

# Oxidation of Aromatic Hydrocarbons

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All benzoic acid and anthraquinone and its derivatives now made in the United States are produced from phthalic anhydride which, in turn, is made by the vapor-phase catalytic oxidation of naphthalene. In addition to these uses, phthalic anhydride is of great importance in its own right, especially in the synthesis of synthetic resins. The present production capacity of phthalic anhydride equipment in the United States is estimated at 70 to 75 million pounds per year. There is no potential shortage of domestic naphthalene for producing phthalic anhydride in much larger quantities than is indicated for future consumption.

**T**OLUENE, naphthalene, and anthracene were for many years oxidized by chemical methods in the liquid phase, respectively, to benzoic acid, phthalic anhydride, and anthraquinone. Later it was found that they could be oxidized to these same products more cheaply by air at elevated temperatures in the vapor phase in contact with various solid catalysts. All three products are now made from one raw material—naphthalene—rather than from what offhand would appear to be their most logical sources. This result has been dictated by economic reasons which the chemical engineer must always recognize as being more important than the chemical reactions themselves, regardless of how intriguing the latter may appear from a strictly scientific standpoint. In order to emphasize this point, it seems proper to trace the histories of these products and point out their economic effects.

The transition of these processes from strictly chemical synthesis to catalytic vapor phase oxidation began during the first World War.

## Phthalic Anhydride

Phthalic anhydride, before the first World War, was produced in Germany in large quantities for the synthesis of phenolphthalein, eosines, rhodamines, and especially indigo, for which there was a large market in Europe, the United States, and the Orient. When the World War broke out in 1914, shipments of indigo from Germany were shut off. A decision had to be made as to whether this important dyestuff should be made from phthalic anhydride or from aniline. Work was started on both processes. It was soon found that the synthesis from aniline was preferable, but there appeared to be enough other possible uses for phthalic anhydride to warrant continuing the effort to produce it.

The German process for producing phthalic anhydride had been reported in patents and in various reference books. This German process was a liquid-phase oxidation of naphthalene using mercury sulfate as a catalyst. The discovery of this process was made possible by the carelessness of a laboratory

If the catalytic oxidation of naphthalene to phthalic anhydride were not known, phthalic anhydride could not occupy its present outstanding importance as an intermediate.

By the old process using sulfuric acid to oxidize naphthalene, the present installed capacity would require an estimated annual consumption of 700,000 to 750,000 tons of 100 per cent sulfuric acid. The cost of contact sulfuric acid plant for this purpose is estimated at close to \$8,000-, 000 and the acid cost alone would probably amount to 25 per cent of the present sales price of phthalic anhydride.

assistant who broke a thermometer in a batch of sulfonated naphthalene combined with the observation of the unsuccessful experiment by an acute chemist. Many important discoveries have been made in like manner. At first this process was carried out in batch stills (1), but it was soon found that the yield of phthalic anhydride could be increased by heating the reaction mixture of naphthalene sulfonic acid, excess sulfuric acid, and mercury sulfate only a short time at a high temperature. An intermittent process was developed to shorten the time of heating. It has been described in several publications (8) but may be summarized briefly as follows:

A flat-bottomed circular shallow pot provided with a scraping agitator was used for the reaction vessel set over gas flames. This was about 6 feet (1.8 meters) in diameter and 2 feet (0.6 meter) deep. Iron balls were placed in the pot to assist in the agitation as well as to act as a warning signal to call for the addition of another charge of reaction mixture. The pot was first coated with catalyst by charging into it 4 kg. of mercury and 120 kg. of concentrated sulfuric acid, and heating it to drive off the bulk of the sulfuric acid. Sometimes copper sulfate was used in addition to the mercury sulfate as the catalyst.

Naphthalene was sulfonated in another vessel using an excess of sulfuric acid. The ratio of naphthalene to sulfuric acid (monohydrate) was about 1 to 14. This mixture of naphthalene sulfonic acid and free sulfuric acid was then fed intermittently in portions of 22 liters, and the gas flames were regulated so as to distill this volume in 15 to 17 minutes. The end of each operation was to be observed by the increased noise of the rotating balls on the bottom of the pot. When this took place, a second charge of 22 liters was to be introduced. The process was to be continued until so much charred material was accumulated as to require cleaning. This was accomplished by running in concentrated sulfuric acid and distilling it off, whereupon the pot was then ready for 2 or 3 days of further operation. Ultimately the residual char accumulated to a point where it had to be dug out of the pot.

The phthalic anhydride distilled off from the pot and was collected in a scrubber where the phthalic was separated from the sulfur dioxide.

During the early days of the first World War attempts were made to produce phthalic anhydride by following the above instructions, but the yield was negligible. It was found that,

if the operation was continued until the balls made an appreciable noise while swirling around on the flat bottom of the pot before the next increment of sulfonated reaction mixture was added, then this was proof that the residue in the pot was a dry carbonized powder. Under these conditions the mercury sulfate was reduced and the catalyst (mercury) had volatilized out of the pot and was no longer available as a catalyst. By careful timing and measuring of the intermittent charges so that the residue was always a sticky mass and not charred and the balls made no noise, then, contrary to the German directions, phthalic anhydride was produced in measurable quantities.

If it had not been for a new synthesis of phthalic anhydride, announced by Gibbs in 1917 as a laboratory process, American chemists undoubtedly through sheer necessity would have found a way to produce it as economically as the Germans. The new process was the direct vapor-phase catalytic oxidation of naphthalene to phthalic anhydride. Its simplicity from an economic standpoint was so attractive that development of the older German process was discarded and American chemical industry embarked upon a new catalytic adventure which many times seemed to be impossible of commercial success. Its raw materials were air and naphthalene with vanadium oxide as the catalyst. Furthermore, there was only one product of consequence—phthalic anhydride. A process making one product from one purchased raw material is always worth investigating.

The Government was anxious to have the method of Gibbs and Conover developed commercially to supply the United States demand for phthalic anhydride because imports from Germany had been cut off. The Gibbs and Conover patent (?) was dedicated to the public. The laboratory discovery of this process was made by placing a few grams of vanadium oxide in a porcelain boat set in a horizontal tube in an ordinary laboratory combustion furnace. A few grams of impure phthalic anhydride at a very low yield were produced per day by this equipment.

A strange but not unusual coincidence was that Wohl in Germany had independently discovered the same synthesis only 2 or 3 months previously, and that led into a complicated patent situation. Suffice it to say, the Wohl patent issued in 1934 (13) in this country about 18 years after he made the invention and will not expire until August 28, 1951, i. e., 35 years after the invention was made.

It was realized that the commercial success of the process would depend upon the exact control of temperature in a high-temperature reaction which was highly exothermic. Furthermore, it is a partial oxidation process, and any complete combustion taking place as a concurrent reaction will develop three times as much heat as the desired highly exothermic reaction itself. For example, the partial oxidation of naphthalene to phthalic anhydride liberates about 6000 B. t. u. per pound of naphthalene, whereas its complete combustion liberates 18,000 B. t. u. per pound. These two reactions always go on concurrently, even in an apparatus with the most ideal temperature control so far developed; consequently the average exotherm may be assumed to be about 10,000 B. t. u. per pound of naphthalene fed into the catalytic zone.

For comparison, the catalytic oxidation of 1 pound of sulfur dioxide to sulfur trioxide, which takes place at approximately the same temperature, liberates about 650 B. t. u.—i. e., only  $\approx 1/15$  as much heat. The  $\text{SO}_2 \rightleftharpoons \text{SO}_3$  reaction is, however, reversible so that if there are hot spots in the catalyst, nothing is destroyed and sulfur dioxide and oxygen will recombine in cooler parts of the catalyst to form sulfur trioxide, whereas with an organic compound such as phthalic anhydride, once carbon dioxide and water are formed, they will not recombine to form phthalic anhydride. Thus

we are concerned with a highly exothermic irreversible reaction which occurs on the surface of a solid catalyst whose heat-transferring properties are very poor. The next point to bear in mind is that any considerable output—say 1 ton of phthalic anhydride per day—might liberate 25,000,000 B. t. u. or approximately 1,000,000 B. t. u. per hour, a large amount of heat to be generated and removed from a solid granular catalyst mass about 5 cubic feet in volume. If the temperature drops too low, unchanged naphthalene comes through to contaminate the product and reduce the output. If the temperature goes too high, complete combustion results, the amount of heat liberated is trebled, and the catalyst or the apparatus itself may be damaged. Clearly this is not a question of simple cooling, but heat must be removed within an upper and lower temperature range.

After trying adaptations of various forms of apparatus, which had been used commercially in other processes, such as contact sulfuric acid, the idea of using a liquid boiling under a selected pressure to fix its temperature as the heat-removing and temperature-sustaining means was selected as worthy of trial. Mercury, for all its other drawbacks, was selected because it is stable, boils at the right temperature under reasonable pressures, does not attack iron, and is liquid at room temperature. The final result was an apparatus which has already been described (4, 5).

The successful large-scale commercial perfection of this type of catalyst chamber about 18 years ago solved the economic factor of catalytic reactions of this kind. Plants using this type of catalytic converter are operating in the United States, England, France, Germany, Italy, and Japan.

The patents covering this kind of apparatus were tested for validity in the United States courts, and infringements stopped. Since then other apparatus for carrying out these reactions have been successful. Patents to Gibbs (6), Thomas (10), and Canon (2) describe typical examples. These and others depend upon the circulation of a nonboiling molten bath by various means with the object of providing as nearly as possible a uniform temperature throughout the bath and also of removing the heat absorbed by the bath from the reaction and thereby holding it within a productive temperature range.

Molten bath types of equipment are in successful operation, but the exact design and proportions of parts were attained only by extensive cut-and-try experiments over a long period of years. Lead baths freeze at 327° C. More expensive alloys have lower freezing points, but special provisions must be taken for preventing their oxidation. Sodium nitrate freezes at 284° C. and the nitrite at 312° C. A mixture of equal parts melts at 221° C. Kirst, Nagle, and Castner (9) recently described a molten salt mixture which is suitable for this purpose. Unlike melted metal baths, these salts do not oxidize, but proper provision has to be made to ensure against their solidification. Stepwise perfection of equipment of this sort is necessary because the bath must rise in temperature to remove heat as it circulates around the catalyst tubes, and mechanical arrangements must therefore be complicated and empirical to assure a constant and uniform temperature throughout the bath in the circuitous spaces between the tubes.

So we see that there is always a considerable variety of solutions of a chemical engineering problem, and that where existing patents may apparently block the path, ingenuity can devise noninfringing methods, provided the economic incentive exists.

The products of reaction are phthalic anhydride, small amounts of maleic anhydride (roughly 5 per cent or less of the phthalic anhydride), still smaller amounts of quinones, and large quantities of carbon dioxide, water, and carbon monoxide.

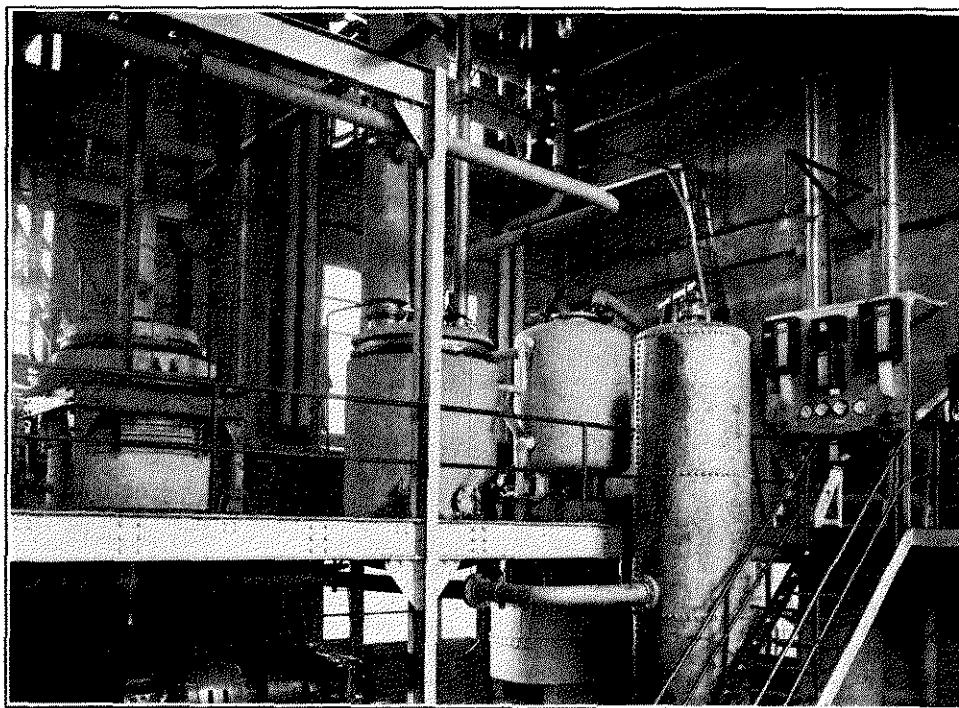


FIGURE 1. OXIDATION EQUIPMENT FOR PRODUCING PHTHALIC ANHYDRIDE BY THE VAPOR-PHASE PROCESS IN A FRENCH PLANT

The reaction products are passed through vapor coolers to cool them quickly to about 125° C. (roughly the dew point of the phthalic anhydride) and then generally through large chambers in which the phthalic anhydride separates out as long needlelike crystals in the earlier sections of the chambers. Maleic anhydride and quinones, owing to their higher vapor pressures, pass on and condense in the later sections. The maleic anhydride is hydrated to the acid by the condensed water of combustion. Various purification methods, such as sublimation and vacuum column distillation, are used to produce commercial phthalic anhydride from the crude chamber condensate.

The recovery of phthalic anhydride from the gaseous reaction products by condensation in large chambers is not an ideal method, largely because of the labor required to empty and clean them. Much work has been done in attempts to simplify this step. Recently the chemical engineers of the Barrett Company modified the condensation by passing the reaction products through a water scrubber in which the phthalic anhydride vapors are hydrated to phthalic acid in the form of a fine suspension in water. Since phthalic acid has a low vapor pressure compared to the anhydride, this permits the use of much more dilute reaction mixtures than can be used when the anhydride is to be condensed directly from the vapor phase to the solid. By the use of dilute mixtures the Barrett Company has changed the oxidation step itself. A new plant vaporizes naphthalene into a large excess of air-reaction gas mixture. This dilute mixture passes through the catalyst, thence through a water scrubber in which phthalic acid is recovered. It is understood that reliance is placed solely upon the large heat-carrying capacity of the dilute gas-naphthalene mixture to absorb the heat of reaction and control the temperature, and no external bath control is used.

There is no market for phthalic acid, and therefore it must be decomposed to the anhydride. Whether this method will compete successfully against the older methods of direct recovery of phthalic anhydride used by National Aniline,

du Pont, Monsanto, American Cyanamid, and Reichhold Chemicals in this country remains to be seen.

The production of phthalic anhydride has grown rapidly during recent years, and has resulted in reduced costs and enlarged markets. Table I shows production and average sales price per pound for the portion sold.

TABLE I. U. S. PRODUCTION AND SALES OF PHTHALIC ANHYDRIDE

Year	Lb. Production	Lb. Sales	Av. Price/ Lb. Sales
1919 <sup>a</sup>	290,677	...	\$0.99
1920 <sup>a</sup>	796,210	...	0.46
1922	1,629,182	1,317,625	0.35
1924	2,787,308	2,277,073	0.24
1926	4,379,108	3,446,175	0.18
1928	6,030,854	5,445,432	0.16
1930	6,693,001	5,614,012	0.13
1932	6,259,000	5,695,000	0.116
1934	20,680,000	13,511,253	0.12
1936	31,244,000	22,905,873	0.12
1937	45,210,784	17,565,905	0.14
1938	27,650,270	14,058,450	0.14
1939	44,274,430	20,380,004	0.14

<sup>a</sup> In 1919 and 1920 sales were not segregated from production.

Production capacity was increased rapidly, particularly after 1932, and the capacity during 1940 is estimated to be between 70 and 75 million pounds.

This accomplishment of making very large quantities of phthalic anhydride affects other syntheses such as anthraquinone and benzoic acid.

### Anthraquinone

Until the first World War anthraquinone was made by the oxidation of anthracene with sodium dichromate. In fact, we may state the proposition in a reverse fashion with as much truth—namely, that anthracene was used as a reducing agent for dichromate to produce chrome-tanning compounds. This process was carried on largely in Germany which enjoyed a large chrome leather industry and anthracene was the cheapest reducing agent especially in view of the fact that anthra-

quinone was a by-product. Such a process naturally appears unusually attractive because two salable products are made; but it has drawbacks, since the market for each must balance the other at all times to prevent overproduction of one.

Anthracene occurs as a constituent of a high-boiling coal-tar fraction which, in addition to oily compounds, contains also phenanthrene and carbazole. As the crude anthracene crystallizes from coal-tar heavy oil, it varies in amount and in composition, but generally contains equal quantities of phenanthrene, carbazole, and anthracene. To produce anthracene, the phenanthrene must first be removed; this may be done by solvent naphtha treatment, but it has no market per se and hence its value is no greater than creosote oil. The cost of its separation must therefore be borne by the carbazole and anthracene. Carbazole must then be separated from anthracene; this has been done either by a solvent such as pyridine or by converting it into its potassium salt by fusion with potassium hydroxide. In the latter method the unreacted anthracene is sublimed out of the melt by means of superheated steam and recovered. There is no present-day use for carbazole. Hence all the cost of producing a high-grade anthracene by the solvent naphtha and the pyridine or the potassium hydroxide treatments must be borne by one third of the constituents—namely, anthracene—and these processes to be successful must recover the solvents and potash for re-use. Such a processing structure is very shaky from an economic standpoint. The only event that would change the picture would be the discovery of new uses for phenanthrene and carbazole. Moreover, the anthracene must not only be very pure but also in finely divided form. When this anthracene is oxidized by dichromate, the anthraquinone must be purified by solution in concentrated sulfuric acid followed by recrystallization by steaming in order to produce an anthraquinone of suitable purity for vat dye manufacture.

The Walter patent (11), based upon work done in 1895 (12), stated that anthracene could be oxidized by air to anthraquinone in the vapor phase in the presence of vanadium oxide as a catalyst and also, as a matter of interest, that toluene could be oxidized to benzaldehyde. These processes were rediscovered by others during the first World War.

It was found that if the phenanthrene was removed from the cake, which was the cheapest step, the carbazole-anthracene mixture could be vaporized and catalytically oxidized to anthraquinone. Here the carbazole is completely burned and the anthracene undergoes partial oxidation to anthraquinone with good yields. This was the cheapest way to get rid of the useless carbazole. But the anthraquinone so made had to go through a concentrated sulfuric acid treatment to make it sufficiently pure. Furthermore, the capacity of an exothermic vapor-phase catalytic converter is limited to an important extent by its ability to take away the heat of reaction and at the same time maintain a desired reaction temperature. Moreover, to burn all the carbazole and partially oxidize the anthracene, a large excess of air must be used which increases the volume of the reaction mixture. If the time of contact between the reaction mixture and the catalyst is to be held constant, the converter capacity is reduced. Therefore, when all the carbazole has to be burned to carbon dioxide and water, the capacity of the converter in terms of anthraquinone produced is very small as compared to its capacity for producing phthalic anhydride from naphthalene. This greatly increases plant investment.

In view of the above facts, it is far better to use phthalic anhydride as a raw material for anthraquinone, and thereby increase the output of phthalic anhydride and simultaneously reduce its cost. Also it should be borne in mind that sufficiently pure naphthalene can be produced for the purpose by the simple process of hot pressing or centrifuging.

The production of anthraquinone by the condensation of

phthalic anhydride and benzene in the presence of aluminum chloride and the conversion of the intermediate product (benzoyl benzoic acid) into anthraquinone by means of concentrated sulfuric acid is well known. The yields are practically quantitative, the process is well worked out, and the anthraquinone, because it goes through the sulfuric purification step inherent in the process, is of high purity. Hence naphthalene, not anthracene, is now the raw material for producing anthraquinone because of a development foreign to the older orthodox methods.

Phthalic anhydride is now condensed also with toluene and chlorobenzene, among other compounds, to form other anthraquinone relatives such as methylanthraquinone and chloroanthraquinone. The latter is converted into aminoanthraquinone. Hence, a new outlet developed for the growing phthalic infant which could not be satisfied by anthraquinone itself.

### Benzoic Acid

Conventional methods dictated toluene as the source of benzoic acid. This was made by chlorination of toluene and hydrolysis of the chlorinated product, but the material so produced was not chlorine-free. The process was long and roundabout. Another method was the oxidation of toluene by manganese dioxide and sulfuric acid which produced a chlorine-free product. Chromic acid was also used to produce chlorine-free benzoic acid from toluene. These were wet oxidation methods. Toluene can also be catalytically oxidized to benzoic acid in the vapor phase with very acceptable yields and purity. But this catalytic method stepped into the irresistible path of the phthalic process and was brushed aside for various reasons, including the comparative values and potential quantities of naphthalene and toluene. The latter is at present in urgent demand as a solvent, particularly for military explosives. So, as in the case of anthraquinone, benzoic acid is now made from phthalic anhydride. This process is described in a patent to Conover (3). The process comprises passing a mixture of phthalic anhydride vapor and a large excess of steam in contact with catalytic agents, such as oxides of copper, zinc, and aluminum (preferably zinc oxide) at about 450° C., and the benzoic acid is condensed in a chamber. The reaction is endothermic.

### Economic Effects

A new process such as the catalytic vapor-phase oxidation of naphthalene to phthalic anhydride has many important economic effects upon other processes and raw materials as mentioned above. To take one example—sulfuric acid—we arrive at surprising figures. We will assume that the old German process, which required the use of 14 pounds of 100 per cent sulfuric acid for each pound of naphthalene oxidized, gave a yield of 1 pound of phthalic anhydride per 20 pounds of sulfuric acid. This figure is considered to be a minimum and may easily have been greatly exceeded. If the 20-pound figure is used, the estimated 1940 installed capacity of 70 to 75 million pounds of phthalic anhydride would require contact sulfuric acid plant equipment to recover 700,000 to 750,000 tons of 100 per cent sulfuric acid per year from the reaction gases. This amounts to about one tenth of the total United States production of sulfuric acid. Low-cost production by this method would dictate not more than a few large phthalic plants and would prevent the purchaser of even large amounts of phthalic anhydride from producing it himself.

It is estimated that the cost of a contact plant to recover this quantity of sulfuric acid would be about \$8,000,000 and then only if the installations were very large. It is further estimated that the cost of recovery of the sulfuric acid, including

make-up, would be at least 25 per cent of the sales price of phthalic anhydride as given in Table I.

The naphthalene used by the old German process had to be pure, otherwise the yield of phthalic anhydride based on sulfuric acid would be correspondingly reduced. The vapor-phase catalytic process uses a lower grade, cheaper naphthalene.

The corrosion and erosion of the German reactors was very high and thus involved a much higher depreciation cost. The plant investment, not including that for the sulfuric acid recovery, was much higher and occupied much more space. The older process required equipment, such as centrifuges, for separating and washing water-soluble acids from the phthalic acid, which now is superfluous. The loss of mercury catalyst was an important cost factor. The operating labor was much greater and the yields were lower.

It is an historical fact that the old synthesis of phthalic anhydride was one of the most important factors in the perfection of the contact sulfuric acid process, but if we were limited to its use today, phthalic anhydride could not be the source of most of its important derivatives now on the market.

The simplicity of oxidation equipment for producing phthalic anhydride by the vapor-phase process is shown in Figure 1. This shows a single oxidation unit capable of producing 600,000 pounds of phthalic anhydride per year which alone, or if necessary in multiples, will make enough product for many consumers of phthalic anhydride.

The potential supplies of naphthalene in the United States, if all coal tar should be processed to recover naphthalene, appear to be ample for any conceivable demand for phthalic anhydride. For example, from past experience, coal tar production may be expected to average about 600,000,000 gallons per year and if all this should be processed for naph-

thalene and converted to phthalic anhydride, about 280,000,000 pounds of the latter could be produced. Of course, not all the tar will be distilled, but the domestic supplies appear adequate and it seems certain that in normal times at least we can depend upon imports to make up any deficiency. The economical separation of naphthalene from coal tar distillates also depends to a large extent upon the simultaneous recovery of phenol and cresylic acids for which there appears to be a comparable market. As a last resort, naphthalene may also be recovered from oil-cracking operations.

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# Economics of Catalytic Oxidation in the Vapor Phase

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**Certain features of catalytic vapor-phase oxidation processes which are important in the economics of these processes are reviewed. Prominence is given to factors, generally economically unfavorable, which in the evaluation of new processes may at times receive insufficient attention.**

**I**N THE manufacture of chemicals, air, because of its cheapness, is the oxidizing agent to be preferred in any case where it can be successfully used. Its field of application is rather severely limited, however, by its properties as a reagent. Except at high temperatures or in the presence of active catalysts, it is inert toward oxidizable substances of many classes; and when reaction is induced by elevation of temperature or by the use of catalysts, the most frequent result is, in the case of a carbon compound, complete combustion sustained by the heat of reaction and, in the case of an inorganic substance, an unfavorable equilibrium or reaction of an undesired kind. Only in exceptional cases can the extent of oxidation be controlled to give a desired product in good yields.

In spite of its limitations air has been found useful as a reagent in two classes of reactions. In one class, substances which are by nature easily oxidized are exposed in the liquid state to air at temperatures generally below 100° C. The heat of reaction is easily dissipated at the low temperature level in the presence of liquids. No unusual apparatus is required; hence oxidations of this kind do not differ in any marked manner from other unit processes carried out with liquid reactants at relatively low temperatures.

In another group of reactions, which are of the greatest importance in the chemical industries, air is used as a reagent at temperatures above 400° C. and in the presence of catalysts. Reactions in this group are carried out in the vapor phase either from necessity or as a matter of convenience. The use