Sulfuryl Chloride[1]

II—Principles of Manufacture from Sulfur Burner Gas

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In this method cheap, dilute gases are dried and brought into contact with active carbon of the proper type, and by cooling and use of absorbents the sulfuryl chloride is recovered for shipment. This is believed to be the first method that has been proposed which permits the use of dilute gases—e. g., 14 per cent sulfur dioxide—in the making of sulfuryl chloride.

I N AN earlier paper[2] a process for the manufacture of sulfuryl chloride from liquid sulfur dioxide was outlined. In order to make sulfuryl chloride available as an agent for the shipment of chlorine from chlorine works to markets for hydrochloric acid, it is necessary that sulfur dioxide be obtained at approximately the same cost as in the manufacture of sulfuric acid, because a salable sulfuric acid is a by-product from the manufacture of hydrochloric acid from sulfuryl chloride. In the present paper a process using a cheaper source of sulfur dioxide, such as a sulfur burner gas containing 14 per cent sulfur dioxide, will be described.

The two most important problems that appear when this dilute sulfur dioxide is substituted for concentrated sulfur dioxide are—first, the absorption of sulfuryl chloride vapors from the stream of inert gases; and second, the effect of temperature on the yield of sulfuryl chloride.

ABSORPTION OF SULFURYL CHLORIDE VAPORS

An ideal absorbent for this purpose should not react with sulfuryl chloride nor introduce impurities that would render hydrochloric acid produced from it unfit for use in food products. It should have a low vapor pressure at the temperature of absorption. Chlorosulfonic acid, SO_2ClOH, meets these requirements. It is the intermediate product of the hydrolysis of sulfuryl chloride and at ordinary temperature has a vapor pressure lower than water.

ABSORPTION OF SULFURYL CHLORIDE BY CHLOROSULFONIC ACID
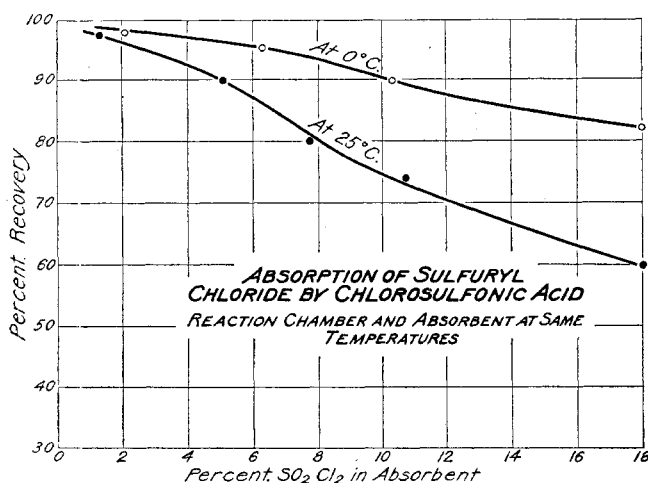REACTION CHAMBER AND ABSORBENT AT SAME TEMPERATURES

FIG. 1

A gas saturated with sulfuryl chloride at 20° C. contains 15 per cent sulfuryl chloride by volume. Chlorine will react with 14 per cent sulfur dioxide at 20° C. to produce a gas mixture approximately saturated with sulfuryl chloride, since one volume of sulfur dioxide makes one volume of sulfuryl chloride vapor. The fact that the gas stream entering

the absorbing tower is saturated permits a high concentration of sulfuryl chloride in the absorbent. In one experiment a mixture of 90 per cent sulfuryl chloride and 10 per cent chlorosulfonic acid at 20° C. was still absorbing sulfuryl chloride vapor from a gas stream carrying 15 per cent sulfuryl chloride. The heat losses in the fractionation of this mixture, therefore, will not be large.

The following experiment shows the action of the absorbent: Dry air at the rate of 187 liters (6.6 cubic feet) per hour was passed through 350 cc. of pure sulfuryl chloride in a 500-cc. graduate into 350 cc. of pure chlorosulfonic acid in a similar graduate. Both cylinders were immersed in a thermostat at 25° C. Folin absorbers were used as gas inlets. The excellent performance of these absorbers when used for the saturation of a gas with a vapor at rapid rates is shown by the fact that when the gas mixture issuing from the saturating vessel was passed through a coil condenser maintained at a temperature only 2 degrees lower than that of the saturator, drops of sulfuryl chloride liquid appeared at the end of the condenser in a few minutes. The completeness of absorption of sulfuryl chloride vapors from the gas stream is shown by the curves in Fig. 1, which define the conditions for equilibrium between the gas and liquid phases at different points in the absorption tower. The percentage recovery obtained by dividing the gain in weight of absorbent by the loss in weight of sulfuryl chloride is plotted against the concentration of sulfuryl chloride in the absorbent. Reading from the curves, a gas saturated with sulfuryl chloride vapor at 0° C. comes to equilibrium with an 18 per cent solution of sulfuryl chloride in chlorosulfonic acid when 82 per cent of the vapor has condensed. At 25° C. an 18 per cent solution will absorb 60 per cent and a 3 per cent solution 95 per cent of the vapor out of a gas mixture saturated with sulfuryl chloride at 25° C.

YIELD OF SULFURYL CHLORIDE

A mixture of chlorine and 14 per cent sulfur dioxide was passed through a body of liquid sulfuryl chloride in which carbon was suspended and the sulfuryl chloride vapor was removed from the exit gases by absorption in chlorosulfonic acid. It was found that when the temperature of the catalyst suspension was maintained at 25° C. the yield of sulfuryl chloride was only 70 per cent. The remainder was uncombined sulfur dioxide and chlorine. These substances are not very soluble in chlorosulfonic acid and consequently pass through unabsorbed. When the temperature of the catalyst suspension was lowered to 0° C. the yield jumped to 98 per cent.

The explanation is simple. The reaction

$$SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$$
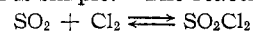
is reversible, and comes to equilibrium at 25° C. when 99 per cent of the sulfur dioxide and chlorine has been combined. The remaining 1 per cent dissolves in the liquid sulfuryl chloride, and the vapor pressure of the solution is considerably higher than that of the pure liquid, as would be expected from Henry's

law. When an inert gas is passed through the solution, the several components of the solution will be removed in amounts proportional to the respective partial pressure which each component exerts. At 25° C. the vapor pressure of pure sulfuryl chloride is 142 mm., and of sulfuryl chloride containing carbon 205 mm. 142 divided by 205 is 69.7 per cent, which checks with the 70 per cent yield of sulfuryl chloride obtained by running the catalyzing chamber at 25° C.

VAPOR PRESSURE
I-Pure SO₂Cl₂ (Trautz)
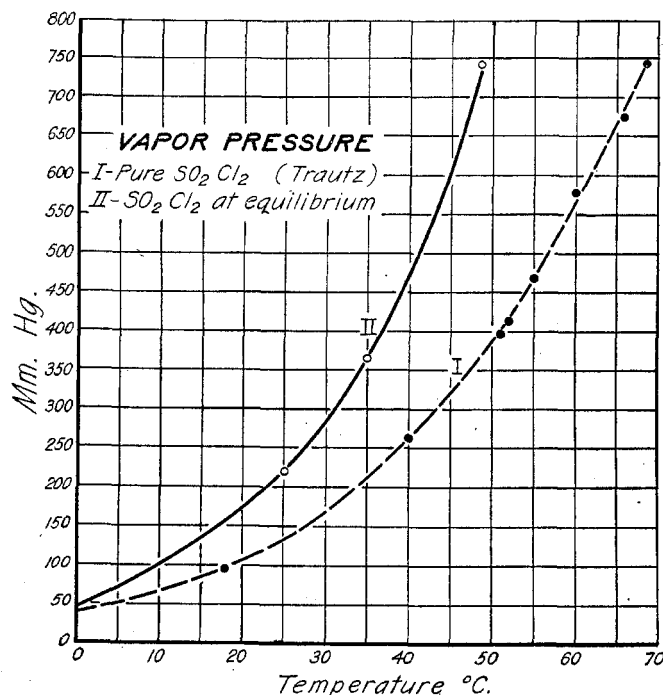II-SO₂Cl₂ at equilibrium

Fig. 2

It is evident that the yield can be increased by making the vapor pressure of the solution more nearly coincide with the partial pressure exerted by the sulfuryl chloride when pure. The curves of Fig. 2 show that the vapor pressure of sulfuryl chloride at equilibrium approaches the vapor pressure of pure sulfuryl chloride as the temperature is decreased. At 0° C. the respective vapor pressures are 40.9 mm. and 44 mm., or a ratio of 93 to 100. In addition to the increase in yield due to the approximation of the two vapor pressure curves at 0° C., there is a further increase in yield due to the comparatively low vapor pressure of sulfuryl chloride at 0° C. At 0° C., 70 per cent of the sulfuryl chloride vapor is condensed from a 14 per cent mixture. These two sources of improvement account for the 98 per cent yield obtained by running the catalyzing chamber at 0° C.

In a larger installation it may prove more economical to decrease the vapor pressure in the catalyzing chamber by the addition of a solvent, or by a combination of cooling and solvent action. It is evident that the substance added to the catalyzing chamber must not poison the catalyst. Pentachlorethane is a suitable solvent.
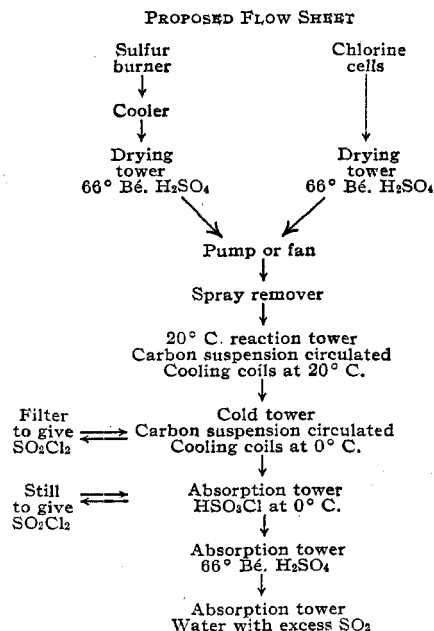
DRYING OF GASES

Several methods are available for removing moisture from the sulfur dioxide and chlorine before entering the catalyzing chamber. Probably the most suitable one is a preliminary drying of the separate gases with 66° Bé. sulfuric acid, followed by electrical precipitation of acid mist from the mixture of sulfur dioxide and chlorine. When the sulfur dioxide and chlorine are mixed, their combined action decomposes the moisture according to the equation

$$SO_2 + Cl_2 + H_2O = H_2SO_4 + 2HCl$$
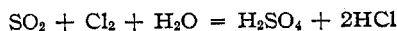
the sulfuric acid separating as a mist and the hydrogen chloride passing through the system as an inert gas. It is obvious that other methods of removing the moisture are available—e. g., reaction with sulfuryl chloride and adsorption of the sulfuric acid on carbon; reaction with chlorosulfonic acid made continuously by action of sulfuryl chloride on 100 per cent sulfuric acid containing a catalyst; and finally, reaction with oleum.

REFRIGERATION

Only a small amount of refrigeration is required, because most of the heat of reaction can be removed by cooling water. The catalyzing chamber is preferably divided in two parts, the first having cooling water coils and the second, brine coils. Both low-temperature cooling water and the use of sulfur dioxide stronger than 14 per cent will decrease the cost for refrigeration, because more of the sulfuryl chloride will be condensed by the cooling water. An estimate of the maximum cost for refrigeration,[3] based on $1.25 per ton of ice and on the worst possible operation during a few weeks in the middle of the summer in West Virginia, with cooling water at 30° C. and using 14 per cent sulfur dioxide, shows a refrigeration cost of $1.00 per ton of sulfuryl chloride. A minimum estimate, based on good operation for the winter months at Niagara Falls with cooling water at 10° C. and using 18 per cent sulfur dioxide, shows a refrigeration cost of 42 cents per ton of sulfuryl chloride. A conservative estimate of the refrigeration requirements for average operation is probably 75 cents per ton of sulfuryl chloride.

PROPOSED FLOW SHEET

Sulfur burner → Cooler → Drying tower 66° Bé. H₂SO₄

Chlorine cells → Drying tower 66° Bé. H₂SO₄

→ Pump or fan → Spray remover → 20° C. reaction tower Carbon suspension circulated Cooling coils at 20° C.

Filter to give SO₂Cl₂ ⇌ Cold tower Carbon suspension circulated Cooling coils at 0° C.

Still to give SO₂Cl₂ ⇌ Absorption tower HSO₃Cl at 0° C.

→ Absorption tower 66° Bé. H₂SO₄ → Absorption tower Water with excess SO₂

The capacity of the catalyzing chamber should be considered in connection with the cooling system. The chemical reaction itself is very rapid. On the basis of one cooling system that the writers have operated on pure sulfur dioxide and chlorine, a catalyzing chamber of 1 cubic foot capacity would produce more than 1 ton of sulfuryl chloride per day. A catalyzing chamber should be designed more on the basis of heat to be removed and on the volume of gases to be handled than upon the rate of the chemical reaction.

[3] Marks, "Mechanical Engineers' Handbook," p. 1737, gives $2.00 as the cost for a ton of refrigeration delivered to consumers in cities, and approximately 50 per cent of this cost is the cost for power. At the lower cost for power prevailing at electrolytic alkali plants the cost of a ton of refrigeration should be less than $1.25.

ABSORPTION SYSTEM

The curves of Fig. 1 show that the percentage recovery of sulfuryl chloride from a gas stream issuing from a reaction chamber at 0° C. decreases much less rapidly when the temperature of the absorbent is 0° C. The divergence of the two curves would be a good deal more pronounced if the reaction chamber were at 0° C. and the absorbent at 25° C. Consequently, it is preferable to circulate the chlorosulfonic acid through this tower at approximately the same temperature as the cold tower.

The objects of the absorption tower (indicated in the flow sheet) in which 66° Bé. sulfuric acid is circulated are—first, to absorb the small amounts of chlorosulfonic acid carried over from the first tower; and second, to produce continuously, if desirable, a fresh supply of chlorosulfonic acid. Sulfur trioxide in the form of oleum or as a solution in sulfuryl chloride can be run into this tower. The sulfur trioxide will react with the traces of dry hydrogen chloride in the exit gases to produce chlorosulfonic acid.

The object of the last tower is to absorb traces of hydrogen chloride, sulfuryl chloride, chlorine, and sulfur dioxide in order that a clean exit gas may be discharged into the atmosphere and any nuisance thereby avoided.

MATERIAL OF CONSTRUCTION

While no experience has as yet been had with plant operations, yet from experience with small-scale operations, the writers feel that the following construction materials will serve well:

Towers should be of acid-resistant brick set in the customary acid-proof cement. Iron will serve for the coils, filter press, and other apparatus. The still for the distillation of the chlorosulfonic acid–sulfuryl chloride mixture should probably be of the type of the ordinary cast-iron nitric acid still, and the condensers should likewise be of one of the types customarily used for nitric acid. This still will be subject to some corrosion, but the amount should not be excessive.

COST ESTIMATE

The total cost of operation, which includes carbon at 7 cents a pound, water, steam, air, repairs, refrigeration, labor at $5.00 per man per day, overhead, interest on investment at 6 per cent, and amortization over a period of three years, is estimated at $12.00 per ton of sulfuryl chloride on a production of 10 tons per day. Taking the cost of sulfur at $20.00, chlorine cell gas at $40.00, and a yield of 92 per cent, the cost of sulfuryl chloride by this process should be about $42.00 per ton.

The Explosibility of Hydrogen Sulfide in Air[1]

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P REVIOUS tests made by the Bureau of Mines on high-sulfur crude petroleums, particularly of Mexican origin, showed that during the distillation and refining thereof the evolved gases may at times contain in excess of 40 per cent of hydrogen sulfide. This gas, when mixed with the proper proportion of air, is explosive, and may thus create additional hazards in the refining of crudes of this class. Hydrogen sulfide gas is also used in many chemical processes as a reducing and precipitating agent, and is liberated as a by-product in other reaction processes. It is therefore desirable as a safety measure to know the proportions of hydrogen sulfide in air which are explosive, or, as termed in this report, are within the "limits of flammability"—that is, mixtures of gas and air in which, if a flame is initiated, it will propagate itself through the entire space without the necessity of the continued presence of the original source of heat.

Exhaustive and careful investigations* have been carried out on the flammable and explosive limits of most of the common combustible gases and vapors, but for hydrogen sulfide no published values were available.

In general, the values reported by the different investigators for many of the common gases differ widely, depending upon the method and procedure employed, such as the size and shape of the explosion chamber, the direction of flame propagation, and the kind and intensity of the ignitions. Profiting by the experiments of previous investigators, the writers used a glass tube 6 cm. in diameter, because Wheeler

Apparatus and procedure for determining the limits of complete flammability of hydrogen sulfide in air have been described.

Tests made in a glass tube 6 cm. in diameter and 215 to 275 cm. long gave the following values for the limits of complete flammability for hydrogen sulfide in air (horizontal flame propagation): (1) lower limit of complete flammability, 5.9 per cent hydrogen sulfide; and (2) upper limit of complete flammability, 27.2 per cent hydrogen sulfide.

and Whitaker[†] have shown that in tubes less than 5 cm. in diameter the cooling effect of the walls exerts a marked influence on the results. The explosion chamber (tube) in experiments in this laboratory was made extra long so as to be certain that a self-propagated flame was produced which would not "die out" before reaching the end. A hot, intense spark was used for igniting the gaseous mixtures. This is very important when making experiments at the upper limit of complete flammability. All tests were made by propagating the flame in a horizontal direction.

TESTING APPARATUS AND PREPARATION OF HYDROGEN SULFIDE

The testing apparatus (Fig. 1) consisted of a glass explosion chamber, a, 6 cm. in internal diameter and 275 cm. (9 feet) (Position B) long, joined in sections. For the preliminary experiments, an explosion chamber only 215 cm. (7 feet) (Position A) long was used. The mixtures were ignited from the nickel electrodes, b and c. The electrodes were connected to the terminals of the secondary windings of a transformer, the primary connections in turn connected directly to a 110-volt alternating current lighting circuit. The transformer used gave a secondary voltage at the electrodes of about 5000 volts and 0.01 ampere of current; d is an ordinary Kipp generator for the production of hydrogen sulfide, which for the preliminary experiments was made by the action of hydrochloric acid on ferrous sulfide.

Hydrogen sulfide prepared in this manner was found to

† J. Chem. Soc. (London), 111, 267 (1917).