

A naphtha solution of isoamyl disulfide ($S = 0.460$ per cent) was refluxed with alcoholic sodium sulfide solution (50 cc. C_2H_5OH , 10 cc. H_2O , and 6 grams $Na_2S \cdot 9H_2O$). After separating, washing, and drying, the oil had 0.459 per cent sulfur; but after treatment with sodium plumbite it had only 0.312 per cent sulfur. That is, the above reaction occurred to some extent, but the sodium mercaptide was at once hydrolyzed and the mercaptan retained in the oil layer until removed with sodium plumbite.

Suggested Analytical Method for Mercaptans, Sulfides, and Disulfides

It seems very probable that an analytical method for mercaptans, sulfides, and disulfides in gasolines could be developed, using sodium plumbite for mercaptans, sodium sulfide for the disulfides, and methyl iodide plus mercuric

iodide for the sulfides. Since the method would depend on analysis of the oil after each treatment, it would probably only be satisfactory for oils containing large amounts of sulfur (over 0.20 per cent). A suitable procedure might be:

1—Remove hydrogen sulfide with sodium carbonate solution and analyze for sulfur.

2—Wash with concentrated aqueous sodium sulfide to remove free sulfur.

3—Wash with 50 per cent alcoholic sodium plumbite containing some solid lead sulfide (to remove mercaptans) and again analyze.

4—Reflux with excess sodium sulfide in 70 to 80 per cent ethyl alcohol, treat with alcoholic sodium plumbite, and again analyze.

5—Finally, shake for several hours with excess methyl iodide and mercuric iodide, pour off the oil layer, distil off methyl iodide (to do this the naphtha being analyzed would have to be fractionated so as to have no portion boiling below about $80^\circ C.$), reflux the bottoms with zinc and acetic acid, and analyze for sulfur.

Oxidation of Ammonia^{1,2}

By Guy B. Taylor

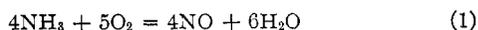
E. I. DU PONT DE NEMOURS & COMPANY, WILMINGTON, DEL.

AMMONIA oxidation in its special sense refers to that industrial process wherein ammonia gas is burned with air on a catalytic surface, producing oxides of nitrogen. Under certain conditions ammonia, cyanogen, or hydrocyanic acid gases can be burned with a free flame, in which case their nitrogen appears in the products of combustion as free nitrogen. If, however, the combustion is carried out on certain surfaces—e. g., platinum or some heavy metal oxide—under suitable conditions, the nitrogen appears in the reaction products as nitric oxide. The oxidation of ammonia to nitric oxide was observed first toward the last of the eighteenth century. Platinum as a catalyst for this reaction was discovered by Kuhlman in 1839. No industrial use was made of the catalytic oxidation of ammonia until shortly before the World War, when Ostwald worked upon it in Germany.

The catalytic oxidation of ammonia is an important technical process because it affords the means of transferring nitrogen combined with hydrogen (or carbon) into nitrogen-oxygen compounds. The primary product of the catalysis is nitric oxide and by suitable series of steps this compound may be converted into practically any compound in which nitrogen and oxygen atoms are directly attached. Syntheses of such compounds are generally effected through the reactions of nitric acid, and up to the present by far the largest technical use of catalytic ammonia oxidation has been in the manufacture of nitric acid. A description of such a nitric acid process is probably the best way to give a clear idea of the general subject of this talk.

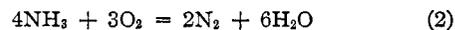
Manufacture of Nitric Acid—Theory

A mixture of ammonia gas and air is passed through a red-hot, fine-meshed platinum gauze, the reaction taking place being represented by the equation

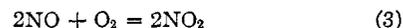


It is possible on an industrial scale to convert 95 per cent or more of the ammonia into nitric oxide. The other 5 per cent breaks down to free nitrogen and all the hydrogen

is converted to water vapor. This secondary reaction may be represented by the equation



After passing the platinum gauze, the gas mixture is cooled and nitric oxide combines with excess oxygen spontaneously to form nitrogen peroxide,



The last step in the process consists in countercurrent absorption of nitrogen peroxide in water to form nitric acid,



The nitric oxide formed in this reaction repeats reaction (3), which is followed by (5) until nearly all of it is converted to nitric acid.

The mechanism of the course of these reactions is important to an understanding of the plant equipment and process details, so a discussion of their peculiarities will be presented before outlining the nature of the plant.

There is no adequate theory to explain reaction (1). Little enough is known to account for any case of contact catalysis, and less about this one. The temperature, $1000^\circ C.$, is higher, and time of contact, 0.0001 second, is shorter than for any other known case of contact catalysis. Practically speaking, the reaction is irreversible, thus differing fundamentally from contact sulfuric acid practice. In spite of the thermodynamic instability of nitric oxide, no upper temperature limit has been found at which the yield falls off, at least up to $1300^\circ C.$ In practice the best temperature seems to be $900-1000^\circ C.$ on account of wear and tear on platinum. At temperatures as low as $500^\circ C.$ the ammonia is almost wholly converted to free nitrogen.

The time factor is important. At excessive rates of gas flow free ammonia passes the catalyst and is destroyed by a secondary reaction between NH_3 and NO . At very low rates the yield falls off, but there is a wide range in rate in which the yield is little affected. The thickness of the contact bed is, in the case of platinum, at most only a few hundredths of an inch. Inert catalyst supports such as are used in sulfuric acid contact plants have never proved suc-

¹ Presented before a General Conference at the Institute of Chemistry of the American Chemical Society, State College, Pa., July 16, 1927.

² Contribution No. 5 from the Du Pont Experimental Station.

cessful for ammonia oxidation, because there must be no exposed inactive surface for breaking down ammonia to free nitrogen.

The effect of the reaction on platinum is remarkable. The gauze loses its characteristic metallic luster and to the naked eye appears gray. Under the microscope the wire appears to be sprouted and covered with platinum sponge. This sprouting effect continues all the time the catalyst is in service, until eventually the wires become so weak they fall apart. When the gauze is used multilayer, the upstream layer sprouts first and may actually disintegrate before the fourth underlayer is appreciably affected.

The statics and dynamics of the reaction between nitric oxide and oxygen have been completely worked out. Reaction (3) is not sensibly reversible under 150° C., so that in ammonia oxidation practice we have only to deal with its rate. Most, if not all, of the gas-phase reactions of nitric oxide are slow enough to measure accurately. Its reactions with oxygen, chlorine, bromine, and hydrogen are actually termolecular and homogeneous. These reactions are among the few known whose reaction order is exactly that indicated by the stoichiometric equation. The reaction between nitric oxide and oxygen is unique among all chemical reactions in that it has a negative temperature coefficient. The cooler the gases the faster they react.

The slowness with which nitric oxide reacts with oxygen accounts for the large sizes of both ammonia-oxidation and arc-process absorption systems. This rate is expressed mathematically in terms of the calculus by the equation

$$-\frac{d(\text{NO})}{dt} = k(\text{NO})^2(\text{O}_2)$$

in which k is a constant at any fixed temperature. The equation states that rate of disappearance of nitric oxide—i. e., its conversion to nitrogen peroxide—is proportional to the square of the nitric oxide concentration and the first power of the oxygen concentration. An interesting deduction from this equation is that if the gas mixture containing nitric oxide and a deficiency of oxygen is diluted with air, nitrogen peroxide will be formed at a maximum rate when oxygen constitutes 7 per cent of the total gas mixture by volume; if pure oxygen is the diluting gas instead of air, this figure is $33\frac{1}{3}$ per cent instead of 7 per cent.

As stated above, the rate increases with decrease of temperature. The value of the reaction rate constant, k , increases about 10 per cent for each 10-degree drop in temperature. The reaction is apparently homogeneous and not a "wall" reaction. Measurements of its rate in small glass tubes passing a few cubic centimeters per minute agree quite well with similar measurements in plant equipment passing thousands of cubic feet per minute. The reaction can be catalyzed by such substances as special charcoal and silica-gel, but these catalysts have found no use in industry because they lose their efficiency by sorption of water vapor, or by becoming wetted by acid mists.

Nitrogen peroxide formed by the oxidation of nitric oxide exists as two molecular species, NO_2 and N_2O_4 . These two species come to instantaneous equilibrium as expressed by equation (4). The equilibrium constant, K_2 , is a function of the temperature and has long been known:

$$K_2 = \frac{\text{N}_2\text{O}_4}{(\text{NO}_2)^2}$$

N_2O_4 is supposed to be colorless and NO_2 , colored brown. The lower the temperature the greater the concentration of N_2O_4 . Nitrogen peroxide boils at 21° C. and freezes at -10° C. Liquid nitrogen peroxide will dissolve nitric oxide (NO) and the green mixture is sometimes said to con-

tain N_2O_3 . There is no very good evidence for the existence of N_2O_3 in the gas phase.

The reaction between nitrogen peroxide and water to form nitric acid (equation 5) was worked out during the war by Burdick and Freed³ at Massachusetts Institute of Technology. Their work has received very little attention by technical writers on nitrogen fixation, but it is undoubtedly the most important contribution to the theory and practice of nitric acid manufacture that has appeared in recent years.

Burdick and Freed assume that the molecular species of nitrogen peroxide reacting with water is NO_2 , that N_2O_4 is inert; N_2O_4 of course dissociates to restore equilibrium (equation 4) as NO_2 disappears by reaction to form HNO_3 . Reaction (5) is reversible, the equilibrium constant being defined by the expression

$$\text{Constant} = \frac{(\text{HNO}_3)^2(\text{NO})}{(\text{NO}_2)^2(\text{H}_2\text{O})}$$

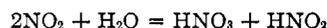
For any one temperature and composition of the liquid phase the partial pressures of nitric acid and water vapors are obviously constant, so that the equilibrium between nitrogen oxides and nitric acid solution may be expressed by a partial constant,

$$K_1 = \frac{\text{NO}}{(\text{NO}_2)^2}$$

Values for K_1 have been determined for all acid strengths up to 65 per cent HNO_3 and temperatures from 10° to 75° C. The values of K_1 are such that the lower the temperature the more the equilibrium is displaced toward HNO_3 .

The values of K_1 decrease with extreme rapidity as the concentration of nitric acid in the liquid phase increases. At ordinary temperatures the partial pressure of nitric oxide in equilibrium with acid much above 60 per cent HNO_3 is so small that reaction (5) practically stops unless a high partial pressure of oxygen is maintained and a long time allowed for the reactions.

Much of the published work on absorption of nitrogen oxides, even at the present time, considers the initial absorption reaction to be



The nitrous acid is supposed to break down to N_2O_3 , then NO and NO_2 . One recent writer⁴ has accounted for the fact that lowering the temperature favors absorption by assuming the primary reaction to be between N_2O_4 and water. None of these complications or assumptions are necessary to explain the facts. A trace of nitrous acid is formed but it can be neglected. On the other hand, it is possible to calculate quantitatively everything that happens, predict equipment sizes, foretell the effect of temperature, etc., by use of the equilibrium constants K_1 and K_2 for reactions (5) and (4) and the rate constant, k , for reaction (3).

Manufacture of Nitric Acid—Practice

The raw materials for the process are ammonia, air, and water. Ammonia may be available either in the liquid anhydrous form or as a 25 per cent solution in water, known in the trade as aqua ammonia or ammonia liquor. In either case ammonia gas is produced from the raw material, mixed with air to form 10 per cent NH_3 by volume, and the mixture passed into the converter or catalytic unit.

The details of ammonia gasification vary according to the construction and operation of the ammonia converter. With liquor there are two general methods: (1) the air-stripping column in which liquor is fed down the column

³ *J. Am. Chem. Soc.*, **43**, 518 (1921).

⁴ *Toniolo, Chem. Met. Eng.*, **34**, 96 (1927).

and air and steam blown in the bottom, in which case the ammonia-air mixture is drawn from the top of the column direct to the converter; (2) separate distillation of ammonia into gas-holders and subsequent mixing with air.

Liquid anhydrous ammonia is gasified by any source of heat (steam, waste heat from the converter, or even cold water).

Converters may be classified, first, into those that employ preheat and those that do not. It is possible to obtain a fair yield without preheat, and some plants abroad are operated this way at catalyst temperatures in the neighborhood of 750° C. But with preheat temperatures of 200° to 300° C. and catalyst temperatures around 1000° C. better yields are obtainable.

Catalyst temperatures have been maintained in three ways: (1) preheating air prior to admixture with ammonia, (2) preheating the ammonia-air mixture, and (3) electrical heating of the catalyst itself. Methods (1) and (2) are, of course, most economically done by heat interchange. In the case of (2) the surfaces coming into contact with the mixture must not oxidize or decompose ammonia. Suitable materials for this purpose are aluminum, nickel, or enameled iron—all of which are or have been used. Method (3) was installed at one of the U. S. Government's nitrate plants at Muscle Shoals. This method can hardly be called economical.

The catalyst most generally used is platinum, though there is report of a successful German plant employing a granular iron oxide mixed with other oxide promoters. The patent literature contains numerous references to various metal oxide combinations. Fair yields can be obtained from some of these catalysts, but they seem to lack the dependability and life of platinum.

The present-day platinum catalyst is constructed of fine-mesh screen (80 to 150 mesh per inch) and wire diameters of 0.001 to 0.003 inch. This screen or gauze is sometimes used single layer but often multilayer in close contact. Four layers is the usual practice in this country and England.

In some types of converters the platinum gauze is placed horizontally and the ammonia-air mixture passed downward in some cases, upward in others. The Parsons and Jones type of converter employs a cylindrical shape passing the mixture inside the cylinder downward. The cylinder form has certain geometrical advantages over planes.

The gas leaving the converter contains nitric oxide, water vapor, nitrogen, and oxygen. It may be cooled and handled in iron pipe down to the dew point, but from that point on it must come in contact with acid-proof materials only. This gas first usually passes to a heat interchanger for preheating the ammonia-air mixture. In some cases its heat is conserved by next passing through a steam boiler.

The gases are now cooled and weak acid is formed from its water vapor condensate reacting with a little nitrogen peroxide. The gases then pass through an empty chamber to allow time for the reaction between nitric oxide and oxygen. Following this chamber are a series of packed towers, over which nitric acid solution is rapidly circulated. Water is fed in the last tower and nitric acid of 50 per cent strength drawn from the first tower. Acid of intermediate strength circulates in the middle towers.

It should be remembered that recovery of nitrogen oxides as nitric acid by absorbing in water is not a case of straightforward solution, but a series of chemical reactions. One of these reactions is the gas-phase oxidation of nitric oxide to nitrogen peroxide, which is slow. This time reaction accounts for the large tower space required. The time of gas travel is a matter of minutes and not of seconds, as would be the case if only solution or a simple reaction between gas and liquid were involved.

It is quite impossible in any reasonable-size absorption system to effect a complete recovery of the nitrogen oxides as nitric acid. A portion of the oxides is generally recovered in alkali towers following the acid towers. In these towers a solution of soda ash is circulated and sodium nitrite is made according to the equation



The size of an absorption system is a function of the following variables: composition of the entering gas, temperature, strength acid delivered, and recovery or efficiency. All these factors are interdependent. The entering gas should contain as little nitric oxide as possible and certainly little enough to avoid reducing nitric acid in the head tower by reversal of reaction (5). In some plants where the oxidation chamber ahead of the absorption towers proper was inadequate, the head absorption tower delivered weaker acid than was supplied to it from the next tower. Lowering the temperature aids acid recovery because it favorably affects the equilibrium of reaction (5) and increases the rate of reaction (3). An uncooled absorption system will generally operate at about 40° C. average temperature and produce 50 per cent strength acid. If the circulating acid in each tower is maintained at 0° C. by artificial refrigeration, the size of the system can be half as large and deliver 60 per cent strength acid at the same recovery.

Concentration of Nitric Acid

The nitric acid with which most of us are familiar, the stock bottle on the laboratory shelf, is generally labeled "68-70 per cent HNO₃." In industry such acid would be regarded as weak. Most large scale users of acid require a strength above 90 per cent HNO₃ for the larger part of their operations. In this particular, the retort process producing acid from Chile nitrate has an advantage over the ammonia oxidation process because it produces high-strength acid directly. Ammonia oxidation acid has to be concentrated, which adds considerably to its cost.

The concentration operation is generally carried out by mixing the weak nitric acid with sulfuric acid and distilling off the nitric acid. The sulfuric acid retains the water, and in order to use it again it must be concentrated either in a contact oleum plant or by boiling out the water.

Industrial Significance

The past industrial significance of the ammonia oxidation process may be stated in a single sentence. Without this process Germany would have lost the World War much sooner for lack of ammunition. As for the present world situation, Germany and most of continental Europe produce nearly all their nitric acid by this process or the arc process. Great Britain and the United States have been slower to adopt it. This country has just begun to produce synthetic ammonia in large enough tonnage to compete seriously with Chile saltpeter in the fixed nitrogen field. At present prices nitric acid can be made cheaper from ammonia than from Chile nitrate. In the next few years the major part of America's acid will undoubtedly be made from ammonia. Niter supply for chamber sulfuric acid plants is so much cheaper by ammonia oxidation than niter pots, that any chamber operator failing to install the process at once is neglecting a major economy.

There are likely to be some developments in the direct utilization of nitrogen oxides to manufacture compounds either now made from nitric acid or not made at all. Ammonia oxidation may play an important role in fertilizer manufacture.