

AN ABSTRACT OF THE THESIS OF

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Title --A Study of the Reaction Between Liquid Chlorine,
--Liquid Sulphur Dioxide, and Water.-----

Abstract Approved--

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(Major Professor)

In the preparation of this thesis, the following work was performed:

Liquid sulfur dioxide and liquid chlorine were reacted with heated water and complete conversion of reactants to hydrochloric and sulfuric acids obtained.

A quantitative study of this reaction was completed. A method of titrimetric analysis was used for both sulfate and chloride determination which gave accurate and consistent results. Quantitative yields of both chloride and sulfate were obtained.

The reaction was treated as an oxidation and reduction system and various substitutes for either water or sulfur dioxide were reacted with the halogen and other halogens were substituted for chlorine.

The literature was reviewed and other methods of production of sulfuric and hydrochloric acids were studied, and comparisons were made.

A brief survey of costs and comparative merits of the process concluded the study.

A STUDY OF THE REACTION
BETWEEN LIQUID CHLORINE,
LIQUID SULPHUR DIOXIDE AND WATER

by

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A THESIS

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A STUDY OF THE REACTION
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Part I

Introduction

In studying the synthesis of sulfuryl chloride which is usually made by the interaction of chlorine and sulfur dioxide gases in presence of a catalyst, it was noted that the reaction is catalyzed by sunlight or ultra violet light, but the literature mentioned (Mellor, 9) that a trace of water is necessary, the anhydrous gases failing to react. Subsequent decomposition of sulfuryl chloride by water yields hydrochloric and sulfuric acids, two important products of commerce.

It was thought interesting to investigate whether water might act as a catalyst in a mixture of the liquid gases, possibly forming sulfuryl chloride which would then hydrolyze forming the acids.

A preliminary test was made by adding heated water to an agitated mixture of the liquid gases in a flask immersed in a dry ice acetone bath. It was evident at once that a reaction of some sort took place explosively immediately upon a drop of water striking the liquid

gases. An excess of water was then added and qualitative tests of the products with silver nitrate and barium chloride revealed heavy precipitates of both chloride and sulfate.

The reaction seemed so efficient it could hardly be other than quantitative. It became the work of this thesis, therefore, to study this reaction of liquid chlorine, liquid sulfur dioxide and heated water, which so far as can be determined has not previously been done. A few experiments were also conducted to demonstrate the versatility of the reaction when regarded as a general oxidation and reduction system, with substitution of reactants other than water. The results obtained in some of these reactions, particularly that of the liquid gases with water, indicate commercial possibilities.

Although the present approach, using liquid sulfur dioxide and liquid chlorine is new, so far as we know, the general reaction of these compounds, particularly in the gaseous state, has been the subject of many investigations. These center both around theoretical and industrial applications.

The latter have been undertaken either to produce sulfuryl chloride or a mixture of hydrochloric and sulfuric acids.

With this latter objective Lunge (1) and Mellor (9) cite a British patent, Haehner, Brit. 717 (16) in which a gaseous mixture of chlorine and sulfur dioxide is allowed to meet with water, or better, hydrogen chloride flowing down in a reaction tower. Gaseous hydrogen chloride escapes at the top and 65% sulfuric acid emerges at the bottom. This same process was patented in France, England, and the United States. Snelling in U. S. 1,430,035 (14) and Welch in U. S. 1,285,856 (15), cite methods of reacting chlorine and sulfur dioxide gases in the presence of actinic rays while water is sprayed into the chamber. Electrical methods of precipitation were employed. Presumably it was found difficult to condense the sulfuric acid spray.

Tobler in U. S. 1,332,581 (10) the halogen and sulfur dioxide gases are conducted into a flowing stream of water. The stream, after passing through a series of packed towers, is subjected to the action of sulfur dioxide alone to sweep out the halogen acid. The drawings of this patent show a sulfur burner from which the sulfur dioxide gas passes directly to the characteristic packed towers so often used in sulfuric acid manufacture.

This method of manufacturing hydrochloric and sulfuric acids from mixing sulfur dioxide and chlorine gases with a stream of water was considered while the manufac-

ture of sulfuric acid was still in experimental development, before the contact and chamber processes had become established as standard methods of sulfuric acid manufacture. Chlorine was an expensive chemical in that period of industrial development and the Deacon process of chlorine manufacture from hydrochloric acid was still much used. Consequently the manufacture of sulfuric and hydrochloric acids from chlorine and sulfur dioxide could hardly have warranted serious consideration at that time.

No methods employed in these early patents reacting chlorine and sulfur dioxide with a stream of water or dilute hydrochloric acid, could produce only weak acids and would involve either considerable loss, or expensive recovery of unreacted gases. The process would be slow and ill suited to mass production of the acids.

It might be pertinent at this time to review some more recent work as cited in the patent literature and elsewhere.

In hydrochloric acid manufacture the trend seems to be toward direct combustion from the elements. Undoubtedly, a few years ago the cost of the elementary gases, hydrogen and chlorine, would have rendered impractical this method of hydrochloric acid manufacture.

Morozov (5) describes semi-factory production of hydrochloric acid from hydrogen and chlorine. The gases

are burned in the presence of pieces of quartz as catalyst.

Osborne in U. S. 2,126,803 (6) describes a method of conducting dry chlorine and ammonia gases into contact with calcium chloride in a reaction chamber heated to 800° and hydrogen chloride and free nitrogen are obtained.

Barstow and Heath, U. S. 1,874,225 (7) chlorine is mixed with an excess of water vapor and the mixture is heated to 1400° - 1600° in the absence of reducing substances and hydrogen chloride is recovered from the reacted gases.

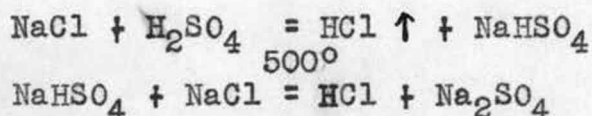
I. G. Farbenind, British 411,818 (8), sulfuric and hydrochloric acids are obtained by reaction of sulfuryl chloride and water in the presence of a substance which is converted to a wetting agent by action of sulfuryl chloride.

A number of processes have been developed in which methane is employed to make hydrochloric acid and hydrogen sulfide gas is used for making sulfuric acid.

The majority of present-day patents in sulfuric acid manufacture are for various catalysts which may be used as substitutes for platinum in the contact process of sulfuric acid manufacture.

A brief description of the long established processes of hydrochloric and sulfuric acid manufacture is given in the following few pages.

The classical method of hydrochloric acid manufacture is the first step in the Le Blanc carbonate process.



In this reaction efficiency depends on the fact that hydrogen chloride is quite insoluble in concentrated sulfuric acid. Water must be excluded for if the HCl were absorbed in the reaction chamber NaHSO₄ would react with the concentrated HCl to precipitate NaCl; hence for both steps of the process to occur, concentrated H₂SO₄ is employed and HCl driven off as a gas and absorbed in a tower system to produce the aqueous hydrochloric acid of commerce.

The disadvantages of this process are principally these three: (1) Concentrated sulfuric acid is required and is in itself expensive. (2) The formerly large market for salt cake for the operation of the Le Blanc process has been curtailed by the development of the Solvay process in Na₂CO₃ manufacture. Where formerly HCl was almost a by-product in the manufacture of Na₂SO₄, now the process is handicapped by producing a product for which there is a limited market. This fact is indicated by the price quotation of salt cake given on a subsequent page. (3) A less pure acid is obtained than by other means. For these reasons other methods of hydrochloric acid manufacture are be-

coming increasingly important, of which the direct combustion of hydrogen and chlorine is perhaps the chief one.

The standard methods of sulfuric acid manufacture are two: the contact and the chamber processes.

The contact process depends on oxidation of sulfur dioxide by oxygen of the air in the presence of a solid catalyst.

The lead chamber process depends on the oxidation of sulfur dioxide with the use of oxides of nitrogen as catalytic material. In this process a small amount of nitrogen dioxide suffices to convert a great deal of sulfur dioxide to sulfur trioxide.

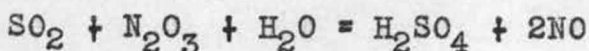
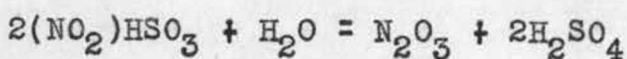
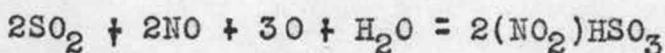
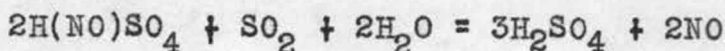
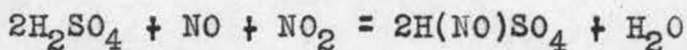
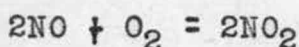
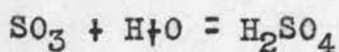
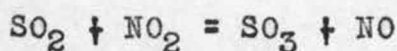
In part, the efficiency of the process depends on the recovery of the oxides of nitrogen. It so happens that an equimolecular mixture of nitric oxide and nitrogen dioxide is absorbed by concentrated sulfuric acid and is released on dilution of the acid.

The reaction occurs in the Glover tower. The sulfur dioxide and oxides of nitrogen mix in rising through this tower and pass into a series of lead chambers. A jet of steam is blown into the chambers. The sulfuric acid formed condenses on the floor of the chambers as 60-70% acid and is drained off.

The unused gases pass into the Gay Lussac tower in which the oxides of nitrogen are absorbed. This tower is

filled with broken tile; concentrated H_2SO_4 trickles down through the tile, probably forming $\text{H}(\text{NO})\text{SO}_4$, which is pumped to the top of the Glover tower and mixed with dilute acid and the released oxides of nitrogen are again reacted with ascending sulfur dioxide.

Possible reactions often cited in the literature for this process follow; the second group is from Mellor (9).



Usually in the contact process a platinum catalyst dispersed in finely divided form on a supporting material as asbestos is maintained at about 400° temperature and the purified sulfur dioxide and oxygen passed over the catalyst. The sulfur trioxide formed is absorbed in 98% sulfuric acid which is usually maintained at that concentration by dilution.

Improvements in this process have mainly centered around the development of cheaper catalysts or catalysts

with longer life as mentioned above.

The present-day manufacture of both hydrochloric and sulfuric acid is frequently associated with their use as a method of utilizing what would otherwise be waste products, such as sulfur dioxide from smelters, or hydrogen from electrolytic processes. Such considerations therefore affect the price structure for these acids.

Part II

Quantitative Procedure

Experimental Work

The experimental work of this thesis is divided roughly into three divisions:

- A. A number of preliminary runs on the reaction between liquid sulfur dioxide, liquid chlorine, and water were carried out to establish successful working conditions and to determine qualitatively the course of the reaction.
- B. Accurate quantitative determination of yields was then made.
- C. A series of qualitative investigations was conducted in which other substances were substituted for one or more of the original reactants. Most of these reactions involving liquid reagents have not previously been recorded in the literature and some indicate interesting possibilities.

The experiment reacting liquid chlorine, liquid sulfur dioxide, and hot water was repeated many times, usually employing simply a three-neck, loosely stoppered flask with an absorption train if desired, that is, a glass tube leading to another flask into which the gaseous products of the reaction were conducted for absorption.

In practice the liquid gases, namely sulfur dioxide and chlorine, were poured from cylinders into the reaction vessel and agitated, hot water was added almost as one would titrate from a burette and the reaction went just as efficiently to an end point as would a volumetric titration. The water seemed to explode immediately on striking the liquid chlorine and hydrogen chloride vapors rose from the reaction. Globules of a liquid that solidified quickly could be seen floating in the solution and were crystals of sulfur trioxide which in one or two instances were isolated from the reaction. As soon as the chlorine had reacted, the reaction stopped and further water added served only to dilute the products.

It would seem possible that with properly controlled conditions, acids as concentrated as desired could be made by this means and easy separation of sulfur trioxide and hydrogen chloride effected, as the hydrogen chloride gas condenses at -85° and the temperature of the bath was about -50° . Sulfur trioxide condenses quickly and has a melting point of about 17° .

In fractionating concentrated solutions of products of the reaction, the characteristic maximum boiling point for hydrochloric acid was observed. As the solution was heated, the temperature remained for some time at 110° , then rose steadily. A concentrated sulfuric acid bath was

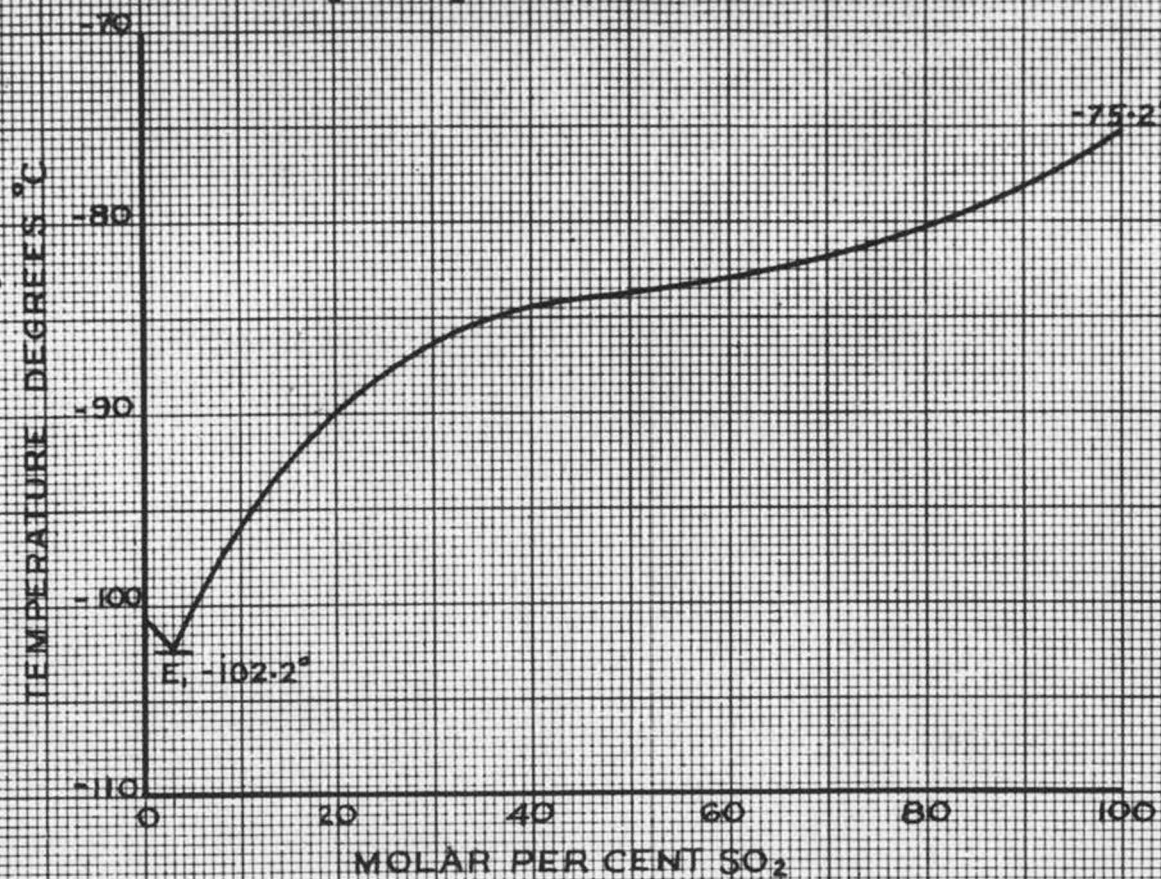
used for heating and the remaining solution darkened with rise in temperature precisely as did the sulfuric acid bath, white fumes came off and the solution boiled about 290° and again at 340° .

Sulfuryl chloride which was originally sought as an intermediate product was never found. Search of the literature reveals that liquid chlorine and liquid sulfur dioxide do not combine except in the presence of a catalyst. This is shown graphically in Figures I and II, pages 13 and 14, where are given the experimental results of T. P. van der Goot (17), on this system.

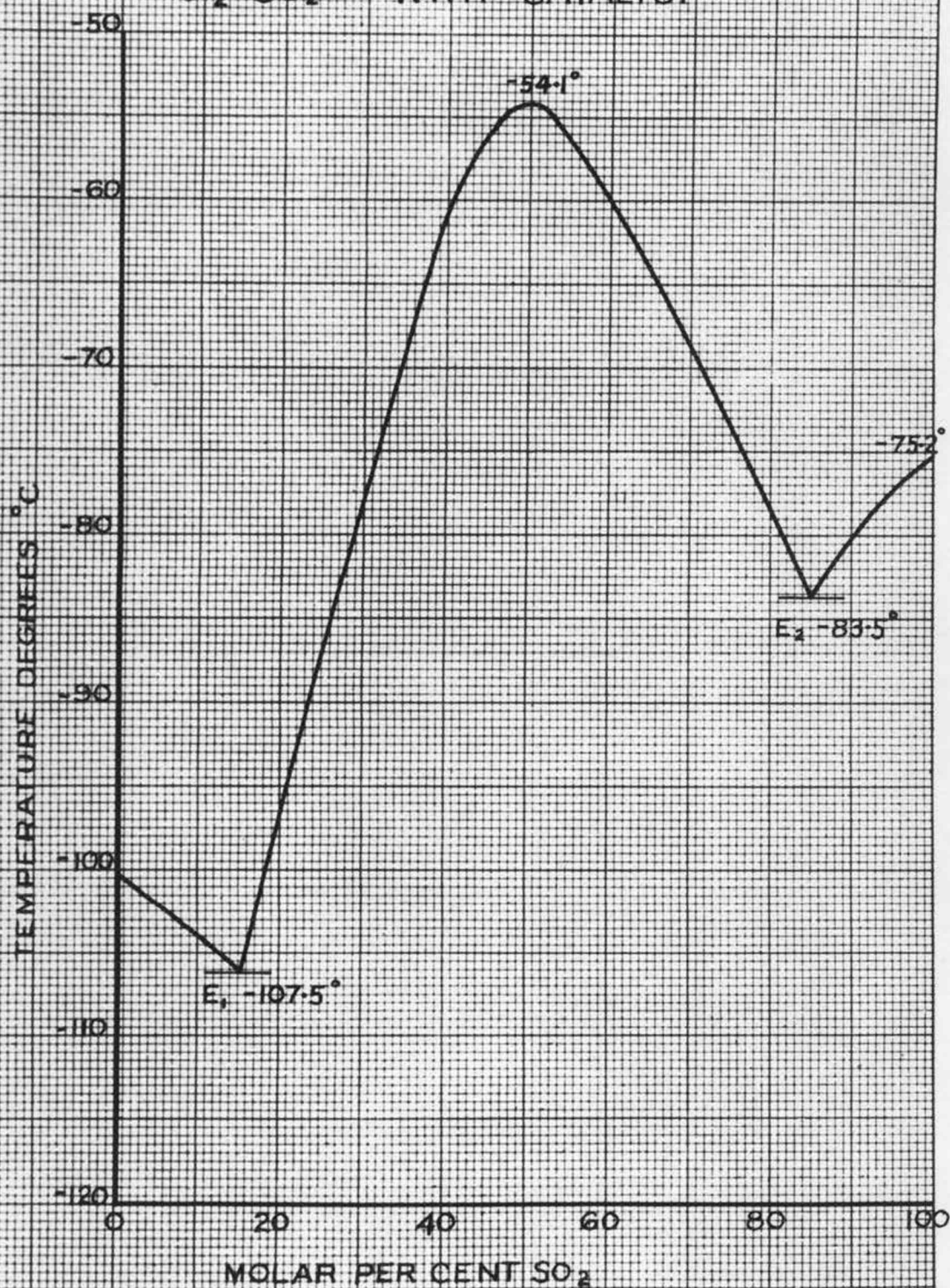
Many catalysts are known to function in this manner but water is apparently not among them. Since chlorosulfuric acid can be made by direct action of hydrogen chloride on fuming sulfuric acid or sulfur trioxide, A. W. Williamson (18) and General Electric Co. U. S. 1,420,335 (19) it might conceivably have been a product of this reaction. This would certainly not be the case however when excess water was added, and the distillation curve of the products did not indicate its presence. However, the fog which almost invariably formed when the products were passed into the absorption flasks could perhaps have contained some of this compound as well as droplets of sulfur trioxide and hydrochloric acid vapor.

Following absorption, however, the only products ever obtained were hydrochloric and sulfuric acids.

FREEZING POINT CURVE OF THE SYSTEM
 $\text{Cl}_2 - \text{SO}_2$ WITHOUT CATALYST



FREEZING POINT CURVE OF THE SYSTEM
 $\text{Cl}_2\text{-SO}_2$ WITH CATALYST



Quantitative Procedure

It was decided that a careful quantitative study should be made of the reaction between liquid sulfur dioxide, liquid chlorine, and heated water.

This presented difficulties because the reaction is somewhat explosive in character. Small quantities of material, it was decided, would have to be used. A tightly closed system was found to be necessary after experiment evidenced the fact that absorption of the evolved gases was otherwise incomplete, due in part to the rapidity of the reaction.

After several types of apparatus were tested or considered, a fairly simple arrangement was devised. A 200 cc. three necked flask was employed as the reaction vessel. From each side neck tubes lead to absorption flasks. Four gas bottles were arranged in a train on one side, the other side neck of the flask opened into a 500 ml. balloon flask. Usually 1250 ml. of solution measured by volumetric flasks was put in the gas bottles as absorption media and another 250 ml. or more was used to rinse out the flasks after the reaction.

The glass tubes leading into the absorption flasks were perforated below liquid level to provide better gas absorption by the liquid from a series of small holes in each tube.

The center opening of the flask was connected by means of glass and rubber tubing to a Pyrex test tube in which water could be heated and poured into the flask by means of atmospheric pressure, since a two-holed stopper in the tube permitted a pinch clamp connection which could be opened to the atmosphere. All stoppers were wired securely when the experiments were made.

The character of the reagents and reaction were such that special techniques had to be devised. A number of unsuccessful runs were made before the results became satisfactory. To secure known amounts of liquid chlorine and liquid sulfur dioxide, the liquids were poured into the calibrated tubes and the tubes were loosely stoppered. Evaporation was relied upon to bring the volumes to the proper levels for the desired stoichiometric proportions, then the sulfur dioxide and chlorine were poured into the reaction flask which was immersed in a chloroform, dry ice bath.

After the liquid gases were in the flask, the center opening was closed with the stoppered connection leading to the test tube of boiling water and secured, all clamps were removed and the boiling water in the test tube was poured into the flask.

Yields were sometimes reduced due to stoppers loosening or the water not entering properly or striking the

sides of the vessel and condensing. After a few trials, however, it was found possible to overcome these faults and to closely duplicate results.

For the quantitative determination of the reaction products it was decided to absorb them in a solution of standard base and to determine the products quantitatively by titration with various standard solutions following in general procedures outlined by Lunge (1) and Dennis (2).

Since the absorption of chlorine itself by base would yield chlorides, water alone was used as absorbing agent in many of the later runs but no evidence ever accumulated that there was any appreciable amount of free chlorine in the reaction products.

Part III

Tables and Discussion

The solutions listed in Table I were made up and standardized.

Silver nitrate was standardized by sodium chloride.

The barium chloride solution was standardized gravimetrically.

Mahin (3) and Scott (4) were consulted as further references in the analytical work.

Table I

Solutions Made Up and Standardized	
Solution	Normality
AgNO_3	0.1001
NaCl	.1000
BaCl_2	.2501
Na_2CO_3	.2000
HCl titre 0.1001 N. AgNO_3 = 0.003649	gm. HCl per cc. 0.1001 N AgNO_3 standard solution
H_2SO_4 titre 0.2501 N. BaCl_2 = 0.01226	gm. H_2SO_4 per cc. 0.2501 N BaCl_2 standard solution

For the estimation of chloride ion the Mohr method was used following standard methods: Scott (4), Dennis

(2), and Mahin (3). In some cases the chloride was also determine gravimetrically in good agreement with the volumetric results.

The determination of sulfate ion proved to be a more complex problem.

At first it was attempted to obtain the sulfate yield by difference. Total acid was to be determined by titration of the excess base used as absorption medium, with standard acid. Then with standard iodine solution and starch indicator the SO_2 content was to be determined and consequently knowing the total acid figure and having the values of chloride and sulfite (ion), the sulfate should be obtained by difference. However, in the initial runs it was found that the titration with standard iodine did not give reliable results.

It became necessary to find a quick, dependable volumetric method of determining the sulfate ion. Outside indicators were tried in titrating with standard BaCl_2 solution but without satisfactory results.

Tetrahydroquinone was employed as indicator, but easily reproducible values could not be obtained.

In a search of the literature, brief mention was found in Lunge (1), Vol. I., p. 101, of a method for determining sulfate by titration of a neutral, boiling solution of the sample with an excess of standard BaCl_2 and back titrating with standard Na_2CO_3 to a phenolphthalein endpoint.

This method was tried with very encouraging results and values obtained were checked gravimetrically as reference to the tables for experimental runs #5 and #6 indicates.

Having established the validity of this method of titrimetric determination of sulfate, it was employed in analyzing subsequent runs.

The technique employed in these titrations was as follows.

For the sulfate, the acidified solution in a porcelain dish or Erlenmeyer was boiled for some time to remove sulfite, then neutralized, using phenolphthalein as indicator, an excess of standard BaCl_2 solution was added with stirring, then using more phenolphthalein as indicator, standard Na_2CO_3 was added with stirring until the solution remained definitely pink.

Several samples of each run were titrated as it was found best to add an excess of about one or two cc.'s of BaCl_2 and then to back titrate with the Na_2CO_3 . The excess barium precipitates as carbonate and a slight excess of Na_2CO_3 gives the basic color change with phenolphthalein. The quantitative results are shown in Tables II to VII.

Without supposition concerning any intermediate steps by which the oxidation may take place the net reaction is

$$2\text{H}_2\text{O}(l) + \text{SO}_2(l) + \text{Cl}_2(l) \rightarrow 2\text{HCl} + \text{H}_2\text{SO}_4.$$

From the stoichiometric proportions, the molecular weights and the approximate specific gravities it is possible to calculate the proportions by volume in which these liquids should be mixed to give the relative amounts called for by the equation as shown in Table II. These volumes by quantitative reaction should produce the weight of products noted.

Table II

Theoretical Volumes of Liquid Reactants				
$2 \text{H}_2\text{O}(1) + \text{SO}_2(1) + \text{Cl}_2(1) = 2 \text{HCl} + \text{H}_2\text{SO}_4$				
(1)	Spec.grav.	1.00	1.434	1.56
	of liquids			
(2)	Proportion by wt.	3.604	6.406	7.091 = 7.292
				9.808
(3)	Proportion by liquid vol.	3.604	4.468	4.547

If the amounts of material listed in Table II were used, about four liters of the standard solution would have been needed for absorption. This would have rapidly depleted the supply and the reaction of such amounts of the liquid gases would have been too violent for safe confinement in the system.

In order to measure quite closely the proper amounts of the liquid gases a series of small pyrex test tubes was calibrated by means of a micro burette.

After this was done a slight excess of the liquid gases could be placed in one of these test tubes and allowed to evaporate down to the mark indicating a desired volume which might then be added to the main reaction flask.

In Table III are shown the amounts of reagents used together with volume of water or base used to absorb the reaction products of the sixteen runs made.

Table III

Experimental Runs					
Run No.	Ml.liquid Cl_2 Used	Ml.liquid SO_2 Used	Total Volume Solution	Absorb. Ml.	
1	0.82	1.21	1820 ml	Alkali	
2	.82	1.21	1750 ml	Alkali	
3	.82	1.21	1600 ml	Alkali	
4	.82	1.21	1500 ml	Alkali	
5	.82	1.21	1750 ml	Alkali	
6	.82	1.21	1520 ml	Alkali	
7	.82	1.21	1000 ml	Alkali	
8	.82	1.21	1100 ml	Alkali	
9	.82	1.21	Discarded	Alkali	
10	.82	.806	1600 ml	Water	
11	.86	1.38	1600 ml	Water	
12	.86	1.38	1870 ml	Water	
13	.86	1.38	1650 ml	Water	
14	.86	1.38	1600 ml	Water	
15	.86	1.38	1300 ml	Dist.water	
16	.86	1.38	1350 ml	Dist.water	

From the absorption products analiquot of 50 ml. was taken and analyzed for chloride and sulfate by the methods described above. From this could be calculated the total

amount of hydrochloric acid and sulfuric acid produced. The first four solutions were analyzed by the indirect method which gave unsatisfactory results, and are not included in the tabulated results. Runs 5 and 6 were analyzed both gravimetrically and titrimetrically with excellent agreement, although the yield of hydrochloric acid was low due to improper manipulation of the apparatus, which was improved in the later runs. The agreement is shown in Tables IV and V. In experiment #5 Table IV, for instance, 0.82 ml. of liquid chlorine was introduced into the reaction flask. The calculated amount of sulfur dioxide for this volume of chlorine would be 0.81 ml. Slightly more than this amount was added so that all yields are calculated on the basis of amount to be expected from the exactly measured volume of chlorine.

The products were collected in a total volume of 1750 ml. and 50 ml. aliquots taken for the determination of Cl and SO_4 from which by suitable factors could be determined the HCl and H_2SO_4 found. 0.82 ml. chlorine should yield 1.318 gm. HCl. From these the percent yield is readily obtained. The data for the remaining runs are summarized in Tables VI and VII.

Table IV

Determination of Cl as HCl

Gravimetrically

#	Tot.vol.ml. absorbed prod.	Vol. Cl ₂ Used	Aliquot part ml.	Wt. AgCl(g)	Wt.HCl in total vol. found	calc.	Percent yield
5	1850	0.82	50	0.083	0.739	1.318	56
6	1520	0.82	50	0.1048	0.812	1.318	62

Titrimetrically

				Ml.AgNO ₃ 0.1001N			
5	1750	0.82	50	5.90	0.761	1.318	58
6	1520	0.82	50	7.00	0.775	1.318	59

Table V

Determination of Sulfate
as H_2SO_4

Gravimetrically

#	Tot.vol.ml. absorbed prod.	Vol. Cl_2 Used	Aliquot part ml.	Wt. BaSO_4 found	Wt. H_2SO_4 in total vol. calc.	Percent yield *
5	1750	0.82	50	0.1194	1.76	100
6	1520	0.82	50	0.1352	1.74	99

Titrimetrically

				Ml. BaCl_2 0.2501N		
5	1750	0.82	50	4.10	1.76	100
6	1520	0.82	50	4.80	1.79	101

* Based on Cl_2 used with excess SO_2

Table VI
Determination of Cl as HCl

Titrimetrically							
Run No.	Total Vol.Ml Absorbed Prod.	Vol.Cl ₂ Used	Aliquot Part Ml.	Ml.AgNO ₃ .1001N	Wt.HCl in total vol. found	Calculated	Percent Yield
7	1000	0.82	50	16.0	1.168	1.318	88
8	1100	0.82	50	14.2	1.126	1.318	85
10	1600	0.82	50	8.10	.906	1.318	71
11	1600	0.86	50	9.96	1.163	1.380	84
12	1870	0.86	50	7.60	1.036	1.380	76
13	1650	0.86	50	11.30	1.360	1.380	98
14	1600	0.86	14	5.760*	1.345	1.380	97
15	1300	0.86	50	13.71	1.300	1.380	94
16	1350	0.86	50	13.76	1.355	1.380	98

*Run #14 was titrated by Microburette

Table VII

Determination of Sulfate as H_2SO_4

Titrimetrically

Run No.	Total vol.Ml. Absorbed Prod.	Vol.Cl ₂ Used	Aliquot Parts Ml.	Ml.BaCl ₂ 0.2501N	Wt.H ₂ SO ₄ Found	in tot. vol. Calc.	Percent* Yield
7	1000	0.82	50	7.10	1.726	1.7673	97.
8	1100	0.82	50	6.41	1.737	1.7673	98.
10	1600	0.86	50	4.35	1.721	1.7673	96.
11	1600	0.86	50	4.54	1.801	1.8541	98.
12	1870	0.86	50	3.80	1.760	1.8541	94(2)
13	1650	0.86	50	4.53	1.830	1.8541	98
14	1600	0.86	50	4.666(1)	1.828	1.8541	98
15	1300	0.86	50	5.80	1.850	1.8541	99
16	1350	0.86	50	5.56	1.851	1.8541	99

* Based on Cl₂ used with excess SO₂

(1) Run #14 titrated by Microburette

(2) In run #12 .84 ml. liquid SO₂ was used, which virtually is the theoretical amount of SO₂ required for reaction with .86 ml. liquid Cl₂.

Part IV

Discussion of Data

In all, sixteen, runs were made with this apparatus, in an effort to check quantitatively the reaction of liquid chlorine, liquid sulfur dioxide, and boiling water.

The first three or four runs gave discouraging results but demonstrated weaknesses in the procedure to be remedied.

The necessity of securing all stoppers, for instance, and the desirability of having a flexible apparatus for prolonged shaking in absorption of products was demonstrated.

In the first three runs in which the acid products of the reaction were water absorbed, namely runs 10, 11, and 12, a study of Tables VI and VII reveals a significant repetition of uniformly high yields of sulfate and varying poor yields of chloride.

Since the validity of the titrations was established gravimetrically, it could hardly be contended that the yield indicated for sulfate is high.

Only one source of error remained, unless the possibility of catalysis could be assumed to account for the high sulfate yield.

In heating the water in the test tube and passing it into the reaction flask, containing the liquid gases, a stopcock was opened to the atmosphere to provide certain flow of the water into the flask. The violent expansion of the gaseous products of the reaction made inevitable some loss of the product through this brief opening of the system, which nevertheless seemed necessary.

In considering how to overcome this source of error the obvious solution would be simply to employ steam pressure to push the heated water or steam into the reaction vessel.

This procedure was employed in the last four runs, maintaining a completely closed system and the almost quantitative results and good agreement between sulfate and chloride yield in each case (see runs #13 and 14, 15 and 16) attest to the soundness of this procedure and locate the difficulty experienced in the earlier runs.

In the completely closed system, runs #13, 14, 15, and 16, the reaction flask was filled almost completely with water siphoned from the absorption flasks; this seems to be an index of the efficiency of the reaction. In all previous runs the flask was filled less completely by siphoning and this in itself indicates a partial loss of gas.

This series of experiments establishes the reaction as practically quantitative in yield. No doubt the system could be further refined by employing directly as the absorption vessel, the large balloon flask to which the contents of the various gas bottles were transferred after reaction, thereby eliminating inevitable small losses in washing and transfer and also reducing the number of stoppered openings and with such a system the yields could be made to very closely approximate the theoretical.

Prolonged shaking of the absorption train was necessary because the SO_3 vapor remained suspended like a white cloud and was especially hard to absorb in the pure water medium. This would present a definite problem were attempt made to apply the process to industrial use.

Because of the apparent high reactions of the liquid chlorine sulfur dioxide mixture, qualitative experiments were tried substituting various oxides, some of them refractory, for the water used in the previous part of the thesis. Oxides of aluminum, magnesium, manganese, chromium, etc., were heated in crucibles and the liquid chlorine, sulfur dioxide mixture added. A violent reaction ensued; in one instance it was noted the contents of the crucible became red hot although no further heat was applied. Such reactions need to be confined to be controlled. Water seemed to facilitate the reaction but was only tried on a separate sample for effect.

The reactions could be pictured most simply as follows: $2 \text{MgO} + \text{SO}_2 + \text{Cl}_2 = \text{MgSO}_4 + \text{MgCl}_2$

Analysis of the products for both anions and cation was made. The analysis was simplified somewhat since the pure oxides were reacted separately, the problem became merely one to determine if the reaction had converted the metal into its soluble salts to any extent. Time prevented quantitative aqueous study.

Solutions of the magnesium residue gave precipitates of the magnesium ammonium phosphate and strong precipitates of both chloride and sulfate were had by the usual methods. Acidification of the solutions prevented a sulfite precipitate if any of this ion should be present. Aluminum gave a positive test in the familiar ammonium acetate alkaline solution with the $\text{H}_3\text{C}_{22}\text{H}_{13}\text{O}_8$, Aluminon reagent. A brick-red precipitate formed.

The manganese residue had a pink tinge in the crucible. A heavy white precipitate of manganese hydroxide developed when alkali was added to the clear solution of the residue of the reaction. The precipitate turned brown almost immediately.

The solution of the reaction with green Cr_2O_3 was tested for chromium by acidifying with acetic acid and gave a yellow precipitate with barium chloride. Alkali precipitated the hydroxide which was soluble in excess of the reagent.

Upon substituting other reagents for sulfur dioxide in the system, the following results were noted.

Liquid hydrogen sulfide was converted to sulfate with some evidence of free sulfur when reacted with liquid chlorine and hot water or steam, as was sulfur dioxide.

It seemed possible that ammonia might be oxidized to nitric acid in the system, although it is well known that under somewhat analogous conditions the explosive chlorides of nitrogen are formed. The chief difference between the present experiments and those studied by other investigators is the addition of the water at an elevated temperature. Liquid ammonia was added to liquid chlorine together with water and small explosions of the material with some flame occurred. It seemed strange to have a solution at -60°C . and upon adding a little water have flames result. With ammonia thus substituted for sulfur dioxide, decomposition of metallic oxides proved to be quite complete, also.

Manganese and magnesium oxides were converted completely to the chlorides even in an open flask. Heavy precipitates of both the anion and cation were obtained on analysis of the solutions.

A possible explanation for which there is qualitative evidence only would be that the nitrogen was oxidized principally to nitric oxide which exercised a solvent

effect on the oxides. On standing, all the solutions became colored a deep yellow, characteristic of nitric acid solutions, which is due to the presence of nitrogen dioxide. Ferrous sulphate solution gave the brown color test for nitrite in the acidified solutions. The qualitative tests were principally taken from Treadwell Hall(11).

Sulfuryl chlorides of benzene and probably a mixture of chlorides were apparently obtained on reacting heated benzene with liquid sulfur dioxide and liquid chlorine. There was some evidence of phenol formation with toluene, liquid chlorine, and hot water. The ceric nitrate test was fair but here again a mixture of compounds was probable as the halogen test on the organic residue was positive. Neither of these reactions was sufficiently investigated due to difficulties encountered in the quantitative work.

Substitution of halogens in the system gave the following results.

If liquid bromine is substituted for liquid chlorine, the liquid sulfur dioxide dissolves the bromine immediately and with boiling water a rapid reaction takes place forming water clear hydrobromic and sulfuric acids. Copious fumes apparently of moist hydrobromic acid are driven off and can be absorbed separately. Very little free sulfur is formed and no free bromine. Reversal of the reaction apparently is negligible, no doubt partly due to rapid

evolution of hydrogen bromide and the low temperature of the products. Analysis of the fuming acid solutions gave heavy precipitates of both bromide and sulfate ion with the proper reagents.

Iodine crystals dissolve in the liquid sulfur dioxide and as hot water is added an efficient reaction occurs, the iodine dissolves rapidly and water clear acid solutions of hydriodic and sulfuric acids are obtained with little free sulphur. The color of free iodine disappears completely. The iodine and sulfate tests again gave heavy precipitates of both ions.

The solubility of iodine in sulfur dioxide is well known but controversy exists concerning the extent of the oxidation of the sulfite to sulfate in the presence of water. In dilute solution the reaction is not complete but under the peculiar conditions imposed here the reaction seemed to proceed far in the direction of completion.

As mentioned above, chlorosulfonic acid is a valuable reagent and can be made by reacting sulfur trioxide and hydrochloric acid under proper conditions. It could conceivably be an intermediate in the reaction of liquid chlorine, liquid sulfur dioxide, and hot water. If this was the case, ethylene should react with it, giving on hydrolysis, alcohol and hydrochloric and sulfuric acids. To test such a supposition liquid ethylene was added to

the reaction of liquid chlorine, liquid sulfur dioxide and water. Analysis of the reaction products evidenced only a quite good yield of a liquid identified by its boiling point as sulfuryl chloride and which decomposed in water to give sulfuric and hydrochloric acids. Gaseous ethylene bubbled into the reaction gave similar results.

This agrees in principle with the observations of H. Schulze (20), that ethylene, charcoal, glacial acetic acid or camphor all serve as catalysts for the combination of chlorine and sulfur dioxide (in the gaseous state) to form sulfuryl chloride.

The results were therefore inconclusive as a test for the presence of chlorosulfonic acid.

Part V

Comparison with Current Methods of Manufacturing

Since the chief reaction studied in this thesis results in quantitative conversion of chlorine and sulfur dioxide into hydrochloric acid and sulfuric acid a brief consideration of possible cost of raw materials and finished products was thought of interest. Since the method must compete with established methods, these are also to be considered. Such a study must of necessity be somewhat academic until trial runs could be made to study necessary conditions for separating the two products when made simultaneously, together with problems involved in the absorption of the sulfur trioxide vapors.

In considering material costs it should be realized that relative costs can only be approximated and frequently material costs are outweighed in importance by other factors which will be mentioned.

The prices quoted are principally taken from Chemical and Engineering News Edition (13) or books on acid manufacture such as American Sulphuric Acid Practice (12).

Sulfur - is quoted at \$16 per ton and it is said
that the cost of production is about
\$4 per ton.

SO_2 - is quoted at $3/4\text{¢}$ per pound, f.o.b. mgf.

Cost of manufacturing liquid SO_2 on the Pacific Coast is \$8 per ton, De Wolf and Larison (12).

H_2SO_4 - cost of production is listed as \$7-\$8 per 1000 lbs. De Wolf and Larison (12).

Cl_2 - is currently quoted at \$1.75 per 100 lbs. (13).

HCl - 20° acid is currently quoted at \$1.75 per 100 lbs. (13)

H_2 - at reduced prices costs approximately 80¢ per lb. or 200 cu. ft.

H_2SO_4 - 66° acid is currently quoted as \$1.50 per 100 lbs. (13)

Salt cake - is \$12-\$15 per ton.

NaCl - is \$12 per ton.

66° H_2SO_4 = 93.2% H_2SO_4

20° HCl = 31.5% HCl

There exists a wide variation in values. SO_2 is often quoted at $3/4\text{¢}$ per lb. and Na_2SO_4 at \$1.45 per 100 lbs. Purity and amounts are reflected in the different price quotations.

In comparing the figures it can be seen that about 300 pounds of pure HCl can be obtained from 100 pounds of Cl_2 and the cost ratio of H_2SO_4 to SO_2 is roughly better than two -- actually is almost three to one.

If we consider Cl_2 at \$1.75 per 100 lbs. and 20°HCl at \$1.75 per 100 lbs. (prices from current issues of Chemical and Engineering News, 13) we find that 20°HCl is 31.5% HCl by weight. Consequently 100 lbs. of anhydrous HCl is worth \$5.40 and it is possible to convert chlorine costing \$1.75 to HCl of the value of \$5.40.

In the case of sulfuric acid, quoting older price quotations but all from the same period (12), it is found that liquid SO_2 costs \$8 per ton and H_2SO_4 \$14 per ton. However, in the production of H_2SO_4 from SO_2 a considerable increase in weight is derived in the course of manufacture.

An increase of almost one third in weight is obtained. Consequently two tons of SO_2 will produce almost three tons of H_2SO_4 , or SO_2 costing \$16 yields \$42 worth of H_2SO_4 .

Hence in both hydrochloric and sulfuric acid manufacture an increase in value of product over cost of materials in the ratio of three to one is indicated for both acids.

The quantitative experiment demonstrates that one can react liquid chlorine and liquid sulfur dioxide and heated water in stoichiometric amounts, completely converting to sulfuric and hydrochloric acids.

A batch process might be devised in which the calculated amounts of reactants are combined and the gaseous products of the reaction perhaps fractionated by passing through cooling coils and the sulfur trioxide absorbed in concentrated sulfuric acid in which it is quite soluble. Or the acid anhydrides could be separated after absorption by distilling off the HCl at 110° .

A more extensive process might be employed in which hot water is continuously added to a large reservoir of the liquid gases and the gaseous products of the reaction fractionated at low temperatures.

It is not known what the costs are for manufacture of hydrochloric and sulfuric acids from waste products. Waste hydrogen is converted to hydrochloric acid by combustion with chlorine and sulfur dioxide is a by product in several industrial processes and is usually converted to sulfuric acid.

However it would seem that a process embodying the following advantages should be economically sound.

1. a process which gives quantitative yields of practically anhydrous HCl and SO_3 if so desired.
2. a process which operates at low temperatures, by which easy fractionation and purification of products are effected.
3. A process which requires no catalysts or preliminary purification of materials.

4. a process which utilizes practically the same raw materials as existing processes namely sulfur or SO_2 and Cl_2 .
5. a process which produces no byproducts of limited marketability but instead produces two acids in great industrial demand.
6. the process may be easily controlled and is capable of rapid and complete conversion of a large amount of reactants for mass production of products. These are features of the process of producing sulfuric and hydrochloric acids from liquid chlorine, liquid sulfur dioxide, and boiling water.

Summary

1. A method of production of HCl and H_2SO_4 , has been developed by use of liquid sulfur dioxide, liquid chlorine, and heated water.
2. The reaction has been found to give quantitative yields of both products.
3. Other halogen acids are similarly obtained by slightly modifying the experiment.
4. The versatility of the reaction when regarded as an oxidation reduction system was demonstrated.
5. A review of the literature failed to disclose that the reaction as performed here had been previously done.
6. Various processes of manufacture were described and compared and costs of production for the manufacture of HCl and H_2SO_4 , indicate that the process is economically sound.

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