concentration, and catalysis imposed in producing product #8. Also, assume that reaction rate varies directly with effectiveness of chlorine dispersion. Then, the time required to produce a product comparable to product #8 (82 per cent TCA) would be 49-hours rather than 90-hours.

Since the chlorinator described by Groggins did not utilize an agitator, the time of reaction for producing TCA could probably be reduced below that estimated in the preceding paragraph.

Summary of Results Pertinent to a Plant Design. The pilot work of this investigation resulted in establishing the following information pertinent to a plant design for the production of TCA. During the first hour of the reaction, the chlorine feed rate should be as high as practical without causing the excessive entrainment. (Cooling may be necessary during this period to maintain 100°C.) The chlorine feed rate should be, at a minimum, 68 per cent in excess of that required for the reaction during the remainder of the reaction period. The temperature of the reaction should be

gradually raised to 160°C (320°F) during the first ten to 15 per cent of the reaction period. The temperature should be maintained at this level for the duration of the reaction. The concentration of red phosphorus recommended by Croggins appeared to be sufficient (0.038 parts per part acetic acid). The chlorinator should be provided with a motor-driven agitator for dispersing the chlorine, and an adequate (ring-type) chlorine distributor, a reflux condenser, and a return condenser. The reflux condenser should be operated with 60°F coolant, and the return condenser with 32°F coolant. The reaction should take place in the absence of actinic light and at atmospheric pressures.

Under the conditions outlined in the previous paragraph, TCA is producible in at least 82 per cent concentrations (63.5 per cent yield based on acetic acid) in a 90-hour reaction period. Comparison of the results of the pilot work with work reported in the literature indicates that the reaction time required in the pilot work may be about 46 per cent higher than that required to produce a comparable product utilizing a commercial type and size chlorinator.

Higher TCA Concentrations Without Further Chlorination. Product #8 was essentially a binary solution of TCA and DCA. Therefore, the freezing point - solubility data given in Figure 12 can be used to estimate the amount of TCA present and the amount recoverable from the product as a separate phase.

By crystallizing TCA out of solution as a separate phase, products rich in TCA could be produced. When product #8 was cooled to 110°F, TCA

began to crystallize out of solution. By cooling such a product to 20°C (68°F), about 600 grams TGA could be crystallized from the 1,146 gram product. If on draining, the liquid retention was ten weight per cent of the solid material, a product containing 96.3 per cent TGA would result. The drained liquid, containing 58 per cent TGA and weighing 486 grams, could be recycled for further chlorination.

Neutralization of TGA. It has been reported<sup>(41)</sup> that chlorinated acetic acids can be neutralized by mixing the acid with dry  $\text{Na}_2\text{CO}_3$ . This report was verified by neutralization of ten grams of product #6 with twice the theoretically required amount of  $\text{Na}_2\text{CO}_3$ . The excess carbonate was used by mistake. Evolution of carbon dioxide on addition of carbonate to the acid, caused considerable foaming during the first minute of reaction, and later if the mixture was not stirred, caused swelling. The mass became doughy within two minutes after carbonate addition. A dry lumpy mass of sodium trichloroacetate (NTA) resulted after heating for 45 minutes at 150°C (302°F). Neutralization of product #6 was investigated at initial acid temperatures of 70° and 212°F. The latter temperature would be the more practical since the mass is all liquid at this temperature, the reaction can be controlled by the rate of carbonate addition, and the product leaving the chlorinators (at 320°F) would not have to be cooled to such a low temperature and then reheated to 150°C. At a temperature of about 200 to 210°C, sodium TGA decomposes. This is a limitation on drying temperature. The doughy mass should be mixed while being neutralized and dried to ensure complete reaction and prevent lumping. A grinder would be required to reduce the dried product to a quickly soluble powder.



Analysis of Chlorinated Acetic Acids. Many analytical methods were investigated for suitable analyses of mixtures of chlorinated acetic acids.

Microscopic Identification. An attempt was made to identify MCA, DCA, and TCA by microscopic examination of mixtures of crystalline salts of these acids. Both sodium and ammonium salts were examined without successful identification. Crystals of MCA and of TCA, observed in the laboratory with the unaided eye, were too similar for differentiation by the investigator. Other optical means of identification of crystals of the acids or their salts would result in a procedure too laborious for practical use. The use of microscopic examination as a means of analysis awaits the finding of suitable salts which have different individual crystal form.

Chromatographic Analysis. Chromatographic analysis of MCA and acetic acid mixtures and mixtures of MCA, DCA, and TCA were investigated. Use of silicic acid as an adsorbent and ether and acetone as eluents and solvents, resulted in no resolution of the mixtures. Temperature ranges of analyses were  $-30^{\circ}$  to  $-10^{\circ}\text{C}$  ( $-24^{\circ}$  to  $14^{\circ}\text{F}$ ), and  $70$  to  $90^{\circ}\text{F}$ . The ratio of acid sample to adsorbent used in the studies were from 0.2 to one, to 0.08 to one. The rates of elution were from one-fourth to five milliliters per minute.

Use of activated alumina as an adsorbent was tried without success. The ratio of acid sample to alumina used was 0.065 to one; elution rate, two milliliters per minute; temperature,  $80$  to  $85^{\circ}\text{F}$ ; and the eluent, ether.

Sucrose, confectioners sugar, was used as an adsorbent and acetone as eluent in chromatography without success. The temperature was 90°F; ratio of sample to adsorbent was 0.04 to one; elution rate was varied from one-half to five milliliters per minute.

Activated carbon was used as an adsorbent, and ether and acetone as eluent and solvent, but with minor success. Ratios of acid sample to carbon used were from 0.31 to one, to 0.06 to one. Rates of sample introduction to the adsorbent column were from one-fourth to two milliliters per minute. Elution rates were varied from one-half to five milliliters per minute. Temperatures tested were the ranges -30 to -10°C (-24 to 14°F) and 70 to 90°F. No appreciable resolution of the acids occurred at the lower temperature range. Resolution, of minor importance, was noted when the procedure given on page 67 was used. On evaporation of the eluent, the fractions were always liquidous. However, further drying in circulating air would vaporize the DCA and leave MCA and TCA in a crystalline form. Since some fractions contained more crystalline material in relation to the original weight of the fraction than did others, it is believed that some resolution did take place. However, at best the analysis was but a crude fractionation to determine the crystalline content of the acid recovered from the adsorbent. Other factors, such as only partial recovery of the acid sample from the adsorbent, evaporation of MCA and TCA, and deliquescence of the acids make the method untenable. The success of the chromatographic method for analysis of mixtures of MCA, DCA, and TCA depends upon the discovery of a suitable adsorbent and eluent. Also,

the usefulness of the chromatographic method will depend upon its ease and time of operation.

Direct Volumetric Analysis for TGA. The method of analysis for TGA as reported by Pool<sup>(46)</sup> was investigated, and the results reported in Table XI. Using Pool's method, three out of four analyses were in error by as much as 50 to 60 per cent. Replications were in error by as much as 40 per cent. This verifies Dalin's<sup>(13)</sup> report that Pool's method was often low by a factor of from 15 to 85 per cent.

It was found, during the investigation, that dilution of the filtrate from the mixture containing barium carbonate, resulted in further precipitation. This was thought likely to be the cause of error. However, as shown in Table XI, a mean error between replications of from six to 68 per cent can be expected. It is quite obvious that this method has no value as an analytical determination. The results put in doubt the quantitative decomposition of TGA to chloroform and carbon dioxide.

Volumetric Analysis of Mixtures of Chlorinated Acetic Acids.

A revised method of analysis for mixtures of MGA, DGA, and TGA, as reported by Dalin<sup>(13)</sup>, was investigated. The results are reported in Table XII. Of three products tested in duplication or triplication (products #4, #6, and #8), replication in two sets of analyses were within 2.2 per cent, and within 4.0 per cent in the third set.

In order to test the effect of smaller amounts of reagents used on the results of analysis, product #8 was tested using different sample weights. A five and an eight-gram sample were used, other

conditions remaining constant. Variation in results were only 4.0 per cent.

The analysis was based on the validity of the assumption that there was no acetic acid present in the acid sample. All products analyzed by this method had been chlorinated at least 30-hours. Since MCA was formed in about 80 per cent concentrations within the first ten to 12 hours of chlorination, the assumption that there was no acetic acid present after 30-hours chlorination seems reasonable. Further substantiation is had in the reported analysis of product #7 at 30-hours.

In volumetric work, there is always some doubt as to the validity of the results, not in regard to duplication but in regard to actuality, until the results of the method have been confirmed as valid. There were two factors observed during the investigation that lend support or confirm this analytical method. The chromatographic work (reported in Table X) shows that the percentage crystalline material recovered during chromatography increased with increase in percentage TCA as reported by this method of analysis. This would indicate that the volumetric method is at least good for comparison purposes.

Further substantiation was had by an observation of the crystallization temperature of the TCA phase in product #8. Product #8 was essentially a binary mixture of TCA and DCA. TCA began to crystallize out at about 110°F. By reference to the TCA-DCA solubility diagram, Figure 12, the percentage of TCA was estimated to be 30. This agrees quite well with the 32.3 and 35.6 per cent TCA values found by volumetric analysis.

The results of analysis for DCA in product #8 at 90-hours were questionable. Results of 36.2 and 35.2 per cent DCA were found. These results, reported in Table XII, of 14.4 and 17.7 per cent DCA were determined by proportioning the total chloride found between TCA and DCA, assuming no MCA present. The assumption of no MCA present was considered valid on the basis of analyses of product #8 at 70 and 80-hours reaction time - no MCA reported. It is not known whether a mistake was made in the procedure for determining DCA (such a mistake hardly likely to occur in two attempts), or whether the asbestos used for a filter medium contained organic matter thus causing a high determination of DCA. This latter explanation seems the more likely. Not as much care was exercised in preparing the asbestos for analysis of product #8 at 90-hours as in the preceding analyses. Further investigation of the application of this method of analysis to mixtures of the acids containing concentrations of TCA greater than 80 per cent would be desirable.

Identification and Separation of TCA by Use of Phenol. The success of this method of identification of TCA depended upon the formation of a phenol-TCA addition compound and its separation by crystallization from the residual phenol, DCA, and MCA. Comparison of the freezing point of the addition compound with the freezing point data of the system phenol-TCA would result in an estimate of the amount of TCA present. It was found that the addition compound would not crystallize from such mixtures of the acids and phenol as a separate phase. The method was discarded.

Pyridine Test for TCA. Fujivara<sup>(22)</sup> reported that a pyridine caustic solution could be utilized to detect  $\text{COCl}_2$  groups. Another

source reported that this test could be used for estimating TCA in one per cent concentrations of less. The method was investigated to determine its usefulness as a means for estimation of TCA. A red coloration appearing in the pyridine layer was a positive test for  $\text{CCl}_3^-$  groups. Known samples of TCA (prepared in the laboratory) were used to determine if there was a concentration limit, below which a positive test would not occur. Results of the study are given in Table XIII. The first 14 tests were made by titrating the hot TCA-caustic-pyridine mixture with caustic until a faint pink coloration appeared in the pyridine layer. It was concluded that the answer had to be known before results could be had within 20 per cent. Tests, other than those reported in Table XIII, were made on solutions containing as little as 0.03 per cent and as much as 50 per cent TCA. In all cases, positive tests for TCA resulted. The pyridine test must be considered as qualitative, only.

Pyridine Test for MCA. The usefulness of pyridine for the quantitative estimation of MCA depends upon the quantitative formation and crystallization of an addition compound of pyridine and MCA. (TCA and DCA do not form an addition compound with pyridine.) It was observed that the addition compound crystallizes out of solution. However, the results are not quantitative (refer to Table XIV).

Analysis of Viscous Material. The viscous material, which formed as a separate phase on the bottom of the reactor soon after the reaction temperature reached  $254^\circ\text{F}$ , was believed to be phosphoric

acid. Volumetric analysis was therefore used to identify the material. It may be pointed out that if the material were phosphorus pentachloride, the analysis would still hold since  $\text{PCl}_5$  hydrolyzes to form  $\text{HCl}$  and  $\text{H}_3\text{PO}_4$ . Table XV contains the results of the analysis. It is seen that the weight of  $\text{H}_3\text{PO}_4$  calculated from the analysis matches the sample weight rather closely. A qualitative test using silver nitrate to form a precipitate of silver salt of neutral sodium phosphate indicated that a phosphate was present.

Evaluation of Analytical Investigation. The only analytical method investigated that produced the desired results was the volumetric analysis for mixtures of MCA, DCA, and TCA as reported by Dalin<sup>(19)</sup>. For mixtures of these three acids, the analysis requires about 12 hours total time to run. If acetic acid is present, the analysis becomes quite long and involved. The method may show poor results when concentrations of DCA fall below 20 per cent, since the backbone of the analysis is the direct determination of DCA.

Further work on chromatography is not recommended because the finding of a suitable adsorbent will involve trial and error investigation and thus success depends to a great extent on chance.

Analysis by Physical Properties. Analysis of mixtures of chlorinated acetic acids may be more convenient by use of two physical properties. Use of density, refractive index, electrical conductivity, and viscosity, in that order should be considered. These properties must be measured at 70°C (158°F) or above, since MCA melts at 69°C. This temperature

limitation may prove to be undesirable. This method of using two physical properties to identify mixtures of three compounds may be particularly useful for mixtures of high MCA or TCA concentrations.



## B. Plant Design for Sodium Trichloroacetate

The accompanying plant design for the production of sodium trichloroacetic acid was made utilizing the information obtained in the pilot work of this investigation. Assumptions were made where data were not available.

General Specifications. In general, the plant design was to follow the process, plant capacity, and operating schedule set up by the Graduate Chemical Engineering Plant Design Class (1949-50) of the Virginia Polytechnic Institute in their plant designed to produce sodium trichloroacetate. Process improvements, indicated by the results of the experimental work, were to be incorporated into the design.

Chemical Process Considerations. Trichloroacetic acid was to be produced by the direct chlorination of acetic acid in the presence of red phosphorus, at a maximum temperature of 320°F (160°C), at atmospheric pressures, in the liquid phase, in the absence of actinic light, and utilizing excess chlorine.

The design was to be for a semi-batch process. Excess chlorine, for driving the reaction toward completion, was to be recovered and recycled. By-product hydrogen chloride was to be absorbed in water to form salable 22°Be acid. The TCA produced was to be neutralized with dry sodium carbonate, dried, pulverized and packed in 50-pound fibre drums.

Operating Schedule. The plant was to be an integral part of a weed-killing concern, and operated only in the interval between growing seasons. The entire output of the plant was to be used by the concern in its weed-killing activities. The plant was to be

designed for a capacity of 5,000 tons TCA per year, and was to be operated for 21 weeks, five days a week, and eight hours a day. The actual daily production operations were considered to be performed during only seven of the eight-hour work period. Thus, 105 days were available for production per annum, or 735 hours. Designed hourly production was then 13,606 pounds.

Concentration of TCA Produced. Since the wood-killing powers of MCA and DCA are nil, the final product should contain that percentage of TCA most economically produced. Utilizing information on equipment costs given in the design by the graduate plant design class and the pilot information of this investigation, the overall plant costs were estimated for producing products containing 50, 60, 70, 80, and 90 per cent concentrations of TCA. The results of these estimates, the estimated unit cost of TCA produced, and the estimated annual net income have been graphically presented in Figure 25.

The estimates show that the 70 and the 90 per cent TCA concentrations should be considered. The increased capital investment required by the 90 per cent over the 70 per cent product is \$1.3 million; but the annual net income is increased \$2.8 million. The 90 per cent product would more than pay for itself during the first year, and thus, is the desirable concentration.

Use of crystallization, and recycle of residual liquors, to produce a 90 per cent TCA product does not appear to be desirable. TCA would have to be produced in 80 per cent concentrations, requiring within one per cent the capital investment of normal 90

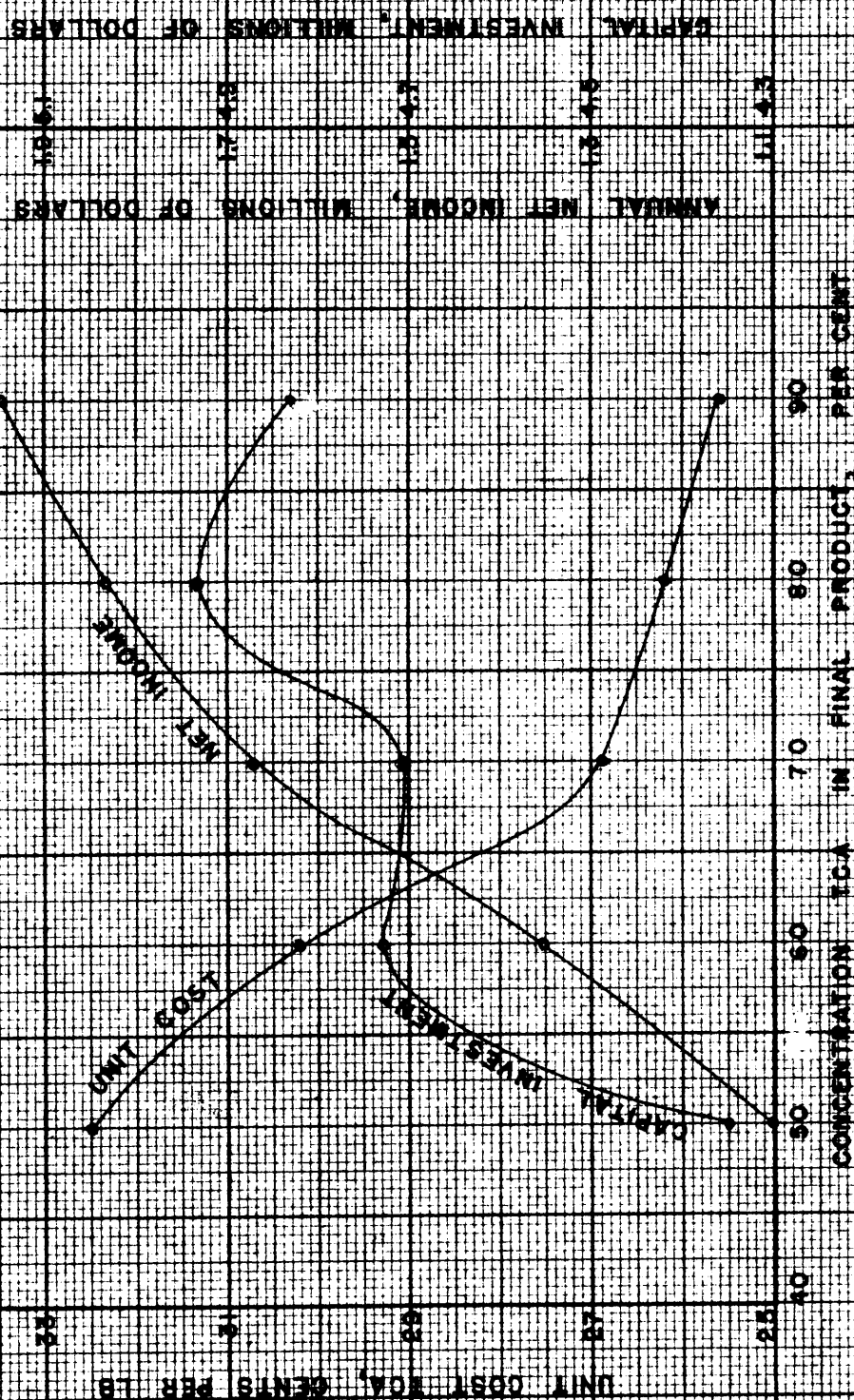


FIGURE 26. ESTIMATED UNIT COST, CAPITAL INVESTMENT, AND NET INCOME VERSUS CONCENTRATION OF TCA IN FINAL PRODUCT

per cent production, and recycling would require additional equipment, materials handling, and labor.

Data and Assumptions for Design. Trichloroacetic acid was produced in concentrations up to 82 per cent in the pilot work, and thus, the experimental data had to be extrapolated for use in designing for a 90 per cent product. However, the extrapolation was not considered likely to lead to erroneous results, since a five to six per cent increase in reaction time requirements would not affect the number of pieces or capacity of equipment necessary. This is due to the peculiarities in the plant operation.

In the discussion of the pilot work (page 120), it was shown that the reaction time required in the pilot work was about 46 per cent greater than that required by more efficient and commercial sized chlorinators. This factor was used in calculating the reaction time required for producing the 90 per cent product.

On page 117, it was shown that the loss of products during pilot work was excessive. Therefore, it was assumed that only half the losses that occurred during the pilot work would occur in the plant to be designed.

On the basis of the decisions given in the three previous paragraphs, the following were calculated and plotted in Figure 26: the degrees of chlorination, yields of TCA, and the reaction times at various concentrations of TCA. The design calculations were based on these curves.

The following data and assumptions were used for the plant design calculations:

1. TCA will be produced by the chlorination of glacial acetic acid in the presence of red phosphorus, between the temperatures of 68 and 320°F, at atmospheric pressures, and in the liquid phase.

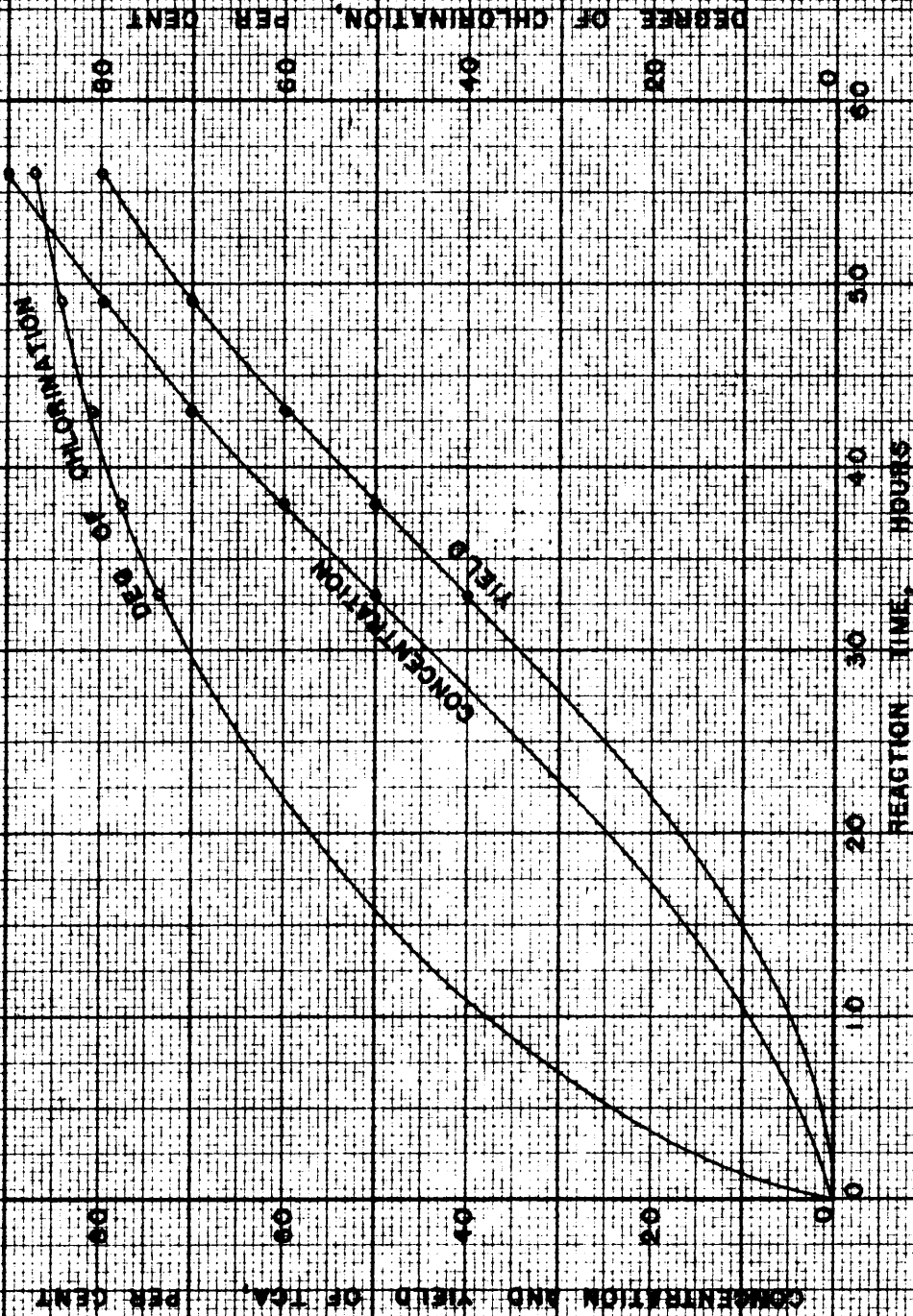


FIGURE 25. CONCENTRATION AND YIELD OF TCA, AND THE DEGREE OF CHLORINATION OF THE REACTION MASS VERSUS REACTION TIME

2. The raw materials will be assumed to have the following compositions:

glacial acetic acid	99.5 % $\text{CH}_3\text{COOH}$
	0.5 % $\text{H}_2\text{O}$
chlorine	100.0 % $\text{Cl}_2$
sodium carbonate	100.0 % $\text{Na}_2\text{CO}_3$
red phosphorus	100.0 % P

3. Red phosphorus will be required in the amount of 0.038 parts per part acetic acid charged to the reactor.

4. The reaction temperature will be maintained at  $212^\circ\text{F}$  during the first three hours of reaction. The temperature will then be raised steadily to  $320^\circ\text{F}$  at eight hours reaction time; the latter temperature being maintained within five degrees during the remainder of the chlorination.

5. The time required to produce TCA in 90 per cent concentrations will be 56 hours.

6. The yield of TCA, in 90 per cent concentrations, will be assumed to be 80 per cent by weight of the theoretical based on acetic acid.

7. The product from the chlorinators will be assumed to have the following composition:

$\text{CCl}_3\text{COOH}$	87.07 per cent
$\text{CHCl}_2\text{COOH}$	9.65
$\text{PCl}_5$	2.37
$\text{CCl}_3\text{COCl}$	0.88
$\text{CHCl}_2\text{COCl}$	0.01
$\text{H}_3\text{PO}_3$	0.015
$\text{H}_3\text{PO}_4$	0.005

8. The heavy, viscous phase in the final product of the chlorinators will amount to 0.059 parts per part acetic acid originally charged to the reactor. It will be assumed to have the following composition:

$H_3PO_3$	47.30 per cent
$H_3PO_4$	14.72
$CCl_3COOH$	34.10
$CHCl_2COOH$	3.88

9. There will be eight reactors in each battery for chlorinating acetic acid, one of the eight producing a finished product of TCA each day. Chlorine will be fed to the reactor of highest TCA concentration, from thence to the reactor of next highest TCA concentration, and so on. The rate of chlorine feed will be such that the gases entering the last reactor in the battery shall contain chlorine in 50 per cent excess of that required by the contents of the reactor.

10. Losses, occurring during the production of TCA, will be due to vaporization only.

11. Decomposition and polymerization of TCA and other products will be negligible.

12. Acetyls (dichloro- and trichloro-) appearing in the final product will be assumed to occur in the same weight ratio as HCA and TCA.

13. It will be assumed that all losses of intermediate and final products that occur during chlorination will be in the form of acetyls and acetic acid. Also, that half of the losses occurring will take place during the first third of the reaction period, and will consist of 60 per cent acetyl chloride, 20 per cent monochloroacetyl chloride, and 20 per cent acetic acid. The remainder of the losses will be assumed to be

distributed evenly over the rest of the reaction period and to consist of 40 per cent mono-, 40 per cent di-, and 20 per cent trichloroacetyl chloride.

14. It will be assumed that half the water entering with the acetic acid reacts with  $\text{POCl}_3$ , and the remaining half leaves in the waste gases.

15. It will be assumed that 30 weight per cent of the  $\text{H}_2\text{PO}_4$  and  $\text{H}_2\text{PO}_3$  formed will be dissolved in the TGA phase; the remainder forming a separate phase containing 25 per cent TGA and DGA by weight, in the same ratio as they occur in the TGA phase.

16. It will be assumed that all  $\text{POCl}_3$  not reacting will be lost as vapors, and that no  $\text{PCl}_5$  will be lost due to vaporization.

17. It will be assumed that one-fourth of the acetyls formed during the entire reaction period will be formed during the first seven hours of the reaction.

18. It will be assumed that one-third of the phosphorus charged to the chlorinator will be chlorinated to  $\text{PCl}_5$  during the first hour of reaction; that one-half will have been chlorinated during the first five hours; and all phosphorus will have been chlorinated after 14 hours of reaction.

19. It will be assumed that the heat of reaction during the first half-hour of the reaction period will liberate heat sufficient to raise the temperature of the reaction mass to  $250^\circ\text{F}$ . Cooling will be required to maintain temperature requirements during the first half-hour; thereafter, external heating will be necessary.



20. TCA will be neutralized with dry sodium carbonate. The temperature of the TCA before sodium carbonate addition will be 212°F (plus or minus ten degrees). The sodium carbonate will be added over a 30 minute period and the neutralized mass dried at 302°F (150°C).

21. It will be assumed that neutralization of TCA will not cause decomposition of the acid.

22. It will be assumed that 0.02 per cent of the final product will be lost in handling and packaging.

23. It will be assumed that the final product will contain 0.5 per cent water.

Proposed Flow Sheet. The proposed flow sheet for the production of sodium TCA is given in Figure 27.

Material Balance. The following material balance is based on a seven-hour day, the data being in pounds per hour.

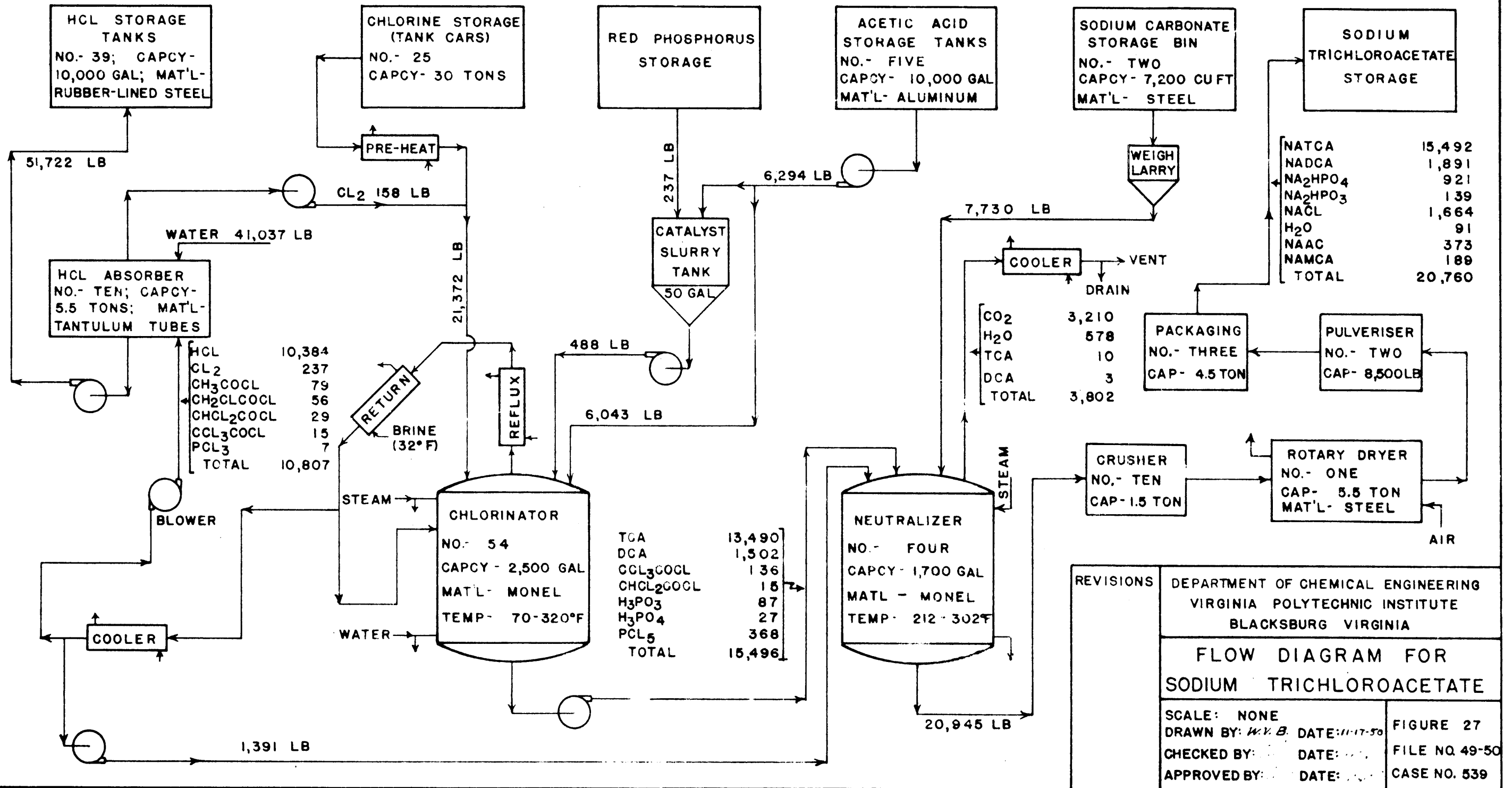
A-1. Red phosphorus storage.

Entering		Leaving	
From phosphorus freight car		To phosphorus slurry tank, B-1	
P . . . . .	237	P . . . . .	237

A-2. Acetic acid storage.

Entering		Leaving	
From acetic acid tank car		To acetic acid feed pump, A-3	
CH <sub>3</sub> COOH . . . . .	6,263	CH <sub>3</sub> COOH . . . . .	6,263
H <sub>2</sub> O . . . . .	31	H <sub>2</sub> O . . . . .	31
Total . . . . .	6,294	Total . . . . .	6,294

ALL WEIGHTS IN POUNDS PER HOUR



REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG VIRGINIA	
FLOW DIAGRAM FOR SODIUM TRICHLOROACETATE		
SCALE: NONE	FIGURE 27	
DRAWN BY: W.V.B. DATE: 11-17-50	FILE NO. 49-50	
CHECKED BY: DATE: .....	CASE NO. 539	
APPROVED BY: DATE: .....		

A-3. Acetic acid feed pump.

Entering		Leaving	
From acetic acid storage, A2		To chlorinators, B-3	
CH <sub>3</sub> COOH . . . . .	6,044	CH <sub>3</sub> COOH . . . . .	6,044
H <sub>2</sub> O . . . . .	30	H <sub>2</sub> O . . . . .	30
Total . . . . .	6,074	Total . . . . .	6,074
From acetic acid storage A2		To phosphorus slurry tank, B-1	
CH <sub>3</sub> COOH . . . . .	250	CH <sub>3</sub> COOH . . . . .	250
H <sub>2</sub> O . . . . .	1	H <sub>2</sub> O . . . . .	1
Total . . . . .	6,294	Total . . . . .	6,294

A-4. HCl storage.

Entering		Leaving	
From HCl pump, H-5		Stored	
HCl . . . . .	10,444	HCl . . . . .	10,444
H <sub>2</sub> O . . . . .	41,035	H <sub>2</sub> O . . . . .	41,035
Cl <sub>2</sub> . . . . .	93	Cl <sub>2</sub> . . . . .	93
CH <sub>3</sub> COOH . . . . .	60	CH <sub>3</sub> COOH . . . . .	60
CH <sub>2</sub> ClCOOH . . . . .	47	CH <sub>2</sub> ClCOOH . . . . .	47
CHCl <sub>2</sub> COOH . . . . .	26	CHCl <sub>2</sub> COOH . . . . .	26
CCl <sub>3</sub> COOH . . . . .	13	CCl <sub>3</sub> COOH . . . . .	13
H <sub>3</sub> PO <sub>3</sub> . . . . .	4	H <sub>3</sub> PO <sub>3</sub> . . . . .	4
Total . . . . .	51,722	Total . . . . .	51,722

A-5. Chlorine storage.

Entering		Leaving	
From producer		To chlorine vaporizer, A-6	
Cl <sub>2</sub> . . . . .	21,214	Cl <sub>2</sub> . . . . .	21,214

A-6. Chlorine vaporizer.

Entering		Leaving	
From chlorine storage, A-5		To chlorinator, B-3	
Cl <sub>2</sub> . . . . .	21,214	Cl <sub>2</sub> . . . . .	21,214

A-7. Na<sub>2</sub>CO<sub>3</sub> storage.

Entering		Leaving	
From Na <sub>2</sub> CO <sub>3</sub> conveyor, A-8		To weigh larry, A-9	
Na <sub>2</sub> CO <sub>3</sub> . . . . .	7,730	Na <sub>2</sub> CO <sub>3</sub> . . . . .	7,730

A-8. Na<sub>2</sub>CO<sub>3</sub> conveyor.

Entering		Leaving	
From freight car		To Na <sub>2</sub> CO <sub>3</sub> storage, A-7	
Na <sub>2</sub> CO <sub>3</sub> . . . . .	7,730	Na <sub>2</sub> CO <sub>3</sub> . . . . .	7,730

A-9. Weigh Larry.

Entering		Leaving	
From Na <sub>2</sub> CO <sub>3</sub> storage, A-7		To neutralizers, C-1	
Na <sub>2</sub> CO <sub>3</sub> . . . . .	7,730	Na <sub>2</sub> CO <sub>3</sub> . . . . .	7,730

A-10. NaTCA storage.

Entering		Leaving	
From packaging, G-1		Storage	
CCl <sub>3</sub> COONa . . . . .	15,492	CCl <sub>3</sub> COONa . . . . .	15,492
CHCl <sub>2</sub> COONa . . . . .	1,891	CHCl <sub>2</sub> COONa . . . . .	1,891
Na <sub>2</sub> HPO <sub>4</sub> . . . . .	921	Na <sub>2</sub> HPO <sub>4</sub> . . . . .	921
Na <sub>2</sub> HPO <sub>3</sub> . . . . .	139	Na <sub>2</sub> HPO <sub>3</sub> . . . . .	139
NaCl . . . . .	1,664	NaCl . . . . .	1,664
H <sub>2</sub> O . . . . .	91	H <sub>2</sub> O . . . . .	91
CH <sub>2</sub> COONa . . . . .	373	CH <sub>2</sub> COONa . . . . .	373
CH <sub>2</sub> ClCOONa . . . . .	189	CH <sub>2</sub> ClCOONa . . . . .	189
Total . . . . .	20,763	Total . . . . .	20,763

B-1. Phosphorus slurry tank.

Entering		Leaving	
From phos. storage, A-1		To phos. slurry pump, B-2	
P . . . . .	237	P . . . . .	237
		CH <sub>3</sub> COOH . . . . .	250
From HAc feed pump, A-3		H <sub>2</sub> O . . . . .	1
CH <sub>3</sub> COOH . . . . .	250	Total . . . . .	488
H <sub>2</sub> O . . . . .	1		
Total . . . . .	488		

B-2. Phosphorus slurry pump.

Entering		Leaving	
From phos. slurry tank, B-1		To chlorinators, B-3	
P . . . . .	237	P . . . . .	237
CH <sub>3</sub> COOH . . . . .	250	CH <sub>3</sub> COOH . . . . .	250
H <sub>2</sub> O . . . . .	<u>1</u>	H <sub>2</sub> O . . . . .	<u>1</u>
Total . . . . .	488	Total . . . . .	488

B-3. Chlorinator.

Entering		Leaving	
From HAc pump, A-3		To TCA pump, B-6	
CH <sub>3</sub> COOH . . . . .	6,044	CCl <sub>3</sub> COOH . . . . .	13,490
H <sub>2</sub> O . . . . .	<u>30</u>	CHCl <sub>2</sub> COOH . . . . .	1,502
Total . . . . .	6,074	CCl <sub>2</sub> COCl . . . . .	136
		CHCl <sub>2</sub> COCl . . . . .	15
From phos. slurry pump, B-2		PCl <sub>5</sub> . . . . .	368
CH <sub>3</sub> COOH . . . . .	250	H <sub>2</sub> PO <sub>3</sub> . . . . .	87
H <sub>2</sub> O . . . . .	237	H <sub>2</sub> PO <sub>4</sub> . . . . .	<u>21</u>
P . . . . .	<u>1</u>	Total . . . . .	15,625
Total . . . . .	488		

From Cl <sub>2</sub> vaporizer, A-6		To HCl cooler, H-1	
Cl <sub>2</sub> . . . . .	21,214	HCl . . . . .	10,384
From Cl <sub>2</sub> compressor, H-4		Cl <sub>2</sub> . . . . .	237
Cl <sub>2</sub> . . . . .	144	CH <sub>3</sub> COOH . . . . .	122
HCl . . . . .	11	CH <sub>2</sub> COCl . . . . .	276
H <sub>2</sub> O . . . . .	<u>3</u>	CH <sub>2</sub> ClCOCl . . . . .	239
Total . . . . .	158	CHCl <sub>2</sub> COCl . . . . .	147
Total . . . . .	27,903	CCl <sub>2</sub> COCl . . . . .	76
		POCl <sub>3</sub> . . . . .	684
		H <sub>2</sub> O . . . . .	19
		PCl <sub>3</sub> . . . . .	<u>14</u>
		Total . . . . .	12,198
		Total . . . . .	27,903

**B-6. TCA PUMP.**

Entering		Leaving	
From chlorinator, B-3		To neutraliser, C-1	
$\text{CCl}_3\text{COOH}$ . . . . .	13,490	$\text{CCl}_3\text{COOH}$ . . . . .	13,490
$\text{CHCl}_2\text{COOH}$ . . . . .	1,502	$\text{CHCl}_2\text{COOH}$ . . . . .	1,502
$\text{CCl}_3\text{COCl}$ . . . . .	136	$\text{CCl}_3\text{COCl}$ . . . . .	136
$\text{CHCl}_2\text{COCl}$ . . . . .	15	$\text{CHCl}_2\text{COCl}$ . . . . .	15
$\text{PCl}_5$ . . . . .	368	$\text{PCl}_5$ . . . . .	368
$\text{H}_3\text{PO}_3$ . . . . .	87	$\text{H}_3\text{PO}_3$ . . . . .	87
$\text{H}_3\text{PO}_4$ . . . . .	<u>21</u>	$\text{H}_3\text{PO}_4$ . . . . .	<u>21</u>
Total . . . . .	15,625	Total . . . . .	15,625

**C-1. Neutraliser.**

Entering		Leaving	
From TCA pump, B-6		To NaTCA conveyor, C-2	
$\text{CCl}_3\text{COOH}$ . . . . .	13,490	$\text{CCl}_3\text{COONa}$ . . . . .	15,495
$\text{CHCl}_2\text{COOH}$ . . . . .	1,502	$\text{CHCl}_2\text{COONa}$ . . . . .	1,891
$\text{CCl}_3\text{COCl}$ . . . . .	136	$\text{Na}_2\text{HPO}_4$ . . . . .	921
$\text{CHCl}_2\text{COCl}$ . . . . .	15	$\text{Na}_2\text{HPO}_3$ . . . . .	139
$\text{PCl}_5$ . . . . .	368	$\text{NaCl}$ . . . . .	1,664
$\text{H}_3\text{PO}_3$ . . . . .	87	$\text{H}_2\text{O}$ . . . . .	273
$\text{H}_3\text{PO}_4$ . . . . .	<u>21</u>	$\text{CH}_3\text{COONa}$ . . . . .	373
Total . . . . .	15,625	$\text{CH}_2\text{ClCOONa}$ . . . . .	<u>189</u>
		Total . . . . .	20,945

**From condensate pump, H-6**

$\text{POCl}_3$ . . . . .	684
$\text{CH}_3\text{COOH}$ . . . . .	122
$\text{CH}_3\text{COCl}$ . . . . .	197
$\text{CH}_2\text{ClCOCl}$ . . . . .	183
$\text{CHCl}_2\text{COCl}$ . . . . .	118
$\text{CCl}_3\text{COCl}$ . . . . .	61
$\text{H}_2\text{O}$ . . . . .	19
$\text{PCl}_3$ . . . . .	<u>7</u>
Total . . . . .	1,391

**To condenser, C-3**

$\text{CO}_2$ . . . . .	3,210
$\text{H}_2\text{O}$ . . . . .	979
$\text{CCl}_3\text{COOH}$ . . . . .	10
$\text{CHCl}_2\text{COOH}$ . . . . .	<u>3</u>
Total . . . . .	3,802
Total . . . . .	<u>24,746</u>

**From weigh lorry, A-9**

$\text{Na}_2\text{CO}_3$ . . . . .	<u>7,730</u>
Total . . . . .	24,746

C-2. NaTCA conveyor.

Entering		Leaving	
From neutralizer, C-1		To crusher, D-1	
$\text{CCl}_3\text{COONa}$	15,495	$\text{CCl}_3\text{COONa}$	15,495
$\text{CHCl}_2\text{COONa}$	1,891	$\text{CHCl}_2\text{COONa}$	1,891
$\text{Na}_2\text{HPO}_4$	921	$\text{Na}_2\text{HPO}_4$	921
$\text{Na}_2\text{HPO}_3$	139	$\text{Na}_2\text{HPO}_3$	139
$\text{NaCl}$	1,664	$\text{NaCl}$	1,664
$\text{H}_2\text{O}$	237	$\text{H}_2\text{O}$	237
$\text{CH}_3\text{COONa}$	373	$\text{CH}_3\text{COONa}$	373
$\text{CH}_2\text{ClCOONa}$	189	$\text{CH}_2\text{ClCOONa}$	189
Total	20,945	Total	20,945

C-3. Condenser.

Entering		Leaving	
From neutralizer, C-1		To atmosphere	
$\text{CO}_2$	3,210	$\text{CO}_2$	2,207
$\text{H}_2\text{O}$	579	$\text{H}_2\text{O}$	5
$\text{CCl}_3\text{COOH}$	10	Total	2,212
$\text{CHCl}_2\text{COOH}$	3		
Total	3,802	To drain	
		$\text{H}_2\text{O}$	574
		$\text{CO}_2$	1,003
		$\text{CCl}_3\text{COOH}$	10
		$\text{CHCl}_2\text{COOH}$	3
		Total	1,590
		Total	3,802

D-1. NaTCA crusher.

Entering		Leaving	
From conveyor, C-2		To NaTCA conveyor, D-2	
$\text{CCl}_3\text{COONa}$	15,495	$\text{CCl}_3\text{COONa}$	15,495
$\text{CHCl}_2\text{COONa}$	1,891	$\text{CHCl}_2\text{COONa}$	1,891
$\text{Na}_2\text{HPO}_4$	921	$\text{Na}_2\text{HPO}_4$	921
$\text{Na}_2\text{HPO}_3$	139	$\text{Na}_2\text{HPO}_3$	139
$\text{NaCl}$	1,664	$\text{NaCl}$	1,664
$\text{H}_2\text{O}$	273	$\text{H}_2\text{O}$	273
$\text{CH}_3\text{COOH}$	373	$\text{CH}_3\text{COONa}$	373
$\text{CH}_2\text{ClCOONa}$	189	$\text{CH}_2\text{ClCOONa}$	189
Total	20,945	Total	20,945

D-2. NaFCA conveyor.

Entering		Leaving	
From crusher, D-1		To rotary dryer, E-1	
$\text{CCl}_3\text{COONa}$	15,495	$\text{CCl}_3\text{COONa}$	15,495
$\text{CHCl}_2\text{COONa}$	1,891	$\text{CHCl}_2\text{COONa}$	1,891
$\text{Na}_2\text{HPO}_4$	921	$\text{Na}_2\text{HPO}_4$	921
$\text{Na}_2\text{HPO}_3$	139	$\text{Na}_2\text{HPO}_3$	139
$\text{NaCl}$	1,664	$\text{NaCl}$	1,664
$\text{H}_2\text{O}$	273	$\text{H}_2\text{O}$	273
$\text{CH}_3\text{COONa}$	373	$\text{CH}_3\text{COONa}$	373
$\text{CH}_2\text{ClCOONa}$	189	$\text{CH}_2\text{ClCOONa}$	189
Total	20,945	Total	20,945

E-1. Rotary dryer.

Entering		Leaving	
From conveyor, D-2		To NaFCA conveyor, E-2	
$\text{CCl}_3\text{COONa}$	15,495	$\text{CCl}_3\text{COONa}$	15,495
$\text{CHCl}_2\text{COONa}$	1,891	$\text{CHCl}_2\text{COONa}$	1,891
$\text{Na}_2\text{HPO}_4$	921	$\text{Na}_2\text{HPO}_4$	921
$\text{Na}_2\text{HPO}_3$	139	$\text{Na}_2\text{HPO}_3$	139
$\text{NaCl}$	1,664	$\text{NaCl}$	1,664
$\text{H}_2\text{O}$	273	$\text{H}_2\text{O}$	91
$\text{CH}_3\text{COONa}$	373	$\text{CH}_3\text{COONa}$	373
$\text{CH}_2\text{ClCOONa}$	189	$\text{CH}_2\text{ClCOONa}$	189
Total	20,945	Total	20,763

To atmosphere

$\text{H}_2\text{O}$	182
Total	20,945

E-2. NaFCA conveyor.

Entering		Leaving	
From rotary dryer, E-1		To pulverizer, F-1	
$\text{CCl}_3\text{COONa}$	15,495	$\text{CCl}_3\text{COONa}$	15,495
$\text{CHCl}_2\text{COONa}$	1,891	$\text{CHCl}_2\text{COONa}$	1,891
$\text{Na}_2\text{HPO}_4$	921	$\text{Na}_2\text{HPO}_4$	921
$\text{Na}_2\text{HPO}_3$	139	$\text{Na}_2\text{HPO}_3$	139
$\text{NaCl}$	1,664	$\text{NaCl}$	1,664
$\text{H}_2\text{O}$	91	$\text{H}_2\text{O}$	91
$\text{CH}_3\text{COONa}$	373	$\text{CH}_3\text{COONa}$	373
$\text{CH}_2\text{ClCOONa}$	189	$\text{CH}_2\text{ClCOONa}$	189
Total	20,763	Total	20,763



F-1. Pulverizer.

Entering		Leaving	
From conveyor, E-2		To NaTGA conveyor, F-2	
$CCl_3COONa$ . . . . .	15,495	$CCl_3COONa$ . . . . .	15,495
$CHCl_2COONa$ . . . . .	1,891	$CHCl_2COONa$ . . . . .	1,891
$Na_2HPO_4$ . . . . .	921	$Na_2HPO_4$ . . . . .	921
$Na_2HPO_3$ . . . . .	139	$Na_2HPO_3$ . . . . .	139
$NaCl$ . . . . .	1,664	$NaCl$ . . . . .	1,664
$H_2O$ . . . . .	91	$H_2O$ . . . . .	91
$CH_3COONa$ . . . . .	373	$CH_3COONa$ . . . . .	373
$CH_2ClCOONa$ . . . . .	189	$CH_2ClCOONa$ . . . . .	189
Total . . . . .	20,763	Total . . . . .	20,763

F-2. NaTGA conveyor.

Entering		Leaving	
From pulveriser, F-1		To packaging, G-1	
$CCl_3COONa$ . . . . .	15,495	$CCl_3COONa$ . . . . .	15,495
$CHCl_2COONa$ . . . . .	1,891	$CHCl_2COONa$ . . . . .	1,891
$Na_2HPO_4$ . . . . .	921	$Na_2HPO_4$ . . . . .	921
$Na_2HPO_3$ . . . . .	139	$Na_2HPO_3$ . . . . .	139
$NaCl$ . . . . .	1,664	$NaCl$ . . . . .	1,664
$H_2O$ . . . . .	91	$H_2O$ . . . . .	91
$CH_3COONa$ . . . . .	373	$CH_3COONa$ . . . . .	373
$CH_2ClCOONa$ . . . . .	189	$CH_2ClCOONa$ . . . . .	189
Total . . . . .	20,763	Total . . . . .	20,763

G-1. NaTGA packaging.

Entering		Leaving	
From conveyor, F-2		To NaTGA storage, A-10	
$CCl_3COONa$ . . . . .	15,495	$CCl_3COONa$ . . . . .	15,495
$CHCl_2COONa$ . . . . .	1,891	$CHCl_2COONa$ . . . . .	1,891
$Na_2HPO_4$ . . . . .	921	$Na_2HPO_4$ . . . . .	921
$Na_2HPO_3$ . . . . .	139	$Na_2HPO_3$ . . . . .	139
$NaCl$ . . . . .	1,664	$NaCl$ . . . . .	1,664
$H_2O$ . . . . .	91	$H_2O$ . . . . .	91
$CH_3COONa$ . . . . .	373	$CH_3COONa$ . . . . .	373
$CH_2ClCOONa$ . . . . .	189	$CH_2ClCOONa$ . . . . .	189
Total . . . . .	20,763	Total . . . . .	20,763

H-1. HCl cooler.

Entering	
From chlorinator, B-3	
HCl . . . . .	10,384
Cl <sub>2</sub> . . . . .	237
CH <sub>3</sub> COOH . . . . .	122
CH <sub>3</sub> COCl . . . . .	276
CH <sub>2</sub> ClCOCl . . . . .	239
CHCl <sub>2</sub> COCl . . . . .	147
CCl <sub>3</sub> COCl . . . . .	76
POCl <sub>3</sub> . . . . .	684
H <sub>2</sub> O . . . . .	19
PCl <sub>3</sub> . . . . .	14
Total . . . . .	<u>12,198</u>

Leaving	
Two condensate pump, B-6	
POCl <sub>3</sub> . . . . .	684
CH <sub>3</sub> COOH . . . . .	122
CH <sub>3</sub> COCl . . . . .	197
CH <sub>2</sub> ClCOCl . . . . .	183
CHCl <sub>2</sub> COCl . . . . .	118
CCl <sub>3</sub> COCl . . . . .	61
H <sub>2</sub> O . . . . .	19
PCl <sub>3</sub> . . . . .	<u>7</u>
Total . . . . .	1,991

To HCl blower, H-2	
HCl . . . . .	10,384
Cl <sub>2</sub> . . . . .	237
CH <sub>3</sub> COCl . . . . .	79
CH <sub>2</sub> ClCOCl . . . . .	56
CHCl <sub>2</sub> COCl . . . . .	29
CCl <sub>3</sub> COCl . . . . .	15
PCl <sub>3</sub> . . . . .	<u>7</u>
Total . . . . .	10,807
Total . . . . .	<u>12,198</u>

H-2. HCl blower.

Entering	
From HCl cooler, H-1	
HCl . . . . .	10,384
Cl <sub>2</sub> . . . . .	237
CH <sub>3</sub> COCl . . . . .	79
CH <sub>2</sub> ClCOCl . . . . .	56
CHCl <sub>2</sub> COCl . . . . .	29
CCl <sub>3</sub> COCl . . . . .	15
PCl <sub>3</sub> . . . . .	<u>7</u>
Total . . . . .	10,807

Leaving	
To HCl absorber, H-3	
HCl . . . . .	10,384
Cl <sub>2</sub> . . . . .	237
CH <sub>3</sub> COCl . . . . .	79
CH <sub>2</sub> ClCOCl . . . . .	56
CHCl <sub>2</sub> COCl . . . . .	29
CCl <sub>3</sub> COCl . . . . .	15
PCl <sub>3</sub> . . . . .	<u>7</u>
Total . . . . .	10,807

H-3. HCl absorber.

Entering	
From blower, H-2	
HCl . . . . .	10,384
Cl <sub>2</sub> . . . . .	237
CH <sub>3</sub> COCl . . . . .	79
CH <sub>2</sub> ClCOCl . . . . .	56
CHCl <sub>2</sub> COCl . . . . .	29
CCl <sub>3</sub> COCl . . . . .	15
PCl <sub>3</sub> . . . . .	7
Total . . . . .	<u>10,807</u>

Leaving	
To HCl pump, H-5	
HCl . . . . .	10,444
Cl <sub>2</sub> . . . . .	93
H <sub>2</sub> O . . . . .	41,035
CH <sub>3</sub> COOH . . . . .	60
CH <sub>2</sub> ClCOOH . . . . .	47
CHCl <sub>2</sub> COOH . . . . .	26
CCl <sub>3</sub> COOH . . . . .	13
H <sub>3</sub> PO <sub>3</sub> . . . . .	4
Total . . . . .	<u>51,722</u>

From water supply line	
H <sub>2</sub> O . . . . .	41,073
Total . . . . .	<u>51,860</u>

To Cl <sub>2</sub> compressor, H-4 . . . . .	
Cl <sub>2</sub> . . . . .	144
HCl . . . . .	11
H <sub>2</sub> O . . . . .	3
Total . . . . .	<u>158</u>
Total . . . . .	<u>51,860</u>

H-4. Chlorine compressor.

Entering	
From HCl absorber, H-3	
Cl <sub>2</sub> . . . . .	144
HCl . . . . .	11
H <sub>2</sub> O . . . . .	3
Total . . . . .	<u>158</u>

Leaving	
To chlorinator, B-3	
Cl <sub>2</sub> . . . . .	144
HCl . . . . .	11
H <sub>2</sub> O . . . . .	3
Total . . . . .	<u>158</u>

H-5. Hydrochloric acid pump.

Entering	
From HCl absorber, H-3	
HCl . . . . .	10,444
Cl <sub>2</sub> . . . . .	93
H <sub>2</sub> O . . . . .	41,035
CH <sub>3</sub> COOH . . . . .	60
CH <sub>2</sub> ClCOOH . . . . .	47
CHCl <sub>2</sub> COOH . . . . .	26
CCl <sub>3</sub> COOH . . . . .	13
H <sub>3</sub> PO <sub>3</sub> . . . . .	4
Total . . . . .	<u>51,722</u>

Leaving	
To HCl storage, A-4	
HCl . . . . .	10,444
Cl <sub>2</sub> . . . . .	93
H <sub>2</sub> O . . . . .	41,035
CH <sub>3</sub> COOH . . . . .	60
CH <sub>2</sub> ClCOOH . . . . .	47
CHCl <sub>2</sub> COOH . . . . .	26
CCl <sub>3</sub> COOH . . . . .	13
H <sub>3</sub> PO <sub>3</sub> . . . . .	4
Total . . . . .	<u>41,722</u>

B-6. Condensate pump.

Entering		Leaving	
From HCl cooler, H-1		To neutralizer, C-1	
POCl <sub>3</sub> . . . . .	684	POCl <sub>3</sub> . . . . .	684
CH <sub>2</sub> COCH <sub>3</sub> . . . . .	122	CH <sub>2</sub> COCH <sub>3</sub> . . . . .	122
CH <sub>2</sub> COCl . . . . .	197	CH <sub>2</sub> COCl . . . . .	197
CH <sub>2</sub> ClCOCl . . . . .	183	CH <sub>2</sub> ClCOCl . . . . .	183
CHCl <sub>2</sub> COCl . . . . .	118	CHCl <sub>2</sub> COCl . . . . .	118
CCl <sub>3</sub> COCl . . . . .	61	CCl <sub>3</sub> COCl . . . . .	61
H <sub>2</sub> O . . . . .	19	H <sub>2</sub> O . . . . .	19
PCl <sub>3</sub> . . . . .	7	PCl <sub>3</sub> . . . . .	7
Total . . . . .	1,391	Total . . . . .	1,391

Preliminary Calculations for Equipment Capacity. Preliminary calculations for equipment capacity appear in Table XVII. The calculations are based on hourly production and the maximum volume of materials handled by the equipment whether it be incoming or outgoing. Densities and specific gravities were taken or calculated from those values given in Table XVII.

Equipment Specifications. The following are the specifications for the equipment required to produce sodium TGA by the proposed process and at the proposed capacity.

A-1. Red phosphorus storage.

Capacity of area: Storage area for two weeks supply red phosphorus, 16,590 lb.

Character of material: Easily combustible.

Containers: 100-lb. drums.

Maximum drums stored: 166.

Dimensions of drum: 16 in. diam. X 21.5 in. height.

Drum arrangement: Drums arranged in racks, three drums high, drums lying horizontal, distance between drums - one inch horizontal and one foot vertically, racks 2.5 feet apart.

Floor area required: 153 ft.

Height of ceiling: 10 ft.

Type of floor: Monolithic concrete.

TABLE XVII

## Results of Preliminary Calculations for Equipment Capacity

No.	Equipment Title	Material Form	Phase	Weight	Temperature	Sp Gr	Density	Volume	
				lb/hr	°F		lb/cu ft	cu ft	gal
A-1	Phosphorus storage	P	S	237	68	2.20	137.0	1.7	12.9
A-2	Acetic acid storage	CH <sub>3</sub> COOH	L	6,263	68	1.05	65.5	95.6	715.0
A-3	Acetic acid pump	CH <sub>3</sub> COOH	L	6,263	68	1.06	65.5	95.6	715.0
A-4	Hydrochloric acid storage	HCl, H <sub>2</sub> O	L	51,722	86	1.12	69.9	741.0	5,540.0
A-5	Chlorine storage	Cl <sub>2</sub>	L	21,214	68	-	97.4	218.0	-
			G	21,214	68	-	0.0064	3,342,000.0	-
A-6	Chlorine vaporizer	Cl <sub>2</sub>	L	21,214	68	-	97.4	218.0	-
			G	21,214	68	-	0.0064	3,342,000.0	-
A-7	Sodium Carbonate stor.	Na <sub>2</sub> CO <sub>3</sub>	S	7,730	68	2.533	158.0	48.9	-
A-8	Na <sub>2</sub> CO <sub>3</sub> conveyor	Na <sub>2</sub> CO <sub>3</sub>	S	7,730	68	2.533	158.0	48.9	-
A-9	Weigh larry	Na <sub>2</sub> CO <sub>3</sub>	S	7,730	68	2.533	158.0	48.9	-
A-10	Sodium TCA storage	NaTCA imp.	S	20,945	68	0.90	56.1	370.0	-
B-1	Phosphorus slurry tank	P, CH <sub>3</sub> COOH	L	487	68	-	87.7	5.5	41.5
B-2	Phosphorus slurry pump	P, CH <sub>3</sub> COOH	L	487	68	-	87.7	5.5	41.5
B-3	Chlorinator	TCA, imp.	L	15,625	320	1.48	92.4	169.4	1,268.0
B-6	TCA pump	TCA, imp.	L	15,625	212	1.54	96.0	163.0	1,201.0
C-1	Neutralizer	TCA, Na <sub>2</sub> CO <sub>3</sub>	L	17,061	212	1.55	96.6	176.2	1,319.0
			S	7,730	68	2.53	158.0	48.9	-
C-2	NaTCA conveyor	NaTCA, imp.	S	20,945	302	0.95	59.2	354.0	2,640.0
D-1	Crusher	NaTCA, imp.	S	20,945	212-302	0.95	59.2	354.0	-
D-2	NaTCA conveyor	NaTCA, imp.	S	20,945	212	0.95	59.2	354.0	-
E-1	Rotary dryer	NaTCA, imp.	S	20,945	302	0.95	59.2	354.0	-
E-2	NaTCA conveyor	NaTCA, imp.	S	20,763	302	0.94	58.6	354.0	-
F-1	Pulverizer	NaTCA, imp.	S	20,763	140	0.94	58.6	354.0	-
F-2	NaTCA conveyor	NaTCA, imp.	S	20,763	86	0.90	56.1	370.0	-
G-1	NaTCA Packaging	NaTCA, imp.	S	20,763	86	0.90	56.1	370.0	-
H-2	HCl Blower	HCl, Cl <sub>2</sub>	G	10,807	32	-	0.102	106,000.0	-
H-3	HCl absorber	HCl	G	10,807	32	-	0.102	106,000.0	-
		H <sub>2</sub> O	L	41,073	59	-	62.42	660.0	4,935.0
H-4	Chlorine compressor	Cl <sub>2</sub>	G	158	86	-	0.180	879.0	-
H-5	Hydrochloric acid pump	HCl, H <sub>2</sub> O	L	51,722	86	1.12	69.9	741.0	5,540.0
H-6	Condensate pump	POCl <sub>3</sub> , HAc	L	1,391	32	1.66	103.6	1.3	10.1

S - Solid phase

L - Liquid phase

G - Gas phase

NaTCA - Sodium trichloroacetate

A-2. Glacial acetic acid storage.

No. required: Five.

Type: Horizontal, fabricated aluminum, closed construction.

Nominal capacity: 10,000 gal.

Character of contents: Glacial acetic acid at 20°C.

Over-all dimensions: Diameter 9 ft. 0 in., length 23 ft. 6 in.

Construction: Standard dished heads.

Connections: Inlet and outlet nozzles 6 in., drain 6 in., gage connections 1-1/2 in.

Material of construction: Aluminum metal.

Available from: General American Transportation Corp.

10 East 49th St., New York 17, N.Y.

A-3. Acetic acid pump.

No. required: One.

Rated capacity: 15 gal. per min.

Type: Buffalo's single suction full ball bearing enclosed impeller pump, no. 1-0L enclosed impeller

Character of liquid: Glacial acetic acid at 20°C.

Total head: 50 ft.

Size inlet: 1-1/2 in.

Size outlet: 1-1/2 in.

Material of construction: Stainless-steel (18-8 Mo) shaft, casing, and impeller, cast-iron base.

Motor: 3/4-hp., 3-phase, 220-volt, a.-c., General Electric Master, 1800 r.p.m.

Available from: Buffalo Pumps, Inc., 506 Broadway, Buffalo 5, N. Y.

A-4. Hydrochloric acid storage.

No. required: 39.

Type: Horizontal, all-weld steel, rubber lined.

Nominal capacity: 10,000 gal.

Character of contents: Hydrochloric acid at 30°C.

Over-all dimensions: Diameter 9 ft. 0 in., length  
23 ft. 6 in.

Construction: In accordance with A.S.M.E. Code U-68;

all-welded with dished heads; shell thickness

1/2 in., head thickness, 5/16 in.

Connections: Inlet and outlet nozzles 3 in., drain 6 in.,  
pressure-vacuum vent valve nozzle.

Material of construction: Rubber-lined mild steel.

Available from: General American Transportation Corp.,

10 East 49th St., New York 17, N.Y.

A-5. Chlorine storage.

Capacity of area: Storage space for two weeks supply liquid  
chlorine, twenty five 30-ton tank cars.

Containers: 30-ton tank cars.

Max. cars stored: 25.

Dimensions of car: Length 33 ft. 10 in., height of  
discharge connection above tank rail 11 ft. 5 in.

Area required: 14,400 sq. ft.

Height of ceiling: 15 ft.

A-6. Chlorine vaporizer.

No. required: One.

Type: Pfandler type FTS, single pass tube side heat exchanger.

Heat transfer area: 290 sq. ft.

Service: Vaporize 21,214 lb. chlorine per hour.

Tube size: 1/2 in. No. 16 BWG copper.

Average length of tubes: 6 ft.

Shell dimensions: Nominal 16 in. diameter, 99 in. over-all length.

Connections: Liquid chlorine inlet 3 in., chlorine gas outlet

8 in., hot water connections 1-1/2 in.

Max. pressure: 160 lb. per sq. in.

Available from: The Pfandler Co., Rochester 3, N.Y.

A-7. Sodium carbonate storage.

No. required: Two.

Type: Readco storage bin, cross feed conveyor.

Capacity: 7,200 cu. ft.

Character of contents: Sodium carbonate, crystalline powder,

bulk density 38 lb. per cu. ft.

Over-all dimensions: Length 20 ft., width 20 ft., height 22 ft.,

minimum angle of repose 45 deg.

Construction: Sheet steel, air tight construction.

Connections: Discharge by multipitch screw conveyor, rate of  
discharge 1240 lb. per hr., rate of charge 480 ton per hr.

Material of construction: Mild steel.

Available: Read Machinery Division, Standard Stokes Co., Inc.,  
York, Pa.



A-8. Sodium carbonate conveyor.

No. required: Two.

Type: Pneumatic.

Capacity: Four tons per minute.

Character of material: Sodium carbonate, crystalline powder,  
density 38 lb. per cu. ft.

Size of conveyor: Dracoo's 4 in. hose nozzle.

Available from: Dracoo Corporation, 4069 East 116th St.,  
Cleveland 5, Ohio.

A-9. Weigh LARRY.

No. required: Two.

Type: Link-Belt travelling weigh larry of 2,000 lb. capacity,  
motor-propelled with gate operating mechanism to center hopper.

Capacity: 2,000 lb.

Character of material: Powdered sodium carbonate.

Hopper dimensions: Length 4 ft., width 2 ft. 10 in., height 3 ft.,  
with chute 7 ft. long.

Track gauge: Width 5 ft. 4 in.

Track length: 45 ft.

Scale position: 7 ft. 6 in. below top of tank.

Track mounting: Track to be supported on overhead beams.

Motor: 2 hp., 220-volt, 60 cycle, 3-phase, a.-c. squirrel-  
cage induction, General Electric, 1,150 r.p.m.

Material of construction: Mild steel.

Available from: Link-Belt Co., 301 W. Pershing Rd., Chicago, Ill.

A-10. Sodium trichloroacetate storage.

Capacity of area: Storage of annual production of sodium TCA, 1,453,410 lb.

Containers: 50-lb. fiber drums.

Max. drums stored: 304,217.

Height of drum storage pile: five drums.

Dimensions of drum: One ft. diameter, 1 ft. 6 in. height.

Floor area required: 61,100 sq. ft.

Height of ceiling: 10 ft.

B-1. Phosphorus slurry tank.

No. required: Two.

Type: Buffalo type B-2, fabricated monel kettle with a standard dished bottom.

Nominal capacity: 50 gal.

Character of contents: Red phosphorus suspended in glacial acetic acid.

Over-all dimensions: Diameter 2 ft. 0 in., straight height 2 ft. 3 in.

Construction: 1/4-in. monel metal, fabricated closed tank.

Connections: Top and bottom.

Top-

1. Manhole, quick-opening cover, Type ME-1/2, diam. 12 in.

2. Inlet, 1-1/2 in. nozzle, Type N-1.
3. Vent, one in. nozzle, Type N-1.
4. Agitator, double propeller off-center agitator, Type A-11, 1/2 hp., Monel propeller and shaft, bronze bearings; drive by direct connected, right angle motor drive with spiral gears; motor- 1/2 hp., 220-volt, 3-phase, 60-cycle, a.-c., squirrel-cage induction, 1800 r.p.m.; gear ratio 5 to 1, agitator 66-150 r.p.m.

Bottom-

Flanged outlet, Type O-1, quick opening gate valve, 4 in.

Supports: Four 3-1/2 in. pipe legs, 12 in. from floor to flanged gate valve.

Material of construction: Monel.

Available from: Buffalo Foundry and Machine Co., Buffalo, N. Y.

B-2. Phosphorus slurry pump.

No. required: One.

Rated capacity: 3,000 gal. per hour.

Type: Single acting diaphragmpump.

Character of liquid: Phosphorus suspended in glacial acetic acid.

Total head: 10 ft.

Size inlet: Three inches.

Size outlet: Three inches.

Material of construction: Hastelloy C.

Motor: 2-1/2-hp., 3-phase, 220-volt, a.-c., General

Electric Master, 1750 r.p.m.

Available from: T. Shriver and Co., Inc., Harrison, N. J.

### B-3. Chlorinator.

No. required: 54.

Type: Buffalo Type B-2, fabricated monel construction.

Nominal capacity: 2,400 gal.

Character of contents: Glacial acetic acid, mixed chlorinated acetic acids, hydrogen chloride, chlorine, acetyl chloride, chloroacetyl chlorides, and red phosphorus.

Over-all dimensions: Eight ft. inside diam., 8 ft. 8 in. outside (jacket) diam., 75 in. straight height.

Construction: Monel metal, 1/2 in. thick, fabricated closed reactor with standard dished top and bottom.

Connections: Top and bottom.

Top-

1. Manhole, Type MB-2, 18 in. diam.
2. Acetic acid inlet, 2-1/2 in.
3. Chlorine inlet, 8 in.
4. Gas outlet, 8 in.
5. Vision peephole, 4 in.
6. Pressure release opening, 8 in.

7. Light-source hole, 4 in.
8. Temperature recorder opening 1/2-in.,  
to extend down inside the reactor 4 ft. 6 in.
9. Agitator, Type A-9, multiple vane, turbine type,  
diam. of propeller 24 in.; gear drive, type B-6,  
(operating in oil tight housing), gear ratio 5 to 1;  
motor, 25-hp., 220-volt, 3-phase, 60 cycle, a.-c.,  
squirrel-cage induction motor, 1800 r.p.m.

Bottom- six in. outlet, Type O-1, with flush seat valve  
having side outlet.

Heating jacket: Type H-1, covers bottom and sides up to three ft.  
straight height above bottom, area 120 sq. ft., steam rate  
1,090 cu. ft. per hr. at 150 lb. per sq. in.

Chlorine distributor: Ring distributor, 3-1/2 in. nom. size monel  
pipe, 1/4-in. holes drilled in opposite sides, two holes to the  
inch, outside ring diam. 48 in.

Supports: Six 3-1/2-in. pipe legs, four feet length.

Available from: Buffalo Foundry and Machine Co.,  
1635 Fillmore Av., Buffalo, N.Y.

#### B-4. Reflux Condenser.

No. required: 5.

Type: Pfandlar type PFH, monel tube, single pass tube side condenser.

Condensing surface: 135 sq. ft.

Dimensions: Nominal diam. 12 in., over-all length 6 ft. 8 in.

Tube size: 3/4-in. 16 BWG.

Tube length: 6 ft.

Materials of construction: Cast iron shell, monel tubes.

Connections: Vapor inlet 7 in., vapor outlet 7 in.,

cooling water connections 1-1/2 in.

Available from: The Pfandler Co., Rochester 3, N.Y.

**B-5. Return Condenser.**

No. required: 54.

Type: Pfandler type PFH, monel tube, single pass tube side condenser.

Condensing surface: 135 sq. ft.

Dimensions: Nominal diam. 12 in., over-all length 6 ft. 8 in.

Tube size: 3/4-in. BWG 16.

Materials of construction: Cast iron shell, monel tubes.

Connections: Vapor inlet 7 in., vapor outlet 7 in., cooling water connections 1-1/2 in.

Available from: The Pfandler Co., Rochester 3, N.Y.

**B-6. TGA Pump.**

No. required: Six.

Type: Single acting diaphragm pump.

Rated capacity: 3,000 gal. per hour.

Character of liquid: Mixture of chlorinated acetic acids.

Total head: 10 ft.

Size inlet: Three inches.

Size outlet: Three inches.

Material of construction: Hastalloy C.

Motor: 2-1/2-hp., 3-phase, 220-volt, a.-c., General Electric Master, 1750 r.p.m.

Available from: T. Shriver and Company, Inc., Harrison, N.J.

C-1. Neutralizer.

No. required: Four.

Type: Seamless jacketed, oval-shaped monel kettle.

Nominal capacity: 1,700 gal.

Character of contents: Chlorinated acetic acids, phosphoric acid,  
sodium carbonate.

Over-all dimensions: 6 ft. 9 in. diam., 6 ft. 9 in.  
straight height.

Construction: Monel metal, 3/8-in. thick, fabricated  
closed kettle.

Connections: Top and bottom.

Top- Dished shaped top with TCA inlet 6 in., sodium  
carbonate inlet nozzle 8 in., gas outlet 8 in.; agitator,  
style D mixer, double motion agitator, direct connected  
vertical gear motor drive, gear ratio 50 to 1; motor  
25-hp., 220-volt, 3-phase, 60 cycle, a.-c., squirrel-  
cage induction, 1,800 r.p.m.

Bottom- bottom outlet for solid mass 8 in., with flush seat  
valve having bottom outlet.

Heating jacket: Covers bottom and sides up to one and  
one-half ft. from top, heating area 75 sq. ft., steam rate  
644 lb. per hour at 150 lb. per sq. in., gage.

Supports: Four 3-in. pipe legs, four foot length.

Available from: Buffalo Equipment Division, Bliss-Knox Co.,  
Buffalo 11, N.Y.

C-2. Sodium TGA conveyor.

No. required: Eight.

Type: Screw Conveyor.

Capacity: 1,100 cu. ft. per hr.

Character of material handled: Sodium trichloroacetate, 2 in. diameter and smaller particles.

Dimensions: 9 in. diam., 10 ft. length.

Material of construction: Mild steel.

Available from: Chain Belt Co. (Perry's Handbook, p. 2232).

C-3. Condenser.

No. required: One.

Type: Pfandler type PFH, monel tube, single pass tube side condenser.

Condensing surface: 135 sq. ft.

Dimensions: Nominal diam. 12 in., over-all length 6 ft. 8 in.

Tube size: 3/4-in. 16 BWG.

Tube length: 6 ft.

Materials of construction: Cast iron shell, monel tubes.

Connections: Vapor inlet 7 in., gas outlet 7 in., cooling water connections 1-1/2 in.

Available from: The Pfandler Co., Rochester 3, N.Y.



D-1. Crusher.

No. required: Ten.

Type: Universal jaw crusher, no. 9.

Capacity: One to 1.5 tons per hour.

Duty: To crush 10.5 tons sodium trichloroacetate per hour from  
1/2 to 2 in. lumps to 1/4 in. or finer particles.

Available: Williams Patent Crusher and Pulverizer Co.,  
St. Louis, Mo.

D-2. Sodium TCA conveyor.

No. required: 10.

Type: Screw conveyor.

Capacity: 105 cu. ft. per hr.

Character of material handled: Sodium trichloroacetate,  
1/4-in. diam. and smaller.

Dimensions: 4 in. diam., 8 ft. length.

Material of construction: Mild steel.

Available from: Chain Belt Co. (Perry's Handbook, Milwaukee,  
Wis. p. 2232).

E-1. Rotary Dryer.

No. required: One.

Type: Atmospheric rotary dryer with agitator.

Capacity: 11,000 lb. per hr.

Character of contents: Sodium trichloroacetate, 1/4-in. diam.  
and smaller particles.

Dimensions: 4 ft. diameter, 15 ft. length.

Connections: Proper openings for charging and discharging.

Agitator: Helical type.

Heating jacket: steam rate 2,000 lb. per hr. of 150 lb. per sq. in., gage steam.

Materials of construction: Stainless steel.

Available from: Bufflovak Equipment Division, Blaw-Knox Co., Buffalo, N.Y.

**E-2. Sodium TCA conveyor.**

No. required: Two.

Type: Screw conveyor.

Capacity: 315 cu. ft. per hr.

Character of contents: Sodium trichloroacetate, 1/4-in. diam. and smaller.

Dimensions: 6 in. diam., 10 ft. lengths.

Material of construction: Mild steel.

Available from: Chain Belt Co., Milwaukee, Wis.

**F-1. Pulverizer.**

No. required: Two.

Type: Raymond roller mill.

Capacity: 8,500 lb. per hr.

Character of contents: Sodium trichloroacetic acid, 1/4 in. diam. and smaller particles.

Size: Raymond No. 4 roller mill.

Available: Combustion Engineering Co., Inc., Raymond Pulverizer Division, Chicago 22, Ill.

F-2. Sodium TGA conveyor.

No. required: Nine.

Type: Screw conveyor.

Capacity: 315 cu. ft. per hr.

Character of contents: Sodium trichloroacetate, 75-mesh and smaller.

Dimensions: 6 in. diam., 10 ft. lengths.

Material of construction: Mild steel.

Available from: Chain Belt Co., Milwaukee, Wis.

G-1. Packaging.

No. required: Three.

Type: Automatic weighing device, type S.C.A.

Capacity: 9,000 lb. per hr.

Character of contents: Sodium trichloroacetate, density 56.1 lb. per cu. ft., dry powder, 75-mesh and smaller.

Size: Type S.C.A., size no. 4, Edtbauer-Duplex Automatic Net Weigher, with No. 21 Vibrox container packer, No. 176N Ideal ball bearing metal elevator, and packing table with belt carrier.

Available: B. F. Gump, Co., 441 S. Clinton St., Chicago 7, Ill.

H-1. HCl Cooler.

No. required: One.

Type: Pfaudler type PFH, single pass tube side.

Condensing surface: 135 sq. ft.

Dimensions: 12 in. diam., 6 ft. 8 in. over-all length.

Connections: Vapor inlet 8 in., gas outlet 8 in., cooling medium inlet and outlet 1-1/2 in.

Material of construction: Monel tubes, cast iron shell.

Available from: The Pfaudler Co., Rochester 4, N.Y.

## H-2. HCl Blower.

No. required: One.

Type: Armored chemical stoneware exhauster.

Capacity: 110,000 cu. ft. per hour.

Character of material handled: Hydrogen chloride, chlorine.

Size: Size 102, chemical stoneware exhauster, suction diam. 8 in., discharge diam. 8 in., max. speed 1,200 r.p.m., max. draft 3-1/2 in. water.

Motor: 3-hp., 220-volt, 3-phase, 60 cycle, a.-c.,

General Electric Master, 1200 r.p.m.

Available from: General Ceramics and Steatite Corp.

Chemical Equipment Division, Kearsbey, N.J.

## H-3. HCl Absorber.

No. required: Ten.

Type: Rand-Klein HCl absorber.

Capacity: 1,134 lb. HCl per hour.

Size of absorber: Cross sectional area of tower 5.94 sq. ft., over-all height of tower 12 ft. 5 in., cooling tubes per rack 11, no. racks 21, max. volume entering gas 1,770 cu. ft. per min., cooling water required (at 15°C) 65 gal. per min.

Operating pressure: One to two atmospheres.

Connections: Gas inlet 15 in., gas outlet 3 in., cooling water inlet and outlet 2 in., feed water inlet (two) 2 in., acid outlet 3 in.

Construction: Frame support of angle iron, permutite shell, tantulum cooling tubes, and berl saddle packing.

Available from: Maurice A. Knight, Akron 9, Ohio.

H-4. Chlorine compressor.

No. required: One.

Type: Chemical stoneware, rotary-type, liquid piston compressor.

Rated capacity: 124 cu. ft. per min.

Character of material handled: Chlorine with two per cent moisture.

Service: Intermittent.

Discharge pressure: 69 in. mercury, gage.

Size: Size VC-2, 1750 r.p.m.

Connections: Suction and discharge diameter 2-1/2 in.

Material of construction: Chemical stoneware.

Available from: General Ceramics and Steatite Corp.,  
Chemical Equipment Division, Keasbey, N.J.

H-5. Hydrochloric acid pump.

No. required: One.

Type: Chemical stoneware, centrifugal.

Rated capacity: Max. 190 gal. per min.

Character of material handled: 22<sup>0</sup>Be hydrochloric acid at  
30<sup>0</sup>C, sp. gr. 1.12.

Service: Continuous.

Total head: 25 ft.

Size: Size ZP-3, max. head 47 ft., 1800 r.p.m.

Connections: Discharge diam. 1-1/2 in., suction diam. 2 in.

Motor: One hp., 220-volt, 3-phase, 60-cycle, a.-c.,

General Electric Master, 1800 r.p.m.

Available from: General Ceramics and Steatite Corp.,

Chemical Equipment Division, Keasbey, N.J.

#### H-6. Condensate pump.

No. required: One.

Type: Centrifugal chemical stoneware pump.

Rated capacity: Max. 50 gal. per min.

Character of material handled: Phosphoryl chloride, acetyl  
chloride, and acetic acid.

Service: Continuous.

Total head: 15 ft.

Size: Size ZP-1, chemical stoneware centrifugal pump, max. head  
33 ft., 2350 r.p.m.

Connections: Suction and discharge diameter one in.

Motor: One-half hp., 220-volt, 3-phase, 60-cycle, a.-c.,

General Electric Master, 1800 r.p.m.

Available from: General Ceramics and Steatite Corp.,

Chemical Equipment Division, Keasbey, N.J.

Recording Flow Meter for Absorption Tower, B-3.

No. required: One.

Type: Bristol 1140-M, recording flow meter with indicating scale.

Medium to be measured: Water at 15°C.

Chart No.: F-40000, 2 $\frac{1}{2}$ -hour.

Power: 110-volt, 60-cycle, a.-c., single phase.

Flow estimate: 2,500 to 3,500 gal. per hr., normal flow 3,000 gal.

Pipe size: 3-1/2 in.

Primary device: Orifice.

Available from: The Bristol Co., 119 Bristol Rd., Waterbury 91,  
Conn.

Recording and Controlling Flow Meter for chlorine flow to B-3.

No. required: Six.

Type: Bristol model 11-5040-M, Ampliset controlling and recording  
flow meter.

Chart No.: F-50000, 2 $\frac{1}{2}$ -hour.

Chart drive: 110-volt, 60-cycle, a.-c., single phase.

Medium to be measured: Liquid chlorine at 20°C, sp gr 1.411,  
flow 3.5 ( $\pm$  0.2) gal. per min.

Pipe size: Eight inch.

Primary device: Orifice.

Controlling device: Pneumatic Synchro Diaphragm Control Valve.

Air pressure available: 25 lb. per sq. in., gage.

Available from: The Bristol Co., 119 Bristol Rd.,  
Waterbury 91, Conn.

Controlling Flow Meter for acetic acid feed to B-3.

No. required: One.

Type: Bristol Model 11-5040-M, Ampliset controlling and recording flow meter.

Chart No.: F-1500, 24-hour.

Chart drive: 110-volt, 60-cycle, a.-c., single phase.

Medium to be measured: Liquid glacial acetic acid at 20°C,  
sp. gr. 1.041, flow 194 gal. per min.

Pipe size: 2-1/2 in.

Primary device: Orifice.

Controlling device: Pneumatic Synchro Diaphragm Control Valve.

Air pressure available: 25 lb. per sq. in., gage.

Available from: The Bristol Co., 119 Bristol Rd., Waterbury 91,

Cycle Controller for acetic acid feed to B-3.

No. required: One.

Type: Bristol Impulse-sequence cycle controller, Model C-500.

Chart No.: 84486, 0 to 60 minutes.

Chart drive: 110-volt, 60-cycle, a.-c., single phase.

Medium to be controlled: Liquid glacial acetic acid at 20°C.

Controller: Two and one-half-inch Pneumatic Synchro Diaphragm control valve.

Air pressure available: 25 lb. per sq. in., gage.

Time cycle operation: Cycle performed once a day; to open and close according to schedule six control valves; the valves regulate the flow of acetic acid to chlorinators.

Available from: The Bristol Co., 119 Bristol Rd., Waterbury 91, Conn.



Pressure Controller for exit gases From Chlorinators. B-3.

No. required: One.

Type: Bristol Convertible Free Vane Air Operated Pressure  
Controller R-5C40-MF, Ampliset.

Medium to be controlled: Hydrogen chloride and chlorine gas  
mixture at 0°C.

Controller: Fifteen-inch Pneumatic Synchro Diaphragm Control  
Valve, direct acting; to maintain gas pressure at 15 ( $\pm 1$ ) lb.  
per sq. inch, absolute.

Chart range: Range from 0 to 50 lb. per sq. in., abs., with  
average pressure of 15 lbs.

Chart rotation: Twenty-four-hour, electrically operated chart,  
110-volt, 60-cycle, a.-c., single phase.

Air pressure available: 25 lb. per sq. in., gage.

Available from: The Bristol Co., 119 Bristol Rd., Waterbury 91,  
Conn.

Automatic Temperature Controller for Chlorinators. B-3.

No. required: 54.

Type: Taylor 5704-124, "Duhl-Duty."

Actuating medium: Mercury.

Chart No.: Cat. No. 220, 25-hour, 60 to 220°C, two-  
degree scale divisions.

Application: To control the temperature of chlorinated acetic acids  
at 100°C and at 160°C ( $\pm 5$ ), by manual setting of the control  
point, control accomplished by regulating steam or cooling water

Flow to chlorinator jacket.

Medium to be measured: Liquid chlorinated acetic acids.

Type of thermometer bulb: Standard long immersion, nickel-plated steel bulb.

Connecting tubing and ambient temperature: 100 ft.

Accuracy tubing subjected to ambient temperatures of 15 to 40°C.

Controller action: Direct.

Power: 110-volt, 60-cycle, a.-c., single phase.

Air pressure available: 25 lb. per sq. in., gage.

Type control valve: Pneumatic Synchro Diaphragm Direct Action Control Valve for steam flow; pneumatic Synchro Diaphragm reverse action control valve for cooling water flow.

Available from: Taylor Instrument Companies, Rochester 1, N.Y.

Safety Head Rupture Disc for Chlorine Gas Holding Tank.

No. required: One.

Type: Black, Sivalls, and Bryson bolted type safety head assembly no. 2.

Flange: A.S.A. Bolting Pattern 150, six-in. steel flange.

Diaphragm: Six-in. monel, rating 60 ( $\pm 3$ ) lb. per sq. in., gage; six diaphragms required.

Available from: Black, Sivalls and Bryson, Inc., Kansas City, Mo.

Safety Head Rupture Disc for Chlorinators, B-1.

No. required: 54.

Type: Black, Sivalis, and Bryson bolted type safety head assembly no. 2.

Flange: A.S.A. Bolting Pattern 150, eight-in. steel flange.

Diaphragms: Eight-inch monel, rating 35 ( $\pm 2$ ) lb. per sq. in., gage; two diaphragms required per assembly.

Available from: Black, Sivalis, and Bryson, Inc., Kansas City, Mo.

Temperature Controller for Rotary Dryer, E-1.

No. required: One.

Type: Taylor 5781-124, "Single-Duty".

Actuating medium: Mercury.

Chart: Cat. No. 220, 24-hour, 60 to 220°C, two-deg. scale divisions.

Applications: To control temperature of dryer at 150°C by regulating steam flow to jacket.

Medium to be measured: Sodium trichloroacetate.

Distance bulb must extend into apparatus: One in.

Connecting tubing and ambient temperature: 40 ft. of tubing subjected to ambient temperatures of 25 to 35°C.

Controller action: Direct.

Power: 110-volt, 60-cycle, a.-c., single phase.

Type of control valve: Three-inch direct acting diaphragm valve to control steam at 150 lb. per sq. in., gage.

Air pressure available: 25 lb. per sq. in., gage.

Available from: Taylor Instrument Companies, Rochester 1, N.Y.

Temperature Controller for Neutralizer. C-1.

No. required: One.

Type: Taylor 5784-124, "Dahl-Duty."

Actuating medium: Mercury.

Chart No.: Cat. No. 220, 24-hour, 60 to 220°C, two-degree scale divisions.

Application: To control the temperature of sodium trichloroacetate at 150°C (±5), by regulating steam flow to jacket.

Medium to be measured: Sodium trichloroacetate.

Distance bulb must extend into apparatus: 1-1/2 in.

Connecting tubing and ambient temperature: 50 ft. of tubing subjected to ambient temperatures of 25 to 35°C.

Controller action: Direct.

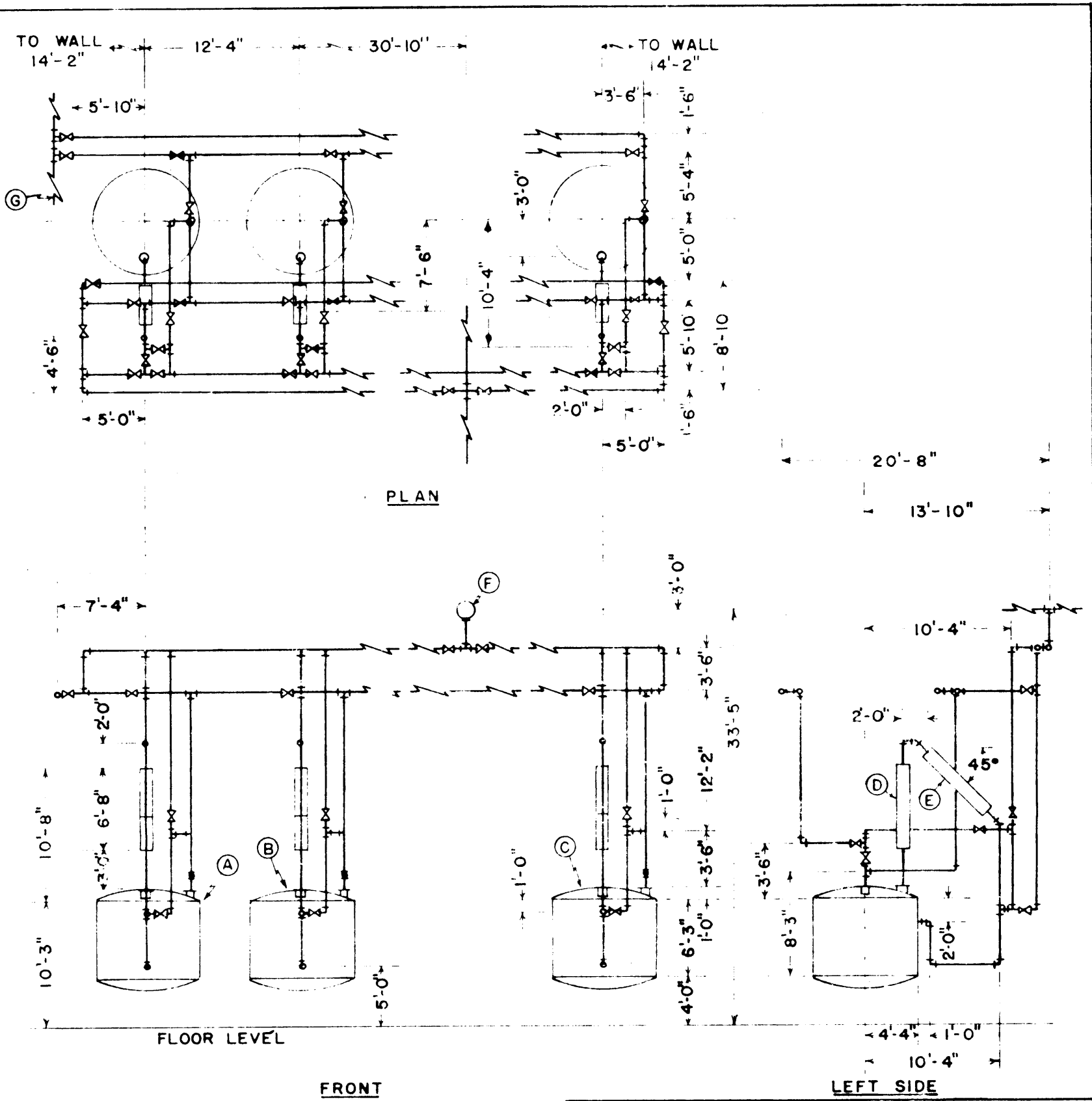
Power: 110-volt, 60-cycle, a.-c., single phase.

Type of control valve: 2-1/2 in. direct acting diaphragm valve to control steam at 150 lb. per sq. in., gage.

Air pressure available: 25 lb. per sq. in., gage.

Available from: Taylor Instrument Companies, Rochester 1, N.Y.

Plant Layout. The plant layout has been given in Figures 28 to 34, in the following sections: liquid manifold system for chlorinators, Figure 28; liquid manifold system for chlorinators, Figure 29; chlorinator section, Figure 30; neutralization - packaging section, Figure 31; HCl absorption section, Figure 32; storage section, Figure 33; and the building and grounds section, Figure 34.



PLAN

FLOOR LEVEL

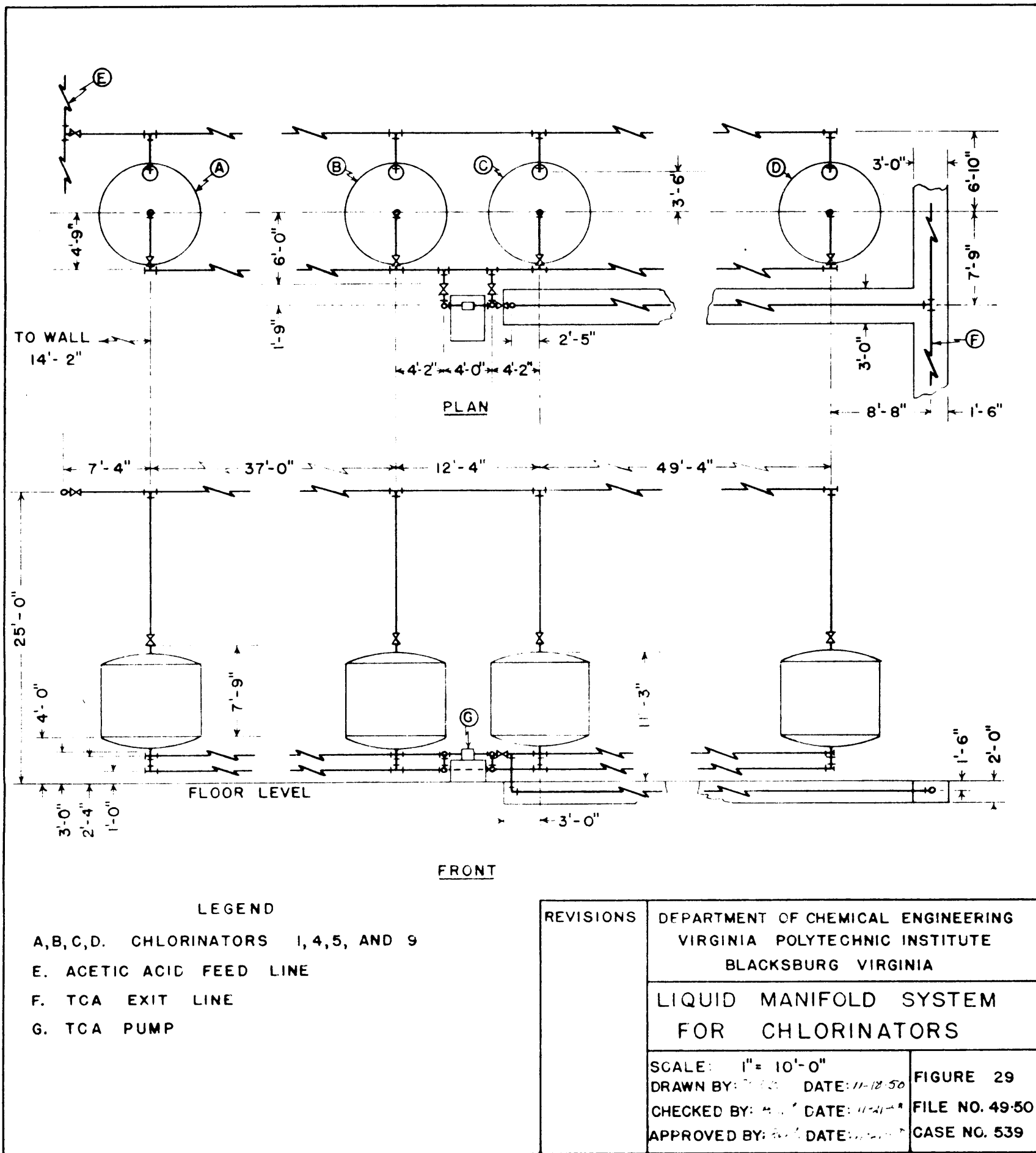
FRONT

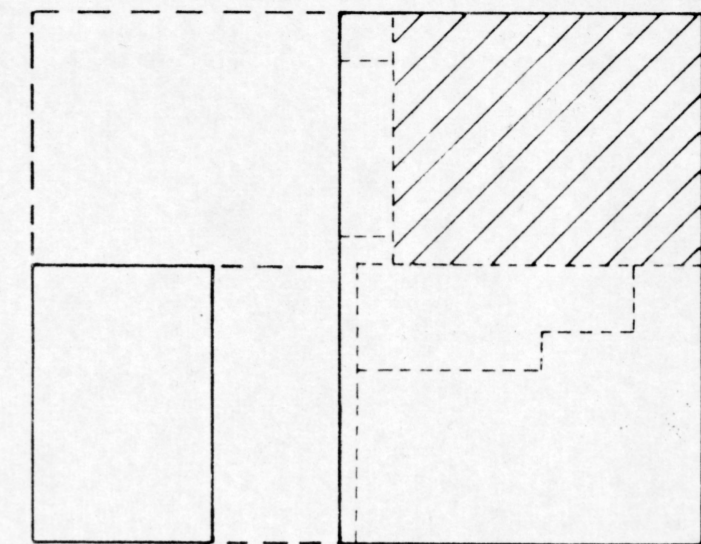
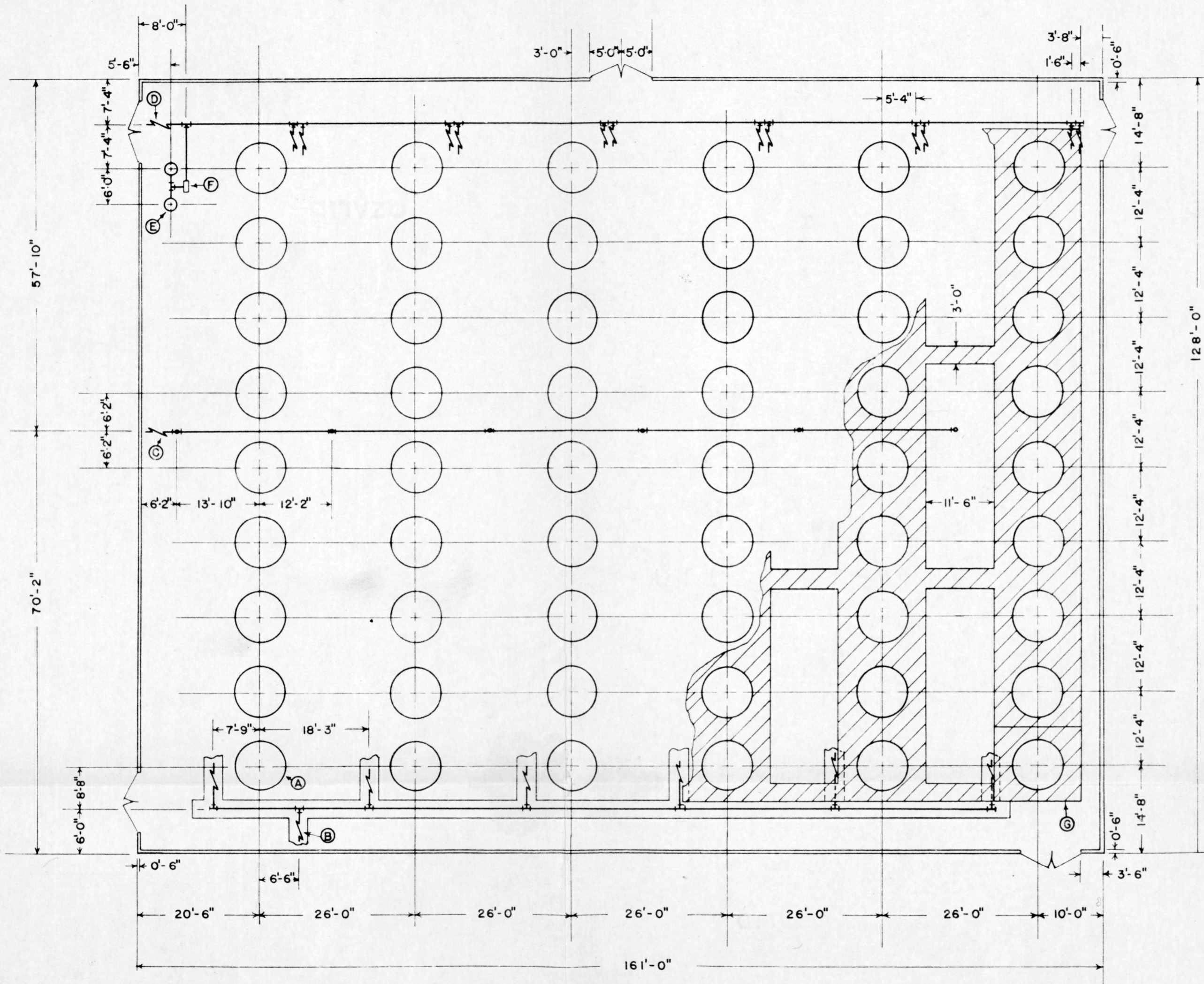
LEFT SIDE

LEGEND

- A, B, C. CHLORINATORS 1, 2, AND 9
- D. REFLUX CONDENSER
- E. RETURN CONDENSER
- F. HCL OUTLET LINE
- G. CHLORINE FEED LINE

REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG VIRGINIA	
	GAS MANIFOLD SYSTEM FOR CHLORINATORS	
	SCALE: 1" = 10'-0"	FIGURE 28
	DRAWN BY: <i>[Signature]</i> DATE: 11-18-50	FILE NO. 49-50
	CHECKED BY: <i>[Signature]</i> DATE: 11-21-50	CASE NO. 539
	APPROVED BY: <i>[Signature]</i> DATE: 11-21-50	

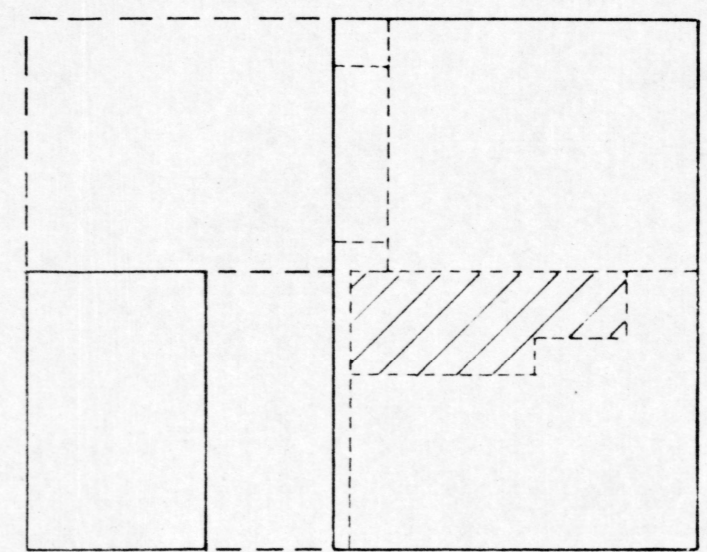
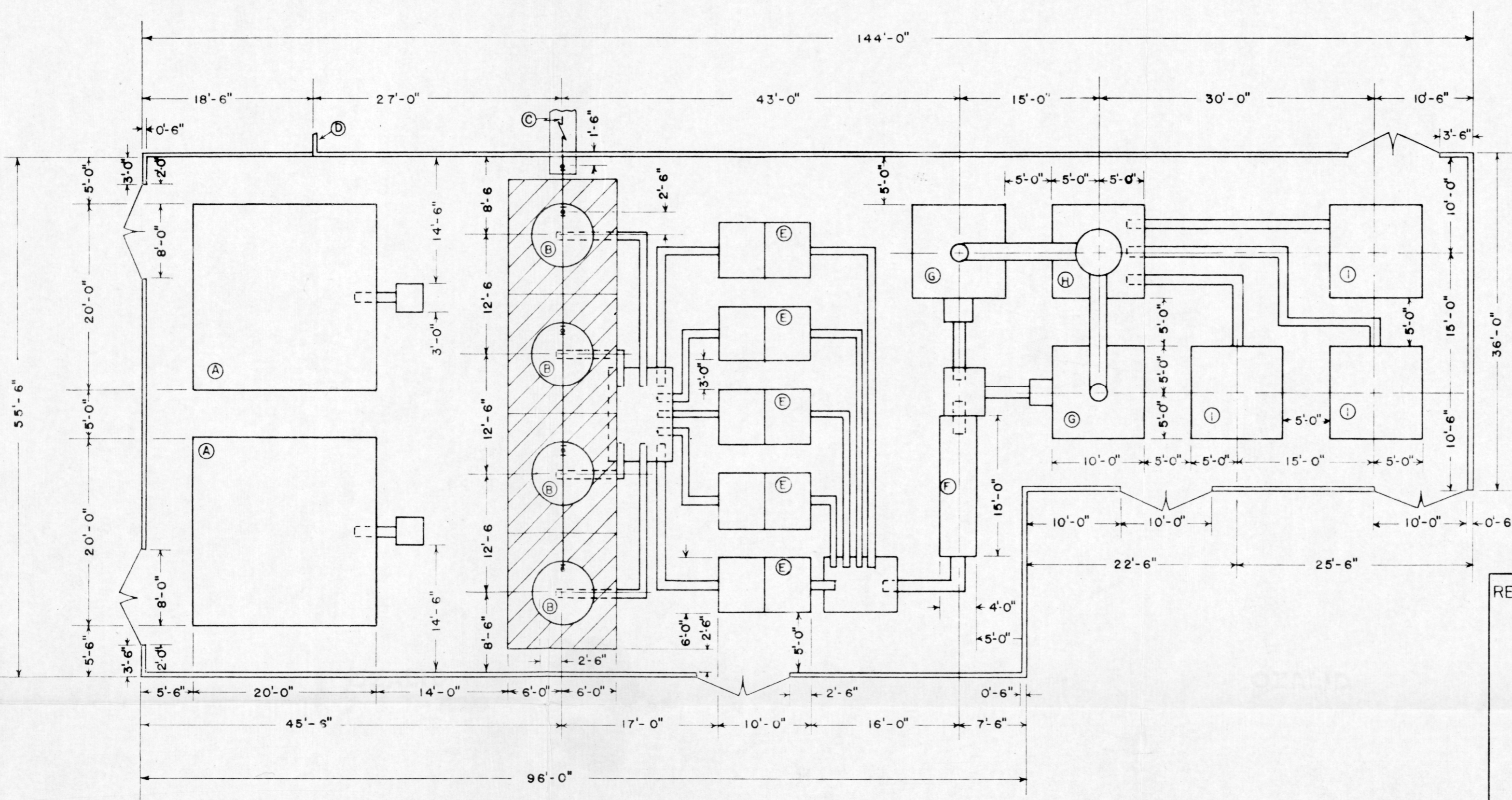




LEGEND

- A. CHLORINATOR 1, BATTERY 1
- B. TCA EXIT LINE TO NEUTRALIZERS
- C. HCL EXIT LINE TO ABSORBERS
- D. CHLORINE FEED LINE
- E. CATALYST SLURRY TANK
- F. CATALYST SLURRY PUMP
- G. BATES GRATES, 4 SECTIONS PER REACTOR

REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA	
	CHLORINATOR SECTION	
	SCALE: 1" = 15'-0"	FIGURE 30
	DRAWN BY: P.K.B. DATE: 11-19-50	FILE NO. 49-50
	CHECKED BY: F.C.V. DATE: 11-21-50	CASE NO. 539
	APPROVED BY: F.C.V. DATE: 11-21-50	

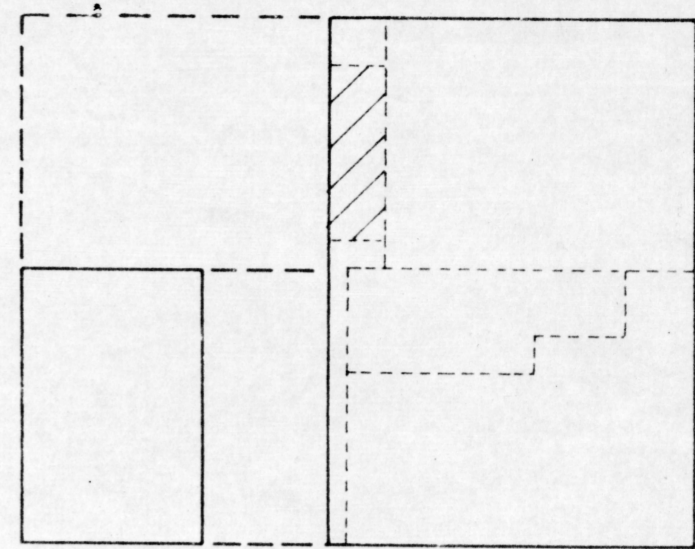
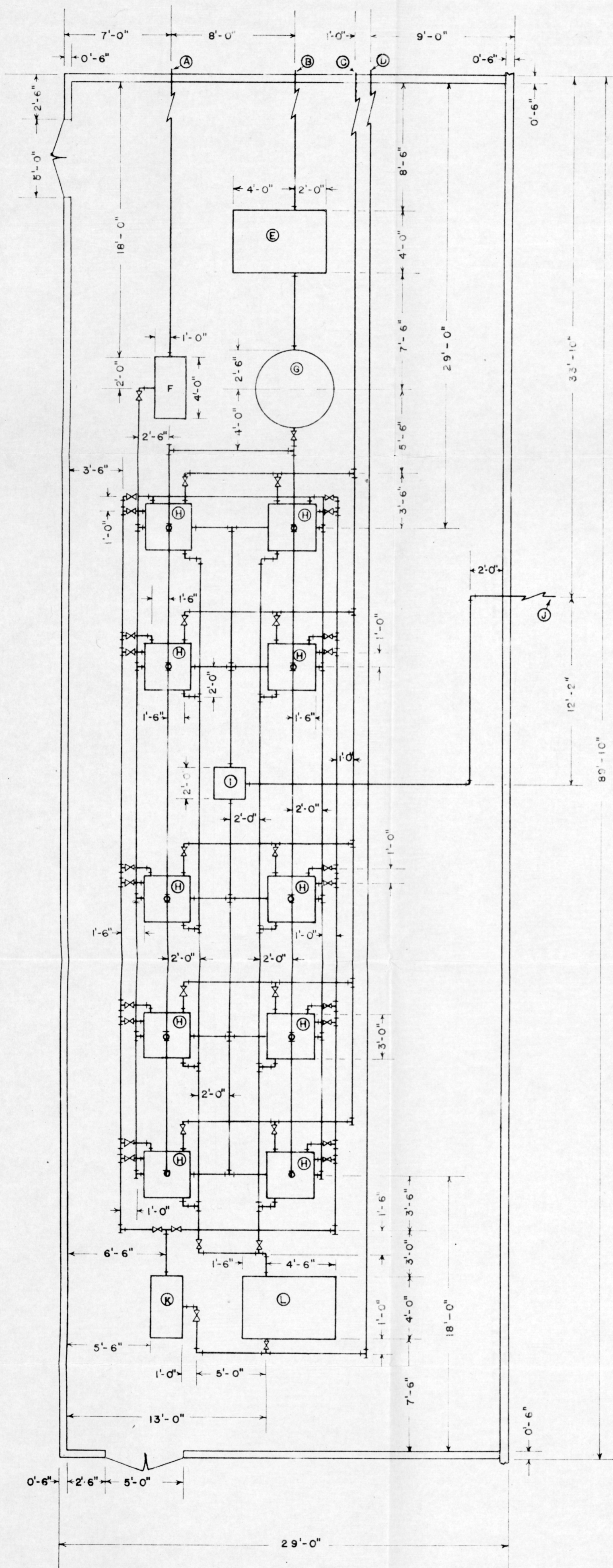


**LEGEND**

- A. SODIUM CARBONATE STORAGE BIN
- B. NEUTRALIZER
- C. TCA LINE FROM CHLORINATORS
- D. WALL, CHLORINATOR SECTION
- E. CRUSHERS
- F. ROTARY DRYER
- G. PULVERISER
- H. COLLECTING BIN
- I. PACKAGING MACHINES

REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING	
	VIRGINIA POLYTECHNIC INSTITUTE	
	BLACKSBURG, VIRGINIA	
<b>NEUTRALIZATION— PACKAGING SECTION</b>		
SCALE: 1" = 10'-0"		FIGURE 31
DRAWN BY: W.Y.B. DATE: 11-19-50		FILE NO. 49-50
CHECKED BY: F.G. DATE: 1-2-51		CASE NO. 539
APPROVED BY: F.L.V. DATE: 11-21-50		

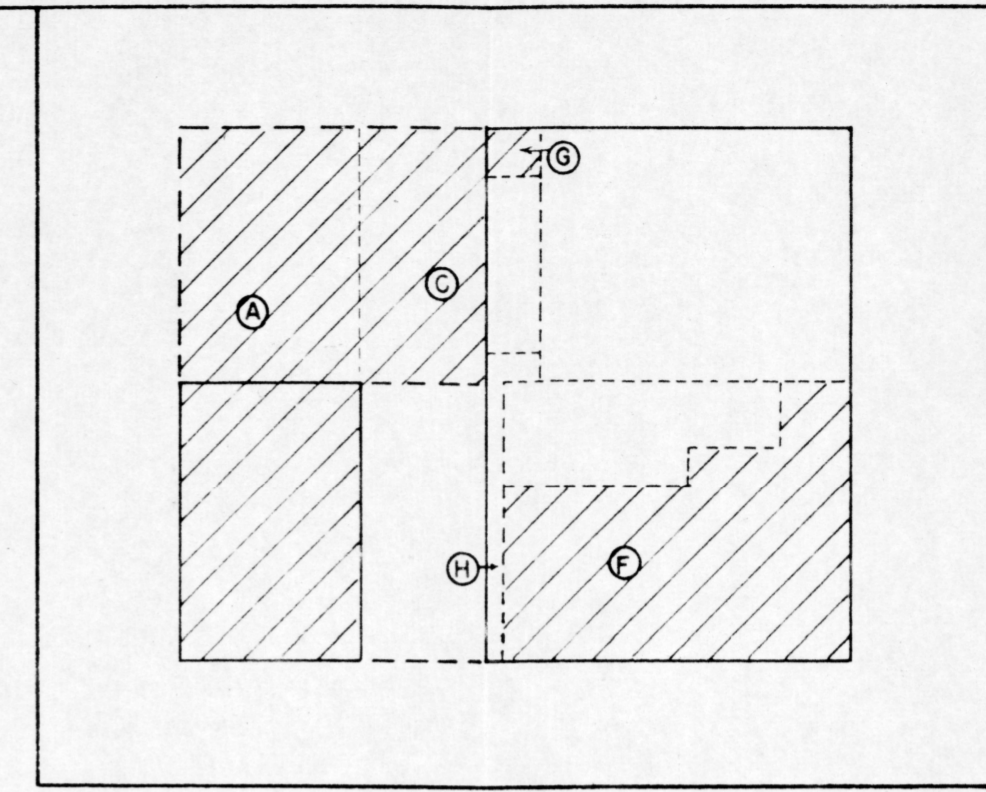
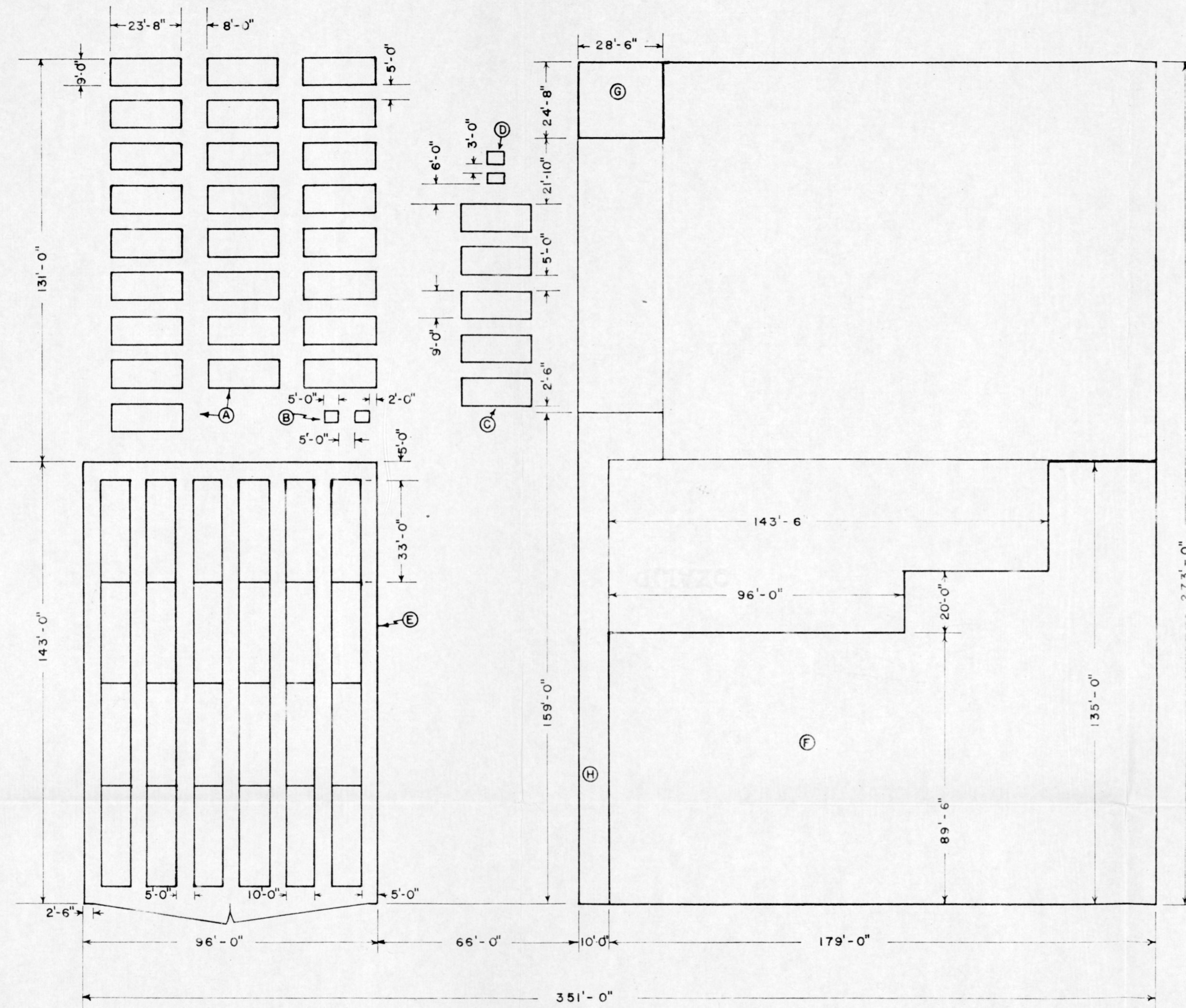




**LEGEND**

- A. HYDROCHLORIC ACID EXIT LINE
- B. CHLORINE TO RECYCLE
- C. COOLING WATER EXIT LINE
- D. COOLING WATER ENTRANCE LINE
- E. CHLORINE COMPRESSOR
- F. ACID PUMP
- G. CHLORINE HOLDING TANK
- H. HCL ABSORBER
- I. HCL BLOWER
- J. HCL LINE FROM CHLORINATOR
- K. FEED WATER PUMP
- L. COOLING WATER PUMP

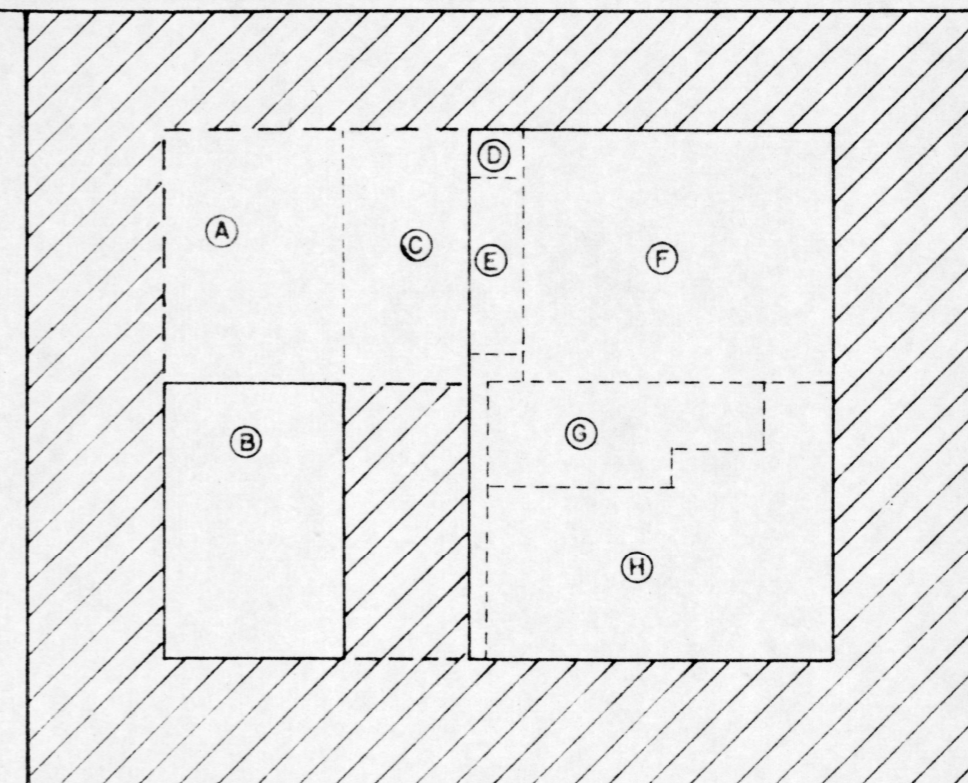
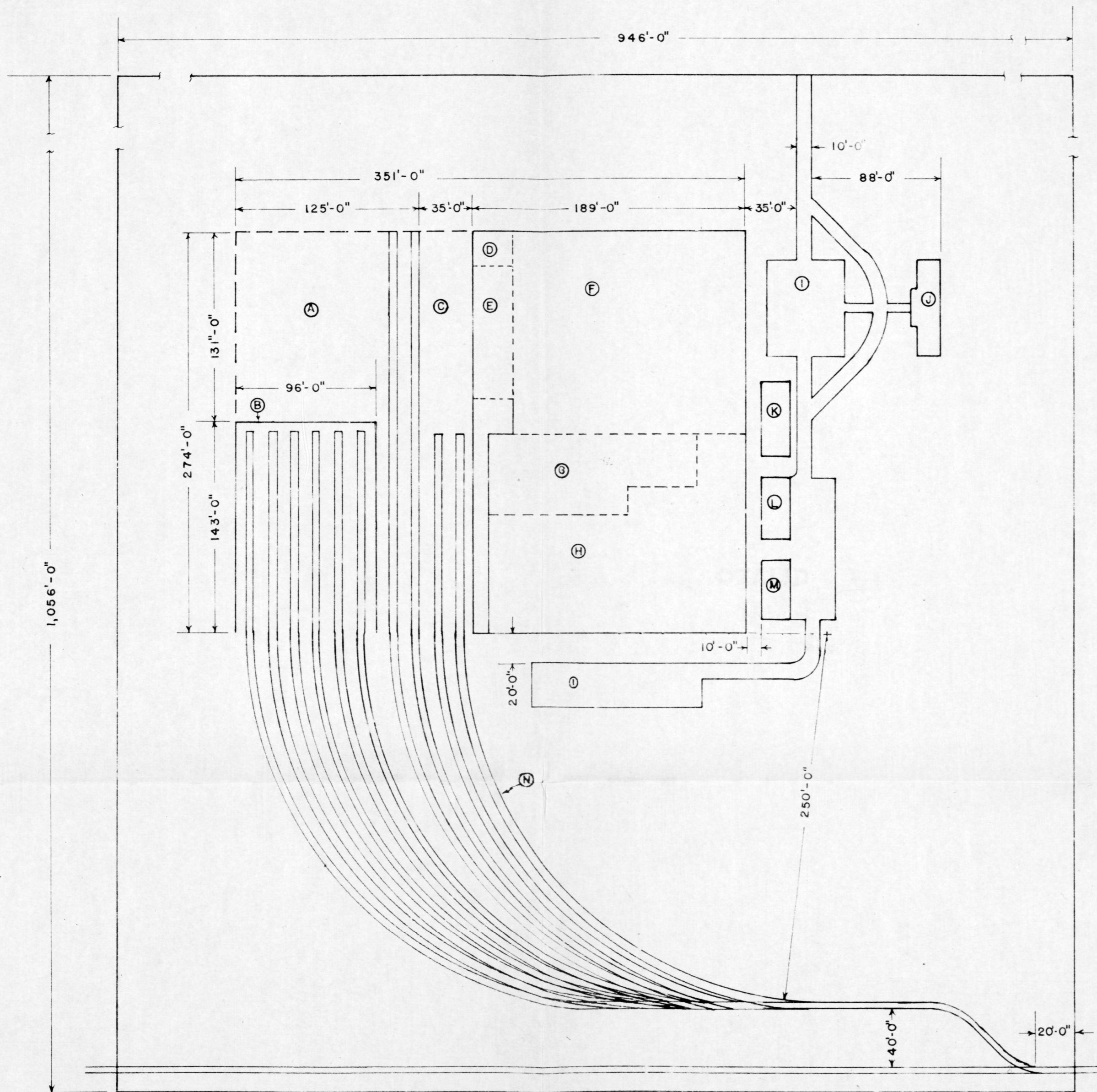
REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA	
	<b>ABSORPTION SECTION</b>	
SCALE: 1" = 5'-0"	FIGURE 32	
DRAWN BY: <i>W.W.B.</i> DATE: 11-19-50	FILE NO. 49-50	
CHECKED BY: <i>F.C.V.</i> DATE: 11-21-50	CASE NO. 539	
APPROVED BY: <i>F.C.V.</i> DATE: 11-21-50		



**LEGEND**

- A. HYDROCHLORIC ACID STORAGE TANKS
- B. HYDROCHLORIC ACID DISCHARGE PUMPS
- C. ACETIC ACID STORAGE TANKS
- D. ACETIC ACID TRANSFER AND FEED PUMPS
- E. CHLORINE TANK CAR STORAGE
- F. PRODUCT STORAGE ROOM
- G. PHOSPHORUS STORAGE ROOM
- H. LOADING PLATFORM

REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA	
	STORAGE SECTION	
	SCALE: 1" = 30'-0"	FIGURE 33
	DRAWN BY: <i>W.B.</i> DATE: 11-19-50	FILE NO. 49-50
	CHECKED BY: <i>F.L.</i> DATE: 11-21-50	CASE NO. 539
	APPROVED BY: <i>F.L.</i> DATE: 11-21-50	



LEGEND

- A. HYDROCHLORIC ACID STORAGE AREA
- B. CHLORINE STORAGE BUILDING
- C. ACETIC ACID STORAGE AREA
- D. PHOSPHORUS STORAGE ROOM
- E. HCL ABSORPTION ROOM
- F. CHLORINATOR ROOM
- G. NEUTRALIZATION - PACKAGING ROOM
- H. PRODUCT STORAGE ROOM
- I. PARKING AREA
- J. ADMINISTRATION BUILDING
- K. MACHINE SHOP
- L. CONTROL LABORATORY
- M. WORKMEN'S DRESSING ROOM, ETC.
- N. RAILROAD SIDINGS

REVISIONS	DEPARTMENT OF CHEMICAL ENGINEERING VIRGINIA POLYTECHNIC INSTITUTE BLACKSBURG, VIRGINIA	
	BUILDINGS AND GROUNDS	
	SCALE: 1" = 60'-0"	FIGURE 34
	DRAWN BY: W.P.B. DATE: 11-19-50	FILE NO. 49-50
	CHECKED BY: P.C.V. DATE: 11-21-50	CASE NO. 539
	APPROVED BY: F.L.V. DATE: 11-21-50	

Daily Plant Operation. The schedules for daily operations have been formulated for the plant on the basis of the following:

1. Daily operations begin at 8:00 AM and end at 4:00 PM, with the half-hour from 12:00 to 12:00 PM set aside for the lunch period.
2. Incoming material shall be stored and checked by warehouse personnel as it arrives.

Product and material storage schedules have not been included in the following paragraphs since such activities occur irregularly.

Chlorinator Schedule. The following is the proposed work schedule for the six batteries of chlorinators and auxiliary equipment:

- 8:00 AM Workers arrive and change to work clothes.
- 8:10 Workers receive instructions for morning operations.
- 8:15 The valves on the six chlorinator batteries are checked for proper setting for operation. Control instruments are checked for proper setting.
- 8:29 Check is made with absorber workers to see that gas lines are open, absorbers are in operation, and the HCl blower is operating.
- 8:30 Chlorine feed line valves are opened.
- 8:31 Periodic check on all instruments and valves maintained during rest of morning.
- 12:00 Lunch period.
- 12:30 PM Period check on all instruments and valves maintained.

- 3:00 PM Valves opened on empty chlorinators for charging with acetic acid. The acetic acid feed pump and cycle control are started. The phosphorus required for charging six chlorinators is brought to the phosphorus slurry tanks, and slurries are readied for charging the chlorinators.
- 3:29 Phosphorus slurry pump is turned on.
- 3:30 Chlorine feed line valves are closed. Acetic acid cycle finished.
- 3:31 Phosphorus slurry charged to chlorinators. Control instruments checked for proper settings for over night temperatures.
- 3:45 Phosphorus slurry pump turned off. Area is cleared of tools and containers. Instrument record charts are turned into the office, and new charts put into place.
- 3:50 Workmen free to shower and change clothes.
- 4:00 Work ceases.

Neutralization - Packaging Schedule. The following is the proposed work schedule for the neutralizers, crushers, dryer, pulverizers, and packaging equipment and auxiliary equipment.

8:00 AM Workers arrive and change to work clothes.

8:10 Workers receive instructions for morning operations.

8:15 Neutralizers checked for proper valve settings. One neutralizer contains product to be discharged, the other three are ready for next batch of TGA. Crushers, dryer, roller mills, and packaging machines are checked for morning operation.

8:20 Crushers, dryer, and roller mills are started. Conveyors are then started. Packaging machines are started.

- 8:30 AM Valves opened on TGA line to neutralisers and TGA pumps started. Valves on steam lines to neutralisers are opened. Weigh harries are filled.
- 8:45 First neutraliser filled with TGA, valve opened to allow TGA to enter second neutraliser.
- 8:46  $\text{Na}_2\text{CO}_3$  introduced to first neutraliser, (N-1).
- 9:00 Second neutraliser (N-2) filled with TGA, valve opened to allow TGA to enter third neutraliser (N-3). Fourth neutraliser (N-4) empty.
- 9:01  $\text{Na}_2\text{CO}_3$  introduced to N-2.
- 9:15 N-3 filled with TGA, valves opened for filling N-4. Neutralisation complete in N-1, contents being emptied.
- 9:16  $\text{Na}_2\text{CO}_3$  introduced into N-3.
- 9:30 N-4 filled. N-1 empty. Neutral. complete in N-2.
- 9:31 TGA pumped to N-1.  $\text{Na}_2\text{CO}_3$  conveyed to N-4. N-2 being emptied.
- 9:45 N-1 filled. N-2 empty. Neutral. compl. N-3.
- 9:46 TGA pumped to N-2.  $\text{Na}_2\text{CO}_3$  conveyed to N-1. N-3 being emptied.
- 10:00 N-2 filled. Neutral. complete in N-4. N-3 empty.
- 10:01 TGA pumped to N-3.  $\text{Na}_2\text{CO}_3$  conveyed to N-2. Neutral. complete in N-4.
- 10:15 N-3 filled. Neutral. complete in N-1. N-4 empty.
- 10:16  $\text{Na}_2\text{CO}_3$  conveyed to N-3. TGA pumped to N-4. Neutral complete in N-1.
- 10:30 N-4 filled. N-1 empty. Neutral. complete in N-2.

- 10:31 AM TGA pumped to N-1.  $\text{Na}_2\text{CO}_3$  conveyed to N-4. N-2 being emptied.
- 10:45 N-1 filled. N-2 empty. Neutral, compl. N-3.
- 10:46 TGA pumped to N-2.  $\text{Na}_2\text{CO}_3$  conveyed to N-1. N-3 being emptied.
- 11:00 N-2 filled. Neutral, compl. N-4. N-3 empty.
- 11:01 TGA pumped to N-3.  $\text{Na}_2\text{CO}_3$  conveyed to N-2. N-4 being emptied.
- 11:15 N-3 filled. Neutral, compl. N-1. N-4 empty.
- 11:16  $\text{Na}_2\text{CO}_3$  conveyed to N-3. TGA pumped to N-4. N-1 being emptied.
- 11:30 N-4 filled. N-1 empty. Neutral, compl. N-2.
- 11:31 TGA pumped to N-1.  $\text{Na}_2\text{CO}_3$  conveyed N-4. N-2 being emptied.
- 11:45 N-1 filled. N-2 empty. Neutral, compl. N-3.
- 11:46 TGA pumped to N-2.  $\text{Na}_2\text{CO}_3$  conveyed N-1. N-3 being emptied.
- 12:00 N-2 filled. Neutral, compl. N-4. N-3 empty. Conveyors, crushers, dryer, roller mills, and packaging machines closed down.
- Lunch Period.
- 12:31 PM Crushers, dryer, roller mills, and packaging machines started. Conveyors started. TGA pumped N-3.  $\text{Na}_2\text{CO}_3$  conveyed N-2. Neutral, compl. N-4.
- 12:45 N-3 filled. Neutral, compl. N-1. N-4 empty.
- 12:46  $\text{Na}_2\text{CO}_3$  conveyed to N-3. TGA pumped to N-4. N-1 being emptied.

- 1:00 PM N-4 filled. N-1 empty. Neutral. compl. N-2.
- 1:01 TGA pumped N-1.  $\text{Na}_2\text{CO}_3$  conveyed N-4. N-2 being emptied.
- 1:15 N-1 filled. N-2 empty. Neutral. compl. N-3.
- 1:16 TGA pumped to N-2.  $\text{Na}_2\text{CO}_3$  conveyed N-1. N-3 being emptied.
- 1:30 N-2 filled. Neutral. compl. N-4. N-3 empty.
- 1:31 TGA pumped N-3.  $\text{Na}_2\text{CO}_3$  conveyed N-2. Neutral. compl. N-4.
- 1:45 N-3 filled. Neutral. compl. N-1. N-4 empty.
- 1:46  $\text{Na}_2\text{CO}_3$  conveyed to N-3. TGA pumped to N-4. N-1 being emptied.
- 2:00 N-4 filled. N-1 empty. Neutral. compl. N-2.
- 2:01 TGA pumped N-1.  $\text{Na}_2\text{CO}_3$  conveyed N-4. N-2 being emptied.
- 2:15 N-1 filled. N-2 empty. Neutral. compl. N-3.
- 2:16 TGA pumped N-2.  $\text{Na}_2\text{CO}_3$  conveyed to N-1. N-3 being emptied.
- 2:30 N-2 filled. Neutral. compl. N-4. N-3 empty.
- 2:31 TGA pumped N-3.  $\text{Na}_2\text{CO}_3$  conveyed N-2. Neutral. compl. N-4.
- 2:45 Neutralisation operations complete. TGA pumps turned off.
- 3:20 Conveyors, crushers, dryer, roller mills, and packaging machines closed down. Area is cleared of accumulated tools or packages. Equipment readied for next days operation. Product containers, not already stored, are stored in warehouse.
- 3:50 Workmen free to take shower and change clothes.
- 4:00 Work ceases.



HCl Absorption Schedule. The following is the proposed work schedule for the HCl absorption units and auxiliary equipment.

8:00 AM Workers arrive and change to work clothes.

8:10 Workers receive instructions for morning operations.

8:15 Holding tank is vented for five minutes, and then vent valve is closed. Valve on gas line connecting absorber to holding tank is opened. Valves on water supply lines to absorber and cooling coils are opened. Motor for cooling pumps are started. HCl blower motor is started. Motor for hydrochloric acid pump is started.

8:29 Report to chlorinator operator that gas lines are clear, absorbers in operation and HCl blower is in operation.

12:00 Lunch Period.

12:30 PM

3:30 HCl blower motor is shut off. Holding tank valve is closed. Motors for cooling and acid pumps are shut off. Feed water and cooling water valves are closed.

3:40 Area cleaned.

3:50 Workers free to take shower and change clothes.

4:00 Work ceases.

Plant Location. Certain factors must be borne in mind in considering the location for the proposed TGA plant. The plant is to be a part of a weed-killing concern which is interested in weed-killing work on railroads in the southeastern part of the country. Only if other demands, such as agricultural, become inviting will the herbicide be produced (by plant expansion) for sale on the market.

The major factors involved in plant location are <sup>(70)</sup> raw materials, market, transportation, labor, plant requirements and power. Location is specified in the southeastern area because of the organization's operations.

Raw Materials. There are a variety of producers of the necessary raw materials in the southeastern area. There are four chlorine producers in Virginia, one in Tennessee, two in West Virginia, one in Alabama, two in North Carolina, and one in Kentucky; or a total of 11 producers. There are two producers of acetic acid in Virginia, one in Tennessee, and two in West Virginia. Soda ash is generally available in the area.

By-Product Market. Availability to a market for hydrochloric acid is a very important factor in location. The credits due to hydrochloric acid sales amount to one-third of the annual net income. Sale of by-product acid depends upon availability to good markets. The main end uses of hydrochloric acid are in the textile and rayon industries, synthetic rubber production, rubber reclaiming, pickling of metals, petroleum, fine chemicals, leather industry, and sugar refining. There are five producers of hydrochloric acid in the Virginia-West Virginia-Tennessee-Georgia area. Therefore, there are good indications of a steady market in the area, due mainly to the textile and rayon operations.

Plant Requirements. The plant requires a large number of railroad sidings and a sizable tract of land (23 acres). Location inside municipal boundaries are thus ruled out. However, the plant requires a plentiful supply of water and power. Location on the outskirts of a municipality or near a hydroelectric plant would be desirable.

Labor. The plant only requires a total of 27 employees. However, availability of services such as electricians are highly desirable. Location in an agricultural district but near a city with available services would be beneficial to both community and organization.

The proposed location is Radford, Virginia. The town, (6,900 population in 1940) is located on the main line of the Norfolk and Western Railway. Suitable locations could probably be purchased on the outskirts of town. Electric power and water are available in large quantities. The area is largely agricultural, however, two other industries (Hercules Powder Co. and Lynchburg Foundry Corp.) are located at Radford, and thus industry is accepted. Various services are available from Roanoke, Virginia, about 41 miles away. Raw materials are available from within the state. The supply of labor is good, both as to the quantity and quality. All-in-all, the major factors to be considered in plant location appear to be satisfied by this location.

Preconstruction Cost Estimation. The preconstruction cost estimate for the TGA plant was carried out utilizing cost data given by Vilhrendt under the following headings: site and building costs<sup>(72)</sup>; equipment costs<sup>(73)</sup>; and operating labor, maintenance and repairs, depreciation, management and marketing, and capital costs<sup>(74)</sup>.

Raw Materials. (Basis: one-day operation)

Acetic acid, gl.	43,851 lb at \$0.11/lb	\$4,823.61
Chlorine	148,463 lb at \$0.02/lb	2,969.26
Phosphorus, red	1,659 lb at \$0.35/lb	580.65
Sodium Carbonate	54,110 lb at \$0.015/lb	811.65

Water, cooling		
reactors	477,000 gal	
absorbers	<u>312,000 gal</u>	
total	789,000 gal at \$0.09	
	per 1,000 gal	71.01

Water, process		
absorbers	20,600 gal	
sanitary	<u>1,350 gal</u>	
total	21,950 gal at \$2.00	
	per 1,000 gal	63.90

Electricity, 220-volt, 60-cycle, three-phase		
reactors	5,435 Kw-hr	
storage	2,200	
dryer	415	
neutralizers	408	
absorbers	352	

Electricity, illumination, 110-volt, single ph.		
reactors	210	
instruments	6	
buildings	1,308	
absorbers	74	
storage	35	
dryers	25	
neutralizers	<u>16</u>	

Total electricity	10,484 Kw-hr at \$0.0122	
	per Kw-hr	127.90

Steam, 150 lb. per sq in., gage		
reactors	21,000 lb	
neutralizers	9,000	
dryer	9,200	
heating	<u>1,850</u>	
total	41,050 lb at \$0.50	
	per 100 lb	205.25

Drums, fiber, 50-lb, for TCA storage		
	2,907 at \$0.20 ea.	581.40

Total per day		<u>\$ 10,234.63</u>
---------------	--	---------------------

Total per 105-day year		<u><u>\$1,074,636.15</u></u>
------------------------	--	------------------------------

Building and Real Estate.

Land, 23 acres at \$125.00 per acre	\$ 2,875
<b>Buildings</b>	
administration	31,730
reactor room	55,940
phosphorus storage room	1,321
product storage room	46,900
neutralization-packaging room	19,150
absorption room	7,010
control laboratory and equipment	9,000
shop and equipment	11,278
locker rooms and toilets	11,338
Railroad sidings, 6,120 ft at \$8.57/ft	52,448
Fencing, 4,004 ft at \$2.00/ft	8,008
Roadways and parking areas, 1,950 sq yd at \$3.00/sq yd	5,880
Personnel facilities, 27 employees at \$150 per person	4,050
Lighting equipment	
interior, 350 fixtures at \$30 ea.	10,500
exterior, 40 fixtures at \$300 ea.	12,000
Drainage, 5.0% of major equipment costs	69,939
Equipment supports, 10.0% of supported equipment costs	33,542
Foundations, 6.0% of other equipment costs	<u>39,687</u>
<b>Total Building and Real Estate</b>	<b>\$ 432,596</b>

The cost of equipment, installed, and labor have been given in

Tables XVIII and XIX.

TABLE XVIII

Cost of Equipment for TCA Plant

No.	Equipment	No. Req'd	Unit List Price	Installation Cost	Freight	Total Unit Cost	Total Cost	
			\$	\$	\$	\$	\$	
A-2	Acetic acid storage	5	10,000	1,000	100	11,100	55,500	
A-3	Acetic acid pump	1	520	78	16	614	614	
A-4	HCl storage	39	5,100	1,275	153	6,528	254,592	
A-5	Chlorine	25	8,500	-	255	8,755	218,875	
A-6	Chlorine vaporizer	1	850	85	10	945	945	
A-7	Na <sub>2</sub> CO <sub>3</sub> storage	2	3,500	350	35	3,885	7,770	
A-8	Conveyor	4	3,600	900	108	4,608	18,432	
A-9	Weigh larry	2	1,800	700	525	3,025	6,050	
A-10	Conveyor	2	3,600	900	108	4,608	9,216	
B-1	Phosphorus slurry tank	2	472	153	14	639	1,278	
B-2	Phosphorus slurry pump	2	1,290	245	12	1,547	3,094	
B-3	Chlorinator	54	8,020	755	150	8,925	481,950	
B-4	Reflux condenser	54	1,850	370	13	2,233	120,582	
B-5	Return condenser	54	1,850	370	13	2,233	120,582	
B-6	TCA pump	6	1,290	245	12	1,547	9,282	
C-1	Neutralizer	4	6,000	580	120	6,700	26,800	
C-2	Conveyor	8	58	20	1	79	632	
C-3	Cooler	1	1,850	370	13	2,233	2,233	
D-1	Crusher	10	1,800	180	18	1,998	19,980	
D-2	Conveyor	10	30	20	1	51	510	
E-1	Rotary dryer	1	450	90	15	555	555	
E-2	Conveyor	2	80	20	1	101	202	
F-1	Pulverizer	2	2,500	25	20	2,545	5,090	
F-2	Conveyor	9	80	20	1	101	909	
G-1	Packaging	3	1,200	120	5	1,325	3,975	
H-1	Cooler	1	1,850	370	13	2,233	2,233	
H-2	Blower	1	2,500	200	3	2,703	2,703	
H-3	HCl absorber	10	950	950	30	1,950	19,500	
H-4	Chlorine compressor	1	1,500	150	2	1,652	1,652	
H-5	HCl pump	1	450	45	2	497	497	
H-6	Condensate pump	1	400	40	2	442	442	
H-2a	Operating floor	7,843 sq ft at \$1.35/sq ft						10,590
C-1a	Operating floor	540 sq ft at \$1.35/sq ft						729
	Total processing						1,398,778	
B-3	Flow control (Cl <sub>2</sub> )	6	900	180	1	1,081	6,486	
B-3	Flow control (HAc)	1	750	180	2	932	932	
B-3	Cycle control (HAc)	1	2,360	480	5	2,845	2,845	
B-3	Pressure control	1	750	150	2	902	902	
B-3	Temperature control	54	750	158	-	908	49,032	
B-3	Safety disc	54	20	5	-	25	1,350	
C-1	Temperature control	4	400	113	1	514	2,054	
E-3	Pressure control	1	300	70	2	372	372	
	Total instruments						63,973	
<b>Total equipment</b>							<b>1,462,751</b>	

TABLE XIX

Labor and Supervision Costs For TCA Plant

Employee	No.	Hourly Rate	Annual Salary	Annual Cost	Cost 22-weeks
		\$	\$	\$	\$
Plant Manager	1	-	10,000	10,000	4,230
Analytical Chemist	1	-	3,000	3,000	1,269
Assistant Superintendent	1	-	5,000	5,000	2,116
Chlorinator Operator	1	2.20	4,576	4,576	1,936
Warehousemen	3	0.75	1,560	4,680	1,980
Chem. Operator Helper	4	1.09	2,267	9,069	3,837
Shipping Clerk	1	1.00	2,080	2,080	880
Neutralizer-Dryer Operator	1	1.28	2,662	2,662	1,129
Chem. Operator Helpers	1	1.09	2,267	2,267	961
Crushing Operator	2	1.09	2,267	4,534	1,922
Roller Mill Operator	1	1.09	2,267	2,267	961
Absorber Men	1	1.23	2,558	2,558	1,082
Packaging Operator	3	1.09	2,267	6,801	2,883
Electricians	1	1.43	2,974	2,974	-
Pipefitter	1	1.39	2,891	2,891	-
Machinist	1	1.43	2,974	2,974	-
Mechanic Helpers	3	1.09	2,267	6,802	-
Watchmen	2	0.75	1,560	3,120	3,120
Total Annual Cost				78,255	
Total Cost 22 Weeks					28,306

Summary of Equipment Costs.

Equipment costs, installed	\$1,462,751
Process piping cost, 25% of installed equipment cost	365,688
Contingency value and contractor's fee at 12-1/2 % installed equipment cost	182,844
	<hr/>
Total equipment cost	\$2,011,283

Fixed Charges.

Taxes, at 25% of total plant cost including building, equipment and real estate	\$ 48,878
Social security, at 1-1/2 % of wages and salaries below \$4,000 per year	300
Unemployment insurance, at 1-1/2 % of wages and salaries below \$4,000 per year	300
Depreciation at 20% of total plant cost	488,776
Insurance at 0.1% of 90% of total plant cost	2,199
	<hr/>
Total fixed charges	\$ 540,453

Working Capital.

Raw material costs (90 days)	\$ 657,677
Labor and supervision (90 days)	15,440
Fixed charges (annual)	540,453
Incidentals	15,000
	<hr/>
Total working capital	\$ 1,228,570

Capital Investment.

Building and real estate	\$ 432,596
Equipment costs	2,011,283
Working capital	1,228,570
	<hr/>
Total capital investment	\$ 3,672,449



Gross Income.

Annual value of product, 11,386,620 lb pure NaFCA at \$0.375 per lb	\$4,269,903
Annual value of by-product, 38,015,670 lb 22°Be HCl at \$0.019 per lb	<u>722,298</u>
<b>Total gross income</b>	<b>\$4,992,281</b>

Annual Costs.

Annual operating costs	
raw material	\$1,074,636
labor and supervision	28,306
maintenance, at 7% of equipment cost	140,790
Fixed charges, management and distribution, at 25% gross income	<u>1,248,070</u>
<b>Total annual costs</b>	<b>\$2,491,802</b>

Net Income.

Annual value of product and by-product	\$4,992,281
Annual costs	<u>2,491,802</u>
<b>Net Income</b>	<b>\$2,500,479</b>

Estimate of "Normal" Wholesale Selling Price.

Raw materials cost		\$1,074,636
Service costs		
labor	\$ 28,306	
fixed charges	540,153	
maintenance (at 7%)	<u>140,790</u>	
Total service	\$ 709,549	709,549
Progress costs (100% of service costs)		709,549
Cost of marketing (50% of service costs)		<u>354,775</u>
Total costs		\$2,848,509
Credits		
hydrochloric acid	\$ 722,298	<u>\$ 722,298</u>
Cost per 11,386,620 lb NaFCA produced		\$2,126,211
Cost per pound of NaFCA produced		0.187

Preconstruction Cost Estimation. The preconstruction cost estimate for the TCA plant was carried out utilizing cost data given by Vilbrandt under the following headings: site and building costs<sup>(72)</sup>; equipment costs<sup>(73)</sup>; and operating labor, maintenance and repairs, depreciation, management and marketing, and capital costs<sup>(74)</sup>. The estimate indicated that to produce 5,000 tons TCA per annum in the form of sodium TCA would require a capital investment of \$3.672 million and a working capital of \$1,229 million. The wholesale selling price was estimated to be \$0.187 per pound sodium TCA or about \$0.14 per pound of the final product. A net income of \$2.50 million was estimated based on the assumption that the sodium TCA produced would sell for \$0.375 per pound sodium TCA contained. The cost estimate bears further examination.

Capital Investment. Of the capital investment, about 55 per cent is required for equipment and piping. This percentage is not unusual in fluid processing plants; a figure of 51 per cent (for plants \$1.0 to \$5.0 million size) being reported<sup>(71)</sup> for fluid processing plants in general. Because of the extremely corrosive nature of the intermediate products, one might suspect higher equipment costs at the outset.

Depreciation. The plant was depreciated at 20 per cent, or over a five-year period. This was done because of the highly competitive nature of the industry and the rapid rate at which new herbicides are being produced.

Net Income. The net income, estimated on page 195, is based on the assumption of a selling price of \$0.375 per pound NaTCA. About one-third of the net income from a TCA plant would be derived

from the sale of by-product hydrochloric acid. In general, the market for hydrochloric acid has been unusually stable for a number of years. However, in certain areas, where demand for the acid is low and transportation costs high, the market often becomes soft. For this reason, availability to hydrochloric acid markets should be weighed heavily in plant location considerations. A possible alternative, in the problem of hydrochloric acid disposal, is the recovery of chlorine by the oxidation of the hydrogen chloride. This latter means has received considerable attention during the past two or three years.

Feasibility of Producing TCA. On the surface, at least, the production of TCA looks promising. However, intimate knowledge of the weed-killing industry and the recent developments in weed-killers is required to accurately ascertain the risk involved.

### Recommendations

As a basis for future study in connection with the production of trichloroacetic acid (TCA) from acetic acid and chlorine, and analysis of chlorinated acetic acids, it is recommended that:

1. Further development work, on a pilot plant scale, be carried out on the process of producing TCA with the purpose of obtaining information leading to a plant design. The work should make use of countercurrent chlorine-acid flow, and utilize the semi-batch process, a chlorinator with adequate condensation and condensate return, agitation, and effective chlorine distribution. The following topics are recommended for study:
  - a. The effect of temperature, chlorine concentration, and catalyst concentration on the rate of reaction.
  - b. The effect of reaction rate on the yield of TCA.
  - c. The determination of the most effective catalyst or combination of catalysts for the process of producing TCA from acetic acid and chlorine. It is suggested that the study include the following catalysts; red phosphorus, sulfur, phosphorus chlorides, sulfur monochloride, acetyl chloride, and actinic light.
  - d. Determination of a scale factor by pilot plant work utilizing reactors of one, three, and nine-liter capacity successively.
  - e. The neutralization of trichloroacetic acid on a pilot plant scale to determine the desirable temperature for the reaction, the time required for neutralization, the drying characteristics of the neutralized mass, and the type equipment best suited for the process.

2. The economic possibilities of utilizing chlorine recovery from by-product hydrogen chloride in connection with TCA production be investigated. Much of the success of an investment in a TCA plant depends upon the sale of by-product hydrochloric acid. Elimination of production of the acid by more complete utilization of the chlorine would ease the risk involved in such a venture.

3. The role of red phosphorus as a catalyst in promoting the chlorination of glacial acetic acid be investigated. It is speculated that the element is not a catalyst in the reaction, but the phosphorus chlorides are. If such speculation is correct, it might be more economical to utilize  $PCl_3$  as the raw catalyst instead of phosphorus.

4. The role of acetyl chloride and chloroacetyl chlorides as catalysts in the production of TCA be investigated. The importance of these intermediate compounds may not be fully appreciated.

5. The application of volumetric analysis, based on Dalin's work and used in this investigation, of mixtures of chlorinated acetic acids low in DCA content (less than 20 per cent) be studied. The unreliable results of analyses of such mixtures are not entirely explained. Also, the limit to which Dalin's method of analysis is applicable has not been reported.

6. The use of physical properties, such as density, refractive index, electrical conductivity, and viscosity as a means of quantitative estimation of mixtures of TCA, DCA, and MCA be investigated. This method promises to be quicker and more reliable over wider ranges of concentration than volumetric analysis.

Limitations

The investigation was limited to a study of the production of trichloroacetic acid from glacial acetic acid and chlorine in the presence of 0.038 parts red phosphorus per part acetic acid by weight and utilizing reactors of liter capacity; reaction temperatures of from 70 to 320°F; atmospheric pressures of from 700 to 725 millimeters mercury, absolute; ratio of chlorine to acetic acid of 1.56 to 2.20 to one; maximum reaction time of 90 hours per batch; absence of actinic light; and production of products of 82 per cent maximum TCA concentration.

## V. CONCLUSIONS

The results of experimental work on the production of trichloroacetic acid from acetic acid and chlorine involved the chlorination of glacial acetic acid in the presence of red phosphorus, utilizing glass reactors of liter capacity; reaction temperatures of from 68 to 320°F; atmospheric pressures; liquid phase; excess chlorine; and a semi-batch process in the absence of actinic light.

A. From the results of the experimental work, it is concluded that:

1. Trichloroacetic acid was produced in an 82 per cent concentration, a 63.5 per cent yield, in a reaction time of 90 hours, and utilizing 68 to 250 per cent excess chlorine.

2. Chlorine distribution in the experimental work, involving the use of a distributor with four 0.25 to 0.75-millimeter diameter openings, was 54 per cent as efficient in its effect on reaction time as that reported for a ring-type chlorine distributor used in conjunction with a 50 to 60-gallon capacity chlorinator.

3. Incomplete condensation of vaporized intermediate and final products from the gases leaving the chlorinator caused the low yield of 63.5 per cent trichloroacetic acid in relation to the 82 per cent concentration produced.

4. Pyrogenation of trichloroacetic acid, in which the temperature did not exceed 320°F, was not a factor contributing to the 63.5 per cent yield of TCA in relation to the 82 per cent concentration produced.

B. A plant was designed for the production of 5,700 tons of sodium trichloroacetate per annum, based on a 105-day year and an eight-hour day. The plant was designed on the basis of the results of the experimental work. From a preconstruction cost estimate of the proposed plant based on 1949 prices, it is concluded that:

1. Sodium trichloroacetate can be produced for \$0.187 per pound.

2. Twenty seven full-time employees are required at a cost of \$28,306 for the 105 days of operation.

3. Equipment costs of \$2,011,283; building and real estate costs of \$432,596; working capital of \$1,228,570; and a total capital investment of \$3,672,449 are required.

4. A annual net income of \$2,500,479 would be realized by such a plant when depreciated at 20 per cent, and assuming a selling price of \$0.375 per pound of sodium trichloroacetate.



## VI. SUMMARY

In 1949, it was found that sodium trichloroacetate, when formulated with sodium chlorate, was a good herbicide, particularly for the hard-to-kill Bermuda grass. However, sodium trichloroacetate was being produced by only two companies, the price was too high for extensive use, and the future demand loomed large over present production. An investigation of the production of trichloroacetic acid (TCA) with the purpose of lowering cost was therefore fitting. Preliminary estimates of the cost of raw materials indicated that production of TCA from acetic acid and chlorine, and neutralization with sodium carbonate, was the most economical process. However, little information of the process was available except catalyst concentration and maximum reaction temperature. Thus, development work on the process was needed.

It was the purpose of the investigation to design, construct, and operate a pilot plant for the production of TCA from acetic acid and chlorine. The results of the pilot work were to be incorporated into a plant design for sodium trichloroacetate.

The pilot work involved the chlorination of glacial acetic acid in the presence of red phosphorus utilizing glass reactors of liter capacity, reaction temperatures of from 70 to 320°F, atmospheric pressures, liquid phase, excess chlorine, and absence of actinic light. The chlorine was metered to the reactors and the waste gases, containing largely hydrogen chloride, absorbed in water. The process was semi-batch; all equipment was made from glass.

From the results of the experimental work under the conditions outlined in the preceding paragraph and utilizing 68 to 250 per cent excess chlorine, it was found that trichloroacetic acid can be produced in 82 per cent concentrations, 63.5 per cent yield, in a reaction time of 49 hours. The results indicated that incomplete condensation of vaporized intermediate and final products in the gases leaving the chlorinator led to the 63.5 per cent yield of TCA in relation to the 82 per cent concentration produced. It was further indicated that appreciable pyrogenation of TCA does not occur in the liquid phase chlorination below 320°F.

A proposed plant design, embodying a semi-batch process with counter-current liquid-gas flow, indicated that sodium trichloroacetate can be produced (1949) for \$0.187 per pound at a rate of 5,700 tons per 105-day year. It was estimated that the plant would require 27 full-time employees at a cost of \$28,306 for the 105 days of operation; equipment costs of \$2,011,283; building and real estate costs of \$432,598; working capital of \$1,228,570; and a total capital investment of \$3,672,449. Estimates showed such a plant, depreciated at 20 per cent, would provide an annual net income of \$2,500,479. A proposed location for the plant is Radford, Virginia.

VII. BIBLIOGRAPHY

1. Alphen, J. van: The Action of Trichloroacetic Acid on Phenols, C.A., 21, 1641 (1927); Rec. Trav. Chim. 46, 144-9 (1927).
2. Arnor, L. E. and H. C. Reits: "Introduction to Organic and Biological Chemistry", pp. 215-16. The C. V. Mosby Co., St. Louis, Mo., 1943.
3. Badger, W. L. and E. M. Baker: "Inorganic Chemical Technology", pp. 125-27. McGraw-Hill Book Co., Inc., New York, N. Y., 1928.
4. Bateman, W. G. and D. B. Conrad: Some Salts of the Halogenoacetic Acids II, J. Am. Chem. Soc. 37, 2553-60 (1915).
5. \_\_\_\_\_ and A. B. Hoel: Some Salts of the Chloroacetic Acids, J. Am. Chem. Soc. 36, 2517-21 (1914).
6. Beebe, R. A.: The Electrometric Titration of Copper Salts by Sodium Hydroxide, J. Phys. Chem. 35, 3677-83 (1931).
7. Bernthsen, A.: "A Text-Book of Organic Chemistry", (Revised by J. J. Sudborough), pp. 176-7. D. Van Nostrand Co., New York, N.Y., 1926.
8. Bousquet, E. W.: Trichloroacetates As Herbicides, C.A., 40, 2264 (1946); U. S. Pat. 2,393,086. (Jan. 15, 1946).
9. Brain, F. H.: Estimation of Trichloroethylene in Air, C.A., 44, 976 (1950); Analyst 74, 555 (1949).
10. Bruckner, H.: Catalytic Chlorination of Acetic Acid to Chloroacetic Acid, C.A., 22, 3819 (1928); Z. Angew. Chem. 41, 226-9 (1928).

11. "Chemical Facts and Figures" (compiled by M. F. Crass, Jr.), p. 100.  
Manufacturing Chemists' Association, Washington, D. C., 1946,  
2d ed.
12. Chlorine, Chem. Eng. 57, 10--263 (1950).
13. Dalin, G. A. and J. N. Haimsohn: Analysis of Chloroacetic Acid,  
Anal. Chem. 20, 470-2 (1948).
14. Dawson, H. M., et. al.: The Elimination of Chloride From Sodium  
Chloroacetate by The Salts of Weak Acids, J. Chem. Soc.,  
517-20 (1943).
15. Drew, T. B. and R. P. Genereaux: Flow of Fluids, "Chemical Engineers'  
Handbook" (J.H. Perry, Editor), p. 845. McGraw-Hill Book Co.,  
Inc., New York, N. Y., 1941. 2d ed.
16. Eisenberg, W. V.: Identification of Chloroacetic Acid as Barium  
Chloroacetate, C.A., 39, 4028 (1945); J. Assoc. Official Agri.  
Chem. 28, 427-8 (1945).
17. Eliel, E. L.: Chromatographic Adsorption, J. Chem. Education 21,  
583-88 (1944).
18. Equipment and Construction Materials, Chem. Eng. 55, 11--99 (1948).
19. Ermolenko, N. F. and D. Z. Ginsburg: Importance of The Constitution of  
Organic Acids for Their Adsorption From Mixed Media, C.A., 33,  
8469 (1939); Colloid J. (USSR) 5, 263-70 (1939).
20. Ferrandis, V. A.: Adsorption From Homogeneous Solutions, C.A., 41,  
4350 (1947); Anales Fis. y Quim. (Madrid) 41, 709-45 (1945).
21. Frenkiel, J. and P. Rombau: Procedure for Determining Monochloro-  
acetic Acid, C.A., 42, 2892 (1948); Chim. Anal. 30, 60 (1948).

22. Fujiwara, K.: New Reaction for the Detection of Chloroform, C.A.,  
11, 3201 (1917); Sitz. Nat. Ges. Rostock 8, 33-43 (1916).
23. Gatterman, L.: "Laboratory Methods of Organic Chemistry", pp. 104-6.  
The MacMillan Co., New York, N. Y., 1932.
24. Gaylord, W. M.: Hydrochloric Acid Versus Construction Materials,  
Chem. Eng. 56, 1-231 (1949).
25. Getman, F. H. and F. Daniels: "Physical Chemistry", pp. 259-60.  
John Wiley and Sons, Inc., New York, N. Y., 1945. 7th ed.
26. Gibb, T. R. P.: "Optical Methods of Chemical Analysis", pp. 202-7.  
McGraw-Hill Book Co., Inc., New York, N. Y., 1942.
27. Gradishar, F. J.: The Development and Evaluation of a Commercial  
Process for The Production of Benzene Hexachloride, pp. 52-9.  
Unpublished Ph. D. Thesis, Library, Va. Poly. Inst., Blacksburg,  
Va., (1948).
28. Groggins, P. H.: "Unit Processes in Organic Synthesis", pp. 169-70.  
McGraw-Hill Book Co., Inc., New York, N. Y., 1947. 3d ed.
29. *ibid*, pp. 186-91.
30. *ibid*, p. 198.
31. *ibid*, pp. 242-3.
32. \_\_\_\_\_ et. al.: Electrochemical Production of Sodium Chlorate,  
Chem. Eng. 44, 302 (1937).
33. Hunt, H. and H. T. Briscoe: The Electrical Conductivity of Organic  
Acids in Water, Alcohols, and Acetone, and the Electronic  
Structures of the Acids, J. Phys. Chem. 33, 1495-1513 (1929).
34. Huntress, E. H.: "Organic Chlorine Compounds", p. 3:1150. John Wiley  
and Sons, Inc., New York, N. Y., 1948.

35. Ismailov, N. A. and M. A. Belbova: Differential Action of Solvents on the Activity of Acid, C. A., 33, 6688 (1939); J. Gen. Chem. (USSR) 9, 453-9 (1939).
36. Jaeger, F. M. and G. Berger: The Action of Ultraviolet Light on the Aqueous Solutions of Certain Organic Acids and Their Salts, C.A., 16, 2847 (1922); Rec. Trav. Chim. 41, 71-81 (1922).
37. Kendall, J.: The Addition Compounds of Organic Acids in Pairs, J. Am. Chem. Soc. 36, 1722-34 (1914).
38. \_\_\_\_\_: The Addition Compounds of Phenols with Organic Acids, J. Am. Chem. Soc. 38, 1309-23 (1916).
39. \_\_\_\_\_ and C. D. Carpenter: The Addition Compounds of Organic Substances with Sulfuric Acid, J. Am. Chem. Soc. 36, 2502-6 (1914).
40. King, G. B. and J. H. Walton: Studies on Phosphoric Acid, J. Phys. Chem. 35, 1745-51 (1931).
41. Lamborn, B. T.: Alkali and Alkaline-earth Metal Salts of Halogenated Fatty Acids, C.A., 42, 8209 (1948); U. S. Pat. 2,446,233 (August 3, 1948).
42. Maryott, A. A.: Conductrimetric Titrations of Acids and Bases in Benzene and Dioxane, C.A., 41, 6493 (1947); J. Research Nat'l. Bur. Standards 58, 527-36 (1947).
43. Pearce, J. N. and A. C. Nelson: The Influence of Solvent on the Decomposition of Trichloroacetic Acid, C.A., 25, 1147 (1931); Proc. Iowa Acad. Sci. 36, 251-60 (1929).

44. Perry, J. H. et al.: Physical and Chemical Data, "Chemical Engineers' Handbook" (J. H. Perry, Editor), pp. 271-367. McGraw-Hill Book Co., Inc., New York, N. Y., 1941. 2d ed.
45. Pickering, S. U.: Solubility of Chloroacetic Acids in Water, J. Soc. Chem. (Lond.) 67, 669 (1895).
46. Peel, J. F. A.: Chloroacetic Acids and Their Estimation and Separation, J. Chem. Soc. 88, 425-6 (1905).
47. Rabinovich, M. A.: Electrotitration of Acids in Benzene Solution, C.A., 32, 4085 (1938); Trav. Inst. Chim. Charkov. 1, 99-107 (1935).
48. Ramsey, L. L. and W. I. Patterson: New Method for the Detection and Determination of Monochloroacetic Acid, C.A., 40, 3369 (1946); J. Assoc. Official Agr. Chem. 29, 100-111 (1946).
49. Redfield, H. L. and G. B. King: Addition Compounds of Phosphorous Acid With Certain Organic Compounds, J. Phys. Chem. 40, 919-25 (1936).
50. Robbins, W. W., A. S. Crafts, and R. N. Raynor: "Weed Control", pp. 1-5. McGraw-Hill Book Co., Inc., New York, N.Y., 1942. 1st ed.
51. Rosenthaler, L.: Analytical Notes, C.A., 27, 3893 (1933); Pharm. Zentralhalle 74, 288-90 (1933).
52. Ruehle, A. E.: Potentiometric Titration in Nonaqueous Solutions, Anal. Chem. 10, 130-1 (1938).
53. Seidell, A.: "Solubilities of Inorganic and Organic Compounds", pp. 9-10. D. Van Nostrand Co., Inc., New York N. Y., 1919. 2d ed.
54. Shedlovsky, T., A. S. Brown, and L. A. MacInnes: The Conductance of Electrolytic Solutions, C.A., 28, 7115 (1934); Trans. Electrochem. Soc. 66, 14 pp. (preprint) (1934).

55. Shreve, R. N.: "The Chemical Process Industries", pp. 670-81.  
McGraw-Hill Book Co., Inc., New York, N. Y., 1945.
56. Shriner, R. L. and R. C. Fuson: "The Systematic Identification of  
Organic Compounds", p. 98. John Wiley and Sons, Inc., New York,  
N. Y., 1935.
57. Skeen, J. R.: Ethyl Alcohol, Chem. Eng. 56, 10-314 (1949).
58. Spence, L. U. and F. O. Haas: Chlorination of Aliphatic Acids and  
Esters, C.A., 39, 4621 (1945); U. S. Pat. 2,379,759 (July 3, 1945).
59. Strain, H. H.: Chromatographic Adsorption Analysis, Anal. Chem. 14,  
245-49 (1942).
60. \_\_\_\_\_: Conditions Affecting the Sequence of Organic Compounds  
in Tswett Adsorption Columns, Anal. Chem. 18, 605-9 (1946).
61. Strosacker, C. J.: Chlorinating Acetic Acid, C.A., 24, 3250 (1930);  
U. S. Pat. 1,757,100 (May 6, 1930).
62. Taylor, J. P.: The Formulation of an Economical Chemical Herbicide to  
Kill Johnson and Bermuda Grass, pp. 1-7. Unpublished M. Sc.  
Thesis, Library, Va. Poly. Inst., Blacksburg, Va., (1950).
63. *ibid*, p. 27.
64. *ibid*, pp. 459-67.
65. Theobald, C. W.: Preparation of Haloacetyl Halides, C.A., 39, 4085  
(1945); U. S. Pat. 2,378,048 (June 12, 1945).
66. Treadwell, F. P. and W. T. Hall: "Analytical Chemistry", pp. 587-8.  
John Wiley and Sons, Inc., New York, N. Y., 1915. Vol. II.  
4th ed.



67. Usanovich, M. and K. Yatsimirskii: Acid-Base Interaction in Acetic Anhydride, C.A., 36, 6444 (1942); J. Gen. Chem. (USSR) 11, 957-8 (1941).
68. Verhoek, F. H.: The Kinetics of the Decomposition of the Trichloroacetates in Various Solvents, J. Am. Chem. Soc. 56, 571-7 (1934).
69. Vilbrandt, F. C.: "Chemical Engineering Plant Design", pp. 287-90. McGraw-Hill Book Co., Inc., New York, N.Y., 1949. 3d ed.
70. *ibid*, p. 388.
71. *ibid*, pp. 420-29.
72. *ibid*, pp. 436-49.
73. *ibid*, pp. 449-514.
74. *ibid*, pp. 514-51.
75. Weiss, J.: The Theory of Chromatography, J. Chem. Soc. 297-303 (1943).
76. Weissenberger, G., F. Schuster, and H. Pamer: Organic Molecular Compounds, C.A., 20, 1785 (1926); Monatsh 46, 281-9 (1926).
77. Wertheim, E.: "Organic Chemistry Laboratory Guide", p. 199. P. Blakiston's Son and Co., Inc., Philadelphia, Penn., 1937.
78. West, C. J. (Compiler): "International Critical Tables", p. 28. McGraw-Hill Book Co., Inc., New York, N. Y., 1933. Vol. 3.
79. *ibid*, p. 33.
80. *ibid*, p. 85.
81. *ibid*, p. 112.
82. *ibid*, p. 123.
83. West, C. J. (Compiler): "International Critical Tables", p.14. McGraw-Hill Book Co., Inc., New York, N. Y., 1933. Vol. 4.

84. West, C. J. (Compiler): "International Critical Tables", pp. 80-1.

McGraw-Hill Book Co., Inc., New York, N. Y., 1933. Vol. 5.

85. *ibid*, p. 102.

86. *ibid*, p. 107.

87. *ibid*, pp. 114-15.

88. *ibid*, p. 124.

89. *ibid*, p. 132.

90. *ibid*, pp. 136-38.

91. *ibid*, p. 148.

92. *ibid*, p. 159.

93. *ibid*, p. 181.

94. *ibid*, p. 227.

95. \_\_\_\_\_ : "International Critical Tables", pp. 142-3.

McGraw-Hill Book Co., Inc., New York, N. Y., 1933. Vol. 6.

96. *ibid*, p. 249.

97. *ibid*, pp. 261-62.

98. \_\_\_\_\_ : "International Critical Tables", p. 12.

McGraw-Hill Book Co., Inc., New York, N. Y., 1933. Vol. 7.

99. *ibid*, p. 34.

100. *ibid*, p. 67.

101. *ibid*, p. 80.

102. *ibid*, p. 122.

103. *ibid*, p. 245.

104. Wilson, J. B. and G. L. Keenan: Identification of Monochloroacetic Acid as the Barium Salt, C.A., 38, 5999 (1944); J. Assoc. Official Agri. Chem. 27, 446-8 (1944).
105. Wilson, J. N.: A Theory of Chromatography, J. Am. Chem. Soc. 62, 1585-91 (1940).

### VIII. ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. F. C. Vilbrandt, Head, Department of Chemical Engineering, Virginia Polytechnic Institute, for suggesting the problem, for his advice, guidance, and criticism during the performance of the experimental work and in the preparation of the written material.

To Mrs. L. W. Claffey for her excellent preparation and editing of the final copies of the thesis, the author wishes to express his appreciation.

The writer wishes to express his gratitude to his parents,  
for their help in making this work possible.

**The vita has been removed from  
the scanned document**