THE CHEMICAL ENGINEERING单元过程—氧化

BY

DONALD B. KEYES
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THE CHEMICAL ENGINEERING
UNIT PROCESS—OXIDATION

BY

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PROFESSOR OF CHEMICAL ENGINEERING

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THE CHEMICAL ENGINEERING UNIT
PROCESS—OXIDATION

I. INTRODUCTION

1. Introductory.—The oxidation of chemical raw materials to produce valuable compounds is a very important unit process in chemical engineering. An example is the manufacture of sulphuric acid by the oxidation of sulphur to sulphur dioxide, and the further oxidation of sulphur dioxide to sulphur trioxide. The price of sulphuric acid has long been considered an index not only of the chemical market, but also of the world industrial market.

It is a well known fact that the air oxidation of any fuel liberates considerable quantities of heat, and is the basic chemical reaction in the production of power. If we leave out of consideration the combustion of fuels and discuss only oxidation of simple chemical compounds, the fact still remains that the basic reaction is usually strongly exothermic, particularly when oxygen is used as the oxidizing agent. Unfortunately, in most of the oxidations as carried out in industry, an intermediate rather than an end product is desired. Any attempt to stop the reaction at the intermediate product will require a careful control of the temperature. This means that the heat must be carried away at a definite and rapid rate from the reaction zone. In certain chemical oxidations an equilibrium is set up and, if the temperature is allowed to rise too high, the action is reversed with corresponding lowering of the yield. An example is the sulphuric acid contact process described later.

Most of these oxidations utilize air as the oxidizing agent, and many of them are carried out exclusively in the vapor phase. In order to maintain a temperature satisfactory for the equilibrium and to prevent the formation of undesirable products, it is necessary to provide a catalyst in order to obtain a practical rate of reaction at the lower temperatures. Usually this catalyst is in solid form, and the problem of contact of the reacting gases with the solid catalyst requires serious consideration. Maintaining a rapid and controlled heat transfer from the catalytic surface is difficult in this case, especially if the reaction is carried out at the higher temperatures.

This is generally done in the laboratory by carrying out the reaction in a small-bore tube. The catalyst is in intimate contact with the walls of the tube, the heat is transmitted to the surface and some
means, such as a boiling liquid bath, for example, is utilized to transfer the heat away from the outside walls of the tube.

It has been found expedient to supply a heat conducting catalyst wherever possible in order to effect the transfer. It has also been found necessary to have the solid catalyst in such a form that considerable surface is exposed in order to supply the necessary contact with the reacting gases in a short distance of travel.

The same conditions prevail in plant-size equipment except that other means of heat removal is sometimes necessary, owing to the large volume of catalyst and reacting gases that are handled and the impracticability of using small tubes. With large scale equipment it is sometimes feasible to place the catalyst between tubes which contain a cooling medium. Of course certain oxidations give off considerably more heat per mol of reacting constituents than others. Where the amount of heat is relatively small, the temperature control mechanism does not have to be nearly so elaborate. In a few cases the oxidation is allowed to continue to its natural completion. Equipment in such cases resembles an ordinary combustion unit or furnace.

A brief description of the equipment and means of operation of actual industrial oxidations will make clear the modern methods of fulfilling these fundamental requirements. The processes that will be considered are: the burning of sulphur to sulphur dioxide; the oxidation of sulphur dioxide to sulphur trioxide, both in the chamber and contact plants; the oxidation of ammonia to nitric acid; and the partial oxidation of certain organic compounds such as naphthalene, kerosene, and the lower hydrocarbons.

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II. Sulphur Oxidation

3. Sulphur Burners.—Sulphur is burned to sulphur dioxide in many sulphuric acid plants. The sulphur itself is usually fairly pure, around 99.4 per cent. It can easily be melted to a liquid, has a fairly high vapor pressure, and its oxidation by means of air can be carried out in equipment resembling that used in the combustion of either coal or oil.

One of the earliest schemes comprised a pan about 5 inches deep
in connection with a combustion chamber. Air was passed over the top and around the sides of the pan, which contained molten sulphur partially vaporized. Combustion began and continued throughout the chamber. The difficulty with this crude arrangement was, of course, the irregularity of the air supply when opening charging doors for feeding the sulphur, and the resulting non-uniformity of the product gases. Approximately 5 to 10 square feet of pan surface (according to the draft applied for air intake) was necessary to burn a ton of sulphur in twenty-four hours.

The modification of this, known as the Vesuvius Burner (Fig. 1) consisted in a series of pans, one above the other, containing molten sulphur. The molten sulphur was allowed to overflow through an outlet on one side of the pan, and across the pan below to another outlet, whence it dropped to a third pan. The sulphur was fed from above through a needle valve. Air entered from the sides, passed over the molten sulphur, and a mixture of sulphur dioxide and gaseous sulphur was carried into a combustion chamber where secondary air was admitted and the final oxidation took place. From 1 to 10 square feet per ton of sulphur per twenty-four hours were necessary in this particular equipment according to the draft. This showed some improvement, of course, over the former crude device. The air control was better, and less labor was required for feeding the sulphur. The sulphur was melted in a tank at the top of the burner by the heat of the burner itself, (combustion of the sulphur) and was admitted at
intervals into the furnace by opening the needle valve at the bottom of the sulphur tank.

Still another arrangement was popular in the old sulphuric acid plants (Fig. 2). This consisted of a revolving horizontal cylinder containing molten sulphur. Sulphur was oxidized by air blown into the cylinder. Considerably more surface is exposed because the horizontal cylinder revolves, carrying the liquid sulphur up the sides and dropping it down again as a spray through the heated air. This is known as the Glens Falls Burner. It can be operated only on pure sulphur containing very little ash.

One inventor by the name of Hurt had the idea of forcing air from a sparge or perforated pipe up through molten sulphur and obtaining a much more perfect contact. Unfortunately, the back pressure was sufficient to increase the power consumption to a point where it was not economical.

Another recent device, the Leonard Burner, utilized molten sulphur which was sprayed over a checker brick in order to present a greater surface for the reaction.

The Chemical Construction Company developed a very satisfactory burner for sulphur (Fig. 3) based on the principle that sulphur can
best be oxidized to SO₂ when converted into a liquid and sprayed into a combustion chamber in the form of minute droplets: the equivalent resembles an ordinary oil burner. The air for this purpose is first scrubbed with concentrated sulphuric acid to remove moisture and then the entrained drops of sulphuric acid are removed by passing the dried air through a packed tower. The two operations can be conducted in one column—the acid spray is introduced near, but not at, the top. A continuous blower picks up the dried air and forces it into the combustion chamber to effect the oxidation of the sprayed sulphur. The sulphur is melted in tanks equipped with steam pipes. The steam, in turn, comes from a waste heat boiler (heated by the sulphur dioxide). It also serves to reduce the temperature of the gas. Part of the insoluble impurities float on the surface of the sulphur bath, while the rest drop to the bottom and can be removed from time to time. The proper design of the nozzles through which the molten sulphur proceeds into the combustion chamber is an essential feature of the equipment.

Othmer* points out in his description of this process that, theoretically, the drier the gas (SO₂) the less the corrosion and the less sulphuric acid is formed, but practically there is a degree of dehydration beyond which no difference in conversion efficiency can be noted. He also states that sometimes there is sufficient steam formed in the waste heat boiler not only to cause the melting of the sulphur but also to operate the sulphur pump and the air blower. The heat available from the combustion of one pound of sulphur is 2170 C.h.u.†

It is realized, of course, that some sulphur trioxide is formed in these operations, and it is often necessary to make an estimate of this percentage. The amount of sulphur trioxide in the gases from the sulphur burner can be approximately determined by assuming that the oxygen unaccounted for in the gas analysis has combined with the sulphur dioxide. Browning and Kress have a method for the direct determination of SO₂ in sulphur burner gases.

4. Pyrites Burners.—Pyrites, FeS₂, is often used as a source of sulphur in the sulphuric acid process. The resulting products not only include the sulphur dioxide, but also ferric oxide, Fe₂O₃ which remains behind as an ash, or cinder.

The simplest design for such a burner would consist of a furnace containing a grate. Such equipment has been used in the industry. In order to cut down radiation losses the furnaces have been put

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*Number references refer to Bibliography, p. 43.
†Centigrade heat units or pound centigrade units.
back to back. In order to control the oxidation they are small in size, for example, 6 feet long and 4 to 5 feet wide, and the fire bed is usually deep. About 50 square feet of grate area per ton of 45-percent sulphur ore per day is required. These burners can only be operated on the lump form of pyrites.

The fine pyrites, on the other hand, is usually burned on trays inside of a steel cylinder lined with fire brick. Air-cooled arms revolve on a central vertical axis and rake the burning ore to the center of the tray whence a down pipe carries the charge to the tray below, and then to the circumference so that the movement is across the tray. This equipment, known as the Herrshoff Burner, varies from 10 to 25 feet in diameter. Two or more arms are used for each tray or cylinder. The air enters at the bottom, is preheated by the hot cinders, passes up through the cylinder, and out at the top. Some air may enter at an intermediate point. These burners are not very efficient in that they require sometimes as high as 100 square feet per ton of ore per day depending on the characteristics of the ore burned, but the control of the product is much better than with the crude device mentioned in the foregoing.

The percentage of sulphur trioxide formed, based on the sulphur burned, can be calculated in a manner similar to that shown in the preceding section. One hundred mols of gas as analyzed is taken as the basis, realizing that no \( \text{SO}_3 \) appears in this analysis. The amount of oxygen accounted for, and the amount of oxygen entering as air is calculated as before, the difference being the amount of oxygen going to \( \text{SO}_3 \). In this case, however, it must be remembered that the equations for the two operations are as follows:

\[
\begin{align*}
4\text{FeS}_2 + 11\text{O}_2 &= 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2 \\
4\text{FeS}_2 + 15\text{O}_2 &= 2\text{Fe}_2\text{O}_3 + 8\text{SO}_2
\end{align*}
\]

In other words, \( \frac{11}{8} \) of the number of mols of sulphur dioxide represent the mols of oxygen going to sulphur dioxide, and \( \frac{9}{15} \) of the unaccounted-for mols of oxygen represent the mols of sulphur trioxide produced on the basis of 100 mols of gas analyzed.

The amount of sulphur dioxide leaving the burner in pounds per hour can be calculated by taking into consideration the number of pounds of sulphur burned and the gas analysis. The air consumption in cubic feet per minute can be calculated from the last-determined figure and also from the gas analysis. The volume of gas leaving the burner can be calculated from the same figures, and the heat
dissipated from the burner can be calculated by taking into consideration the following equations:

\[ S + O_2 = SO_2 + 69 \, 300 \text{ C.h.u.} \]
\[ S + \frac{1}{2}O_2 = SO_3 + 91 \, 900 \text{ C.h.u.} \]

This will give the amount of heat involved per mol, and from this the total number of C.h.u. evolved on the basis of 100 mols of gas analyzed. The heat capacity of the gases is known, and the amount of heat absorbed by the gasses can be determined, providing the temperature of these exit gases is also known. The difference between this and the heat emitted is the heat dissipated.

III. Sulphur Dioxide Oxidation

5. Contact Sulphuric Acid Process.—It is a well known fact that the catalytic oxidation of sulphur dioxide to trioxide is strongly exothermic, and at the higher temperatures the equilibrium, which exists, is not favorable for good yields of sulphur trioxide. Unfortunately, the present commercial catalysts do not cause the reaction to take place at any appreciable speed at low temperatures and a compromise between rate and yield is necessary. Often two catalytic beds are used, the first at a high temperature giving low conversions (60 to 80 per cent) but necessitating only a short time of contact and a relatively short path through the catalyst material, and a second at a much lower temperature, which necessitates a considerably longer time of contact, and therefore a much deeper bed of catalyst.

The minimum temperature necessary is approximately 400 deg. C. At 500 deg. C. the reaction over the catalyst is about forty times as fast, but the conversion is considerably below 95 per cent.

There should be a uniform temperature horizontally throughout the catalyst bed, and for ideal operating conditions a gradual temperature gradient vertically, from a high temperature down to the 400 deg. C. which is optimum for high yields.

The original crude design of the catalyst chamber consisted of short cylinders packed with platinum catalyst on asbestos. Good conversions could not be obtained with cylinders of large diameter, because the heat liberated was not taken care of except by radiation from the surface.

The next improvement known as the Schroeder-Grillo equipment,
consisted in an outer shell through which the gas was passed upwards and then down through an inner cylinder containing the catalyst arranged in layers. The downward movement of the gas gave better distribution and tended to prevent channeling. The upward movement through the outer shell caused the gas to be preheated, and at the same time roughly regulated the temperature within the catalyst body. Baffles were inserted between layers of catalyst. The catalyst consisted of platinum metal on magnesium sulphate as a support.

The Audianne process employed tubes in the catalyst bed for preheating the air. The catalyst surrounding these tubes was hard to remove for revivification. The cross-section temperatures, as in the other equipment, were nonuniform.

The Mannheim process employed two catalyst chambers, one containing ferric oxide (pyrites cinders), and the other platinized asbestos. Fifty per cent of the conversion was realized over the iron oxide at approximately 600 deg. C. The same difficulties were apparent in this equipment as in the former ones.

In recent years there has been developed in this country, largely by Jaeger, the internal heat exchange converter. The original equipment was a modification of the Audianne method previously described. This in turn was preceded by the Knietzch development (Fig. 4) in which the catalyst was placed within the tubes, and the gas was preheated in its passage around the tubes.

Tentelew built a catalyst chamber unique in design, a perforated plate containing truncated cones. The catalyst was placed upon the perforated plates and the cones protruded through the catalyst bed and caused the gases above to be preheated. The final catalyst was placed on perforated plates in a small cylinder below the main cham-
ber. The movement of the gas was downward. Platinum on asbestos was used for the catalyst.

Jaeger and Bertsch first developed an ingenious arrangement which consisted of a series of tubes inserted into the catalyst layer. The gas to be preheated passed up through a vertical tube and down through a tube which surrounded the first, closed at its upper end. The gas then passed upward through a screen and the catalyst layer. This gave far more efficient preheating of the gases, and at the same time permitted a much better cooling of the catalyst layer. The temperature through a horizontal section of the catalyst bed was maintained at a much more uniform value. More cooling tubes were placed in the center than at the periphery in order to create this uniformity of temperature, thus overcoming the drop in temperature due to radiation.

A further development (Fig. 5) along these same lines occurred later, when a second series of tubes was placed in the upper catalyst layer. These tubes were inverted and air for cooling purposes was passed through them. This permitted the upper and deeper catalyst bed to be operated at a much lower temperature. The heat, of course, can be saved by utilizing the heat capacity of the outlet gases for some other purpose. Recent installations have abandoned the use of cooling tubes in the upper layer of catalyst. The lower set of tubes has been extended into the gas space between the catalyst layers. This affords sufficient cooling for the purpose.

The catalyst used was a complex vanadium zeolite. The gases were preheated to about 300 deg. C. and passed up through the catalyst bed. They contained 7 to 8 per cent sulphur dioxide (the remainder air). The temperature at the bottom of the lower catalyst bed was approximately 460 to 480 deg. C. The maximum temperature
reached in this lower bed was around 600 deg. C. and the temperature at the top of the lower bed was approximately 465 to 475 deg. C. The outlet gases from the upper bed were at a temperature of about 280 deg. C. The catalyst was supported on a layer of quartz, which in turn was supported on a perforated plate or screen.

Another common modern type of burner operates on the principle of multipass conversion* (Fig. 6). In other words, at least two converters and two heat exchangers are used. The cool sulphur dioxide is first passed through a large heat exchanger and then to a small hot heat exchanger on the outside of the tubes. Next it passes to the top of the smaller converter, down through the layers of catalyst and out at the bottom. It is then returned to the tubes of the first heat exchanger in order to heat the incoming gases. Thence, it passes to the top of the second or larger converter, again down through the catalyst bed, out at the bottom, and to the tubes of the second heat exchanger. Thence it passes on to the purifying, cooling, and absorption equipment.

The temperature of the gases at the top entrance of the smaller

*The multipass conversion is an invention of J. B. S. Herreshoff.*
The vanadium zeolite catalyst is quite popular in the United States. If this catalyst is used, it is necessary to have only two layers in the first converter and three in the second. Baffles between the thick catalyst beds are necessary in order to obtain proper distribution of the gases. Furthermore, a spreading plate is used at the top of the converter in order to prevent channeling of the gases. The first converter usually has about 30 per cent of the catalyst, and the second, 70 per cent. Sometimes the catalyst is in the form of pellets especially designed for the purpose in order to cut down the back pressure and save power, while at the same time sufficient surface is exposed for the reaction. Heat is recovered from the $\text{SO}_2$ gas by means of air heaters.

The advantage of this multipass system is usually that a stronger or more concentrated gas can be used due to the fact that there is a greater opportunity to absorb heat. On the other hand, more power is required because of the additional back pressure. There is considerable argument at the present time as to the respective advantages of the internally-cooled and the multipass converter. In justice to both of these types, it might be said that special plant conditions dictate which is the more efficient. From a fundamental standpoint, it can easily be seen that the internally-cooled converter removes the heat as fast as it is formed, and requires a small cross section or necessitates the use of tubes. It is said that in the American type of internally-cooled converter the temperature of entering gases is 60 to 80 deg. C. higher than in the two-pass system; less space is utilized; the original equipment costs more; and the necessary repairs are more costly. However, the tubes do not break easily.

It is claimed that in the externally-cooled or multipass system about 80 per cent conversion for an 8-per-cent gas at 585 deg. C. is obtained in the first converter, though the entrance gases are not at as high a temperature, with a relatively small amount of catalyst. This first converter is said to require only about 30 per cent of the total catalyst, and the total amount of catalyst is less than in the internally-cooled equipment. It is believed by some engineers that
the multipass system is more flexible as far as the gas used is concerned. On the other hand, with sulphur which gives a constant concentration of sulphur dioxide, this flexibility is not important.

The material for construction for these converter shells is generally cast iron, though recently steel has been used with apparent success. Chromium steel might be more satisfactory from some standpoints, but it is too costly at the present time. What is needed is not only an anti-corrosive alloy, but also one that will prevent the depositing of a ferric sulphate scale on heat exchanger tubes. Such a scale naturally cuts down the heat transfer and decreases the efficiency of the unit. Furthermore, it should be remembered that ferric sulphate in the presence of moisture and oxygen, is in itself a very corrosive agent. It is certainly far more corrosive towards iron and steel than is concentrated sulphuric acid.

6. Catalysts for Contact Process.—The vanadium zeolite catalyst introduced by Jaeger in this country has shown excellent results. One hundred and thirty-five liters of 7-per-cent gas per hour per 200 cc. of contact mass (675 liters of gas per liter of catalyst per hour space velocity) give conversions of 97.0 to 98.8 per cent. No drop in yield was noted at a rate of 150 liters of this same gas per hour, and the drop was barely visible at 200 liters per hour. There was less than 1 per cent drop in conversion at 300 liters per hour.

It is interesting to note the conversions with various concentrations of sulphur dioxide. The rate of passage of the gas was 150 liters per hour over 200 cc. of contact mass (750 liters of gas per liter of catalyst per hour space velocity). The conversions to SO\(_3\) were as follows: at a concentration of 5 per cent SO\(_2\) the conversion was 99.5 per cent; at 6 per cent, 98.8 per cent; at 7 per cent, 98.5 per cent; and at 8 per cent, 98.0 per cent. At 9 per cent the conversion was still about 97 per cent. These were plant tests.*

*Judge Nelson McVicar filed an opinion on June 17, 1932 in U. S. District Court, Western District of Penn. No. 2556. in the patent suit between the General Chemical Company and the Selden Company in which he gave the following interesting description of the preparation of the Selden Company’s vanadium catalyst.

*A water solution of potassium silicate is sprinkled on superfloss, otherwise known as kieselguhr, wetting the surfaces of the particles, and they are thoroughly mixed for one-half an hour by rolling, raking and shoveling.

*Aluminum hydroxide is made from aluminum sulphate and ammonia, and this aluminum hydroxide is transformed into potassium aluminate by the addition of potassium hydroxide.

*A water solution of this potassium aluminate is then sprinkled on the potassium silicate and superfloss mixture and the product is thoroughly mixed for one-half hour by rolling, raking and shoveling. The potassium aluminate unites with the potassium silicate to form a zeolite which is a potassium aluminum silicate of jelly-like consistency. The mass is forced through a screen to form it into lumps of zeolite containing and diluted by superfloss particles. The potassium aluminate and potassium silicate are added in the proportion of two combining parts of the former to five combining parts of the latter to form the zeolite gel.

*A complex vanadium compound is prepared by adding ammonium vanadate to potassium aluminate and potassium hydroxide in the proportion of one combining part of potassium aluminate to three combining parts of ammonium vanadate.

*This complex vanadium compound, in the form of a thick gelatinous suspension just
It was thought that 80 per cent of the sulphur dioxide was oxidized over the first 10 per cent of the catalyst.

Besides the Jaeger catalyst, Holmes and Elder\textsuperscript{13} have prepared in the laboratory a special catalyst from potassium metavanadate, ferric chloride, and water glass. Potassium metavanadate is added to a solution of ferric chloride in equivalent quantities. A precipitate is formed which is peptized in an excess of ferric chloride. This solution is added to water glass. The catalyst, promoter, and support are then coprecipitated. Laboratory tests indicated that this catalyst gave conversions of 91 to 97 per cent, thus comparing favorably with the Jaeger catalyst made and used in the laboratory according to the patented process.

Scott and Layfield\textsuperscript{12} developed another vanadium catalyst in the laboratory. Potassium hydroxide was added to an ammonium vanadate solution. Water glass was added and the solution mixed with a barium chloride solution. The resulting precipitate was allowed to stand for two hours and then dried at 200 to 300 deg. C. for another two hours.

The conversions over this particular catalyst were very good. Two hundred to 400 cc. of gas per minute gave a 98 to 99 per cent conversion at 500 deg. C. When the rate was increased to 600 to 700 cc. of gas per minute, the conversion dropped to 97.3 per cent.

Fifteen hundredths of a pound of ammonium vanadate were used in making one pound of catalyst, which occupied 78 to 80 cubic inches. Larger scale tests indicated that at 450 deg C., 17 to 35 cubic feet per hour of this gas over this catalyst gave 98.0 to 98.8 per cent conversion. The production of sulphuric acid was 0.35 to 0.75 pounds per hour.

Further tests at an increased rate of 50 cubic feet per hour at 500 deg C. gave 97.3 per cent conversion, producing one pound of sulphuric acid per hour.

Calculations from these results indicate that one pound of vanadium produced from 5 to 10 pounds of sulphuric acid per hour at capable of being poured, is poured on the lumps of zeolite diluted with superfloss and is mixed to only a slight extent, without penetrating the zeolite jelly.

"The coated lumps are compacted between rollers, then forced through a screen to separate them into small lumps and then compacted into pellets.

"Prior to filing the Bill of Complaint, and for a short time thereafter, these pellets were delivered directly to the users without being treated with sulphur dioxide, and without any further treatment other than mere drying. Beginning some time after the filing of the Bill of Complaint, the defendant has formed its pellets in a Stokes pill machine, and to prevent sticking in this machine has added a small amount of stearic acid as a lubricant before pelleting. It has then calcined or sulphated the pellets by heating with a very dilute mixture of air and sulphur dioxide containing about 1% sulphur dioxide, gradually increasing the amount of sulphur dioxide until the pellets are gradually but thoroughly calcined. After the calcining the pellets have been cooled with a blast of cool air through the calciner to reduce the temperature from about 500° C. to a temperature at which the pellets can be removed."
450 deg. C. with a 98 per cent conversion, and 13 pounds of sulphuric acid per hour at 500 deg. C. with a 97 per cent conversion.

Thompson\textsuperscript{14} has reviewed the general situation regarding platinum versus vanadium catalysts. He feels that the platinum catalyst, when properly employed, is more economical, and that the percentage of platinum in modern platinum catalysts has been too much reduced. He states that with a larger percentage of platinum the life of the catalyst is increased, higher concentrations of gas (up to 10 per cent sulphur dioxide) and higher space velocities are permissible, high overloads are possible, there is a low kindling temperature, and it is possible to use a greater range of concentrations of sulphur dioxide in the gas.

He makes some calculations based on various assumptions which indicate that the platinum catalyst costs $0.17-0.37 less per ton of sulphuric acid produced than the vanadium catalyst. He points out that a simpler converter is required in the case of platinum, and the possibility of operating with high percentages of sulphur dioxide means considerable saving.

Some plant tests indicate that platinum silica gel is a desirable catalyst because it is not affected by arsenic. Thompson, however, points out that dust must be removed, and along with it, arsenic, in any satisfactory operation regardless of whether or not it poisons the catalyst.

Most of the poisons for contact sulphuric acid catalysts are dusts; therefore, dust separators have been largely used for gas purification.

7. Calculations on Converter Design.—Lewis and Ries\textsuperscript{10} have published an excellent academic method for the calculation of temperatures, etc., prevailing in a converter for the oxidation of SO\textsubscript{2} to SO\textsubscript{3}.

The converter, as indicated in Fig. 7, is merely a diagrammatic sketch illustrating the fundamental principles involved, and is not a design for practical purposes. It will be noticed that their fundamental method of operation consists in passing the entering gas through a preheating coil at the top of the converter and then through intermediate heating coils between layers of catalysts until it reaches the bottom, where the gas is allowed to enter the converter, passing up through the successive layers of the catalyst and out at the top. It will also be noticed that there are valves present in the line so that any heating coil may be by-passed if the calculations indicate it advisable. Also, the amount of flow through any heating coil can be controlled. It should be recognized that these heating coils act as cooling coils as far as gases inside the converter are concerned.
The conversion is maintained considerably above 90 per cent up to 400 deg. C. and then begins to fall off; it is quite low at approximately 525 deg. C. It is evident that a rough range of temperature of operation should be between 400 deg C. and 530 deg. C., remembering that the speed of reaction caused by a catalyst is considerably greater at the higher temperature.

Lewis and Ries have taken an 8-per-cent sulphur dioxide gas as their basis for operation and they have assumed a practical conversion of 60 per cent for the first layer of catalyst at the bottom, with a top temperature of 530 deg. C.

The oxidation of one mol of sulphur dioxide to one mol of sulphur trioxide gives off 22 500 C.h.u. On a basis of 100 mols of gas, the heat capacity per degree would be 760 C.h.u. This would mean that 0.6 of 8, or 4.8 mols of SO₃ would be formed in this first layer of catalyst. 4.8 × 22 500 C.h.u. is equal to 760 C.h.u. × 530 deg. C. — C₁, the temperature of the outlet gas. The simple solution of this equation results in a temperature of C₁ of 388 deg. C.

Lewis and Ries assume that the conversion in the second layer of catalyst rises from 60 per cent to 90 per cent. Looking on their chart,
it will be found that a temperature of 480 deg. C. is necessary for this 90 per cent conversion. The 8 mols of entering sulphur dioxide \( \times (0.9 - 0.6) \times 22500 + (530 - 480 \text{ deg}) \times 760 \text{ C.h.u.} \) gives the amount of heat that must be absorbed, or 92 000 C.h.u. Dividing the 92 000 by 760 gives a temperature drop of the gases of 121 deg. C. The 121 deg. C. subtracted from the 388 deg. C. gives a temperature of 267 deg. C., the inlet temperature of the gases to the second layer of catalyst.

It can easily be seen that this simple process could be carried on throughout the various layers of catalysts and the necessary temperatures calculated. From these temperatures it is evident how much cooling is desired in each section. The cooling can be accomplished by adjusting the by-pass valves and permitting the requisite amount of gas to go through each cooling coil.

8. Chamber Process for Sulphuric Acid.—The reaction that takes place in the ordinary chamber process for the manufacture of sulphuric acid is essentially catalytic in nature, but differs from the contact process in employing homogeneous catalysis under conditions such that the intermediate steps are more evident. The so-called catalyst is nitrogen oxides. Air is used as the oxidizing agent, and water is necessary. This reaction takes place not only in the chambers themselves, but also in the Glover tower, which precedes the chambers. The Gay Lussac tower is used for the recovery of the nitrogen oxides, and their return to the Glover tower. The finished product comes from the bottom of the Glover tower. An excellent description of the fundamental equations involved in the oxidation process is given in Badger and Baker's book entitled “Inorganic Chemical Technology.” The reactions that take place in the Glover tower are represented by the following equations:

\[
2 \text{SO}_2 + 2 \text{NO} + \frac{3}{2} \text{O}_2 + \text{H}_2\text{O} = 2(\text{ONO})(\text{OH})\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{N}_2\text{O}_3
\]
\[
2 \text{(ONO)(OH)SO}_2 + \text{SO}_2 + 2 \text{H}_2\text{O} = 3 \text{H}_2\text{SO}_4 + 2 \text{NO}
\]

A substance known as nitrosyl sulphuric acid is formed in the first equation. This is the active agent or intermediate product formed
by the catalyst with the sulphur dioxide and water, or it may be considered as the real catalyst.

In the upper part of the tower, this compound is hydrolyzed with water, forming sulphuric acid and $N_2O_3$, as indicated in Equation (2). The $N_2O_3$ is carried out with the gases to the chambers, where it reacts again.

In the intermediate zone of the Glover tower the nitrosyl sulphuric acid is formed according to Equation (1), while in the lower portion of the tower it reacts with the sulphur dioxide to form sulphuric acid and NO. The NO is carried up through the tower and reforms nitrosyl sulphuric acid. The more concentrated sulphuric acid comes out as a product from the base of the tower.

Most of the nitrosyl sulphuric acid found at the top of the tower comes from the Gay Lussac tower where the nitrogen oxides are recovered. The burner gas, $SO_2$ and air, enters the Glover tower near the bottom.

About 20 per cent of the acid formed in the entire process is made in the Glover tower.

9. Construction of Glover Tower.—The modern Glover tower is a packed column, sometimes lead sheathed outside, of brick construction with a checkered brick packing. Not much time of contact is needed. Approximately 0.10 to 0.15 cubic feet of space per pound of sulphur per 24 hours is required. The rate of gas flow can be fairly high, usually around one cubic foot per second per square foot of tower cross-section.

The brick structure is put together with an acid-proof cement. The walls of the lower part are around 12 to 16 inches thick, and the upper part 8 to 12 inches. Usually the tower is square or circular in cross-section. A lead pan underneath is always provided, and lead-covered steel corners are often used. The pipe lines to the tower are of lead or wrought iron, and often of an iron-silicon alloy. The floor of the tower should be above the ground in order to permit gravity flow from the base. There is a free space at the bottom in order to facilitate the distribution of the gases under the packing. A brick arch supports the packing. Hexagonal stoneware blocks with a spiral center are sometimes used as packing in the upper part. Sometimes it is advisable to cover the top of the packing with quartz for proper distribution of the liquid. The temperature at the top generally runs around 100 deg. C.

Briefly, the Glover tower resembles in construction a scrubbing column for corrosive liquids and gases. Fortunately, the time of con-
tact necessary is not great, and, therefore, the relatively simple design described in the foregoing has proved to be satisfactory.

Fairlie in his recent book on sulphuric acid manufacture shows a practical, though empirical, method for determining the dimensions of a Glover Tower. He states that 28 per cent to 31 per cent free space (cross-section) can be realized with the modern packing. Twenty to twenty-five square feet of cross-section per one thousand cubic feet of gas per minute (the gas volume calculated at standard conditions) should be allowed. Furthermore, 700 to 800 cu. ft. of contents per 1000 cu. ft. of gas per minute (the gas volume calculated at standard conditions) should be used. It must be remembered in estimating the height and diameter that allowance must be made for the top and bottom sections where there is little or no reaction, and for the space occupied by the walls and floor.

10. Lead Chambers.—The reaction taking place within the catalytic chambers is not definitely known. However, Badger and Baker in their book entitled “Inorganic Chemical Technology,” give a satisfactory description of what takes place. Nitrosyl sulphuric acid plus sulphuric acid in the form of a mist seems to concentrate in the center or hotter portions of the chamber. It is in the center of the chambers that the sulphur dioxide reacts with water and NO. Along the walls, where it is cooler, water condenses and hydrolyzes the nitrosyl sulphuric acid, forming more NO. Any N₂O₅ will react with sulphuric acid to form the nitrosyl sulphuric acid plus water. This occurs in the first chamber. Later the nitrosyl sulphuric acid hydrolyzes, forming N₂O₃, which, in turn, in the presence of a large excess of water, will react at low temperatures with SO₂, when the concentration of the latter is small, to reform nitrosyl sulphuric acid.

The conventional, air-cooled lead chambers vary from 50 to 25 feet in length, 16 to 80 feet in height, and 30 to 60 feet in width. Anywhere from 6 to 16 cubic feet of space may be used per pound of sulphur burned per 24 hours.

As lead has a very low tensile strength, 500 pounds per square inch, and as it can itself only support approximately 90 feet of sheeting, it is necessary to build a steel support on the outside of these chambers. Furthermore, there is a tendency for the pressure within these chambers to vary over a range of about 0.5 lbs. per square inch. The lead sheets must, therefore, be attached in various places to the steel outer structure. This is done by means of a lead strap burned on to the main sheet.

Corrosion is most severe in the first chamber, and on the lead
bottoms of all the chambers. Any uncooled spots will be subject to severe corrosion. There is also considerable corrosion in the last chamber where the sulphur dioxide is exhausted.

It should be remembered that the heat of reaction must be taken care of as in the contact process. It is found desirable to use intermediate cooling towers, because the heat transfer from these chambers is exceedingly poor.

Stoneware atomizers for water entrance are used. Duriron, Lewis, LaBour and Ceco centrifugal pumps and air lifts have been found to be quite effective for handling acid and have replaced the acid eggs. The Lewis pump with no stuffing box has attracted considerable interest, due to the fact that there is no leakage at the glands.

11. Other Types of Chamber Construction.—It has long been recognized that the heat transfer difficulty in the air-cooled lead chamber is a serious one. Much more heat is liberated in the chamber process than in the contact process, since the product is dilute H₂SO₄ solution rather than SO₃. Perhaps one of the simplest schemes for improving the situation has been to make the chambers in the form of a truncated cone, permitting water to run down the surface of the lead sides. This is known as the Mills-Packard tower. Such a tower is approximately 48 feet high, and has a base diameter of 20 to 35 feet and a top diameter of 12 to 32 feet, according to size. The water is distributed down the sides by using a perforated lead gutter at intervals. Six towers are used. The first operates at about 185 deg. F. and the last at 86 deg. F. It is estimated that the efficiency of these towers is about 2.5 times that of the ordinary type which is air cooled. From 2 to 5 cubic feet of space is necessary per pound of sulphur burned per 24 hours.

Another interesting development is the Gaillard-Parrish turbo-disperser. This is used in connection with relatively tall towers and consists of a turbine operating a whirling spray at the top of each tower (Fig. 8). Liquid sulphuric acid plus the necessary water, etc., is shot out from this whirling spray to the walls of the tower. It is necessary with this device to use intermediate coolers between towers, owing to the increased capacity. About 2 to 3.5 cubic feet of volume per pound of sulphur burned per day is all that is necessary. Usually three chambers or towers are used, the first one operating at about 100 deg. C., in which 50.6 per cent of the conversion takes place; the second at 52 deg. C. with a conversion of 33.4 per cent; and the last at 32 deg. C. with a conversion of 16 per cent. Nineteen per cent of the
heat given off in the reaction is thought to be removed by the dispersed liquid sulphuric acid. Only 0.685 square feet of surface per pound of sulphur burned per day is required.

It has long been realized that there is rather poor mixing in the ordinary lead chamber and that the contact with the “catalyst” is not what it should be. Therefore, it is not surprising to find that attempts have been made to utilize packed towers in the place of the ordinary lead chamber. Such a scheme was developed by Larison\(^{21,24}\) of the Anaconda Company. It is claimed that one cubic foot of volume is all that is necessary per pound of sulphur burned per day. The system consists of five cells or towers arranged in a block, lead lined, packed with acid-resisting material, and irrigated with pre-cooled chamber acid. The acid is distributed at the top, and the gas flow is either up or down.

One of the most interesting experiments ever published on this general subject is known as the Kaltenback pipe process.\(^{19}\) This was a laboratory scheme in which cooled pipes packed with filling material were utilized in place of chambers. The results obtained on this scale were quite remarkable.

12. *Gay Lussac Tower.*—The main function of this tower is to
provide time for the oxidation of NO (following the consumption of SO₂) to nitrogen peroxide NO₂, which is absorbed with the excess of NO as N₂O₅. The sulphur dioxide must be low; otherwise it will react with the nitrosyl sulphuric acid and the water to produce not only sulphuric acid but NO, which escapes through the top of the tower. On the other hand, some sulphur dioxide must be present in the last chamber, otherwise N₂O₅ becomes oxidized to NO₂ or N₂O₄—only slightly soluble in 60 deg. Bé sulphuric acid.

The construction is very similar to that of the Glover tower, but the reactions are much slower in Gay Lussac towers and they operate at a lower temperature. Therefore, considerably more packing is necessary in order to obtain a satisfactory time of contact. Usually this is brought about by using two Gay Lussac towers in place of one. Stoneware rings are employed as packing.

Fairlie outlines a method of design for the Gay Lussac Tower. He states that gases containing 2 per cent niter require 30 to 60 seconds of contact for gas velocities of 3 to 1 ft. per second.

An average niter loss of 3 per cent based on the sulphur burned, with an average time of contact for the gases of 45 seconds and a free space in the packing of 50 per cent would normally require 1500 cu. ft. of actual packing space per 1000 cu. ft. of chamber exit gas per minute. The gas volume is calculated at 55 deg. C. This is equivalent to 1200 cu. ft. of packing space per 1000 cu. ft. of 6-per-cent SO₂ burner gas per minute (gas volume calculated at 100 deg C.), or approximately 1640 cu. ft. of burner gas per minute (gas at standard conditions).

The ratio of the tower diameter to the height varies from 1/2 to 1/6. One-fifth or one-sixth are better values for practical design. The diameter should be approximately 10 ft. providing the volume of gas handled is not very large. This diameter is impractical for large volumes, and may be increased to 30 ft. In this case a ratio of diameter to height of 1/2 should be taken, otherwise the tower would be far too high from an economic standpoint.

If the desired velocity is 2 ft. per sec. and 35 seconds time of contact seems to be sufficient, then the packed region in the tower would be 70 ft. high, giving a total height of 80 ft., allowing for free space at the top and bottom and the thickness of the floor. In such a case it would be necessary to have two columns in series each about 35 ft. high.

The cross-section of the tower can be determined by multiplying the necessary cubic feet of packed space per one thousand cubic feet
of exit gas at the actual exit temperature per minute by the number of one thousand cubic feet units of this gas, and dividing the result by the total height of the packed space. The method of calculating the inside diameter is obvious.

13. Pressure System.—Berl has shown that it is possible to produce 66 deg. Bé. acid at lower operating cost in the chamber process, providing high pressure is employed. His work was done in the laboratory. The chief engineering difficulty in the commercial development of this process is the removal of the excessive heat produced.

14. Calculations.—Lewis and Radasch, in their book “Industrial Stoichiometry,” give an excellent example of a method of calculating efficiencies, chamber capacities, etc.

In order to obtain the sulphur efficiency of the entire process, it is advisable to calculate all sulphuric acid values on the basis of 100-per-cent sulphuric acid. The total sulphuric acid produced per day on this basis is obtained by adding the number of tons of 100-per-cent sulphuric acid produced per day in the Glover tower to that produced in the chambers. The total sulphur burned per day in terms of 100-per-cent sulphuric acid is calculated by multiplying 98/32 times the tons of sulphur. From the two figures, it is possible to obtain the sulphur efficiency.

Another common question is the percentage of total acid made in the Glover tower. Using as a basis 100 mols of burner gas, the mols of oxygen accounted for can be calculated. The total number of mols of oxygen put in can be obtained from the nitrogen figure, and the difference represents the mols of sulphur oxidized to SO₃ in the burner. Calculations concerning the Glover tower gas must now be put on a new basis. In other words, the nitrogen content of the two gases must be the same in order to compare them on a molal basis. By noting the loss of sulphur dioxide, it is a very simple matter to find the number of mols of sulphur dioxide oxidized to sulphuric acid in the Glover tower. Combining this figure with the SO₃ formed in the burner gives the total amount of sulphuric acid coming from the Glover tower. This over the total mols times 100 will give the percentage.

Another question is the percentage of acid returned to the Glover tower from the chambers for concentration. The total mols of sulphuric acid from the Glover tower minus the amount previously calculated as made in the tower, gives the amount of sulphuric acid obtained from the chambers for concentration.
A certain amount of water is evaporated in the Glover tower and sent on to the chambers. We assume no water is added or lost in the tower. The water evaporated in the tower comes from the chambers and from the water in the burner gas. The water in the burner gas can be determined from the humidity of the air, the vapor pressure of the water at that temperature, and the barometric reading. This can be expressed in tons of water per day. The tons of acid from the chambers per day times the per cent water plus this last figure gives the total water introduced into the tower. This figure minus the water returned as steam to the chambers gives the water in the exit acid from the tower.

In order to determine the amount of water necessary to be fed to the chambers, the water present in the acid from the Glover tower is added to the water coming from the chambers and entering the tower and the water combined with the total SO₃. The difference between the water in the chamber acid and the water in the Glover discharge is returned to the chambers as steam. This difference should be subtracted from the total water as calculated above. From it must also be subtracted the water entering with the air for the burner gas.

IV. OXIDATION OF AMMONIA TO NITRIC ACID

15. Process.—This oxidation takes place in several stages. The first step is the oxidation of ammonia to NO and water, as indicated in the reaction

\[ 4\text{NH}_3 + 5\text{O}_2 = 4\text{NO} + 6\text{H}_2\text{O} \]

This occurs on the surface of a platinum gauze catalyst, and 95-percent conversions can be obtained.

This oxidation of ammonia to NO is unique in that it is the only catalytic process that can be operated effectively at a high temperature, 1000 deg. C., and with a very short time of contact, 0.0001 second. It is also irreversible. This means that very little contact between the gases and the solid catalyst need be provided, and the temperature control is not important.

Two secondary reactions may take place. One involves the decomposition of ammonia and the oxidation of hydrogen to water.

\[ 4\text{NH}_3 + 3\text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O} \]

The other is the reaction between ammonia and nitric oxide to form nitrogen and water.
The first side reaction takes place only to the extent of about 5 per cent. The second side reaction is serious when excessive rates of gas flow are used or when the rates are very low. In other words, a curve showing the relation between percentage conversion to NO and rate of gas flow passes through a maximum.

Due to the nature of these reactions the catalyst bed need be only a few hundredths of an inch in thickness. An inert packing for the catalyst is not desirable because it has a tendency to catalyze the decomposition of ammonia.

A further oxidation is necessary to form NO₂. This does not require a catalyst, however, and is represented by the following equation:

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \]

This reaction is interesting because at 150 deg. C. it becomes reversible, and because it has a negative temperature coefficient. According to the rate equation, the maximum production when air is used requires 7 per cent by volume of oxygen, and when oxygen is used, \( 33\frac{1}{3} \) per cent. The velocity constant for the reaction increases 10 per cent with each drop of ten degrees in temperature. Catalysts such as activated charcoal and silica gel have been tried but are soon ruined by the presence of water absorbed on their surface. A further reaction sometimes occurs, NO₂ polymerizes to N₂O₄, which is colorless. The NO₂ has a reddish-brown color. This, however, is in equilibrium, and it is thought that only the NO₂ can be absorbed in the scrubbing liquid.

The scrubber or absorber which exists beyond the second oxidation chamber converts the NO₂ and water to HNO₃ and NO. The NO in turn is oxidized by the oxygen present to NO₂. The process is repeated. The equation is as follows:

\[ 3\text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 + \text{NO} \]

In this case the nitric acid and the water have a fairly constant composition, and, therefore, constant partial pressure, for any particular temperature. The equilibrium constant can then be expressed by the ratio of the partial pressure of NO to the partial pressure of NO₂. This constant decreases with an increased concentration of HNO₂, and is greater at the lower temperature.

There are several other theories regarding the formation of nitric acid, but we have selected this one from the work of G. B. Taylor because it seems to fit the conditions most accurately.
16. **Ammonia-Oxygen Mixers.**—Before the ammonia enters the catalyst chamber, it is necessary to mix it with air. A stripping column is employed when aqueous ammonia is used. On the other hand, the shipment of aqueous ammonia is sometimes prohibitive on account of freight charges on the water content. It is, therefore, desirable to make aqueous ammonia from the anhydrous ammonia. This can easily be done in an air stripping column. There is, however, generally no difficulty in using compressed anhydrous ammonia. The liquid NH₃ is easily vaporized by passing it through a coil immersed in a tub of warm water (that discharged from the acid coolers will do), and the gaseous ammonia is mixed with air.

17. **Converters.**—There has been considerable development in the construction of the converter in recent years. Results obtained by calculations and also from plant operations indicate that it is necessary either to preheat the gases (counter current heater) or to heat the catalyst in order to obtain high conversions. One of the original methods tried was an electrically-heated platinum gauze. The electrical energy was costly, and the method is no longer popular. The modern method is either to preheat the air or to preheat both the air and the ammonia to a temperature of about 200 to 300 deg. C. The amount of ammonia in the gases is generally held around 10 per cent.

One of the original catalyst chambers used in this country consisted of an electrically-heated platinum gauze within an aluminum box. Another type (Fig. 9) consisted of a cylindrical gauze through which the gases passed after they had first been preheated. The whole was contained in a fire-brick chamber with peep holes for observation directly opposite the catalyst. The connections at the top and bottom were made of aluminum, and the gas flow was downward. Three to 4 layers of 80-150 mesh gauze were used. The platinum wire was 0.001 to 0.003 inches in diameter. The refractory material was employed in order to radiate heat back to the catalyst. The exit gases were at about 800 deg. C. In this particular type 70 pounds of ammonia were oxidized per day per Troy ounce of platinum consumed. This represented a 7-per-cent loss of platinum per year. The cost was approximately $0.03 per pound of nitric acid.

It has been found more recently by other investigators that a cylindrical gauze is not necessary, and that the flat gauzes are equally effective. Several layers are still used. Their relative position is not important.

Considerable argument has occurred over the question of what poisons this catalyst. W. S. Landis has maintained that his experi-
ence has shown that no common poison has any appreciable effect. The principal thing to be remembered is to activate the catalyst with the particular gas that is to be used. It is, of course, quite essential not to have any oil present in the ammonia. It is recognized today that phosphine is a poison for the platinum catalyst.

The second oxidation takes place in an empty chamber, where time is required to oxidize the NO to NO₂. No particular difficulty has been found with this operation.

18. Absorber.—It will be noted under theory that the absorber not only acts as an absorber of NO₂, but also provides a space for the NO formed to oxidize to NO₂. These towers were originally built of stoneware, but chromium-iron alloys have replaced this material. Packing material (bubble cap plates for the high pressure process) is used to give the necessary time of contact. It is desirable to cool the gases before they come to the absorber. This is usually done by employing waste heat boilers. Modern equipment goes further and supplies cooling arrangements within the scrubbing tower.

The final product contains between 50 and 55 per cent HNO₃.
Water is added as the scrubbing medium, and also dilute acid. More than one tower can be used for this purpose. The gases go to a condenser after the conversion to nitric acid and are returned for further oxidation, whereas the liquid goes to a cooler and to storage.

It is sometimes profitable to absorb the residual nitrogen oxides in a sodium carbonate solution, as they are usually so dilute that it is impractical to oxidize them back to NO₂.

19. Pressure System.—An increase in pressure would increase the capacity of any unit. Fauser has found that raising the pressure from one atmosphere to 5 has increased the kilograms of nitric acid produced per day per gram of platinum from 2.76 to 12.8, and the tons of ammonia oxidized per day per square meter of platinum from 0.7 to 3.3, while the yield remained approximately the same, 91.6 to 91.2 per cent. The absorber, requiring 1200 seconds at atmospheric pressure, required only 59 seconds at 5 atmospheres.

Low temperatures are favorable for absorption, but an increase in pressure from 1 to 6 reduces the cooling necessary from 4.5 to 1.

The power increase is very small, and, if necessary, the compressed gases can be used to drive a turbine connected with a pump to reclaim some of this energy.

In the process described by Fauser (Fig. 10) the gases were first put under pressure, passed through a filter, and then through the converter to a preheater. Any dilute acid formed was extracted beyond this point and returned to the top of the absorber. The acids passed through a second oxidizing chamber and then to the bottom of the absorber. The liquid at the bottom of the absorber passed through a secondary column in order to free it from any nitrogen dioxide and other gases. This second absorber or bleacher utilized compressed oxygen gas entering at the base. The final product was removed at the bottom. The gases from this bleacher were returned to the top of the second oxidizing chamber. The gases from the absorber were passed through the preheater and to a turbine or motor which operated the pump.

The development of chromium-iron alloys, making possible the construction of a compressor to operate with corrosive gases, led Fauser to put pressure only on the absorbing system and to operate the conversion at atmospheric pressure. His experiments show that he obtained 91 per cent conversion at 4 atmospheres, and 95 to 96 per cent at one atmosphere. The catalyst at the lower pressure was less affected by poisons.

In these experiments he changed the absorbing system to utilize a
series of cylindrical tanks in place of a filled column. The liquid ran from one to another by gravity. The gases passed from a sparge pipe through the liquid, coming in contact with the vapors and out at the top, then into the sparge pipe of the tank above. He claims that this type of absorber gave a longer time for oxidation, better cooling, and required less power.

Taylor, Chilton, and Handforth\(^4\) favor the application of pressure to the entire system, and do not favor the use of chromium-iron alloy for pump construction. Their converter (Fig. 11) consists of a 4-layer gauze cylinder made of platinum-rhodium alloy, containing 10 per cent rhodium. They obtained 96 per cent conversion. Their finished plant was very flexible, operating satisfactorily on 3 to 25 tons of ammonia per day. They concluded that refrigeration or cooling of the absorber did not pay.

Their absorber consisted of a bubble column, 5\(\frac{1}{4}\) feet in diameter and 40 feet high, with special cooling device. They point out that this pressure system operates at a lower cost for the same capacity. The acid concentration was higher, 8 to 10 per cent. This means 50 to 60
per cent less concentration of the product is necessary in order to obtain the 90 per cent acid required.

V. OXIDATION OF ORGANIC COMPOUNDS

20. General Considerations.—The complete oxidation of organic compounds results in the formation of carbon dioxide and water. Since these products are of less value than the original substances, there is no economic advantage in complete oxidation. On the other hand, whenever partial oxidation is possible quite often a compound is formed that is more valuable than the original. Partial oxidation of organic compounds requires a much better temperature control, and, therefore, a much better heat transfer from the reaction zone than do the oxidations previously considered.

Aromatic hydrocarbons are relatively stable towards oxidation and require generally a large excess of oxygen for the process. There seem to be points of resistance. In other words, it is sometimes relatively simple to stop the oxidation of an aromatic hydrocarbon at the point where an intermediate compound is formed. Naphthalene to phthalic anhydride is an example. On the other hand, if the aromatic
hydrocarbon has a side chain, the side chain resembles an aliphatic compound, for it is relatively unstable.

Aliphatic hydrocarbons not only are unstable in comparison with aromatic hydrocarbons as far as oxidation is concerned, but require relatively small amounts of oxygen. There are apparently no points of real resistance in the common types of aliphatic hydrocarbons. The actual conversion, or the yield per pass, is small. A short time of contact is necessary; low temperatures as well as low oxygen concentrations are essential to obtain reasonable yields of the product. Perhaps the worst feature of the partial oxidation of these compounds is the tendency to form complex mixtures. The resulting product, because of its complexity, is difficult to separate into its constituents. It is, therefore, almost impossible to obtain any satisfactory yield of a pure compound by the partial oxidation of an aliphatic hydrocarbon.

A common method of oxidizing an organic compound is to pass its vapor, along with air, through a heated tube over a solid catalyst. In order to prevent the temperature from rising to the point where complete oxidation takes place, it is necessary to conduct the heat rapidly from the surface of the catalyst, where the reaction takes place, to the outer system. First of all, it is thought desirable to use a catalyst that is a heat conductor or a catalyst on a backing that is a heat conductor. The greatest resistance, however, occurs between the solid catalyst and the walls of the tube. This contact must be sufficient to provide a satisfactory flow of heat in order to prevent an undue rise in temperature on the catalyst surface. It has been found by workers in industry that most of this heat transfer in commercial installations does not take place by conduction, but by radiation to the walls of the tube. In order to increase the absorption, the "blackness" of the tube surface is undoubtedly an important factor. The heat capacity of the gases is an important feature in removing the heat from the catalyst surface, and often times a vapor such as steam is added. The nitrogen in the air acts not only as a diluent but as a heat absorber.

The actual resistance to heat flow of the tube itself is not of any great importance, especially if the tube is made of metal. In other words, the selection of a particular metal for this purpose need not be considered.

After the heat has gone through the tube walls, it must be removed from the outer surface. Considerable development has taken place in recent years in providing a more efficient heat transfer from the outer surface to the surroundings. Radiation was first used for this purpose.
The more recent type of catalyst chambers, however, employ a boiling liquid on the outside of the tube to absorb the heat and carry it away. A boiling liquid is advantageous not only because of its high heat capacity, but also on account of its latent heat. Furthermore, it will be noticed that a boiling film does not present high resistance to heat flow. The vapors can be condensed and returned, and, if necessary, the liquid itself can be taken out, cooled, and returned. An additional feature is the fact that the temperature of the boiling liquid can be changed by the application of pressure or vacuum. Thus, by controlling the pressure on the system, it will act as a thermostat by maintaining the temperature at the outer surface of the catalyst tube at the point desired.

In a few cases it is possible to operate these oxidation processes at a sufficiently low temperature so that one of the reactants is in the form of a liquid. The higher heat capacity of the liquid is desirable. In this case, however, if the other reactant is a slightly soluble gas such as oxygen or air, it usually becomes difficult to obtain the necessary surface of contact.

The time of contact is important in all of these processes that are operated in the liquid or vapor phase. The surface of the catalyst exposed to a unit volume of reactant, therefore, is also important. The extensive surface of aerogels has been recognized, and recent experiments show the value of silica aerogel as an oxidizing catalyst.

Perhaps one of the most unfortunate conditions that must be met is the fact that most organic compounds are sensitive to heat and have a tendency to break down even though they are not oxidized. This means that it is essential to bring the organic liquid or gas to be oxidized to the necessary temperature in a minimum length of time. The difficulties are increased as the unit becomes larger.

Still another difficulty presents itself. Most of these partial oxidation products are not only sensitive to high pressure, but are also capable of being further oxidized at high temperatures, if sufficient time is allowed. This, in turn, means that the products must be promptly chilled or their temperature greatly reduced immediately after they are formed. Again extremely rapid heat transfer is necessary.

We may divide the oxidation process into three periods. In the first period, the reactants are heated to a high temperature, and this heating operation must be extremely rapid. In a second or reaction period, it is necessary to maintain a definite temperature on the surface of the catalyst. The heat transfer must, therefore, be controlled within
certain narrow limits. Finally, in the cooling period, an extremely rapid heat transfer is again required.

Air, the common oxidizing agent, is usually added in one of two different ways. It may be passed through the organic liquid, at a temperature such that the required concentration of the organic compound in the gaseous mixture is maintained, or it may be mixed with the vaporized organic compound. Either or both of the gases may be preheated to the required temperature.

21. Converters.—The converters that have been used for the oxidation of organic compounds where the liquid phase was present are extremely simple in construction. This type of converter consists of a bubbling device in which the oxygen gas is allowed to pass through the liquid. Heat is absorbed by the excess liquid present and removed from the system in various simple ways. Such equipment has been used commercially in the air oxidation of acetaldehyde (concentrated water solution) in the presence of the liquid product, concentrated acetic acid, and the dissolved catalyst, manganese acetate.

On the other hand, where both the organic liquid and the air or oxygen are in the gaseous phase, much more elaborate construction is required.

One of the first converters used for the purpose of oxidizing aromatic hydrocarbons was developed by Downs46 (Fig. 12). This consisted of a chamber through which air passed downward after being preheated by electrical resistant members, and then through a thin layer of solid catalyst where its temperature was raised to a point beyond which complete conversion could take place. The resulting gases were cooled by an indirect cooling system such as a coil, and
passed through the next layer of catalyst below, and so on until the conversion was satisfactory. This intermittent heating and cooling of the gas did not give adequate control.

Conover had a somewhat similar but more elaborate device (Fig. 13) in which the horizontal catalytic chambers were completely enclosed by a cooling zone through which water or some other similar cooling medium was passed. The gases passed horizontally through the catalyst tubes and out. Much more cooling space than catalyst space was provided, and the probabilities are that the reaction was often times quenched, thus causing poor conversion.

Downs then invented an apparatus (Fig. 14) for the utilization of a boiling liquid. The boiling liquid was placed in a sealed vertical tube, which was inserted in the catalyst bed. The upper half of the tube was surrounded by a water condenser. The lower half was in the catalyst bed. The gases passed through the catalyst, around the boiling liquid and out.

A much better design (Fig. 15) was just the reverse, in which a
tube containing the catalyst was surrounded by the boiling liquid. The vapors from this boiling liquid were condensed by a reflux condenser, and returned to the surrounding chamber. Gas entered at the top and passed down through the catalyst which was surrounded by the boiling liquid, and out the bottom of the tube. Square tubes were used in order to obtain more surface per unit of volume. A commercial unit had tubes that were from \( \frac{3}{8} \) to \( \frac{3}{4} \) inch on a side. These square or rectangular tubes were also used because a number of them would fit more effectively in a given cross section. In the case of naphthalene oxidation, a thousand tubes were used, \( \frac{3}{4} \) inch on a side, 36 inches long. They were housed in a cylindrical shell 36 inches in diameter. Instead of a tube sheet, the tubes were welded together at the top, thus affording only a relatively small space for the cooling liquid. Mercury was used because of its high boiling point. It should be noted that mercury vapor is quite toxic; both the vapor and the liquid are heavy; and it is a poor conductor. However, if the equipment can be kept tight, there is very little loss of mercury to the atmosphere, very little danger involved, and the rapid agitation due to boiling materially increases the heat transfer and neutralizes the effect of the poor conductivity. Mercury can easily be purified by simple distillation and used over again. The losses per year in a commercial plant are approximately 1 per cent.

The boiling point of mercury at the pressure of one atmosphere is 375 deg. C. In the case of the oxidation of naphthalene, 425 deg. C. is usually necessary. In other words, the reaction takes place first at 400 deg. C. and later on at 450 deg. C. It is a simple matter to apply
pressure to boiling mercury to raise the temperature to the reaction temperature. The pressure is applied by the addition of some inert gas like nitrogen or carbon dioxide. Of course, it is necessary to keep the temperature below the maximum in order to prevent complete oxidation of the hydrocarbons to carbon dioxide and water.

The amount of surface exposed is 4.35 square inches per cubic inch of volume for the $\frac{3}{4}$-inch tubes, and 6.4 square inches per cubic inch of volume for the $\frac{5}{8}$-inch tubes.

Sixteen thousand to eighteen thousand pounds of naphthalene were used in this unit per 24 hours. The heat of reaction for the naphthalene oxidation is 6000 B.t.u., but some complete oxidation took place, so this figure generally rose to approximately 10 000 B.t.u. per pound of naphthalene oxidized in practice. The plant in question liberated 21 000 000 B.t.u. per day in the converter.

Mercury-cadmium alloys have been suggested and used by Jaeger.44 A 12-per-cent cadmium-mercury alloy will boil at 375 deg. C.; a 25-per-cent cadmium alloy boils at 425 deg. C. and is satisfactory for this process; and a 40-per-cent cadmium alloy will boil at 430 deg. C. One good point about this alloy is that it is liquid at 100 deg. C. and, therefore, can be moved about at this comparatively low temperature.

Mercury, lead, and tin alloys containing 40 per cent mercury, 30 per cent lead, and 30 per cent tin have a boiling point of 425 deg. C. These have also been suggested.

Downs46 has utilized boiling sulphur. This element is cheaper and lighter than mercury. It has a boiling point of 444.6 deg. C. at the pressure of one atmosphere and for practical purposes it must be utilized with reduced pressure. The apparatus is considerably lighter.

Diphenyl59 and "Dowtherm" should be mentioned as possible substitutes for mercury.

Still other experiments have been performed with boiling anthracene. Rapid circulation is necessary to prevent decomposition of the anthracene.

The catalyst for the aromatic hydrocarbon oxidation using these converters is usually vanadium pentoxide on a carrier. The carrier must not be pumice, however, because the high temperature existing causes the decomposition of the hydrocarbon wherever the carrier is exposed to its vapors.

One of the original converters (Fig. 16) used by Gibbs46 for this oxidation consisted of a series of horizontal tubes. The entering gas was passed through a central tube and then returned through tubes
containing the catalyst. The catalyst tubes were jacketed by a cooling chamber. In this case the cooling medium was a fused salt, such as sodium and potassium nitrate. The Monsanto Company have used a similar type in which the catalyst tubes are vertical. This is to prevent the catalyst from stratifying and permitting the gas to pass through a free space above it.

Jaeger has developed several interesting catalyst chambers for the oxidation of various hydrocarbons. He recommends for naphthalene oxidation catalyst tubes surrounded by a fused salt bath. The non-boiling bath is circulated by means of an agitator and cooled...
directly by the incoming gases in a chamber separated from the catalyst bed.

He modifies this equipment for the oxidation of toluene to benzaldehyde by interspersing heat exchange elements (tubes through which gas flows) among the catalyst tubes and not providing for positive circulation of the fused salt bath. This simplification is possible due to the fact that this reaction is not excessively exothermic.

Jaeger shows a more elaborate design (Fig. 17) for maximum control of temperature in the catalyst bed, and applies it to the oxidation of anthracene to anthraquinone. The fused salt bath is circulated by means of an agitator around both catalyst tubes and tubes in which the gaseous products are flowing. The course of the circulated bath is directed by means of baffles.

22. Pressure Oxidation.—Considerable work has been done on the use of high pressure for the catalytic oxidation of the lower hydro-
The results of this work showed that the chief products were alcohols and aldehydes. The greater the pressure, the greater the alcohol content of the product. The chemical composition of the catalyst was of little moment. Its physical characteristics, however, were important. The temperature range was between 300 and 400 deg. C. The pressure was between 1500 and 3500 pounds per square inch. Low oxygen concentration was used, around 15 molar per cent. A short time of contact was necessary, and, as would be expected, the higher hydrocarbons reacted more than the lower (Fig. 18).

These high pressures had a tendency to keep down the decomposition of the product, but in order to obtain a reasonable percentage of conversion, it was necessary to have quick preheating of the incoming gases and rapid cooling of the products. It should be remembered that the explosion hazards are greater wherever a large concentration of oxygen is heated to a high temperature in the presence of combustible material. These dangerous conditions occur principally at the point of the introduction of the oxygen into the system and when a high temperature exists. The safest method is to saturate the hydrocarbon with oxygen after it has been brought to the required pressure and temperature. Never heat the hydrocarbon-oxygen mixtures directly.

In spite of the use of higher pressures, conversions per pass based on the hydrocarbon used were low and the products were a complex mixture of aldehydes, alcohols, acids, and ketones.
### VI. Bibliography

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