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REPORT NO. 42

HYDROGEN PEROXIDE

PART ONE

CHAPTER I – INTRODUCTION AND NOMENCLATURE
CHAPTER 2 – FORMATION AND MANUFACTURE, I. DIRECTLY FROM WATER OR OXYGEN
CHAPTER 3 – FORMATION AND MANUFACTURE, II. FROM PEROXY COMPOUNDS
CHAPTER 4 – CONCENTRATION, PURIFICATION, STRUCTURAL MATERIALS, HANDLING

A Monograph Prepared with
Support from the
Office of Naval Research
Contract No. N5ori-07819
NR-092-008

BY

W. C. Schumb
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PREFACE

A program of fundamental studies of the properties, formation, and reactions of hydrogen peroxide has been sponsored at M. I. T. since 1945 by the U. S. Navy, Bureau of Ordnance, and later the Office of Naval Research. For some time it has been apparent that the growth of basic knowledge of this chemical, as well as the development of various practical applications, would be furthered by a compilation and evaluation in the form of a monograph of the scientific and technical knowledge available.

The present report constitutes part I (Chapters 1 - 4) of such a monograph. The remaining parts (II, III and IV) will be issued in the near future as Report Numbers 43, 44 and 45. The Table of Contents gives a detailed outline of the material presented in Part I and indicates the contents of the other three parts by listing the headings of the chapters which each of them will contain.

The literature appearing up to January 1, 1953, has been consulted in the preparation of Part I of the monograph. It has not been attempted to cite every reference on hydrogen peroxide, but all publications which appeared to the authors to have some present-day usefulness are quoted. Patents have been treated in the same fashion as other publications and it has not been attempted to prepare an exhaustive list of them. In some cases, particularly in the chapters on manufacture, various U. S. Government reports of German practice give much more complete information than available elsewhere, and references are accordingly made to them rather than to patents.

Arrangements have been made for this monograph subsequently to be published in book form. The authors will appreciate errors being called to their attention or receiving the comments of readers on the material presented.

The authors wish to thank Dr. Max E. Bretschger and Mr. Russell E. Cushing for the photographs of the German manufacturing plants reproduced in Chapters 2 and 3. The photographs of Chapter 4 are through the courtesy of the Buffalo Electro-Chemical Company, Division of Food Machinery and Chemical Co.

Walter C. Schumb
Charles N. Satterfield
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September 15, 1953

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CHAPTER ONE

INTRODUCTION AND NOMENCLATURE

Hydrogen peroxide has been recognized as a chemical compound since 1818. In July of that year Louis Jacques Thenard reported to the Paris Academy of Sciences a method of preparation of what he first believed to be "oxygenated acids." Before the year was out Thenard had read a number of further papers resulting from studies on these "acids" and had come to the conclusion that instead he had discovered a new compound: oxidized water. A thorough examination of the technique of preparation and chemical properties of this new compound was made by Thenard, leading him to observe that it was rather unstable, that it represented a novel form of chemical combination, and perhaps most interesting, that it could be decomposed vigorously by certain substances without discernible effect on the decomposing agents.

These three outstanding observations have been the basis for continuing interest in and study of hydrogen peroxide since its discovery. As knowledge of the properties of hydrogen peroxide has grown throughout the years, it has gradually become apparent that hydrogen peroxide is not an inherently unstable substance, although a widely reactive one. It has taken a unique position in the scheme of chemistry due to the type of chemical bond which characterizes it, and it has received wide attention in the study of catalysis.

To the purely scientific interest in hydrogen peroxide there must be added the ever growing realization of its technical usefulness. Paralleling improvements in the methods and techniques of manufacture there has been a constant broadening of the field of application for hydrogen peroxide and increase in its production.

A short historical account, recapitulating the main currents in the study and application of hydrogen peroxide, is of value in understanding the state of present knowledge, scientific and technical, regarding this substance and in serving as a frame of reference for evaluation of the older literature.

THE DISCOVERY OF HYDROGEN PEROXIDE

Credit for discovery can be assigned with certainty in the case of hydrogen peroxide. Although Davy (1) and Gay-Lussac and Thenard (2) had undoubtedly formed hydrogen peroxide in the course of their studies of the alkali metals, Thenard was clearly the first to notice its occurrence, and his prompt publication of extensive studies of the technique of its preparation and its properties leaves no doubt regarding his recognition of the nature of the new compound. It was by chance that Thenard made the experiment which brought hydrogen peroxide to his attention, but the course of events which placed Thenard in a position to make the discovery can be traced quite clearly (3).

In 1806 Humphrey Davy lectured before the Royal Society "On Some Chemical Agencies of Electricity," for which he was awarded a prize of 3000 francs established by Napoleon for significant electrical research. The award, made by a French committee, was given in spite of the fact that England and France were then at war, and Napoleon was irritated that no French scientist could be found worthy of the prize. On being told that France did not possess a voltaic pile with which experiments could be conducted as Davy had, Napoleon ordered two to be built and presented to the Ecole Polytechnique. Gay-Lussac and Thenard were to be placed in charge of this work. The most interesting of Davy's discoveries with the pile had been the formation of metallic sodium and potassium, and while Gay-Lussac and Thenard were awaiting the completion of the great French batteries they turned their attention to the preparation of the alkali metals by chemical means, succeeding very well with the method of reducing molten caustic with red hot iron. This process surpassed the electrical method of preparation both in ease and quantity of production. The piles, when they became available, proved to be of inferior construction, but the work initiated by Napoleon's pique led to wide investigations by Gay-Lussac and Thenard (2) which were of considerable importance to the development of chemistry.

The fact of interest here is that the work included the preparation of the oxides of the alkali and alkaline earth metals by various means. In this manner these substances were available to Thenard and he became familiar with them. It was recognized at this time that each of a number of metals formed more than one type of combination with oxygen and that the different combinations contained different ratios of metal to oxygen. According to the accepted belief, a metal combined with more than the "proper" amount of oxygen would give off the excess oxygen when treated with an acid.

FIG. 1(4)- LOUIS JACQUES THENARD, 1777-1857

As a result of a statement made to his students which he realized had not been verified, Thenard was led to make an experiment with barium peroxide, which according to the hypothesis, should be an "excess oxygen" compound. He dissolved barium dioxide in a dish of nitric acid kept cold with an ice bath and, to his surprise, no gas evolution was to be seen. He allowed the mixture to stand overnight, and on returning to the laboratory in the morning saw that bubbles of gas were being generated in the liquid. Placing a little of the liquid in a test tube and warming it, Thenard identified the gas given off as oxygen by the simple experiment of plunging a glowing splint into the tube.

Thenard's first conclusion was that he had caused the acid to become oxygenated. Since oxygen was in the center of interest in the chemistry of the day, the desire to know more of its reactions and combining proportions undoubtedly motivated Thenard to make his broad investigation of the new "oxygenated acid." After a short period of experimentation Thenard found that all the acid and barium salts could be eliminated from the active solution, leaving a liquid which could be evaporated without solid residue remaining. From this he concluded that he had in fact oxygenated water, forming a compound of definite proportions.

THE SCOPE OF THENARD'S WORK

A very adequate knowledge of the character of hydrogen peroxide, the problems of its preparation from barium peroxide, and its chemical nature can be gained from studying the publications of Thenard.*

It is of interest to review his work briefly since it was the most comprehensive and able study of hydrogen peroxide made in the nineteenth century, and since substantial portions of his work were apparently overlooked for several decades after his death. In the year following the discovery Thenard presented nine papers (5) and a summary of his work (6). A complete account of the work was included in the third and succeeding editions of his Traité de Chimie (7) and

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* By Thenard's express wish his name is written without an accented e.

two later papers were presented on the subjects of preparation (8)(1832) and catalytic decomposition (9)(1856) of hydrogen peroxide. The work was followed with interest by foreign scientists and a number of comments and short translations or notices (10) are available.

A large part of Thenard's work was concerned with the perfection of practical measures for the preparation of stable, concentrated hydrogen peroxide. Although various accounts (3) differ regarding the acid used by Thenard for the first preparation of hydrogen peroxide, his first paper (5) makes it clear that it was nitric acid. Then, after demonstrating that a number of other acids would react with barium peroxide to produce an oxygen-rich solution, Thenard chose hydrochloric acid as the most effective. It permitted rapid reaction with the barium peroxide unimpeded by formation of insoluble barium salts around the reacting particles yet allowed excess acid and barium chloride formed to be removed later by chemical precipitation methods. Thenard recognized that it was also possible to form hydrogen peroxide by the action of acid on the peroxides of potassium, sodium, strontium, and calcium, but he used none of these in the preparation of hydrogen peroxide because of the more convenient separation by precipitation possible with barium.

Thenard recommended that the preparation of barium dioxide be undertaken with barium nitrate, recrystallized to free it as far as possible from iron and manganese. The nitrate was decomposed by heating in air in a porcelain retort, the resulting barium oxide then peroxidized by heating to redness in a tube through which a stream of oxygen was rapidly flowing. The barium peroxide was dampened and ground, then dissolved in hydrochloric acid. Sulfuric acid was then added to slight excess, precipitating barium sulfate and regenerating hydrochloric acid. Thenard recognized that formation of a precipitate of good filtering quality depended upon the proportion of sulfuric acid added; too much or too little impaired the separation of barium sulfate. The procedure of barium peroxide solution and sulfuric acid precipitation was repeated several times, making it possible to enrich the solution until it contained 125 volumes of available oxygen for each volume of solution, or about 33 weight % H_2O_2. The concentrated solution thus produced still contained hydrochloric acid plus dissolved impurities from the barium peroxide and the acids. The impurities were removed by first chilling the liquid in ice and supersaturating it with barium oxide, which precipitated iron, manganese, silica, and alumina. Thenard later (8) suggested the addition of phosphoric acid at this step to precipitate iron and manganese as phosphates. The filtering of this solution was carried out as quickly as possible to avoid decomposition on the collected precipitate. To the filtrate from this operation was now added silver sulfate containing no free silver oxide. The separation of silver chloride which followed also served to clear the solution; until this time it had remained turbid. It was now necessary to remove the sulfuric acid from the solution by precipitation of barium sulfate. This step was carried out with the solution cold, barium being added as the oxide.

The solution of hydrogen peroxide, freed of barium sulfate, was allowed to remain somewhat acidic for better keeping. It could now be further concentrated by evaporation of the water under vacuum. In this manner Thenard was able to prepare essentially anhydrous hydrogen peroxide.

Gasometric analysis for the oxygen content of the hydrogen peroxide solutions was easily carried out, the oxygen being liberated from the solution either by heating or by addition of a catalyst such as silver oxide or manganese dioxide. In the Traité de Chimie, Thenard gives the details of an analysis of a sample of density 1.452 g/cc which produced 476 volumes of oxygen per volume of liquid. The temperature at which the density was determined is not given, but on the assumption that it was near 15°C. these values are very close to the presently accepted ones for pure, anhydrous hydrogen peroxide. In addition, the weight of oxygen collected in this experiment was within 1 per cent of that to be expected from a portion of anhydrous hydrogen peroxide of the weight of the sample taken.

The oxygen content of this hydrogen peroxide of density 1.452 g/cc could not be increased by prolonged exposure to vacuum, leading Thenard to conclude "that the most highly oxidized water is a peroxide of hydrogen which contains essentially twice as much oxygen as pure water, and that every time that the hydrogen peroxide does not contain this amount of oxygen, it can be regarded as a mixture of pure water and hydrogen peroxide."

In view of the later contention that hydrogen peroxide is an unstable material this preparation by Thenard of pure hydrogen peroxide, essentially anhydrous, is remarkable. It would seem that no chemist for many years to come took the pains to provide himself with hydrogen peroxide of anything like the purity and stability of that made by Thenard. The stability on storage of this material was probably not comparable to modern standards (Thenard himself suggested that it be kept in glass surrounded by ice in a cool cellar), but with Thenard's recognition of the importance of avoiding heavy metal impurities and the stabilizing action of acid it was undoubtedly a very adequate preparation for the study of the nature of hydrogen peroxide.

Thenard used both concentrated and dilute hydrogen peroxide in his studies of its properties. He found it impossible to freeze the pure material (it is now known that concentrated hydrogen peroxide solutions greatly supercool), and the disproportionation of hydrogen peroxide between solid and liquid when 10 wt.% material was partially frozen was not complete enough to make concentration by crystallization practical. In the light of later statements to the contrary, it is of interest to note that Thenard observed that the evaporation of hydrogen peroxide could be continued to dryness under reduced pressure without sensible decomposition occurring. Thenard apparently was unable to determine the boiling point of any of his solutions; decomposition always became severe on heating much above room temperature. He observed that detonation did not occur when the hydrogen peroxide was thrown on a red hot metal plate.

Thenard tasted his hydrogen peroxide; it recalled the taste of a metallic solution to him and was somewhat nauseating. The whitening of the skin caused by contact with hydrogen peroxide was also noticed. He reported hydrogen peroxide to have practically no odor.

Thenard's comprehensive observations of the reactivity of hydrogen peroxide are of most interest. In all he cites the reactions of more than 130 substances, including metals, oxides, salts, acids, and bases, comprising compounds of 40 of the elements and diverse organic materials. The earliest reported test is that of the failure of acid hydrogen peroxide to act on gold, perhaps a lingering reminder of the old alchemy. Most of the substances which Thenard tested for their action with hydrogen peroxide caused decomposition. In this decomposition some substances were chemically altered as with the reported oxidation of arsenic, molybdenum, tungsten, and chromium, which took up a part of the oxygen of hydrogen peroxide. A few metals, such as tin, antimony, and tellurium were observed to have no action, even on concentrated hydrogen peroxide. The decomposition of hydrogen peroxide was always accompanied by the generation of considerable heat; this, in a reaction involving the evolution of oxygen, Thenard found difficult to understand in the light of the then current theory.

Observations of the effective decomposing action of such substances as silver oxide, lead, manganese dioxide, and platinum were made even while the compound was still regarded as an oxygenated acid. For some of these Thenard gave a complete description of the chemical action accompanying the catalytic decomposition of hydrogen peroxide. With silver oxide, for example, he described the reduction to silver metal which occurs on the addition of silver oxide to hydrogen peroxide, the complete solution which takes place when acid is added, and the precipitation of silver metal and continuation of hydrogen peroxide decomposition brought about by subsequent neutralization. After a few such observations of the decomposition had been made, Thenard perceived that "in these decompositions, chemical action is evidently missing; it is necessary then, to attribute these actions to a physical cause; but these actions are dependent on neither heat nor light, whence it follows that they are probably due to electricity." More of these catalytic reactions were to be observed, and in cataloging the reactions of hydrogen peroxide, Thenard was careful to distinguish between decompositions occurring with and without chemical alteration of the decomposing agent.

This work constitutes one of the earliest recognitions of catalysis. Its mechanism remained obscure to Thenard. With his observation that animal matter such as fibrin of the blood and the tissues of the organs was effective in decomposing many successive portions of hydrogen peroxide, he supposed that the action was caused by the same force as that exerted by the metallic or inorganic catalysts. This notion was to continue in the literature in the classification of such catalysts as platinum as "inorganic ferments." But Thenard could not "conceive how an organ, without being absorbed or changed, can continually act on a liquid to transform it to new products." It remained for Berzelius (11) to collect the scattered observations of catalytic action of which Thenard's were an important part, giving a name and recognition to this important branch of chemistry.

Although Thenard had some considerable accomplishments in applied chemistry, he found only two uses for hydrogen peroxide. He suggested that it be used in medicine where an external irritant was needed, and that it be used to restore old paintings. Disfiguring black spots resulting from the action of hydrogen sulfide in the air on white lead in a painting could be quickly removed by brushing on dilute hydrogen peroxide. Thenard himself applied this technique to a painting by Raphael with great success.

Hydrogen peroxide was firmly placed in the scheme of chemistry at the conclusion of Thenard's work. It may be admitted that the knowledge of modern chemistry makes possible a more coherent interpretation of his work, but it must be judged as a competent piece of research. Somewhat overshadowed by the reputation of his close friend, Gay-Lussac, in matters of a more fundamental nature, Thenard deserves more recognition than is generally accorded him.

EARLY STUDIES OF HYDROGEN PEROXIDE

With hydrogen peroxide called to their attention, the chemists after Thenard set about to explain its constitution, to fit it into the framework of chemical affinities. This was the period of the organization of chemistry, and the problem of accounting for the nature of hydrogen peroxide received its share of attention. Within the period of Thenard's lifetime (to 1857) there appeared about three dozen papers dealing with hydrogen peroxide, on reactions, preparation, and constitution, and mention of hydrogen peroxide found its way into the treatises of chemistry. In this period the antozone theory of Schönbein was established. This was the most energetic, even if not useful, consideration of hydrogen peroxide since Thenard's original researches, and Schönbein's work forms the core of the literature on hydrogen peroxide until the decade 1870-1880. In these years Schönbein's theory was struck down and the notions regarding the nature of hydrogen peroxide merged into a chemistry containing the fundamentals of modern views. The decade of the seventies thus provides a natural division between literature of historical interest and the beginning of an accumulation of knowledge on hydrogen peroxide which represents a real advance over the facts known to Thenard.

For a decade after the discovery of hydrogen peroxide no new researches appeared; the textbooks, e.g., those by Silliman, Turner, Gmelin (12), presented a faithful account of Thenard's work. The first new considerations of hydrogen peroxide appearing in the literature were attempts to explain the mechanism of its decomposition, and these are characterized by lack of recourse to experiment. Thus, a theory presented by Faust (13) in 1830, accounted for hydrogen peroxide decomposition as a kind of electrolysis, the decomposing agents taking the role of the electrodes in the electrolysis of water. Liebig (14), aroused by Thenard's view (15) that the character of hydrogen sulfide was similar to that of hydrogen peroxide, conceived that the affinity of oxygen for another substance in an oxide must be greater than the force necessary to compress the oxygen from its normal state in the atmosphere to the small volume it occupies in the oxide. Any disturbing influence would therefore cause the tendency of oxygen to reassume its gaseous state to preponderate over the affinity, decomposing the oxide. Mitscherlich (16) pointed out that the rate of hydrogen peroxide decomposition on solids was proportional to the extent of solid surface provided and concluded that the attraction exerted by the atoms of solid bodies might induce reaction and decomposition. In 1848, Playfair (17) reviewed the theory of catalytic decomposition, showing that the theories of Liebig and Mitscherlich did not account for all the examples of catalytic decomposition to be seen. In Playfair's view the attractions of water and another substance for oxygen might be so balanced as to set the oxygen of hydrogen peroxide free, but he suggested that more attention to the problem of catalysis would be necessary before a complete understanding could be reached.

The foregoing generalizations do not seem to have contributed greatly to the understanding of the true nature of hydrogen peroxide. A more forceful explanation, one which gained wide acceptance and at the same time stimulated a healthy antagonism, was shortly to appear. This was the ozone-antozone theory of Schönbein. Schönbein had discovered ozone in 1840, and his life (18) thereafter was almost completely devoted to the study of the compounds of oxygen.

Schönbein's development of the ozone-antozone theory can be followed in all essentials in a very few papers (19), largely letters to Faraday, although he published voluminously. Indeed, the last of some 364 papers by Schönbein listed in the Royal Society Catalogue is concerned with the occurrence of hydrogen peroxide in the atmosphere. An original discovery of Schönbein's, that a number of substances such as ether, turpentine, and phosphorus were slowly oxidized in air and so became effective as bleaching agents, was the starting point of this theory. Being mindful of the similar bleaching action of ozone, Schönbein concluded that this action was due to the formation of ozone, or as he later put it, to the transformation of ordinary oxygen into ozone, in which form it united with the substance being oxidized. This theory at once explained how such an energetic effect as bleaching could be accomplished by ordinary oxygen and was at the same time in accord with Schönbein's conception of the nature of ozone. He had originally held ozone to be a compound of oxygen and hydrogen, but now regarded it as an allotropic, active form of oxygen. Apparently he visualized no difference in structure between oxygen and ozone, but only a difference in activity or polarity.

Schönbein at first concluded that the available oxygen in hydrogen peroxide was present as ozonized oxygen. Knowing then that ozone itself reverted to ordinary oxygen on being heated or in contact with various substances, the parallel action of hydrogen peroxide was thus explained as being due to the ozonized oxygen, which retained, while compounded with water, the properties it exhibited alone. Since certain metal oxides were known to be reduced while decomposing hydrogen peroxide, it appeared to Schönbein that the oxygen in these oxides must also be in the ozonized form and that ozonized oxygen must have the property of combining with itself to form common oxygen.

Schönbein shortly altered this preliminary viewpoint to a form which seemed to him most comprehensive in accounting for the reactions of oxygen. He now postulated three modifications of oxygen: two oppositely polarized, active forms and ordinary oxygen. These active forms stood in the relation to one another of plus to minus, the negative being ozone and the positive being an entity for which Schönbein coined the name antozone. The signs arose from their "electromotive bearing."

This idea allowed the following systematizations of the reactions of oxygen. Common oxygen was chemically inactive and formed by the mutual neutralization of ozone and antozone. Ozonized oxygen was produced by the electric spark or the slow oxidation of phosphorus and was identical with a part of the oxygen occurring in a group of oxides to be known as ozonides, e.g., MnO_2, PbO_2. Another group of substances were to be known as antozonides, including hydrogen peroxide, the peroxides of the alkali metals, and some organic compounds such as ether, turpentine, and the essential oils. On being brought together, an ozonide and an antozonide produced a reciprocal catalysis with the disengagement of ordinary oxygen which left the original ozonide and antozonide compounds in combination with only that portion of oxygen that had not been polarized. An example of this action was the catalytic decomposition of hydrogen peroxide by lead dioxide, known to result in water, oxygen and lead monoxide. Schönbein symbolized this as:

$$(HO + \oplus) + (PbO + \ominus) \longrightarrow HO + PbO + 2O.$$

Such was Schönbein's basic thesis. It was stated nearly completely in 1859, but until his death in 1869, he was tireless in experimenting with new ways of producing and testing for ozone and antozones. He found that the amalgams of several metals produced hydrogen peroxide (and therefore antozone) when shaken with water in the presence of air. A species of fluorspar which was known to have a disagreeable halogen-like odor was found by Schönbein to produce hydrogen peroxide when triturated with water. Schönbein therefore concluded that the smell was that of antozone. In the extension of his theory Schönbein was forced to make several modifications of the accepted chemistry. The observations that ozonides such as manganese dioxide furnished chlorine on reaction with hydrochloric acid while with antozonides such as barium peroxide, hydrogen peroxide was produced, led Schönbein to conclude that, just as water could become chemically associated only with antozone, hydrochloric acid could only associate with ozone to produce chlorine. This was in essence a return to the oxygen theory of acids which Davy had dispelled.

These researches and theories of Schönbein are frequently contradictory among themselves. Thus, at one time he stated that he perceived the distinctive smell of antozone on treating barium peroxide with sulfuric acid. Later, on adding barium peroxide to sulfuric acid containing the ozonide potassium permanganate,, he identified the smell of ozone. In spite of the awkwardness of the theory, Schönbein found a number of supporters. Schaer (20) presents a lengthy exposition of Schönbein's theory as late as 1869. Foremost among Schönbein's supporters was Meissner (21). Meissner demonstrated a new phenomenon associated with the supposed antozone, an experiment which was later to be interpreted quite differently and to lead to the rejection of the ozone-antozone theory.

On passing electrified oxygen through water or into moist air, Meissner found that a mist was formed. From this he concluded that electrified air contains ozone and a substance he named atmizone (from the Greek, to smoke). The mist was to be attributed to the presence of the atmizone. Later, Meissner concluded that atmizone was identical with Schönbein's antozone and spent considerable effort in separating it from ozone and studying its properties. To Meissner it seemed that this cloud formation might explain the smoke from tobacco, chimneys, and gunpowder and that the "copious rains which follow great battles" might be due to the action of antozone on the atmosphere.

Other workers furnished further embroidery to the antozone theory: Lenssen (22) supposed that oxygen was positively polarized in acid hydrogen peroxide, and negatively polarized in alkaline hydrogen peroxide; Clausius (23) proposed the theory that ozone and antozone retained their opposite charges in forming oxygen, these charges holding them together in a diatomic molecule; Osann (24) believed the cloud was caused by the formation of ammonium nitrate; Phipson (25) considered hydrogen peroxide to be one of the most electro-negative bodies known. These and further minutiae of this ozone-antozone theory are discussed by Fox (26) and Birckenbach (27).

Opposition to the ozone-antozone theory was overlooked for a long period. In 1854, Brodie (28) reported experiments on the catalytic decomposition of hydrogen peroxide and discussed them with considerable insight. At this time he asserted that there must be distinguished two means of decomposition of hydrogen peroxide: 1) the reaction which results in the reduction of the decomposing agent, and 2) the further, catalytic action of this reduced form. Later Brodie (29) refuted Schönbein's views, stating that it was unnecessary to depart from the accepted chemistry and postulate special modifications of oxygen. Brodie admitted that oxygen might exist in different polar states in its combinations but asserted that the combining properties of the elements depended upon physical conditions and upon the associated chemical substances. Where hydrogen peroxide was concerned, Brodie extended his separation of its reactions into the categories catalytic and stoichiometric, and pointed out that an apparent overall reaction might well represent the sum of several individual reactions.

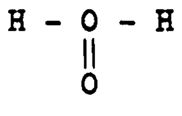
Weltzien (30) agreed with Brodie that common chemistry was all that was necessary to explain ozone and antozone. Weltzien pointed up the suggestion of Brodie that too much attention was being paid to the role of oxygen in its compounds with total neglect of the contribution of the nature of the other elements as in the differentiation of such oxides as PbO_2 and BaO_2. Most important was Weltzien's suggestion that there was no reason why hydrogen peroxide should not vaporize to a certain extent, as during its formation from BaO_2, and so give the reactions of antozone.

The work of Brodie and Weltzien should have perhaps been sufficient to discredit Schönbein, but more proof was required. In the study of ozone it was soon to be demonstrated by the work of Andrews and Tait, Soret, and others, that the vapor density of ozone was 3/2 that of oxygen, requiring a considerably different concept of the structure of ozone. The final banishment of antozone was to come through the work of von Babo (31) and Engler and Nasse (32). In a well-considered paper based on good experimental evidence, von Babo shows how he could never obtain the fumes described by Meissner unless nitrogen or an oxidizable substance was present. In the supposed tests for differentiating between ozone and antozone, von Babo found that a test for antozone might be positive in the presence of ozone if easily oxidizable substances were present which could form hydrogen peroxide.

Engler and Nasse, writing in 1870, recognized that formation of hydrogen peroxide by the reaction of ozone with water was quite possible. These workers passed oxygen through an electrical discharge tube and trapped out ozone before leading the gas through water. No clouds were seen to form. On placing calcium chloride (believed to trap antozone) in the stream before the contact with water, thus allowing ozone to pass through it, the clouds were obtained. This was regarded as evidence that the supposed antozone was merely hydrogen peroxide formed on the reaction of ozone with water. In addition, Engler and Nasse cited the evidence of chemical reactions which were contradictory to Schönbein's scheme of the relationships between the classes of ozonides and antozonides.

By these researches the ozone-antozone controversy was settled and the identity of hydrogen peroxide was reestablished. Fairley (33) and Leeds (34) reviewed the evidence in the late 1870's and were critical of the generation of chemists which had been led astray. There still remained, however, the necessity of adopting a structural formula for hydrogen peroxide which would account for the loosely-held oxygen atom and its reducing action. Birckenbach (27) reviews the numerous views on this subject which apparently include all the possible plane and spatial configurations of the symbols for two hydrogen atoms and two oxygen atoms as well as several forms containing oxygen-hydrogen ratios greater than one. The theories of structure were based almost entirely on geometrical considerations; no real basis was laid for an understanding of the properties of hydrogen peroxide. It seems that most chemists were content to assume, as Heyes (35) did, that one oxygen of the molecule was quadrivalent and not attached to either of the hydrogen atoms, i.e., as in formula I rather than formula II:

I



$$\begin{array}{c} H - O - H \\ \| \\ O \end{array}$$

II

$$H - O - O - H$$

Formula I could account for the formation of water and the ready loss of one oxygen which might further act alone in an oxidation. The reducing properties of hydrogen peroxide might then be explained by the loss of both oxygen atoms together to form molecular oxygen while the hydrogen atoms united to form water with the oxygen of a compound being reduced. The present-day conception of the structure of hydrogen peroxide, which differs from the above, is presented in Chapter 6.

This review of some of the early studies of hydrogen peroxide has covered the period from the discovery until about the year 1880. During the next three or four decades, scientific interest in this substance was directed primarily to studies of catalytic decomposition phenomena and reactions. Few studies were made to obtain quantitative data on the physical properties of hydrogen peroxide until the work (36) of Otto Maass and his students, beginning about 1920, which established many of the important properties with high precision.

THE TECHNICAL DEVELOPMENT OF HYDROGEN PEROXIDE

Until the establishment in the twentieth century of electrochemical processes the practical method for the preparation of hydrogen peroxide remained that of the action of an acid on an alkali peroxide or alkaline earth peroxide, as discovered by Thenard. First to suggest an improvement on Thenard's process was Pelouze (37), who, in 1832, suggested that fluosilicic acid be used as the acid to react with BaO_2. This reaction produces a precipitate of barium fluosilicate and shortens the procedure of preparation. The process was popular for many years, probably because less skill was necessary to form an easily separable precipitate with fluosilicic acid than with sulfuric acid.

A number of early chemists proposed impossible procedures for the preparation of hydrogen peroxide. For example, the early uncertainty regarding the differences between the nature of the alkali peroxides and such "peroxides" as MnO_2 and PbO_2 brought proposals and even assertions such as those of Kastner (38), Lampadius (39), and Baudrimont (40) that hydrogen peroxide could be prepared by the action of acid on MnO_2 or PbO_2. Not all these proposals were accepted; the assertion of Kirchner (41) that hydrogen peroxide could be prepared by letting chlorine act on water held in a bladder was promptly denounced (42).

Further changes suggested for the alkali peroxide process did not come into use when serious manufacture was commenced. Duprey (43) showed that carbon dioxide could be used as the acid to form hydrogen peroxide from a barium peroxide slurry. Much later a cyclic procedure based on reconversion of barium carbonate to the peroxide was patented by Bale and Sims (44) and studied by Fawsitt (45), but these and other systems suggested at the time were not suitable for the technology of the day. Davis (46) stated in 1879 when the manufacture of hydrogen peroxide had been established that nearly all hydrogen peroxide was made by the action of hydrofluoric or fluosilicic acid on barium peroxide. Other systems such as the proposal of Hofmann (47) that fluosilicic acid be reacted with air-blown molten potassium did not receive practical attention. One circumstance which encouraged and perhaps even made practical the manufacture of hydrogen peroxide from barium peroxide was the commercial availability of barium peroxide in large amounts resulting from the introduction in 1879 of the Brin process (48) for oxygen manufacture (49). This process, depending on alternate oxidation of barium oxide in air followed by thermal decomposition at a higher temperature of the barium peroxide, stimulated a large production of barium peroxide, amounting to 10,000 tons annually in Europe by 1901 (50). Squibb (51) has presented a detailed description of the operation of a hydrogen peroxide factory of that day.

Figure 2 reproduces a painting which depicts a typical early commercial process for manufacture of hydrogen peroxide. The scene represents the hydrogen peroxide plant of Bernard Laporte in Shipley, Yorkshire, shortly after its beginning in 1888. The operations shown in the painting have been described by Mr. V. W. Slater (52) as follows:

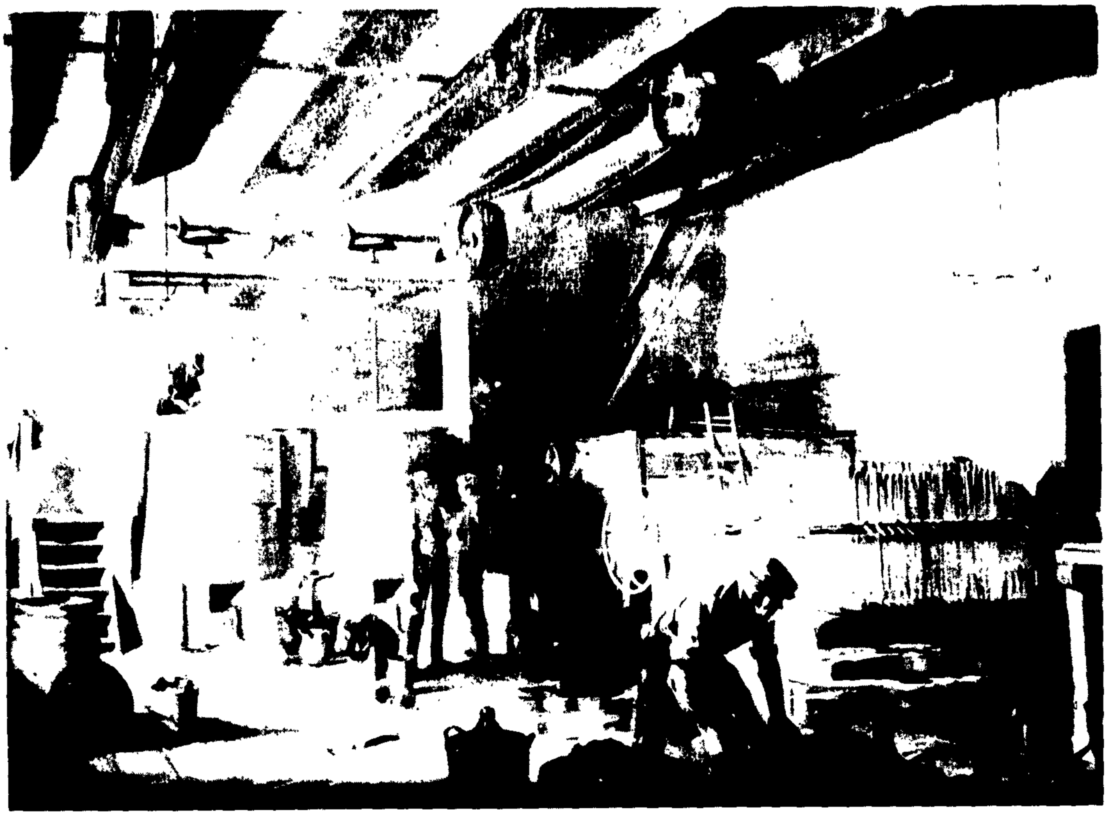


FIG. 2 - EARLY HYDROGEN PEROXIDE PLANT (FROM A PAINTING BY F. OLDHAM, FOR LAPORTE CHEMICALS, LTD.)

"The picture depicts two hydrogen peroxide making vats to the left; these have been filled with weak hydrogen peroxide washings from a previous making, or with water. Some hydrochloric acid, phosphoric acid or hydrofluoric acid was then added to give a solvent solution for barium peroxide. The barium peroxide was added to the vat simultaneously with sulphuric acid so that the barium peroxide was dissolved by the solvent acids which were almost immediately liberated with the precipitation of barium sulphate. The whole process was operated as an art rather than a science since the workmen had to control the feed of barium peroxide and sulphuric acid so that at no time was there excess barium peroxide which would have decomposed the hydrogen peroxide nor excess free sulphuric acid which would coat the barium peroxide particles with barium sulphate and so lock up the BaO_2. The workman practiced his art by means of a glass rod and litmus paper. The picture shows the workmen pouring in a jug of solvent acid.

"When the making was finished the slurry of hydrogen peroxide and barium sulphate was pumped through the filter press, depicted on the right of the picture, into the storage tank shown at the back. The barium sulphate was then washed, the washings being used for the next making.

"Note that the building is fitted with gas lighting, that is before the advent of electricity for this purpose. The hydrogen peroxide solution had a final treatment for stabilization and adjustment of acidity after which it was pumped through a clearing press to its final storage which is shown on the extreme right of the picture and from which the carboys were filled for sale."

While manufacture was being established using the barium peroxide process, discovery and study was made of the present day process of electrolytic manufacture, as well as a number of other processes which have never been commercially practical but which continue to present intriguing potentialities. Formation of hydrogen peroxide during the electrolysis of sulfuric acid was recognized by Meidinger (53) in 1853. It had been known since Faraday's work that an ozone-like odor was given off in the electrolysis and that the volume of oxygen evolved in a given experiment was sometimes observed to be less than one half the volume of hydrogen. Meidinger realized that the deficiency of oxygen must have been retained in the solution, presumably as dissolved ozone or hydrogen peroxide, and concluded that it was hydrogen peroxide. From his studies Meidinger found that the "hydrogen peroxide" was formed most abundantly when (1) the sulfuric acid specific gravity was 1.4, (2) the temperature was as low as possible, and (3) the intensity of the electric current was made great by use of a small electrode.

Other workers, Bunsen, Rundspaden, and Leblanc (54), confirmed the preparation of peroxy compounds by electrolysis of sulfuric acid, but it was not until the work of Berthelot, (55) in 1878, that an understanding of the process was gained. Berthelot showed that it was in fact peroxysulfuric acid, a compound which he had only recently discovered, that was initially formed in the electrolysis. This in turn slowly hydrolyzed to form hydrogen peroxide and sulfuric acid. Further study by Elbs and Schoenherr and others (56) made possible the establishment of manufacture of hydrogen peroxide by an electrolytic process in 1908; thereby encouraging a thorough, modern investigation of the process in 1912, by Reichel (57), who reviewed its history.

Another process which received early attention is that of the formation of hydrogen peroxide in the course of combustion of hydrogen. Investigated by Struve, Böttger, Schuller, and Traube (58) between the years 1869-1885, and even patented, the process was never used for manufacture. The results of these and considerations of other procedures for preparation and manufacture of hydrogen peroxide are, like the wealth of early work on the reactions of hydrogen peroxide which has not been cited here, not of great importance in gaining a perspective of the historical development of hydrogen peroxide. Although a variety of methods of preparation were investigated during this period, most of these reactions have not attracted more than passing commercial interest. This subject is considered in more detail in Chapters 2 and 3.

At about the time manufacture of hydrogen peroxide was commenced, some fresh consideration began to be given to the questions of the stability of hydrogen peroxide and the possibility of working with concentrated solutions, both widely misunderstood subjects. Typical of the confusion which existed were the results of Harcourt (59) who claimed that glass deliberately made dirty with oil, or varnished, was much more effective than clean glass in preventing the decomposition of dilute hydrogen peroxide. Schöne (60), in 1878, pointed out that conflicting statements regarding the properties of hydrogen peroxide might be due to impurities present. Schöne reviewed methods for preparation with respect for purity, and was himself able to produce 99.1 wt. % hydrogen peroxide. Davis (46) presented what are probably the first published figures on decomposition in storage. A sample of 9-volume peroxide standing in his laboratory was 20% decomposed in 11 weeks; further decomposition was not noticed for 8 weeks after the addition of a few drops of ether. Berthelot (61), after a study of the decomposition rate over periods of a month or more, concluded that stability depended on freedom of the solution from alkali.

Most of these efforts were to a large extent rediscoveries of facts or attitudes known to Thenard, but long ignored. A number of suggestions such as that by Mann (62) for the purification of commercial hydrogen peroxide by reprecipitation of BaO_2 and subsequent treatment with acid amount to no more than the laborious procedure with which Thenard worked. The suggestion that various additives might stabilize hydrogen peroxide was a new idea, however, and became a standard and necessary procedure. Kingzett (63) made a broad investigation of the properties of many salts and organic compounds in restraining the decomposition of 5% hydrogen peroxide. Alcohol, ether, camphor, menthol, and thymol were judged the best preservatives, Kingzett preferring alcohol. A study by Talbot and Moody (64) of commercial solutions of hydrogen peroxide in 1892, revealed none suitable for analytical purposes due to the number of additives and acid residues present.

Probably most important in beginning to displace the notion that hydrogen peroxide is an inherently unstable substance was the work of Hanriot (65) and of Wolffenstein (66). Hanriot demonstrated in 1885 that it was possible to vaporize hydrogen peroxide by distillation under reduced pressure, with substantial recovery of the product in condensed form; by this means he prepared 64% hydrogen peroxide. Wolffenstein asserted that hydrogen peroxide free from alkali, all traces of heavy metal compounds, and solid matter, was highly stable and that a

3% solution of such hydrogen peroxide could be concentrated to 50% by evaporation under reduced pressure to keep the temperature below 75°C., without loss by decomposition. Wolffenstein was able to prepare a 99.1% solution, and this result has been widely quoted. The difficulties of a manufacturer in attaining the standard which Wolffenstein set are well illustrated by Fawsitt (45), and the considerable work of Kebler, Warren, and Ruddiman (67) in testing the stability of commercial 3% solutions provides a basis for judging the stability at a time (1912) when manufacture was a well established procedure. Most of the samples examined by Kebler, Warren and Ruddiman were stabilized with acetanilide. The presence of this additive appeared to confer greater stability on the samples, but the effect varied widely and one particular manufacturer's product, containing no acetanilide, was reported to be as good or better than the stabilized samples. This was probably a good indication of the variation in care of preparation and consequent purity. Although decomposition varied from 1% to 90% over the one-year test period, a 10% decomposition was about the usual and this was considered acceptable.

It does not seem possible to establish with certainty when a manufacturing operation for the production of hydrogen peroxide for sale was first set up. The evidence of von Schrötter (68) and Cameron (69) indicates that 3% hydrogen peroxide was commercially available by 1867 or 1869. This was a preparation marketed by E. H. Thiellay and thought by Hofmann (70) to have been manufactured by the firm of Hopkin and Williams of London. According to von Schrötter, a factory for hydrogen peroxide manufacture was to be established in Berlin by Schering in 1873. Bourgougnon (71), in the United States, speaks of having attempted preparation for the market in 1873, and of manufacture on a commercial scale in 1878. Davis (46) stated that hydrogen peroxide of sufficient purity for chemical work was commercially available in 1879. Lange (72) placed the beginning of factory-scale production at the year 1881, and it is certain that manufacture was under way in Brooklyn, New York by the Oakland Chemical Co. in

1881 (73) and that Bernard Laporte established a factory in Shipley, Yorkshire in 1888 (49). From this evidence it appears that manufacture has been steadily maintained since at least 1880.

The price of some of the first hydrogen peroxide to reach market was very high; nearly $5 per pound for the sample examined by von Schrötter (68) in 1874. That this price allowed a very substantial profit is shown by the price of about $1 per pound or less in quantity quoted by Hofmann (70) in 1876. Leeds (34) speaks of imported hydrogen peroxide available in New York in 1879 at about $2 per pound and of 0.8% material available a year later at $1 per pound. Similarly high prices prevail today for small quantities of hydrogen peroxide sold at retail, but its use in commerce would never have been possible if such prices prevailed. Bourgougnon (71) discussed the cost of manufacture in 1878, setting a figure of about 6 cents per pound. The cost sheet for operation of a factory in 1902 given by Fawsitt (45) makes the cost about 4 cents per pound. By 1909 the value of hydrogen peroxide manufactured in the United States is given at about 9 cents per pound by the U.S. Census (74). All of the above figures are for the 10 volume or 3 wt. % hydrogen peroxide commonly marketed until the advent of the electrolytic process, which made it relatively easy to produce more concentrated solutions.

The price of hydrogen peroxide in more recent times at the point of manufacture has decreased steadily due both to competitition and the increasing volume of sales. In 1924, before the advent of electrolytic manufacture in the United States the price for the 27.5% hydrogen peroxide common in commerce was about 36 cents per pound of solution. After the beginning of electrolytic manufacture, this price dropped to about 30 cents per pound in 1927 and to about 24 cents per pound in 1929. By 1940, the price had declined to 20 cents per pound, and after a further decline during the war years to a low of 15 cents per pound rose to a level of about 20 cents per pound of solution in 1950.

It is probable that technological improvements to the electrolytic processes which could permit a reduction of manufacturing cost have reached the point of diminishing returns and that substantial cost reduction in the future can only be brought about by development of new manufacturing processes. It should be noted that the delivered price per quantity of hydrogen peroxide in solution is at a minimum for solutions of intermediate concentration. The minimum is determined by the costs of transportation, packaging, etc., of the water ballast in the dilute solutions balanced against the costs of concentration.

The quantity of hydrogen peroxide manufactured has advanced with few breaks throughout the years. Until shortly after the war of 1914, production was relatively steady, but beginning about 1925, increasing use, largely in the textile industry, encouraged a rise in production which continues uninterruptedly. In Figure 3, prepared by the Stanford Research Institute (75) from figures of the U.S. Census (74), the course of manufacture in the United States can be seen. By the year 1955, United States production capacity is expected to be 165 million pounds expressed as 27.5% hydrogen peroxide solution per year (76). World-wide productive capacity in 1939 is estimated to have been 100 million pounds of 27.5% hydrogen peroxide; the United States thus accounted for about one quarter of the production. Few reliable data on the extent of post-war manufacture have been published, probably because of military security. Manufacture has been carried out in most industrially advanced nations of the world. Before the war of 1939, factories were located in England, France, Germany, Austria, Italy, and most of the other European countries as well as in Australia, Korea, Japan, and the United States. Only some 10% of the production in 1939 was accounted for by the barium peroxide process, making the location of most factories, which use the electrolytic process, a matter of balance between proximity to markets and the availability of electrical energy at low cost.

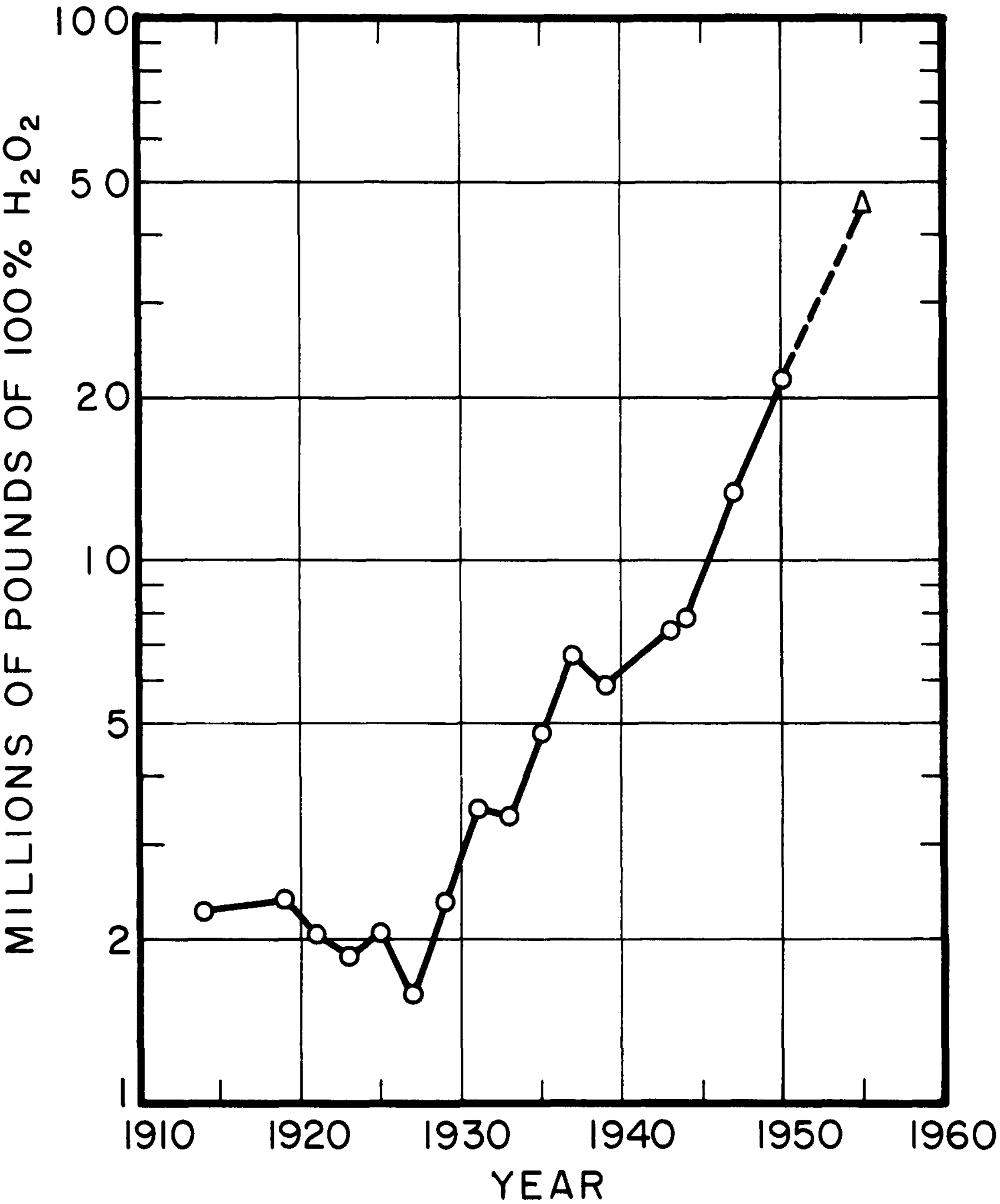


FIG. 3 - PRODUCTION OF HYDROGEN PEROXIDE IN THE UNITED STATES

The manufacture of hydrogen peroxide in the United States was begun in 1881 (73). By 1912, Brewer (77) estimated that there were more than a hundred manufacturers, all dependent upon barium peroxide imported from Europe. The loss of this source of supply during the war of 1914 was largely made up by production from the Rollin Chemical Company of Charleston, West Virginia, which had been organized in 1913. Other plants manufacturing barium peroxide were established in California after the war, meeting stiff competition from renewed imports. One of these, the Barium Products, Ltd., of Modesto, California, was purchased in 1929 by the Westvaco Chemical Company. This company, a division of the Food Machinery and Chemical Corporation since 1948, has continued production of hydrogen peroxide by the barium peroxide process, first in California, and since 1941, in Cartaret, New Jersey.

The first manufacture of hydrogen peroxide by the electrolytic process in the United States was commenced by the Roessler and Hasslacher Chemical Company in 1926, at Niagara Falls, New York. This company had begun manufacture of hydrogen peroxide in 1909 and was acquired by E. I. duPont de Nemours and Company in 1928. At nearly the same time production by the electrolytic process was begun by the Buffalo Electro-Chemical Company, which had been established in 1925, and became a subsidiary of Food Machinery and Chemical Corporation in 1951. These two concerns are now said to supply about 90% of the total U. S. production (78).

The Pennsylvania Salt Manufacturing Company has also manufactured hydrogen peroxide by the electrolytic process for some time. Other chemical manufacturers (79) have produced smaller quantities of hydrogen peroxide by the barium peroxide process, largely for the pharmaceutical or fine chemical trade. New producers of hydrogen peroxide in significant quantities may be expected to enter the trade in the future as the use is expanded and particularly as new processes are developed. In 1951, the duPont Co. announced the construction of a plant to produce hydrogen peroxide at Memphis, Tennessee by a new undisclosed process. Further details of the history of hydrogen peroxide manufacture in the United States are given by Haynes (80).

The development of the use of hydrogen peroxide on a scale sufficiently large to support manufacture was initially a slow process. There were some early suggestions for its use, such as that of DeSondalo (81) in 1843, that it be used to refresh the air in meeting places and mines, suggestions which were either impractical or too advanced for the time. Some use of it was made in medicine in several ways, as an irritant, antiseptic, Lister spray, etc., and there was a period when it was believed to be a specific for the treatment of diphtheria. Richardson (82) was an early proponent of the use in medicine, and this use, largely as an antiseptic, has continued through times of alternate professional medical approval and disregard.

The use for bleaching, which is of greatest importance, was suggested as early as 1862 by Chevreul (83) and Tessié du Motay (84). Use as a cosmetic in the bleaching of the hair provided a market for the first manufactured hydrogen peroxide. Both Cameron (69) and von Schrötter (68), whose accounts are helpful in marking the beginning of manufacture, had as tasks to establish the composition of a fluid fashionable for bleaching the hair, von Schrötter's preparation bearing the commercial label "Eau fontaine de jouvence golden." Hofmann (70) says that it is apparently to this that "is due that offensive blonde shade of hair which holds an intermediate place between ash gray and bright yellow, and attracts the attention of the spectators and the curiosity of observers by its piquante unnaturalness."

Other applications to bleaching which followed shortly were in the preparation of ivory, bone, silk, bristles, and feathers where the action of hydrogen peroxide was found to be unrivaled, and relative expense was a secondary consideration. The superiority of bleaching with hydrogen peroxide slowly won its acceptance in the treatment of other materials;

straw, hides, wool, and wood, so that by about 1890, manufacturers were less dependent on fashion and had begun to serve a steady market. Papers by Ebell, Gohring, and Delmart (85) reveal the extent of the early use of hydrogen peroxide.

THE LITERATURE OF HYDROGEN PEROXIDE

A conservative estimate would place the number of references dealing with hydrogen peroxide in the technical and commercial literature at three to four thousand. For those having special interests it may be helpful to outline the scope of the literature and to make reference to some reviews which exist.

The historical account which has been presented is by no means complete; several subjects studied at length before the beginning of the twentieth century, such as the chemical reactions of hydrogen peroxide, its occurrence in the atmosphere, and its use in medicine, have been mentioned only briefly. A certain portion of such work will warrant later citation, but much of it has been superseded and is of little interest.

Three books on the subject of hydrogen peroxide have been published, all in the German language. Birckenbach (27) wrote in 1906, chiefly on the subject of analysis for hydrogen peroxide, but the book also contains long sections on history, manufacture, and uses. Books by Machu (86) and Kausch (87) are recent, and each contains nearly two thousand references. Each of these books provides direction to the significant literature up to the time of publication on such subjects as physical and chemical properties, manufacture, and well-known uses. The book of Birckenbach remains of value on the subject of analysis and is useful for historical material. Machu, writing first in 1936 and in a second edition of 1951, devotes about one fifth of his book to the subject of peroxy compounds other than hydrogen peroxide. Machu presents a discussion of the literature of hydrogen peroxide, concentrating particularly on manufacture. A valuable feature of this monograph is an annotated list of patents. The book by Kausch (1938) gives an essentially complete compilation of references to the literature, in a form which is in effect an annotated bibliography. Peroxy compounds other than hydrogen peroxide are not treated by Kausch, but the discussion of the uses of hydrogen peroxide is more extensive than in Machu.

Several early papers of a general nature are of value. Already mentioned have been Davis (46), Leeds (34), and Fawsitt (45). The paper of Leeds discusses the ozone-antozone theory and presents a bibliography on hydrogen peroxide to the year 1879. Mason (88) in 1881, presented what appears to be a knowledgable review of all phases of the subject of hydrogen peroxide. Koller (89) thoroughly discussed its use in bleaching in 1892. The extensive review by Neumark (90) in 1913, coming at the end of a period in which a pattern of use and understanding had been developed, is valuable as a summary.

Modern reviews on hydrogen peroxide to be recommended are by Reichert (91), Slater (92), Shanley and Greenspan (93), Shanley (94), Milas (95), and Mitteau (96). A valuable summary of the chemical properties of hydrogen peroxide, with particular reference and comparison to analogous compounds is given by Yost and Russell (97). Historical reviews of the manufacture of hydrogen peroxide are given by Bretschger and Shanley and by Löwenstein (98). The earlier series of the Index Catalog of the Surgeon General's Office (99) are invaluable in learning of applications made of hydrogen peroxide in medicine. Some more obscure uses of hydrogen peroxide, with emphasis on the patent literature, are covered by Lange (72).

THE NOMENCLATURE OF PEROXIDE COMPOUNDS

In naming peroxide compounds it is necessary to indicate the presence of peroxide structure and to differentiate peroxides from other oxygen-containing compounds. A number of practices for naming peroxide compounds have been proposed or are in use; the most satisfactory system can be developed by consideration of the various types of oxygen compounds.

The oxygen atom unites with oxygen and with other elements in chemical bonds which are largely of covalent or shared electron nature. Each oxygen atom may acquire, through sharing, up to two electrons. Molecules formed only of oxygen are O_2, O_3, and O_4; linking of a number of oxygen atoms larger than four apparently does not occur. In compounds of oxygen with other elements linkage of as many as four oxygen atoms together may occur and the joining of more than four has been postulated. If the discussion is restricted to the compounds of oxygen with other elements in which linking of oxygen with oxygen is limited to two oxygen atoms, the compounds made possible by combination of oxygen with an element, M, capable of contributing one electron per atom to a covalent bond may be listed as: MO_2, MO, M_2O_2, and M_2O. Combination of oxygen with a more electronegative element, as in OF_2, need not be considered here. The ratio of element M to oxygen or the combining proportion of oxygen in this series is 1/2, 1, and 2. It is convenient to give these numbers a negative sign to express the electronegative or electron accepting nature of oxygen. Including molecular oxygen, O_2, in the series with a ratio of zero it is then possible to refer to the nominal valences or oxidation numbers 0, -1/2, -1, and -2 of oxygen. In so doing it is not intended to indicate that the bonds formed by oxygen in these states are predominantly electrostatic or ionic in nature, but only to facilitate identification and the balancing of reactions.

Compounds containing oxygen as O_2^- or of oxidation number -1/2 are presently called superoxides, *e.g.*, potassium superoxide, KO_2. This class of compounds may be regarded as derivatives of the acid HO_2. The molecule or radical HO_2, logically named hydrogen superoxide, is, however, generally termed perhydroxyl (100) (see below). However, it should be noted that the term "superoxide" was at one time used in the same sense as "peroxide" and that in German *Wasserstoffsuperoxyd* and *Wasserstoffperoxyd* both mean hydrogen peroxide.

Substances containing the group -O-O- or $O_2^{=}$ or oxygen of oxidation number -1 are properly called peroxides or peroxy compounds. Other designations such as the use of the prefixes super-, hyper- or hol- (86) or the use of the term oxate (101) have been proposed, and there is some variation in the designation of the parent compound, hydrogen peroxide,* but through usage and agreement of the International Union of Chemistry (102) the designations peroxide and peroxy are preferred.

The most familiar oxygen compounds, containing $O^{=}$ or oxygen of the oxidation number -2, are simply termed oxides with an ordinal prefix such as mono-, di-, etc. to indicate the number of oxygen atoms, as in manganese dioxide, MnO_2.

Where a third element occurs in a compound of oxide oxygen the presence of oxygen may not be indicated by the name, but the presence of the suffixes -ate or -ite in the name of the compound usually, but not always, indicates oxide oxygen since many of the radicals bearing these suffixes in the radical name carry oxygen.** Certain oxides of the formula MO_2

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* Hydrogen dioxide and peroxide of hydrogen are fairly common in English; the French retains Thenard's first designation, *eau oxygénée*, which usage is followed in the Italian *acqua ossigenati* and the Spanish *agua oxigenada*; *Wasserstoffsuperoxyd* is common in German, but these names are not used as root words in naming other peroxy compounds.

** The suffix -ate denotes roughly "that which is acted upon by," as in lead acetate, or "lead that is acted upon by acetic acid." The names of many inorganic radicals are derived from the names of salts formed by oxygen-carrying acids which have acted upon an alkali, *e.g.*, sulfate, from the salts of sulfuric acid. The suffix -ite is used similarly, indicating only presence of a different oxidation state.

such as PbO_2 and MnO_2 have been called peroxides, but this is incorrect. The term dioxide seems most suitable here, both in indicating structure and avoiding confusion with true peroxides.

It is important to emphasize that the prefix per- does not denote peroxide compounds uniquely (103). The prefix, coming from the Latin, meaning thoroughly or perfectly, was originally introduced into chemical nomenclature by Thomson (104) in 1804, in the term peroxide to denote a compound in which a metal was combined with as much oxygen as possible. Combination with the largest proportion of other elements was later designated in the same way, as in the term perchloride, now obsolete. Under this system the name hydrogen peroxide to distinguish H_2O_2 from H_2O was quite correct. This usage of the prefix per- became accepted, but with the growth of understanding of the nature of chemical combinations two changes in significance have come about: (1) The etymological meaning has been inverted, in that the implied state of the element in combination with the largest proportion of oxygen or another element is emphasized by the use of the prefix in the name of a compound (105). For example, in the name permanganate Thomson's original intention of indicating manganese combined with the largest possible quantity of oxygen is achieved, but in modern usage attention is focused on the implied high <u>oxidation state</u> of the manganese which is a consequence of its presence in small proportion to the oxygen. (2) It has been realized that oxygen combines in different proportions or has more than one oxidation state and that this fact is not indicated by the use of the prefix per- alone. Thus if lead dioxide, PbO_2, were called lead peroxide a difference in structure of fundamental importance between PbO_2 and a true peroxide such as barium peroxide, BaO_2, is not distinguished.

The meaning implied by the use of the prefix per- in present-day chemistry may then be given (106) as: (1) a compound or radical containing an element in its highest state of oxidation *e.g.*, perchloric acid, $HClO_4$, containing heptavalent chlorine; (2) the presence of the peroxide group, -O-O-, e.g., sodium peroxide, Na_2O_2; to these must be added a third less common meaning, (3) exhaustive substitution or addition, e.g., perhydronaphthalene, $C_{10}H_{18}$.*

Since in true peroxide compounds the oxidation state to be indicated by the name is that of the oxygen, which, in addition, is not formally in its highest oxidation state, the use of the prefix per- should be restricted to the meanings in (1) and (3) and the term peroxide, the adjective peroxy, or the prefix peroxy- used only for compounds in group (2) if composition is to be indicated unambiguously**(108). An example of this is the distinction between perchloric acid, $HClO_4$, and peroxymonosulfuric acid H_2SO_5. Thus $Na_2S_2O_8$ is designated as sodium peroxydisulfate.

Two exceptions of this practice in use are acceptable. The acid anion of hydrogen peroxide, O_2H^-, is termed perhydroxyl ion in preference to the more cumbersome peroxyhydroxyl. The radical HO_2, properly called hydrogen superoxide, is generally termed perhydroxyl radical by analogy of formula and due to the frequently postulated formation of hydrogen peroxide from it in gas-phase reactions. The name peroxide ion is reserved for $O_2^=$.

Hydrogen peroxide addition compounds, that is, compounds carrying hydrogen peroxide of crystallization, such as $2Na_2CO_3 \cdot 3H_2O_2$, have been commonly called perhydrates in parallel with the term hydrate. The term perhydrate might easily be taken to indicate and differentiate a substance hydrated to the greatest possible degree. At the same time the word form perhydr- does not designate hydrogen peroxide well. A more desirable name would be one which did not allow misinterpretation of the

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* This usage has recently been approved (107), and it may be expected to become more familiar as the completely halogenated hydrocarbons assume increasing importance.

** The German language avoids confusion between per- and peroxy through the use of the prefix über- to designate highest state of oxidation in non-peroxidic substances.

intended meaning of per- and which clearly indicated hydrogen peroxide without introducing confusion with water, if the word forms hydr- or hydro- are used. Improved substitutes for the term perhydrate that have been suggested are peroxate, hydroperoxate, or hydroperoxidate. The last term is derived most nearly in parallel with the term hydrate to express the meaning "that which is added to or acted upon by hydrogen peroxide." The term hydroperoxidate* is accordingly recommended and used here. Peroxide compounds or hydroperoxidates may also carry water of crystallization as in the examples, $Na_2O_2 \cdot 8H_2O$, sodium peroxide octahydrate, and $Na_2SO_4 \cdot 2H_2O \cdot H_2O_2$, sodium sulfate dihydrate hydroperoxidate. The constitution of some peroxy compounds has not been proven clearly; it is questioned whether the peroxy oxygen exists as a peroxide or as a hydroperoxidate. In this case, the compounds are generally referred to simply as peroxides.

Several categories may be established for substituted hydrogen peroxides; among the inorganic compounds are the metal salts of hydrogen peroxide, metal hydroperoxides and metal peroxides, and the peroxyacids; among organic compounds are the alkyl derivatives of hydrogen peroxide, alkyl hydroperoxides, and alkyl peroxides, the acyl hydroperoxides or peroxyacids, the acyl peroxides, and the acyl alkyl peroxides or peroxy esters.

The following practices are used in designating substituted hydrogen peroxides or compounds which may be regarded as derivatives of hydrogen peroxide. The organic mono derivatives and the salts of the weak acid H_2O_2, which can both be written as ROOH, (_e.g._, NaOOH or CH_3OOH), are termed R hydrogen peroxides or, more commonly, R hydroperoxides if the element or radical R is _not_ an acid or acyl (-COR) radical. The disubsti-

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* Suggested by Professor Austin M. Patterson.

tuted structures ROOR, ROOR', or RO_2, (e.g., NaOONa, $CH_3OOC_2H_5$, or BaO_2), where R is not an acid radical are termed R or di R peroxides or RR' peroxides. If both R groups or both R and R' are acyl groups these compounds are also termed R RR' peroxides.

The compounds ROOH, or ROOR, where R is an acid radical or an acyl radical except as noted above, e.g., CH_3CO O O H or HSO_3-O-O-SO_3H, are called peroxy acids. With substitution of dihydroxy acids such as carbonic acid it is possible to formulate three compounds, for example, HOCO-O-O-H, peroxymonocarbonic acid, HOCO-O-O-COOH, peroxydicarbonic acid, as well as H-O-O-CO-O-O-H, diperoxycarbonic acid. These names indicate the manner in which the source of the acid properties is indicated, although it is not to be implied that these acids or similar ones are necessarily known to exist. Salts of these acids are named in the usual manner, as in C_6H_5CO-O-O-Na, sodium peroxybenzoate. Compounds ROOR' where one R group but not the other is an acyl radical are called peroxy esters as in C_6H_5CO-O-O-$C(CH_3)_3$, perbenzoic acid, t-butyl peroxy ester or more commonly, t-butyl peroxybenzoate. One particular difference in behavior between these compounds and ordinary esters is that on hydrolysis the peroxy esters yield acid and hydroperoxides rather than peroxyacid and alcohol.

Many more complex peroxides are possible among the thousand or so known peroxy compounds. If they are termed peroxides or the designation peroxy is used to indicate the presence of one or more peroxide groups no misunderstanding should arise. The structure of a group of compounds formed through reaction of unsaturated compounds with ozone and known as ozonides (109) or oxozonides has not been established definitely. These compounds may contain peroxide oxygen, but they are not designated as peroxides.

LITERATURE CITATIONS - CHAPTER ONE

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CHAPTER TWO

FORMATION AND MANUFACTURE,

I. DIRECTLY FROM WATER OR OXYGEN

For about sixty years following the discovery of hydrogen peroxide it remained essentially a laboratory curiosity, made in small quantities by the reaction of barium peroxide with an acid. The introduction in 1879 of the Brin process for manufacturing oxygen from barium peroxide made this latter chemical commercially available, and by the end of the following decade 3 wt. % hydrogen peroxide was being produced in modest amounts in Europe and Britain by reaction of barium peroxide with phosphoric acid, hydrofluoric, fluosilicic or other acids and sold for bleaching silk, hair, feathers, wool, etc., and as a disinfectant for treatment of wounds.

The discovery by Berthelot in 1878, that peroxydisulfuric acid may be produced by electrolysis of sulfuric acid solutions and readily hydrolyzed in solution to yield hydrogen peroxide and sulfuric acid, plus the demonstration by Hanriot in 1885, that hydrogen peroxide could be vaporized from the hydrolyzed solutions if the temperature were kept low by reduced pressure, led to the establishment in 1909 of the first of the commercial electrochemical processes (1). These processes permitted the production of a relatively pure and therefore highly stable hydrogen peroxide in substantially higher concentrations than formerly and largely superseded the barium process which is now used only to a relatively small degree where markets exist for by-product barium sulfate. Although hydrogen peroxide is at present produced principally by electrochemical processes via peroxydisulfates, a number of other methods have been studied for potential commercial application and carried to at least the pilot plant stage. Hydrogen peroxide is perhaps unique in the wide variety of reactions in which it may be formed and in the large fraction of these reactions which have been seriously considered as methods for commercial production of this chemical. Since an understanding of manufacturing processes must rest on a knowledge of the characteristics of the chemical reactions involved, manufacturing technology will be considered in juxtaposition with the relevant basic chemistry, the subject material being classified by the character of the chemical reactions involved.

The reactions in which hydrogen peroxide is formed may be conveniently divided into two groups. The first group, which are considered in Chapter 2, consists of those reactions in which hydrogen peroxide is formed directly from water or oxygen by thermal, photochemical, electrochemical, electric discharge or other types of processes. The second group of reactions, considered in Chapter 3, consists of those in which hydrogen peroxide is formed from other peroxy compounds such as the inorganic peroxides and the peroxydisulfates. The principal methods of manufacture now used are therefore discussed in Chapter 3.

THERMAL FORMATION FROM WATER

Small amounts of hydrogen peroxide have been obtained by subjecting water and oxygen to high temperatures followed by sudden cooling, as for example, by passing mixtures of water vapor and oxygen at high velocity through hot magnesia capillaries or by burning strips of magnesium sheet and directing the flame against ice (2).

The reaction: $H_2O(g) + 1/2\ O_2\ (g) \longrightarrow H_2O_2(g)$ is highly endothermic; the most accurate thermodynamic data at present give $\Delta H^{o}_{298} = 25.35$ kcal/g.mole and $\Delta F^{o}_{298} = 29.93$ kcal/g.mole. Although the formation of hydrogen peroxide by this reaction is favored by higher pressures and temperatures, even at 1500^{o}K. and 1000 atmospheres pressure, for example, a mixture containing initially one mole of water per one-half mole of oxygen will form only 2.1 x 10^{-4} moles of hydrogen peroxide under equilibrium conditions. It thus appears that the hydrogen peroxide formed from water in experiments such as the above results from a series of reactions occurring under conditions far from equilibrium. A recent French patent (3) claims the formation of hydrogen peroxide from water vapor and oxygen at a pressure of several thousand atmospheres and a temperature of 3500-4000°C. It is proposed to obtain these conditions by rapid adiabatic compression of the gases, followed by very rapid cooling by expansion to prevent decomposition of the product. However, no experimental data are quoted and the idea does not appear to have been reduced to practice. Substantial quantities of hydrogen peroxide could exist in equilibrium under the conditions specified but the technical problems involved in such a process would be extremely difficult.

THERMAL REACTION OF HYDROGEN AND OXYGEN

Observation of the formation of hydrogen peroxide by combustion of hydrogen in oxygen was recorded by Böttger (4) in 1878 and a patent was obtained by M. Traube (5) in 1884 for a process of manufacturing hydrogen peroxide by introducing water into a flame formed by the combustion of carbon monoxide, hydrogen, water gas, illuminating gas, etc. Several other investigations in the following two decades showed that in order to obtain hydrogen peroxide in readily detectable amounts it was necessary to cool the combustion gases rapidly as, for instance, by directing the flame against water or ice.

Proper interpretation of these results could not be made until considerably later when the equilibrium relationships involved could be accurately determined. It has been seen above that if complete equilibrium were established between oxygen, hydrogen, water, and hydrogen peroxide under any combination of temperature and pressure which is technically feasible at present, the amounts of hydrogen peroxide present would be vanishingly small. However the reaction: $H_2(g) + O_2(g) \longrightarrow H_2O_2(g)$ is

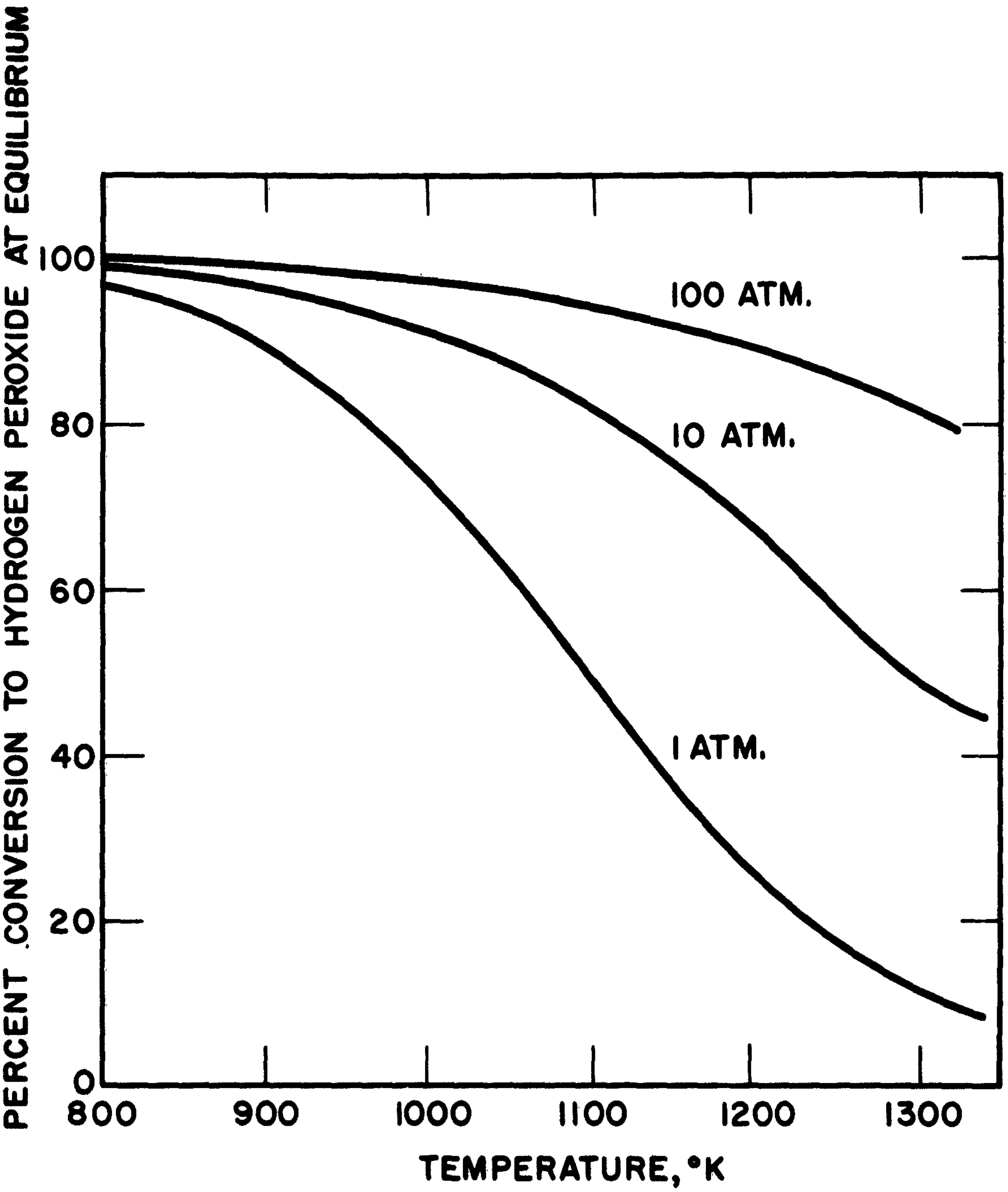

FIG. 1 – CALCULATED CONVERSION UNDER EQUILIBRIUM CONDITIONS OF AN EQUIMOLAR MIXTURE OF HYDROGEN AND OXYGEN TO HYDROGEN PEROXIDE VAPOR. (ASSUMING NO WATER FORMATION)

exothermic and it is interesting to note that if it were possible to suppress the reactions forming water, a high concentration of hydrogen peroxide could exist in equilibrium with hydrogen and oxygen. The extent of this conversion is indicated in Figure 1, which was calculated from the thermodynamic data of Chapter 5. The percent conversion to hydrogen peroxide of a mixture at equilibrium containing initially equimolar quantities of hydrogen and oxygen is plotted as a function of temperature for three values of the total pressure. It is seen that if reaction to form water could be prevented, substantially all of the hydrogen and oxygen will be converted at equilibrium to hydrogen peroxide at temperatures below about 900°K., although if water is present the amounts of hydrogen peroxide which can exist in equilibrium with it are minute.

It is apparent that in the reaction of hydrogen and oxygen, hydrogen peroxide is formed as a relatively unstable intermediate and ordinarily transitory compound in the overall series of combustion reactions and it does not exist in appreciable concentrations when in complete equilibrium with the other chemical species present. Some understanding of the formation and destruction of hydrogen peroxide can be obtained by considering the general kinetics of the reaction between hydrogen and oxygen. This overall reaction is very complex. It involves the formation and disappearance of species such as H, O, OH, HO_2, and H_2O_2 by a large number of simultaneously and successively occurring reactions, the relative importance of each varying significantly with the temperature, pressure, ratio of hydrogen to oxygen, physical configuration of experimental equipment, and chemical nature of surfaces exposed to the reacting mixture. The thermal reaction of hydrogen and oxygen has been studied in considerable detail, particularly by Hinshelwood and co-workers (6) in England and by Lewis and von Elbe (7) in the United States. The theory of the underlying reaction mechanisms is in a high state of development, but the fact that some uncertainties exist on the relative importance of alternate reaction schemes is not surprising in view of the large number of experimental variables found to be of significance, and the large number of possible reactions involved.

The reaction mechanisms which have been proposed are derived from a variety of studies, including various reactions initiated photochemically or by electric discharge, interpretation of emission and absorption spectra of individual species and of reacting mixtures, as well as interpretations of various studies of explosion limits of hydrogen and oxygen and of reaction rate measurements near the explosion limits, all being considered in the light of the energy relationships and the energies of activation involved in the individual reaction steps. The character of the explosion limits will first be presented together with a summary of the individual reaction steps believed to be of importance, and their role in the thermal reaction. This will be followed by consideration of specific studies of the thermal reaction in which formation of hydrogen peroxide has been of primary interest. Subsequently there will be considered the formation of hydrogen peroxide from water or the elements on excitation by thermal, electrical, photochemical and radiochemical means. A more detailed consideration of the general hydrogen-oxygen reaction and explosion limits may be obtained from Laidler (8), Hottel and Williams (9), and in the references previously cited.

Explosion Limits of Hydrogen-Oxygen Mixtures

Mixtures of hydrogen and oxygen of a wide range of composition explode spontaneously at gas temperatures above about 600°C. unless the pressure is below about 1 mm. of mercury. At temperatures below 400°C. the rate of reaction is very slow, and no explosion will occur unless initiated by an external source such as a spark or hot wire. A stoichiometric mixture of 2 mols of hydrogen per mol of oxygen at, for example, 500°C. and 400 mm. of mercury will react homogeneously at a steady, measurable rate. If the pressure is gradually reduced isothermally, the rate will diminish; but at a critical pressure of about 100 mm. of mercury, the mixture will spontaneously explode. The pressure at which this occurs is known as the second or upper explosion limit. If the same initial mixture at 550°C. is gradually compressed isothermally, the reaction rate will slowly increase and again a spontaneous explosion will occur, at a pressure of about 1000 mm. of mercury, known as the third explosion limit. Likewise, the same initial mixture at 550°C. but at a very low pressure will react slowly until the pressure is increased to about 1 mm. of mercury, at which the first explosion limit is reached. These limits for auto-ignition of explosions vary somewhat with mixture ratio and nature of the containing vessel; the variation with temperature and pressure is shown in Figure 2. It is apparent that the existence of the second explosion limit* cannot be explained as a thermal explosion, since in such a case the minimum temperature for auto-ignition is that at which the rate of heat production by homogeneous reaction just exceeds the rate of heat loss by conduction and consequently a pressure <u>increase</u>, which would not markedly affect the rate of heat conduction but would strongly increase the reaction rate, should cause a <u>lower</u> auto-ignition temperature.

To explain these explosion limits and other observations, it is postulated that the hydrogen-oxygen reaction proceeds

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* It is important to note that the term <u>explosion limit</u> is used in the scientific and technical literature in two different senses. In one sense, as used above, it refers to the limiting combinations of pressure and temperature at which a gas of a given composition just fails to explode <u>of itself</u>. In the other sense, it refers to the limits of composition outside of which an explosion cannot be propagated by external ignition, such as a spark or flame. The latter concept is also referred to as the <u>explosive composition limits</u> or <u>ignition limits</u> and will be so referred to in this book in order to avoid confusion. The explosive composition limits also vary somewhat with pressure and temperature; higher pressures and temperatures usually, but not always, increase the explosive composition range. The explosive composition limits for hydrogen and oxygen mixtures are 9.2 and 91.6% hydrogen at room temperature and atmospheric pressure (10).

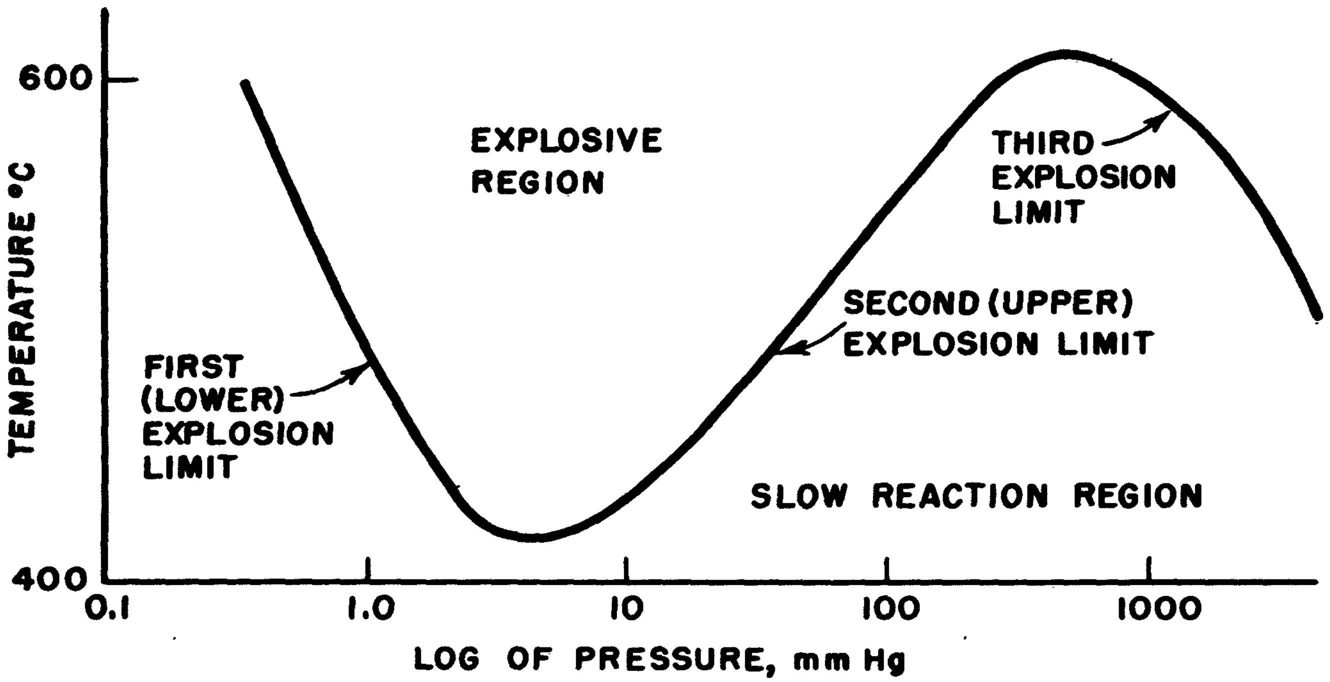

FIG. 2 — EXPLOSION LIMITS IN THE HYDROGEN-OXYGEN SYSTEM

by the formation of free atoms and radicals as intermediates, known as chain carriers, these being produced and consumed by simple steps involving the reaction of one or two species at a time, or perhaps three at higher pressures. If reactions producing more than one atom or radical for each one consumed occur to a sufficient extent (chain branching), then the consequent self-accelerating reaction will lead to an explosion.

The quantitative evaluation of the reactions involved is greatly simplified by considering conditions under which steady-state reaction rates occur and making the assumption that under these circumstances, the chain-carrying intermediates are present in constant but small concentrations during the course of the reaction. The rates of the separate individual reactions, including diffusion and subsequent reaction on the walls, are formulated as simple expressions in accordance with the laws of mass action. These equations are then solved simultaneously, by setting the net rate of formation of intermediates equal to zero and eliminating the concentrations of intermediates, thereby obtaining an expression for the rate of product formation in terms of the rate constants for the individual reactions and functions of the concentrations of the original reactants.

An explosion is therefore predicted to occur for those sets of operating variables in which the rate of product formation approaches infinity. By proposing various reaction schemes and comparing the predicted character of the explosion limits with those found experimentally, it is possible to eliminate certain schemes from consideration and arrive at one or several plausible sets of reactions for each general area of experimental conditions. Further guidance may be obtained from consideration of the characteristics of the reaction near the explosion limit, and the other types of studies described above.

Steps in the Thermal Hydrogen-Oxygen Reaction

Reactions which appear from various studies to be of probable importance in hydrogen combustion are listed in Table 1.* The table also lists for each reaction the change of enthalpy and the activation energy. Values of the latter have been determined or estimated for only a few cases; the enthalpy figures are well established and are probably accurate within 1 - 2 kilocalories for all species except HO_2. The value used here is from the recent and careful analysis of Evans, Hush and Uri (10a); it is probably accurate to within a few kilocalorie units. The values of energies of activation are, of course, difficult to determine and their accuracy is generally unknown. The figures here are from Jost (10), most of which were originally published by Geib (10b). That for reaction 5 refers to a two-body collision.

There is general agreement that at low pressures below the first explosion limit (approximately 0.1 to 5 mm. of mercury) combustion proceeds by reactions 1, 2 and 3, and with destruction of O, H and OH on the walls (reactions 15_H, 15_O and 15_{OH}).

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* The table follows the reaction-numbering scheme used by Hottel and Williams (9) which is based on that of Lewis and von Elbe (7) except for numbers 9 and 10 which the latter do not include in their present scheme, and 15, to which they do not give a number. Hottel and Williams note that Hinshelwood and co-workers use the same numbering on 1, 2, 3, 5; but that they call 6 and 10, 4 and 6; and their combination of 12 and 13 they call 5. No. 9 is suggested by Voivodskii (11). Other reactions discussed later will be numbered consecutively starting with 16. No reactions here bear the numbers 4 or 8; these were used at an earlier date by Lewis and von Elbe to designate reactions later discarded.

TABLE 1*

Steps in the Thermal Hydrogen-Oxygen Reaction

	Enthalpy Change, ΔH_R, kcal	Energy of Activation, ΔE_A, kcal
Two-body collisions combining to produce chain-branching:		
1. $OH + H_2 \longrightarrow H_2O + H$	+ 4.3	7
2. $H + O_2 \longrightarrow OH + O$	+17.1	14 to 20
3. $O + H_2 \longrightarrow OH + H$	+ 3.5	7 ± 2
Three-body gas-phase reactions: (M = any third body)		
5. $H + H_2O_2 + M \longrightarrow H_2O + OH + M$	-65.7	5
6. $H + O_2 + M \longrightarrow HO_2 + M$	-36	0
Two-body gas-phase reactions:		
7. $HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH$	-12	—
9. $HO_2 + H_2O \longrightarrow H_2O_2 + OH$	+37	—
10. $HO_2 + H_2 \longrightarrow H_2O + OH$	-45	7
11. $HO_2 + H_2 \longrightarrow H_2O_2 + H$	+20	—
Surface reactions:		
12. $2HO_2 \xrightarrow{surface} H_2O_2 + O_2$	-29	—
13. $2\,H_2O_2 \xrightarrow{surface} 2H_2O + O_2$	-48.4	
14. $H_2 + O_2 \xrightarrow{surface} H_2O_2$	-33.6	
15_H. $H \xrightarrow{\text{diff'n. to surface}}$ free-valence destroyed		
15_O. $O \xrightarrow{\text{diff'n. to surface}}$ free-valence destroyed		
15_{OH}. $OH \xrightarrow{\text{diff'n. to surface}}$ free-valence destroyed		
Chain-carrier initiating reactions:		
i. $H\ O + M \longrightarrow 2\,OH + M$	+ 54.2	—
o. $H_2 + M \longrightarrow 2\,H + M$	+103.6	—

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* See footnote on page 54.

Because of the importance of diffusion as the chain-breaking mechanism, the first explosion limit pressures vary as an inverse function of the vessel diameter, and inert gases tend to make mixtures explosive by hindering the diffusion of chain carriers to the wall. Note that neither HO_2 or hydrogen peroxide appears in this reaction scheme at very low pressures. At higher pressures (above the second explosion limit--about 10 to 100 mm. of mercury) three-body collisions become more probable and reaction 6 becomes important; the HO_2 thus formed may subsequently disappear according to reactions 7, 9, 10, 11 or 12. It is noted that reactions 9, 11, 12 and 14 produce hydrogen peroxide which may then be destroyed by 5, 7 or 13. At a given pressure between the second and third limit, an increase in temperature towards the explosive limit will increase the importance of the chain branching reactions 2 and 3 over the straight-chain reactions cited. Experimental evidence at present is insufficient to indicate clearly for any given set of conditions the relative importance which may be placed on alternate combinations of these reactions. However, it is apparent that at higher pressures (approaching the third explosive limit-above about 400 mm. of mercury) reaction 6 continues to increase in importance but reactions involving diffusion to the vessel surface diminish in importance to reactions involving direct collisions. It is interesting to note that hydrogen peroxide is apparently not formed by homogeneous gas phase reactions at very low pressures unless, as will be shown later, substantial quantities of <u>atomic</u> hydrogen are introduced into the system. However, it will also be shown subsequently that hydrogen peroxide can be formed <u>heterogeneously</u> at these low pressures by condensation of OH radicals on walls cooled below -180°C. It has been proposed that the initiation of the thermal reaction is by the small amounts of atomic hydrogen formed by molecular collisions (Hinshelwood) or by decomposition of hydrogen peroxide (Lewis and von Elbe) formed via an unspecified path.

Formation in the Thermal Hydrogen-Oxygen Reaction

The experimental results reported in the various papers will first be summarized, followed by an interpretation of the data in terms of the probable mechanisms involved. One of the first quantitative studies of hydrogen peroxide formation by reaction of hydrogen and oxygen was that of Pease (12) who passed continuously a mixture of these gases at atmospheric pressure through a tube at 550°C. and then into a vessel cooled to -79°C.; concentrations of several percent of hydrogen peroxide were obtained. In further experiments, spherical vessels 4.3 cm. in diameter containing 95% hydrogen and 5% oxygen were heated for a short time and then rapidly cooled to -79°C. The products contained up to 25 wt. % hydrogen peroxide. At sub-atmospheric pressures, but within the explosive composition limits, no hydrogen peroxide was obtained.

More recently, Poljakow and co-workers (13) have published a series of papers on the formation of hydrogen peroxide by explosions of hydrogen and oxygen in a small glass reaction vessel immersed in liquid air, and similar studies have been reported by Egerton and Minkoff (14). In both studies the hydrogen peroxide yield, expressed as a percentage content of the condensate, was found to be affected by a large number of variables, including the nature of the vessel wall, wall temperature, gas composition, pressure, vessel configuration, method of mixing the gases, and the amount of product frozen on the wall. In Poljakow's studies the hydrogen peroxide yield was but slightly affected by wide variations in the temperature of his platinum ignition wire or by the length of the induction period which preceded the explosion, even though the time of the induction period varied considerably with wire temperature. Higher wire temperatures were needed to initiate explosions in small diameter vessels and with gases containing a large fraction of hydrogen. In some studies the ignition wire was heated to a relatively low temperature under which conditions the gas mixture reacted slowly without explosion. Here the variation of hydrogen peroxide yield with changes in experimental conditions was similar to that observed with explosions, except that the yield was about one tenth as great. Tanner (15) also found that the hydrogen peroxide yield in a similar apparatus was unaffected by whether initiation was by spark or a hot catalyst surface. Tanner also reported that lead tetraethyl in the vapor significantly increased the hydrogen peroxide yield and decreased the violence of the explosion.

Poljakov's experiments were made with bulbs 25, 35 and 45 mm. in diameter, at total pressures of from 60 to 120 mm. of mercury, and with hydrogen-oxygen ratios of from 1 to 4 or 5, the upper composition limit being the maximum which could be exploded. Both gases were passed over calcium chloride and premixed before introduction into the reaction vessel. In each vessel, the hydrogen peroxide yield increased as the pressure was decreased; it also reached a maximum with hydrogen-oxygen ratios of about 2.5 - 4.0. In general at lower pressures, maximum yields were found at the lower composition ratios. The yields increased with decrease in vessel diameter, a maximum of about 3% hydrogen peroxide being reported in the 25 mm. diameter bulb. At the low hydrogen-oxygen ratios, ozone was reported in the condensed products, although the analytical method used was not recorded. The formation of ozone would account for the low hydrogen peroxide yields attained with these gas compositions, since hydrogen peroxide and ozone react rapidly with one another. It was also found that if the ignition wire were surrounded by a platinum grid, then no hydrogen peroxide was formed on the cooled walls of the vessel.

In another set of experiments, successive explosions were initiated in cylindrical tubes of enameled metal varying from 10 to 35 mm. in diameter and from 80 to 300 mm. in length, initiation here being by a spark rather than a hot wire. Passage of a detonation wave through a narrow tube of 2 - 3 mm. diameter produced no peroxide. In large diameter tubes, however, substantial yields of hydrogen peroxide were obtained. There is considerable scatter in the data but the following trends are clear: as with the spherical vessel, hydrogen peroxide yields increased with pressure decrease from 150 mm. of mercury to 50 mm. of mercury, for any given tube and decreased with an increase in diameter for a fixed length.

Egerton and Minkoff studied the hydrogen-oxygen reaction by a considerable variety of methods, including the use of single and multiple explosions and flow experiments using continuous spark ignition. In the single explosion studies a Pyrex tube 130 to 140 x 14 mm. was used in a procedure similar to that of Poljakov except that the vessel, immersed in liquid air during the explosion, was allowed to warm up to room temperature after only one explosion, and the amount of hydrogen peroxide present was determined colorimetrically by comparison with standard solutions, using titanous chloride reagent. The hydrogen peroxide yields were in general somewhat higher than those reported by Poljakov but show the same trend of maximum yield at hydrogen-oxygen ratios of 2.5, and increasing yield with decreasing pressure down to about 40 - 30 mm. of mercury. Further decrease in pressure to 20 mm. of mercury, however, produced a <u>decrease</u> in yield, a result also found by Poljakov who reported a maximum yield at about 45 mm. mercury pressure in one set of runs in a cylindrical vessel 100 x 10 mm.

Addition of 5% argon or nitrogen to a hydrogen-oxygen mixture ratio of 1.7 caused a slight decrease in yield at the pressures studied, 20 to 60 mm. of mercury. A few experiments with successive explosions, as used by Poljakov, showed that the yield decreased with number of explosions, which was attributed to the insulating effect of the condensed film of water and hydrogen peroxide. This same insulating effect was found in the flow studies of Egerton and Minkoff where premixed hydrogen and oxygen gas were passed over a continuous spark in a cylindrical tube immersed in liquid air. Under optimum conditions, initial yields of 30 - 35% hydrogen peroxide decreased quickly with time to a steady value of 10 - 15% which remained approximately independent of thickness of the ice film.

In the various types of experiments, use of cellophane, aluminum, or boric acid treatments on glass resulted in the same yield as with glass surfaces; potassium chloride on glass decreased the yield. These effects parallel the known activities of these surfaces in the decomposition of hydrogen peroxide. The variation of yield with experimental conditions was in general the same in the continuous flame experiments as in the explosion studies reported by both Poljakov and Egerton and Minkoff. The yield increased with a decrease in tube diameter from 24 to 14 mm., and showed a maximum at total pressures of 40 - 60 mm. of mercury, with much lower yields at 30 and 80 mm. of mercury. An increase in wall temperature from -180°C. to -79°C. decreased the yield from 15% to 6%.

In order to establish the seat of formation of hydrogen peroxide, Egerton and Minkoff measured the absorption from a beam of ultra-violet light passed through the tube during the explosions, and compared it to that they obtained with hydrogen peroxide vapor and that reported for hydrogen peroxide vapor by Dawsey, Rice and Urey (16). Although substantial absorption occurred, interpreted at the time as caused by hydrogen peroxide vapor, more recent studies by these workers indicate that the absorption was actually due to a fog of liquid water (14).

Hydrogen peroxide has also been identified by Holt and Oldenberg (17) as being present in the continuous thermal reaction of hydrogen and oxygen at about 540°C. and 1 atmosphere pressure, by similar measurements of the absorption spectrum of the reacting mixture. The amount of peroxide present in the gas phase as determined by the amount of absorption at 2537 Å was found to be strongly affected by the surface conditions of the Pyrex tube reactor, which varied with age and its previous history. An old tube roughened by many experiments gave practically no hydrogen peroxide under otherwise favorable conditions. With a satisfactory tube, formation of peroxide was favored by high hydrogen-oxygen ratios.

A study of the reaction between hydrogen peroxide and hydrogen at 470 - 500°C. and 1 atmosphere pressure by McLane (18) showed that the hydrogen peroxide disappeared more rapidly in the presence of hydrogen than with an inert gas, but the dependence of reaction rate on concentrations was complicated and did not permit a clear understanding of the reaction mechanism. The reaction rate of hydrogen-oxygen mixtures was appreciably accelerated by addition of small amounts of hydrogen peroxide under experimental conditions where the rate is normally very small.

Two patents by Cook (19) describe the formation of hydrogen peroxide by passing a mixture of hydrogen with generally less than 10% oxygen, at 5 - 35 atmospheres pressure and at 400 - 650°C. through a tube on which is fused a lining of boric acid or borates which retards the decomposition of hydrogen peroxide. The experimental conditions in each case are chosen to be such that the temperature is a few degrees below the point where rapid water-forming combustion would take place. Examples given indicate conversion to peroxide of 3 - 5% of the input oxygen, accounting for 10 - 20% of the oxygen reacting, when the product was condensed at room temperature.

Addition of water vapor in amounts of 1 - 40% increased the hydrogen peroxide yields; nitrogen up to 25% had little effect; hydrocarbon gases and chlorine in small amounts did not seriously interfere with the essential reaction but did enter into side reactions. Nitrogen dioxide, other nitrogen oxides, and carbon monoxide were reported as being harmful.

Mechanism of Hydrogen Peroxide Formation in the Thermal Hydrogen-Oxygen Reaction

On considering the various observations it is apparent that at sub-atmospheric pressures and wall temperatures at that of liquid air, some of the hydrogen peroxide must be formed on the walls of the containing vessel, probably by the freezing out of hydroxyl radicals

$$OH + OH \xrightarrow{surface} H_2O_2 \qquad (16)$$

It has been well established (20) that on passage of an electric discharge through water vapor, the hydrogen peroxide found on condensing the discharge products in a cold trap is formed by reaction 16 and it is also known that this process becomes less efficient at higher wall temperatures, and is negligible at wall temperatures much above -180°C. It is also possible that the reaction

$$HO_2 + HO_2 \xrightarrow{surface} H_2O_2 + O_2 \qquad (12)$$

is significant in hydrogen combustion at some temperature levels. The formation on the wall of hydrogen peroxide from hydroxyl radicals, however, will not explain the presence of hydrogen peroxide distributed in the gas phase, or the fact that the peroxide yield goes through a maximum at a pressure of about 40 mm. Hg. Egerton and Minkoff, who present an excellent discussion of the probable mechanism of hydrogen peroxide formation, propose the following explanation for this effect of pressure on hydrogen peroxide yield. It is postulated that HO_2 is formed in an activated state (designated by an asterisk) by direct association of H and O_2 in two-body collisions

$$H + O_2 \longrightarrow HO_2^* \qquad (6a)$$

Although the HO_2^* would have a short life because of its excited state, it is possible under certain conditions that a substantial fraction might collide and react before disintegrating. At low pressures presumably most will disintegrate into OH and O before encountering a third body. At higher pressure, however, and with excess hydrogen, the excess energy in the activated HO_2^* should permit the following reaction:

$$HO_2^* + H_2 \longrightarrow H_2O_2 + H \qquad (11a)$$

The hydrogen peroxide may well be produced in an active form, so that unless the energy of formation of the peroxide is removed on the cold walls, the hydrogen peroxide decomposes, most probably into two hydroxyls. Further increases in pressure result in the formation of a higher proportion of stabilized HO_2 radicals by collisions with other molecules, and an increase would occur in the number of three-body collisions forming stabilized HO_2 by

$$H + O_2 + M \longrightarrow HO_2 + M \tag{6}$$

Since reaction 11 is endothermic, only a small proportion of <u>unactivated</u> HO_2 radicals would presumably disappear by this reaction, and would be consumed instead by processes such as

$$HO_2 + H_2 \longrightarrow H_2O + OH \tag{10}$$

$$\text{or } HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH \tag{7}$$

thereby resulting in a smaller concentration of hydrogen peroxide.

It should be noted that this mechanism involving excited HO_2^* would not be expected to be significant at pressures above the second explosion limit where three-body collisions would become more probable. The above hypothesis explains most of the observations made at low pressures; increased tube diameter increases the time for hydrogen peroxide molecules to reach the walls and thus reduces the probability of the peroxide molecules being stabilized, likewise the combination of hydroxyls on the wall would be less probable. The manner in which lead tetraethyl increases the amount of hydrogen peroxide formed, as reported by Tanner, is not clear. Possibly the lead tetraethyl preferentially removes atomic hydrogen particles which move at relatively high velocities, and which Geib (21) has shown to destroy hydrogen peroxide rapidly.

At super-atmospheric pressures, the formation of hydrogen peroxide probably occurs via HO_2 from reaction 6, followed by formation of hydrogen peroxide by reaction 11. Here, the HO_2 is unactivated, and the energy required could be supplied by three-body collisions. The increased peroxide yield in the presence of water vapor may be due to its effectiveness as a third body for reaction 6, or it may form hydrogen peroxide by

$$HO_2 + H_2O \longrightarrow H_2O_2 + OH \qquad (9)$$

Another possibility is that the effect is due to adsorption of water on the tube surface (see, for example, Badin (22)) which may thereby enhance the relative effect of

$$2\ HO_2 \xrightarrow{\text{surface}} H_2O_2 + O_2 \qquad (12)$$

over

$$2\ H_2O_2 \xrightarrow{\text{surface}} 2\ H_2O + O_2 \qquad (13)$$

Manufacture by Thermal Reaction of Hydrogen and Oxygen

The direct formation of hydrogen peroxide by thermal reaction of the elements has the potentiality of being a simple, straight-forward process which could yield a pure and highly stable product from relatively inexpensive starting materials. Although a number of patents have been granted on processes for making hydrogen peroxide by combustion of hydrogen and oxygen or from water (23) no actual commercial application is known, as of 1952. This is primarily due to the low yields of hydrogen peroxide which have been obtained under conditions which are economically feasible.

Variables which particularly affect the yield are the character of the vessel surface, the total pressure, the hydrogen-oxygen ratio, and the temperature to which the products are cooled. It has been seen that at very low pressures hydrogen peroxide is apparently not formed by homogeneous reactions and none is obtained even by the most rapid cooling of the reaction products to room temperature. As the pressure is increased, homogeneous formation occurs to an increasing extent, and small yields of hydrogen peroxide may be obtained by cooling to room temperature, the yield increasing at super-atmospheric pressures.

At all pressures, the yield is substantially increased by cooling the products to temperatures well below ambient but this is offset industrially by the cost of low temperature refrigeration. Hydrogen peroxide may be obtained from substantially all ratios of hydrogen and oxygen, but the yields appear to be greatest with a large excess of hydrogen. At atmospheric and higher pressures it is desirable to use a mixture of hydrogen and oxygen lying outside the explosive composition limits (between 9.2 and 91.6% hydrogen at 1 atmosphere pressure) in order to decrease the hazards involved. At 1 atmosphere pressure a yield of 0.5% hydrogen peroxide based on hydrogen has been reported from a hydrogen-air flame quenched in water. Replacing the air with oxygen raised the yield to 2.5% (24). A process involving low temperature cooling (25) proposes the use of a non-explosive mixture of oxygen and hydrogen at 100 to 250 atmospheres pressure, this being cooled initially to a temperature slightly above the critical temperature (-80°C. at 100 atm. or -10°C. at 250 atm.) and conducted over platinized pumice stone, or "Eisenasbest," a fibrous silica formed in iron manufacture. Reaction may be initiated by electrical heating. The reaction products are quenched by introducing a stream of oxygen, hydrogen or nitrogen cooled to -80°C. or cooling may also be obtained by expansion to atmospheric pressure. It is interesting to note that this proposed technique of cooling avoids the problems which would be involved if the heat were transferred through a low-temperature cooling surface, from which the solid peroxide and water would need be continuously removed. The yields in the above process are reported to be 80 - 90 percent, based on the oxygen entering.

The continuous thermal reaction at atmospheric pressure and 500 - 625°C. was studied during the 1930's at the R. and H. (now the Electrochemicals) Division of the duPont Co., by passing mixtures containing 1 - 3% oxygen in hydrogen, or 1 - 3% hydrogen in oxygen or air through a Pyrex or silica tube and scrubbing the products with water at ambient temperature (26). The course of the reaction was very sensitive to surface effects, as has been found elsewhere. The selectivity of oxygen reacting to form hydrogen peroxide was greatest at the shortest reaction times at which, however, the peroxide gas-phase concentration was extremely low. The maximum readily reproducible volume concentrations were 0.04 to 0.06% hydrogen peroxide, obtained in hydrogen containing 3% oxygen; this corresponded to 20 - 30% of the oxygen reacting. Air containing 3% hydrogen gave about the same hydrogen peroxide gas-phase concentration, but at a yield of 10 - 15%. However for a technical process to be satisfactory it was estimated that a minimum volume concentration of 0.25 to 0.50% hydrogen peroxide vapor in the product gas must be achieved; otherwise the cost of heating and circulating the gas mixture is prohibitive.

Patents have been issued on methods for forming hydrogen peroxide by contacting hydrogen and oxygen in the presence of water with certain active metals such as palladium, but no experimental data were disclosed (27).

ELECTRIC DISCHARGE PROCESSES

Discharge in Water Vapor

The reactions of the products of an electrical glow discharge in water vapor have been studied by numerous investigators (28), and particularly by Oldenberg, Rodebush and their respective co-workers (29, 30, 31, 32, 33). An excellent summary and interpretation of the various experimental results to date is given in a paper by Rodebush, Keizer, McKee and Quagliano (33). The principal experimental results are as follows. The maximum yield of hydrogen peroxide occurs at a water vapor pressure of 0.1 - 0.2 mm. of mercury in the discharge tube, with as rapid a vapor throughput as possible, and with the products condensed as quickly as possible in a liquid-air cooled trap. If solid carbon dioxide is used instead of liquid-air, no hydrogen peroxide is obtained and frequently very little water. If the trap is maintained at liquid-air temperature but is separated from the discharge tube to allow an increased time for reaction, the amount of peroxide produced decreases to zero, and practically no water is condensed in the trap. If a liquid-air trap is placed adjacent to the electric discharge, practically all of the oxygen entering in the form of water is recovered in the trap as water or hydrogen peroxide.

Although complex ionization processes occur in the discharge, spectroscopic determinations indicate that the products of dissociation leaving the discharge tube are almost entirely atomic hydrogen and hydroxyl, both being uncharged, and no significant amount of atomic oxygen is obtained unless a very strong discharge is used at low pressures of water vapor. (The formation of atomic oxygen may also be detected by the appearance of an afterglow in the presence of nitric oxide.) With a discharge of moderate intensity, (e.g. 1000 volts at 60 cycles in a tube 30 mm. in diameter and 2 meters long), dissociation of water is complete, since essentially none is found in a condensation trap placed sufficiently far downstream. It is believed that the primary step in the formation of hydrogen peroxide here is by condensation of hydroxyl radicals on the walls of the liquid-air cooled trap and not by gas phase reactions. This is shown by the fact that yields as high as 60% hydrogen peroxide have been readily obtained and by the fact that absorption spectrum studies of Frost and Oldenberg (29) showed no trace of peroxide in the gas phase after passage of an electric discharge through water vapor, although their apparatus could detect partial pressures of hydrogen peroxide as low as 0.01 mm. mercury. Following the initial formation of H and OH in the discharge, the relative degree to which the three competing reactions:

$$H + OH \xrightarrow{surface} H_2O \qquad (17)$$

$$OH + OH \xrightarrow{surface} H_2O_2 \qquad (16)$$

$$H + H \xrightarrow{surface} H_2 \qquad (18)$$

occur on the cold wall of a trap presumably determines the composition of the products. The failure to obtain hydrogen peroxide at temperatures of -78°C. in the trap is attributed to the low condensation point of hydroxyl radicals since they do not form an associated condensed phase.

Numerous investigations confirm that the OH formed in the discharge disappears rapidly, thus suggesting a homogeneous mechanism. Three possibilities are:

$$OH + OH \longrightarrow H_2O_2 \qquad (16)$$

$$OH + OH \longrightarrow H_2O + O \qquad (19)$$

$$OH + OH \longrightarrow H_2 + O_2 \qquad (20)$$

In the studies of Rodebush et al, the fact that the yield of water and hydrogen peroxide decreased to zero as the distance from the discharge tube to the trap is increased, and the fact that no atomic oxygen could be detected under these conditions lead to the conclusion that only reaction 20 is involved at these low pressures. At higher total pressures, or under other conditions,

$$H + OH + M \longrightarrow H_2O + M \qquad (17)$$

may become important.

The rate of disappearance of OH radicals has been determined by measurement of the absorption spectrum at various time intervals following their production in an electric discharge (29, 30). OH radicals were found to persist for as long as 0.4 seconds when the discharge was passed through water vapor, but disappeared in less than 0.01 second if produced by a discharge in hydrogen peroxide, thus indicating their removal by reaction with hydrogen peroxide.

Reactions of Oxygen and Atomic Hydrogen

Concentrations of 20 to 50 percent of hydrogen atoms may be obtained by passage of an electric discharge through hydrogen, usually at pressures of about 1 mm. of mercury or less, and the atomic hydrogen thus produced may exist for considerable lengths of time before re-combination. Boehm and Bonhoeffer (34) and Geib and Harteck (35) studied the reaction of oxygen with atomic hydrogen at pressures of 0.1 to 0.5 mm. of mercury and at wall temperatures from 30°K. to 200°K. The product was essentially 100% H_2O_2 at 30°K. but the yield decreased at higher wall temperatures and became negligible at about 200°K. These authors reported that their product vigorously evolved oxygen when warmed to about -115°C. and suggested that hydrogen peroxide of a different structure than normal (written by them as $H_2O \longrightarrow O$) was first produced, which then decomposed on warming to -115°C.

A similar phenomenon was observed by Jones and Winkler (36) on the condensed products from water vapor dissociated by an electric discharge. Products collected at trap temperatures below -150°C. evolved oxygen when warmed above -120°C., leaving water and hydrogen peroxide in the trap.

This same phenomenon has also been observed very recently by Giguere, Secco, and Eaton (37), who have compared their product to deuterium peroxide formed in the same manner, and have also studied the infra-red spectra of both. Their studies indicate that the deposit contains some normal hydrogen peroxide plus something else which has not been identified with certainty but which is transformed irreversibly into normal hydrogen peroxide at -115°C. No clear and positive evidence has yet been developed to support the Geib and Harteck hypothesis that an abnormal form of hydrogen peroxide is actually formed.

Geib and Harteck proposed that hydrogen peroxide was formed in their experiments by

$$O_2 + H + M \longrightarrow HO_2 + M \qquad (6)$$

followed by

$$HO_2 + H + M \longrightarrow H_2O_2 + M \qquad (21)$$

$$\text{or} \quad HO_2 + HO_2 + M \longrightarrow H_2O_2 + O_2 + M \qquad (12)$$

where M may be a third molecule or (most likely) the wall. The authors favored these reactions over reactions 1, 2 and 3, because the latter group is believed to require substantial activation energy. As the wall temperature is raised, it was postulated that the HO_2 or H_2O_2 molecules cannot transfer enough energy to the wall to become stabilized and H_2O, O or OH are formed instead. However, it is also possible that OH could be formed by the homogeneous reactions 2 and 3, followed by their diffusion to the wall where they will react to form hydrogen peroxide if the temperature there is sufficiently low.

Badin (22) has reported the results of similar studies of the molecular oxygen-atomic hydrogen reaction at a pressure of 0.27 mm. of mercury, and using a large excess of atomic hydrogen. He found that for constant surface conditions the rate of formation of hydrogen peroxide is proportional to the oxygen concentration, over a considerable range, and the results were not affected by passing the oxygen as well as the hydrogen through the electric discharge. The rate data are consistent with the mechanism of equation (6) followed by (21).

At a condensing temperature of -196°C. all the inlet oxygen appeared as water and hydrogen peroxide, which were formed in about equimolar quantities. At higher condensing temperatures, water increased and peroxide decreased until at -79°C. no peroxide was formed. Increasing the distance between the point of mixing and the condensing trap reduced the hydrogen peroxide found to a trace while the amount of water formed was only slightly changed. These results are similar to those which have been found on passing an electric discharge through water vapor (see below).

In order to account for the simultaneous formation of water with hydrogen peroxide, Badin proposed the reaction

$$HO_2 + H \longrightarrow [HO - OH]^* \qquad (21a)$$

which competes with reaction 21 in consumption of HO_2 radicals. The $[HO - OH]^*$ is analogous to the activated HO_2^* proposed by Egerton and Minkoff and may be either stabilized on a cold surface or split into two OH radicals which then form water by

$$H + OH + M \longrightarrow H_2O + M \qquad (17)$$

The activation energy required for the reaction $H_2 + HO_2$ makes it less likely than 17. However, since the amount of water formed does not increase with reaction time, some OH must also disappear by

$$OH + OH \longrightarrow H_2 + O_2 \qquad (20)$$

The character of the surface in the zone of reaction was found to have a marked effect on the amount and nature of the condensable products, as would be expected at very low pressures. The amount of condensable products in a liquid-air trap downstream from the reaction zone decreased with increasing wall temperature in the reaction zone. At surface temperatures between 0 and 250°C., a potassium chloride surface practically eliminated hydrogen peroxide, a Pyrex surface gave an intermediate amount of peroxide which decreased with temperature, and a surface treated with phosphoric acid gave the maximum formation of hydrogen peroxide, substantially unaffected by temperature and about ten times that obtained with potassium chloride. Badin suggests that the surface effects are associated in some way with the amount of water present on the surface, a chloride surface being "dry" and phosphoric acid being "wet." The decrease of condensable products with increased wall temperature must be due to the reforming of hydrogen and oxygen from OH or HO_2.

Little or no reaction has been observed if atomic oxygen is produced in a discharge tube and then is mixed with molecular hydrogen, even if the reacting gases are cooled in a liquid-air trap. If any reaction does occur, water is formed, and not hydrogen peroxide. Apparently the recombination reaction of oxygen atoms is much more rapid than their reaction with hydrogen. Because of this fact and the stronger bond in the oxygen than in the hydrogen molecule, it would be expected that passage of an electric discharge through a mixture of excess hydrogen and oxygen should give about the same results as passage through hydrogen alone followed by mixing with molecular oxygen.

Passage of an electric discharge through air or oxygen containing water vapor also produces hydrogen peroxide (2) but in smaller yields than are obtained by using a mixture of hydrogen and oxygen containing a large excess of hydrogen.(see below). This is attributed to a rapid decomposition of the hydrogen peroxide by the ozone which is simultaneously formed. The use of an excess of oxygen in a hydrogen-oxygen mixture gives low yields of hydrogen peroxide, presumably for the same reason.

Manufacture by Electric Discharge

It has been seen that hydrogen peroxide cannot be produced by passage of an electric discharge through a hydrogen-oxygen mixture at low pressures (about 1 mm. of mercury) except by wall reactions occurring at surface temperatures well below -79°C. Interest in the industrial potentialities of such a process is therefore directed to reactions at about atmospheric pressure, at which hydrogen peroxide is apparently produced by homogeneous reactions and can be removed by cooling to room temperatures. Here the use of gas mixtures containing less than about eight to ten mole percent of oxygen is recommended in order to be outside the explosive range of composition. Although at 1 atmosphere pressure increased yields of hydrogen peroxide are obtained by cooling to sub-atmospheric temperatures (38), as in the thermal reaction of hydrogen and oxygen, this does not sufficiently compensate for the high cost of such low temperature refrigeration. In all cases an electric discharge of the corona or brush type is desired rather than an arc type breakdown of the gas. Proposed processes have been patented by Dawsey (39) and studied by the I. G. Farbenindustrie at Leverkusen, Germany (24), but the greatest progress thus far towards commercial feasibility was probably made in the studies of J. Krutzsch at the Electrochemische Werke, Munich, Germany, from 1931 to 1945 (40).

Experimental studies were carried out on a small laboratory apparatus of 4 - 20 watts power, used primarily to study the effect of variation of gas composition, temperature, voltage, frequency, etc., and some studies were also made with a 10 kilowatt apparatus. A 100 kilowatt pilot plant was almost completed but never operated due to military action. The proposed process has been described by Krutzsch in terms of a 2000 kilowatt plant, to produce 100 kg./hour of 10 wt. % hydrogen peroxide, the design and predicted operating characteristics being based on a scale-up from the results of studies on the 4 - 20 watt and 10 kilowatt pieces of apparatus.

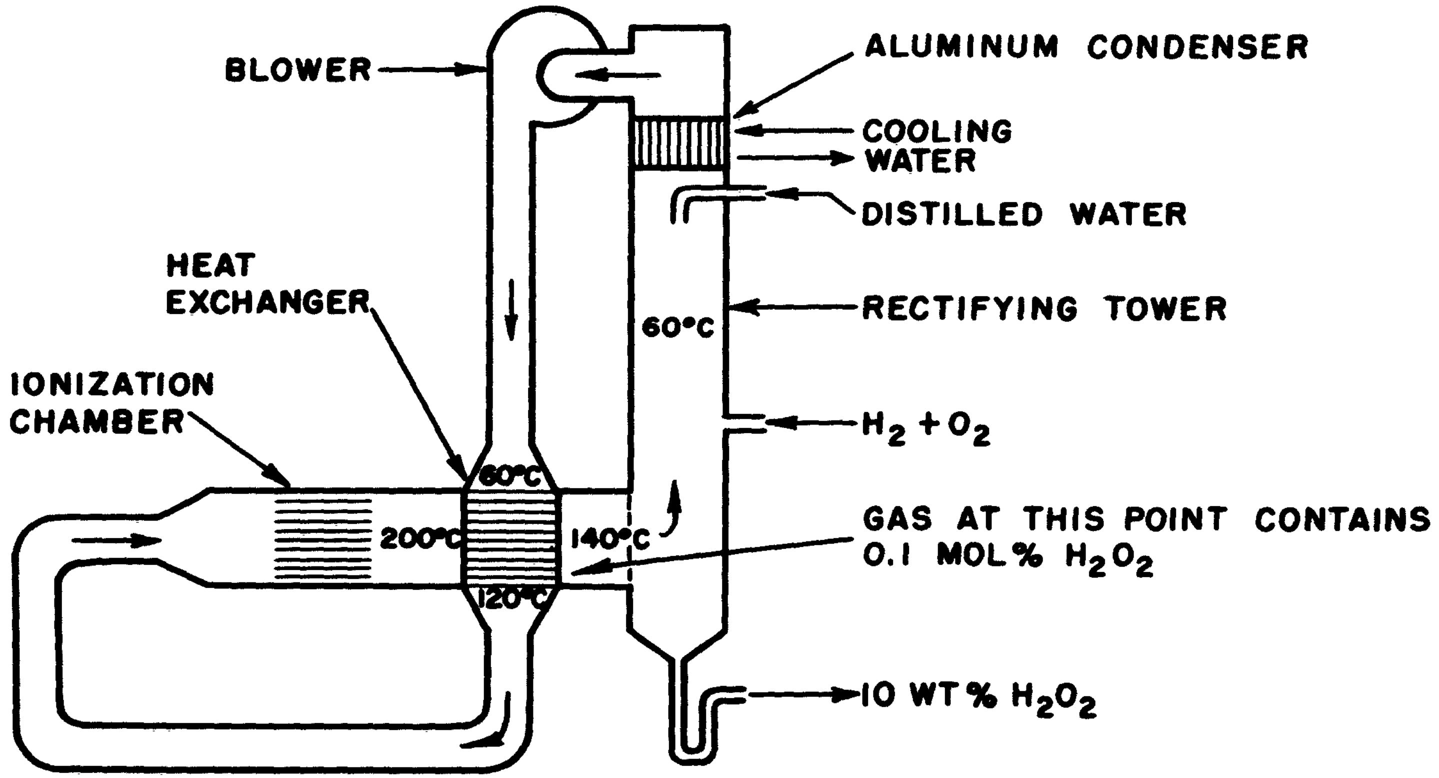

FIG. 3–THE KRUTZSCH ELECTRIC-DISCHARGE PROCESS

A gas mixture containing 95% hydrogen, 5% oxygen and some water vapor is circulated through the apparatus at slightly above atmospheric pressure by a blower, (see Figure 3). The gases are heated by a heat exchanger and then enter the ionization chamber. This is essentially a high capacity condenser consisting of a large number of quartz plates each 5mm. thick, and 50 cm. square, coated on one side with an electrically conducting layer consisting of high purity aluminum and etched on the other side by treatment with hydrofluoric acid. The aluminum sides are placed back to back and the gas flows through 5 mm. spaces between the non-conducting surfaces, the plates plus the spacers being built up as in a sandwich, two plates per spacer. The plates are connected electrically in parallel and an alternating potential of 12,000 volts and 9,500 cycles/second is applied. The electric discharge appears at a power of 0.96 kilowatts per pair of plates. The gases from the ionization chamber are cooled in the heat exchanger and then enter a rectifying column made of stoneware and packed with glazed porcelain rings. Distilled water is added at the top and cooling supplied by a pure aluminum condenser. The cooling water rate in the condenser controls the temperature and thereby the water vapor content of the recycled gases. Make-up hydrogen and oxygen are added and peroxide-free gases are recycled by the blower. The point of introduction of the gases is unimportant since the composition change per pass is very low.

Studies on the 20 watt laboratory apparatus showed a maximum yield of hydrogen peroxide per quantity of energy consumed at an average temperature of 160°C. in the ionization chamber and with water vapor present in an amount corresponding to a saturation temperature of 60°C., and these conditions were recommended for use in the large plant. The gas temperature was expected to rise from 60°C. to 120°C. in the heat exchanger, and then to 200°C. in the exit from the ionizer. Although energy yields were a maximum in the laboratory apparatus at a frequency of 1000 cycles/second, the lowest studied, the use of 9,500 cycles/second was recommended for the larger plant, apparently in order to decrease the quantity of expensive quartz plates required for a given production capacity.

It was reported that the energy yield increased with decreasing average peroxide concentration in the gases, which presumably occurred when a decreased residence time was used in the ionizer and thereby a lower degree of reaction. At the recommended operating conditions, 70 moles of hydrogen peroxide were produced per 30 moles of water, but the conversion per pass was so low that the peroxide concentration in the gases entering the rectifying column was only 0.1 percent. At optimum conditions there was obtained an ionizer efficiency of about 40 kw. hours per kilogram of hydrogen peroxide produced (calculated as 100% H_2O_2). The following energy consumptions were quoted by Krutzsch for the 2000 kw. plant, allowing for the inefficiencies in electrical conversion, and assuming the hydrogen and oxygen were produced by electrolysis.

ionization	2560 kw.
electrolysis	469 kw.
blower	98 kw.
auxiliary equipment	5 kw.
	3132 kw.

or 62.6 kw. hour/kg. H_2O_2

The concentration of hydrogen peroxide leaving the tower is determined by the amount of water introduced below the condenser. A 10 wt. % hydrogen peroxide solution could be easily obtained, but operation to produce higher concentrations significantly increased the amount of decomposition in the tower.

The heat exchanger is a very critical part of the plant. Although it increases the heat economy of the process, a substantial amount of the hydrogen peroxide formed may decompose in the exchanger before reaching the rectifying tower. This was shown to be a surface effect; increasing the surface about eight-fold at constant volume decreased the amount of peroxide recovered by about 20%, but increasing the residence time in the exchanger from 0.35 sec. to 1.1 sec. and keeping the amount of surface at a constant low value had no effect on the amount of peroxide recovered. In order to reduce the decomposition to a minimum, an extremely high purity (99.9%) aluminum was required. The amount of decomposition on wet surfaces is generally far below that on dry surfaces, apparently due to the protective effect of the liquid film. Direct quenching of the gases from the ionizer would possibly eliminate these difficulties, but gas preheating would then require a large amount of energy because of the high recycle rate per quantity of peroxide produced.

The energy yield and selectivity of hydrogen conversion to hydrogen peroxide varied strongly with both the water content of the hydrogen-oxygen mixture and the temperature in the ionizing chamber. However, the water vapor concentration giving the maximum energy yield did not necessarily correspond to that giving maximum selectivity of hydrogen to hydrogen peroxide.

A wide variety of dielectric materials were studied for their effect on the energy yield of hydrogen peroxide; quartz plates were about the most satisfactory. "Luvican" plates (N-polyvinylcarbazole) gave higher energy yields than quartz but could not be heated above 150°C. It was found that with good insulating materials, the surface properties of the dielectric had a much more important effect on the energy yield than the internal properties and that the effect of the surface of the dielectric seemed to be due principally to its influence on the electric discharge and not on the decomposition of hydrogen peroxide vapor. A wide variety of surface coatings on quartz were studied but most of these were organic and deteriorated.

Operation of the process at 1.5 atmosphere pressure was reported as being less efficient than 1 atmosphere pressure, and the use of a gas mixture containing 8.8% argon on a dry basis was reported to increase the yield slightly.

The capital investment for the Krutzsch process is of the order of that required for the electrolytic processes, but labor requirements are low, and the equipment does not deteriorate rapidly. The large quantities of cooling water required in the electrolytic process are not needed here and the cost of production would not vary greatly with size, in comparison with electrolytic plants, so that the discharge process might be of interest for small plants. The hydrogen peroxide produced by this process was of high purity since no chemicals other than hydrogen and oxygen are used, and it was found to have a good stability on storage. However, at the present state of development, the high electrical consumption makes the process of commercial interest only where very cheap power is available. Nevertheless, it is possible that the total cost of the process could be significantly reduced by modifications, such as operating the ionizer at lower frequency and using plates of a cheaper material giving higher yields than quartz, for example, plastics which are stable at relatively high temperatures. Krutzsch indicated that operation at sub-atmospheric pressure might be most efficient, and it is also possible that additions of other materials than argon to the gas stream might be effective.

In the electric discharge studies at I. G. Farbenindustrie, Leverkusen, an apparatus was used consisting of a central glass tube carrying a platinum wire immersed in water (i.e., tube full of water) forming one pole, which was then placed in a wider glass tube, water jacketed, which formed the other pole. The preferred annular separation was 0.5 mm., but it could be increased to 2 - 6 mm. The most favorable results were obtained with a gas mixture containing 4 to 6% oxygen, the remainder being hydrogen. Water vapor in the gas improved the yield but this may have been in part due to the more rapid removal of hydrogen peroxide from the system by its being washed out with the water condensed simultaneously. The energy yields of this process at optimum conditions were substantially less than those obtained by Krutzsch and it was regarded as being generally less satisfactory.

Hydrogen peroxide or peroxy compounds are also formed if a spark or glow discharge is struck between an electrode and an aqueous solution of an electrolyte or if both electrodes are placed in the gas phase near the surface of the liquid (41). The yield of hydrogen peroxide is frequently in substantial excess to that corresponding to Faraday's law, and varies with the nature of the electrolyte, the pH of the solution, the nature of the gas surrounding the electric discharge and its pressure, and the direction of flow of the electric current. With sulfuric acid in the presence of oxygen, Klemenc (42) reports that hydrogen peroxide, H_2SO_5, and $H_2S_2O_8$ may be formed in yields of about three times that corresponding to Faraday's law, or up to twelve times if sodium stannate is added, which acts as an inhibitor for peroxide decomposition. The results are difficult to interpret in terms of fundamental mechanisms since hydrogen peroxide may be formed in the vapor phase, or by combination of gaseous ions with electrolytic ions opposite sign, or by electrolytic processes, and may disappear by gas or liquid phase decomposition, the rate of the latter being affected by such variables as pH, temperature, nature of solutes present and the catalytic nature of the electrode submerged in the solution. There is a sharp potential drop at both electrodes; in Klemenc's apparatus this was about 400 volts at the cathode and 70 volts at the anode. Accordingly power consumption is much greater than that in the electrolytic processes or even in Krutzsch's gaseous discharge process. In similar studies reported by A. Muta (43), the hydrogen peroxide yield was 9 gm./kw.hr.

The glow discharge electrolysis has been recently investigated by Davies and Hickling (44) who used a set of conditions which was sufficiently simple to yield reproducible results and to permit considerable fundamental interpretation of the data. An electrical discharge was passed at reduced pressure between the liquid surface of a dilute solution of an inert electrolyte, and an anode withdrawn from the solution. Here the amount of hydrogen peroxide formed initially was directly proportional to the quantity of electricity passed and essentially independent of the current density, electrolyte volume, and various other factors affecting the nature of the discharge, although the initial yield varied with the concentration of electrolyte and pH. The yield dropped as each experiment proceeded, due to decomposition of the hydrogen peroxide formed, and none was detected if a highly alkaline solution were used. The results were consistent with the assumption that the discharge is primarily through water vapor and that the ions in the gas phase generated hydroxyl radicals in the liquid water mainly by electrolytic action. The hydroxyls are then postulated to dimerize to form hydrogen peroxide, which in turn would be destroyed by further reaction with hydroxyl radicals.

IRRADIATION PROCESSES

Processes induced by radiation may be divided into two groups generally designated respectively as photochemical and radiochemical.

Photochemical processes are those in which absorption of radiation leads to the formation of excited molecules which then initiate secondary reactions involving atoms, free radicals or molecules. The extent and character of the initial reactions is usually highly specific to the wave length, and thereby the quantum energy of the radiation. The radiation must usually be in the ultra-violet spectral region for photochemical processes to occur. Radiochemical processes, on the other hand, proceed from the absorption of higher energy radiation such as X and γ , or cathode rays, and fast particles such as protons, α , and β rays, generally termed "ionizing radiations." Here a certain proportion of the energy absorbed produces excited molecules or radicals, but the remainder produces ion pairs, which then generate more free radicals and atoms. Radiochemical processes are characterized by the appearance of ionization and results which are in general independent of the energy of the individual particle or quantum and dependent instead on the total energy absorbed. The initial processes occurring under ionizing radication therefore involve the simultaneous formation of both charged and uncharged species and are far more complex than those occurring in photochemical initiation. However, the reactions following the initiation processes are generally similar in nature, with the effects being more pronounced, the greater the energy of the radiation.

Photochemical Reaction of Hydrogen and Oxygen

The formation of hydrogen peroxide on ultra-violet radiation of hydrogen-oxygen mixtures will be considered first. Coehn and Grote (45) were able to detect the formation of a small amount of hydrogen peroxide on passing a hydrogen-oxygen mixture rapidly through an irradiated quartz vessel, but none was detected in a slow passage or in a static experiment. The very low peroxide concentrations produced are probably a consequence of the hydrogen peroxide absorbing radiation at least as readily as the original hydrogen and oxygen, with subsequent destruction of the excited molecule. For this reason, and since only that radiation which is absorbed is effective in causing reaction, most of the studies have been made with the addition of a photosensitizing agent which has a higher absorptivity than the hydrogen-oxygen mixture alone. Mercury vapor has been extensively used as a sensitizer because of its strong absorptivity for the wave length 2537 Å which can be readily produced by a mercury vapor discharge tube. Even at the low mercury vapor pressure existing at room temperature (*e.g.*, 0.0028 mm. mercury at 30°C.) the intensity of incident radiation is reduced to one half by passage through a depth of only a few millimeters of the mercury vapor. The excited mercury atoms in turn transfer their energy by collision with the other species present.

Although a number of studies of the mercury-sensitized hydrogen-oxygen reaction have been reported (46, 47, 48, 49, 50) the results of a given experimenter may vary considerably from run to run, and the results of different investigators are often difficult to reconcile.

In the more recent studies, mixtures of hydrogen and oxygen were dried, saturated with mercury vapor at room temperature and then passed continuously through a quartz tube which is of sufficient diameter that the mixture of hydrogen, oxygen and mercury vapor will absorb practically all of the 2537 Å light entering. This tube in turn was irradiated by a mercury vapor lamp. Water and peroxide were removed from the effluent gases by cooling in a trap surrounded by liquid air or solid carbon dioxide or by bubbling through water. The amount of incident light (assumed to be completely absorbed) and thereby the quantum yield of the reaction (number of molecules formed per quantum of energy absorbed) is determined against some standard; for example, uranyl oxalate has been used as an actinometer. The reaction vessel is filled with an uranyl oxalate-oxalic acid solution and the amount of radiation entering in a known period can then be calculated from the known reaction characteristics of this system. In general, maximum yields of hydrogen peroxide have been obtained at hydrogen-oxygen ratios of 5 to 10. More than 90% of the oxygen reacting was converted to hydrogen peroxide in some of the experiments, but this varied considerably in different runs and in different investigations, due possibly to variable decomposition of HO_2 or hydrogen peroxide by mercuric oxide or mercury which may deposit on the tube walls.

Quantum yields for the overall reaction of hydrogen and oxygen have been reported by Marshall (46) as about 6.6, later revised to 2.5; Frankenburger and Klinkhart (49) reported quantum yields of about 1, but they measured the amount of light absorbed in their reaction vessel using monochloracetic acid as an actinometer and another study (51) on the properties of monochloracetic acid shows that their quantum yield was actually substantially less than unity. In the most recent work of Volman (50) quantum yields of about 0.3 - 0.5 are reported for the overall reaction. These results indicate that at least at room temperatures, the hydrogen-oxygen reaction at one atmosphere pressure may involve short chains or possibly none at all, although as the temperature is increased to approach the explosion limit, undoubtedly chain length also increases. It is important to note that except for the photochemical initiation of the reaction, the characterisitcs of particular reaction steps would be expected to be the same here as for the thermal reaction under the same conditions.

In studies with mixtures containing 1 - 3% oxygen, Frankenburger and Klinkhardt (49) reported hydrogen peroxide yields of up to 20 gm. of hydrogen peroxide per k.w. hour of electricity supplied to the lamp. The mercury vapor lamp radiated up to 5% of the electrical energy input as resonance light of 2537 Å. The hydrogen peroxide yield was unaffected by temperature variation between 50 and 200°C., and pressure changes from 1 to 11 atmospheres. However, it is highly unlikely that pressure and temperature would be unimportant at higher oxygen concentrations. Volman's studies at atmospheric pressure and 40°C. showed little change in the total moles of water plus hydrogen peroxide formed with variation in hydrogen-oxygen ratio from about 0.5 to 10. The hydrogen peroxide yield was lowest at low hydrogen-oxygen ratios, but did not increase significantly with an increase in the ratio above about 2.

The first step of the photochemical reaction initiated by 2537 Å radiation is frequently postulated as the formation of hydrogen atoms from a hydrogen molecule by collision with a mercury atom excited by the absorption of a quantum of energy. The postulate is based on the fact that the quantum energy (112 kcal./g. mole) is sufficient for disruption of the hydrogen molecule bond (103 kcal./g.mole) but not the oxygen molecule bond, (116.4 kcal./g. mole). However, species such as H_gH, H_gO, H_gOH, or ozone may also be formed from the initial excited mercury atom (52), so the character of the initial reaction is far from settled.

Nevertheless, the low quantum yield does indicate that the formation of hydrogen peroxide probably proceeds largely by reactions such as

$$HO_2 + HO_2 + M \longrightarrow H_2O_2 + O_2 + M \qquad (12)$$

or

$$H + HO_2 + M \longrightarrow H_2O_2 + M \qquad (21)$$

where M is the wall or a third body, rather than by reactions producing a free radical or atom as one of the products. Since high yields of hydrogen peroxide have been obtained under some circumstances, it is probable that water is formed primarily by destruction of HO_2 or hydrogen peroxide, which may occur on mercury and its compounds, by wall reactions, or by further gas-phase reactions, possibly involving ozone. It is known that ozone is formed by ultraviolet irradiation of oxygen, and Volman (50) has shown that ozone and peroxide react rapidly in the gas phase.*

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* Several studies of the ozone-hydrogen peroxide reaction in aqueous solution have been reported, the most extensive of which was that of T aube and Bray (53), who proposed the following mechanism:

(1) $H_2O_2 + O_3 \longrightarrow OH + HO_2 + O_2$ (22)

(2) $HO_2 + O_3 \longrightarrow OH + 2\,O_2$ (23)

(3) $OH + O_3 \longrightarrow HO_2 + O_2$ (24)

(4) $OH + H_2O_2 \longrightarrow HO_2 + H_2O$ (25)

The proposal by earlier investigators that hydrogen peroxide is formed via

$$2\ OH + M \longrightarrow H_2O_2 + M \qquad (16)$$

is now untenable (20).

Other possible explanations for the low quantum yield here are the deactivation of excited mercury atoms without production of hydrogen atoms, combination of hydrogen atoms to form hydrogen on the wall, or the reforming of hydrogen and oxygen by gas-phase reactions such as

$$OH + OH \longrightarrow H_2 + O_2 \qquad (20)$$

the OH coming from the decomposition of hydrogen peroxide or the hydrogen peroxide-ozone reactions. The disappearance of hydrogen peroxide and HO_2 may also occur by wall reactions involving mercuric oxide or H_gOH as intermediates.

The non-sensitized reaction of hydrogen and oxygen has been studied most recently in a flow apparatus by Smith and Kistiakowsky (54) and Smith and Napravnik (55) using ultraviolet light in the spectral regions 1719 - 1725 Å, and 1850 - 1862 Å, total pressures of from 1140 to 95 mm. mercury, and mixtures of all compositions of hydrogen and oxygen. The products consisted of ozone, hydrogen peroxide and water. Lowering the oxygen concentration increased the quantum yields of hydrogen peroxide and water; increasing the oxygen concentration increased the quantum yield of ozone. Lowering the pressure below 1140 mm. mercury at constant gas composition increased the water and hydrogen peroxide yields and decreased the ozone yield, with the effect being particularly pronounced at the lowest pressures studied. At a constant pressure of 190 mm. mercury, increasing the temperature from 25 to 280°C. decreased the quantum yield of ozone (until none was detected with a hydrogen-oxygen ratio of 9 at

150°C. and increased the quantum yield of water and hydrogen peroxide with the temperature coefficient of the quantum yield increasing very rapidly at temperatures of 230 - 280°C.

At the pressure of 190 mm. mercury, maximum quantum yields of hydrogen peroxide were obtained with the minimum oxygen concentration studied (10%) but the ratio of moles of water formed to moles of hydrogen peroxide formed remained approximately 5 to 10 as the temperature and pressure were varied.

The sudden rise in quantum yield with temperature found by Smith and Napravnik is similar to that reported by Taylor and Salley (56) for the mercury-sensitized reaction at 1 atmosphere pressure and near 300°C. and by others who have studied the thermal reactions. It is indicative of the lessening importance of non-chain reactions such as 12 and 21 and the increasing importance of chain carrying reactions such as

$$HO_2 + H_2 \longrightarrow H_2O_2 + H \qquad (11)$$

and $$HO_2 + H_2 \longrightarrow H_2O + OH \qquad (10)$$

and of two-body branched-chain reactions,

$$H + O_2 \longrightarrow OH + O \qquad (2)$$

and $$O + H_2 \longrightarrow OH + H \qquad (3)$$

followed by

$$OH + H_2 \longrightarrow H_2O + H \qquad (1)$$

These also probably account for the increase in quantum yield with lower pressure, at a constant temperature.

The reaction mechanism here differs from that in the mercury-sensitized reaction in that the primary step in absorption of the 1862 - 1854 Å radiation is probably the formation of excited oxygen molecules, while the 1725 - 1719 Å radiation dissociates oxygen molecules directly into one normal plus one excited oxygen atom. This is presumably followed by interaction of oxygen atoms with molecules of oxygen and hydrogen by reactions such as have been specified previously for the thermal reaction. Ozone is presumably formed by

$$O + O_2 + M \longrightarrow O_3 + M \qquad (26)$$

or by collision of an excited oxygen molecule with a normal oxygen molecule. The fact that with increasing temperature the ozone disappears before the rapid rise in temperature coefficient occurs, clearly indicates that its disappearance is in no way related to the appearance of long chains as the temperature is increased.

A number of other materials besides mercury would be expected to act as sensitizers for the hydrogen-oxygen photochemical reaction if they have a sufficiently high absorptivity in this spectral range.

Little work has been done on this subject, but it is possible that substances such as the halogens, hydrogen halides, hydrogen sulfide, ammonia, and nitrogen dioxide might be effective, since they will dissociate under ultraviolet radiation to yield H, O or other atoms (52, 57) which might then initiate further reactions of hydrogen and oxygen. The mechanism here, of course, would be different than with mercury vapor since the sensitizer itself is destroyed in the process of generating the free radicals and atoms although the halogens or the hydrogen halides might be reformed by other reactions after dissociation.

Photochemically activated atoms of the inert gas, xenon, might also be effective since they bring about dissociation of molecular hydrogen to hydrogen atoms in similar fashion to mercury (52).

$$Xe + h\nu \longrightarrow Xe^*$$

$$Xe^* + H_2 \longrightarrow Xe + 2H \qquad (1)$$

Small amounts of hydrogen peroxide have been detected by Kernbaum (58) on ultraviolet illumination of water for ten hours. According to Tian (59) a steady-state hydrogen peroxide concentration is developed on exposure of water to 1900 Å light, the magnitude of which is increased if oxygen is dissolved in the water.

In this connection it is interesting to note that small amounts of hydrogen peroxide (0.04 - 1 mg./liter) are claimed to have been found in rain, snow, fog, dew, etc. by a number of investigators, although the analytical procedures are open to doubt. For example, Schöne (60) in Moscow in the 1870's reported that rains produced from polar winds contained less "peroxide" than those from the south, that rain falling in the summer contained more "peroxide" than that falling at autumn, and that the "peroxide" content of water vapor condensed from the air increased in amount as the sun rose over the horizon. Schöne's conclusion that the phenomenon observed is due to the action of the sun's rays seems quite reasonable. H. Matsui (61) recently reported similar results from a study in Japan; rain water was reported to have 0.35 - 0.86 mg. H_2O_2 per liter while water from snow had 0.08 - 0.15 mg./l. and this content apparently varied with the strength of ultraviolet radiation at the time of sampling. However the analytical techniques used for the detection of peroxide in the above studies involved the oxidation of an iodide salt to free iodine, the quantity of which was then determined by a colorimetric technique. Unfortunately other oxidizing agents such as ozone, nitrites, and nitric oxide, would also give the same reaction, as discussed in Chapter 10, so the actual character of the oxidizing species present is still uncertain. It is known that ozone and nitrogen oxides are formed in the atmosphere, and in industrially-polluted air there may also be sulfur oxides, as well as organic peroxy compounds (62). The solution in water of oxygen increases the amount of hydrogen peroxide formed on ultraviolet illumination, a phenomenon also observed with ionizing radiation. Hydrogen peroxide has also been reported as forming on photochemical oxidation of oxalates in the presence of manganous ion (Mn^{++})(63) and of paraldehyde (64), and on irradiation of aqueous solutions of potassium iodide and potassium bromate (65).

Several white pigments are claimed to act as sensitizers for a number of photochemical processes; thus the formation of hydrogen peroxide from water has been reported to be sensitized by zinc oxide and zinc carbonate as well as CdO, SnO_2, and ThO_2. A number of attempts have been made to correlate the photochemical activity of such pigments with the degree of chalking or "weathering" of paints in which they are incorporated, but with little success thus far. Zinc oxide has been studied most frequently and its effect has been found to extend from the ultraviolet to the visible range of 4000 - 4700 Å. However, zinc compounds are known to have a stabilizing effect on the decomposition of hydrogen peroxide in storage and these results may represent at least in part merely the variable degrees of preservation of hydrogen peroxide formed. Increased amounts of hydrogen peroxide are found on the further addition in the presence of zinc oxide, of a wide variety of organic compounds, of which the following have been cited (66); glycerol, glucose, glycine, dextrose, benzidine, ethylamine, phenol, acetone, alcohol, acetic and benzoic acid, and inorganic substances like sodium hydroxide. Hydrogen peroxide concentrations of the order of 10^{-5} and 10^{-6}g.moles/liter are formed.

The effect of many of these organic materials may be primarily that of stabilizing the hydrogen peroxide after it is formed, since the highest peroxide concentrations were found with substances like phenol and acetanilide which are known effectively to inhibit the photochemical and thermal decomposition of hydrogen peroxide. However, it is also probable that some hydrogen peroxide is formed via photochemical autoxidation of the organic molecules. Hydrogen peroxide is also formed on exposure to ultraviolet light of solutions or suspensions of biological sensitizers such as dried yeast extract and chlorophyll (67); again photochemical autoxidation of the organic substances probably accounts for at least a part of the hydrogen peroxide formed.

Effect of Ionizing Radiation

The large variety of processes which may occur when water in the liquid or vapor phase or aqueous solutions are subjected to ionizing radiation make it difficult to interpret the various observations which have been made of the formation of hydrogen peroxide by such bombardment. Much of the early knowledge of the processes involved is the result of studies by H. Fricke and collaborators (68). The present state of knowledge of this field has been recently presented by Allen (69, 70), Dainton and Collinson (70, 71), Krenz (72), Burton (70) and in a series of papers by a group of investigators in France (73 - 77). The bombardment of water by all types of ionizing radiation results in the ultimate formation of hydrogen and oxygen gases and hydrogen peroxide. It has been generally believed that the oxygen is produced from secondary reactions involving hydrogen peroxide decomposition. For example, Allen (69) has shown that with fast electron or atomic pile radiation (fast neutron plus γ radiation), very short exposures produce hydrogen peroxide but no oxygen; the oxygen appears only on longer exposures. On the other hand Lefort (73) reports that on α-ray bombardment of water, yields of hydrogen peroxide and oxygen are constant throughout an initial period of the reaction, indicating that they are both formed initially in the decomposition of water. With x-ray bombardment, the amount of hydrogen peroxide formed is greatly dependent on the amount of oxygen dissolved in the water.

It has been found that the heavy particles from radioactive sources are much more effective than x- or γ-radiation, per quantity of energy absorbed, in producing chemical change in water. Thus x-ray radiation produces only minute amounts of decomposition of pure water (free from oxygen) while for higher energy radiation, Allen reports the following values for molecules of liquid water decomposed per 100 e.v. of energy absorbed, as calculated from the quantity of hydrogen gas evolved: 0.1 - 0.4 for tritium β radiation (about 5 k.e.v.), 0.2 - 0.5 for 1 m.e.v. electrons, 0.54 for 8 m.e.v. deuterons, about 1 for atomic pile radiation, (mixed γ rays and fast neutrons), and 2.0 for α rays.

The reactions which occur under ionizing radiation are not well understood. At present there is no known way of measuring the number of ion pairs (positive ion plus an electron) formed per quantity of ionizing radiation absorbed in water. It is generally postulated that about half of the energy absorbed goes to the formation of electronically excited water molecules and the other half of the energy forms ion pairs. This proceeds from the assumption that the same amount of energy, namely 30 - 35 electron volts, is needed to produce one ion pair in liquid water as is required in air. Since roughly one half this amount of energy is needed to ionize one water molecule, the other half is assumed to be dissipated in the form of activated water molecules. Some of these activated water molecules are deactivated by collisions, others may form H and OH radicals. However the probability is high that the radicals formed by dissociation of an activated water molecule, being close together, would immediately recombine to form water.

The extent to which OH and H radicals from activated water molecules may take part in other reactions is unknown but is believed to be slight. However, the reactions proceeding from the ionized water molecule and the ejected electron are more significant, although the mechanisms proposed are still speculative. The first reaction of the ionized water molecule, H_2O^+, is generally postulated as

$$H_2O^+ + H_2O \longrightarrow H_3O^+ + OH$$

$$\text{or} \qquad H_2O^+ \longrightarrow H^+ + OH$$

The electron is usually postulated as being captured by

$$H_2O + e^- \longrightarrow H + OH^-$$

although Haissinsky and Magat (74) propose that instead the following reactions proceed:

$$H_2O + e^- \longrightarrow H_2 + O^-$$

$$O^- + H_2O \longrightarrow OH + OH^-$$

This proposal is supported by some experimental results. Secondary reactions involving neutralization of charged particles and reactions between charged particles and uncharged particles or molecules are believed to produce more H and OH radicals which may then recombine to form water, or to form hydrogen or hydrogen peroxide. Oxygen may then appear from reactions involving hydrogen peroxide.

The marked effect of type of radiation on the energy yield in water decomposition probably lies in the degree of separation between the H and OH radicals produced in the ionized path (71) or abnormal distribution of the H and OH radicals. For example, it has been proposed that the positive ions formed along an α -, p- or d- particle track each rapidly dissociate into H^+ and an OH radical, while the electron from the primary process is not captured until it has traveled some distance from the path. This results in an excess of OH radicals along the center of the track and an excess of H radicals in the area surrounding the center, which increases the probability of combination of two OH radicals to form hydrogen peroxide, and two H atoms to form hydrogen molecules. With x-, γ - and β -rays it is reasonable to postulate that the OH and H radicals would be produced in much lower concentration and be more evenly distributed, which would increase the probability of reforming water. Little information is available about the relative energy yields in water vapor versus liquid water. However, the close approach of water molecules and hydrogen bonding in the liquid phase would be expected to cause significant differences in the mechanisms of the reactions in the two phases.

Pure liquid water (free from dissolved gas or other solutes) bombarded by 1 m.e.v. electron or Van de Graaff x-rays, reaches a steady-state hydrogen peroxide concentration of the order of a few micromoles per liter (69), with a corresponding steady-state partial pressure of hydrogen gas over the water amounting to a few millimeters mercury pressure; the hydrogen peroxide concentration is so low that it was undetected by a number of earlier investigators. The fact that a steady state is reached indicates that the hydrogen peroxide and hydrogen dissolved in the water continue to react with H and OH to reform water by processes such as

$$OH + H_2 \longrightarrow H_2O + H \qquad (1)$$

$$H + H_2O_2 \longrightarrow H_2O + OH \qquad (5)$$

This is not a thermodynamic equilibrium, but merely a steady-state condition which is reached when, under bombardment, the opposing reactions are equal in magnitude. The steady-state concentrations of hydrogen peroxide and hydrogen were found to increase with intensity of the radiation, thus the steady-state pressure of hydrogen was reported as varying from 1 - 2 cm. for 1 m.e.v. to over 1 atmosphere for α-rays. The energy yield, of course, drops to the extent that back-reactions are allowed to occur.

Additional evidence of the formation of H and OH radicals in the x- and γ-ray irradiation of pure, air-free water comes from Dainton's studies of the polymerization of vinyl compounds such as acrylonitrile and methacrylonitrile in dilute aqueous solution under such bombardment. It is well established that free radicals such as OH can initiate such polymerization reactions (52, 78) and the OH groups in the final polymer may be detected by infrared spectroscopic analysis.

The solution of air or oxygen in water markedly increases both the initial rate of formation of hydrogen peroxide and its steady-state concentration under x-ray irradiation, although the presence of oxygen is without effect under α-ray bombardment (76). Decreasing pH also increases the amount of hydrogen peroxide formed on x-ray irradiation (79). In recent studies (76) it has been reported that on irradiation of ice formed from water saturated with oxygen, the amount of hydrogen peroxide produced per quantity of energy absorbed from x-ray bombardment diminished with decreasing temperature in the range 0°C. to -116°C., no peroxide being detected below -116°C. Water saturated with oxygen at 0°C. formed substantially more peroxide than did ice at 0°C., and the peroxide yield continued to rise with temperature up to 20°C., the highest studied. This temperature effect was not observed with α-rays, although a marked discontinuity in hydrogen peroxide yield was again observed at the transition from water to ice.

There is considerable uncertainty about the mechanisms involved here in the formation and destruction of hydrogen peroxide, and it is probable that the type of radiation markedly affects the overall course of reaction.

The initial reactions postulated to occur from ionized molecules and electrons have been discussed above. If dissolved oxygen is also present, the initial reaction is postulated to be:

$$H + O_2 \longrightarrow HO_2^* \qquad (6a)$$

From this point on, various reaction schemes have been proposed involving the formation of hydrogen peroxide from the HO_2 radical, and destruction of hydrogen peroxide and HO_2 by various free radical reactions. Reactions involving ionic species are also included to account for the effect of pH on experimental results.

The decomposition of hydrogen peroxide under radiation is considered in more detail in Chapter 8. A variety of studies have been reported of the effects of radiation on aqueous solutions; there are conflicting reports on whether the addition of the solute increases or does not affect the amount of water decomposition. In general, reducing solutes are oxidized and oxidizing solutes are reduced. The processes occurring are usually consistent with the postulated initial formation of H and OH radicals from the water, followed by reactions of these radicals with the solute, although Lefort and Haïssinsky have reported a case in which arsenite in aqueous solution appeared to be converted to elemental arsenic by direct action of radiation (75). In a number of cases the rate of formation of hydrogen peroxide is increased; for example, dissolved halide ions increase the quantity of hydrogen peroxide formed, iodide being more effective than bromide, which is in turn more effective than chloride.

The fact that hydrogen peroxide is formed by irradiation of water, and particularly in the presence of oxygen, has led to speculation and the development of some evidence that the damage done to living things by excessive radiation may operate through a chemical mechanism involving free radicals such as OH or hydrogen peroxide, or both. The processes occurring are, of course, extremely complex but since the main constituent of most cells (about 70 percent) is water, the formation of these species should be highly probable. The inhibiting effect of hydrogen peroxide on biological processes is discussed elsewhere. Two pieces of evidence are striking: (1) It has been noted that addition of hydrogen peroxide to bacteria can cause mutant strains to appear, similar to those produced by radiation of the bacteria. (2) It has also been found that in atmospheres deficient in oxygen, rats can survive much larger doses of radiation, and x-raying of plants and fruit flies produces a smaller percentage of chromosome aberrations and mutations than in air. This is consistent with the pronounced relationship found, under x-ray bombardment, between the amount of hydrogen peroxide formed and the amount of oxygen present.

Sonic and Ultrasonic Vibrations

Vibrational waves and particularly those of a frequency above the hearing range of the human ear, (above about 15 - 20 kilocycles/second) have been found to induce or to accelerate a wide variety of chemical reactions. The formation of small amounts of hydrogen peroxide has been reported as occurring on the subjection of water to ultrasonic waves of frequencies of 400, 500, 540 and 985 kilocycles/second, (81, 82, 83), and by sonic waves of 9 kilocycles/second (84). The effect does not occur unless oxygen, air, or some gas is dissolved in the water. In the presence of air, the formation of nitrous and nitric acids has also been observed. The small magnitude of the effect (several hours of ultrasonic irradiation may produce about 20 mg. H_2O_2/liter) has increased the difficulty of establishing the facts, and the mechanism by which ultrasonic energy is utilized is still uncertain.

Since the conversion of water and oxygen to hydrogen peroxide, or of water to hydrogen peroxide and hydrogen, is highly endothermic, it is evident that the mode of action of the ultrasonic vibrations here cannot merely be that of supplying an energy of activation, which may be its principal role in some exothermic reactions. The quantity of hydrogen peroxide produced becomes a maximum when the experimental conditions are such as to produce maximum cavitation--the appearance of "cavities" or bubbles in liquid when subjected to vibrations or sound under certain conditions. The bubbles are presumably formed during the negative cycle of the sound wave when the water is under tension rather than compression. Cavitation does not usually occur in a degassed liquid, and high pressures also prevent its occurrence.

The close relationship of hydrogen peroxide formation to degree of cavitation is illustrated by the experiments of Polotskii (85) who found that when the pressure (temperature unspecified) was varied from 20 to 4180 mm. mercury, no peroxide was formed on ultrasonic bombardment of water at pressures below 100 mm. mercury, but the amounts increased with pressure up to a maximum at about 1520 mm. mercury and then fell with further pressure rise to zero yield at about 4180 mm. mercury. Polotskii also produced non-ultrasonic cavitations by introducing steam at 150°C. and 250°C. from a capillary of 0.5 mm. diameter into water at 20° and 50°C. With water at 20°C., and steam at 250°C., 0.255 mg. H_2O_2/50 ml. water was found after 20 minutes, and 0.635 mg./50 ml. after 60 minutes. The amounts of hydrogen peroxide formed in this manner with water at 50°C. were 2 - 2.5 times less than at the lower temperature; a decrease in steam temperature also slightly lowered the amount of hydrogen peroxide formed.

A large number of investigators have advanced theories to explain the correlation between cavitation and chemical reaction. The theories fall into two general groups. One proceeds from the fact that various scintillation and luminescent phenomena are observed when cavitation occurs and attributes the chemical reactions to electrical phenomena occurring at the liquid-gas interface of the bubbles. These are postulated to give rise to charged particles and/or to produce free radicals, either of which react to form the products observed. Another possibility cited is the generation of photons which could cause photochemical reactions. The other group of theories proposes that the momentary local high pressure and temperature produced when the bubble collapses initiate reactions by the direct formation of atoms and free radicals such as H and OH.

The formation of hydrogen peroxide by ultrasonic bombardment of water has been recently studied in detail by Schick (83); he also discusses previous studies of chemical reactions under ultrasonic bombardment and gives extensive literature references. He found that no peroxide was formed in the absence of a dissolved gas; in the presence of oxygen, hydrogen peroxide was formed but no significant quantities of hydrogen were produced. These confirm previous studies.

In the presence of helium instead of oxygen, hydrogen and hydrogen peroxide are produced, plus some oxygen gas (the oxygen may have been released by decomposition of the peroxide formed). Over a pH range, maximum peroxide formation occurred at pH = 4. Most likely this is due to the fact that hydrogen peroxide has a maximum stability at this pH, as discussed in Chapter 9. Over a temperature range of 10 - 85°C., the maximum rate occurred at 45°C. Various possible interpretations of this result were suggested, including the effect of temperature on (1) the properties of water, (2) nucleation rates, (3) rates of growth of bubbles, (4) reaction mechanism in the bubbles, and (5) the rate of decomposition of hydrogen peroxide.

A particularly interesting finding was the observation that in a closed system, starting with water and helium, a steady-state gas pressure of 1 - 2 cm. Hg. was attained, independent of intensity over the range studied. The gas consisted primarily of hydrogen plus some oxygen, while hydrogen peroxide was formed in the liquid. The steady-state condition could also be approached by starting from hydrogen and hydrogen peroxide, in which case the hydrogen was consumed. These results are similar to those obtained by radiochemical bombardment, described previously, and Schick suggests that the same reactions involving free radicals are occurring here. Under optimum conditions (45°C. and absorbed bombardment intensity of about 21 watts/75 ml.) the hydrogen peroxide yield was about 0.01 molecules/100 electron volts, compared to values of 0.2 - 2.0 reported by Allen (69) for the number of water molecules decomposed under bombardment by various radiochemical sources. Schick also found that ultrasonic irradiation of aqueous solutions of 4, 4', 4" hexamethyl triamino triphenyl methane or of carbon tetrachloride produced oxidation which could not be attributed to reaction with hydrogen peroxide and this conclusion coincides with studies of other oxidation phenomena which have been reported under ultrasonic irradiation (86). It is possible that hydroxyl radicals are the active species here.

A substantial number of studies have been reported of other chemical reactions occurring in aqueous medium under ultrasonic bombardment. For detailed discussion, the reader is referred to the book by Bergmann (81).

AUTOXIDATION

The term <u>autoxidation</u> is applied to the reactions which occur between molecular oxygen and various substances at approximately room temperatures. The reactions are generally slow and a large variety of substances may undergo such reaction. Thus autoxidation occurs in such diverse processes as the rusting of iron, the polymerization of drying oils, the weathering of coal, the rancification of fats and oils, the metabolism of bacteria, and the biological oxidation processes involved in the assimilation of food.

The reactions are markedly affected by positive and negative catalysts; frequently they are autocatalytic and they may initiate polymerization reactions. In view of the complexity of any one autoxidation process and the wide variety of substances which undergo autoxidation, it is not surprising to find many different theories regarding the mechanisms of these reactions. Each theory usually adequately explains certain model experiments or groups of studies but then becomes more general and tenuous as attempts are made to extrapolate it to more complex and less-well-understood autoxidation phenomena, as in the extrapolation of the mechanism of oxidation of organic molecules to explain the action of enzymes and biological processes. Only a brief summary will be given here of the principal theories.

With compounds like aldehydes and olefins, it is believed that the oxygen first adds directly to the $>C = C<$ or $C = O$ bond

$$R + O_2 \longrightarrow R \cdot O_2$$

The RO_2 is usually an unstable intermediate and it may then react with a second molecule to give the final product

$$R \cdot O_2 + R' \longrightarrow RO + R'O$$

as in conversion of benzaldehyde to benzoic acid via the peroxy acid, where R and R' are both benzaldehyde molecules, or the intermediate may decompose by other reactions. This type of mechanism frequently bears the term "Bach-Engler," after the two principal proponents of the theory.

With saturated compounds, there have been two main theories in the field which differed principally on whether the initial step involves "activation" of hydrogen and its transference to the oxygen molecule--a dehydrogenation reaction:

$$RH_2 + O_2 \longrightarrow R + H_2O_2$$

or whether the oxygen is "activated" and forms an addition product:

$$RH + O_2 \longrightarrow ROOH$$

It is readily seen that a critical test between the two theories for a given reaction would be the experimental determination of whether hydrogen peroxide or an organic peroxide is initially formed. Unfortunately there are relatively few systems in which the evidence is unequivocal. This is due to the fact that most of the organic peroxides formed are very unstable and decompose rapidly with initiation of polymerizations and isomerizations, and they may also form hydrogen peroxide, as by hydrolysis of peroxy acids. Likewise hydrogen peroxide will frequently react rapidly to form organic peroxides, be decomposed by catalysts, or will likewise initiate polymerizations and isomerizations. Since in most of these systems the reactions destroying hydrogen peroxide are usually relatively rapid, hydrogen peroxide has actually been detected in only a small number of autoxidations, although it is postulated by analogy to exist as a transitory intermediate in many reactions for which no direct evidence is available. A part of the problem also has arisen from analytical difficulties or distinguishing between hydrogen peroxide and organic peroxides.

The meaning of the term "activation" has undergone considerable modification with time and the two theories have become generally fused with the recognition that the first step in any autoxidation is presumably the formation of some combination of oxygen with the autoxidizable substance (often designated as donor, or substrate) or with a catalyst, or both. This would be true whether the autoxidizable substance is a metal, metal salt, or completely organic. The catalyst may also be a metal, metallo-organic compound, or completely organic, and may be of a simple structure or very complex, like an enzyme. The initial combination may then change into a better defined peroxide (organic) or it may split off hydrogen peroxide.

Autoxidation reactions are catalyzed by a wide variety of substances but consideration of the various catalytic reactions and mechanisms involved is beyond the scope of this book.

Biological Systems

The role of hydrogen peroxide in biological processes will be considered only briefly. All animals and many bacteria obtain their energy by oxidation of organic substances to carbon dioxide and water. This involves a chain of reactions many of which are unknown or but poorly understood; however, somewhere in the chain there must be reaction with oxygen. These reactions are profoundly affected by the presence of "biological catalysts"--enzymes.

Theories of the mode of biological oxidation are based to a considerable extent on the "model reactions" of chemical compounds of known structure, as well as on experiments on simple living organisms like bacteria and on the actions of enzymes on non-living matter. As in autoxidation of non-living matter, the two principal theories in the past have focused on "activation" of hydrogen versus that of oxygen. The first commonly bears the name of Wieland who based his work principally on model reactions and the second the name of Warburg who developed his theory particularly from studies on cell respiration and iron systems and emphasized the importance of "oxygen activation" in which enzyme iron is first converted to an iron peroxide, whereupon this complex directly oxidizes the substrate.

Hydrogen peroxide formation has been detected in a number of enzyme and biological systems, but only if the system is free from heavy metals or the enzymes catalase and peroxidase, both of which decompose hydrogen peroxide. Thus hydrogen peroxide has been found in a number of reactions catalyzed by certain oxidizing enzymes (oxidases) and by the purine dehydrogenase of milk. Hydrogen peroxide is not detected in cells which require oxygen in their metabolism (aerobic) since these always contain catalase, but it has been found on exposure to oxygen of certain bacteria devoid of catalase such as pneumococci and streptococci which live anaerobically. Hydrogen peroxide inhibits the aerobic growth of anaerobic organisms such as these, which indicates that the destruction of these organisms which occurs on contact with air may well proceed via their forming hydrogen peroxide which is a poison to their metabolism. There is also evidence that the antibacterial activity of human saliva is caused by the presence of streptococci. Thus, ether extracts of streptococci have been found to inhibit the growth of diphtheria bacteria and staphylococci, and the effect has been traced to the hydrogen peroxide content (87).

There is now evidence that the antibacterial activity of penicillin may be due to hydrogen peroxide which it forms by enzyme action in the presence of glucose and oxygen (88). In one set of experiments the growth of Staphylococcus aureus was found to be delayed by as little as 0.0003% hydrogen peroxide while concentrations of 0.0027% or higher were bactericidal.

In other studies the amounts of hydrogen peroxide required to prevent the growth of various Gram-positive and Gram-negative organisms were found to be of the same order as those produced by antibacterial penicillin media. The optimum antibacterial activity of penicillin occurs under those conditions in which hydrogen peroxide formation is also favored, i.e. (1) presence of oxygen, (2) presence of glucose or similar sugars, and (3) absence of appreciable amounts of catalase. Thus, penicillin B failed to produce antibacterial activity in anaerobic experiments and fresh horse or other serum, which contains catalase, is antagonistic to the action of penicillin.

The following examples give additional evidence of the inhibiting effect of hydrogen peroxide on biological processes.

(a) The fermentation of sugar by _Lactobacillus bulgaricus_ in contact with air is found to cease before the sugar is all consumed, while hydrogen peroxide accumulates during the fermentation process (89). In an inert atmosphere, such as nitrogen, fermentation proceeds until the sugar is consumed and no hydrogen peroxide is formed. The amount of peroxide formed was found to vary directly with the oxygen content of the gas.

(b) In the presence of egg yolk, spermatozoa develop hydrogen peroxide which in turn inhibits sperm respiration.

(c) It has been suggested that the destructive action of ascorbic acid on such bacteria as the tubercle bacillus is due to hydrogen peroxide which is known to be formed on reaction of ascorbic acid with oxygen.

For more detailed discussion of autoxidation and biological oxidation, the reader is referred to the books or reviews by Milas, Wieland, Oppenheimer and Stern, and Dufraisse and Chovin (90).

Autoxidation of Metals

Small amounts of hydrogen peroxide have been found on the exposure of a number of metals to oxygen and moisture, using a qualitative color test such as with titanium or the "Russell effect" to detect the hydrogen peroxide. The latter test rests on the fact that photographic plates are highly sensitive to very small amounts of hydrogen peroxide. Thus Russell found that a number of substances including several metals, particularly when freshly abraded, gave photographic images when held near a photographic plate in the dark, and this was conclusively traced to the emanation of hydrogen peroxide. The detection of hydrogen peroxide by one of these techniques has been reported on the oxidation of the following metals: zinc, lead, tin, silver, mercury, copper, aluminum, cadmium, magnesium, iron (91, 92). It is highly probable that hydrogen peroxide is also formed on oxidation of a number of other metals. It is most difficult to detect it on those metals which are also active peroxide decomposition catalysts, such as iron, copper, and lead. It is apparent that the hydrogen peroxide concentration produced in autoxidation of metals is determined by the relative rates of the formation and decomposition reactions and whether or not it is detected by a particular investigator depends upon the sensitivity of his particular test and also on the conditions of his experiment. Higher concentrations of hydrogen peroxide are found on freshly abraded metal surfaces and at least in the case of aluminum, in weak to moderate acid or weakly alkaline aqueous media. The metal becomes cathodic during the oxidation. Making the metal anodic suppresses the formation of hydrogen peroxide, making it more cathodic enchances its formation.

It is not clear whether both water and oxygen must be present for hydrogen peroxide to be formed although this is highly probable. In one test a sample of aluminum in dry nitrogen gave a faint photographic image, but it probably had absorbed oxygen and/or water from the air before being placed in the inert atmosphere.

It now seems quite probable that the oxygen corrosion of many metals, such as the rusting of iron, involves hydrogen peroxide formation--a theory which was first proposed by Dunston, Jowett and Goulding (93) in 1905 but received at that time little support. The possible mechanisms involved, which are still somewhat obscure, are discussed later in this chapter.

Hydrogen peroxide forms readily on contacting mercury or amalgamated metals with oxygen in acidic solutions or in a medium consisting principally of an alcohol. Thus Furman and Murray (94) found that on shaking mixtures of mercury, hydrochloric acid and oxygen together, hydrogen peroxide and mercurous chloride are formed, with some mercuric salt appearing in the initial stages of the reaction; shaking mercury with pure water and oxygen gives a soluble mercury compound but no peroxide. These results may be due to the fact that the catalytic activity of mercury is at a minimum in acid solutions. Müller and Barchmann (95) obtained solutions containing as high as 3.77% hydrogen peroxide by contacting oxygen with a 3% cadmium amalgam at 0°C. in a medium consisting of ethyl alcohol and 50% sulfuric acid; cadmium sulfate was simultaneously formed. Patents have also been issued for the formation of hydrogen peroxide by contacting an amalgam containing about 0.0003% to 0.001% of an alkali metal with oxygen in the presence of water or a liquid such as methyl alcohol containing some water (96). The corresponding alkali is simultaneously produced. The amalgam may be produced by electrolysis of alkali compounds with a mercury cathode or by dissolving alkali metal in mercury.

Small amounts of hydrogen peroxide are also formed when gold is dissolved in aqueous potassium cyanide solutions using air agitation (97).

The fact that hydrogen peroxide can be formed by autoxidation of metals has caused considerable difficulty and interference with microanalytical procedures if they are carried out in the presence of air. For example, in a microvolumetric determination of iron, the element is dissolved in acid and then reduced with silver. However it is necessary to exclude air in the procedure to avoid the formation of small amounts of hydrogen peroxide which would otherwise interfere with the determination (98).

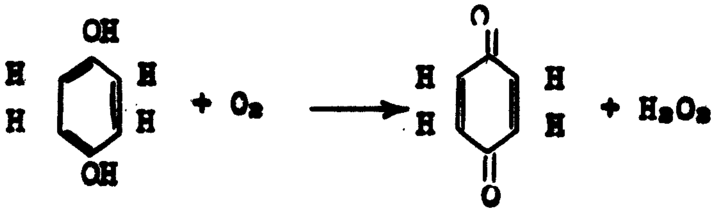
Autoxidation of Organic Compounds

It has been seen that autoxidation of organic substances is believed to involve the initial formation of a peroxide; if the organic compound contains hydrogen atoms which can be easily split off, then a dehydrogenation occurs with formation of hydrogen peroxide. However, these reactions which produce hydrogen peroxide generally proceed relatively slowly in the absence of catalysis. The exceptions are certain aromatic compounds such as polyphenols like hydroquinone or dihydroxymaleic acid, hydrazo compounds, and hydro derivatives (leuco forms) of certain dyes which are converted into quinones, such as methylene blue and anthraquinone vat dyes. The reaction may be represented as:

(27)

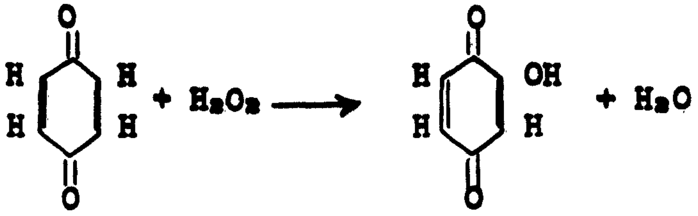
where R is oxygen, or a nitrogen structure such as NH or NR".

The complicated autoxidation of hydroquinone and its homologues in mildly alkaline solution has been studied by James, Snell and Weissberger (99). The first step is probably the formation of quinone and hydrogen peroxide:



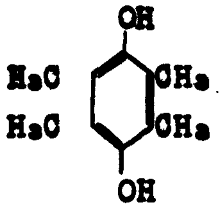
(28)

However, quinone reacts rapidly with hydrogen peroxide to form hydroxy quinone

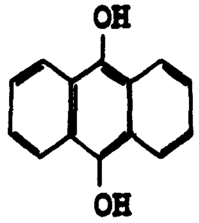


(29)

and no hydrogen peroxide has been detected experimentally until the work of the above authors in which 2-methyl-benzothiazole-metho-p-toluene sulfonate was added to the reaction mixture to "tie-up" the quinone on formation. Ordinarily the hydroxyquinone is formed and polymerizes to humic acids, $(C_6H_4O_3)_x$. If the reactive hydrogen atoms attached to the benzene nucleus are replaced by other inactive atoms or groups no reactions subsequent to the autoxidation occur and the quinone and hydrogen peroxide formed can then be readily isolated. Thus, autoxidation of durohydroquinone, (I), or anthrahydroquinone (II) results in the quantitative formation of hydrogen peroxide and the corresponding quinone-type structure.

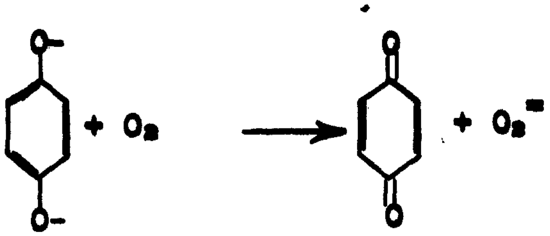


durahydroquinone (I)



anthrahydroquinone (II)

In the pH range of 7.2 - 8.2 the rate of oxidation of various hydroquinones is proportional to the square of the hydroxyl-ion concentration, from which the above authors concluded that the first step in the reaction is formation of the doubly-charged anion of the quinone which then reacts with oxygen



(30)

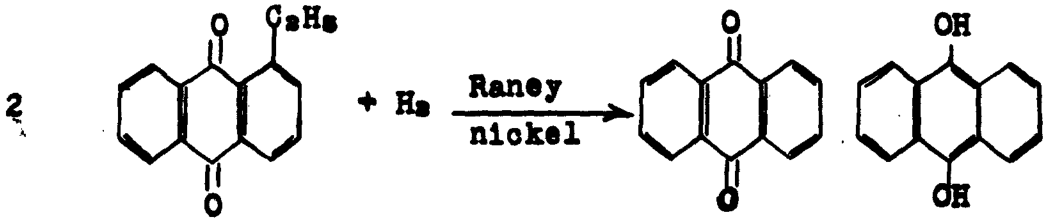
The rate is strongly catalyzed by small amounts of the quinone and is not always proportional to oxygen concentration, suggesting that reaction 30 may proceed in more than one fashion and may involve the intermediate formation of a complex structure--perhaps a charged radical.

The formation of hydrogen peroxide during the oxidation of reduced (leuco) anthraquinone and anthraquinoid vat dyes has been studied by Atherton and Turner (100) who suggest that hydrogen peroxide formation may be an intermediate step in oxidations of cellulose which are initiated or accelerated by changes in the dye system.

Manufacture by Autoxidation Processes

Several patents have been issued on a method of producing hydrogen peroxide by contacting a solution of a cyclic, polynuclear hydroquinoid such as anthrahydroquinone with oxygen, removing the hydrogen peroxide formed by extraction with water, reducing the quinone structure with hydrogen to the hydroquinone and recycling to the oxidation stage (101). This process (often bearing the term Riedl-Pfleiderer) was studied at the I. G. Farbenindustrie, Ludwigshaven, Germany, using 2-ethyl anthraquinone, and led to the construction and operation during World War II of a small plant having the capacity of about 5 metric tons of 20% hydrogen peroxide per 24-hour day and plans to erect two plants, at Heidebreck, Silesia, and at Waldenberg (102). Originally these were planned to have a capacity of 2000 metric tons of hydrogen peroxide per month, calculated as 100% hydrogen peroxide, but the plans were scaled down to about one third in 1944, and the plants were each partially completed when construction was stopped.

In the German process, shown in Figure 4, 2-ethyl anthraquinone,* was dissolved in a solvent called "Paralk," chosen after extensive investigation. It consisted of a 50:50 mixture of benzene and secondary alcohols of chain length $C_7 - C_{11}$, the latter being produced by ketonization of $C_4 - C_6$ fatty acids from paraffin oxidation, followed by hydrogenation of the ketone to secondary alcohols. The choice of the 2-ethyl homolog rather than anthraquinone itself was apparently based on a more favorable solubility and reaction rate of this compound. Hydrogenation of the anthraquinone with Raney nickel catalyst was stopped at the half-way stage of the quinhydrone because of the lower solubility of the fully reduced hydroquinone.



(31)

Reduction took place continuously at 30 - 36°C. and 1 - 2 atmospheres of hydrogen pressure, with Raney nickel catalyst suspended in benzene added continuously at the rate of about 3 - 5 gm. of catalyst per kilogram of hydrogen peroxide finally produced. The benzene must be thiophene-free, and the hydrogen must be carefully purified to avoid poisoning the catalyst. Hydrogen efficiencies of about 90% were reported for laboratory operations and about 80% for the pilot-plant, at the residence time used of

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* 2-ethyl anthraquinone was prepared by condensation of ethyl benzene and phthalic anhydride in the presence of aluminum chloride, followed by heating with fuming sulfuric acid to close the ring with removal of water.

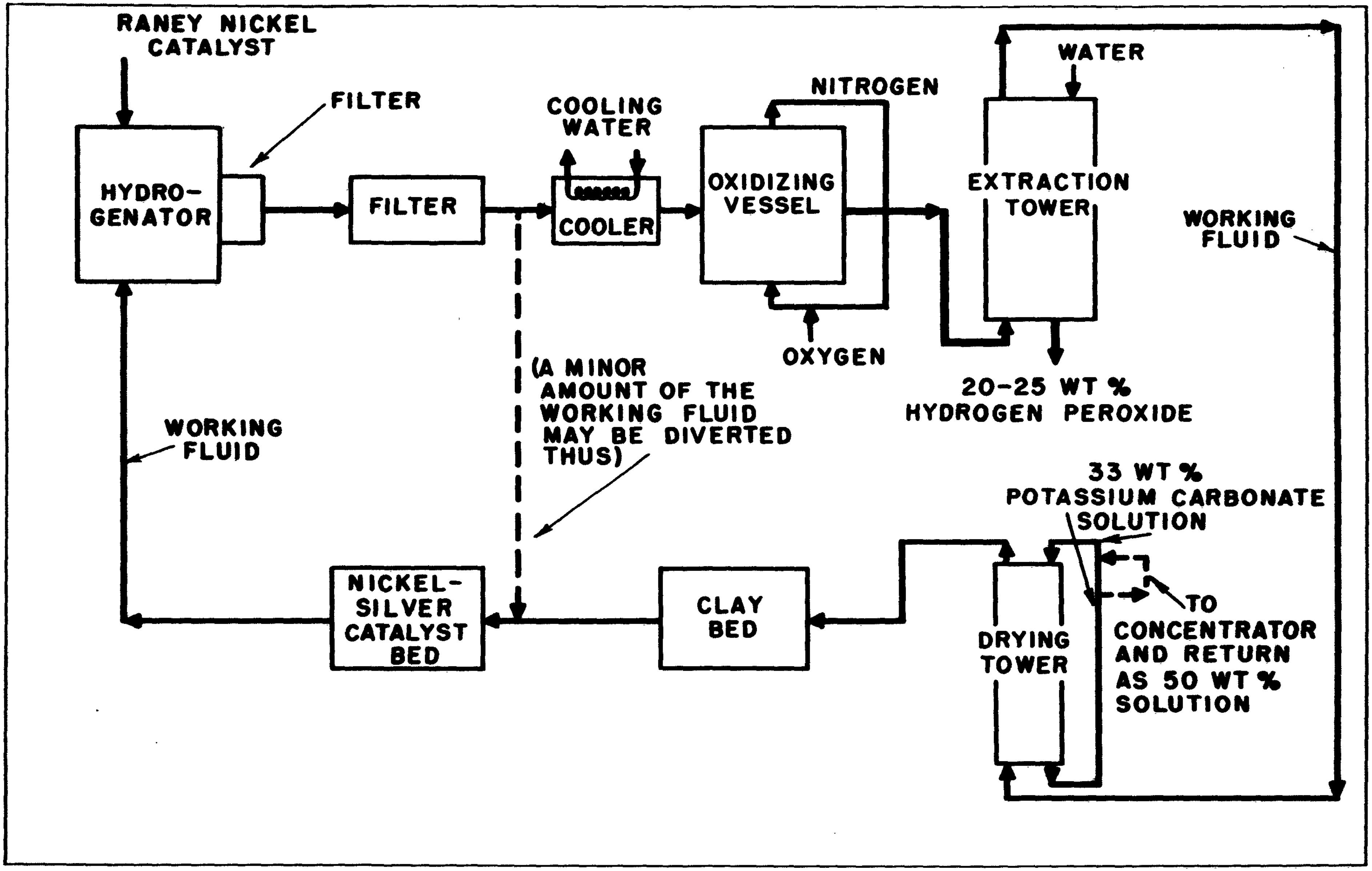


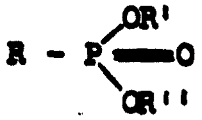
FIG. 4 – FLOWSHEET OF THE RIEDL-PFLEIDERER 2-ETHYL ANTHRAQUINONE PROCESS

one-half hour. The solution must be carefully filtered to remove the finely divided catalyst before autoxidation or otherwise the hydrogen peroxide subsequently produced will be decomposed. Consequently the solution was removed through a filter barrier and then passed through a separate filter. The solution was then cooled and passed to the oxidizing vessel. In this next step, the oxygen was diluted with nitrogen to avoid forming vapor mixtures of explosive composition. The exit gas stream, principally nitrogen, was fortified with oxygen and recirculated, thus avoiding loss of solvent. Air could be used instead of oxygen in this step if a sufficiently nonvolatile and otherwise suitable solvent were substituted for the Paralk, and a somewhat longer oxidation time accepted.

No water was added until after the oxidation step, when the hydrogen peroxide was removed from solution by countercurrent extraction with water in a packed tower. With the German use of 100 gm. of ethyl anthraquinone per liter of solution, the theoretically maximum concentration of hydrogen peroxide in the working solution is 7.2 gm. H_2O_2/liter. Actually about 5.5 gm. H_2O_2/liter were obtained during the half-hour oxidation and this yielded a 20 - 25 wt. % hydrogen peroxide solution on water extraction.

After extraction the anthraquinone solution contained about 0.1 - 0.3% water, plus small amounts of hydrogen peroxide (0.17 gm./liter has been quoted as typical) as well as oxidized organic matter such as organic acids, aldehydes, ketones, etc. These would poison the nickel hydrogenation catalyst and must therefore be removed before recycling. In the German process it was dried with a 33 wt. % potassium carbonate aqueous solution, which also removed some of the peroxide, and the organic materials and water traces were removed by adsorption in a clay bed. The remaining hydrogen peroxide was decomposed by a bed of a supported nickel-silver catalyst and a small amount of reduced solution (about 10%) from the hydrogenator was sometimes added to the recycle liquid before entering the catalyst bed to assist in the removal of hydrogen peroxide and dissolved oxygen. The small amount of water thus produced remained in the working solution.

The large amounts of solvent which must be recirculated per quantity of product produced emphasize the critical importance which must be placed on its careful choice. Thus, the solvent should have as high dissolving power as possible for the autoxidizable substance in both the quinone and hydroquinone forms; the solvent should be readily non-volatile to reduce solvent losses and fire and explosion hazards; it should be insoluble in water so that the hydrogen peroxide may be removed as a pure aqueous solution; and it should be stable to oxidation. A high distribution coefficient for hydrogen peroxide between water and the solvent is important in order to produce hydrogen peroxide in reasonable concentration and yield. A variety of solvents have been proposed for this purpose in addition to the Paralk used in Germany; like Paralk they consist usually of a mixture of two solvents, one of which is a good solvent for the quinone, the other for the hydroquinone; recent patents (103) propose a mixture of a hydrocarbon such as benzene, with an organic phosphonate having the structure



$$R - P(=O)(OR')(OR'')$$

(*e*.*g*., dioctyl styrenephosphonate) or a mixture of benzene with an organic triphosphate ester (*e*.*g*., tributyl phosphate). The ester of a dibasic acid, like dibutyl sebacate or dihexyl succinate has also been proposed for use by itself. Hydrogen peroxide is substantially insoluble in some of these esters, which would permit separation of a highly concentrated hydrogen peroxide directly by decantation.

The hydrogen peroxide solution produced will be saturated with respect to the organic (working) solution, and all decomposition and oxidation products will gradually migrate into the hydrogen peroxide product. The nature of the inorganic and organic impurities in the hydrogen peroxide produced will, consequently, depend not only on the nature of the working solution but also on the extent to which it is purified during recycling, and also on the various materials of construction used. The 20 - 25% hydrogen peroxide produced in the German pilot plant contained about 0.4 mg./liter of iron (from the hydrogenation vessel, valves, etc.), about 0.8 mg./liter of nickel (from the Raney nickel), and other inorganic contaminants such as aluminum. The organic content in the crude hydrogen peroxide solution varied up to about 1500 mg./liter, expressed as carbon. This consisted primarily of benzene and oxidation products (fatty acids) of the Paralk component of the solvent. (Water saturated with benzene at 25°C. contains 620 mg./liter of carbon.) Little organic matter was believed to come from ethyl anthraquinone or its oxidation products, and the Paralk itself is quite insoluble. On storage for six months the carbon content dropped to about 800 mg./liter of carbon (104).

This process appears to be economically more attractive than the presently used electrolytic processes since it avoids the high consumption of electricity and high capital investment associated with the latter, although a more exact evaluation must rest on a number of important factors on which no reliable data or information have been published. These include the rate of deterioration of suitable solvents and of the anthraquinone, the cost of plant construction and maintenance, the possibility that further purification steps may be needed to remove organic impurities in the hydrogen peroxide, and the stability of the final peroxide product, particularly during a possible subsequent concentration step. The possibility that organic peroxides may form in the working fluid or be extracted into the hydrogen peroxide product also introduces a potential hazard. During the reduction step, some anthraquinone is reduced to the tetrahydroquinone, which is more difficult to oxidize in the subsequent oxidation step; the working fluid in the German process was reported to contain 30 - 40% of the anthraquinone in the form of the tetrahydro derivative. However, the tetrahydrohydroquinone is more soluble in a benzene-cyclohexanol solvent than hydroanthraquinone.

The fact that two large plants to use this process were planned and partially constructed in Germany indicates the serious consideration which will be given to it in the future.

Hydrazobenzene Autoxidation

Reaction of oxygen with an aryl hydrazo compound such as hydrazotoluene yields hydrogen peroxide and the azo compound, analogous to the reaction of oxygen with anthrahydroquinone:

$$\text{R-NH-NH-R} + O_2 \longrightarrow \text{R-N=N-R} + H_2O_2 \qquad (32)$$

The oxidation of hydrazobenzene in alcohol or benzene solution was studied by Walton and Filson in 1932 (105), who proposed it as a method for making concentrated hydrogen peroxide, and hydrazobenzene and related compounds have been studied for use in such a process as disclosed in a series of patents from the Mathieson Alkali Works (106). The hydrazo compound is dissolved in an unreactive solvent immiscible with water, such as benzene. The oxidation may be performed with either air or oxygen and negligible side reactions occur. The hydrogen peroxide can be removed by water extraction. However, the reduction of the azo compound to the hydrazo form, required in a commercial cyclical process, appears to be considerably more difficult than the corresponding step with 2-ethyl anthraquinone. Catalytic reduction with hydrogen causes some splitting of the N=N bond; thus para azobenzene forms substantial amounts of aniline; electrolytic reduction has also been suggested but the most satisfactory is the use of a metal in aqueous alkaline solution. Tin, zinc, iron and sodium have been suggested; iron causes significant formation of aniline; of the others sodium is the cheapest. A preferred use is as a sodium amalgam, e.g., 0.2% sodium, as proposed in several patents. This could be formed in a conventional mercury electrolytic cell, and the mercury recycled to the cells from the azo reduction step. Caustic soda would thus be produced as a by-product.

Oxidation of hydrazobenzene proceeds relatively slowly; use of amino substituted compounds with water increases the rate but they form emulsions which are difficult to break; certain alkyl-substituted compounds like p-hydrazotoluene are the most satisfactory since they are more readily oxidized than the benzene compounds and yet do not form emulsions. This process was considered in Germany during World War II but discarded in favor of the anthraquinone process.

Hydrazine Autoxidation

Studies of the autoxidation of dilute aqueous hydrazine solutions (0.25 to 1 molar) by Gilbert (107) and Audrieth and Mohr (108) have shown that some hydrogen peroxide is formed as an intermediate although water, nitrogen and traces of ammonia are the final products found. In studies with a 0.635 molar hydrazine solution, Audrieth and Mohr found that addition of 8-hydroxy quinoline, which is an inhibitor for peroxide decomposition, resulted in much higher hydrogen peroxide concentrations than were otherwise found, and markedly decreased the rate of autoxidation of the hydrazine.

In concentrated hydrazine, however, addition of 8-hydroxy quinoline or substances having a catalytic effect on peroxide such as catalase or potassium iodide, did not affect the basic oxidation rate.

OXIDATION OF HYDROCARBONS

The reaction of hydrocarbons with oxygen can give rise to peroxides plus a wide variety of other substances including carbon monoxide and dioxide, hydrogen, water, unsaturated compounds (from saturated hydrocarbons), organic acids, ketones, aldehydes and alcohols. The state of basic knowledge and theory of these very complex reactions is understandably much less developed than in the less complex yet still involved and imperfectly understood reactions of hydrogen and oxygen. If reaction is carried out at substantially elevated temperatures, peroxides are usually not isolated unless the gaseous mixture is quenched after a short reaction time, but it appears that they are formed in the initial steps of essentially all hydrocarbon oxidations. The hydrocarbon combustion reactions have two prominent characteristics: (1) After the reaction mixture is brought to reaction temperature, a time lag of varying length, called an induction period, usually occurs before noticeable reaction takes place. Small amounts of additives may have a marked effect on the length of this induction period and on the products formed. (2) The characteristics of the reaction are profoundly affected by an increase in the amount of surface present or by a change in its nature. Both of these phenomena are characteristic and indicative of chain reactions involving free radicals.

It is frequently difficult to tell whether the peroxides isolated from the reaction mixture are hydrogen peroxide or organic in nature, and until fairly recently few attempts were made to determine their structure. Conclusions as to the character of the peroxide have been based on such evidence as (1) the composition of the gas and liquid produced on decomposition of the peroxide (*e.g.*, hydrogen peroxide yields oxygen and water; a hydroxy alkyl peroxide on alkaline decomposition yields hydrogen and an acid; methyl hydroperoxide evolves carbon dioxide on decomposition by platinum black (109)), (2) various color tests, such as that with titanium salts, whose sensitivity is somewhat different for various types of peroxides, (3) characteristics of the reaction with acid potassium iodide (*e.g.*, methyl hydroperoxide reacts in the presence of ferrous sulfate catalyst but not in the presence of ammonium molybdate (110)), (4) formation of insoluble inorganic peroxides such as calcium peroxide or sodium peroxy borate on suitable additions to the product, indicating presence of hydrogen peroxide or hydroxy alkyl hydroperoxides, (5) comparison of absorption spectra with those of known peroxides (111), (6) determination of partition coefficients with ether (112), (7) by chromatographic separations (110), and (8) estimates of the rate of thermal decomposition of various peroxides at the temperature level of the reaction zone.

The problem of analysis of the condensed mixtures formed by hydrocarbon oxidation is complicated by the reactions which can occur between the species present. In a recent study several analytical methods were evaluated and compared for determining quantitatively the total peroxide, the total aldehyde, the formaldehyde, and the methanol content of aqueous solutions containing hydrogen peroxide, acetaldehyde, formaldehyde, and methanol (112a). These are the principal condensable components formed on partial oxidation of propane.

The character of the peroxides formed has been studied primarily in the oxidation of the simpler hydrocarbon molecules. Under suitable conditions hydrogen peroxide may be formed on oxidation of ethane, propane, butane, ethylene and probably a number of larger molecules of similar types.* Of these propane has been the subject of several studies and will be considered here as an example of this type of reaction. It represents the smallest hydrocarbon molecule containing both secondary and primary carbon atoms and is of interest from the industrial viewpoint because it is readily available in petroleum operations. In both static and flow experiments the reaction rate of rich mixtures of propane and higher saturated hydrocarbons shows a negative temperature coefficient over a certain temperature range. For example, Pease (112) found a maximum in the rate at about 330°C., dropping to a minimum at about 380°C., and then rising with further temperature increase, when studying a 50:50 mole ratio of propane and oxygen at 200 mm. of mercury total pressure. Likewise in a recent study (113) a maximum rate of oxygen consumption was found at 375°C., dropping to a minimum at 425°C.,

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* The peroxides isolated from methane combustion are primarily organic; little hydrogen peroxide is produced.

and then increasing at higher temperatures, when studying a 5.5:1 mole ratio of propane and oxygen reacting under flow conditions at 1 atmosphere pressure. Similar results have been reported by Harris (114), Chernyak and Shtern (115), and Kooijman (116).

In a typical flow experiment, the gases are allowed to react for a few seconds and then cooled to room temperature in a surface condenser. This produces a liquid phase containing water, hydrogen peroxide and organic peroxides, aldehydes, and methyl alcohol, plus a gas phase containing unsaturated hydrocarbons (propylene and ethylene), methane, carbon monoxide, unreacted propane, and small amounts of uncondensed liquid-phase constituents. Small or negligible amounts of hydrogen, carbon dioxide, and organic acids are formed under conditions yielding maximum amounts of peroxide (113, 116).

The peroxide in the condensed phase is found to be either hydrogen peroxide or a hydroxy alkyl peroxide of the type R - CH(OH)-OOH or R - CH(OH)-OOCH(OH)-R, which is presumably formed from reaction of hydrogen peroxide with one or two molecules of aldehyde when the mixture is cooled. The evidence for this view is based upon (1) the fact that under suitable conditions essentially all of the peroxide present in the product can be isolated as calcium peroxide or as a peroxy borate and (2) the fact that various alkyl peroxides have been found to have enormously greater rates of homogeneous decomposition in the vapor phase than hydrogen peroxide. Although alkyl hydroperoxides (ROOH) have been reported on low temperature oxidation of hydrocarbons (e.g., 100 - 150°C.), the estimated half life of such species at the reaction temperature here is so short that detectable amounts could hardly exist. The maximum hydrogen peroxide concentration in the reacting gases has been found with propane-oxygen mole ratios of 3 to 10, at reaction temperatures of 465 - 485°C., and a contact time of 3 - 4 seconds (113, 116).

Hydrogen peroxide is also formed in the lower temperature region, around 375°C., but in substantially lower yields, based on the oxygen reacted. Instead larger amounts of partially-oxidized products such as aldehydes and alcohols are formed. A typical set of experimental data are shown in Figure 5 (113) for reaction at a temperature of about 475°C. This shows the change in product composition as reaction proceeds, the latter expressed as percent of the inlet oxygen reacted. It is seen that the hydrogen peroxide concentration goes through a maximum. The decrease on further reaction may possibly be caused by heterogeneous decomposition on the reactor walls, although insufficient evidence is available to indicate clearly whether this, or further homogeneous reaction, is the cause. The amounts of hydrogen peroxide isolated vary greatly with the character of the surface present. Coating the walls with potassium chloride essentially eliminates hydrogen peroxide formation. Maximum amounts are found when the reactor is made of the most inert materials such as borosilicate glass, particularly after being washed with hydrofluoric acid, or when the surfaces are coated with borates.

Mechanism of Propane Oxidation

The overall mechanisms of hydrocarbon oxidation are understandably less well understood than for the hydrogen-oxygen system, although the nature of some of the individual reactions involved is fairly well known. The subject has been recently examined (113, 117) and also discussed in the books by Lewis and von Elbe (7) and Laidler (8) as well as in the other references cited above. A detailed consideration of the various reaction steps in hydrocarbon oxidation would be too lengthy to present here. However, the experimental evidence (113) indicates that hydrogen peroxide is formed in the following fashion, again taking propane as an example.

The first step is postulated to be removal of a hydrogen atom from a propane molecule to form a propyl radical, by attack from oxygen or other radicals. The propyl radicals

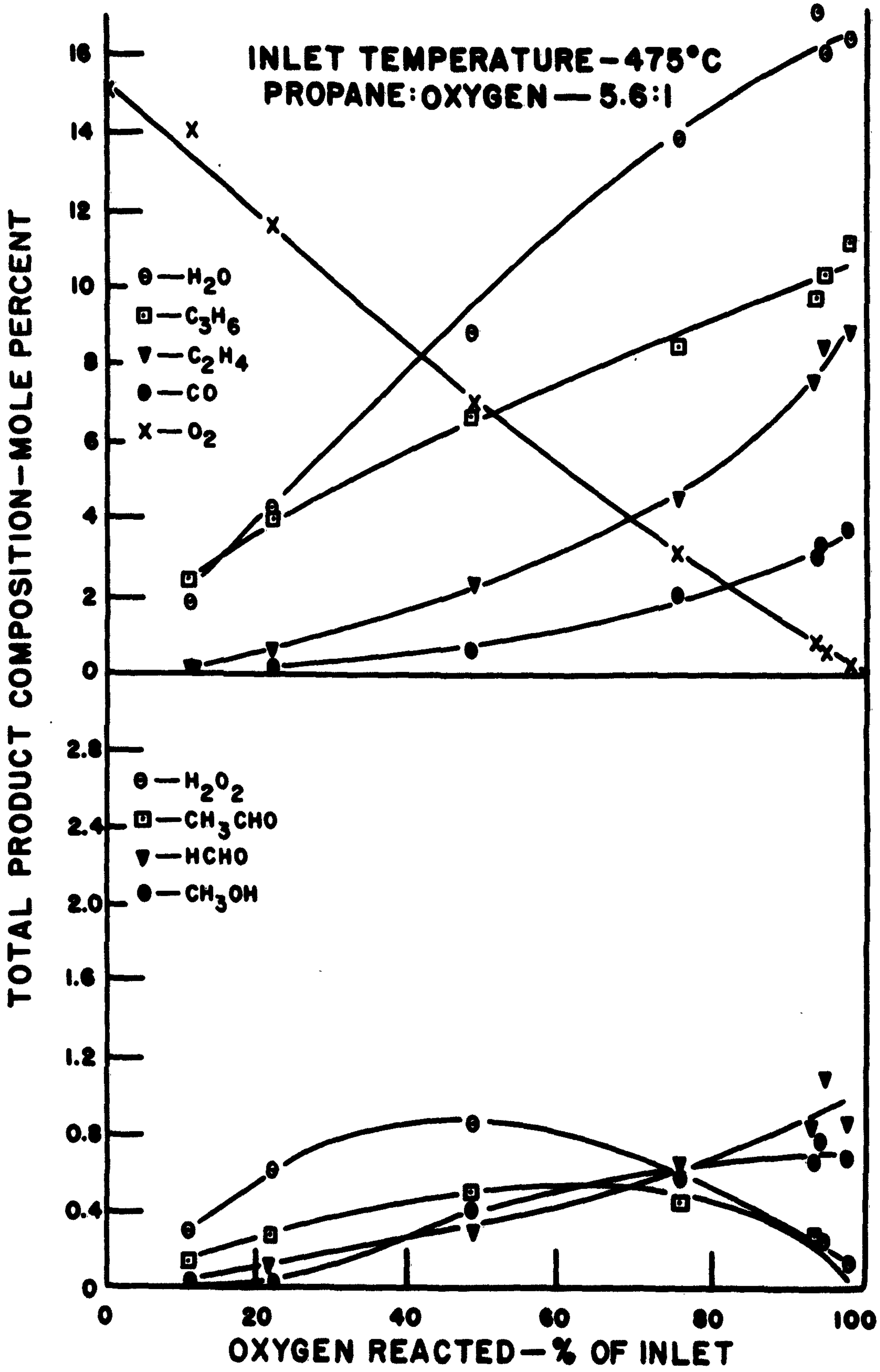

FIGURE 5
PRODUCTS OF PROPANE OXIDATION

may be either primary or secondary and there are indications that the subsequent reaction may be somewhat different for the two types. Thus it appears that at least under the conditions of interest here, most of the primary propyl disappears by reaction 33.

$$C_3H_7 \longrightarrow C_2H_4 + CH_3 \qquad (33)$$

Most of the secondary propyl radical is believed to react with oxygen according to reactions 34 and 35.

$$C_3H_7 + O_2 \longrightarrow C_3H_7\dot{O}O \begin{array}{ll} \nearrow \text{oxygenated organic compounds} & (34) \\ \searrow C_3H_6 + HO_2 & (35) \end{array}$$

Whether or not the hydroperoxide radical actually exists as more than a transitory intermediate complex is speculative. As the temperature is increased, say from 375°C. to 475°C., reaction 35 becomes more important relative to 34.

Hydrogen peroxide is believed then to be formed by reaction of perhydroxyl radical with propane

$$HO_2 + C_3H_8 \longrightarrow C_3H_7 + H_2O_2 \qquad (36)$$

The formation and destruction of HO_2 and hydrogen peroxide is also postulated as being involved in the water-catalyzed reaction between carbon monoxide and oxygen (7, 118).

Manufacture by Organic Oxidation Processes

The possibilities of technical production of hydrogen peroxide by partial oxidation of hydrocarbons have been studied by several investigators (116, 113, 119, 120). Of the low molecular weight starting materials, the saturated hydrocarbons ethane and propane are most suitable; the use of larger molecules containing the dihydrobenzene structure, for example, dihydronapthalene, has also been patented. Optimum operating conditions for oxidation of the paraffins are difficult to specify because maximum conversion of oxygen to peroxides may occur under somewhat different conditions than those at which the greatest yield of peroxide is obtained per volume of gas passing through the reactor. Optimum temperatures here are in the range 400 - 500°C.*

The process may be attractive where hydrocarbon gases are available essentially at their value as fuel; its advantages are the low costs involved in handling gases and liquids, the relative simplicity of the equipment relative to electrolytic processes, the low amounts of electricity required, and the formation of substantial amounts of olefins as by-products; its disadvantages are the low fraction of gas mixture which is converted to peroxide and olefin per pass and particularly the problems and cost of separating hydrogen peroxide from the condensate, in which it forms hydroxy alkyl peroxides with the aldehydes present. However, it might be feasible industrially to use the peroxide-containing condensate directly in place of hydrogen peroxide as the starting material in certain organic syntheses.

Several methods of separating the hydrogen peroxide have been studied. One (116) is based on the fact that an equilibrium is established in the liquid phase between hydrogen peroxide, aldehyde, and hydroxy alkyl peroxides, thus:

$$H_2O_2 + RCHO \rightleftharpoons RCH(OH)OOH \qquad (37)$$

$$RCH(OH)OOH + RCHO \rightleftharpoons RCH(OH)OOCH(OH)R' \qquad (38)$$

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* It is interesting to note that patents on the formation of organic peroxides by liquid phase oxidation of higher molecular weight hydrocarbons specify optimum temperatures of about 200 - 300°F., (ca. 120°C.)(121).

Addition of calcium oxide to the mixture results in the precipitation of calcium peroxide in amount equal to the sum of the hydrogen peroxide and monohydroxy hydroperoxide present, (113, 122). From this it is inferred that reaction 37 is reversible under the precipitation conditions. The dihydroxy peroxide formed from formaldehyde by reaction 38 is quite unstable in alkaline media and decomposes rapidly.

Since both reactions 37 and 38 are shifted to the right by higher ratios of aldehyde to hydrogen peroxide, it is seen that it is desirable to minimize aldehyde formation in the oxidation step to minimize the separation problem and reduce decomposition in the condensate. Hydrogen peroxide can be regenerated from the calcium peroxide by treatment with carbon dioxide, and the oxide regenerated by calcination of the calcium carbonate formed.

When substantially more hydrogen peroxide than aldehyde is present, the organic peroxides may be decomposed to non-peroxidic acids by heating, and the organic acids thus formed removed by distillation under vacuum, leaving hydrogen peroxide behind (123). This requires that the aqueous peroxide solution be kept sufficiently dilute so that explosive mixtures are not formed, and also may involve a loss of a considerable portion of the peroxides initially formed.

Alternately, it has been reported that heating the condensate with dilute sulfuric acid and methyl alcohol forms acetals that are more volatile than the aldehydes and can therefore be distilled off under vacuum, driving reactions 37 and 38 to the left (124). A recent examination of this proposal confirmed that addition of methyl alcohol aided in the removal, but not by the formation of the acetal (124a). The effect is apparently due instead to the lowered boiling point of the mixture, which decreases the rate of peroxide decomposition.

Various methods of separating hydrogen peroxide from the products of propane oxidation have been recently studied (124a).

The principal problem in the separation is caused by the presence of formaldehyde which reacts rapidly with hydrogen peroxide to form organic peroxides; these peroxides decompose much more rapidly than those formed from acetaldehyde.

The formation of hydrogen peroxide on gas-phase oxidation of hydro-aromatic compounds (120) is technically interesting because a compound such as 1-4 dihydronaphthalene may be prepared by sodium reduction of naphthalene in ethanol, and on oxidation the napthalene is reformed, thus suggesting a cyclic process. The ratio of hydrogen peroxide to carbonyl compounds in the products may be quite high. Under optimum conditions, mole ratios of from 10 to 100 are cited for corresponding hydrogen peroxide yields based on oxygen of 60 to 83%. The more favorable selectivity occurs at smaller degrees of reaction. This process is similar to the cyclic processes involving autoxidations of ethyl anthrahydroquinone or hydrazobenzene, except that oxidation here is in the gas phase at elevated temperatures and substantial deterioration of the "working substance" occurs on oxidation.

OXIDATION OF ALCOHOLS

Non-catalytic, gas phase, partial oxidation of primary or secondary alcohols with oxygen or air can also produce high yields of hydrogen peroxide and aldehyde or ketone (125). Thus, an equimolal mixture of isopropyl alcohol and air reacted at about 485°C. and bubbled through ice water after contact time sufficient to react 46% of the oxygen entering, gave an aqueous solution of hydrogen peroxide and acetone representing an hydrogen peroxide yield of 81% and acetone yield of 97% based on the oxygen reacted according to:

$$(CH_3)_2CHOH + O_2 \longrightarrow (CH_3)_2CO + H_2O_2 \qquad (39)$$

Similar yields are obtained in the presence of water vapor but lower selectivities were found with most of the other alcohols studied. Oxidation of a primary alcohol leads to the formation of the corresponding aldehyde. The high selectivity of oxygen to form hydrogen peroxide on reaction with isopropyl alcohol and the fact that such difficultly-separable compounds as aldehydes are formed only to a slight extent would seem to make this process of possible commercial interest.

AMMONIA OXIDATION

Stephens and Pease (126) report that under certain conditions the product gases from non-catalytic combustion of ammonia and oxygen slowly colored starch-iodide test paper and bleached acidified permanganate, indicating the presence of a trace of peroxide. The products were very largely nitrogen and water.

REACTIONS INVOLVING FLUORINE

Fluorine is an extremely powerful oxidizing agent and will convert aqueous solutions of sulfates, carbonates, borates, phosphates, etc., to peroxy compounds, with reduction of the fluorine to hydrogen fluoride. Contact of fluorine with water alone will result in the formation of some hydrogen peroxide and hydrogen fluoride, plus various other oxidizing agents such as oxygen, F_2O and possibly ozone. Little is known about the nature of the reaction because of the uncertainty of methods of analysis for the products. In one experiment, Fichter and Bladergroen (127) passed fluorine in contact with 50 cc. of water held in a platinum dish and externally cooled with ice; a maximum concentration of 0.2% of hydrogen peroxide was found after 20 minutes, after which the peroxide concentration decreased with time. They attributed the peroxide disappearance to reaction with ozone, since an "ozone odor" was detected after the first half hour and since passage of fluorine into an aqueous potassium hydroxide solution at -20°C. produced a material having properties similar to potassium ozonate, but it is equally possible that the hydrogen peroxide was decomposed by other species present. Hückel (128) reports that the reaction of fluorine with water or ice forms F_2O, hydrogen peroxide, hydrogen fluoride and oxygen, but only traces of ozone at most.

In recent studies by Davis and others (129), fluorine gas and water vapor were contacted in a flow apparatus at room temperature and atmospheric pressure, using excess fluorine and nitrogen as a diluent. The products were condensed at liquid oxygen temperature, and separated into fractions by heating to dry ice and room temperature, successively, and then analyzed by the following spot tests: (1) tetramethyl base, (2) benzidine, (3) potassium bromide - fluoroscein, (4) activated silver, (5) potassium iodide - starch, and (6) acid-base. (These tests are described in Chapter 10.) These indicated the presence of hydrogen fluoride, oxygen, hydrogen peroxide, ozone, and probably some fluorine oxides.

REDUCTION OF OXYGEN ON A CATHODE

Traube showed in 1882 that the presence of oxygen at the cathode in an electrochemical process causes the formation of hydrogen peroxide and in his and subsequent studies it was found that the current yield of hydrogen peroxide varies greatly with the physical and chemical character of the electrode, the concentration of dissolved oxygen and hydrogen peroxide in the electrolyte, temperature, the current density, and the pH and composition of the electrolyte. With the use of various metallic cathodes in an electrolytic cell, low current densities (e.g., 0.02 amp./dm^2) and a dilute acid electrolyte, almost theoretical current yields of hydrogen peroxide have been obtained, with the yield decreasing rapidly as the peroxide concentration or current density was increased (130, 131). However, the maximum hydrogen peroxide concentrations produced are a fraction of 1%. Higher peroxide concentrations with good current yields have been obtained by operating the electrolytic cell under higher oxygen pressure, to increase the concentration of dissolved oxygen. For example, Fischer and Priess (131) made an extensive study of the effects of pressure and were able to obtain a 2.7% hydrogen peroxide concentration with an 83% current yield and 1.3% hydrogen peroxide with 90% current yield at 100 atm. of oxygen pressure, the highest studied, using a gold sheet cathode, platinum anode, 1% sulfuric acid as the electrolyte, and a current density of 2.3 x 10^{-2} amp./cm.^{2}, with corresponding cell voltage of about 2. Attempts to obtain higher peroxide concentrations than this led to much lower yields, as did also operation at lower oxygen pressures. The low peroxide concentrations obtained are presumably caused by the further reduction to water of the hydrogen peroxide formed. Müller and Mehlhorn (132) describe an electrolysis apparatus using a mercury cathode and special stirrer which they designed to transport rapidly into the solution the peroxide formed on the cathode, thereby minimizing further reduction to water. A number of patents have been issued on methods of carrying out the cathode reduction, particularly involving operation under pressure and the use of various specific metallic electrodes (133), but these have little commercial interest today. Patrick and Wagner (134) recently reported studies of oxygen reduction at an iron cathode with very low current densities (about 10^{-6} amp./cm.^{2}). No hydrogen peroxide was detected in weak acid media (pH = 4.25) but yields of from 5 to 36% were obtained in experiments at pH values of 6.5 and 11.1. The highest yield was obtained at pH = 11.1 and at the lowest current density studied. The authors proposed that this was due to peroxide existing largely as the negatively charged perhydroxyl ion in basic media and consequently being repelled from the cathode while hydrogen peroxide molecules existing in neutral or acidic solutions would remain near the electrode and be further reduced. However, another possible explanation is the fact that the catalytic activity of iron compounds reaches a peak in weakly acidic media and this may well have caused the disappearance of all the peroxide formed (see Chapter 8).

A number of studies have been made of the reduction of oxygen on a dropping mercury electrode (135, 136, 137, 138) since this reaction is sometimes involved in polarographic analyses, and the reactions on amalgamated metal electrodes have also been investigated (139). The reduction in the polarographic apparatus clearly proceeds in two stages. As the voltage is increased, the first current wave is interpreted to correspond to the reduction of oxygen to hydrogen peroxide generally written as:

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \qquad (40)$$

or $$O_2 + 2H_2O + 2e^- \longrightarrow H_2O_2 + 2OH^- \qquad (40a)$$

A further increase in voltage leads to a second current wave which corresponds to reduction of the hydrogen peroxide to OH^- or water.

$$H_2O_2 + 2e^- \longrightarrow 2OH^- \qquad (41)$$

or $$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \qquad (41a)$$

The actual mechanisms involved are not well established, but the question of whether or not the reactions are reversible can in principal be determined by comparing the variation of the potential with pH at each point of a current wave, with the change in potential predicted from independent thermodynamic data. Different investigators disagree on whether or not reaction 40(40a) can be made reversible in the polarographic apparatus, although 41(41a) is agreed to be irreversible. A detailed study of the mercury electrode by Iofa, Shimshelevich, and Andreeva (136) led to the conclusion that the reduction of oxygen to hydrogen peroxide here is a first-order reaction for oxygen in both acid and alkaline solutions. The reaction was postulated to proceed via O_2^-, HO_2 and HO_2^-, with the rate determined by the step: $O_2 - e^- \longrightarrow O_2^-$. The reduction of hydrogen peroxide was also found to be a first-order reaction.

The reduction of oxygen on various metal surfaces has also been studied recently by Delahay (140), with the amount of hydrogen peroxide formed determined by a polarographic technique. Hydrogen peroxide formation was favored on aluminum, zinc and magnesium but only small amounts were detected on nickel, iron, silver, copper, tin and lead. These results may be interpreted in terms of the relative rates of three simultaneously-occurring processes: the rate of formation of hydrogen peroxide on a given metal surface, the catalytic activity of the metal for decomposition of hydrogen peroxide, and the possibility of occurrence of other reactions which consume the metal electrode.

W. G. Berl measured the potential which is established on passing oxygen over a graphite electrode (141) and found that the variation of the potential of this half cell on adding various amounts of potassium hydroxide and hydrogen peroxide to the electrolyte corresponded to that which would be predicted from independent thermodynamic data for the half cell reaction 42, after allowing for ionization of hydrogen peroxide and formation of KHO_2:

$$OH^- + HO_2^- \longrightarrow O_2 + H_2O + 2e^- \qquad (42)$$

The standard electrode potential for this reaction is calculated to be 0.0745 volt. Berl concluded that this half cell reaction is reversible and that the mechanism involved is

$$O_2 + 2e^- \longrightarrow O_2^=$$

$$O_2^= + H_2O \longrightarrow HO_2^- + OH^-$$

This mechanism seems more plausible than that generally assumed previously, which postulated the initial splitting of the oxygen molecule to uncharged oxygen atoms and ignored the formation of HO_2 or hydrogen peroxide.

Minute amounts of peroxide were produced with current efficiencies of up to 86% by Fischer and Krönig (142) when the oxygen electrode (on smooth platinum) was made a part of a galvanic cell using hydrogen as the anode and the cell was short-circuited, but considerable polarization occurred and a maximum of only a 3-milliampere current was withdrawn. Only traces of hydrogen peroxide were found if more active forms of platinum were used as electrodes. Berl (141) also reports that by "suitable" operation of a cell containing an oxygen electrode, the electrical or chemical energy can be converted completely to hydrogen peroxide, whether the cell is operated by impressing a potential upon it (electrolysis) or by connecting the oxygen electrode to a suitable anode to form a galvanic cell which generates a current as well as hydrogen peroxide. It is interesting to note that the use of a metallic electrode with oxygen gas instead of graphite or carbon generally gives low and irreversible potentials, varying irregularly with time, which is usually attributed to the formation of oxides which can set up local self-polarizing currents between metal and oxide. No difference was found between graphite and activated carbon in the potentials developed in the above studies by Berl although in his electrolysis cells, the hydrogen peroxide yield was markedly affected by the character of the electrode.

Manufacture by Cathodic Reduction of Oxygen

The use of an activated carbon cathode for commercial production of hydrogen peroxide by oxygen reduction in an electrolytic cell has been studied by E. Berl (143). The critical factor in the peroxide yield is the nature of the electrode--it is necessary that it consist of a highly active, activated carbon of good electrical conductivity. Thus, graphitized retort carbon is unsuitable and best results were obtained with a carbon formed from an oil refinery acid sludge neutralized with potassium compounds--the carbon so formed being more active than if sodium compounds were used. The electrode is formed with a hollow center and is made porous so that oxygen can be fed through it and into the cell. The most effective carbon electrodes in the electrolytic cell are those which have a large porous surface area and also are the most active in decomposing a hydrogen peroxide solution; however, the rate of such decomposition is decreased when a potential is impressed upon the carbon electrode.

With an active carbon electrode and a basic potassium electrolyte, a current efficiency of over 90% is reported for the formation of hydrogen peroxide in 2 -5% concentration, and 65% for the production of about 25% peroxide. These efficiencies are somewhat better than those cited with the use of metallic electrodes (133). The cell potential varies with the current density; 1.4 volts is quoted for a density of a "few" amp./dm.^{2}, and 2.8 - 3.3 volts at 20 - 35 amp./dm^2. At the latter current density, a 12 - 15% hydrogen peroxide solution can be prepared with 70 - 80% current yield and power consumption of about 7.5 kwh. per kilogram of hydrogen peroxide. This is about one half of the power consumption required for the electrolytic peroxydisulfate processes. However, it is necessary to use an alkaline electrolyte in the cells, potassium compounds being preferred to those of sodium, and therefore for recovery of hydrogen peroxide from the electrolyte, it must first be neutralized and then distilled. Alternately, the dissolved peroxide could be removed by conversion to an insoluble peroxide from which hydrogen peroxide could be regenerated, using techniques similar to those proposed for recovery of hydrogen peroxide from the condensed products of hydrocarbon oxidation. The yields of the cathode reduction process are decreased somewhat if air is used instead of oxygen. The process offers the potentiality of simultaneously forming oxygen, chlorine or peroxy compounds at the anode and hydrogen peroxide at the cathode, but this would be difficult to do technically.

The making of a suitable electrode for the process appears to be more of an art than a science, and the effectiveness of the electrode varies with time. It appears that it would probably be necessary to replace the carbon cathodes in the cells with fresh ones fairly frequently and regenerate to restore their activity. Some development work on the Berl process was done by the Mathieson Alkali Works in the 1930's, and the process was also considered by several other companies in the United States and Germany (144). However, it has never been used commercially.

The reduction of oxygen on the activated carbon electrode has also been studied recently by Mizuno (145) who obtained the same general results as Berl. The current efficiency of electrolysis was generally low in NaOH although an 8% NaOH solution was reported to give the same current efficiency as a 20% potassium hydroxide solution. Higher current efficiencies were obtained with uniform oxygen flow around the cathode, and by keeping the solution below 20°C. With the best electrode studied, a 4% hydrogen peroxide solution was prepared with 80% current efficiency by electrolyzing 150 cc. of 20% potassium hydroxide (plus 0.1% sodium fluoride) for 3 hours at a cathode current density of 3.51 amp./sq.dm. and a current concentration of 26.7 amperes/liter. The activated carbon electrodes used here did not establish a reversible potential in a half cell containing 20% potassium hydroxide as did those of Berl, but the potential which was developed by the electrode in such a test was found to be related to its activity and the results of the electrolysis using the electrode. Two studies have also been reported of the formation of hydrogen peroxide in the absorption of acids and oxygen on an activated charcoal (146).

It appears probable that in all of the oxygen electrode cells, the oxygen is first reduced substantially quantitatively to hydrogen peroxide by reaction 1. However, as the peroxide concentration increases, the equilibrium potential for reaction 2 approaches that for the formation by 1 and hydrogen peroxide then becomes destroyed. In addition, catalytic decomposition may occur throughout the electrolyte, particularly if it is highly alkaline, and in some cases possibly on the electrode as well.

Depolarization of Primary Cells

The reduction of oxygen is also of interest as a method of depolarizing the cathode of a primary cell and thereby permitting higher cell potentials and current flow. Thus in the "Edison" primary cell consisting of a carbon cathode and zinc anode in caustic soda electrolyte, the battery housing is designed to allow access of air to the cathode, so that hydrogen peroxide is formed instead of hydrogen gas. However here it is desired that the peroxide thus produced be destroyed as rapidly as possible in order to obtain the highest possible cell potential. A study by Weisz and Jaffe (147) of the potentials established by a carbon-oxygen cathode confirmed Berl's results in basic solutions and showed that in acidic solutions the oxygen is also reduced but not reversibly. In the basic solutions of an air-depolarized cell it was shown that peroxide was formed in accordance with Faraday's laws, and that this peroxide was not reduced to water on the electrode, but was removed from the cell by catalytic decomposition only. The potential of the discharging cell at all current densities using an alkaline solution was found to be that predicted for thermodynamic equilibrium between oxygen and peroxide, after allowing for the internal resistance barrier. Another study of air-depolarized alkali carbon primary cells (148) confirmed the above observations that the oxygen absorbed from the air is converted to hydrogen peroxide and further showed that in the particular cells studied, a portion of the hydrogen peroxide migrated to the zinc anode and depolarized it, and caused corrosion of up to 40 - 70% over the amount of zinc dissolved by the current. The e.m.f. of the cell was raised 10 - 20% by incorporating a peroxide decomposition catalyst into the electrode or by depositing it on the surface. Silver nitrate and potassium permanganate were most effective in the first method, but better results were obtained by depositing palladium chloride on the surface. The use of catalyzed electrodes also increased the cell capacity by 30 - 50% due to the reduced corrosion of zinc.

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CHAPTER THREE

FORMATION AND MANUFACTURE, II. FROM PEROXY COMPOUNDS

In this chapter are considered the formation and manufacture from non-peroxidic reactants, of peroxy compounds other than hydrogen peroxide, and the reactions of these peroxy compounds to produce hydrogen peroxide. Two groups of reactions are found in this category: (1) the formation of inorganic peroxides and their subsequent reactions with acids to release hydrogen peroxide, and (2) the formation of peroxydisulfuric acid and peroxydisulfates by electrolysis, and their subsequent hydrolysis to release hydrogen peroxide. The second group form the basis for the principal hydrogen peroxide manufacturing processes used today.

INORGANIC PEROXIDES

Barium Peroxide

Barium oxide reacts with oxygen to form barium peroxide according to the equation:

$$BaO + 1/2\ O_2 \longrightarrow BaO_2 \qquad \Delta H = -19{,}000\ \text{cal} \qquad (1)$$

The reaction will go to the right if, at the temperature specified, the partial pressure of the oxygen is greater than that which exists in equilibrium with a mixture of barium oxide and barium peroxide. The system is univariant and the equilibrium partial pressure varies with temperature as follows:

T, °C.	P_{O_2}, atm.
620	0.015
700	0.0861
787	0.1855
835	0.945
853	1.220
868	1.534

It is seen that barium peroxide may be formed from air at atmospheric pressure at temperatures of about 790°C. or lower, although in practice temperatures of about 500°C. are used in order to obtain reasonably rapid reaction rates under favorable equilibrium conditions. The peroxidation is usually carried out by blowing air over the oxide which is contained in an externally heated muffle furnace. The reaction proceeds fairly rapidly if the barium oxide is dry, finely divided, and highly porous and if carbon dioxide and moisture are removed from the air. Under these conditions a product containing 88 - 90% barium peroxide may be readily obtained. The use of oxygen instead of air substantially increases the rate of peroxidation but may not be justified economically. Air alone has been used in all industrial operations up to the present time.

A high yield depends principally upon starting with a sufficiently porous form of barium oxide, a manufacturing problem much greater than that of conversion of the oxide to the peroxide, since decomposition of a barium salt at a high temperature level may be accompanied by sintering which produces a hard and unreactive oxide. During the nineteenth century barium oxide was produced almost exclusively from barium nitrate which decomposes fairly rapidly at temperatures of 600 - 800°C., but the operation was very troublesome and expensive since a molten mixture of nitrate, nitrite and oxide is formed. This necessitated small batch operations in externally heated closed crucibles, and involved a number of problems in the handling and recovery or disposal of the nitrogen oxide fumes which were formed. This process was displaced in the very early part of the twentieth century by oxide from barium carbonate.

Barium Oxide from Barium Carbonate

The decomposition of barium carbonate involves the formation first of an intermediate

$$2BaCO_3 \longrightarrow BaO \cdot BaCO_3 + CO_2 \qquad \Delta H = 63{,}000 \text{ cal.} \qquad (2)$$

followed by

$$BaO \cdot BaCO_3 \longrightarrow 2BaO + CO_2 \qquad \Delta H = 2{,}100 \text{ cal.} \qquad (3)$$

The equilibrium partial pressures of carbon dioxide above the solid mixture are as follows (1):

Reaction(2)

T, °C.	P_{CO_2}, atm.
1120	0.0330
1145	0.0504
1195	0.1116
1220	0.161
1255	0.272
1300	0.503
1350	0.967
1352	1.0

Reaction(3)

T, °C.	P_{CO_2}, atm.
1120	0.014
1250	0.09
1450	0.987

This indicates that temperatures above about 1450°C. are needed for complete calcination. However, above 1350°C. the solid phase liquifies and even at temperatures down to about 1050°C. considerable sintering and softening may occur (2). The presence of impurities will, of course, also greatly enhance the tendency to melt and to sinter. Consequently whenever it has been necessary to produce a porous barium oxide in practice, the decomposition temperature has been substantially lowered, usually by adding carbon which lowers the partial pressure of carbon dioxide by converting it to carbon monoxide.

Although barium carbonate occurs naturally, for example as the mineral Witherite, it is too impure for direct use in a barium peroxide process. Instead the starting material is usually the more common mineral, barytes ($BaSO_4$), which is first reduced to barium sulfide with carbon. The barium sulfide is then extracted from the insoluble impurities by leaching with hot water, and barium carbonate is precipitated from the solution by treatment with carbon dioxide gas or sodium carbonate.

$$BaS + H_2O + CO_2 \longrightarrow BaCO_3 + H_2S \qquad (4)$$

The calcination of barium carbonate here is substantially more difficult than that of calcium carbonate because of the stratagems which must be invoked to produce a porous and reactive barium oxide of high purity and to avoid operating at excessively high temperatures. As in calcining limestone, a large heat requirement must be supplied at a high temperature level to a material whose oxide has a strong slagging character. However, to form the porous and reactive barium oxide it is necessary either (a) to add to the carbonate a compound such as barium nitrate or barium peroxide which decomposes and swells up the mass, yet introduces no impurity, or more commonly (b) to lower the decomposition temperature by decreasing the partial pressure of carbon dioxide above the carbonate-oxide mixture. This usually is accomplished by addition of carbon in the form of lampblack, coal dust, petroleum coke, or tar, which converts the carbon dioxide formed to carbon monoxide.

In principle the heat required for the calcination could be evolved directly in the charge by burning additional carbon, for example using a rotary kiln and supplying the additional carbon either as pulverized solid with the air, or in the barium carbonate charge, or both. However oxidation to carbon monoxide releases only slightly more than one quarter of the amount of heat released by formation of carbon dioxide. Consequently the fuel consumption would be very high and if it consisted of powdered coal, would probably cause an unacceptably high impurity content in the product. In practice, the kilns have been designed so as not to allow combustion gases to come in direct contact with the charge, in contrast to conventional limestone kilns. Consequently the heat must be transferred through the retort wall, as is done, for example in by-product coke ovens. The kiln construction is therefore substantially more expensive and operating costs are higher than with limestone calcination.

The form of carbon used should have a minimum ash content since the alumina and silicate compounds in the ash may produce a fused or sintered mixture with the barium oxide. The use of excess carbon (e.g. constituting 25 - 30 wt. % of the initial mixture) permits calcination at higher temperatures without excessive sintering but the excess must then be removed by oxidation at a sufficiently high temperature that the carbonate is not reformed; for example, contact with air for one half-hour at 1350°C. or above has been cited as being effective. The carbon could also be removed by reaction with steam,

$$C + H_2O \longrightarrow CO + H_2 \qquad (5)$$

but temperatures above 988°C. would presumably be required at atmospheric pressure to prevent the formation of barium hydroxide.* The carbon-barium carbonate mixture is usually calcined batchwise in crucibles on a small scale or in shaft

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*The partial pressure of water vapor in equilibrium with barium hydroxide and barium oxide is, for example, 1 atmosphere at 988°C. and 0.125 atmosphere at 786°C.(1). Therefore it would be expected that gases containing water vapor, such as the products of combustion, at temperatures below approximately 800 - 1000°C. would convert barium oxide into the hydroxide.

furnaces or revolving kilns. Sometimes in the latter processes vacuum or an inert gas sweep has been used to help lower the carbon dioxide partial pressure and consequently the decomposition temperature (3). The excess carbon is then removed by contact with very high temperature air. Heating is supplied from electric resistances or indirectly from combustion gases. As would be expected, use of an electric arc furnace is reported to produce a hard, non-porous, and therefore unsuitable form of barium oxide. In all these operations it is important to obtain uniform and carefully controlled temperatures to avoid sintering. Also, the barium oxide formed must be kept from contact with gases containing carbon dioxide at temperatures below that of calcination to avoid reforming the carbonate. Likewise gases containing water vapor may cause formation of barium hydroxide, which has a melting point of about 400°C.*

Bollo and Cardenaccio have patented a process (4) in which addition of a metallic catalyst is purported to permit the direct formation of barium peroxide from the carbonate. In view of the equilibrium relationships discussed above, this appears highly doubtful; it is probable that the barium peroxide they found was formed on cooling the calcined charge in air.

Processes exist for conversion of barium carbonate to the hydroxide by high temperature reaction with steam or by calcination in the presence of silicates to lower the temperature, followed by leaching with water. However, severe technical difficulties would be involved in attempting to dehydrate the molten barium hydroxide to barium oxide at the very high temperatures required. It has been proposed to mix charcoal with the barium hydroxide and operate at about 1200°C. The charcoal would give a more porous product and lower the temperature required by reacting with the water vapor according to reaction 5. However, direct calcination to the oxide appears technically preferable here.

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* See footnote on page 149.

Reaction of Barium Peroxide with Acid

The reaction of barium peroxide with excess acid will result in the complete conversion of barium peroxide to hydrogen peroxide under equilibrium conditions.* In manufacturing practice, the choice of the acid depends upon several factors including: (a) the effect on the purity and stability of the product and on the maximum hydrogen peroxide concentration which can be obtained without serious decomposition, (b) the rate and degree of barium peroxide conversion readily obtainable, (c) the filtering characteristics of the barium salt, if insoluble, (d) the use to which the barium salt formed is to be put and (e) the desirability of forming an insoluble barium salt to remove it from the product solution. Usually the barium peroxide has been reacted with either (1) phosphoric acid or (2) sulphuric acid to which has been added small amounts of hydrochloric or phosphoric acid. If the barium peroxide were reacted with an acid other than sulfuric, the barium salt formed was converted with sulfuric acid to barium sulfate--the only barium salt having an appreciable market--and the original acid regenerated. In principle, the barium salt could be decomposed to barium oxide and recycled to the peroxidation step but unfortunately those acids which are the most satisfactory for reaction with barium peroxide (e.g., sulfuric, phosphoric) form barium salts which are thermally stable and difficult to reconvert to barium oxide; other acids offer difficulty because of cost, insufficient hydrogen ion strength, or because of the problem of conversion of the salt to barium oxide. With the advent of the electrochemical manufacturing processes, which can produce directly a more concentrated and stable product, the barium processes have been generally displaced and now exist only where a suitable market exists for

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* Lewis and Randall (5) measured the equilibrium constant for the reaction $BaO_2(s) + H_2O \rightleftharpoons Ba^{++} + H_2O_2 + 2OH^-$ and reported a value of about 15×10^{-12} for $K = (Ba^{++})(OH^-)^2(H_2O_2)$, where the concentrations are expressed in g. moles/liter.

by-product barium sulfate, also known as blanc fixe. Only a small fraction of present United States and world production is by this process. The simplicity of the equipment required and relative ease of operation make the barium process of interest where a small-scale operation is to be considered, particularly if the commensurate market is for low concentrations of hydrogen peroxide and is relatively near the manufacturing plant. To the present time no industrial barium process has been reported in which the barium salt is reconverted to barium oxide for recycle although it would appear that modern improvements in solids handling techniques and high-temperature operations might make such a cyclical barium process competitive.

The maximum hydrogen peroxide concentration obtainable by the direct reaction of barium peroxide and an acid is usually limited economically to about 6 - 8% hydrogen peroxide because of the thick slurry required at these concentrations and the increasing loss in active oxygen at higher concentrations. Although higher concentrations can be produced by recycling dilute hydrogen peroxide to fresh barium peroxide-acid mixture, the high degree of peroxide decomposition incurred makes concentration by distillation economically preferable.

Hydrogen peroxide has a maximum stability in weakly acidic media, but is much less stable in alkaline solutions than in moderately strong acid media (see Chapter 9). The stability is decreased by tiny amounts of heavy metal ions like iron or copper, by the presence of solid particles, and by the solution of larger quantities of almost any substance. Although pure barium peroxide is relatively insoluble in water, the barium oxide invariably present in the commercial product dissolves to produce a basic medium, and therefore it is desirable to use a fairly strong acid and to contact acid and solid in such a manner as to keep the solution acidic. It is preferable to use an acid which forms an insoluble barium salt and thereby removes the barium from solution (such as sulfuric acid, carbon dioxide, or phosphoric acid); although if such an acid is used, it is necessary to avoid precipitation of the salt in such a fashion that it coats the particles of barium peroxide and protects them from further reaction. Thus, practically no hydrogen peroxide has been found by reaction of concentrated sulfuric acid with unhydrated barium peroxide at 20°C. or of 10 - 50% sulfuric acid at temperatures below 0°C. The solid residue was found to contain most of the initial barium peroxide (6); presumably the particles were coated with insoluble barium sulfate. If the barium peroxide is agitated with water to convert it to the hydrate, $BaO_2 \cdot 8H_2O$, before acid treatment, the formation of hydrogen peroxide is enhanced, presumably because the barium peroxide particles become separated from one another and more readily soluble, but a substantial fraction of the initial peroxygen may be decomposed due to the high alkalinity which exists in the hydration step. Consequently dilute hydrochloric or phosphoric acids have been used instead for hydration.

Addition of a few percent of hydrochloric or phosphoric acid to the sulfuric acid substantially increases the rate of reaction and permits substantially complete conversion. The mechanism of this phenomenon and of the reaction in general can be explained in terms of the film theory, according to which the zone immediately surrounding each barium peroxide particle is a relatively stagnant region across which mass transport occurs principally by molecular diffusion of ions and molecules. Although the degree of turbulence actually increases continuously with distance from the particle surface, it is convenient to visualize the existence of a completely stagnant film, as presented in Figure 1, in which the reaction occurs and in which mass transport is by ion and molecular diffusion alone. Because of the limited solubility of barium peroxide, hydrogen ions diffusing inwardly probably react near the surface of the solid barium peroxide and oxide mixture forming hydrogen peroxide and barium ions, which then diffuse outward. If the acid anion forms an insoluble barium salt, the anions will likewise diffuse inwardly, tending to precipitate the salt on the surface of the particles where the barium ion concentration is greatest, and thereby coating them over. However if a small amount of a second acid is added whose barium salt is soluble, such as hydrochloric acid, then in the initial stage of the reaction the solid particle will become surrounded with a film of chloride ions by the selective precipitation of sulfate ions from the sulfate-chloride anion mixture around the particle. As a consequence, barium ions will diffuse further away from the particle surface, perhaps beyond most of the "stagnant film," before encountering sufficient sulfate ion concentration to produce precipitation. Such a precipitate would be relatively non-adherent to the original particles.

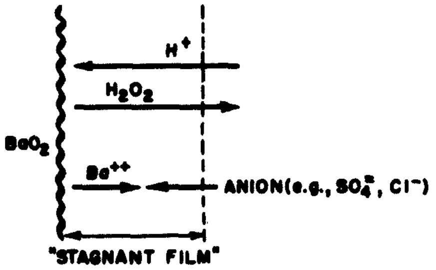

FIG. 1 - INFERRED DIFFUSION OF SPECIES IN THE REACTION OF AN ACID WITH BARIUM PEROXIDE

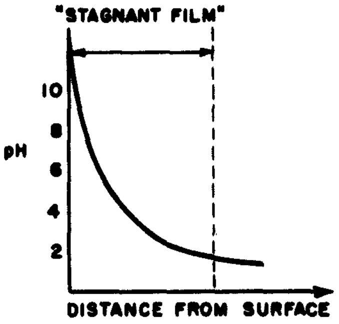

FIG. 2 - INFERRED VARIATION OF pH WITH DISTANCE FROM BARIUM PEROXIDE SURFACE DURING REACTION

The pH will be at a maximum value, probably highly alkaline, next to the particle surface and will decrease with distance from the surface in a manner as indicated in Figure 2. Since the hydrogen peroxide is formed in an alkaline and therefore unstable medium, minimum hydrogen peroxide decomposition is obtained by reducing the time in which the hydrogen peroxide remains in this unstable zone by (a) increasing its rate of diffusion outwards or (b) decreasing the thickness of the alkaline region. The rate of diffusion is increased by temperature and by increased concentration gradient. The temperature cannot be appreciably altered because of the rapid increase in decomposition rate with temperature, but the concentration gradient is kept high by maintaining the hydrogen peroxide concentration in the main body of the liquid to a low value--3 to 8%.

The thickness of the alkaline region can be reduced by (a) using a strong acid to maintain a low pH in the main body of the liquid and therefore a steep pH gradient, and (b) using sufficient agitation so that the maximum slip velocity between particle and fluid is obtained, and thereby minimum film thickness. Good agitation is also needed to break up agglomerated clumps of particles as well as to insure good mixing, since in the reactor alkaline regions in a gross sense must likewise be avoided.

It is seen that the formation of an insoluble barium salt around the reacting particles will not only reduce the rate of reaction, but also reduce the rate of diffusion of hydrogen peroxide out of the alkaline zone, and therefore decrease the yield of hydrogen peroxide.

Reaction of Barium Peroxide with Phosphoric Acid

Phosphoric acid forms three salts with barium; the phosphate is present principally in the form of the highly insoluble $Ba_3(PO_4)_2$ in basic media, as the slightly soluble $BaHPO_4$ in dilute or concentrated acid. Thus, rapid and complete conversion of the barium peroxide can be obtained by allowing the reaction to occur in an acid medium, with final adjustmant of the pH, for example by addition of barium hydroxide, to precipitate the phosphates largely as $BaHPO_4$. The phosphates of iron, copper, and other impurities precipitate at the same time, leaving a relatively stable hydrogen peroxide solution. The impurities can then be removed from the phosphate precipitate by addition of phosphoric acid

$$BaHPO_4 + H_3PO_4 \longrightarrow Ba(H_2PO_4)_2 \qquad (6)$$

to render the barium phosphate soluble, and then the impurities, which remain insoluble, are removed by filtration and the phosphoric acid is recovered by treatment with sulfuric acid and reused

$$Ba(H_2PO_4)_2 + H_2SO_4 \longrightarrow BaSO_4\downarrow + 2H_3PO_4 \qquad (7)$$

Various alternate schemes have been proposed differing in minor details from the above (7). Thus barium peroxide or barium carbonate can be used for adjustment of pH, or metaphosphoric acid used in place of the ortho form and the phosphoric acid or phosphates can be purified in various alternate ways before recycling. It also has been proposed to treat the phosphoric acids with excess concentrated nitric, hydrochloric, hydrofluoric, fluosilicic or fluoboric acid, to precipitate the corresponding barium salt, the phosphoric acid filtrate being heated to drive off the remaining volatile acid before recycling. In another proposal, the barium phosphate is reduced with carbon to form elemental phosphorus and barium carbide. The phosphorus can be converted to phosphoric acid and the barium carbide reacted with water to yield acetylene and barium hydroxide solution and the latter converted to barium carbonate with an alkali carbonate. However, the large number of steps and technical difficulties involved in many of these proposals suggest that they are probably relatively uneconomical.

The high thermal stability of the phosphates prevents their being economically converted directly to barium oxide. Therefore, the ultimate by-product produced with the phosphoric acid process has always been the same as that of sulfuric acid--barium sulfate. The cost of the extra operations involved in the phosphoric acid process in comparison with the sulfuric is apparently offset economically by the ability to produce somewhat higher hydrogen peroxide concentrations directly without excessive decomposition. The hydrogen peroxide solution resulting from phosphoric acid treatment is reported to be purer and more stable than that produced from sulfuric acid since the common impurities such as iron and copper form more soluble sulfates than phosphates, and phosphoric acid has a general stabilizing effect.

Reaction of Barium Peroxide with Other Mineral Acids

The reaction of hydrochloric or nitric acids with barium peroxide has never been used on a technical scale because of the problem of removing the soluble barium salts from the hydrogen peroxide solution formed, although patents have been issued for such reactions (8). In a subsequent distillation process, the low volatility of hydrogen peroxide to water would tend to keep the hydrogen peroxide in the still pot and thus in a solution saturated with barium salts and in contact with precipitated salts--conditions highly favorable for catalytic decomposition. However, in the use of ion exchange resins to separate the hydrogen peroxide formation step from the salt formation step, which is described later in this chapter, a mineral acid forming a soluble salt is preferred.

Hydrofluoric and fluosilicic acids were used on a small scale in the nineteenth century, the insoluble barium salts being treated with sulfuric acid to produce barium sulfate and regenerate the acid.

Reaction of Barium Peroxide with Carbon Dioxide

The reaction of barium peroxide with carbonic acid has been the subject of a number of investigations because of the possibility of being able to calcine the barium carbonate formed to barium oxide for reuse in the process and thus avoid by-product barium salts which are in less demand than hydrogen peroxide. However, the low solubility of carbon dioxide and the fact that carbonic acid is weakly ionized increase the alkaline zone of instability around the reacting particles, and cause more hydrogen peroxide decomposition than occurs with the use of stronger acids. The solubility of carbon dioxide can be increased by pressure, but not the degree of dissociation, and even at 25 atmospheres pressure of carbon dioxide, the hydrogen peroxide yield falls rapidly on attempts to obtain hydrogen peroxide concentrations above about 3 - 4%. Small amounts of barium bicarbonate are formed in solution (2 gm. barium bicarbonate per liter at 1 atmosphere pressure of carbon dioxide) but none exists in the solid phase, the insoluble barium carbonate being the only compound present. The bicarbonate remaining in solution at the end of a run can be converted to insoluble carbonate by adding base, *e.g.* barium hydroxide. As in the formation of insoluble barium sulfate from barium peroxide and sulfuric acid, the reaction rate and hydrogen peroxide yield are enhanced here by addition of small amounts of acids forming soluble barium salts. The use of formic, acetic, propionic, nitric and other acids has been proposed. A comparison between acetic acid and hydrochloric acid showed the latter to be somewhat more effective (6), presumably because of its much greater degree of ionization. The addition of ammonium salts has also been recommended (9), or Na_2HPO_4 (10), which would also inactivate iron or other impurities present in the barium peroxide.

The most extensive studies of the carbon dioxide reaction with barium peroxide are those of Askenasy and Rose (6), who also summarize the work of previous investigators and give extensive literature references. In their studies, a stream of carbon dioxide gas was passed up through the barium peroxide slurry contained in an autoclave, the contents being maintained at a constant pressure and agitation supplied solely by the upward passage of the gas. About 7 minutes was sufficient to obtain substantially complete reaction of the barium peroxide; the hydrogen peroxide yield increased with pressure, particularly when higher slurry concentrations of barium peroxide were studied. In one series of experiments at room temperature in which complete conversion of barium peroxide to hydrogen peroxide would have given about a 2.5% hydrogen peroxide product, reaction for 7 - 10 minutes gave a 76% yield at 1 atmosphere, rising to 82% at 5 atmospheres and about 87% at 10 - 40 atmospheres. In a second series, in which complete conversion would have given about a 5 wt. % hydrogen peroxide product concentration, the actual yield of 57% at 5 atmospheres rose to 71% at 10 atmospheres and 79% at 25 atmospheres. Other studies at 25 atmospheres gave hydrogen peroxide yields of 80 - 90% for final concentrations of 1 - 2 wt. % hydrogen peroxide and 76 - 80% for 4 wt. % final concentration, but attempts to obtain higher concentrations resulted in markedly lower yields. It is possible to obtain higher concentrations by reaction of barium peroxide slurry in a dilute hydrogen peroxide solution but substantial decomposition occurs. Although no noticeable decomposition occurs on passing carbon dioxide through a slurry of pure barium carbonate and dilute hydrogen peroxide, the experimental data indicate that extending the contact time of carbon dioxide with the technical grade barium peroxide from 10 to 30 minutes caused a substantial drop in hydrogen peroxide concentration. Addition of an acid forming a soluble barium salt increases the above yields; for example, addition of hydrochloric acid to form a 1% solution in the water allowed the formation of a 5.5% product concentration with 90% yield, but this introduces the problem of removing from the solution the barium salt formed. The addition of hydrochloric acid produces a coarse, almost sandy, and easily filterable precipitate in comparison to the fine-grained and slimy barium carbonate formed from carbon dioxide alone.

In order to obtain the yields above, it is necessary to carry out the reaction very carefully to avoid the formation or maintenance of hydrogen peroxide in an alkaline medium, this being particularly important when the higher product concentrations are desired. Thus, when starting with a batch of barium peroxide slurry, a carbon dioxide pressure of 20 atmospheres or more should be reached as quickly as possible, in order to obtain an acid medium rapidly. Alternately, as proposed by Doerner (11), the barium peroxide is added to the carbonic acid solution under pressure at a sufficiently slow rate to maintain the slurry acidic. (He reports yields of 50 - 80% for operation at

100 pounds/square inch.) The precipitate formed should be removed immediately after blow-down of the autoclave. The reason for this is that the pressure release discharges most of the acidity of the slurry, so if it is allowed to stand after blow-down, small amounts of unreacted barium peroxide or oxide can make the slurry alkaline, which will cause extensive hydrogen peroxide decomposition. Under some circumstances the hydrogen peroxide decomposition can become so rapid that the rise in temperature produces a self-accelerating decomposition which will destroy all the hydrogen peroxide in a few moments. The considerable variation in results and low yields found by some earlier investigators can be attributed at least in part to their being unaware of the importance of the above factors, and also possibly to the use of a less pure form of barium peroxide. As in reaction of barium peroxide with other acids, it is important to remove the exothermic heat of reaction and to keep the slurry at room temperature or, preferably, near 0°C. since moderate increases in temperature will markedly lower the yield. The problem of heat removal becomes particularly important in the higher slurry concentrations, and in some cases ice has been added to the reaction mixture to aid in cooling.

At atmospheric pressure and with slow addition of carbon dioxide to a barium peroxide slurry to allow the solution to remain alkaline, Wolfenstein and Peltner (12) found that the barium peroxide disappeared without the formation of hydrogen peroxide, but the hydrogen peroxide was suddenly produced as the slurry became acidic on continued introduction of carbon dioxide. They attributed this phenomenon to the formation of barium peroxycarbonate, an insoluble compound moderately stable in alkaline media but decomposing in acid media to form hydrogen peroxide and barium carbonate. They also formed this compound by passing carbon dioxide slowly over barium peroxide hydrate at 0 - 5°C. The formation of barium peroxycarbonate in an alkaline medium suggests the possibility of commercially producing moderate hydrogen peroxide concentrations at atmospheric pressure from dilute carbon dioxide gas concentrations as occur, for example, in flue gases. After conversion of the barium peroxide, the peroxycarbonate precipitate could be removed and then treated with a small amount of an acid to generate barium carbonate and hydrogen peroxide. In the experiment quoted by Wolffenstein and Peltner, a 1.95% hydrogen peroxide solution was prepared with an 87% yield in a run lasting for 3 hours.

S. Mizuno et al (13) separated the hydrogen peroxide formed in their experiments on the electrolytic reduction of oxygen by addition of barium hydroxide to the electrolyte, thereby precipitating barium peroxide. This was converted to hydrogen peroxide by reaction with carbon dioxide gas, keeping the liquid weakly alkaline. Under the best conditions, a 1.65% hydrogen peroxide solution was obtained at a yield of 73.67%. Askenasy and Rose reported that no barium peroxycarbonate was formed in their studies, a result to be expected since they analyzed only their final product and their final solutions were acidic. It has been reported by several workers that the hydrogen peroxide produced from carbon dioxide is purer and more stable than that produced from reaction with sulfuric acid, which is probably due to the very low solubility of the carbonate salts of the impurities. Lunge (14) mentioned that in 1890 a plant in France used the reaction of barium peroxide with carbon dioxide ~~under~~ pressure, but no report has been published of a company using this process in more recent times.

Manufacture of Hydrogen Peroxide from Barium Peroxide

Only one plant in the United States has been reported to use a barium peroxide process, a division of Food Machinery and Chemical Co. at Carteret, New Jersey. The barium peroxide is produced by Barium Products, Ltd., in Modesto, California, and shipped to New Jersey for conversion to hydrogen peroxide (15). The only barium peroxide process of which details have been published is that of Kalichemie in Honningen, Germany (16). The plant is rather old and the operations might be substantially modified in a modern installation. However, in the absence of other information, it will be described briefly. This plant produced about 2000 - 3000 metric tons/year of hydrogen peroxide calculated as 30% solution, plus 3000 - 4000 metric tons/year of barium peroxide, and about 37,000 metric tons/year of barium carbonate, plus by-product barium sulfate and smaller amounts of barium hydroxide, sodium peroxycarbonate and perborate.

Powdered barytes analyzing 94% barium sulfate were mixed with a coarsely powdered coal and reduced to barium sulfide in revolving kilns fired with powdered coal (see flow sheet, Figure 3). Two thirds of the coal required was mixed with the barytes, and the remaining one third was blown into the revolving kiln with the air countercurrent to the solid charge. The reaction is:

$$BaSO_4 + 4C \longrightarrow BaS + 4CO \qquad (8)$$

The maximum temperature reached in the kiln was 1000°C. and the hot clinker leaving was cooled in a second revolving cylinder with part of the air required for the combustion. (In the presence of solid carbon, little carbon dioxide is formed.) Sixty-five to 80% of the solid consisted of water-soluble barium sulfide, the higher content being obtained with low-ash coals. Per 100 tons of 100% barium sulfide produced, 170 tons of barytes and a total of 40 tons of coal were required.

The clinker left the coolers at 100 - 150°C. and was then transferred to the leaching tanks. Extraction was carried out countercurrently in groups of mild steel tanks. Each group consisted of 4 tanks, each containing a 1.5 metric ton charge of clinker. Fresh clinker was contacted with the most saturated solution, and the relatively exhausted clinker with fresh water. At each extraction step, the solution was heated to 60°C. with live steam and after 4 - 5 hours the liquor was pumped off after the solid was allowed to settle. The waste, now containing only 5 - 6% barium sulfide on a dry basis, was discarded.

Barium carbonate was precipitated from the above liquor, containing 180 g./liter of barium sulfide, by countercurrent treat-

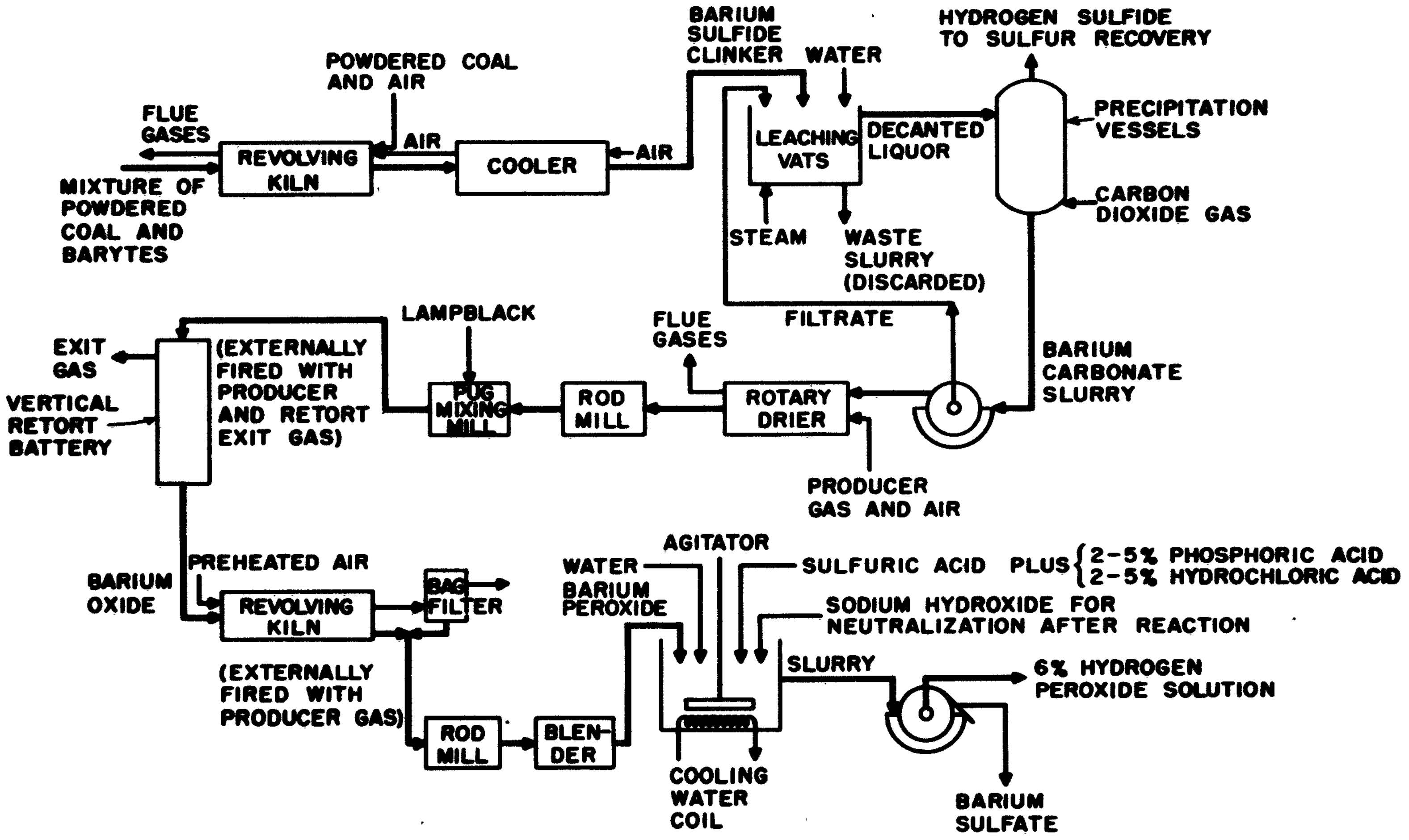

FIGURE 3 – FLOWSHEET FOR THE MANUFACTURE OF HYDROGEN PEROXIDE AT KALICHEMIE, BARIUM PROCESS STARTING WITH BARYTES

ment with carbon dioxide in groups of cast iron cylindrical vessels, each vessel having a volume of 12 cubic meters. The reaction is:

$$BaS + CO_2 + H_2O \longrightarrow BaCO_3 + H_2S \qquad (4)$$

Each group again consisted of 4 tanks, the first 3 containing solution and the fourth acting as an entrainment separator. The oldest solution was treated with the fresh carbon dioxide, which then passed to the second oldest and finally newest solution. Each solution was in contact with carbon dioxide for 6 to 9 hours--2 to 3 hours in each stage of the operation--which stripped all sulfur compounds from solution. The exit gas, analyzing about 90% hydrogen sulfide and 10% carbon dioxide, was then burned and the sulfur recovered. The total pressure drop through the system was about 1 atmosphere, so entering carbon dioxide was fed at 2 atmospheres. The barium carbonate slurry was filtered on rotary vacuum filters of plain cast iron or mild steel, the filtrate was returned to the extraction vats, and the wet cake was dried in producer-gas-fired mild steel rotary driers. Parallel feed was used since countercurrent feed was claimed to be unsatisfactory. The dry product analyzed 98 - 99% barium carbonate and had a total sulfur content of 0.8 - 1.2%, calculated as barium sulfate.

For reduction to barium oxide, the carbonate was mixed in a pug mill with lampblack containing 0.03 - 0.05% ash, in the ratio of 1 part lampblack to 10 parts barium carbonate. Reduction was carried out in retort batteries, externally fired with producer gas plus exit gases from the retorts, which consisted of 18 - 20% carbon dioxide and the remainder essentially carbon monoxide. Each retort consisted of a vertical pipe 4 meters long and 20 cms. inside diameter, made of lengths of acid-resistant stone. Each charge, consisting of 70 kg. of mixture initially and about 50 kg. after calcining, was heated for 12 hours at 1200°C., and then dropped without cooling into steel trucks. It was reported that no difficulty was encountered in emptying the tubes or fluxing of tubes by barium oxide. The product was 93 - 94% barium oxide, the remainder being unreduced barium carbonate and ash, and was produced as particles about 7 mm. in size. About 1 ton of coal was said to be used per ton of barium oxide produced, to supply producer gas for the retorts and for the barium peroxide production described next.

Peroxidation was carried out batchwise in horizontal, cast iron revolving cylinders, externally heated with producer gas. Air was preheated to 150 - 200°C. in a heat exchanger on the exit flue from the calcination furnaces and passed over a 3 metric ton charge at 1000 cubic meters/hour, and then through bag filters. It was said that the charge temperature was about 300°C., although this seems somewhat low.

At the start of the reaction the oxygen was completely removed from the air, and reaction was complete in 14 - 16 hours yielding a product having the following average analysis:

BaO_2	87 - 88%
$BaCO_3$	3 - 5%
$BaSO_4$	1 - 1.5%
SiO_2	0.2 - 0.3%
Al_2O_3	0.1 - 0.2%
Fe	0.02%

The barium oxide content was not reported, but presumably constitutes the remainder.

The barium peroxide as produced was principally of less than 1 mm. particle size, plus some lumps of up to 1 cm. After cooling it was ground in a rod mill to pass a screen of 100 meshes/cm. and mixed in a blender to obtain uniform quality. Reaction with acid to form hydrogen peroxide was carried out batchwise in mild steel vats lined with tile held in putty, each vat being 3 meters in diameter and 2 meters high, and fitted with a lead cooling coil and a pitch-pine agitator. In a given run, 1.4 cubic meters of water were added to the vat, and then 2 metric tons of barium peroxide. Seventy percent sulfuric acid containing 5% phosphoric acid and 5% hydrochloric acid (some figures indicate only 2% each of hydrochloric and phosphoric acid) was run in over 2½ to 3 hours together with sufficient water to keep the concentration of liberated hydrogen peroxide at about 6%. Cooling water kept the batch to a temperature of 30 - 35°C. After reaction was complete, sodium hydroxide was added to neutralize the slight excess of acid used and to bring the final pH to about 4. The hydrogen peroxide yield from the barium peroxide was reported to be 90%. The slurry was filtered on rotary vacuum filters of rubber-covered mild steel construction, using polyvinyl chloride filter cloth. The 6% hydrogen peroxide produced was stored in tile-lined mild steel tanks and no stabilizer was added unless it was to be stored for a long time. For concentration to 30% hydrogen peroxide solution, the solution was vaporized under vacuum and fractionally condensed (distillation and concentration processes are discussed in Chapter 4). Figures leading to a cost evaluation on the entire operation are not available but the following operating factors were cited for the <u>single</u> step of production of 6% hydrogen peroxide from barium peroxide, per 100 kg. of hydrogen peroxide contained in the product.

BaO_2	560 kg.
H_2SO_4 (as 100%)	350 kg.
H_3PO_4	10 kg.
HCl	11 - 12 kg.
NaOH (30%)	11 kg.
Electricity	30 KWH
Steam	25 - 40 kg.
Water (process plus cooling)	16 m^3
Man-hours	5

Hydrogen Peroxide from Sodium Peroxide

Hydrogen peroxide may be produced by reaction of an acid with sodium peroxide in similar fashion to the reaction with barium peroxide. However, most sodium salts are water-soluble, which greatly increases the problem of separation of the hydrogen peroxide from the salt solution without substantial decomposition, as discussed previously.

Sodium peroxide is made by oxidation of metallic sodium, which in turn is produced by electrolysis of sodium chloride dissolved in alkali fluorides and calcium chloride. At 1952 market prices in the United States, hydrogen peroxide from electrolytic processes sold for about 35% more than sodium peroxide, per mole of available oxygen. Therefore, to the extent that a substantial differential exists between the two delivered prices at a given location, hydrogen peroxide may be produced from sodium peroxide, usually at the point of use and for applications where the sodium salt remaining in solution is innocuous. At the present time this is usually done only where the final solution is to be used immediately in alkaline bleaching operations, as of wood pulp and other cellulosic materials. The relative competitive position between hydrogen/peroxide and sodium peroxide is also discussed in Chapter 11.

The sodium peroxide reaction may also be used to produce hydrogen peroxide as a by-product in a process where the focus of attention is on preparing a sodium salt by reaction of the proper acid with a basic sodium compound. For example, moderately soluble sodium fluoride can be prepared from hydrofluoric acid and sodium peroxide, and then artificial cryolite, $Na_3(AlF_6)$, can be precipitated from the solution by adding aluminum fluoride (17)--a process reported to have been used for some time in France.

A recent patent (18), proposes the use of ion-exchange resins to effect the separation of soluble salts in the acid reaction with sodium peroxide. An aqueous sodium peroxide solution is converted to a hydrogen peroxide solution by passing it through a bed of cation-exchange resin initially in the acid state. Organic resins composed of a sulfonated condensation product of formaldehyde and a polyhydric phenol are used since inorganic ion-exchange materials cause excessive decomposition. Subsequent acid treatment of the resin regenerates it to the acidic form and removes the adsorbed sodium ions as the sodium salt. It is necessary to treat the resin in each regeneration step with 2 to 5 times the amount of acid required for complete removal of the sodium ions alone, using, for example, 2 - 20% solution of a strong acid like hydrochloric, sulfuric, or nitric acid. This excess acid treatment removes iron and other catalytic polyvalent heavy metal ions which would otherwise cause substantial peroxide decomposition. Hydrogen peroxide decomposition is also reduced by (1) pre-cooling the sodium peroxide solution to 5 - 10°C., since the reaction develops heat, (2) adding small amounts of stabilizers to the solution, such as sodium silicate, a soluble magnesium salt, or a soluble pyrophosphate, and (3) by keeping the alkalinity of the solution entering the bed to a reasonable minimum by using a solution containing preferably 0.5 - 2.5% of sodium peroxide. Under these conditions, hydrogen peroxide yields of 90 - 99% are claimed. The concentration can be increased to 20 - 30% hydrogen peroxide if desired by recirculating the hydrogen peroxide solution through the resin bed with addition of sodium peroxide to the dilute solution before it enters the bed, although presumably a higher fraction of the peroxygen is then lost. This process can also be applied to other peroxides including, it is claimed, barium peroxide, although no experimental data are cited. However, operation with an insoluble peroxide would be expected to be somewhat more difficult, particularly if it were desired to recover an insoluble barium salt directly from the resin.

Peroxidation of Other Alkaline Earth Oxides

All inorganic peroxides other than barium and sodium peroxide are usually prepared from sodium peroxide or by mixing hydrogen peroxide with appropriate salts or hydroxides. The hydrogen peroxide can be regenerated from these compounds by acid treatment such as has been described.

At a given temperature, the equilibrium partial pressure of oxygen which exists above an alkaline earth peroxide increases in the order: barium peroxide, strontium peroxide, calcium peroxide. Consequently it is far more difficult to form strontium peroxide or calcium peroxide from the oxide by direct reaction with air or oxygen. As with barium peroxide, the equilibrium oxygen pressure increases rapidly with temperature, so that the temperature required for favorable equilibrium for formation of either calcium or strontium peroxide is so low, even at superatmospheric pressures, that the rate of reaction is exceedingly slow. Little work has been attempted on peroxidation of these two oxides.

The equilibrium partial pressure of oxygen above a mixture of strontium peroxide and strontium oxide is reported to be equal to 1 atmosphere at 215°C. Traces of strontium peroxide have been obtained by heating strontium oxide in air, and Fischer and Plötze (19) were able to obtain yields of up to 16% strontium peroxide by heating strontium oxide at a temperature of about 410°C. under 100 atmospheres of oxygen. A patent by Pierce (20) claims the formation of 85% strontium peroxide at temperatures of 400 - 500°C., and 105 - 126 kilograms/sq.cm. (102 - 122 atmospheres). Since there is little demand for strontium salts, hydrogen peroxide could at present be manufactured commercially only in a cyclical process, for example, via strontium carbonate, but the calcination problems involved are similar to those with barium carbonate since strontium carbonate decomposes at about 1340°C., and in addition the peroxidation step would be far more difficult.

Equilibrium in the system calcium peroxide-calcium oxide-oxygen is still somewhat uncertain because of the slow reaction rates at the low temperatures involved. A recent study (21) indicates that 1525 psia.

oxygen pressure exists at equilibrium above the solid at about 111°C. Traces of calcium peroxide have been formed from oxygen and calcium oxide over a reaction time of several days (21, 22) but this reaction appears not to be a practicable route for manufacture of calcium peroxide, and thereby hydrogen peroxide.

FORMATION BY ELECTROLYTIC PROCESSES

Hydrogen peroxide and other peroxy compounds can be formed by electrolytic oxidation on the anode. It is also possible to form hydrogen peroxide directly on the cathode by reduction of oxygen which is dissolved in the electrolyte or bubbled over the cathode. These cathode processes are discussed in Chapter 2.

Only small amounts of hydrogen peroxide as such have been detected on anodic oxidation, and these only in highly basic media. Thus Riesenfeld and Reinhold (23) reported that slight amounts of hydrogen peroxide were detected on electrolyzing a saturated potassium hydroxide solution at -40°C., but none was detected with sodium hydroxide solution under the same conditions. The yield with the potassium hydroxide solution dropped at higher temperatures. In studies at 2 - 4°C., Rius (24) obtained a maximum current yield of 5.35% using a 6.3N solution of potassium hydroxide plus potassium fluoride, with the yield decreasing with time. In other studies at room temperature, no hydrogen peroxide or only traces have been reported. Most of the studies have been made with electrodes of platinum, which is a hydrogen peroxide decomposition catalyst, and the difficulty of detecting hydrogen peroxide in many cases may have been caused by rapid catalytic decomposition on the anode. Burgin (25) used zinc anodes coated with a protective layer of zinc hydroxide or zinc carbonate, which are much less active catalysts and obtained a current yield of about 60% with an electrolyte at 0°C.

containing 5 molar sodium hydroxide and 1 molar boric acid, but this high yield was obtained only at low peroxygen concentrations in the electrolyte.

Glasstone and Hickling (26) have proposed a theory that anodic oxidations in general proceed via the formation of hydrogen peroxide on the anode as an intermediate. It is postulated that discharge of hydroxyl ions at the anode produces OH radicals which then combine irreversibly to form the hydrogen peroxide. The theory is supported by a large amount of evidence including the parallelism between direction of anodic oxidation reactions under varying experimental conditions and that expected if hydrogen peroxide were truly an intermediate, as well as the influence of various hydrogen peroxide decomposition catalysts and of various anode materials on the reactions observed.

Meidinger stated in 1853 that hydrogen peroxide was formed in electrolysis of water strongly acidified with sulfuric acid, a statement which was reiterated by Bunsen in 1854, Hoffman in 1867 and others. However, Berthelot in 1878 (27) showed that the substance formed on the anode was instead peroxydisulfuric acid, $H_2S_2O_8$, which decomposed to yield hydrogen peroxide. It is now well known that peroxydisulfates may be formed in high current yields from solutions of sulfuric acid, or from sulfates in acid or neutral solution, and these reactions form the basis of the commercial processes most widely used today.

Other peroxy compounds such as peroxyborates and perexycarbonates can also be formed on the anode, but these are of relatively less industrial interest, and are not considered in this book.

Theory of Formation on Anode

The observations on amount and kind of peroxygen compounds formed on the anode may be interpreted by considering the standard oxidation-reduction potentials for the reactions which may take place on the anode in water or in various solutions (28).

$$2H_2O \longrightarrow H_2O_2 + 2H^+ + 2e^- \qquad (9)$$

$E^o = -1.77$ volts (1 normal acid)

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (10)$$

$E^o = -1.229$ (1 normal acid)

$E^o = -0.82$ (neutral solution)

$$4OH^- \longrightarrow O_2 + 2H_2O + 4e^- \qquad (11)$$

$E^o = 0.401$ (1 normal base)

$$H_2O_2 \longrightarrow O_2 + 2H^+ + 2e^- \qquad (12)$$

$E^o = -0.682$ (1 normal acid)

$$2HSO_4^- \longrightarrow S_2O_8^= + 2H^+ + 2e^- \qquad (13)$$

$E^o = -2.18$

$$2SO_4^= \longrightarrow S_2O_8^= + 2e^- \qquad (14)$$

$E^o = -2.06$

The potentials are given in volts, and apply to unit activities (essentially one normal solution) of the various species and at a temperature of 25°C. Under thermodynamically reversible conditions, the process having the lowest negative (most positive) potential will occur first and it is seen that under such equilibrium conditions neither hydrogen peroxide nor peroxydisulfate but only oxygen would appear on the anode. The corresponding theoretical cell potential would be 1.229 volts in 1 normal acid or 0.82 volts in neutral solution. However, in actual electrolytic processes, a reaction requiring a higher potential but which is relatively rapid may occur preferentially to one of lower potential but which is relatively slow if the potential drop in the cell is raised above the higher value, as by the use of high current densities and by choice of an electrode material which has a high electrode potential. The fact that little hydrogen peroxide is found when a cell is operated under sufficiently high potential that reaction 9 may occur to some extent may be attributed to reaction 10 being more rapid than reaction 9, or to the fact that the hydrogen peroxide formed could disappear by reaction 12 as soon as a low hydrogen peroxide concentration had appeared. The high instability of hydrogen peroxide in alkaline media could also account for its disappearance by non-electrolytic decomposition processes in high pH media. Anode surfaces can also cause substantial decomposition.

In sulfuric acid the solution contains principally bisulfate ions and the formation of peroxydisulfate most probably occurs by reaction 13. Neutral sulfate solutions contain principally sulfate ions and the corresponding anode reaction is most probably by reaction 14.

Most materials are too catalytically active or unstable to be used as electrodes for these processes. Platinum has been preferred to other metals because it is stable and has a high electrode potential, thereby permitting reactions such as 13 and 14 to occur. However, platinum is an active decomposition catalyst for hydrogen peroxide, which contributes to the other processes which cause its destruction.

The formation of peroxydisulfates in high concentration and good current yield by electrolysis is made possible by the fact that, unlike hydrogen peroxide, they are not readily decomposed on the platinum anode under the cell operating conditions. In order to obtain the high anode potential needed for their formation, polished platinum anodes are used, which have a high electrode potential drop. A high anode current density is also applied, which causes a large overvoltage and minimizes the fraction of the current consumed in the undesired formation of oxygen. Certain additions to the electrolyte in small amounts, such as fluoride or thiocyanate compounds or urea, raise the anode potential somewhat and enhance this effect, probably by being adsorbed on active centers of the platinum anode and acting as inhibitors for the formation of oxygen.

Considerable disagreement exists as to the mechanism of formation on the anode of both hydrogen peroxide and peroxydisulfates (29 - 32), although one involving direct combination of ions seems most probable, viz. equations 13 and 14 for sulfate solutions in acid or neutral media, or combination of two hydroxyl ions to form hydrogen peroxide in alkaline media (hydroxy radicals may possibly form as intermediates). There are various indications that in acid media hydrogen peroxide is not formed on the anode as an intermediate which then reacts with the sulfate to form peroxydisulfate, nor does this apparently occur in the electrolytic formation of peroxycarbonates and peroxyborates (33). In sulfuric acid solutions not containing sulfate salts, maximum peroxydisulfuric acid formation occurs at moderately high acid concentrations and little is formed in dilute acid solutions. This fact has been frequently cited as "evidence" that peroxydisulfuric acid is formed from bisulfate rather than sulfate ions. Although this may well be true--since the anions in relatively high acid concentrations are principally bisulfate--the lower current yields in dilute acid probably result from the lower total cation concentration rather than from the existence of primarily sulfate instead of bisulfate ions, since two of either cation must combine to form the peroxydisulfate ion. The fact that in neutral sulfate solutions high salt concentrations are required to obtain high current yields supports this viewpoint.

It has also been claimed that the presence of nascent oxygen is necessary for the reaction to occur, thus:

$$2HSO_4^- + O + H_2O \longrightarrow H_2S_2O_8 + 2OH^- \qquad (15)$$

However no justification has been offered for this mechanism and it appears far more probable that evolution of oxygen on the anode is needed solely for its polarizing action to produce the high potential required for the formation of peroxydisulfate. Since oxygen evolution proceeds at a lower potential, its formation will always be thermodynamically favorable if the potential is high enough to form peroxydisulfate. Oxygen formation probably cannot be completely eliminated, but in practice it may be reduced to a minor fraction of the current consumed.

Peroxydisulfuric Acid from Sulfuric Acid

Peroxydisulfuric acid decomposes to yield oxygen and sulfuric acid only at a very slow rate at room temperature, but it will readily hydrolyze to yield peroxymonosulfuric acid (Caro's acid), H_2SO_5,

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4 \qquad (16)$$

The H_2SO_5 may then be destroyed at the anode:

$$SO_5^= + O \longrightarrow SO_4^= + O_2 \qquad (17)$$

or may form hydrogen peroxide,

$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2 \qquad (18)$$

or be destroyed by hydrogen peroxide,

$$H_2SO_5 + H_2O_2 \longrightarrow H_2SO_4 + O_2 + H_2O \qquad (19)$$

The hydrolysis reaction 16 and reactions 18 and 19 are non-electrolytic and may occur anywhere in the solution. To obtain a high yield of peroxydisulfuric acid from sulfuric acid it is necessary to avoid as far as possible the formation of peroxymonosulfuric acid, not only because of the readiness with which it enters into the above reactions but also because it causes depolarization of the anode which lowers the cell potential and thereby strongly reduces the current yield for formation of peroxydisulfuric acid.

Many studies have been made to determine the effect on peroxydisulfuric acid formation of changes in the many variables involved in cell design and operation, and these have been presented in considerable detail by Machu (34). The maximum <u>current yield</u> of peroxydisulfuric acid occurs with minimum total residence time of the electrolyte in the cells, since the increasing formation of peroxymonosulfuric acid with time leads to the loss of active oxygen. On the other hand the <u>concentration</u> of peroxydisulfuric acid in the electrolyte continues to increase with residence time. Therefore in a manufacturing process the optimum cell residence time is established by an economic balance. As the peroxydisulfate concentration is allowed to increase, power cost and cell investment per pound of hydrogen peroxide produced increase, but cost of recovery of hydrogen peroxide from the peroxydisulfate decreases. The necessity for a high anode current density (of about 1 amp./sq. cm.) has already been mentioned. A maximum limit on current density is set by the increasing rate of hydrolysis of peroxydisulfuric acid to the peroxymonosulfuric acid and consequent loss of active oxygen at values much above 1.5 amp./sq. cm.--due at least in part to an increase in the local temperature on the anode. It is important to keep the electrolyte as cool as feasible in order to minimize the effect of this increase in peroxydisulfuric acid hydrolysis rate with temperature and also because a temperature rise decreases the cell potential and thereby lowers the current yield. Electrolyte temperatures of 15 - 25°C. are used commercially.

It has been seen that much of the loss of active oxygen is the result of reactions taking place in the electrolyte in contrast to those occurring on the anode itself. It would therefore be expected that the highest current yields would be obtained with a minimum ratio of electrolyte volume to anode surface, which would maximize the extent of electrode reactions relative to electrolyte reactions. Consequently, peroxydisulfuric acid cells are designed with a small volume of electrolyte in the anode compartment (anolyte) and operate with "current concentrations" of about 500 amperes per liter of solution.

Ammonium Peroxydisulfate

Replacement of a portion of the sulfuric acid by ammonium sulfate gives higher current yields than are obtained with sulfuric acid alone, the maximum occurring with a neutral solution of ammonium sulfate. This is because of the fact that in neutral solutions side reactions, particularly the formation of $SO_5^=$, occur only to a slight extent. Here the peroxydisulfate ion is probably produced by direct union of two sulfate ions

$$2SO_4^= \longrightarrow S_2O_8^= + 2e^- \qquad (14)$$

Again a high anode current density is required to furnish the high cell potential needed for high current efficiency. If a neutral solution is used, however, the cathode becomes alkaline and gaseous ammonia is released at the cathode by the overall reaction:

$$2(NH_4)_2SO_4 \longrightarrow (NH_4)_2S_2O_8 + 2NH_3 + H_2 \qquad (20)$$

Consequently commercially there is used a solution containing initially a molar concentration of sulfuric acid slightly greater than that of ammonium sulfate, so that the entire solution remains acidic throughout the electrolysis and therefore negligible ammonia is lost in the cells. The excess acid present allows hydrolysis to occur readily on heating which is the next step in the process. The initial solution may thus be regarded as being an acidic solution of ammonium bisulfate.

Although sodium and potassium sulfates in acid solution can also be converted to the peroxydisulfates by electrolysis and in good current yields (35) these reactions are not usually feasible commercially because of the low solubility of the corresponding peroxydisulfates, which precipitate out in the cells and on the electrodes and are difficult to remove. When these salts are desired as end products, they are manufactured by appropriate reactions with peroxydisulfuric acid or ammonium peroxydisulfate.

During electrolysis of ammonium bisulfate, hydrolysis of the $S_2O_8^=$ ion formed is much slower than in the peroxydisulfuric acid electrolysis because of the higher pH. Consequently much lower current <u>concentrations</u> (amperes/liter) can be used (but not current density) and the cells may contain a relatively large volume of electrolyte. Likewise higher electrolyte temperatures, 30 to 40°C., can be used without significant hydrolysis of the product and are indeed even required to prevent precipitation of the product salt from solution.

With both sulfuric acid and ammonium bisulfate solutions, extreme purity of chemicals and equipment is required to avoid excessive decomposition, which may occur particularly in the subsequent hydrolysis at elevated temperatures. Most heavy metals cannot be used for construction purposes if they will come in contact with the electrolyte. A portion of the recirculated electrolyte is constantly treated to keep the concentration of these catalytically-active heavy metal ions, such as iron and platinum, to a minimum.

Mixed Sulfate Solutions

According to a recent British patent (36), addition of sodium sulfate or other sulfates such as lithium, magnesium, or zinc sulfate to an aqueous solution of ammonium sulfate and sulfuric acid can form a system in which the saturation concentration of total peroxydisulfate can be increased by about 50 - 100 percent over that attainable in acid ammonium peroxydisulfate solutions alone. Accompanying increases in the current concentrations and current density permit the plant capacity to be almost doubled. Current efficiencies of 82 - 85%, which equal those obtained with the ammonium bisulfate electrolyte alone, are claimed but the cell voltage and power requirements were not given. Experimental data given indicate a hydrolysis efficiency of about 80%, which equaled that obtained with an ammonium bisulfate control solution, but is slightly less than that reported for other plants using the all-liquid ammonium bisulfate process.

Cell Design

Many materials have been considered for use as anodes, but only platinum has been found to supply satisfactorily the two principal requirements of inertness to the electrolyte and high electrode overvoltage. The platinum may be supported on tantalum or ebonite-covered metal. Fortunately the necessity for very high anode current densities reduces the required anode surface to a minimum. The only requirement for the cathode is that it be inert to the electrolyte. Consequently, it may consist of graphite, of lead, or of a lead coil through which cooling water can be circulated. Although lead is an active decomposition catalyst, the cathode becomes inactive by formation of inert lead sulfate on the surface. In all the electrolytic processes it is necessary to prevent diffusion of peroxydisulfate ions to the cathode where they would be destroyed, and consequently a porous porcelain diaphragm is commonly used to separate the anolyte from catholyte. In the Pietzsch-Adolph ammonium peroxydisulfate process, the cathode is wrapped with asbestos rope which acts as the diaphragm and thereby eliminates the use of a catholyte. In all cells it is desirable to maintain the flow rate of anolyte above a certain minimum to prevent overheating. The desired peroxydisulfate concentration could be obtained by recirculating the liquid through the cell but in a large industrial installation it is more convenient to pass the electrolyte through a number of cells in series, these often being physically arranged in steps to permit flow by gravity. If the cell design provides for both anolyte and catholyte, the liquid from the hydrolysis step is passed through all the catholyte chambers of the cell series first, and then through all the anolyte chambers. With a suitable diaphragm no change occurs in the composition of the catholyte during its passage through the cells except for the destruction of any residual active oxygen remaining from the hydrolysis and that due to a small amount of diffusion through the diaphragm. The important commercial cells are described in more detail in succeeding sections.

Hydrolysis of Peroxydisulfuric Acid and Peroxydisulfates (34, 37)

The compounds produced in the electrolytic cell are subsequently subjected to hydrolysis to generate hydrogen peroxide. Peroxydisulfuric acid is hydrolyzed directly (Weissenstein process); the acid ammonium peroxydisulfate solution may either be hydrolyzed directly (Loewenstein, Laporte processes) or converted to the relatively insoluble potassium peroxydisulfate, which is then acidified and hydrolyzed (Pietzsch-Adolph process).

In each case an acid medium is required for the reaction and it is in effect peroxydisulfuric acid which is actually hydrolyzed, a reaction which proceeds in two steps as indicated previously:

$$H_2S_2O_8 + H_2O \rightleftharpoons H_2SO_5 + H_2SO_4 \qquad (16)$$

$$H_2SO_5 + H_2O \rightleftharpoons H_2SO_4 + H_2O_2 \qquad (18)$$

The reactions are reversible and 16 occurs much more rapidly than 18. For example, Palme (38) found that with a mixture of potassium peroxydisulfate and sulfuric acid at 50°C., the velocity constant for 16 was 40 times greater than for 18. Increasing the acid concentration increases both rates, that at 10 normal being 8.5 times greater for both reactions than at 5 normal.

In order to accomplish the hydrolysis with a high yield of hydrogen peroxide, it is necessary to minimize the decomposition of hydrogen peroxide and reaction with peroxymonosulfuric acid.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (21)$$

$$H_2SO_5 + H_2O_2 \longrightarrow H_2SO_4 + H_2O + O_2 \qquad (19)$$

Reaction 19 will occur in the liquid phase and 21 in either the liquid or vapor phase. This requires that the hydrogen peroxide be volatilized from the solution substantially as rapidly as it is formed, which is accomplished by operation at elevated temperatures and reduced pressure. A variety of different methods for carrying out the hydrolysis with low active-oxygen loss have been proposed and used, involving various means of obtaining optimum concentrations and temperatures; the most important will be described in the next section.

The direct hydrolysis of an ammonium peroxydisulfate solution has been more difficult to carry out with a high hydrogen peroxide yield than that of peroxydisulfuric acid because it is necessary to concentrate the acid ammonium peroxydisulfate solution before sufficiently rapid hydrolysis will occur and under these conditions solid matter may crystallize out on various portions of the apparatus and cause substantial decomposition of the hydrogen peroxide formed. This problem was overcome by using climbing film evaporators in which concentration and hydrolysis took place simultaneously with no opportunity allowed for solid to collect on the walls (Loewenstein process) or later by using a two-step operation in which the solution is first concentrated under vacuum with partial hydrolysis and then the liquid enters a still where the hydrolysis is completed in the presence of steam (Laporte process). It is necessary in both cases that the electrolyte be very pure in order for this hydrolysis to be carried out without excessive decomposition.

The conversion to the potassium salt before hydrolysis has the following advantages: (1) most of the catalytically active impurities such as iron and platinum remain in the solution, yielding a purer peroxydisulfate for hydrolysis, and (2) the relatively low solubility of the potassium peroxydisulfate produces a lower hydrolysis rate and therefore more opportunity for the hydrogen peroxide to be removed from solution before decomposition or reaction with peroxymonosulfuric acid occurs. The disadvantages are the extra processing steps involved, and particularly the costs involved in handling solids. With each hydrolysis process, fractional condensation of the vapors produced yields a solution containing up to about 35 weight percent hydrogen peroxide.

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COMMERCIAL ELECTROLYTIC PROCESSES

Over 80% of the present world production of hydrogen peroxide is by processes which involve the electrochemical formation of peroxydisulfuric acid or ammonium peroxydisulfate followed by a hydrolysis step to yield hydrogen peroxide and sulfuric acid or ammonium bisulfate, of which the latter are recycled to the cells.

Their advantage over the old barium peroxide processes lies in the ability to produce directly a more concentrated hydrogen peroxide solution (up to about 35 wt. % hydrogen peroxide versus 6 - 8% from barium peroxide) of greater purity and stability. Their chief disabilities are the high capital investment, the electricity consumption, and the extensive and continuing purification of chemicals and electrolyte required. These processes were first developed in Germany and Austria and were expanded there before and during World War II to capacities much greater than existed in any other country, in order to supply hydrogen peroxide which was then concentrated for military uses. A large quantity of detailed information concerning these particular plants became available at the end of the war in the reports of various teams of investigators from the United States and Great Britain, and form the basis for the following discussion. A report by Bretschger, Crewson and Cushing (42) is a particularly detailed and valuable source of information, being written by highly qualified experts in the field. Except for the patent literature, little information has been published about the electrolytic processes used elsewhere, although they are believed to be essentially as described below.

The installed capacities of the various processes in Germany and Austria were as follows: (expressed as metric tons per year of 100% hydrogen peroxide, although produced generally as 35%)

Process	Prewar Capacity	Maximum Wartime Capacity (1944)
Potassium peroxydisulfate	2,600	15,800
Peroxydisulfuric acid	1,700	2,700
Ammonium peroxydisulfate	700	800
Barium peroxide	700	700
	5,700	20,000

In addition to the above, at the end of the war 22,000 additional tons of annual capacity to use the potassium peroxydisulfate process was under construction as well as another 52,000 tons of capacity to utilize the ethyl anthraquinone process. This compares to a pre-1939 world capacity of about 12,000 tons/year calculated as 100% hydrogen peroxide, including that in Germany and Austria.

The maximum war-time distillation capacity in Germany and Austria for concentration to 80 - 85% hydrogen peroxide, reached in 1944, was 17,000 tons/year, with an additional 66,000 tons/year under construction, all expressed as 100% hydrogen peroxide.

Information on capacity in Japan is meager and conflicting (39). Prewar capacity, which utilized the ammonium peroxydisulfate method, was apparently about 700 tons/year expressed as 100% hydrogen peroxide but produced as 30%. In 1944 it was decided to construct manufacturing and concentration capacity for 28,800 tons of 80% H_2O_2/year, expressed as 100% product, but only a small portion of this huge capacity was ever actually built and much was destroyed. Estimates of the maximum production of 80% hydrogen peroxide actually reached vary from 100 to 600 metric tons/month, with the lower figure appearing more probable. There has been little information published on hydrogen peroxide production or production capacities since World War II. A large portion of the peak German capacity was subsequently destroyed or dismantled.

Figures on the rate of production in the United States over the years are given in Chapter 1. The history of the development of commercial processes is also traced briefly in Chapter 1. In 1952 the Defense Production Authority of the United States Government established an expansion goal for the annual U. S. production capacity calling for an increase of 22.3 million pounds per year by January 1, 1955, over the production capacity of 23.1 million pounds per year in 1951. Applications for special tax amortization certificates of necessity by private companies had been received by 1952 to cover the entire proposed expansion. These figures refer to a 100% hydrogen peroxide basis (40).

The important characteristics of each of the electrolytic processes are summarized below:

Peroxydisulfuric Acid (Weissenstein) Process (41, 42)

This process, the oldest electrolytic one, was first brought into operation in 1908 by the Oesterreichische Chemische Werke, Weissenstein, Austria. The capacity at Weissenstein (1945) was about 75 metric tons/month, calculated as 100% H_2O_2, but produced as 30% H_2O_2. The process is also used by the Deutsche Gold und Silver Anstalt (Degussa), Rheinfelden, Germany, which had a monthly capacity (1944) of 160 metric tons as 100% H_2O_2, with additional capacity under construction, and the process is also used in a number of other plants in Europe and the du Pont Co. plant in Niagara Falls, N. Y., U. S. A. A flowsheet is shown in Figure 4.

As operated at Weissenstein and Rheinfelden in 1944, 24 to 26 cells are arranged in series with respect to both solution and electricity, and placed in cascades so that solution flows from one cell to the next by gravity. The cell room in Degussa is shown in Figure 5. Each cell used in this process consists of a ceramic tub about 100 cm. long by 15 cm. wide by 50 cm. deep. A lead coil, through which cooling water is passed, is set in the tub and it serves simultaneously as the cathode and the cooling coil. Inside the lead coil, 10 vertical cylindrical porcelain diaphragms are spaced equidistantly, and inside each diaphragm is fitted a glass vessel which serves to restrict the volume of the anolyte chamber. Cooling water

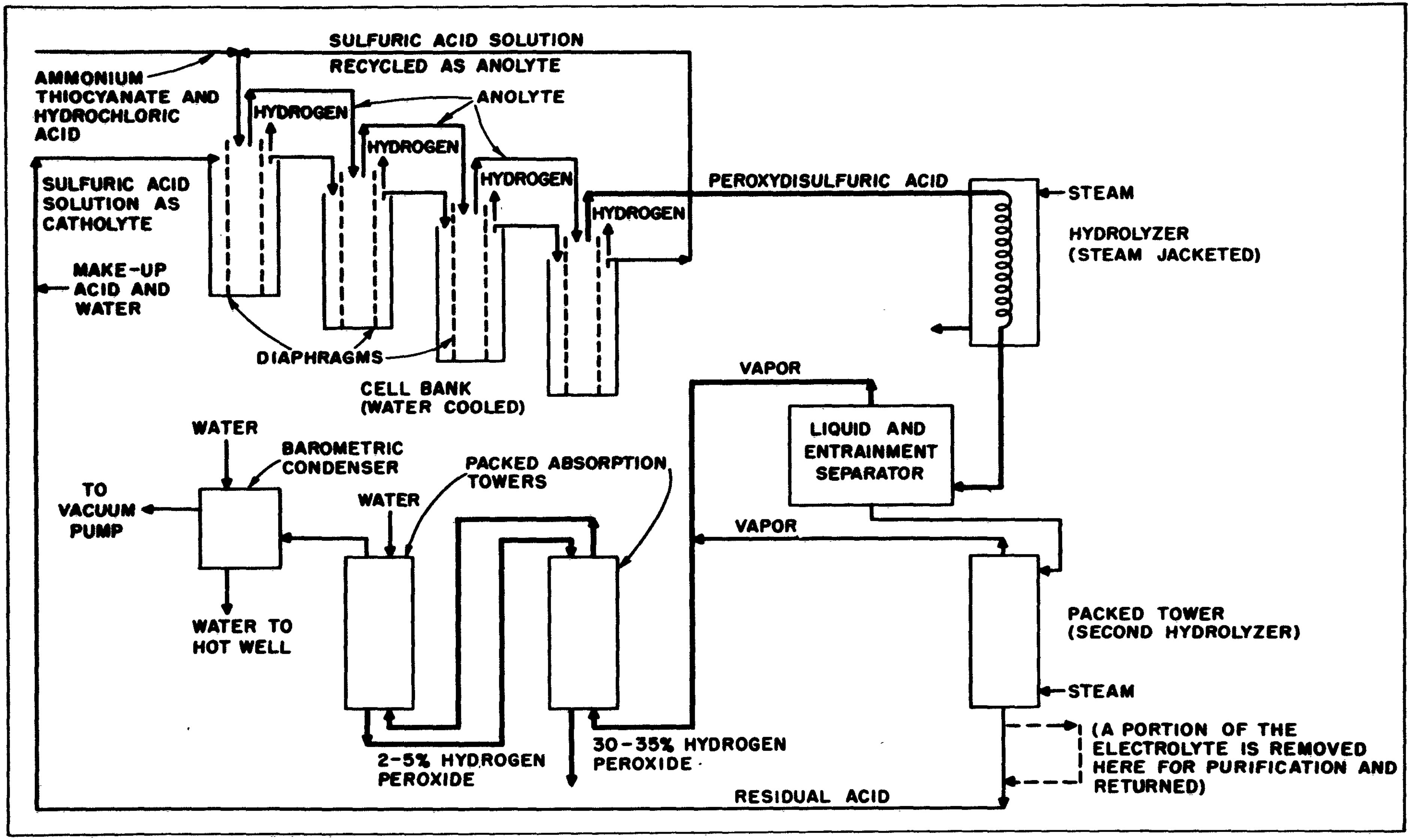

FIG. 4-FLOWSHEET FOR THE PEROXYDISULFURIC ACID ELECTROLYTIC PROCESS

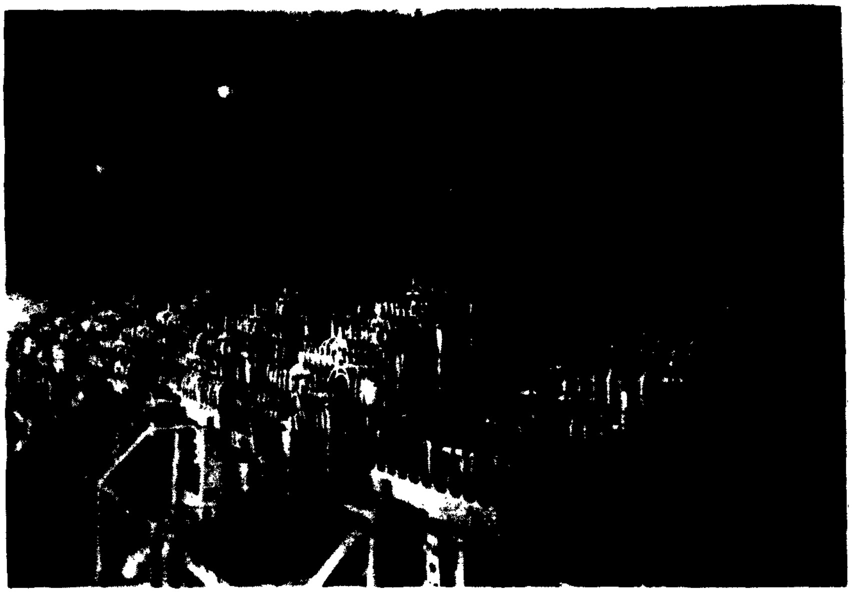

FIG. 5 - PEROXYDISULFURIC ACID CELL ROOM, DEGUSSA

is passed inside the glass vessel. Each anode consists of 11 vertical platinum strips equispaced within the thin annulus between glass vessel and diaphragm, each strip sealed to a lead ring resting on top of the diaphragm. All ten anode sets inside one tub are connected in parallel. In a preferred anode construction the bottom portion of the strip is platinum and the top is tantalum, the two being spot-welded together. The dimetal anode has a longer life and the lower electrical resistance of the combination lowers the cell potential slightly. (A zirconium-platinum combination would also be satisfactory although perhaps difficult to manufacture; tantalum, zirconium, and their salts do not cause significant peroxygen decomposition (43).)

A solution containing 500 gm./liter of sulfuric acid flows through the catholyte chambers of the cascade of cells in series, during which no significant change in concentration or chemical composition occurs, and then is pumped back to flow through the anolyte chambers in series. The hydrogen is evolved into the air of the cell room, which must be well ventilated. A solution of ammonium thiocyanate and hydrochloric acid is added before the solution enters the first anolyte chamber, in amounts equivalent to 0.15 gm. HCNS and 0.037 gm. of hydrochloric acid per liter of anolyte. The catholyte operates usually about 5°C. cooler than the anolyte. Cooling water is passed through the cathode lead coils and anode glass inserts with the aim of keeping the anolyte temperature down to 20 - 30°C. The electrolyte leaving the last cell contains 25 - 30 gm. of peroxydisulfuric acid per 100 cc. of solution. The average potential drop per cell is about 5.5 - 5.7 volts with the all-platinum anode and 5.2 - 5.3 volts with the platinum-tantalum combination. A current density of about 0.86 amp./sq. cm. is used; densities higher than 1 amp./sq. cm. cause excessive platinum loss. A corresponding current efficiency of 72% is reported.

The electrolyte is hydrolyzed by passing it continuously through a long steam-jacketed lead coil in which the liquid is evaporated to about one half its original volume, 80 - 90% of the peroxydisulfuric acid is hydrolyzed, and the resulting hydrogen peroxide is vaporized. Hydrolysis of peroxydisulfuric acid to the peroxymonosulfuric acid occurs fairly near the inlet. Evaporation of water along the tube increases the acid concentration and thereby accelerates the rate of hydrolysis of the peroxymonosulfuric acid to hydrogen peroxide. Most of the hydrogen peroxide formation appears to occur towards the exit, where the acid concentration is high. The liquid and vapor are then separated. The liquid is run into the top of a packed porcelain tower into the bottom of which steam is fed countercurrent to the liquid. The steam provides heat for hydrolysis of remaining peroxy sulfuric acids and also prevents too high an acid concentration in the liquid. Most of the remaining active oxygen in the liquid is thus converted to hydrogen peroxide and removed as vapor. The liquid leaving the tower contains some hydrogen peroxide plus the two peroxy sulfuric acids, equivalent to about 2.6 gm. of peroxydisulfuric acid per 100 cc. of solution, and this is destroyed by electrolysis in the cathode compartments of the cells.

The overall reactions are:

In the cell,

$$2H_2SO_4 \longrightarrow H_2S_2O_8 + H_2 \qquad (22)$$

In the hydrolyzer,

$$H_2S_2O_8 + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2 \qquad (23)$$

The vapors from the hydrolyzers are fed to two groups of packed absorption towers in series and operated under vacuum, from which an aqueous solution containing 30 - 35% hydrogen peroxide is produced. The product from the rectifying tower contains about 4 gms. of sulfuric acid per liter. This is partly neutralized to produce a slightly acidic product and stabilizers are added before shipment.

The efficiency of peroxygen recovery in the overall hydrolysis and distillation operation is reported to be about 85%. To keep impurity concentrations to a minimum, about 5% of the recycled acid is continuously withdrawn, purified by distillation in quartz apparatus, and returned to the system. Some of the operating factors are reported to be as follows, on the basis of 1 kg. of product calculated as 100%: power for cells, 14 - 16.2 kwh.; total process power including 10% loss in AC-DC conversion, 21.5 kwh.; steam for hydrolysis and distillation, 27.5 kg.; sulfuric acid makeup, 0.5 - 0.9 kg.; process labor, about 0.1 man-hours; platinum loss 0.0025 - 0.003 gm., platinum investment per 1000 kg./month capacity, 815 gm. platinum or 334 gm. of platinum and 3340 gm. of tantalum in bimetallic anodes. The peroxydisulfuric acid process has the advantage of lower labor costs than the potassium peroxydisulfate process described below, but cell current efficiency and hydrolysis efficiency are both lower than in the potassium peroxydisulfate process.

Potassium Peroxydisulfate (Pietzsch and Adolph or E.W.M.) Process (42, 44)

This process was first operated in 1910 by the Elecktrochemische Werke, Munich (E.W.M.) in a plant in Hollriegelskreuth and is used in the Henkel Co. plant in Düsseldorf, and elsewhere. It was the process picked for most of the World War II expansion in Germany, very large plants being erected at Bad Lauterberg (capacity 1100 tons/month expressed as 100% hydrogen peroxide) and Rhumspringe (capacity actually constructed, 700 tons/month as 100% hydrogen peroxide). A flowsheet is shown in Figure 6.

An acid ammonium bisulfate solution is first electrolyzed to give ammonium peroxydisulfate in solution:

$$2NH_4HSO_4 \longrightarrow (NH_4)_2S_2O_8 + H_2 \qquad (24)$$

Potassium bisulfate is then added to precipitate potassium peroxydisulfate and the ammonium bisulfate is purified and returned to the cells:

$$(NH_4)_2S_2O_8 + 2KHSO_4 \longrightarrow K_2S_2O_8 + 2NH_4HSO_4 \qquad (25)$$

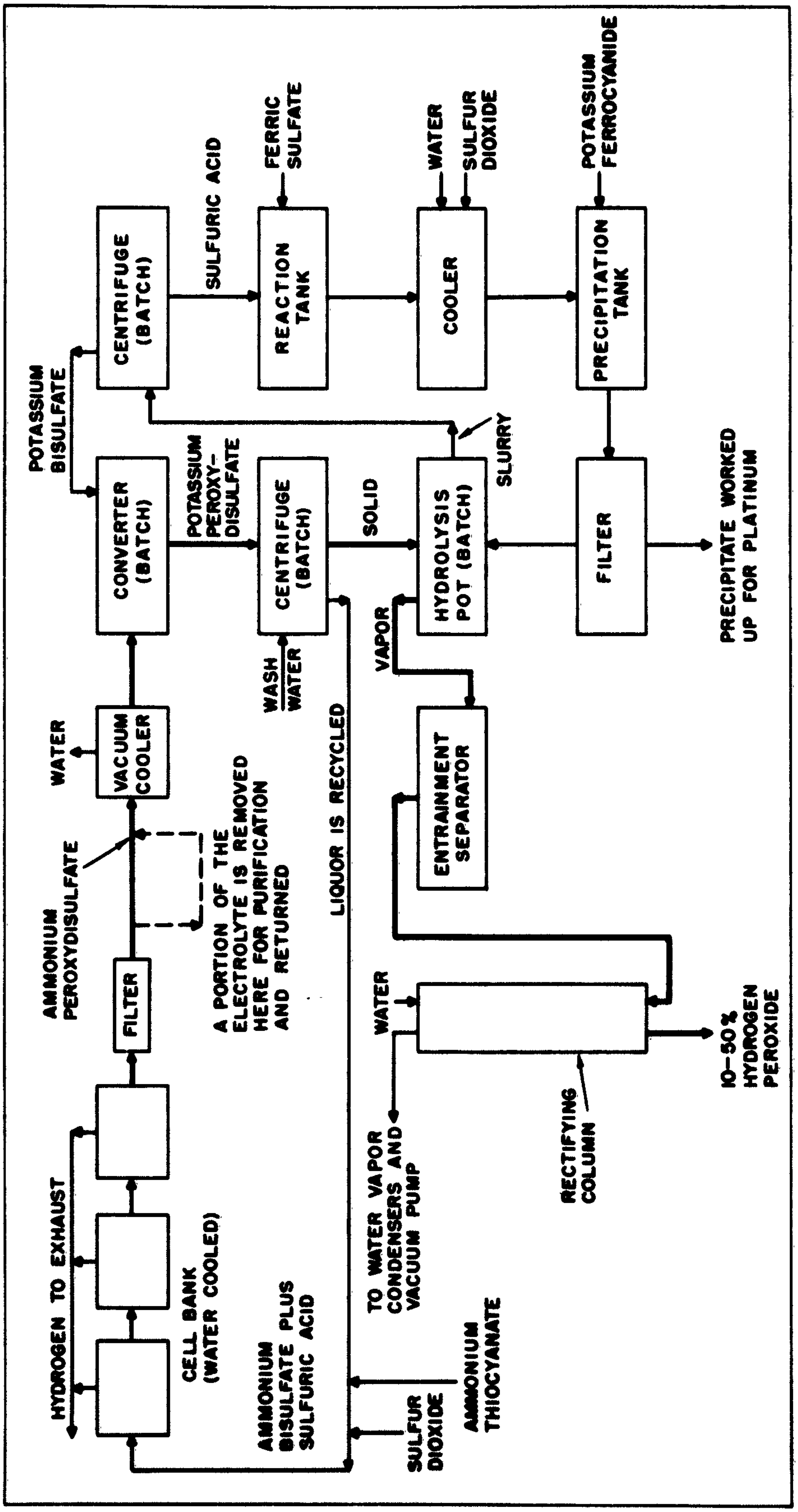

FIG. 6—FLOWSHEET FOR THE POTASSIUM PEROXYDISULFATE PROCESS

Sulfuric acid is added to the potassium peroxydisulfate slurry and the mixture is steam distilled to produce hydrogen peroxide vapor which is fractionally condensed.

$$K_2S_2O_8 + 2H_2O \xrightarrow{H_2SO_4} 2KHSO_4 + H_2O_2 \qquad (26)$$

The solid potassium bisulfate is centrifuged from the above slurry and returned to the stage represented by equation 25. The residual sulfuric acid is purified and returned to the hydrolysis step.

Figure 7 shows the detail of the top of an E. W. M. type electrolytic cell, and Figure 8 shows the cell room at the Bad Lauterberg plant, containing E. W. M. type cells. At E. W. M. each cell consists of a stoneware tub 28" x 31½" and 34" deep containing no partitions. Each tub contains parallel vertical rows of anodes (14 per row), cathodes (15 per row), and cooling tubes (16 per row) placed in the following sequence: cooling tubes, cathodes, anodes, cathodes, cooling tubes, with the sequence repeated 5 times. Thus one tub contains 70 anodes, 150 cathodes and 160 cooling tubes, all the anodes and all the cathodes, respectively, being connected in parallel electrically. In other plants using this process the number of cathodes, anodes, and coolers per tub may be slightly different. The cell is enclosed with 7 graphite blocks which rest on the top of the tub and extend across it. Several can be seen in Figure 7, below the bus bars. The central 5 blocks support the electrode and cooler assemblies. The maximum cell size is apparently set by the difficulty of manufacturing the large stoneware tub. The cell construction is quite complex and will not be described in complete detail here. Each anode consists of a vertical aluminum rod coated with hard rubber which supports around it a circular grid of vertical platinum wires which form the true anode. Each cathode is a vertical rod of graphite coated with paraffin to minimize corrosive attack, and closely wound over its entire length with asbestos rope 3 mm. in diameter, which wrapping acts as the cell diaphragm. Thus the catholyte compartment is only

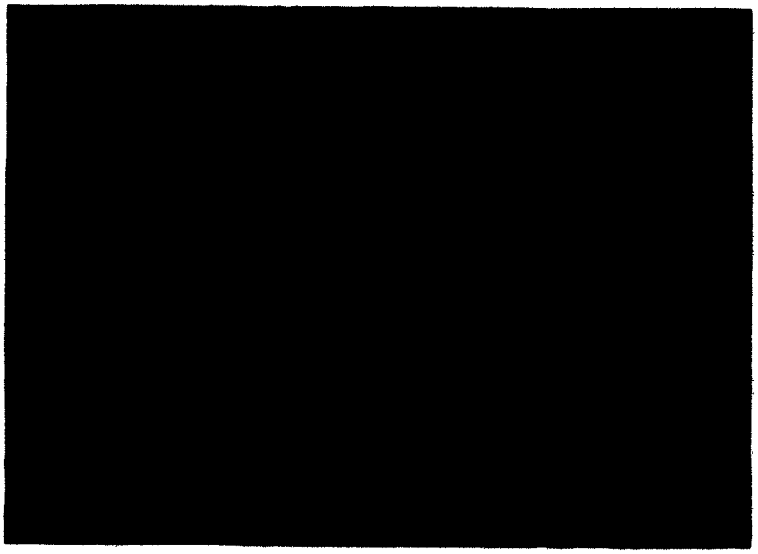

FIG. 7 - E.W.M. PEROXYDISULFATE CELL DETAILS.

FIG. 8-CELL ROOM, BAD LAUTERBERG, (E.W.M. TYPE)

the tiny volume between the asbestos cord and the rod. Each carbon block suspends two rows of cathodes. Between these in each block is a row of holes for entrance of the anode assembly to the cell, and outside the two cathode rows are two other rows of holes for the cooler assemblies. Electrical contact to the cathodes is made by an aluminum plate resting on the blocks and connected to the bus bars at both ends. Suitable holes are provided in the plate to match those in the carbon blocks to allow entrance to the anode assemblies and coolers. The anode assemblies are insulated where they pass through the holes in the carbon blocks and aluminum plates and are suspended from aluminum bars above the blocks, the bars being connected at both sides to bus bars. The cathode current density is 0.03 - 0.05 amps./cm. Higher cathode densities lead to hydrogen polarization and formation of free ammonia gas on the cathode. The current concentration is about 18 amp./liter. Each cooler consists of two vertical concentric glass tubes so that the water flows down through the center and then rises in the annulus. The tubes are connected to hard rubber double manifolds which are suspended above the carbon blocks. Use of glass is to avoid corrosion. In Figure 7 can be seen the hard rubber headers and the top of the outer row of coolers. The glass tubes seen prominently on top give a visual indication of cooling water flow. After assembly of the cell, the cracks between blocks, and blocks and tub, are sealed with wax. From 7 to 11 tubs are connected in series with glass nipples for flow of the electrolyte, all the tubs being at the same level. All 28 tubs at E. W. N. were in series with respect to flow of electricity. The hydrogen is removed from one end of the cell into pipes by an exhauster fan, air being allowed to enter the cell at the other end to keep the hydrogen concentration very low. This mixed gas is then discharged to the atmosphere.

Each cell uses 4600 amperes at a current density of 1 - 2 amperes/cm^2. The platinum loss from the anodes per ampere hour is a minimum at 2 - 4 amp./cm.^{2} and under these conditions the anodes last three to five years before replacement is necessary. Alloying the platinum with 0.1% iridium also reduces the platinum loss somewhat. Each cell contains about 340 liters of solution, and normal flow rate is 1500 liters/hr. through each group of tubs in series. Aluminum is frequently used for bus bars since even traces of copper in the electrolyte would cause significant catalytic decomposition. During operation the ammonium ion concentration at the cathode slowly increases and the pH consequently increases.

$$2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2 \qquad (27)$$

When the solution at the cathode becomes alkaline, ammonia gas is released to the atmosphere and potassium sulfate precipitates out. The cell voltage starts at 5.2 but in the German operations slowly increased until it averaged 6.2 volts at the end of six days operation, with an average during the week of 5.9 volts. The cell banks were then shut down for one day to allow the potassium sulfate to redissolve. Some individual cells increased in voltage more rapidly and they were individually cut out of the circuit when they exceeded 6.5 volts. Consequently, about 90% of the cells were in operation on the average, and the entire cell room was shut down one day in seven.

The electrolyte solution has the following typical concentration:

	Concentration (Normality)	
Component	Entering Cells	Leaving Cells
$(NH_4)_2S_2O_8$	0.6	1.2
$(NH_4)_2SO_4$	4.0	3.4
H_2SO_4	1.4	0.8
K_2SO_4	0.4	0.4
NH_4CNS, g./l	0.1	0
KNO_3, g./l (Max.)	2.5	2.5

About 40 - 110 ppm. of iron may also be present. An increase in nitrate ion content, which is formed by oxidation of ammonium ion, would result in decreased current efficiency.

The concentrations of ammonium peroxydisulfate and potassium sulfate in the entering liquor are determined by the equilibrium relationships in the previous precipitation of potassium peroxysulfate. Consequently the concentrations will vary with the temperature and amount of potassium bisulfate added in that step. In order to increase the percent recovery of peroxydisulfate as the potassium salt, which would lower the ammonium peroxydisulfate content in the liquid entering the cells, it is necessary to increase also the potassium sulfate content. However this causes an increase in the salting-up rate in the cells.

Optimum operating temperature for the cells is 38°C.; excessive peroxygen decomposition occurs at higher temperatures and excessive salt precipitation at lower temperatures.

The electrolyte leaving the cell bank (see Figure 6) flows to a vacuum cooler where evaporation of water lowers the temperature to 28°C., and then to 18-8 stainless steel tanks equipped with means for cooling and stirrers where potassium bisulfate in the form of a damp cake is added to precipitate half of the peroxydisulfate as the potassium salt. The final temperature is 14 - 16°C. and the precipitated product still contains about 10 - 20% ammonium peroxydisulfate from occlusion. The potassium peroxydisulfate is batch centrifuged, washed, and then carted to the hydrolyzing units. The mother liquor is treated with sulfur dioxide to destroy any peroxymonosulfuric acid present by reducing it to sulfuric acid, ammonium thiocyanate is added to increase the anode potential and then the liquor is returned to the cells. The destruction of peroxymonosulfuric acid reduces the loss of platinum from the anodes.

The hydrolysis was carried out in stoneware retorts in batches of 1000 kg. potassium peroxydisulfate, to each of which was added 250 - 300 liters of 18N sulfuric acid. The hydrolysis units at the Bad Lauterberg plant are shown in Figure 9. Steam was added through a perforated pipe for 4½ hours and the vapors were removed under vacuum. The retort operated at 75 - 85°C. and 45 - 55 mm. Hg. pressure. The vapors passed to a packed column to remove entrained liquid and then to a fractionating column in which reflux was provided by either a water spray or an aluminum condenser. Figure 10 shows the rectification columns in the Bad Lauterberg plant. The vapor entering the column from the retort varied in concentration from about 10% wt. hydrogen peroxide at the beginning of the hydrolysis to less than 1% wt. at the end. Liquid from the bottom of the fractionating column varied from about 50% hydrogen peroxide at the beginning to 3% or less at the end. An average concentration of 35% hydrogen peroxide was obtained with an overall efficiency of 85 - 91%--most of this loss being due to decomposition and the rest lost in pot residue or vapor from the rectification tower. However, this vapor generally contains negligible hydrogen peroxide; it is condensed and the non-condensable gases passed to a vacuum pump. Figures on the impurity content of the hydrogen peroxide vary; from 2 to less than 0.25 gms. sulfuric acid/liter are quoted by various sources.

After distillation was complete, the retort was washed out with 300 liters of 15N sulfuric acid and the slurry was cooled and centrifuged. The bisulfate was carted to the potassium peroxydisulfate precipitation tanks and all of the sulfuric acid filtrate was purified in the following operation, before recycling to the process.

Peroxygen compounds were first decomposed by heating with steam to 105°C. and adding ferric sulfate. After 1½ to 3 hours of standing in a series of stoneware tanks, the acid was cooled to 60 - 80°C. in a tantalum cooler, and diluted to 10N to precipitate the iron. Traces of active oxygen remaining were destroyed by adding SO_2, and then the acid was treated in batches with $K_4Fe(CN)_6$, using air agitation, to precipitate remaining iron as Prussian blue--using rubber-lined steel tanks with tile

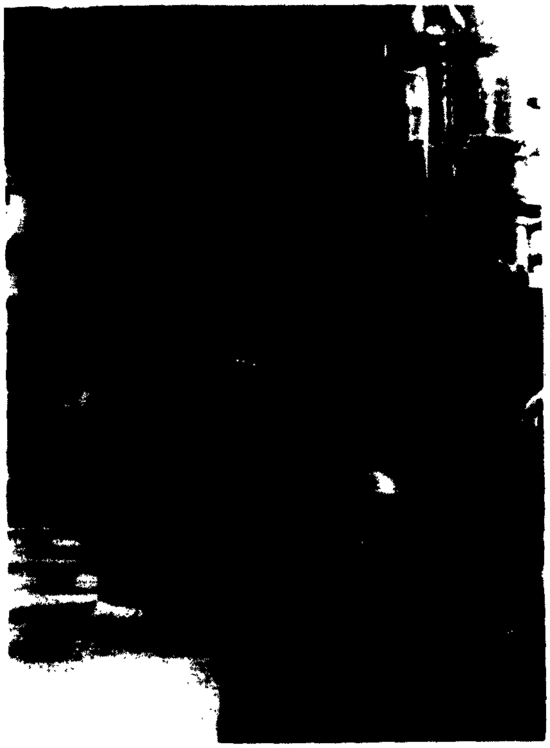

FIG. 9 - POTASSIUM PEROXYDISULFATE HYDROLYSIS UNITS AT BAD LAUTERBERG

FIG. 10–RECTIFICATION COLUMNS FOR 35% HYDROGEN PEROXIDE, BAD LAUTERBERG

facing. The precipitate was filtered by gravity through ceramic filter tubes and treated to recover about 40% of the platinum lost from the anodes. The acid filtrate was concentrated to 18N in a stoneware retort heated by a gold alloy (30% silver) coil and operated at 10 mm. Hg. pressure. (Silver is added to the gold to give a harder metal.) After concentration the filtrate contained 5 - 10 ppm. iron.

Iron and platinum may also be precipitated by making the solution slightly alkaline with ammonia, but if this is done directly, the quantity of ammonia required would increase the concentration of ammonium sulfate in the system above that desired. Therefore if this technique of purification is used, 1 - 5% of the electrolyte after hydrolysis is passed slowly through a set of cells to bring the sulfuric acid concentration down to 0.2N, the peroxydisulfate content increasing to 1.8N. Then 0.3 equivalents of ammonia are added to the liquor in a Haveg tank to precipitate the iron and alumina and provide just sufficient ammonium ion to make up for losses from the system. Alternately, ammonia could be added to precipitate impurities and the excess ammonium sulfate removed by diverting a portion of the regular electrolyte stream to stoneware evaporators. This operation also removes small pieces of graphite, asbestos fibers, etc.

Some of the operating factors are reported to be as follows, on the basis of 1 kg. of product calculated as 100% hydrogen peroxide and produced as 35%, and for production in a plant having the capacity of about 150 tons/month or larger. Power for electrolysis: 12.9 - 13.2 kwh. for the cells, plus 10 - 15% loss in AC to DC conversion, and 2 - 2.5 kwh. for miscellaneous process uses; process steam, 13 kg. for distillation and 25 - 28 kg. total; water 1 - 2.5 $m.^3$; (this figure will vary considerably with water temperature); sulfuric acid, 0.08 - 0.15 kg.; ammonium hydroxide 0.03 - 0.1 kg.; potassium sulfate, 0.020 - 0.03 kg.; ammonium thiocyanate, 0.025 - 0.075 kg.; $K_4Fe(CN)_6$, 0.002 - 0.01 kg.; sulfur dioxide 0.005 - 0.075 kg.;

ferric sulfate, 0.01 - 0.08 kg.; net platinum loss, -.0014 - 0.0027 gm.; platinum investment, 330 gm. per 1000 kg./month capacity; process labor, about 0.28 man-hour. Depreciation on equipment at 15% per year and on buildings at 5% per year and maintenance accounted for 35 - 40% of the total manufacturing cost in Germany. The total cost of producing 80% hydrogen peroxide by this process, including overhead and depreciation, was 2.25 Reichsmarks per kilogram of contained hydrogen peroxide, which corresponds to 41 cents/pound at an exchange rate of 40 cents per mark. This process has the advantage over that using sulfuric acid alone, of producing a purer product, of having a higher cell current efficiency, (about 82 - 84% versus 72% for peroxydisulfuric acid and about 84% for the "all-liquid" ammonium peroxydisulfate process) and a slightly higher hydrolysis efficiency (about 85 - 91% versus 85 - 88% for peroxydisulfuric acid and 85% for the Elchemie ammonium peroxydisulfate process), plus the fact that much larger cells can be conveniently used. However operation is somewhat more complex and involves substantially higher labor costs. In particular, the use of an asbestos diaphragm wound around the cathode in the electrolytic cell causes salting-out to occur at the cathode with accompanying gradual rise in cell potential. Consequently the cells must be shut down from time to time. Furthermore the higher average cell potential largely nullifies the advantage of high current efficiency. The handling of solids and the batch hydrolysis operations both require considerable labor time. It appears that of the three processes, an all-liquid ammonium peroxydisulfate process is generally the most efficient if the hydrolysis step can be carried out with reasonably high yield, and this process is of interest particularly in large installations and where labor costs are high, as in the United States. Thus, it was estimated in 1945 that in the potassium peroxydisulfate process labor costs accounted for about 30 - 35% of the production cost in war-time Germany, but that it would be about 70% in the United States. The potassium peroxydisulfate process with batch hydrolysis may be more competitive in small plants. The decision to use it in war-time Germany seems to have been based partly on political considerations as well as on a purely technical basis. The E. W. M. type cell can be used quite satisfactorily in an all-liquid process, as discussed below.

Ammonium Peroxydisulfate "all-liquid" (Lowenstein or Laporte) Processes (142, 145)

An all-liquid ammonium peroxydisulfate process was not put into commercial use until about 1927 because of the problems associated with the hydrolysis reaction, as previously discussed. This type of process is used by Elchemie Co. in Kufstein, Austria (capacity about 65 tons/month as 100%), by Laporte, Ltd. in Luton, England, and by the Buffalo Electrochemical Co. in Buffalo, N. Y., and was studied at the Electrochemische Werke, Munich, during 1940-1945 with the expectation of its probably replacing the solid potassium peroxydisulfate process. This appears to be the most economical of the three electrolytic processes if the hydrolysis step is carried out with reasonably high yield, since the cell efficiency is greater than with the peroxydisulfuric acid process, and labor costs are less than with the potassium peroxydisulfate process.

The flowsheet is similar to that shown in Figure 4 for peroxydisulfuric acid, except that somewhat different equipment is used for the hydrolysis.

In the process used at Elchemie Co., variously termed the "Lowenstein," "Riedel-deHaen" or "Riedel-Schering" process, the electrolytic cells consist, as usual, of platinum anodes and lead cathodes in a stoneware tub, but the physical arrangement is different from the cells previously described. The details of one tub are shown in Figure 11 and the cell room at Elchemie is shown in Figure 12. Each rectangular tub is divided into six symmetrical compartments by two lateral and one longitudinal stoneware partitions. Each compartment is a separate cell and is divided by two porous ceramic diaphragms into one central anode and two side cathode compartments. A double row of vertical glass coolers down the center for cooling the anode compartment, is flanked on either side by a parallel row of four verti-

FIG. 11-PEROXYDISULFATE CELL DETAILS, ELCHEMIE

FIG. 12 - PEROXYDISULFATE CELL ROOM, ELCHEMIE

cal anodes (eight in all). Outside and parallel to the anode rows are the diaphragm plates (not visible in the picture) and then lead plates which are the cathodes. Cooling in the cathode chamber is supplied by coils of lead tubing. Eleven tubs (2 parallel groups, 33 cells each) were placed in series at Elchemie, the difference in height between tubs being about six inches, to produce flow by gravity. The ammonium bisulfate solution passes through all the cathode chambers and then through all the anode chambers. The tubs are covered with loosely-fitted hoods so that air can enter to dilute the hydrogen evolved and the gas mixture is then exhausted. Current efficiencies of 82 - 84% are obtained with anode current densities of 0.4 - 1.1 amp./sq. cm. and corresponding cell voltages of 5.0 - 5.2. The anode current concentration is about 17 amp./liter, and the cells operate at 28 - 33°C.

Typical concentrations (in gms./liter) of the electrolyte are as follows:

	Entering catholyte	Exit anolyte
H_2SO_4	260	160
$(NH_4)_2SO_4$	210	76
$(NH_4)_2S_2O_8$	0	232

In these particular cells the catholyte concentration changes appreciably during passage through the cells, with ammonium ions migrating through the diaphragm to the catholyte side and sulfate ions migrating to the anolyte side.

At Elchemie hydrolysis is obtained by passing the liquor from the cells through 2 banks in series of steam-jacketed, climbing-film evaporators made of lead. The first bank consists of 28 tubes in parallel, arranged in 2 lines, each tube being fed at a controlled rate. The lower end of this bank is shown in Figure 13. The bank of evaporators is surmounted by a separator, which can be seen in Figure 14, a view of the hydrolysis and concentration room. Water was added to the liquor from the first evaporator bank before it passed

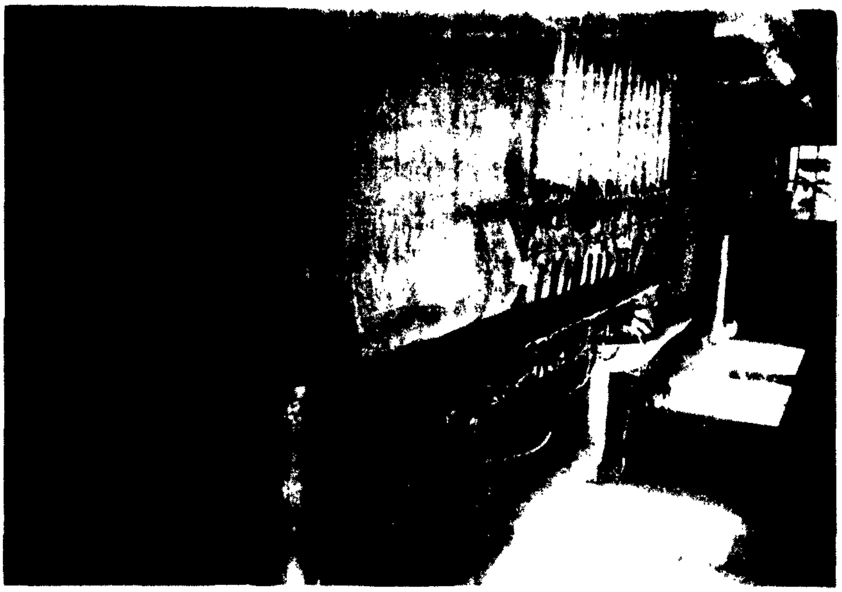

FIG. 13 - PEROXYDISULFATE HYDROLYSIS TUBES, LOWER END, ELCHEMIE

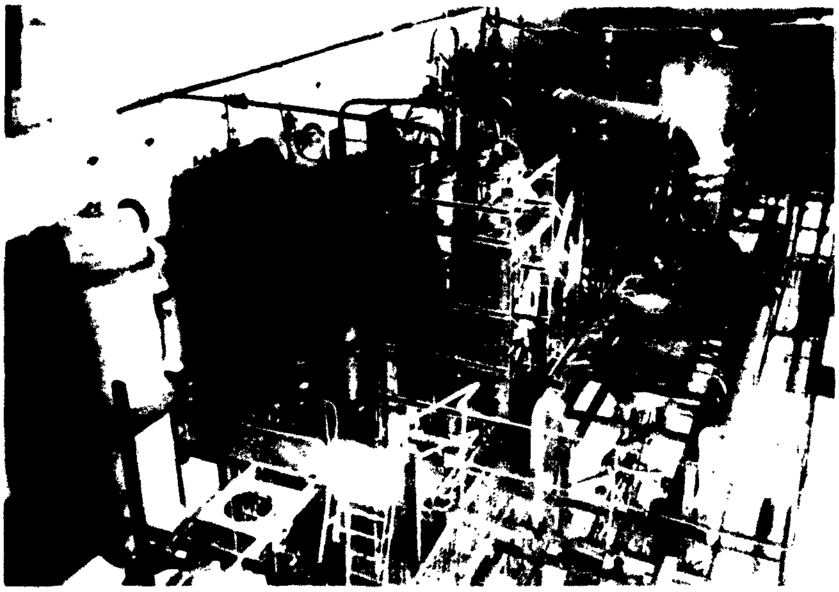

FIG. 14 - PEROXYDISULFATE HYDROLYSIS AND DISTILLATION ROOM, ELCHEMIE

to the second, presumably to prevent precipitation of ammonium salts. The vapor is rectified under vacuum in a series of 3 columns to produce a 30 - 35 wt. % hydrogen peroxide solution. The distillation-hydrolysis efficiency on the basis of peroxygen recovery is about 85%; about 10% is lost by decomposition. Very few materials are satisfactory for fabrication of the evaporator tubes; lead tubes are rapidly corroded and must be replaced every 30 to 45 days; however, addition of 0.2 to 2.0% antimony to the lead results in substantially longer life.

A more efficient hydrolysis method is that used by Laporte, Ltd., and a similar method was developed at the Electrochemische Werke, Munich (EWM). This involves a two-step operation in which the solution is first concentrated and partially hydrolyzed but with little hydrogen peroxide formation, followed by a steam distillation under vacuum to complete the hydrolysis and remove the hydrogen peroxide. Evaporation to about half the entering volume takes place in a stoneware vessel equipped with a Krupp V4A (an 18-8 stainless steel containing 2.2% molybdenum) steam coil. After a residence time of about 5 minutes, the liquid passes to a perforated plate or packed column where it is heated with tantalum heaters and steam is blown in counter-current to the liquid. A hydrolysis-distillation efficiency of 96% is reported for the German process.

In the use of the Pietzsch-Adolph type cells with the all-liquid process, a higher sulfuric acid content is required than in the potassium peroxydisulfate process, in order to hydrolyze the peroxydisulfate; a typical concentration entering the cell is 4.0N ammonium sulfate and 5.0N sulfuric acid. The increased acid content reduces the cell current efficiency to about 75%, makes necessary a higher current concentration and a lower cell temperature (about 27°C.), but since no potassium enters the electrolyte, the cells should not "salt up," and the cell voltage is reduced from 5.9 to about 4.6.

Operating figures for the Elchemie installation showed the following, per kilogram of product calculated as 100% hydrogen peroxide but produced as 30% solution.

Electricity: 13.4 kwh. for cells, 17.0 total, including AC to DC conversion loss and other process requirements; steam for distillation, 75 kg. reported but 50 kg. calculated from a heat balance; platinum investment 522 gm. per 1000 kg./month capacity calculated as 100%. Platinum loss 0.006 gm.; process labor 0.26 man-hours.*

As indicated previously, it appears that the all-liquid ammonium peroxydisulfate process is generally the most economical of the electrolytic processes if the hydrolysis step can be carried out with reasonably high yield.

Several minor modifications of the all-liquid ammonium peroxydisulfate process as described above have been patented or used, differing in such factors as the design of the electrolytic cells and the concentration of the chemicals used as well as differences in the hydrolysis equipment. For example, the Henkel Company at Düsseldorf, whose main hydrogen peroxide production was by the Pietzsch-Adolf process, also operated the Schmidt process on a small scale between 1938 and 1944. As operated by Henkel (46), large electrolytic cells having both anolyte and catholyte compartments were used with an electrolyte more acidic than those used in other ammonium peroxydisulfate processes. Typical concentrations (in gms./liter) were:

	Catholyte feed	Anolyte feed
H_2SO_4	325	285
$(NH_4)_2SO_4$	195	235
Available oxygen as H_2O_2	4	0

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* Labor cost figures for all three processes are rather uncertain since they will vary substantially with plant size. However, this reported figure seems somewhat high in relation to 0.1 man-hours quoted for the peroxydisulfuric acid process and 0.28 for the Pietzsch-Adolph process, since the latter definitely requires substantially more labor than the two all-liquid processes.

Cell voltages varied from 5.0 to 5.2 and the current efficiencies averaged about 88%. Hydrolysis and distillation was obtained by allowing the liquid to flow downward on the inside walls of vertical steam-jacketed porcelain tubes. The vapor passed to an entrainment separator and rectification tower similar to those previously described. Maximum distillation efficiencies of around 80 - 85% were obtained, but the Schmidt unit, at least as constructed and operated at Henkel Co., was regarded as inferior to the Pietsch-Adolf process.

Effect of Alternating Fields

Superimposition of an alternating current on the direct current flowing through a cell can cause reducing and oxidizing reactions to occur successively on one electrode. Some studies of the formation of hydrogen peroxide on a zinc anode under such conditions have been reported (47). The hydrogen peroxide has been postulated as being formed under the influence of the direct current and then reduced by the negative phase of the alternating current, but interpretation of the experimental data is very difficult.

The formation of hydrogen peroxide and peroxy compounds under the influence of an electric discharge is discussed in Chapter 2.

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CHAPTER FOUR

CONCENTRATION, PURIFICATION, STRUCTURAL MATERIALS, HANDLING

CONCENTRATION

In most non-military uses of hydrogen peroxide, e.g., bleaching, only a very dilute solution is required. However the product is manufactured in substantially higher concentrations in order to reduce the cost of packaging, transportation and storage per pound of contained hydrogen peroxide. Thus in the electrolytic processes, a mixture of water and hydrogen peroxide vapor is produced by peroxydisulfate hydrolysis and it is simple to condense fractionally this vapor to produce a product containing about 28 to 35 wt. % hydrogen peroxide. Somewhat higher concentrations could be produced directly but at the penalty of lower recovery of hydrogen peroxide. A very small amount of impurities may be present in the electrolytic product as the result of mechanical entrainment. In most cases this impurity content is sufficiently innocuous that an acceptable stability is obtained and the product is shipped directly to the customer with no further processing beyond one or more of the following: (1) adjustment of the pH to give maximum stability, (2) addition of a small amount of stabilizing compounds to inhibit catalytic decomposition, and (3) addition of corrosion inhibitors to reduce attack on the aluminum containers commonly used for shipment. Additional purification steps which may be required are described in a succeeding section. The direct product of the barium peroxide process, which contains up to about 8 wt. % hydrogen peroxide and generally undergoes similar final processing, is frequently shipped directly to the user without concentration, although here the high water content increases the transportation and handling cost per pound of contained peroxide and therefore tends to limit the area in which the product may be economically marketed.

For use in power-producing devices and in a few other applications, such as preparation of some organic compounds, a highly concentrated hydrogen peroxide solution is desired. Several methods of concentration have been used in laboratory procedures. Extraction of the hydrogen peroxide with ether followed by removal of the ether under vacuum has been used but is extremely hazardous, since unstable organic peroxides may be formed. In principle water may be removed by selectively freezing it out. However, hydrogen peroxide solutions greatly supercool, so that seeding is required. Recent studies indicate that on freezing, water and hydrogen peroxide actually form separate pure phases, but because of occlusion of mother liquor, the actual degree of separation obtained on freezing may be small. (See Chapter 5.)

The high relative volatility of water to hydrogen peroxide makes it possible in principle to concentrate dilute hydrogen peroxide solutions by simply distilling off water. However, three problems exist: (1) the nonvolatile impurities are concentrated as well as the peroxide and the resulting concentrated solution is consequently more unstable. Even the addition of substantial quantities of stabilizers may not produce an acceptable stability if the impurity content is appreciable. High purity is necessary for high stability. (2) The rate of decomposition of liquid hydrogen peroxide increases about 2.3 fold for each 10°C. rise in temperature. (3) Hydrogen peroxide vapors above certain concentration limits will readily explode on contact with a bit of catalytically-active material or with non-catalytic materials at slightly elevated temperatures. These problems are met by the use of relatively inert materials of construction and by distillation under vacuum which lowers the temperature and also avoids the explosive composition region. For some purposes, a relatively high impurity and stabilizer content may be innocuous and a lower stability acceptable, particularly if not too high a peroxide concentration, _e.g._, 35 wt. % is to be produced. Here a simple concentration, removing water under vacuum, may suffice. However, at high concentrations (_e.g._, 80% and greater) high purity is needed for good stability and it is necessary that the peroxide solution be further purified either before or during the distillation and concentration.

Techniques of preparing highly concentrated hydrogen peroxide solutions on a commercial scale were first developed by the Elektrochemische Werke, Munich, in Germany with work starting as early as 1936, and were used in World War II in Germany to supply solutions for military use containing 80 to 85 wt. % hydrogen peroxide. Similar processes were developed during the war in England and the United States, as well as in Japan, where the German manufacturing details were made available.

The necessary high purity is obtained in each of these processes by a two- or three-stage distillation in which the peroxide solution is completely volatilized, leaving the non-volatile impurities behind, and then the hydrogen peroxide vapor is concentrated by rectification. In Germany concentration units were operated at Bad Lauterberg and by the Elektrochemische Werke, Munich (E.W.M.) and construction was underway at the end of the war on units at Rhumspringe, Heydebrecke and Waldenburg, the last two designed to concentrate a peroxide solution prepared by the ethylanthraquinone process and containing initially 20 - 30 wt. % hydrogen peroxide. The two plants which were actually operated utilized 30 - 35% hydrogen peroxide from electrolytic processes and differed from one another in only minor detail. The flowsheet is shown in Figure 1 (1).

A 30 to 35 wt. % hydrogen peroxide solution to which stabilizers have been added* was fed continuously to the first retort. If decomposition is negligible, the vapor leaving the

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* In Germany, 200 p.p.m. of sodium pyrophosphate and 100 p.p.m. of 8-hydroxyquinoline were added to the 30 - 35 wt.% product from the Pietzsch-Adolph electrolytic process, plus a small amount of phosphoric acid if the highest concentrations were being made. Sodium stannate was preferred for the product of the anthraquinone process. With a purer initial product substantially lower stabilizer concentrations could presumably be used.

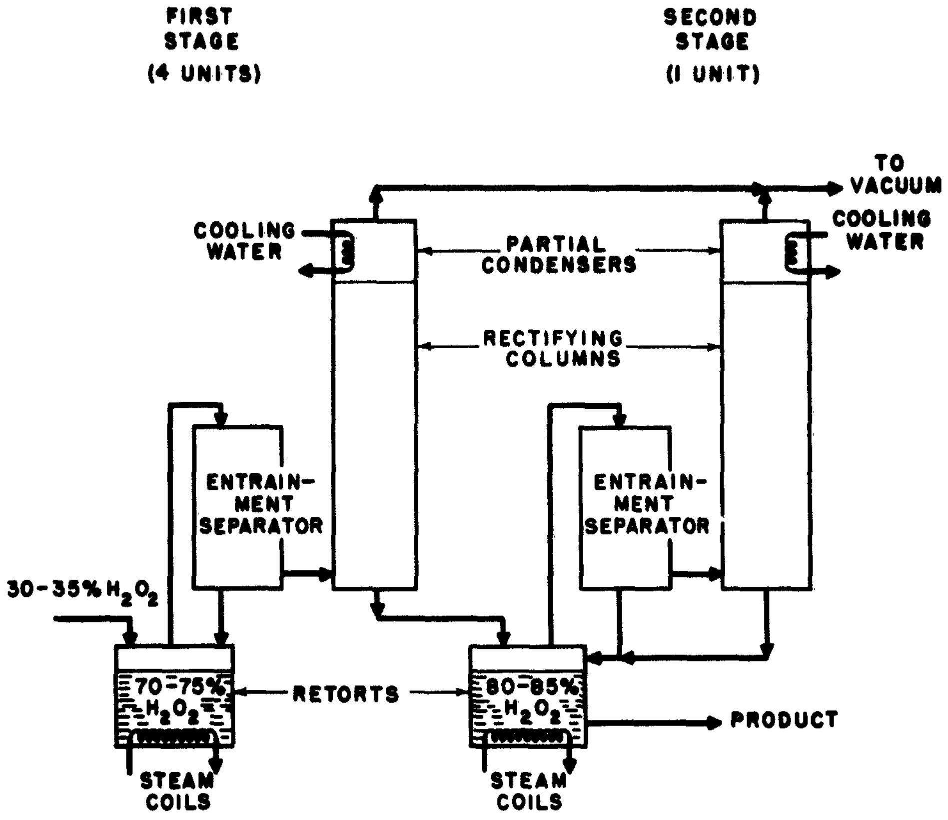

FIG. 1 - FLOWSHEET FOR CONCENTRATION OF HYDROGEN PEROXIDE, E.W.M. PROCESS.

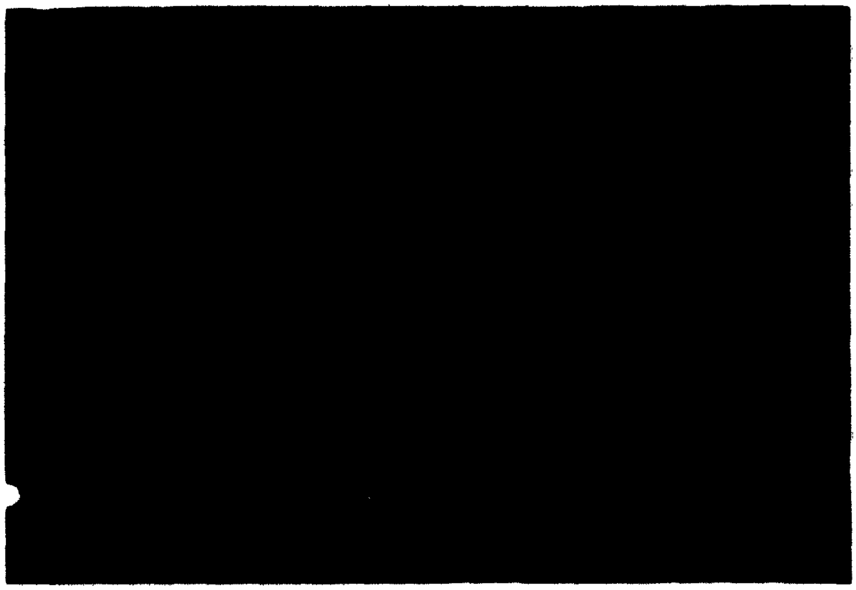

FIG. 2 - GENERAL VIEW OF CONCENTRATION RETORTS, E. W. M.

retort will have the same concentration as the liquid entering, but the liquid contents of the retort will be in equilibrium with the vapor and therefore contain 70 to 75 wt. % hydrogen peroxide. The vapor passed through an entrainment separator filled with packing, such as Raschig rings or pieces of quartz, and then to a packed rectification column. Equipment was generally constructed of stoneware except for heat transfer surfaces.

Reflux was provided by an aluminum partial condenser, as shown in the figure, or by adding water, and the exit vapor--essentially 100% water vapor--went to a jet condenser with a barometric leg backed by a vacuum pump or steam ejector. The purified bottoms from the first tower were run to a second retort, the vapors from which were passed through another entrainment separator and rectification tower.* The condensate from the second tower was returned to the second retort from which the concentrated product, containing 80 - 85% hydrogen peroxide, was continuously removed and passed through a cooler. The concentration of impurities and the stabilizers gradually increased in the first retort with accompanying increase in decomposition rate and amount of foaming so that distillation was discontinued after about 120 hours of continuous operation and the first retort emptied. These periodic impure residues could be steam stripped in a separate apparatus to recover the hydrogen peroxide. On restarting operation, the first retort was filled with feed solution and condensate from the first tower was returned to the first retort until the concentration was built up to 70 to 75%, after which it was switched to the second retort. Four first-stage units were required to supply one second-stage unit. In the German processes, a small amount of stabilizer was also added to the second retort and therefore it remained in the final product. A general view of the concentration retorts at the E. W. M. plant is shown in Figure 2.

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* In the Bad Lauterberg plant, as a safety measure, the condensate from the first tower was cooled and stored instead of going directly to the second retort.

If the hydrogen peroxide is relatively pure at this stage, very little or no stabilizer is needed, as shown by the fact that a 90 wt. % hydrogen peroxide now being commercially produced in the United States contains only a few parts per million of stabilizer at most.

A critical point in the design of a hydrogen peroxide concentrator is the nature of the steam coil. It is essential that it not be corroded by the hot peroxide solution or possible impurities present and that it cause minimum hydrogen peroxide decomposition. The German process used a polished coil of Krupp V14A stainless steel (17.5% Cr., 12.5% Ni., 4.7% Mo., 0.07% C. max.)--this alloy was apparently needed because of the free sulfuric acid content in the feed liquid. Tantalum has also been used elsewhere. The process operated with 28 - 32 mm. Hg. absolute pressure at the top of the rectification towers and retort pressures of 50 - 60 mm. Hg.; the difference was largely due to the pressure drop through the packing. Corresponding retort temperatures were 62 - 66°C. in the first and 69 - 72°C. in the second. The maximum concentrations regularly produced in Germany were 85 wt. %, and 90 wt. % was the maximum commercially produced in the United States in 1952. Since at all compositions, the vapor contains a larger fraction of water than the liquid in equilibrium with it, in principle essentially 100% hydrogen peroxide could be produced by rectification. However, it would be necessary to operate at very low pressures to avoid the formation of an explosive vapor composition (see later). The maximum concentration commercially produced by distillation is therefore limited by the explosive limits of the vapor at the minimum pressure readily obtainable in the final retort. This minimum pressure in turn is largely determined by the minimum pressure drop obtainable through the rectification tower.

Under the above conditions, 95% hydrogen peroxide recovery was claimed in Germany if the residue is not considered, or 98% recovery if it were included. The concentrating process planned for the 2-ethylanthraquinone product was the same as the above in principle although slightly different in design and had an efficiency of 81 - 85%; about 10% of the loss was pot residues which were discarded because of their organic content which could form explosive peroxy mixtures; about 4 - 8% was decomposition loss. The following utility and labor requirements were quoted for concentration from 35 to 82% hydrogen peroxide, per kg. of contained hydrogen peroxide; power 0.10 kwh.; steam 5.8 kg.; water at 11°C., 0.4 cubic meters; process labor, 0.020 man hours; 8 cubic meters/hr. of vacuum displacement at 40 mm. Hg. for 1000 kg./month capacity. Cost figures for German operation indicated that the cost of concentration was about one fifth the cost of production of 35% product by the electrolytic processes.

A potentially hazardous feature of the above process is the fact that large quantities--several hundred gallons--of highly concentrated hydrogen peroxide solution are held continuously at high temperatures, although no explosions occurred at either German plant during several years of operation. A British process (2) minimizes this hazard by substituting a climbing film evaporator for the retort so that only a small amount of hot concentrated liquid is present at one time; and this technique is undoubtedly preferable to that used in the E. W. M. process. Data quoted show a loss as low as 1 percent of the hydrogen peroxide in the concentration process from 28 to 90 wt. % using this equipment. A similar method using climbing film evaporators was also developed during the war to a pilot-plant size by Elchemie Co., Kufstein, Austria, independent of the E. W. M. process which was the one actually used in Germany (3), and several patents on similar processes have been issued (4). In an alternate process (5), the hydrogen peroxide inventory is held to a minimum by spraying the crude solution into a cylindrical vaporizing vessel with heated walls, operated under vacuum and in such a manner that the liquid is vaporized practically instantaneously. The exit vapor may then be concentrated as above. Hydrogen peroxide may also be purified without hazard at lower concentrations by conventional vacuum distillation (6). This is often done in the laboratory.

The principal problem in the concentration by distillation and rectification of hydrogen peroxide manufactured by an organic process is that of minimizing the amounts of organic substances in the highly concentrated product, while avoiding the accumulation of organic substances to hazardous concentrations in the vaporization section of the distillation apparatus. The detailed techniques will vary with the nature and amounts of the impurities characteristic of the method of production. Although impurities which are relatively volatile in the system can be easily removed, it is difficult to predict what the actual vapor-liquid equilibrium relationships will be in any given case since hydrogen peroxide readily reacts with various organic substances, particularly those containing oxygen, such as aldehydes and alcohols, to form complex and unstable compounds of lower volatility than either of the reactants.

The 20 wt. % hydrogen peroxide solution produced in the German ethyl anthraquinone process contained dissolved organic material equivalent to about 1300 - 1600 mg. of carbon per liter of solution. This was believed to be primarily benzene (which constituted part of the solvent for the ethyl anthraquinone) and fatty acids and other oxygen-containing compounds formed by oxidation of the secondary alcohols which constituted the remainder of the solvent (see Chapter 2). On concentration of this product in pilot-plant sized apparatus of similar design to the German plants described above, it was found that the organic content of the hydrogen peroxide in the first still retort (determined as carbon) tended to approach asymptotically a limiting value characteristic of the particular crude solution being studied. This indicates that as the organic content of the still pot increases, the rate of disappearance of the organic residues by oxidation and volatilization also increases. The percentage of the original carbonaceous material in the crude solution which remained in the final pot residues varied in the range of 5 - 30%, indicating that most was carried over either by volatilization or entrainment.* It was

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* Considerable difficulty was encountered with foaming caused by soaps formed from fatty acids reacting with potassium salts used in drying the working solution.

reported that no difficulty was encountered with sudden decomposition or explosion even when the carbon content of the bottoms was as high as 20 - 25 gm./liter (7). However, as shown below, this concentration approaches the explosion limits of solutions of organic substances in aqueous hydrogen peroxide, and higher concentrations of organics definitely would be very hazardous.

One patent has been issued (8) on a distillation method for purifying the product of the para-azo-toluene process.

A highly concentrated or essentially anhydrous hydrogen peroxide may also be produced by reaction of an acid with a peroxy compound in a non-aqueous medium, the medium being so chosen that it can be separated by vacuum distillation from the hydrogen peroxide formed (9). The example of sodium peroxycarbonate reacted with sulfuric acid in the presence of anhydrous methanol has been quoted. Sodium sulfate precipitates out and the alcohol may be removed under vacuum. However the lower alcohols such as methanol and many other organic compounds in which hydrogen peroxide is quite soluble are known to form sensitive and highly explosive mixtures over a wide composition range with hydrogen peroxide and water (see below). Therefore the use of methanol in this process is extremely hazardous. Another technique is to remove the water from an aqueous solution of hydrogen peroxide by treatment with an ester of boric acid to form insoluble boric acid plus hydrogen peroxide in an alcoholic solution, the alcohol coming from the ester hydrolysis (10). In this reference it is claimed that the anhydrous solutions of hydrogen peroxide in alcohols such as amyl, butyl and benzyl are stable at room temperature and not explosive, although if so this is presumably due to the limited solubility of hydrogen peroxide in the particular liquids specified.

PURIFICATION

The degree of purity required of the technical product is usually set by either (1) the minimum acceptable degree of stability on storage, or (2) the use to which the hydrogen peroxide is to be put. Thus for medical and some military applications a very high purity is desired, entirely apart from the necessity for good stability. In a number of plants using the electrolytic processes, the rectification and condensation of the vapors from the peroxydisulfate hydrolysis produce a product to which no further processing is required beyond the additives described in the section on concentration. If further purification is needed, this may be accomplished by total distillation under vacuum, particularly when it is desired to produce a more concentrated product. A number of other techniques have been used. One is to produce a colloidal suspension of stannic hydroxide in the hydrogen peroxide solution by addition of an appropriate tin compound and careful adjustment of the pH so that a stannic oxide precipitate is formed which adsorbs heavy metal ion impurities. The precipitate is then removed by settling or filtration (11). The tin remaining in solution acts as a very effective stabilizer. In the purification process once used by the du Pont Co., the product of the peroxydisulfuric acid hydrolysis, which may contain a small amount of sulfuric acid, was first treated with barium hydroxide to remove sulfate and other anions and then catalytic cations such as iron were removed by precipitation of stannic hydroxide (12). The process has been described in detail (13).

Another technique of interest is to remove the ionic impurities by applying an electric potential. Inorganic salts ionize in hydrogen peroxide, which behaves as a non-electrolyte like water. Consequently anions and cations will each migrate to the oppositely charged electrode. Several patents have been issued on purification techniques based on this principle (14) but to the authors' knowledge it has never been used commercially on hydrogen peroxide solutions. Of course this process cannot remove uncharged impurities as would occur for example, in the product of an organic manufacturing process.

A very recent development has been the proposed use of organic ion-exchange resins to remove the heavy metal ion impurities (15).

If the hydrogen peroxide were formed by some organic process, such as by partial oxidation of hydrocarbons, which simultaneously produced amounts of organic impurities, it might be necessary to purify the crude product by adding a suitable reagent to precipitate out a peroxide compound which then could be reconverted to hydrogen peroxide. For example, addition of calcium hydroxide would form insoluble calcium peroxide which could be removed, washed and converted to hydrogen peroxide by treatment with acid (see Chapter 2).

STRUCTURAL MATERIALS

In considering what materials may be suitable for contact with hydrogen peroxide in any given piece of equipment, attention should be focused on two factors, (1) the effect of the material on the decomposition rate of the peroxide, and (2) the effect of the hydrogen peroxide on the material. In addition, with hydrogen peroxide concentrations of about 45 wt. % or more, the possibility of forming detonatable mixtures by contamination with organic substances may exist. It is usually found that the effect on the stability of the hydrogen peroxide is the major factor involved in the choice of a suitable material. Very few materials exist which are satisfactory for handling hydrogen peroxide of the various concentrations under all conditions of storage, manufacture and use.

The rate of decomposition of hydrogen peroxide is affected by a large number of variables such as (1) concentration, (2) pH, (3) temperature, (4) nature and quantity of impurities and stabilizers present in the peroxide, (5) time of contact (*e.g.*, a peroxide solution may slowly leach out impurities from a container wall and thus increase the rate of decomposition with time. On the other hand, a carefully cleaned inert metal surface substantially free of harmful impurities is usually slowly passivated on contact with peroxide, leading to a decrease in the rate of decomposition with time), (6) physical and chemical nature of the surface (in general, the smoother the surface, the lower the rate of decomposition).

The interrelationships between the effects of these variables are frequently curious and complex. Thus, in one instance, the addition of a small quantity of phosphate stabilizer to a quantity of peroxide stored in an aluminum container was found to increase substantially the rate of decomposition. It was finally found that portions of the container were constructed of two different types of aluminum; the addition of the phosphate compound increased the electrical conductivity of the peroxide and thus the rate of electrolytic corrosion. This in turn released contaminants to the peroxide solution which markedly increased the rate of decomposition. Such an effect may be experienced wherever dissimilar metals are used in the construction of apparatus for containing and conveying hydrogen peroxide. With stainless steel and aluminum, for example, a white, powdery deposit is built up on the aluminum at the points of contact.

Since the handling of highly concentrated hydrogen peroxide sets more stringent requirements than that of dilute solutions, materials for use with a 90% solution will be considered first, followed by examination of suitable materials for contact with more dilute solutions. As might be expected, tests of the rate of decomposition in contact with most surfaces are difficult to reproduce, even with careful control of variables, and it is common for the decomposition rates carefully measured by different laboratories under ostensibly the same conditions to vary by several fold. Therefore, to obtain a general picture of the conditions under which various materials are suitable for use with concentrated hydrogen peroxide, a qualitative method used by the Buffalo Electrochemical Co. (16), and reported by Davis and Keefe (19), will be presented here. Materials are grouped into four general classifications as follows:

"<u>Class 1</u>: Materials which are highly compatible and can be used for long-time contact with hydrogen peroxide. Irrespective of length of contact, these materials will not contaminate the hydrogen peroxide. Typical use for a material of this class would be for the construction of long-time storage containers such as tanks, tank cars, or drums."

"Class 2: Materials which are satisfactory for repeated short-time contact with high strength hydrogen peroxide. These materials can be used for transient contact with the solution prior to storage of the hydrogen peroxide or for limited contact of the hydrogen peroxide prior to prompt use. Such limited contact time should not exceed 4 hours at 160°F. or 1 week at 70°F. Typical uses for materials of this class would be as valves or pumps in a peroxide transfer line, or as high-pressure storage tanks."

"Class 3: Materials which should be used only for short-time contact with hydrogen peroxide prior to prompt use of the hydrogen peroxide. These materials can be used for repeated contact with hydrogen peroxide, but no one period should exceed 1 minute at 160°F. or 1 hour at 70°F. prior to immediate use. These materials might cause sufficient contamination of the solution to render it unsuitable for storage."

"Class 4: Materials which are not recommended for any use with high strength hydrogen peroxide. They are materials which cause immediate excessive decomposition of the hydrogen peroxide, are rapidly attacked by the hydrogen peroxide, or form explosive mixtures with concentrated hydrogen peroxide."

The classification number is a figure of merit for the construction material considered. Accordingly, a Class 1 material could be used for Class 2 or Class 3 uses if desired, but a Class 3 material is restricted to the uses specified for it.

The classification assigned to a number of materials by the Buffalo Electrochemical Co. is shown in Table 1. It should be noted that this applies only to highly purified, 90% hydrogen peroxide solutions. Small amounts of impurities, even though relatively non-catalytic in themselves, such as mineral acids, may lead to corrosion of the material and subsequent increase in decomposition rate. With hydrogen peroxide concentrations less than 90 wt. %, it will frequently be possible to use lower-class materials than are indicated below. Materials which are reported by the Buffalo Electrochemical Co. to have given satisfactory performance in extensive usage are underlined in Table 1.

The rate of decomposition of concentrated hydrogen peroxide with a number of materials has been recorded in reports of German practice (17). Bellinger and co-workers (18) report a large number of quantitative results of stability tests of concentrated hydrogen peroxide in contact with various metals and other materials, including the effects of various surface treatments of the metals. Structural materials which have been used in various manufacturing processes and in various applications are also described in Chapters 2, 3 and 11. Various types of equipment which have proven satisfactory for use with concentrated hydrogen peroxide, such as pumps, valves and pipe connections, are described and pictured by Davis and Keefe (19).

Certain general comments may be made about conditions under which materials have been used at various hydrogen peroxide concentrations.

Aluminum

The rate of corrosion of aluminum is increased in both acid and alkaline media and therefore aluminum is not recommended for use with dilute alkaline bleaching solutions. Beside the general corrosion caused by acid or alkali, localized pitting is produced by contaminants such as chlorides; this can be prevented by addition of a small amount of nitrates, such as 0.05 wt. % or less of ammonium nitrate (21). Containers used for storage should be made of a highly pure aluminum (99.6+ % pure) containing a minimum copper content. They must be carefully cleaned, as by treatment with dilute sodium hydroxide solution followed by pickling for several hours in 35 - 50 wt. % sulfuric, phosphoric, or nitric acid, followed by washing with water (22). It is important that all surfaces be free of foreign matter, such as might be left behind by welding or forming operations, and also that they be as smooth as possible. It is generally found that an aluminum surface gradually becomes more inert on prolonged contact with hydrogen

TABLE 1

CLASSIFICATION OF MATERIALS ACCORDING TO RECOMMENDED USE WITH 90 PERCENT HYDROGEN PEROXIDE*

Material	Classification Number
Metals:	
Aluminum-99.6% (or more) pure 2S Alloy	1
43,3S,52S,56S,61S,63S,150S, B214,355,356,A360	2
24S	3
13,40E,53S,214,75S	4
Copper	4
Durimet 20	2
Durimet T	4
Hasco-O-Seven	2
Hastelloy B and C	3
Inconel	4
Iron or carbon steel	4
Lead	4
Magnesium alloys	4
Malin Wilstabrite	2
Manganese-containing alloys	4
Monel	4
Multimet N-155	3
Refractalloy 26,27,70	3
Stainless steel AISI type	
303,304,309,310,316,317,318 321,322,347,613 (extra low carbon) 304 (extra low carbon)	2
443,446,440	4
Stainless "W"	2
Stellite No. 6	4
Tin, CP or 99.0% pure	1
Universal Cyclops 19-9DL	3
Worthite	3
High Polymers:	
Borosilicate glass	1
Buna S & N	4
Geon 8372	4
Hycar	4

TABLE 1 (continued)

Material	Classification Number
Koroseal	
116,117,700 (molded or extruded, unpigmented)	2
Neoprene	4
Nylon	4
Pliovic	2
Polyvinyl chloride	2
Polyethylene, (Visqueen, Polythene, Trithene, Jescolite 231), Halogenated Polyethylenes, (Teflon, Kel-F)	1
Polystyrene	2
Saran	2
Silicone Rubber	4
Teflon-impregnated glass cloth	1
Thiokol	4
Tygon 2807	4
Veloform	2
Vinylite	2
Wood, cork, hydrocarbon lubricating oils, and other oxidizable substances	4
Lubricants:	
Aroclors	4
Fluorolubes	1
Halocarbon Oils	1
Kel-Flo Polymers	1
Paraffin	4
Perfluorolube Oils	1
RPM Hydraulic fluid	4
Silicones	4
Skydrol	4
Ucon Hydrolube U-4	4

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* Adapted from a table prepared by the Buffalo Electrochemical Co., Buffalo, N. Y. The classification scheme is described in the text.

peroxide, which is attributed to the formation of an inert oxide film. Consequently containers to be used with concentrated peroxide are frequently "passivated" after cleaning by filling them with dilute peroxide for some time; this technique also is a good test of the adequacy of the preparation and cleaning of the container.

An inert oxide coating on aluminum may also be attained by anodic oxidation (23), which is reported to give better inertness of Class 2 aluminum alloys than can be obtained by chemical treatment. A patent has been issued which claims that treatment of the aluminum surface with an aqueous solution of arsenic acid and hydrazine hydrate makes the metal "resistant" to concentrated hydrogen peroxide (24). The method has not been tested in the United States to the present authors' knowledge, and appears of doubtful usefulness. Aluminum is the best practical material to use for containers of neutral hydrogen peroxide solutions where it is important to minimize rate of decomposition, as in storage vessels.

Stainless Steel

Many of the stainless steels are resistant to corrosion by hydrogen peroxide over a wide pH range but even when carefully cleaned and polished they cause somewhat greater rates of decomposition than do suitable aluminum surfaces. Stainless steel has given excellent service when used as linings or for the construction of tanks, vats and other equipment to hold dilute peroxide bleaching solutions (20). As with aluminum, it is important that the surfaces be carefully cleaned, for example, with nitric acid, and that they be as smooth as possible. Thus with the 300-type stainless steels, wrought or machined surfaces are relatively serviceable but rough-cast surfaces are not. The rough surface also allows chromium, which is catalytically-active, to be leached into the peroxide, causing a decrease in its stability. Cast surfaces generally contain inclusions of the mold material, which is likely to be catalytic.

Tin

Tin is reported to be passive in neutral and slightly acid peroxide concentrations up to 50% or possibly higher, but is corroded by alkali solutions, unless inhibited by addition of sodium silicate (20). Pure tin has been satisfactory for pumps, pipelines, etc., but tin platings are frequently unsuitable, particularly with concentrated peroxide. Tiny imperfections such as pinholes allow the peroxide to contact the undersurface where it decomposes, liberating oxygen gas and forming blisters which break away the plating. Pure tin, treated with hydrochloric acid and rinsed with clean water, is suitable for gasket material in contact with liquid peroxide or its hot vapors, and shredded tin has been used in pump packings. Within the limitations mentioned, block tin is probably the most inert of the commonly available materials of construction for use with hydrogen peroxide, although its cost and weakness as a structural material restrict its usefulness; a temperature limitation is also imposed by the unacceptable allotropic modifications which occur below 13°C. and above 203°C.

Tantalum

Tantalum is highly inert and resistant to corrosion under a variety of conditions but its use is limited by its high cost.

Lead

Lead compounds are active decomposition catalysts. Lead equipment can only be used satisfactorily where sulfates are present to form a coating of inert lead sulfate. Lead has been used in several applications in hydrogen peroxide manufacturing plants using the electrolytic peroxydisulfuric process and in the bleaching of raw wool where sulfates are present.

Iron

Ordinary iron and carbon steels cannot usually be used in contact with hydrogen peroxide because of the formation of rust which is an active decomposition catalyst. The only steels which resist the rusting action of concentrated peroxide are those containing more than about 13% chromium or the 18-8 chromium-nickel stainless steels, of which the latter are much more resistant. Iron equipment has only been used with very dilute alkaline peroxide solutions to which sodium silicate has been added to inhibit corrosion, but even here other materials are generally preferable. High-silicon iron alloys like Duriron have been used in pumps for handling dilute alkaline bleaching solutions. Under certain conditions an iron surface may become passive in hydrogen peroxide solution, but this action cannot be depended upon in practice.

Copper

Copper is a decomposition catalyst and equipment made of copper or alloys containing a substantial percentage of copper is unsuitable.

High Polymers

The polyvinyl chlorides, polyvinylidene chlorides and their copolymers, polyethylene and halogenated polyethylenes are generally satisfactory for use as tubing, hoses and gaskets with all concentrations of hydrogen peroxide. The completely halogenated polyethylenes, such as Teflon and Kel-F, are reported to withstand the action of concentrated peroxide up to about 160°F. and polyethylene up to about 120°F. (19). These are the most satisfactory plastic gasket and packing materials. Low molecular weight polyethylene may be used advantageously as a sealant or luting for pipe threads. Concentrated peroxide may slowly leach out the plasticizer contained in the polyvinyl chloride polymers and there is a tendency for these polymers to become slowly hardened in use.

Trifluorovinyl chloride polymers (Fluorolubes), available as oils and grease-like materials, are in general inert to hydrogen peroxide and provide safe and non-catalytic lubricants for machinery, ground glass joints, and the like, and manometer fluids for use with hydrogen peroxide.

The use of polymers as coating materials is not recommended with concentrated peroxide, and no satisfactory paints to withstand the action of hydrogen peroxide have yet been developed. As with tin plate, hydrogen peroxide penetrates to the under surface and decomposes, releasing oxygen gas which peels off the coating. Most rubbers are fairly rapidly deteriorated by contact with peroxide.

Wood

Wood may spontaneously inflame in contact with highly concentrated peroxide. For very dilute peroxide solutions wooden tanks and pipes made of cypress and pine have been fairly satisfactory although the life expectancy has been reported as being only about four to six years (20); the use of type 316(18-8) stainless steel is preferable wherever feasible.

Transite and Concrete

Tanks and pipes made of these materials have been found suitable for the dilute, mildly alkaline solutions used in bleaching operations, particularly when sodium silicate is present; they are not recommended for high concentration peroxide. Type 316(18-8) stainless steel is a preferred material for this use. Acid-proof tile tanks, and tile-lined concrete tanks have been satisfactory for bleaching solutions.

Nickel

Nickel and Inconel have very slight catalytic effect on hydrogen peroxide of all concentrations and are resistant to corrosion in neutral and alkaline media. Inconel is resistant to some acid solutions but nickel is unsatisfactory. Monel, which contains 30% copper, is unsatisfactory except with the very weak alkaline bleaching solutions. All three substances have been used for this purpose.

Glass and Ceramics

Glass is highly inert and has been used satisfactorily for storage and handling of various concentrations of hydrogen peroxide. The principal disability here is its fragility. Glass containing a high silicate content such as borosilicate (Pyrex) glass causes less decomposition than soda glass, which is more alkaline; indeed soda glass vessels may be regarded as unsuitable for storage of highly concentrated hydrogen peroxide. Glass-lined vessels have been used for dilute hydrogen peroxide; they would be expected to give results similar to soda glass. The rate of decomposition of peroxide is accelerated by exposure to sunlight, so glass containers are frequently colored to reduce the magnitude of this effect. Ceramics and stoneware of low iron content are relatively inert and have been used satisfactorily for storage containers, although aluminum is generally preferred for this purpose today.

STORAGE AND HANDLING

Containers for storage and transportation of concentrated peroxide are usually made of high-purity aluminum, treated as described above. Glass is sometimes used for very small quantities (less than a pound) of concentrated peroxide or for somewhat larger quantities of peroxide at concentrations below about 35 wt. %, but its use is more hazardous because of the danger of breakage. Flexible containers made of a suitable polymer have been used in a few instances; e.g., polyethylene bottles have now almost replaced the small, glass or wax-lined bottles used for reagent grade hydrogen peroxide. As noted above, plastic-lined equipment is unsatisfactory for concentrated solutions. Normal rates of decomposition to be expected in storages are discussed in the chapter on stability. A number of techniques for coating storage container surfaces to make them more inert have been described and used, such as covering with a thin wax layer, but in general these tend to peel off on use. It now appears that the most satisfactory method of obtaining maximum stability in a metal container is by using a highly pure aluminum, treated as described, and then passivated by long contact with peroxide.

In 1952 in the United States, hydrogen peroxide was commercially available from the manufacturers in strengths of 27.5, 35, 50 and 90 wt. %. The 27.5 and 35 wt. % concentrations were sometimes shipped in glass carboys each containing up to 120 pounds of solution. All four concentrations were also available in 30-gallon aluminum drums, or in railroad or truck aluminum tank cars, holding 4000 to 8000 gallons, all containers being equipped with appropriate venting devices, usually of the Bunsen valve type. Typical drums and tank cars are shown in Figures 3 and 4.

The drum on the left in Figure 3 is used for hydrogen peroxide solutions of moderate concentrations, or for highly concentrated solutions in carload lots only. That on the right, used for 90 wt. % concentrations in single drum shipments, has a "false head" enclosing an upper chamber above the drum proper. The closures and vent are designed so that if the drum is accidentally laid on its side, any leakage of contents through the vent in the drum proper will be caught in the upper chamber, thereby preventing outside spillage of highly concentrated peroxide. Both drums have drainage holes in the top rims so that rain water or other liquids will not collect around the vent holes. Small amounts of stannate or phosphate compounds or both are usually added as stabilizers.

Information on techniques of storage and handling and on special apparatus such as racks, spouts and siphons are available from the various manufacturers and will not be considered in detail here. The important precautions to observe are (1) to avoid contact with active catalysts, such as materials containing iron, copper, manganese and most other metals, and dust and alkaline substances, which can cause rapid decomposition, (2) to avoid contact with organic substances, which can be set on fire or form explosive mixtures with concentrated peroxide, (3) to always allow for proper venting of any piece of equipment in which peroxide

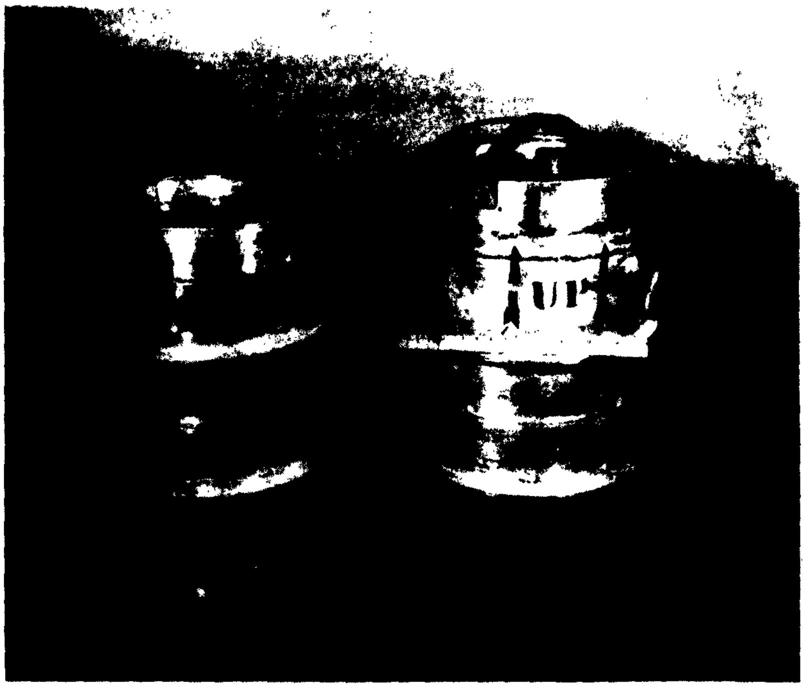

FIG. 3 - ALUMINUM STORAGE DRUMS FOR HIGHLY CONCENTRATED HYDROGEN PEROXIDE

FIG. 4 - ALUMINUM RAILROAD TANK CARS FOR SHIPPING HYDROGEN PEROXIDE

may be stored or held* and (4) to avoid excessively high temperatures. The physiological effects of hydrogen peroxide are described below. Hydrogen peroxide of about 50 wt. % or less generally does not start a fire immediately when spilled on combustible material such as clothing, but when allowed to dry, the water evaporates preferentially and the accompanying concentration of the hydrogen peroxide may lead to spontaneous inflammation. Dirty material containing catalytic impurities of other combustible material such as wood or clothing, particulary wool, will often ignite spontaneously with highly concentrated peroxide. Any type of spillage is best handled by flushing with large amounts of water. Clothing made of polyethylene, polyvinyl chloride, Neoprene, or Orlon (polyacrylonitrile) is resistant to hydrogen peroxide. Dacron (a polycondensation product of terephthalic acid and ethylene glycol) has been recently recommended as being particularly inert and resistant.

All storage containers should have a vent to release the oxygen developed by decomposition and so designed to minimize the possibility of contamination of the contents. The heat developed by the normal rate of decomposition on storage is easily dissipated to the surroundings. However, it is possible for gross contamination of more concentrated peroxide solutions to produce such a rapid rate of decomposition that the accompanying heat cannot be dissipated. In this event, a self-accelerating decomposition develops with accompanying temperature and pressure rise which will cause the container to explode even if vented, in a manner analagous to rupture of a pressure vessel. To avoid this possibility, large storage vessels for concentrated peroxide are usually equipped with temperature indicators and provision for rapid dumping and dilution of the contents if an abnormal rate of

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*It is dangerous to use stopcocks in lines containing concentrated hydrogen peroxide. Gas released by decomposition of the liquid trapped in the bore when the cock is closed can build up to sufficiently high pressures to burst the cock, particularly if it is made of glass.

decomposition develops. Mercury thermometers should not be used for this purpose because of the danger, if breakage occurs, of contaminating the peroxide with mercury, which is catalytically active.

Shanley (25) has calculated heat balances for various combinations of storage container size and hydrogen peroxide concentration and degree of instability, which make possible estimations of the critical conditions under which a self-accelerating decomposition can develop. The time-temperature histories of several self-accelerating cases are also predicted.

The shipment of hydrogen peroxide in the United States is governed by the regulations of the Interstate Commerce Commission, which classifies hydrogen peroxide for this purpose as a "corrosive liquid" to bear a white label. The specifications are fairly detailed with respect to type and design of containers, and vary with the concentration handled. For hydrogen peroxide concentrations exceeding 10 wt. %, only glass or earthenware bottles or carboys, suitably boxed and/or cushioned, or suitable aluminum containers are allowed for use. For hydrogen peroxide concentrations between 37 and 52 wt. %, glass container capacity must not exceed 1 gallon; for concentrations above 52 wt. %, glass container capacity must not exceed 1 quart. The specifications on packing the glass containers inside another protective container likewise increase in stringency with increase in hydrogen peroxide concentration. Consequently any substantial quantities of hydrogen peroxide of concentrations greater than 37 wt. % are shipped in aluminum containers. More details may be obtained directly from the Interstate Commerce Commission or in the handbook by Sax (25a).

PHYSIOLOGICAL ACTION

Hydrogen peroxide is not toxic in the usual sense, but concentrated solutions (*e.g.*, 27 wt. % and above) are strong primary irritants to the skin and respiratory passages. On contact the peroxide solutions cause a whitening of the skin, accompanied by itching or a stinging sensation; the stinging is usually relieved by prolonged flushing with water and the skin ordinarily returns to its normal color shortly thereafter without leaving any visible evidence of the contact. Longer contact or higher concentrations can cause blistering. The vapors from hydrogen peroxide are lachrymatory and cause irritation of the mucous membranes of the nose and throat. The inhalation of vapors saturated at room temperature with 90% hydrogen peroxide for moderate periods of time, such as might occur in gross spillage, is believed to offer no major respiratory hazard (26). Liquid hydrogen peroxide is highly irritating to the eyes and may lead to injury. In case of contact, the eyes should be flushed with water and medical attention obtained immediately. Solutions of hydrogen peroxide should not be swallowed since, unless very dilute, they can result in internal bleeding caused by excessive irritation. Animal experiments also indicate that 90% hydrogen peroxide is absorbed when applied to the skin (26).

In handling substantial quantities of concentrated peroxide it is advisable to wear clothing, boots and gloves of polyvinyl chloride, polyethylene, Orlon or (preferably) Dacron and to carefully avoid spillage on any part of the body. Goggles or face masks should be worn when handling solutions of more than about 3 - 5 wt. % concentration.

EXPLOSIVE CHARACTERISTICS: (7, 18, 27, 28, 29)

A considerable variety of studies have been made of the extent to which it is possible to cause explosive decomposition of pure, aqueous, hydrogen peroxide solutions. The usual technique is to subject the sample to the impact produced mechanically or, more frequently, by the detonation of a blasting cap or quantity of an explosive such as pentaerythritol tetranitrate (P.E.T.N.), and to compare the destruction produced to that which occurs under a similar test using water instead of hydrogen peroxide. For aqueous hydrogen peroxide solutions containing no organic admixtures, a continuous gradation of explosive effects is observed as the hydrogen peroxide concentration is increased and other experimental conditions varied. The degree to which the explosive effect of the initiator is enhanced by the presence of a hydrogen peroxide solution instead of water increases as each of the following is increased: temperature, hydrogen peroxide concentration, vessel diameter, degree of confinement, and magnitude of the initiating explosion. Hydrogen peroxide concentration is the most important variable.

It is difficult to obtain a propagating detonation even in 100% hydrogen peroxide. In one series of experiments (7) using containers 25 - 30 mm. in diameter, it was found necessary to use strong stainless steel tubes for the container and 30 grams of P.E.T.N. as the initiator to insure complete detonation in each test. As less extreme conditions are applied, it appears that the hydrogen peroxide immediately around the initiator detonates, but the detonation wave "runs down" after a certain distance which depends upon conditions. For example, longer and longer pieces of the tube container remain intact plus larger quantities of undecomposed peroxide. Several examples of the results obtained under various experimental conditions will be cited to indicate the regions of hazard. The following all apply to hydrogen peroxide at atmospheric temperatures. One hundred percent hydrogen peroxide is not detonated by mechanical impact such as a drop hammer or by gunfire. It has not been detonated under the more severe initiating conditions consisting of the explosion of a No. 8 blasting cap, when the hydrogen peroxide was confined in a 21 mm. diameter aluminum tube buried in loose, moist sand. Initiation by 10 grams of P.E.T.N., however, caused complete detonation under the latter conditions and also when the aluminum tube was unconfined. A No. 8 blasting cap causes partial detonation if the 100% peroxide is held in a reinforced container. Partial detonations have been obtained at concentrations as low as 90% using 10 grams of P.E.T.N. as initiator and substantial confinement.

Partial detonation of an 85% solution was obtained in one case in Germany when a large quantity (200 kg.) was initiated by the explosion of 25 kg. of a 50:50 mixture of trinitrotoluene and cyclonite (symmetrical trimethylene-trinitramine). A number of studies have shown that various forms of mechanical impact such as dropping weights, rifle and machine gun fire will not detonate 90% hydrogen peroxide. There is considerable evidence that even with powerful initiation and strong confinement, solutions containing up to about 95 - 96% hydrogen peroxide will not support a propagating detonation. In the Trauzl lead block test, in which the tested substance is subjected to impact by a blasting cap under great confinement, enhancement of the explosive effect of the cap was reported at concentrations as low as 60%. The effects increased continuously as peroxide concentration was increased, with very rapid changes over the last few percentage points as 100% was approached.

It is reported that explosive effects are more readily obtained on addition of alkalies to the peroxide, although additions of stabilizers or catalysts are without effect. Hydrogen peroxide solutions in the solid state are reported to have considerably less tendency to detonate than in the liquid state.

The detonation velocity of aqueous solutions containing 96 - 100% hydrogen peroxide has been found to be about 6500 meters/sec., as determined by the Dautriche and by an optical method (7). Although three different detonation velocities have been observed in a given mixture of hydrogen peroxide with an organic compound (see below), only one detonation velocity has been found with pure aqueous hydrogen peroxide.

A few organic materials, particularly if contaminated with heavy metals or alkaline substances, may react violently on contact with concentrated hydrogen peroxide solutions. Other oxidizable materials such as the mono and polyhydric alcohols show no immediate visible evidence of reaction on mixing, yet form detonatable mixtures if their mutual solubility is fairly high or if the oxidizable material becomes dispersed in the hydrogen peroxide solution. The impact sensitivity and the explosive effect of such mixtures varies somewhat with the

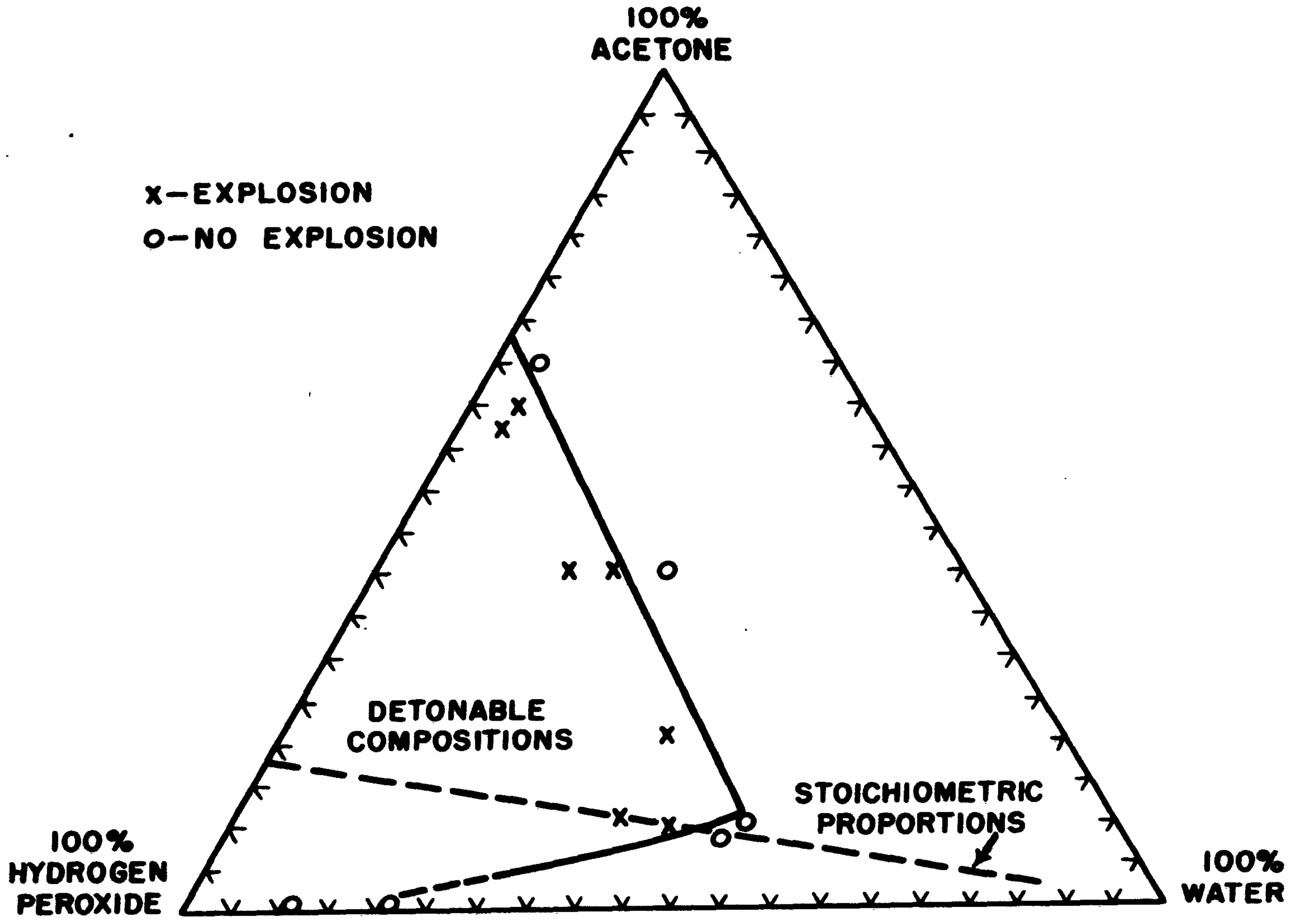

FIG. 5 – RANGE OF EXPLOSIVE COMPOSITIONS FOR ACETONE–PEROXIDE–WATER MIXTURES, FROM SHANLEY AND GREENSPAN[29]

nature of the organic material, but more strongly with the concentration of the hydrogen peroxide and the relative ratios of the two. Shanley and Greenspan (29) have reported the regions of detonatable composition for solutions of several organic substances in aqueous hydrogen peroxide. Figure 5, which shows their results for acetone- hydrogen peroxide - water mixtures, is typical of the various solutions studied. Ninety percent hydrogen peroxide containing several percent of a soluble organic substance is usually detonatable, but detonations have not been observed when 90% peroxide formed less than 30 volume % of the final mixture.

The most pronounced effects are observed with the ratio of the organic substance to hydrogen peroxide equivalent to complete oxidation (stoichiometric ratio). A wide variety of organic substances in concentrated hydrogen peroxide solution have been tested for detonatability. In every case it has been found that if the organic material is sufficiently soluble, a region of detonatable composition exists. Examples include solutions of methyl, ethyl, propyl, and butyl alcohols, formic, acetic, and priopionic acids, allyl and benzyl alcohol, acetonitrile, polyhydric alcohols such as glycerine, dioxane, quinoline and ethyl acetate. The stoichiometric solutions of unsaturated alcohols are more sensitive to detonation than those of saturated alcohols; the latter in turn are more sensitive than solutions of organic acids, using as a criterion the amount of primer required to set off the characteristic high-velocity detonation wave instead of a second low velocity wave (see below). Some of these organic solutions in concentrated hydrogen peroxide are highly sensitive to detonation by mechanical impact. Thus solutions of methyl alcohol in concentrated hydrogen peroxide, contained in a glass vessel, have detonated when dropped from a height of a few feet onto a concrete floor. It should also be noted that many of these organic solutions in concentrated hydrogen peroxide which may initially show no visible evidence of reaction, actually are slowly oxidized, forming mixtures having new explosive properties, and sometimes increased sensitivity.

The explosive characteristics of solutions of methyl alcohol, ethyl alcohol, and glycerine in concentrated hydrogen peroxide have been extensively studied (7). Such mixtures can be ignited with a flame. Small quantities burn with a "hissing" sound, larger quantities soon detonate after catching fire. The presence of impurities can produce spontaneous decomposition leading to inflammation and detonation. Detonation or deflagration, depending upon the conditions and quantity studied, occurs on heating to about 130 - 140°C.

Detonation velocities of stoichiometric mixtures of these three compounds dissolved in concentrated hydrogen peroxide (80% or more), as well as many others, have been measured by the Dautriche and optical methods (7). Under suitable conditions a detonation velocity of about 7000 meters/second is found, which does not vary greatly with the nature of the organic admixture. However, as the peroxide concentration or the primer impulse is continuously decreased, or other variables such as degree of confinement, tube diameter, etc., are gradually changed, the detonation velocity suddenly drops to about 2300 meters/second. Under even milder conditions a third detonation velocity of about 750 meters/second is obtained. The brisance, as measured by the degree of compression of a lead or copper block, likewise suddenly becomes much less. In other words, it is possible to obtain two markedly different and discrete degrees of explosive effect by changing the priming charge, or other variables.

Under conditions giving the higher detonation velocity, these organic mixtures with hydrogen peroxide have a brisance comparable to or surpassing that of picric acid, although lower than nitroglycerine. Lead block expansion values are found to be higher than for nitroglycerine, presumably because of the relatively high gas volume released by the peroxide explosives.

At atmospheric pressure vapors containing 26 mole % or more hydrogen peroxide (the remainder being an inert gas such as oxygen or nitrogen or water vapor) can be exploded by a spark, by contact with catalytically-active materials initially at room

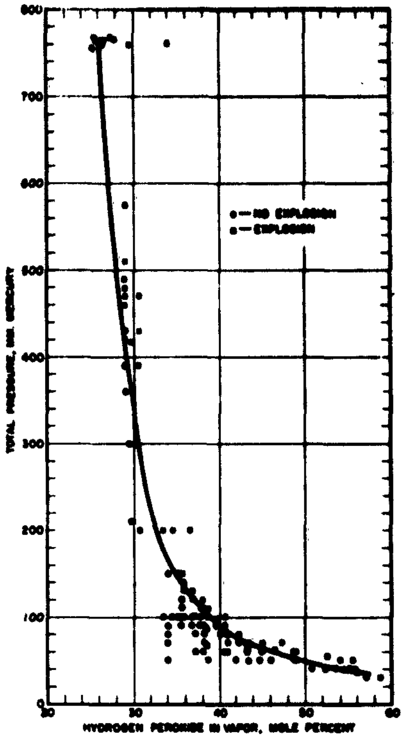

FIG. 7 - EFFECT OF TOTAL PRESSURE ON IGNITION LIMIT
SPARK-GAP INITIATION

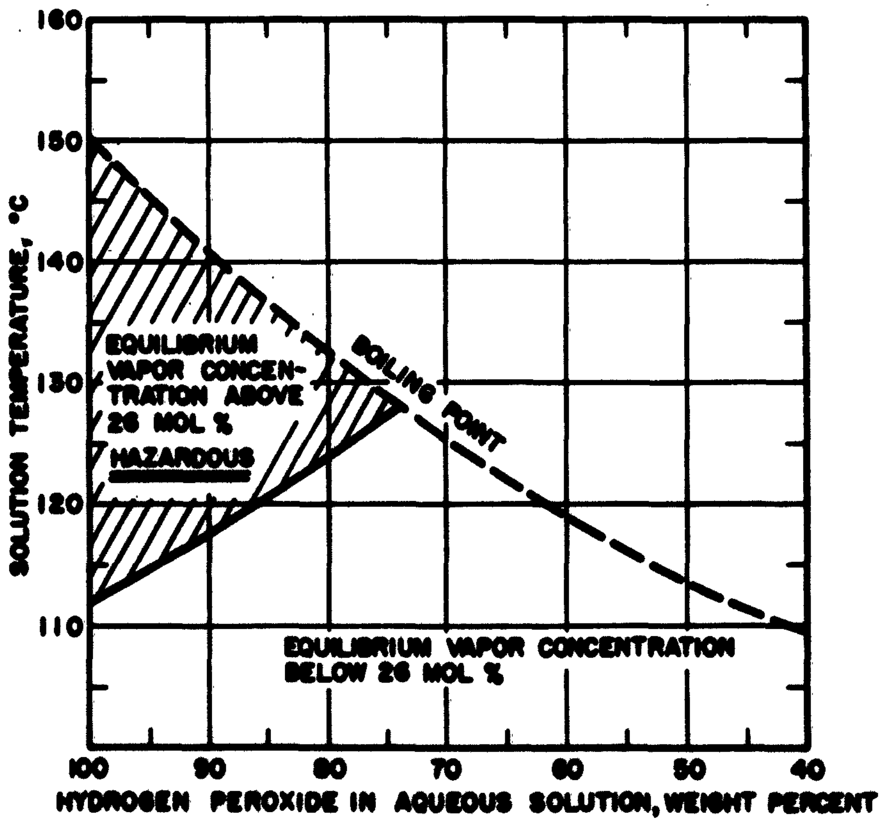

FIG. 6 - COMBINATION OF TEMPERATURE AND LIQUID COMPOSITION PRODUCING EQUILIBRIUM VAPORS IN EXPLOSIVE REGION
TOTAL PRESSURE 1 ATMOSPHERE

temperature, or by "non-catalytic" materials like aluminum which are at temperatures of about 150°C. or higher (30). There is reason to believe that explosions which have been reported as occurring on heating pure aqueous hydrogen peroxide solutions to temperatures near the boiling point may well have occurred in the vapor state, and not in the liquid. The minimum temperatures at which a hazardous vapor mixture can exist above aqueous peroxide solutions at atmospheric pressure have been calculated from the established explosion limit and from vapor-liquid equilibria. They are shown as a function of liquid concentration in Figure 6. It is interesting to note that because of the high relative volatility of water to hydrogen peroxide, the danger of vapor phase explosion on storage of liquid hydrogen peroxide will be encountered only with highly concentrated solutions at elevated temperatures--such as might be reached in a fire or with gross contamination. Under such circumstances, however, it is probable that the accelerating decomposition reaction at these temperature levels would cause pressure rupture of an enclosed or vented vessel at about the time that a vapor of explosive composition was being formed. The rate of dissipation of the heat of normal decomposition by convection from a standard storage drum is quite adequate to keep the temperature of the contents at not more than a few degrees above the surroundings, even at ambient temperatures as high as 150°F.

As the pressure is decreased, the minimum hydrogen peroxide concentration in the vapor which can be exploded increases as shown in Figure 7. This figure indicates the hazardous regions which should be avoided in concentrating peroxide solutions by vacuum distillation. The explosive composition limit is not affected by the ratio of water vapor to oxygen in the inert gas. The explosive characteristics of hydrogen peroxide vapor are also discussed in Chapter 7 on decomposition.

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