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REPORT NO. 44

HYDROGEN PEROXIDE

PART THREE

CHAPTER 7 – CHEMICAL PROPERTIES

CHAPTER 8 – DECOMPOSITION PROCESSES

A Monograph Prepared with
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BY

W. C. Schumb
C. N. Satterfield
R. L. Wentworth

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Departments of Chemistry and Chemical Engineering Cambridge, Mass.

Division of Industrial Cooperation Project 6552

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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 III (Chapters 7 and 8) of such a monograph. The remaining parts (I, II and IV) bear the report Numbers 42, 43, and 45. Report No. 42 was issued September 15, 1953, Report 43 was issued December 1, 1953, and Report 45 was issued November 1, 1953. The Table of Contents presented in this report gives a detailed outline of the material presented in Part III and indicates the contents of the other three parts by listing the headings of the Chapters which each of them contains.

Literature appearing up to about July 1, 1954 has been consulted in the preparation of Part III 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.

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.

Walter C. Schumb
Charles N. Satterfield
Ralph L. Wentworth

December 31, 1954

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CHAPTER SEVEN

CHEMICAL PROPERTIES

The discussion of the chemical properties of hydrogen peroxide has been divided among three chapters. In this chapter the general chemical behavior and the stoichiometric reactions of hydrogen peroxide are described. The following chapter deals with decomposition processes, that is, reactions in which stoichiometric proportions are not or cannot be observed. Chapter nine discusses the subject of the stability of hydrogen peroxide. This division is an arbitrary one, but serves to separate and focus attention on two topics which, for hydrogen peroxide, assume outstanding importance in the discussion of chemical properties. Some duplication and overlapping of the discussion has occurred because of this organization, and it is suggested that when information regarding a particular subject is desired the content of all three chapters be considered since the same subject may receive treatment from differing points of view in each.

It will be useful first to consider some broad classifications of the chemical behavior of hydrogen peroxide. Then in an order of increasing complexity the character of hydrogen peroxide may be considered from the standpoints of the thermodynamics, rates, and mechanisms of its reactions. Discussions of such subjects as the properties of hydrogen peroxide as an acid, properties as a reaction medium, studies of its reactions in non-aqueous solvents, and isotopic tracer experiments involving hydrogen peroxide which have been made then follow. References and as much discussion as space allows of specific reactions, grouped according to the periodic table, are then given. Following the discussion of chemical reactions will be found sections dealing with organic reactions and biological action.

CLASSIFICATION OF REACTIONS OF HYDROGEN PEROXIDE

Four categories may be established for classifying the reactions of hydrogen peroxide. These deal only with the net or over-all result of the reactions.

Decomposition Processes

A reaction which became evident upon almost the discovery of hydrogen peroxide was;

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (1)$$

This was interpreted to be the self-decomposition of hydrogen peroxide. Further study has indicated, however that except at high temperatures in the vapor phase, reaction (1) does not usually occur without the action of some other substance. In most cases a chemical change in the other substance cannot be observed or else the change is not a stoichiometric one, that is, the number of moles of interacting substance which become changed does not bear a simple or consistent ratio to the number of moles of hydrogen peroxide converted to water and oxygen. These <u>decomposition processes</u> will be discussed in the next chapter.

Fortunately, hydrogen peroxide may react in more orderly fashion than just indicated, and these stoichiometric reactions provide the subject matter of this chapter. These reactions have been classified, for example by Halssinsky (1), as follows: 1) Oxidation or reduction reactions, 2) Peroxide group transfer, and 3) Addition-compound formation.

Oxidation or Reduction Reactions

These are reactions in which the other reactant and the oxygen of the hydrogen peroxide undergo a change in valence. An example of a net oxidation by hydrogen peroxide is:

$$H_2O_2 + 2Fe^{++} + 2H^{+} \longrightarrow 2Fe^{+++} + 2H_2O \qquad (2)$$

Similarly, as an example of reduction by hydrogen peroxide there may be cited:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2 \qquad (3)$$

It has been pointed out by Steinbach (2) that an infinite number of sets of compatible coefficients may be chosen for the reduction reactions of hydrogen peroxide, but this only arises because of the possibility of adding multiples of reaction (1) without affecting the balance of the reduction reactions.

The dual nature of hydrogen peroxide, that is, its ability to act as both an oxidizing and reducing agent, is to be emphasized. This property, which contributes so much to the variety and complexity of hydrogen peroxide chemistry, has sometimes been overlooked. In a larger sense this is only a reflection of the intermediate position of hydrogen peroxide between water and molecular oxygen in the oxidation-reduction scale. There is no reason to consider this as '' paradoxical'' (3); molecular oxygen is certainly to be considered legitimately as the oxidation product of hydrogen peroxide.

Peroxide Group Transfer

No change in valency of the oxygen in hydrogen peroxide is involved when this peroxide group is transferred to another molecule. An example of such a metathetical reaction is:

$$H_2O_2 + Ba(OH)_2 \longrightarrow BaO_2 + 2H_2O \qquad (4)$$

It may be pointed out, somewhat in anticipation of the discussion of the mechanism given below, that transfer of the peroxide group intact from molecule to molecule is much the same as formation of molecular oxygen from hydrogen peroxide, even though valence change is assumed to occur in one case and not in the other.

Addition-compound Formation

The hydrogen peroxide molecule as a whole may be attached to another molecule to form addition compounds or hydroperoxidates which are analogous to hydrates.

$$3H_2O_2 + 2Na_2CO_3 \longrightarrow 2Na_2CO_3 \cdot 3H_2O_2 \qquad (5)$$

is an example of such a reaction.

Of these three classes of reactions most of this chapter will be concerned with the first, or oxidation-reduction reactions. The inverse of these classes of reactions, that is, reactions for the formation of hydrogen peroxide, are discussed in Chapters 2 and 3. Additional information about reactions falling in the last two classes will also be found in Chapter 12.

THERMODYNAMICS OF HYDROGEN PEROXIDE REACTIONS

A considerable understanding of the chemical properties of hydrogen peroxide can be obtained from thermodynamic data that allow the calculation of chemical equilibria involving hydrogen peroxide. The thermodynamic quantities required for this purpose are derived in Chapter 5 and are summarized here in Table 1, along with similar data (4) for some other substances. These free energy values may be combined with those for other reactants and products to obtain the total free energy change of the reaction of interest. Thus the equilibrium constant may be calculated through use of the relation $\Delta F^\circ = -RT\ln K$ and a measure is obtained of the degree to which a hydrogen peroxide reaction may proceed to completion.

<u>Half-cell Electrode Potentials</u>

A more convenient method than the use of free energy data to express the tendency to reaction is afforded by the use of half-cell electrode potentials.[*]

For hydrogen peroxide acting as an oxidizing agent the half-cell reaction may be written:

$$2H_2O \longrightarrow H_2O_2 + 2H^+ + 2e^- \qquad (6)$$

For this reaction the potential is:

$$E = -1.76 - \frac{0.05916}{2} \log (a_{H_2O_2} \cdot a^2_{H^+}) \qquad (7)$$

For reaction in terms of the perhydroxyl ion formed in basic solution the half-cell reaction becomes

$$3OH^- \longrightarrow HO_2^- + H_2O + 2e^- \qquad (8)$$

---

[*] In an appendix to this chapter, p. 99 , there is presented a brief review of the use of electrode potentials in the chemistry of hydrogen peroxide.

and the potential is then given by:

$$E = -0.87 - \frac{0.05916}{2} \log \left(\frac{a_{HO_2^-}}{a^3_{OH_2^-}} \right) \tag{9}$$

For hydrogen peroxide acting as a reducing agent the half-cell reaction is:

$$H_2O_2 \longrightarrow 2H^+ + O_2 + 2e^- \tag{10}$$

and has a potential:

$$E = -0.693 - \frac{0.05916}{2} \log \left(\frac{p_{O_2} \cdot a_{H^+}}{a_{H_2O_2}} \right) \tag{11}$$

In basic solution this becomes:

$$OH^- + HO_2^- \longrightarrow O_2 + H_2O + 2e^- \tag{12}$$

with a potential:

$$E = 0.084 - \frac{0.05916}{2} \log \left(\frac{p_{O_2}}{a_{OH^-} \cdot a_{HO_2^-}} \right) \tag{13}$$

These values for the electrode potentials, which were developed in Chapter 5, of hydrogen peroxide show that it is a powerful oxidizing agent. Of the substances which can exist in solution and which have been tabulated in lists of electrode potentials, hydrogen peroxide is capable of oxidizing all but a few. In considering possible reactions of hydrogen peroxide, then, it may be assumed that oxidation of all but the strongest oxidizing agents such as fluorine or ozone will be possible at some pH. As a reducing agent, however, hydrogen peroxide is not particularly outstanding.

TABLE 1

FREE ENERGIES OF FORMATION OF HYDROGEN PEROXIDE AND RELATED SPECIES, AT 25°C and 1 atm

Substance	$\Delta\underline{F}^\circ$, kcal/mole
H_2O_2 (g)	-25.24
H_2O_2 (l)	-28.77
H_2O_2 (aq)	-31.95
O_2H^- (aq)	-15.23
H_2O (g)	-54.635
H_2O (l)	-56.690
OH^- (aq)	-37.595

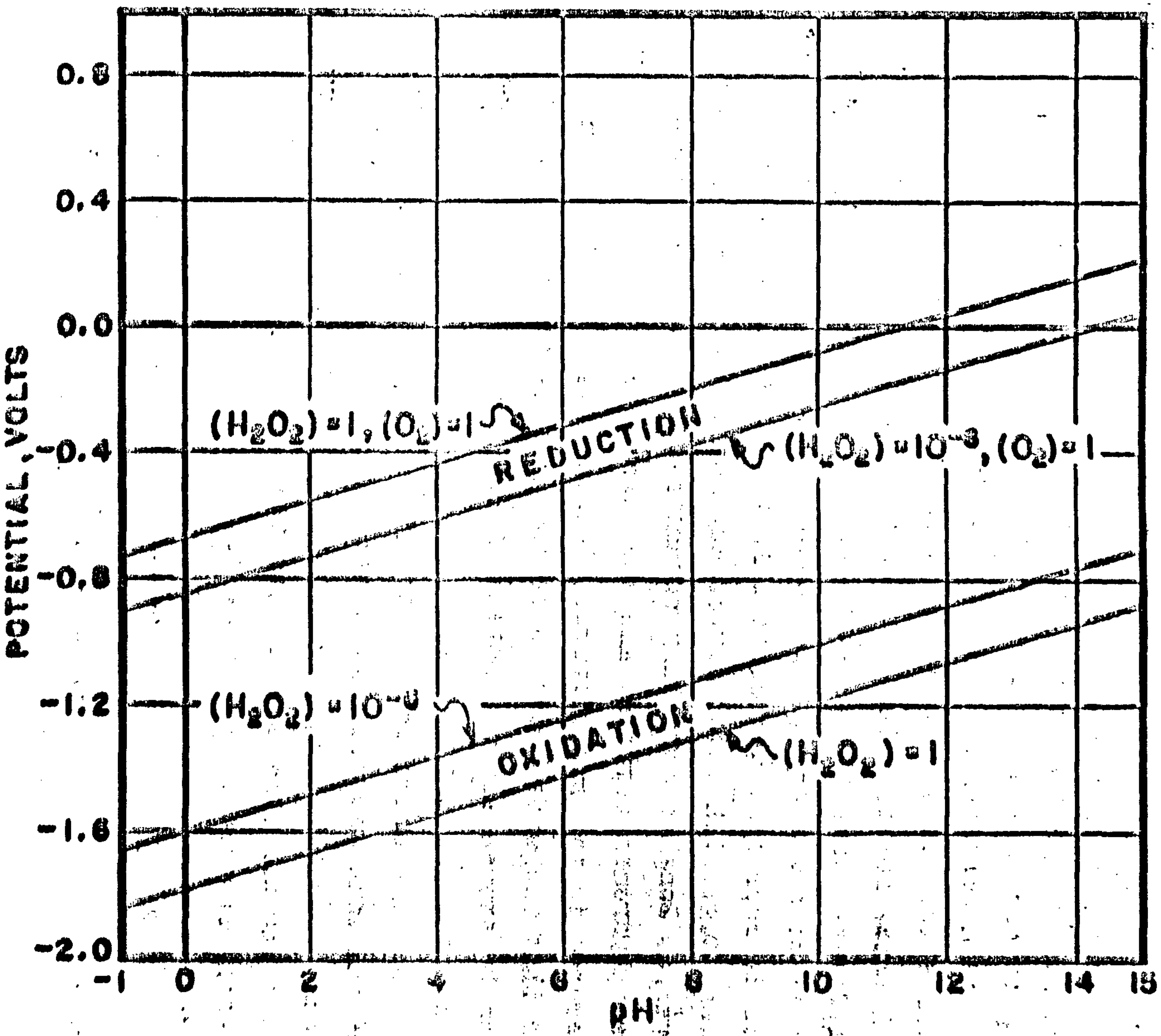
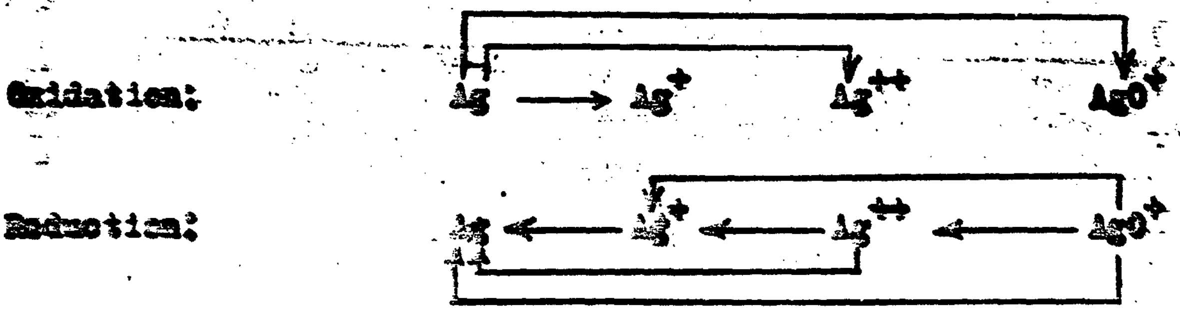


FIG. 1 – POTENTIAL – pH DIAGRAM FOR HYDROGEN PEROXIDE – WATER SOLUTIONS AT INDICATED CONCENTRATION AND PRESSURE

Such a common reducing agent as thiosulfate outstrips it and there is no comparison with the strong reducing agents such as the alkali or alkaline earth metals.

The information provided by these electrode potentials is shown graphically in Figure 1, which was presented in essentially the same form by Delahay, Pourbaix, and Van Rysselberghe (3). Such a potential-pH diagram, easily constructed (5), illustrates the dependence of the potential on the concentration of hydrogen peroxide and of hydrogen ion. By superposing on Fig. 1 similar curves for other half-cell reactions it may be determined at a glance whether the potential is favorable for reaction over the whole of the composition range. Fig. 1 shows how the electrode potentials of hydrogen peroxide at different concentrations are linearly dependent upon pH and parallel to one another. It should be pointed out that if it is chosen to represent the potentials in terms of some other species, e.g., O_2H^-, the curves may not be linear and parallel. However, as long as a rapidly established equilibrium exists between hydrogen peroxide and the other species there is no real difference in two such figures. Furthermore, unless it is known that the other species is the true reactant, little is gained by expressing the potential in terms of a species, the concentration of which must be laboriously calculated.

Once the comparison of the potentials of hydrogen peroxide and some reactants of interest has been made, it may be found useful to summarize the information in the following fashion, as illustrated here for the system of silver and hydrogen peroxide in the range of 10^{-7} to 1 molal acid in the presence of one molal hydrogen peroxide:

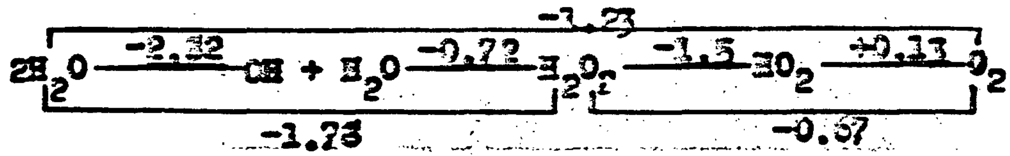


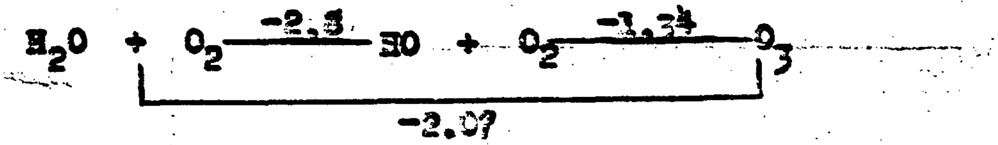
In this diagram the presence of an arrow indicates that the equilibrium is such that the connected substances coexist or that the reaction could go substantially in the indicated direction. The diagram could of course have been prepared for other limits of concentration.

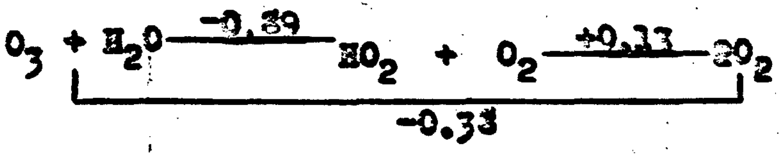
Relative Thermodynamic Potential

Another means for typifying the tendency to reaction of hydrogen peroxide relinquishes the opportunity to show the effect of concentration and instead demonstrates the relation of hydrogen peroxide reactions to those of oxygen in other valence states. With this method there is constructed the following oxidation potential diagram, taken from Latimer (4), which shows the values of E^0 for a group of related equilibria.

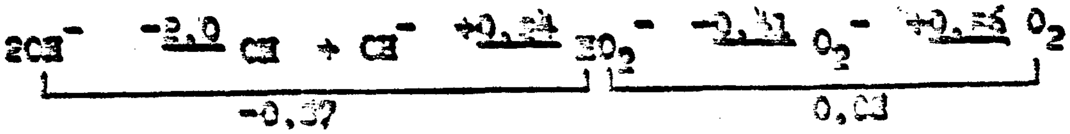
ACID SOLUTION







BASIC SOLUTION



Similar diagrams have been presented for other elements.

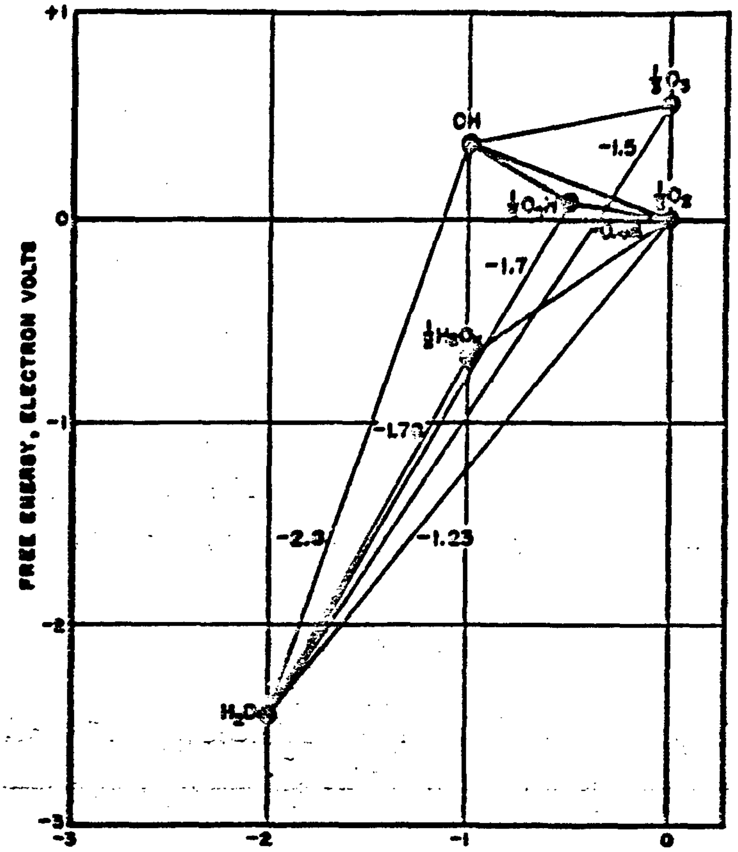


FIG. 2 - OXIDATION STATE - FREE ENERGY DIAGRAM FOR OXYGEN COMPOUNDS IN ACID SOLUTION

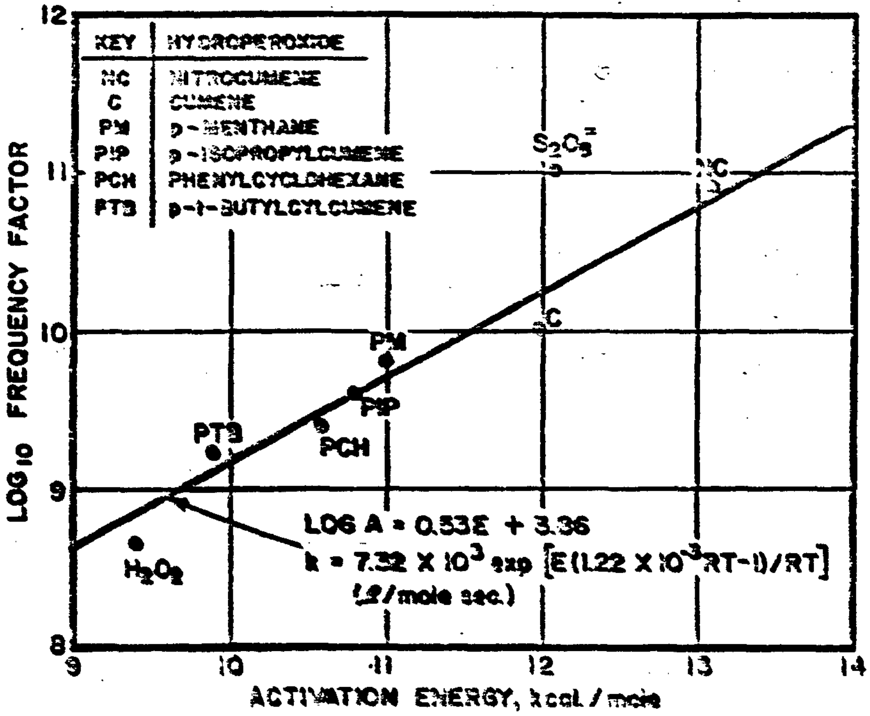


FIG. 3 - RATE FACTORS FOR REACTION OF PEROXIDES WITH FERROUS ION, FROM ORR & WILLIAMS.

The information shown by the foregoing potential diagram may be presented graphically in a way suggested by Frost (7) and adopted for the construction of Fig. 2. The basis for Fig. 2 is found in the relation $\underline{E}^0 = -\Delta\underline{F}^0/\underline{n}\mathcal{F}$, showing that if free energy is expressed in electron volt units (1ev = 23.06 k cal/mole) the potential of a reaction will be given by the slope of a line on a potential-free energy diagram. Such a diagram has certain limitations; some study is required to learn (7) to interpret it, and it may be criticized for laying undue stress on the formal oxidation state of oxygen.

THE RATES OF HYDROGEN PEROXIDE REACTIONS

The study of the rates at which the reactions and decomposition processes of hydrogen peroxide proceed reveals many apparent inconsistencies. Some of its reaction rates, namely with certain ions of the halogens, are so predictable that they have achieved classic status, being given as examples in textbooks and earning a place in the National Bureau of Standards tabulation (8). On the other hand it is often a matter of the greatest difficulty to obtain reproducibility of the most qualitative sort in making measurements of the rate of decomposition with a heterogeneous catalyst. Cobalt metal, for example, can maintain a state of passivity in concentrated hydrogen peroxide for long periods and then unaccountably burst into violent activity. Such catalytic decomposition or the homogeneous decomposition of hydrogen peroxide vapor can occur at an explosive rate, yet at the same time the pure substance is quite stable in storage and has been characterized (9) generally as a slow oxidant except with powerful reducing agents. An other important question, not yet settled, is whether the rate of decomposition of the purest hydrogen peroxide can be reduced to zero in the liquid state at the commonly encountered conditions of storage. From the standpoints of both experience and theory it appears that an unmeasurably slow rate of decomposition is potentially attainable, but in practice only to be approached asymptotically because of the impossibility of eliminating container surfaces and the last traces of impurities.

Solid hydrogen peroxide has been reported to be surprisingly inert. For example, chilled 0.5% permanganate solution, particles of rust, and other catalysts if added judiciously so as not to allow thawing were found (10) to cause no decomposition of 90 wt % hydrogen peroxide at -55°C. Only when melting was permitted to occur did decomposition begin.

Although no attempt has been made to collect and tabulate reaction rate data for hydrogen peroxide decomposition or its reactions with other species, it is instructive to consider briefly the range of rates encountered, and the temperature coefficients as typified by the Arrhenius activation energies observed. No measurements on a gas phase decomposition of hydrogen peroxide have yet been identified unambiguously as being that of the purely homogeneous decomposition, although the results of McLane (11) obtained from experiments at 467 to 542°C indicated that at least part of the decomposition observed was homogeneous. His results yield an activation energy of 40 to 50 kcal/mole. It is reasonable to suppose that it is only at such high temperatures that the thermally activated homogeneous decomposition of hydrogen peroxide can occur at measurable rates. This fact has been pointed out by Hart (12), who cited the following reasoning. As reference to the thermodynamic data of Chapter 5 will show, the most likely initial step in the homogeneous decomposition of hydrogen peroxide is dissociation into two hydroxyl radicals. Using the energy change of this reaction as an estimate of the activation energy and an assumed collision factor of 10^{14}, near room temperature only about one hydrogen peroxide molecule in 10^{27} undergoes this dissociation per second. Near 300°C one molecule in 10^{5} reacts per second on this basis, allowing for slight decomposition by chain reaction of reasonable length. At 600°C all hydrogen peroxide would decompose in a fraction of a second, even without contribution from chains.

Even with allowance for the uncertainties involved, this estimate makes it clear that other studies of vapor phase decomposition, cited in Chapter 3, dealt only with heterogeneous decomposition. A temperature range of 25 to 420°C is covered by these studies, and activation energies ranging from 4 to 20 kcal/mole were reported.

This conclusion may also be applied to decomposition in the liquid phase. As discussed in Chapter 9, a highly purified sample of hydrogen peroxide in a Pyrex container will decompose at a rate consistent with an activation energy of about 15 kcal/mole, and the process is assumed to be largely heterogeneous. Homogeneous liquid phase reactions of hydrogen peroxide also exhibit activation energies in this range, for example, values ranging from 10 to 27 kcal/mole are observed for reaction with a number of ions of the halogens (13).

To be compared with these values are those obtained in the study of the reactions of various substituted peroxides. For the homogeneous decomposition proceeding by homolytic O-O bond fission in either the gas or liquid phases a number of peroxides, such as diethyl peroxide, dibenzoyl peroxide, di-*tert*-butyl peroxide, cumene hydroperoxide, and peroxysulfate exhibit activation energies of about 30 to 40 kcal/mole. The activation energies for reaction with other substances fall below this range, as low as 10 kcal/mole. A more detailed comparison of several peroxides undergoing the same process, namely reaction with ferrous ion, is provided by Fig. 3, which was published by Orr and Williams (14). As these data indicate, there is a direct relationship between the frequency factor and activation energy for this particular reaction. At a given temperature the relationship is such that all the substitutions on hydrogen peroxide indicated make the reaction rate slower. This may be contrasted with the higher reaction rates observed for the uncatalyzed homogeneous decomposition of organic peroxides relative to that of hydrogen peroxide. Orr and Williams (14) have interpreted the results of the ferrous ion reaction shown in Fig. 3 to show that repulsion of an electron excess into the O-O bond gives a low activation energy by increasing the availability of electrons for coordination with ferrous ion in the activated complex.

A general guide for comparing the stability of peroxides has been put forward by Walsh (15), who stated that, up to a point, the O-O bond energy is increased by negative charge transfer. Some observations consistent with such a generalization were listed earlier by Walsh (16) as follows: acyl peroxides decompose appreciably even at room temperature, and are more reactive than aryl (acyl substituents are electron attracting, aryl, repelling), dialkyl peroxides are more stable than the corresponding hydroperoxides, which in turn decompose less readily than hydroxy alkyl peroxides, $HOOCH_2OH$, and among alkyl hydroperoxides stability increases in the order primary, secondary, tertiary. Walsh (15) emphasized that charge transfer affects bond strength, but not necessarily bond dissociation energy, and that activation energy may not be concerned solely with O-O bond fission.

This principle of charge transfer is of undoubted importance, but it is not clear that the effects of charge transfer have yet been recognized and codified into a consistently reliable theory. For example, barium peroxide, a nearly completely ionic substance, is notably stable. On the other hand, work cited in the discussion below has demonstrated that addition of electron repelling substituents to acyl peroxides increases their rate of decomposition. It would appear that any comparison which is made should deal with similar processes, that is, breaking of the same bond in the same environment by a consistently homogeneous or heterogeneous process involving the same or equivalent co-reactant, initiator, or catalyst. For example, if the rate of homogeneous gas phase decomposition is considered it appears that organic peroxides are less stable than hydrogen peroxide. The instance of reaction with ferrous ion on the other hand shows hydrogen peroxide to be the most reactive of the peroxides considered. In particular a distinction should be made between the susceptibility of a peroxide to explosion or detonation and the rate at which it undergoes reaction under well defined conditions.

MECHANISM OF HYDROGEN PEROXIDE REACTIONS

The description of a hydrogen peroxide reaction according to the foregoing classifications can be made with high precision and certainty, or may at least in principle be so determined. However, when it is required to know the mechanism of a reaction, i.e., to have some knowledge of the intermediate states assumed by the participating atoms and electrons, then no such certainty can be offered. This is a subject for which satisfactory theory has only recently begun to be developed, and improvement to much more useful levels of refinement may be expected. In the following paragraphs a number of suggestions regarding mechanisms will be reviewed briefly. Perhaps the most important conclusion to be reached is that neither the scope of experimental facts nor the most advanced theory allow any generalizations by which the mechanism of hydrogen peroxide reactions can be predicted or even classified unequivocally at present.

Net Reaction Equations as Descriptions of Mechanism

The chemistry of hydrogen peroxide provides excellent instances to illustrate how inadequate net equations are to describe mechanism. If a net reaction such as (3), which shows the oxidation of hydrogen peroxide by potassium permanganate, is considered, there immediately arises the question of whether the interaction of ten molecules is really involved. Reaction (3) can also be written in slightly different manner by adding one more sulfuric acid molecule to the reactants and expressing the potassium salt product as the bisulfate, $KHSO_4$. The latter uncertainty is relieved if it is recalled that this reaction is ordinarily conducted in aqueous solution where certain of the reactants and products are in ionized form. Thus it is reasonable to eliminate as inert, ions of potassium, sulfate, or bisulfate giving:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \longrightarrow 2Mn^{++} + 8H_2O + 5O_2 \qquad (14)$$

In one respect, however, this procedure has complicated the matter; thirteen reacting molecules now replace the original ten. In addition it is uncertain at which point the application of ionization should be stopped. It is known that hydrogen peroxide can ionize to a slight extent in aqueous solution to form hydrogen and perhydroxyl ions. Although there is no hesitation about showing the potassium permanganate as completely ionized it will be recognized that hydrogen peroxide is a weak acid, and unless the reaction is carried out in basic solution little perhydroxyl ion will be present. It might be insisted that perhydroxyl ion is the reactive form even if present only in small proportions. Whatever the merit of this suggestions, it necessarily leads to further increase in the number of reactant molecules written in the net equation.

Stepwise Reactions

This elementary discussion has demonstrated the inadequacy of net equations as mechanistic descriptions. The usual idea offered in explanation is that net reactions show only the sum of a series of individual reactions. For example, it has been suggested that in the case of the action of hydrogen peroxide as a reducing agent, as in the permanganate reaction under discussion, the hydrogen peroxide must first oxidize the substrate, followed by a reduction by water, thus:

$$H_2O_2 + 2H^+ + 2M^+ \longrightarrow 2M^{++} + 2H_2O \qquad (15)$$

$$2M^{++} + 2H_2O \longrightarrow 4H^+ + 2M + O_2 \qquad (16)$$

Two objections are immediately raised to this. It may often be incredible that an oxidized substance being reduced by hydrogen peroxide should first be oxidized even higher. Even if it is insisted in the face of an exceedingly unfavorable energy relationship that higher oxidation may occur in minute proportion there remains the further criticism that in both reactions (14) and (15) there has in fact been an assumption of mechanism, namely that embodied in the reactions written to express the half-cell potentials, (6) and (10). The form of these reactions too has no relation to mechanism, only net results regarding the energy and nature of the reactants and products being of concern. A number of other half-reactions can be listed, and in the absence of any additional basis for choice, combinations of these or perhaps of others as well certainly merit consideration.

$$H_2O_2 \longrightarrow HO_2 + H^+ + e^- \qquad (17)$$

$$OH + OH^- \longrightarrow H_2O_2 + e^- \qquad (18)$$

$$OH + 2OH^- \longrightarrow O_2H^- + H_2O + e^- \qquad (19)$$

$$O_2H^- + OH^- \longrightarrow O_2^- + H_2O + e^- \qquad (20)$$

$$O_2H \longrightarrow O_2 + H^+ + e^- \qquad (21)$$

Even if no direct experimental evidence for the existence of some of these intermediates were available, their consideration for the simplification in the molecularity of reactions seems reasonable.

An additional idea regarding mechanism has been touched on in the above discussion. The thought that exceedingly small proportions of uncommonly highly oxidized substrate may be active in hydrogen peroxide reactions has been frequently expressed. Perhaps even more use of this has been made in explaining decomposition processes, as in the following chapter. The rather high-standing oxidation potential of hydrogen peroxide permits reasonable consideration of this idea. In the absence of any direct knowledge that such an oxidation is not possible, the only limitation entering the problem is the reaction rate permitted by the small concentration of oxidized substrate. Presumably it might be calculated that small concentration is consistent with an observed rate, but it is likely that a convincing calculation would in turn depend on such a detailed knowledge of mechanism that the purpose would be defeated. Another idea similar to this has been advanced repeatedly. It is possible that hydrogen peroxide reacts with substrate molecules to form peroxides or hydroperoxides which may be more powerful reactants than hydrogen peroxide. Where such a hypothesis has been advanced it has been seldom that the actual existence of the peroxide has been demonstrated or that its thermodynamic potential has been known.

Recent re-evaluations of the concepts of oxidation and reduction (17),(18) may be helpful in considering these ideas. The usefulness of the terms oxidation and reduction is best limited, according to Mulliken (19), to description of net processes and to the formalistic assignment of charge to atoms. To deal with the actual (or supposed) mechanism of reaction the concept of tendencies toward electron acceptance or repulsion are brought into consideration. Some aspects of this which are of importance in interpreting the reactions of hydrogen peroxide are mentioned below.

Atom Positions and Electron Distribution. Earlier theorists were troubled by a fancied lack of geometrical accessibility of the oxygen in hydrogen peroxide, leading to the previously discussed insistence on the trigonal structure. Inadequate observation impeded progress; for example, Bancroft (20) wrote: "the chemistry of hydrogen peroxide is a hopeless subject for the phenomenological or Baconian experimenter because misleading experiment is everywhere." This interesting statement has been widely noticed and even cast into French by Thiesse (21). It seems to imply that speculation will come nearer the truth than experimental results. There is no doubt that the large literature of hydrogen peroxide abounds in poorly reported and imprecise experiments over narrow ranges of conditions. Nevertheless, observations of precision can be made and these can be interpreted validly. The framework for such an interpretation must be based on a consideration of electronic theory, as used in the preceding chapter to determine structure. This approach adds to the concern about the relative positions of the atoms the requirement that the electron distribution about the atoms also be considered. Most of the development of such theory has been due to organic chemists (22,23) rather than to physical or inorganic chemists, but its extension and application to hydrogen peroxide reactions is perfectly feasible.

In order to follow and describe atomic position and electron distribution throughout a reaction it is useful to visualize the reaction as occurring in a number of stages even though such stages cannot in fact be separately distinguished experimentally. For example, Coulson (24) divides them into (1) the initial stage of approach of reactants before reaction begins, (2) the polarized state with the reactants recognizable but in a perturbed state, (3) the transition state with energy at a maximum and reactants rearranged and fused into a transition complex, and (4) the final state with the products separated. Thus, in order for a net chemical change to be observed with hydrogen peroxide it may be necessary for subsequent or parallel steps of activated complex formation and bond breaking to occur among the products of the initial reaction or with additional hydrogen peroxide. In some cases no bonds in the hydrogen peroxide need be broken, in others one, two, or all must be broken.

The magnitude of the energy necessary to form the activated complex (25) is of considerable importance since it determines the rate of reaction, or, indeed whether the reaction can proceed at all. The energy available for this is not unlimited being derived in "thermal" reactions from the kinetic energy of the reacting molecules. The circumstance which permits continued consideration of a mechanism involving the breaking of a strong bond is the fact that bond-breaking (or any of the other reaction steps) does not occur as a discrete act. It is not necessary to supply all this energy and break the bond completely because the bond-breaking and bond-forming procedures go forward together. This process is not limited to the breaking and forming of covalent bonds, but as Ingold points out (ref. 22, p.44) may also be effected by solvent interaction as in covalent fission and simultaneous ion solvation.

A feature of the greatest importance, to be emphasized in all discussions of mechanism is the charge distribution in the molecules undergoing reaction. With hydrogen peroxide the most important factor is the concentration of negative charge in the oxygen. This may be expressed in different ways by different authors according to the point of view or the reaction mechanism contemplated. Thus the polar nature of the OH bond may be emphasized. Or the presence of the lone pairs of electrons on the oxygens may be pointed out. Generally this fact is merely expressed by referring to the electron accepting nature of the oxygen, *i.e.*, its electronegative character. It should be noted that electronegativity is a relative term and one not yet amenable to strict definition. For example, an isolated atom or group is regarded as possessing a certain electronegativity. When some reaction or molecular interaction is allowed to occur, however, the relative magnitude of that electronegativity is changed. As Sanderson (26) points out, it is reasonable to suppose that on the formation of a chemical bond the interacting atoms change in average electronic density in such a way as to bring them each to equal electronegativity in the molecule. Such a process is limited by the degree of electron transfer which may occur; when a group of high electronegativity combines with a group of low electronegativity even complete electron transfer may not be sufficient to bring about equality, *e.g.*, peroxide ion, $O_2^{=}$, remains quite electronegative in its various combinations.

In this consideration of charge distribution it is necessary to use care in distinguishing between the kinetic order of a reaction and its molecularity. The kinetic order is concerned only with the order of concentration to which the rate of reaction is observed to be proportional. The molecularity of the reaction refers to the number of molecules taking part in a reaction. The phrase "taking part" receives differing interpretations, particularly with respect to the solvent, Ingold (ref. 22, pp. 315, 356) wishes to close the definition more strictly, limiting molecularity to "the number of molecules necessarily undergoing covalency change." Others, e.g., Swain (27), point to the importance of interactions of one reactant with solvent or other solutes in such a way to prepare it for reaction. It is possible that interaction with an adjacent molecule, ordinarily thought of as inert, might cause redistribution of the charge in the hydrogen peroxide molecule in such a way that one end of the molecule might be substantially positive with respect to the other end, facilitating the approach, and therefore the reaction with another molecule or ion and its shell of solvation. The reaction may then be typified as requiring a concerted push-pull by solvent and reactant and could be considered termolecular. Ingold (22) regards such interactions as too diffuse and general to allow classification of reaction type. These ideas and conflicts have been reviewed by Remick (28). Other solutes as well as solvents can also assume such a role in reaction mechanisms; for example, electron transfer (oxidation) from Cr^{++} to Fe^{+++} is catalyzed by the presence of chloride ion (29). This entire group of effects due to the assistance of electrostatic or other forces is well expressed by Mulliken's term (19); "environmental cooperation".

These ideas are to a large extent new and controversial. Much of the reasoning involved is intuitive, but the basic premises are sound and provide a useful basis for discussion of mechanism. The terminology and the validity of various viewpoints on mechanism are discussed by Mulliken (19). This source is also of value in indicating how much systematization is possible although the elaborate nomenclature adopted will not appeal to many.

Characteristics of Hydrogen Peroxide in its Reactions

Hydroperoxidate Formation. The simplest reaction of hydrogen peroxide, at least in visualization, is the addition of the molecule as a whole to another molecule, that is, formation of a hydroperoxidate. In the analogous formation of hydrates several methods of binding are currently recognized as possible, and the water of hydration or crystallization is thus distinguished according to the designations, coordinated water, anion water, lattice water, or zeolitic water. Experimental background is inadequate to establish such categories for the analogous compounds with hydrogen peroxide, especially for the less sharply defined classes of lattice and zeolitic binding. The brief observation by Willstätter (30) that alum may form a hydroperoxidate suggests a possible instance of lattice binding, but the study by Münzberg (31) casts doubt on this. More recently it has been observed (32) that an amine permutite is capable of taking up hydrogen peroxide. It is also unclear whether stable coordinate bonding of the hydrogen peroxide molecule as a whole occurs. The improving description (33) of the electronic nature of the coordinate bond promises to throw light on this important question. It is suggested that coordinate bonding of hydrogen peroxide cannot occur without seriously reducing the stability of the molecule. It appears likely that the shift of charge away from the oxygen atoms required in the formation of a coordinate bond would either cause disruption of the molecule or induce its ready reaction. Such a function seems to be provided by the enzymes peroxidase and catalase, and it is suggestive in this respect that nearly all the heavier metals are excellent decomposition catalysts. If valence bond breaking is induced by formation of a coordinate bond it seems most reasonable that this would occur at the hydrogen-oxygen bond to leave a perhydroxyl ion.

The definite hydroperoxidates which have been shown to occur are most acceptably understood as hydrogen bonded compounds analogous to the class of anion water compounds mentioned above. The process of forming hydrogen bonds appears to be simple mechanistically. The nature of the hydrogen bonding which occurs with hydrogen peroxide is briefly discussed in connection with the associative properties in Chapter 6. It is seen how the electronegative character of oxygen, the polarity of the OH link, and the small size of the hydrogen atom contributed to the formation of these bonds. It is also pointed out that these bonds are too weak to be long maintained in the gas or liquid phase; only in solids do they maintain identity. From these qualities it is easily appreciated that hydroperoxidates (and hydrates as well) are formed with compounds containing the highly electronegative atoms such as nitrogen, oxygen, and fluorine. References to studies of these hydroperoxidates are given in Chapter 12. Most of the information relates only to the occurrence of these compounds, and little can be said about the mechanism of formation, which is assumed to be little more than suitably oriented collision and adherence. In many cases these reports of occurrence need confirmation. Münzberg (31) found by microscopic examination that many of the reported hydroperoxidates were in fact only inclusions of mother liquor in the crystal mass, and reported negative results for a large number of salts tested for hydroperoxidate formation. Interesting facts regarding the nature of the bonds formed are provided by the observations of Husain (34) that the capacity of phosphates to bind hydrogen peroxide increases in the order: primary phosphate, secondary phosphate, pyrophosphate. With each salt type the potassium salt was found to bind more firmly than the sodium salt. Münzberg (31) found it a rule that only di-or polybasic acids could bind hydrogen peroxide. It was observed as a result of the study (35) of the formation of hydroperoxidates by wool that hydrogen peroxide is bound more firmly by amino groups than by carboxyl or hydroxyl groups. Similarly it was concluded (36) that the amino group was responsible for the absorption of hydrogen peroxide on an ion exchange resin. Levi and Battaglino (37) observed that hydrated hydroperoxidates retained the hydrogen peroxide more tenaciously than the water.

Valence Bond Breaking Processes. In other reactions of hydrogen peroxide one or more of the valence bonds of the molecule is broken, and along with this, certain electron transfer processes may occur. Five possible net processes can be readily discerned. These may be written as follows, in which the dots represent the electrons of a covalent bond and the broken lines indicate the separation to be visualized.

$$HO{:}OH \longrightarrow 2\ OH \qquad (22)$$

$$HO : | OH \longrightarrow OH^- + OH^+ \qquad (23)$$

$$HOO \,/\, H \longrightarrow \cdot O_2H + H \qquad (24)$$

$$HOO : | H \longrightarrow O_2H^- + H^+ \qquad (25)$$

$$HOO | : H \longrightarrow O_2H^+ + H^- \qquad (26)$$

The two cases (reactions (22) and (24)) in which the two electrons are shared by the products are examples of homolytic valence bond fission. Since each product has an odd electron these are termed free radical mechanisms. The three cases (reactions (23),(25), and (26)) in which both electrons of the broken bond remain with one of the product molecules result in the formation of charged products. These processes are termed ionic mechanisms and occur by heterolytic fission. Other ionizing processes involving removal of an electron from the molecule as a whole can be visualized, but the energy requirements for such ionizations (see p.77, Chapter 6) are several fold those of the reactions just discussed and do not come into consideration with any chemistry so far reported. With the advent of studies of decomposition processes initiated by ionizing radiation such ions may be found to be of importance (38). The ion $H_2O_2^-$ mentioned by Weiss (38) is difficult to imagine, although combined electron impact, splitting of the hydrogen peroxide, and incorporation of the electron into a product may occur. Reaction (26) is a rather unlikely one for hydrogen peroxide to undergo and will not be considered further.

It is often not immediately possible to choose the most likely of reactions (22) to (25) to suit a particular set of reaction conditions, although there are a few principles for guidance. In decomposition processes occurring in the vapor phase, whether thermal or photochemical, reaction (22) is the most likely, reaction (24) being next most probable. Reaction with other substances in the vapor very likely also occurs solely through free radicals. In the liquid phase the factors of environmental cooperation make the ionic reactions (23) and (25) more likely. This comes about through reduction of the direct energy requirement to bring about these ionic reactions; as discussed above, the temperature level of concern in liquid phase reactions is too low to permit significant thermal activation of the unassisted disruption to free radicals. With the introduction of energy to the liquid *via* photochemical or ionizing radiation, however, free radical reactions can again occur.

Because the electron shells of hydrogen peroxide are complete, it is necessary that the molecule be split before further electrons can be accepted. Likewise in order to donate an electron or a share in an electron, it is likely that the molecule must be split. The focus of attention is subsequently on the more novel or uniquely reactive fragment. In the case of reaction (23) this is the OH^+ ion, an electrophilic or electron accepting entity, which is analogous to the carbonium ions. In reaction (25) it is the O_2H^- ion, a nucleophilic or electron donating entity. The hydroxyl free radical probably deserves classification as an electron accepting body, while both electron accepting and electron donating roles have been assigned to the perhydroxyl free radical. Other characteristics of processes involving free radicals have been described by Waters (39), and free radical and ionic mechanisms of organic peroxides have been compared by Tobolsky and Mesrobian (ref. 40, pp.57-59).

Electron Transfer. It has been noted that electron exchange may accompany the valence bond-breaking which occurs in reaction. This provides another way of typifying hydrogen peroxide reactions, introduced by Browne (41), who pointed out that in acting as an oxidizing agent hydrogen peroxide accepts two electrons, whereas some other oxidizing agents accept only one electron. Brown used this as a basis for classification, inventing the terms mono- and di-delectronator. The distinction is a valid one, but the less cumbersome terms, one- or two-electron change, seem preferable. A slight alteration and stiffening of Brown's definition is also in order. All net oxidation-reduction reactions of hydrogen peroxide involve two electron changes, but these may be imagined to occur in two steps or at once. Taube (42) has stated a definition quite distinctly. A net change, formally represented as

$$A^{++} + B = A + B^{++} \tag{27}$$

is referred to as an example. This reaction is presumed to proceed through an activated complex AB^{++}. The distinction between a one electron change and a two electron change is not concerned with the flow of electrons in the complex but rather with the question of whether evidence can be found for the existence of the intermediate species A^+ and B^+. If these exist (and can be demonstrated) then the reaction proceeds <u>via</u> one electron changes. If the demonstration of their existence cannot be made then it is presumed that the change is a two electron one. Taube points out that the insensitivity of tests[a] for such intermediates as A^+ and B^+ may cause misleading conclusions. There has consequently been some difference of opinion regarding the possibility that hydrogen peroxide may act by both one and two electron changes. Uri (43) reasserted the claim of Haber and Weiss that hydrogen peroxide never reacts with a substrate making a bivalent change or simultaneously with two substrates making monovalent changes in the direct production of oxygen or water. On the other hand, both Taube (42,44) and Christiansen (45) have cited evidence that two electron changes do indeed occur with hydrogen peroxide. The extensive discussion by Cahill and Taube (44) illustrates the problems involved here. These authors sought to determine from oxygen isotope tracer experiments whether the oxidation of ferrous ion by hydrogen peroxide proceeded as a one electron transfer to the ferric state or a two electron

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[a] Tests for free radical intermediates, on the other hand, are highly sensitive; for example Tobolsky and Mesrobian (40) cite eleven methods for demonstrating their presence.

transfer to the Fe(IV) state, i.e., whether reaction (28) or (29)

$$Fe^{++} + H_2O_2 = Fe^{+++} + OH + OH^- \qquad (28)$$

occurred in one step involving the formation of only one activated complex;

$$Fe^{++} + H_2O_2 = Fe(IV) + 2OH^- \qquad (29)$$

The initial bond-breaking step in the hydrogen peroxide molecule would appear to be classified as the same in both cases.

It can be appreciated that if Fe(IV) were the ultimate product of reaction, this net result could equally well be achieved by carrying out reaction (28) and following this by electron transfer from ferric ion to hydroxyl radical. Unless the latter interaction is quantitative, however, some alternate reaction of hydroxyl radical would very likely change the kinetics or net result. Cahill and Taube concluded that oxidation was in fact proceeding by both the one and two electron transfer mechanisms.

This matter was discussed by Higginson, Sutton, and Wright (47) from several points of view, and on the basis of experiment they came to the interesting conclusions that the rate of oxidation by hydrogen peroxide of several ions of multivalent metals correlated better with the electrode potentials of the metals for one electron steps than with those for two electron steps. Although they admit the correlation may not be valid, it is suggestive of preference for one electron changes. The limitations of a description according to electron order should be kept in mind. Just as discussed above in regard to the concepts of oxidation and reduction it is often difficult to suggest a clear-cut path of actual electron transfer. Thus, as has been noted (47), the concept may be only equivalent to stating that net oxidation or reduction occurs, although as defined above the usage carries a definite implication of detailed knowledge of mechanism.

This discussion of terminology and its drawbacks illustrates again the difficulty of organizing under one system ideas about mechanism differing in level of detail. For example, the reaction in which ferrous iron is oxidized to ferric iron while producing a hydroxyl radical and a hydroxyl ion from hydrogen peroxide, could be classified as proceeding by an ionic mechanism or a free radical mechanism, according to whether reaction (22) or (23) is believed to occur at the approach of the Fe^{++} ion. It is believed that the ionic mechanism is more likely, although the paths followed by the electrons exchanged cannot be followed in detail. At the same time this is an important process for the generation of free radicals, and the subsequent reactions may be the same ones possible following an initial free radical dissociation. Also the product ions likely exist in association. Thus there exists considerable room for confusion in describing an ionic reaction involving electron transfer to produce a free radical and a complex ion. Part of the uncertainty of designation arises from the point of view; in this example interest is centered on the hydroxyl free radical product. It is perhaps appropriate to point out that free radicals no longer deserve special status as extraordinary molecules. They are especially reactive to be sure, but the theory of valence accounts for their structure well, moderating the astonishment with which they were regarded when first proposed (39). Also, certain of the ions, i.e., the ferrous ion or the Hg^{+} ion, could just as well be termed free radicals or radical-ions.

Another characteristic of hydrogen peroxide which contributes to uncertainties about its mechanism of reaction when ionic cleavage of the OO bond is considered is the identity of the two halves of the molecule. With other peroxides ROOR' or ROOH there is a preferred direction of charge migration. And in the elementary related example of hydroxylamine the tendency is always to dissociate to NH_2^{+} and OH^{-} rather than to NH_2^{-} and OH^{+} because of the greater electron affinity of OH(43). With hydrogen peroxide, however, there is no tendency for charge to migrate in one direction except as induced by the approach of other molecules.

Classification According to Bond Breaking Process. From the foregoing discussion there emerges the idea that the first step of a hydrogen peroxide reaction involves the formation of one of the entities OH^+, O_2H^-, OH, or O_2H as a more or less independent intermediate. The degree of independence possessed by such species has been discussed (ref. 40, pp.107-112) for the similar case of organic peroxide reactions. Electron exchange may occur nearly simultaneously. This classification of reactions indicated by equations (22) to (25) (with the exclusion of O_2H) was proposed by Derbyshire and Waters (49), who were of the opinion that each of these species has well-defined characteristics allowing discrimination. As a means of classification of the detailed mechanism of hydrogen peroxide reactions the practice will be adopted here of referring to reactions involving initial formation of two OH radicals as *hydroxyl radical mechanisms*; those involving formation of OH^+ and OH^- will be termed *hydroxyl ion mechanisms*. Similarly, if O_2H is believed to be first produced this will be called a *perhydroxyl radical mechanism*, and if dissociation to O_2H^- and H^+ is thought to occur, reference will be made to a *perhydroxyl ion mechanism*.

It will be observed that the two ionic mechanisms are to be associated with the concepts of acid-base catalysis. The O_2H^- ion will be recognized as the anion resulting from dissociation as an acid. Conviction that the OH^+ ion has independent existence comes less easily. It has been suggested (50) that there occurs the reaction

$$H^+ + HOOH = HOOH_2^+ \qquad (30)$$

and that the OH^+ ion subsequently may appear through

$$HOOH_2^+ = H_2O + OH^+ \qquad (31)$$

One striking difference between the two ionic mechanisms lies in the fact that in one case (OH^+) the two oxygen atoms of the hydrogen peroxide molecule are separated at the beginning. When perhydroxyl ion is involved the oxygen atoms remain together, at least initially, and offer the opportunity for them to remain so bound in the oxidation to molecular oxygen. Without isotopic labelling the difference may not be apparent, however. For example, both hypochlorous ion (ClO^-) and molecular chlorine (Cl_2) react with hydrogen peroxide to yield oxygen and chloride ion. In the former case there may be visualized the reaction of ClO^- and OH^+ to form ClOOH. In the latter case the interaction of Cl^+ and O_2H^- may yield again, ClOOH. This chlorine hydroperoxide has not been isolated, and indeed, as the remarks of Chapter 6 indicated, it could be expected to be quite reactive. The presence of the electronegative chlorine should enhance both ionization of the hydrogen and separation of molecular oxygen. These two sets of proposed reactions may very well not occur exactly as detailed, but as a means of visualizing the bond-breaking and electron transfer steps occurring, this procedure illustrates how the resulting molecular oxygen may come solely from the hydrogen peroxide or may contain a contribution from the substrate as well. In actual fact, both hypochlorite and chlorine have been shown to produce oxygen solely from the hydrogen peroxide molecule (46), indicating that the mechanism supposed above may be correct for molecular chlorine, but not for hypochlorite, which must involve O_2H^-. Of course the ions OH^+ and O_2H^- need not always react further. They may be the means of hydroxylation or of hydroperoxide formation directly.

Other characteristics of hydrogen peroxide reactions have been pointed out. The addition of oxygen to both organic and inorganic compounds which possess unshared electrons frequently occurs (ref. 39, p.245). Examples are:

$$As(OH)_3 + H_2O_2 = H_3AsO_3 + H_2O \qquad (32)$$

$$R_2S + H_2O_2 = R_2SO + H_2O \qquad (33)$$

The work of Halperin and Taube (51) showed that in an instance of such addition of an oxygen atom, namely the oxidation of sulfite to sulfate, hydrogen peroxide adds two oxygen atoms to the sulfite in the initial step, although the net process requires the addition of only one.

Waters (ref. 18, p.86) has pointed out that the organic free radicals which attack hydrogen peroxide have a structure which favors maintenance of a high electron density at the site of the odd electron. Such molecules induce chain continuation, whereas those in which the charge is more evenly distributed do not disrupt the hydrogen peroxide in such a way as to produce further radicals. The more commonly thought of reaction with hydrogen peroxide to produce hydroxyl free radicals is the one in which a metal ion is oxidized by a one valence step. Evans, Baxendale, and Park (52) found by initiating polymerization that chromous, mercurous, cuprous, titanous, manganous, and ferrous ions were capable of generating hydroxyl radicals. A feature of importance regarding the transmission or propagation of hydroxyl free radicals in aqueous solutions is the fact that hydroxyl may exchange with water in the reaction:

$$\mathrm{O^{*}H + H_2O = H_2O^{*} + OH} \qquad (34)$$

This possibility (53) has been tested experimentally (54,55). It provides a means whereby the hydroxyl radical may have an apparent long existance. Exchange with other species might produce a less reactive free radical, impairing the efficiency of the process.

The perhydroxyl radical on the other hand must be generated by an oxidizing agent. The possible rôle of this radical has been given less consideration than that of hydroxyl. A basis for speculation about perhydroxyl was provided by Baer and Stein (56), who studied the reduction of ceric ion by hydrogen peroxide and proposed the reactions:

$$\mathrm{Ce^{+4} + H_2O_2 = HO_2 + H^{+} + Ce^{+3}} \qquad (35)$$

$$\mathrm{Ce^{+4} + HO_2 = O_2 + H^{+} + Ce^{+3}} \qquad (36)$$

The mechanisms here are quite different from those involved in the iron-hydroxyl radical system. These reactions are rapid (compared to the slow ferrous ion reaction), and no path exists for reoxidation of the cerous ion. The system was studied at high acid concentrations and there was no evidence that reaction occurred between the hydrogen peroxide and the perhydroxyl assumed to be present. This accords with the hypothesis that hydrogen peroxide reacts only with the superoxide ion, O_2^-, which is the acid dissociation product of perhydroxyl. It cannot be said, however, that this study of ceric ion reduction is to be interpreted as unequivocal proof of a mechanism involving perhydroxyl radicals. A two electron mechanism involving the complex cerium dimers suggested by Heidt and Smith (57) may also be considered.

Electron Distribution in Hydrogen-Oxygen Species. To summarize and unify these ideas regarding the general characteristics of hydrogen peroxide reactions attention is called again to the earlier remarks regarding the electronegative or electron-acquiring character of oxygen. This is the thread running through all the chemistry of hydrogen peroxide, and it is exceedingly useful to keep in mind. As an aid in visualizing the electronic environment of oxygen in some of the simpler radicals or ions of interest, the representation of Figure 4 may be useful. This figure shows schematically the probable distribution of electrons in the three perpendicular $2p$ orbitals of oxygen for hydrogen-oxygen compounds and ions containing one or two oxygen atoms without reference to hybridization effects.

It may be seen that in the water molecule one oxygen atom receives the charge transferred to it by two hydrogen atoms; in hydrogen peroxide each oxygen atom has much less charge transferred to it. This trend would continue to the oxygen molecule, O_2, but for the intervention of the circumstances allowing stabilization through formation of the the three-electron bonds. Two misconceptions regarding the latter should be mentioned. The fact that the oxygen molecule bears two unpaired electrons has encouraged reference to it as a biradical, implying structural similarity to free radicals. As noted by Waters (ref. 13, p.73), however, the presence of the two three-electron bonds must vitiate this comparison considerably, and the unreactivity of oxygen relative to that of the free radicals attests to this fact.

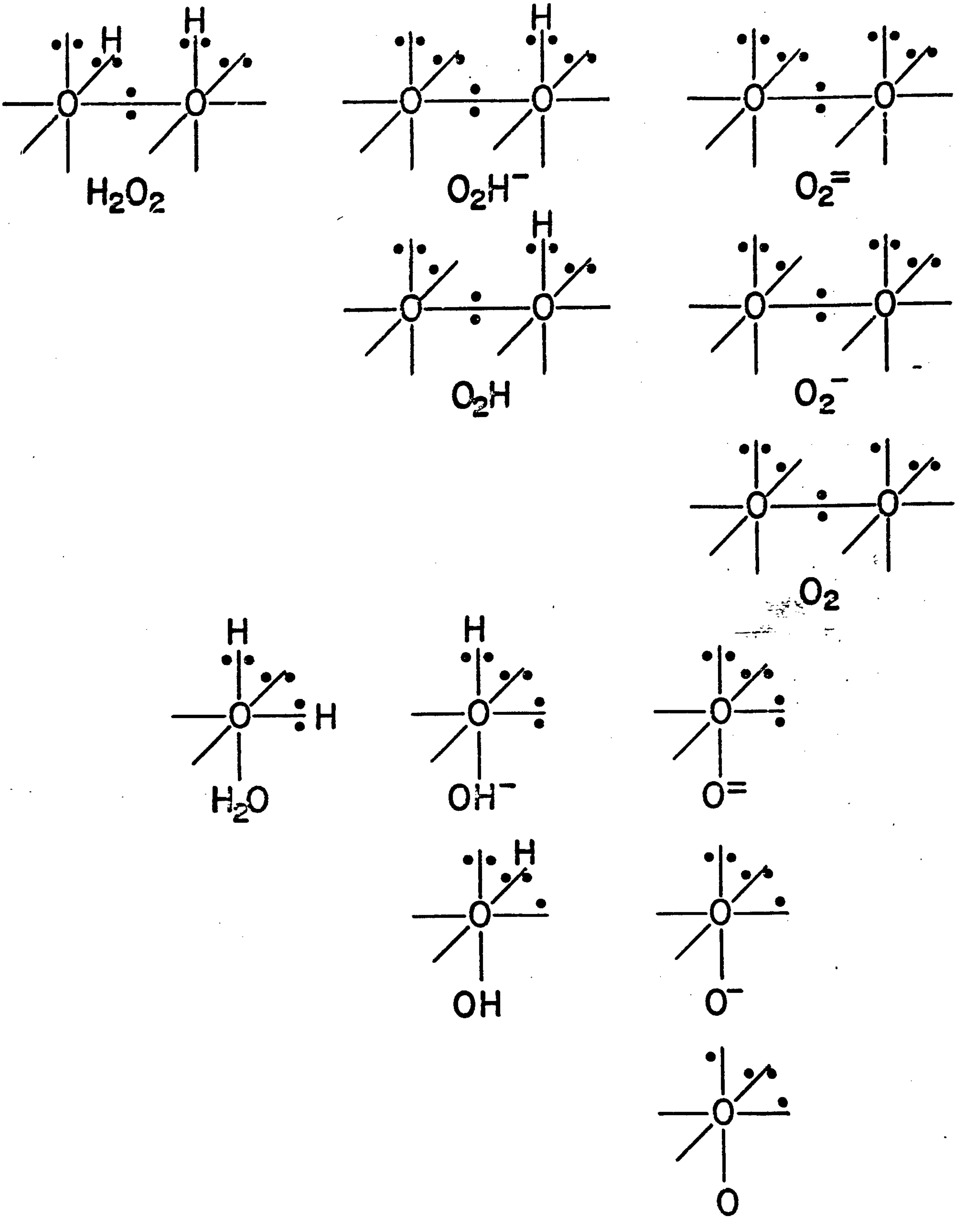

FIG. 4 – A REPRESENTATION OF THE ELECTRON DISTRIBUTION IN THE p ORBITALS OF SOME HYDROGEN – OXYGEN COMPOUNDS AND IONS

A considerable energy is required to uncouple these odd electrons from their three-electron bonds. Another misconception, corrected by Walsh (15), stems from regarding molecular oxygen as "double-bonded." According to this viewpoint "opening the double bond" should expose the full reactivity of the oxygen molecule, and any intermediate such as HO_2 should share this reactivity. If the two three-electron bonds are considered, however, it will be seen that only one need be broken at a time, and that one such remaining bond should confer considerable remaining stability. The basis for the suggestion above that the superoxide ion, O_2^-, is more reactive than perhydroxyl radical, O_2H is also shown. The sketch of the electronic structure of O_2^- and O_2H shows that although each may form a three electron bond, in the superoxide ion there is present in addition the repulsion of two parallel lone pair-filled orbitals. Thus it is not inherently necessary to assume (ref. 13, p.74) that upon the formation of a superoxide, RO_2, from molecular oxygen the full reactivity of the oxygen is exposed in a manner analogous to that of other elements in saturated radicals.

Reference to Fig.4, may also aid in considering Walsh's postulate (15) that although charge transfer to the peroxide group strengthens the bond between the oxygen atoms this process can only be carried so far; further charge transfer weakens the bond. There are several aspects of this, and it is uncertain just how far this reasoning can be carried. For example, the free peroxide ion, $O_2^{=}$, has a structure isoelectronic with the fluorine molecule, F_2, and the repulsion of two sets of two parallel filled orbitals might be thought to contribute to reactivity. The relatively unreactive nature of barium peroxide would appear to refute this, however, it is difficult to determine just how far the process of charge transfer has proceeded in this case. It is clear that the $O_2^{=}$ ion lacks the extra stabilization of the extra bonding in the oxygen molecule, and it is this fact which permits the statement (46) that removal of electrons from $O_2^{=}$ strengthens the bond between oxygen atoms.

Examples of Hydrogen Peroxide Reaction Mechanisms

Hydroxyl Radical Mechanisms. Reactions and decomposition processes of hydrogen peroxide which proceed *via* hydroxyl radical mechanisms have been proposed for the vapor phase with thermal, electric discharge, and photochemical initiation. In the liquid phase this mechanism has been suggested only for photochemical initiation. The actual presence of hydroxyl radicals was demonstrated by Frost and Oldenberg (58) in a study of the decomposition of hydrogen peroxide vapor in an electric discharge. The photochemical decomposition of the vapor was studied by Volman (59) and that of the liquid by Hunt and Taube (60), evidence for reaction *via* hydroxyl radical being presented in both studies. The thermal decomposition of hydrogen peroxide has been studied and presumed to proceed by the same process, but the evidence is either indirect or confused by the coincident occurrence of heterogeneous catalytic decomposition which may proceed by the same or a different mechanism. For example, McLane (11) reported a pure homogeneous thermal decomposition to occur in addition to the heterogeneous decomposition at 500°C, and the explosive decomposition of the vapor, which is certainly propagated homogeneously, has been observed (61). There is a very definite energetic limitation upon the extent of homogeneous thermal decomposition, as indicated in the discussion of rates of reaction. Thus the thermal decomposition which occurred in the experiments of Stone and Taylor(62) conconcerning photochemical generation of hydroxyl radicals from hydrogen peroxide was certainly heterogeneous. The absence of any pathway to thermal homogeneous decomposition of hydrogen peroxide vapor at low concentrations and temperatures is further illustrated by the demonstration of Stone and Taylor that carbon monoxide would not react with hydrogen peroxide vapor near 100°C even though heterogeneous decomposition was simultaneously occurring. However, carbon monoxide reacted avidly when the system was illuminated with actinic light. These results show that no significant propagation of radicals possibly generated by the heterogeneous decomposition occurs at low concentration and that thermal activation of a hydroxyl radical mechanism cannot occur at 100°C. The details of photochemical and thermal decomposition processes, both homogeneous and heterogeneous, are discussed in the next chapter. Hydroxyl radical mechanisms are universally accepted as playing the important rôle in most such processes, and the above discussion indicates the extent of the experimental and theoretical evidence for this belief.

<u>Hydroxyl Ion Mechanisms</u>. Only relatively recently have reactions of hydrogen peroxide been proposed to occur <u>via</u> hydroxyl ion mechanisms. It appears that Ross(50) was the first to mention this possibility. Ross studied the acid catalyzed oxidation of thiodiglycol and triethylamine by hydrogen peroxide and suggested that the effectiveness of hydrogen peroxide for this purpose was due to the ease with which the OH^+ group could be donated. The action through the mediation of the $HOOH_2^+$ ion was believed to be fast because its product was not an OH^- ion, involving separation of charge at the critical step of the reaction. This idea has also been borne out by Overberger and Cummins (63), who successfully explained in this way the results of a similar study of the formation of sulfoxide from <u>p</u>, <u>p</u>'- dichlorobenzyl sulfide by hydrogen peroxide. The same reasoning was applied by Derbyshire and Waters (49) to explain their observations of the hydroxylation of mesitylene by hydrogen peroxide. These authors proposed that this mechanism might also lead to an understanding of reactions in which hydrogen peroxide adds an oxygen atom by coordination to molecules having atoms with a lone pair of electrons. This viewpoint was applied to inorganic reactions of hydrogen peroxide by Edwards (64,13) in an exposition of the mechanism of reaction by electron donor molecules. In a general approach(64) Edwards regarded hydrogen peroxide as an oxyanion source (O_2H^-) which through combination with protons formed an electron acceptor, <u>i.e.</u>, $HOOH_2^+$, which has OH^+ as its anhydrous form. In a specific study (13) of hydrogen peroxide reactions with various halogen ions Edwards correlated a large body of rate measurements and showed them to be consistent with the theories of general acid catalysis. Edwards (13,65)

also showed that a high proportion of the catalysis was due to solvent, the observed rate being more than 50 % due to solvent catalysis at pH greater than 3 in several cases. No specific mechanism was championed, but it was pointed out that the facts were consistent with what is here termed a hydroxyl ion mechanism. This work (65) also reveals that the kinetic law for a hydroxyl ion mechanism may be at the same time consistent with that for a mechanism in which no breaking of the O-O bond occurs. Several instances of oxidation of hydrogen peroxide fall in this class, for example, the oxygen isotope tracer experiments of Cahill and Taube (46) showed that the oxygen derived from the reaction with hypochlorite (one of Edward's examples) came completely from the hydrogen peroxide, eliminating O-O bond breaking from consideration. The operation of the hydroxyl ion radical mechanism in the decomposition of hydrogen peroxide in perchlorous acid solution was believed unlikely by Bunton and Llewellyn(66), although their tracer experiments and the supposed net reaction were not given in detail. Some hydroxylation reactions of hydrogen peroxide, said to be catalyzed by certain metals, were suggested by Mugdan and Young(67) to be of the hydroxyl ion mechanism, but occuring *via* peroxy acid formation.

Perhydroxyl Radical Mechanisms. There appears to be no certain instance of a thermally or photochemically initiated hydrogen peroxide decomposition which occurs *via* a perhydroxyl radical mechanism, which is quite reasonable when the unfavorable energy requirement relative to the alternate hydroxyl radical path is considered. Hunt and Taube (60) could find no justification for consideration of this as an initiating mechanism in their study of the photochemical decomposition of liquid hydrogen peroxide. It is true that the problem of the detection of the perhydroxyl radical(68) has only recently received attention; on the other hand, in the case of hydrogen peroxide the appearance of perhydroxyl through autodecomposition also involves the production of a hydrogen atom, a well-known and kinetically unique particle. It is possible that a perhydroxyl radical mechanism could be operative in the often postulated reaction

$$OH + H_2O_2 = H_2O + O_2H \qquad (37)$$

Perhydroxyl Ion Mechanisms. The perhydroxyl ion mechanism for the decomposition and reaction of hydrogen peroxide has gained more attention than the preceeding ones. When the fact is known that this dissociation readily occurs by proton transfer to water or other solutes, and the observation has been made that hydrogen peroxide decomposes at an accelerated rate at high pH, it is reasonable to assume that the perhydroxyl ion is particularly reactive. In spite of this, the mechanism underlying the heightened rate of decomposition in alkaline solutions is still uncertain. A rather direct demonstration of the occurrence of a perhydroxyl ion mechanism is the case of the surprising means whereby sulfite is oxidized to sulfate by hydrogen peroxide (51). In the initial stage of this reaction two oxygen atoms derived from a hydrogen peroxide molecule are attached to the sulfite, thus forming as an intermediate, peroxymono sulfurous acid. Subsequent rearrangement forms the sulfate, leaving no doubt that perhydroxyl ion mechanism is responsible. A similar study by tracer techniques (16) demonstrated that hypochlorite reacts with hydrogen peroxide by this mechanism, as mentioned earlier. Edwards(69,65) has treated such reactions as those of substitution or replacement on oxyanions, pointing out in particular the importance of the equilibrium of such substitution in determining whether it may be possible to demonstrate the presence of certain peroxides, e.g., peroxyboric acid and similar disputed substances. Thus, although a peroxide may exist in solution, a rapidly established equilibrium via substitution (hydrolysis) with hydrogen peroxide may reveal only the presence of the latter. It has been pointed out (65) that such a circumstance is likewise important in affecting the success of an analytical scheme for a mixture of peroxides, such as discussed in Chapter 10. Many substituted peroxides do not act as reducing agents, which permits determination of hydrogen peroxide in their presence. If the substitution or hydrolysis equilibrium is rapid, however, advantage cannot be taken of such a difference.

Since such processes are readily imagined to entail the formation of intermediate hydroperoxides, thus renewing the much older idea of unstable peroxide intermediates, the recent work of Davies, Foster, and White (70) is of interest. Alcohols, carboxylic esters, 2-butyl sodium sulfate, or olefins were reacted with 90 wt.% hydrogen peroxide to form alkyl hydroperoxides and these authors found support for the assumption that the reactions occurred <u>via</u> a perhydroxyl ion mechanism involving carbonium ions. It was pointed out in particular how the highly polar nature of concentrated hydrogen peroxide should favor reactions involving the appearance of charges. The formation of peroxy acids from oxygen isotope-labelled carboxylic acids, at least for the case of peroxyacetic acid, was shown by Bunton, Lewis, and Llewellyn (71) to go forward by direct replacement of the hydroxyl group by the perhydroxyl group. Bunton (72) had earlier published evidence that the oxidation of α-diketones by hydrogen peroxide occurred through action of perhydroxyl ion. The reaction of hydrogen peroxide with benzeneboronic acid appears to provide (73) an instance of direct addition of perhydroxyl ion. A last example of perhydroxyl ion mechanisms is the conversion of benzonitrile to benzamide by hydrogen peroxide, which as a net process involves the transfer of one oxygen atom to the substrate in a manner requiring the action of two molecules of hydrogen peroxide. This was made the subject of a well-planned study by Wiberg (74), who suggested that a hydroperoxide is first formed, then decomposed at the attack of the second molecule of hydrogen peroxide. As outlined by Wiberg the first reaction appears to involve the already-formed perhydroxyl ion, and the second step could be said to take place by inductive dissociation of a second hydrogen peroxide molecule.

<u>Reaction Mechanisms of Other Peroxides</u>

Although it is not the purpose of this monograph to treat peroxides other than hydrogen peroxide with any degree of completeness, a study of other peroxides can lead to increased understanding of the nature of the parent compound. The facts available are limited largely to organic peroxides; inorganic peroxides and peroxy acids, with the possible exception of peroxydisulfuric acid, have unfortunately received practically no study that is of immediate value in studying reaction mechanisms. The characteristics of organic peroxide reaction mechanisms have been the subject recently of an excellent review (40) and therefore need not be repeated here; the remarks below are intended to show how the bonding between the oxygen atoms in the peroxide group is affected by substitution and to demonstrate how reaction mechanisms similar to those just outlined for hydrogen peroxide are also in operation for other peroxides.

The importance of both of these topics is implied in the classification presented by Tobolsky and Mesrobian (ref. 40, p.107). These authors suggested the following to be the predominant characteristics of the reaction of some types of organic peroxides: alkyl hydroperoxides, dialkyl peroxides, and diacyl peroxides decompose by homolytic dissociation, acyl hydroperoxides (peroxy acids) decompose heterolytically, and the alkyl-acyl peroxides (peroxy esters) include examples reacting by both ionic and radical mechanisms. This appears to be a good characterization, but should be applied with care in new and unfamiliar cases. The factors such as solvent, concentration, and temperature influencing the occurrence of one mechanism or another have been reviewed by Leffler(75) and Bartlett(76). An example of how these factors operate to change the mechanism of decomposition has been provided by Leffler(77), who showed that the mechanism of decomposition of *p*-methoxy-*p'*-nitrobenzoyl peroxide could be changed from free radical to ionic according to environmental conditions in spite of the fact that the symmetrical parent compound, benzoyl peroxide, decomposes *via* free radicals under a wide range of circumstances, even those favoring ionic dissociation.

An outstanding difference observed between the reactions of hydrogen peroxide and organic peroxides is the markedly lower energy required for dissociation of organic peroxides into free radicals by breaking at the O-O bond. It was recounted above how this energy requirement seriously limits the opportunity for hydrogen peroxide to decompose by a homogeneous, thermally activated free radical mechanism, necessitating intervention by catalysts or the introduction of energy electrically or photochemically if free radical decomposition is to occur. Among many organic peroxides so far studied this energy requirement is some 20 kcal/mole less than that needed for hydrogen peroxide, and as a consequence thermally initiated free radical mechanisms are favored. Otherwise it is presumed that decomposition would not be observed in many of the non-polar solvents used. This difference is illustrated strikingly by an observation made by Brown (78). In studying the homogeneous free radical decomposition of benzoyl peroxide the rate was not affected by increasing the amount of platinum surface exposed to the system in contrast to the marked effect of platinum on hydrogen peroxide.

Among organic peroxide decompositions proceeding via free radical mechanisms occurring by breaking at the O-O bond two of the most extensively studied have been those of di-*tert*-butyl peroxide and benzoyl peroxide. The di-*tert*-butyl peroxide decomposes quite homogeneously, the products varying according to concentration and environment; recent reviews (40) have summarized these results. Benzoyl peroxide behaves similarly; studies of it of particular interest here are those of the effect of substitution on the rate of its decomposition. Swain, Stockmayer, and Clarke (79) found that the symmetrical substitution of electron repelling groups on benzoyl peroxide increased the rate of decomposition while electron attracting groups decreased the rate; this relationship could be represented by a plot of Hammett's sigma function (80). To explain this behavior it was pointed out that in benzoyl peroxide the two oxybenzoate groups can be considered to be dipoles attached in repulsion (the negative ends being together at the peroxide link), and that the addition of electron repelling groups would be expected to enhance this relation, presumed already to be unstable, accounting for the rise in decomposition rate. The facts presented have been verified by others (81,82,83), and such factors as effect of solvent (81), validity of the Hammett relation for this case (82,83), and possible effects of position of substitution (82,83) have been studied in addition. The interesting feature of this is that the effect of substitution runs counter to the proposal cited before, *i.e.*, that negative charge transfer to the peroxide group tends to stabilize it. It may be that in this case the maximum in the benefit of this charge transfer process has been passed, but this cannot yet be verified.

An interesting suggestion is that of Cooper (83), who pointed out that in such a diacyl peroxide there may exist equivalence of oxygen atoms such as has been demonstrated for the analogous sulfur compound tetramethyl thiuram disulfide (84). This equivalence might be expected to alter the stability relationships of the peroxide group. Further study will be necessary to establish such an effect, especially in view of the demonstration by Blomquist and Berstein (85) that similar effects of substituents are to be found with tert-butyl peroxy benzoate, an asymmetrical, monoacyl compound having the radical fission tendency of both parent compounds.

Ionic reaction mechanisms for organic peroxides analogous to the hydroxyl ion path for hydrogen peroxide appear to be well established. Kharasch and Burt (86), for example, proposed that in the generalized equation for the so-called acid cleavage of unsymmetrical dialkyl peroxides the carbinol is always formed from the radical, R, of greatest electron attracting power.* The interesting conclusion was also reached that the susceptibility of hydroperoxides to such acid cleavage paralleled the facility with which such hydroperoxides may be formed by autoxidation of the corresponding hydrocarbons. Among hydroperoxides undergoing acid cleavage, i.e., ionic dissociation at the O-O bond, and which have received considerable study, are cumene hydroperoxide, peroxyacetic acid, and decalin and tetralin hydroperoxides. The study (87) of decalin and tetralin hydroperoxides has shown how the mechanism of decomposition of these peroxides may be changed from a free radical one to one in which both homolytic and heterolytic processes occur by changing chiefly the polarity of the solvent. A similar relation holds for cumene hydroperoxide. At 100° in a non-polar solution a free radical dissociation occurs (88). At room temperature in aqueous solution an ionic reaction with ferrous iron readily occurs (89, 90, 91). Some interesting facts have been brought out by study of this reaction. In going from the radical mechanism to the ionic mechanism involving ferrous ion the frequency factor was reduced from about 10^{12} to 10^{9} and the activation energy lowered from 30 to 11 kcal/mole (90). These figures may be compared with similar

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* $ROOR' \xrightarrow{H^+} ROH + R'O^+$ (38)

ones for hydrogen peroxide: the activation energy for a radical decomposition of hydrogen peroxide is, as noted before, unattainable, whereas the frequency factor and activation energy for the ferrous ion reaction of hydrogen peroxide are approximately the same as that for cumene hydroperoxide as shown in Fig. 3. Thus by the free radical path the rates are of completely different orders of magnitude, by the easier ionic path the hydrogen peroxide decomposes about four times faster than cumene hydroperoxide. It might be concluded on this basis that substitution of the cumyl group makes the O-O bond less stable with respect to the free radical mechanism and more stable with respect to the ionic mechanism. Study of the effect of further substitution on the cumyl group (14,92) indicates that addition of groups of increasing electron donating power increases the rate of reaction of the cumene hydroperoxide. These facts appear to be in opposition to the postulate mentioned above regarding the effect of charge transfer to the O-O group on its stability, but it is difficult to sort out the varying contributions to the different processes of energy transfer, activation, and orientation involved. A somewhat more readily understood hydroxyl ion mechanism seems to occur in the reaction of peroxy acids to form epoxides with olefins. Swern (93) showed how in the case of peroxyacetic acid the addition of electron-donating substituents to the olefins enhanced the rate of attack by the electron attracting peroxy acid; and Waters (94) has given an excellent discussion of the probable course of this reaction. In addition to this interpretation Bartlett (76) has suggested an alternate mechanism which is less easily cataloged according to the classifications of hydroxyl or perhydroxyl ion mechanism.

The acid dissociation of some alkyl and acyl hydroperoxides was studied by Everett and Minkoff (95); this is of course the process analogous to the perhydroxyl ion mechanism in hydrogen peroxide. The results of this study provide a quantitative measure of the acid strength of the peroxy acids; these are clearly weaker acids than the parent carboxylic acids yet much stronger than the corresponding non-acyl hydroperoxides. The comparable change in acid strength in going from an alcohol to a carboxylic acid is of course notable. These relationships were explained by pointing out that the effects of substitution on the ease with which the CH bond is broken must be transmitted through the O-O link in the hydroperoxides and peroxy acids. In the alkyl hydroperoxides substitution of an alkyl group for one hydrogen in hydrogen peroxide causes a charge shift toward the oxygen, but the avidly electronegative O-O group retains this charge transfer, the terminal hydrogen being little affected. In the analogous water-alcohol case this charge transfer is of course seen in the resulting much stronger binding of the hydrogen ion to the alcohol. In the acyl hydroperoxides or peroxy acids the substitution of the acyl group is thought to draw charge away from the OO group. This results in the hydrogen ion being less strongly held, but the effect is not as marked as in passing from water to carboxylic acid, which loses the hydrogen ion much more readily. These results appear to be in agreement with the postulated strengthening of the peroxide link by charge transfer to it. A similar situation appearsto occur in the base catalysed decomposition of tertiary hydroperoxides cited by Tobolsky and Mesrobian (40). This substance is thought to form the salt at low and high sodium hydroxide concentrations. An intermediate optimum concentration permits ionization and subsequent rapid decomposition by an induced attack of the hydroperoxide.

This brief review of other peroxide reaction mechanisms may be concluded by providing some references to the behavior of peroxydisulfuric acid. It seems that in common with organic peroxides, this substance can decompose homolytically as well as heterolytically. Morgan (96) demonstrated the initiation of polymerization by peroxydisulfate. Kolthoff and Miller (97) suggested that the uncatalysed decomposition involved formation of two sulfate radicals, whereas an acid catalysed decomposition was also possible and proceeded <u>via</u> sulfur tetroxide formation but it has been shown (98) that the latter mechanism cannot involve equilibrium between sulfate and peroxysulfate ions. A related and industrially important reaction, the hydrolysis of peroxymonosulfuric acid, appears to occur (66) by transfer of the perhydroxyl ion.

ISOTOPE EXCHANGE IN HYDROGEN PEROXIDE REACTIONS

The evidence regarding reaction mechanisms which is offered by studies of the fate of the peroxide oxygen in hydrogen peroxide reactions has a value all out of proportion to the small number of such studies, justifying discussion of them separately. Tracer experiments have also been made to determine the course of atoms of substrate molecules in hydrogen peroxide reactions, but the results of these are less general and will be cited in the discussion of the reactions of the various elements.

Tracer experiments with the hydrogen of hydrogen peroxide would also be of value, but, as might be expected, the hydrogen of hydrogen peroxide exchanges spontaneously and quickly with that of water. This was established by Erlenmeyer and Gärtner (99), who measured the deuterium content of three cuts from the distillation of a mixture of 2% D_2O containing about 10% H_2O_2. No difference in deuterium content of the three cuts was evident if allowance was made for the effect of distillation itself in concentrating the samples in deuterium content. Hydrogen may be traced if reaction with some substance which does not exchange with water or hydrogen peroxide is under consideration. Such an experiment was carried out by Wirtz and Bonhoeffer (100) to show that the molecular hydrogen resulting from the reaction of formaldehyde and hydrogen peroxide in alkaline solution is derived solely from the formaldehyde. The use of heavy water in studies of solvent effects is discussed below.

Studies of hydrogen peroxide reactions which have been made with oxygen isotopes are summarized in Table 2. Several conclusions are immediately clear from the results presented. The three experiments with formation reactions (103, 108, 111) show that molecular oxygen maintains its integrity on being reduced to hydrogen peroxide; no oxygen derived from water or catalyst is incorporated into the hydrogen peroxide formed. In similar fashion the balance of the experiments provide evidence that the oxygen in solvent water does not participate in decomposition or reaction of hydrogen peroxide; no exchange occurs between water and the molecular oxygen or oxygenated products formed. Also of importance are observations of isotope fractionation, that is, changes in the proportions of two isotopes on going from reactant to product. This is defined mathematically in slightly different fashions by different authors. There are two ways in which fractionation can occur in hydrogen peroxide. One is solely a rate phenomenon in which the isotope ratio in a product differs according to the distance from completeness of reaction. Thus, Bunton and Llewellyn (66) found O^{16} more abundant in the first one percent of gas evolved in a decomposition than in the last, although there was no net change in isotope ratio on going from reactant to product. Since the O-O bond apparently does not break when molecular oxygen is produced, this is interpreted to signify that the net process of abstracting two hydrogen atoms is more easily accomplished with O^{16} than with O^{18}. The second kind of fractionation that can occur is made possible by the formation of more than one product, *e.g.*, molecular oxygen and water. It was found by Dole, Rudd, Muchow, and Comte (107) that an enrichment of about 2% of O^{18} occurred in the oxygen gas obtained on complete decomposition with certain inorganic catalysts, whereas catalase gave no such enrichment. Similar studies, which included certain reducing agents, were made by Cahill and Taube (36). The conclusion permitted seems to be that in oxidation to molecular oxygen the O-O bond is not broken and no fractionation occurs. When hydrogen peroxide is reduced, however, the bond is severed and fractionation may occur. The various sources listed in Table 2 give considerable discussion of the implications of these experiments in regard to mechanism, some of which were drawn upon in the treatment above. Approaches have also been made to the explanation of observations of fractionation in terms of absolute reaction rate theory. A review by Dole (114) discusses this and relates tracer experiments on hydrogen peroxide with such studies on other oxygen compounds.

It is of interest to compare and contrast these results with similar ones for peroxysulfate and hydrazine. As the last few entries in Table 2 show, exchange of labelled oxygen can occur between solvent water and some of the oxygen in peroxysulfate or

TABLE 2

ISOTOPE EXCHANGE STUDIES

Reference	Reaction	Reagent, Solvent	Result
Taylor & Gould (1934) (101)	Catalytic Decomp. of 30% H_2O_2	Normal H_2O , Pt	Fractionation, O^{18} more easily evolved
Bentley (1948) (102)	Catalytic Decomp. H_2O_2	Catalase, $FeSO_4$ in 1.6 % H_2O^{18}	No O^{18} in O_2 gas
Collinson & Dainton (1948) (55)	——	H_2O^{18}, hν	Said to demonstrate $OH + H_2O_2 \rightarrow H_2O + O_2H$ faster than $OH + H_2O \rightarrow H_2O + OH$
Bentley & Neuberger (1949) (103)	Glucose + $O_2 \rightarrow$ Gluconic acid + H_2O_2	By notatin in H_2O^{18} or with O_2^{18}	$H_2O_2^{18}$ formed from O_2^{18} but not from H_2O^{18}
MacKenzie & Milner (1951) (104)	$O_2^{18} + H_2O \rightarrow H_2O^{18}$	Metallic oxides, hydroxides, organic substances.	No exchange oxygen gas to water
"	"	H_2O_2 or its decomp. catalysts: Pt or catalase	Exchange catalyzed

le 2, Cont'd.

Reference	Reaction	Reagent, Solvent	Result
Winter & Briscoe (1951)(105)	Catalytic Decomp. 10% H_2O_2	MnO_2, Fe_2O_3, Pd and Pt on asbestos in H_2O^{18}, heated	No loss of H_2O^{18} as O_2
''	15% $H_2O_2 + Na_2SO_3 \longrightarrow H_2O + Na_2SO_4$	H_2O^{18}	No loss of O^{18} from H_2O^{18} to sulfate.
aertschi (1951)(106)	$5H_2O_2$(0.13 to 0.4 mol/1) + $2MnO_4^- + 6H^+ \longrightarrow 2Mn^{++} + 8H_2O + 5O_2$	0.4% $KMnO_4{}^{18}$ in acid, 0.4 % H_2O^{18} at 0 to 45°C	No enhancement of ratio O^{18}/O^{16} (=0.21%) in evolved O_2.
''	Catalytic Decomp. H_2O_2	Unspecified catalyst in H_2O^{18} at various pH's	O^{18}/O^{16} ratio in evolved O_2 independent of that in H_2O_2, but fractionation occurs
Dole, Rudd, Muchow & Comte (1952)(107)	Catalytic Decomp. 1% H_2O_2 (derived from Na_2O_2)	MnO_2, Pt, Au, $Fe(OH)_3$, Catalase in normal or O^{18} enriched H_2O	No effect of O^{18} content of H_2O on O^{18} content of O_2, but inorganic catalysts fractionate oxygen

Table 2, Cont'd.

Reference	Reaction	Reagent, Solvent	Result
Dole, Rudd, Muchow & Comte (1952)(107)	$O_2^x + H_2O^y \longrightarrow O_2^y + H_2O^x$	Prolonged contact with Catalase or Hemoglobin	No exchange
Bunton & Llewellyn (1952)(66)	Catalytic Decomp. H_2O_2	12% H_2O^{18} with O^{18} labelled Pt, Ag, MnO_2, Fe^{++}, Fe^{+++}, Ce^{++++}, MnO_4^-, $Cr_2O_7^{--}$, H_5IO_6, HBr, Br_2, HOCl	No O^{18} in O_2 gas
''	''	12% H_2O^{18} cont. 60-70% $HClO_4$, Catalyst unspecified	''
''	''	Normal H_2O	Fractionation occurs; marked $\bar{c}$ Fe^{++}, Fe^{+++}, Pd, less marked with $KMnO_4$.
''	$H_2O_2 + 2H_2SO_4 \longrightarrow H_2S_2O_8 + 2H_2O$	Unspecified	Peroxide oxygens transferred without separation.
Bentley & Neuberger (1952)(108)	Uric acid + $O_2^{18} \longrightarrow H_2O_2$	Normal H_2O, uricase	Oxygen in H_2O_2 derived solely from O_2

Table 2, Cont'd.

Reference	Reaction	Reagent, Solvent	Result
Forchheimer & Taube (1952, 1954)(54)	7%$O_3 + H_2O^{18} \rightarrow O_3^{18} + H_2O$	0.04 M HClO$_4$ in 1.4% H_2O^{18}	No exchange if acid; extensive exchange if alkalin
"	"	Same as above plus 9×10^{-4} M H_2O_2	Some exchange
Halperin & Taube (1952)(51)	$H_2O_2 + H_2SO_3 \rightarrow H_2O + H_2SO_4$ (1% dithionate formed)	In HCl or pH5 acetate buffer, either H_2O_2 or $SO_3^=$ + H_2O cont. O^{18}	Two atoms O derived from H_2O_2 found in $SO_4^=$ for each $SO_3^=$ oxidized
"	$H_2O_2^{18} + 1/4\ S_2O_3^= \xrightarrow{MoO_3}$ $1/2\ SO_4^=\ \ 3/4\ H_2O + 1/2\ H^+$	In pH 5 acetate buffer	One atom O derived from H_2O_2 found in $SO_4^=$ for each $S_2O_3^=$ oxidized
Hart, Gordon & Hutchison (1952)(109)	$O_2^{18} + H_2O \rightarrow O_2 + H_2O^{18}$	At pH 11.8	No exchange
"	"	Same with 0.18 MH_2O_2	Exchange
"	$O_2^{18} + H_2O + h\nu \rightarrow O_2 + H_2O^{18}$	pH range 2 to 12	Exchange occurs with γ-radiation; at pH 12, H_2O_2 inhibits exchange
Cahill & Taube (1952)(46)	$H_2O_2 + X \rightarrow X_{red} + O_2$, concentrations unspecified	In normal H_2O and 1.2% H_2O^{18} with Ce(IV), MnO_4^-, Cl_2 + Cl^-, HClO, and Cr_2O_7	O^{18}/O^{16} ratio independent of H_2O^{18} content

Table 2, Cont'd.

Reference	Reaction	Reagent, Solvent	Result
Cahill & Taube (1952) (46)	Catalytic Decomp. H_2O_2; concentrations unspecified	In normal H_2O and 1.2% H_2O^{18} with Fe^{+++}, I^-, I_2, Br^-, Br_2, MnO_2, & Pt	"
"	Reaction or Catalytic Decomp'n	In normal H_2O with Fe^{++}, Fe^{+++}, Sn^{++} Ti^{+++}, Cr^{++}, Cu^+ Ce^{+++}, Cl_2, HOCl, I^-, Br^-, Mo(V) with various additives, pH's	Fractionation of oxygen observed
Hunt & Taube (1952) (60)	30% $H_2O_2 + h\nu \longrightarrow O_2$	In 1.6% H_2O^{18}	O^{18}/O^{16} ratio in O_2 same as in H_2O_2; fractionation
"	0.037M H_2O_2 containing 1.6% $H_2O_2^{18} + h\nu \rightarrow O_2$	In normal H_2O having normal O_2 bubbled thru it.	O_2 evolved enriched in O^{18} over H_2O_2 i.e., fractionation
Baertschi (1952) (110) (quoted by Christiansen)	$H_2O_2 \longrightarrow O_2$ concentration unspecified	In H_2O^{18}	No O^{18} in O_2
Wiberg (1953) (74)	$C_6H_5CN + 2H_2O_2 \longrightarrow C_6H_5CONH_2 + O_2 + H_2O$	In H_2O^{18}	Water derived from benzamide gave 0.03% excess abundance over normal; 0.6 to 0.7% excess expect. if oxygen had been derived from solvent water used

Table 2, Cont'd.

Reference	Reaction	Reagent, Solvent	Result
Bunton, Lewis & Llewellyn (1954) (71)	$RCOO^{18}H + H_2O_2 \longrightarrow RCOOOH + H_2O^{18}$	Acetic and formic acid in normal H_2O_2 + H_2SO_4 aqueous solution	Hydroxyl oxygen from carboxylic acid appears as water. No exchange of O^{18} between H_2O_2, RCOOOH, water, and the carboxyl oxygen.
Calvert, Theurer, Rankin and MacNevin (1954) (111)	$ZnO + O_2 + H_2O + h\nu \longrightarrow H_2O_2$	O_2^{18} in H_2O	O in H_2O_2 formed comes solely from O_2
Kolthoff & Miller (1951) (97)	Thermal Decomp. 0.1M $K_2S_2O_8 \longrightarrow O_2$	In H_2O^{18} at various pH's	O_2^{18} derived from water varying proportion depending on pH (increased O^{18} with decreased pH)
"	$K_2S_2O_8$ solution	In H_2O^{18} at 50 and 90°	No O^{18} exchange in alkaline solution, in 0.5M H_2SO_4, 2% exchange at 90°, 0.4% at 50°
Riesebos and Aten (1952) (112)	$K_2S^{35}O_4$ solution	In $K_2S_2O_8$ in H_2O	No exchange of S^{35} with unlabelled $K_2S_2O_8$

Table 2, Cont'd

Reference	Reaction	Reagent, Solvent	Result
Elkeles & Brosset (1953) (113)	$S_2O_8^{=} + S^{*}O_4^{=} \longrightarrow S_2^{*}O_8^{=} + SO_4^{=}$	$(NH_4)S_2O_8$ in aqueous $H_2S^{35}O_4$	No exchange of S^{35}
Eager & McCallum (1954) (98)	" " " "	In water and conc. HAc	" " "

the molecular oxygen resulting from its decomposition. At the same time several studies show that sulfate does not exchange with peroxysulfate, and it is therefore concluded that the *peroxide* oxygen in peroxysulfate does not exchange with water, just as is the case with hydrogen peroxide. In the thermal decomposition in solution, however, oxygen derived from water does appear in the molecular oxygen produced, a result distinctly different than that obtained with hydrogen peroxide. Experiments with hydrazine (115) have demonstrated that, as with hydrogen peroxide, alternate paths for its reaction exist which involve either breaking or preservation of the N-N bond; when molecular nitrogen is produced it appears that no N-N bond breaking occurs. It would be of interest to be able to extend the comparison to persulfides, for which similar mechanisms have been suggested (116).

HYDROGEN PEROXIDE SOLUTIONS AS A REACTION MEDIUM

The discussion of reaction mechanisms has emphasized the importance of the interaction of hydrogen peroxide with the solvent and with other solutes as well as with the reactants. In this section attention may be drawn to some of the characteristics of hydrogen peroxide solutions which affect reactions in them. The physical nature of hydrogen peroxide solutions is discussed in Chapter 6. Studies referred to there emphasize the high dielectric constant of hydrogen peroxide and its similarity to water. Differences do exist, but are for the most part not yet well-explained. For example, Bamberger and Nussbaum (117) pointed out some time ago that water and hydrogen peroxide both dissolve most readily those organic substances which are rich in hydroxyl groups, but that with increasing molecular weight of solute only more concentrated hydrogen peroxide will function as a solvent. Among inorganic solutes there are found substances both more and less soluble than in water. The conductances of salts in hydrogen peroxide solutions, on the other hand, are much the same as in water, whereas, acids are found less conducting (118), indicating decreased mobility of the hydrogen ion in hydrogen peroxide. References to studies of such physical properties as solubility and conductance are tabulated in Chapter 5. For the most part these considerations have received little attention in studies of the reactions of hydrogen peroxide. For example, although reports have been given (119)

TABLE 3

SOLUTE ACTIVITY OF HYDROGEN PEROXIDE IN AQUEOUS SOLUTION

H_2O_2 Concentration		H_2O_2 Activity	
Mole fr.	wt.%	Mole fr.	Molar
0	0	0	0
0.01	1.871	0.0103	0.5724
0.02	3.710	0.0213	1.180
0.03	5.517	0.0329	1.824
0.04	7.293	0.0451	2.506
0.05	9.039	0.0581	3.225
0.06	10.755	0.0718	3.980
0.07	12.443	0.0861	4.782
0.08	14.103	0.1013	5.621
0.09	15.735	0.1171	6.502
0.10	17.34	0.1338	7.424
0.20	32.07	0.3445	19.12
0.30	44.73	0.6406	35.56
0.40	55.73	1.020	56.64
0.50	65.37	1.470	81.62
0.60	73.90	1.967	109.2
0.70	81.50	2.481	137.7
0.80	88.31	2.981	165.5
0.90	94.44	3.445	191.2
0.91	95.02	3.488	193.6
0.92	95.60	3.531	196.0
0.93	96.17	3.574	198.4
0.94	96.73	3.616	200.7
0.95	97.29	3.653	203.0
0.96	97.84	3.699	205.3
0.97	98.39	3.739	207.5
0.98	98.93	3.779	209.8
0.99	99.47	3.819	211.9
1.00	100.0	3.857	214.1

of the effect of salts on heterogeneous catalytic decomposition, it appears that in only one instance (120) has a study been made of the primary salt effect in a case of acid-base catalysis. Similarly, the activity of hydrogen peroxide in its solutions has seldom been considered. Data available in Chapter 5 afford an opportunity to calculate the solute activity of hydrogen peroxide in aqueous solutions. This is defined (121) for mole fraction units by the equation $a = p_H (x_H / p_H)^*$, where the starred quantity is the limiting value at infinite dilution. Values in both mole fraction and molar units calculated in this manner have been tabulated in Table 3. The activity of 1.5-molar hydrogen peroxide in salt solutions was measured by Livingston (122).

Acid Properties of Hydrogen Peroxide

Hydrogen peroxide is a weak acid, that is to say, the thermally activated transfer of a proton from a hydrogen peroxide molecule to a water molecule occurs to a small degree:

$$H_2O_2 + H_2O = H_3O^+ + O_2H^- \qquad (39)$$

Early workers with hydrogen peroxide recognized that it is weakly acidic (123), but the dissociation constant was not measured until 1912 by Joyner (124). Joyner employed classical methods, determining the hydrolysis of sodium hydroperoxide by observation of ester saponification, measurement of distribution coefficient, and measurement of conductivity. By these methods he obtained the average value 7×10^{-13} for the acid dissociation constant of hydrogen peroxide at 0°C. Direct thermochemical measurement yielded the value 8.6 kcal/mole for the heat of dissociation allowing the calculation of the value $K = 2.4 \times 10^{-12}$ at 25°C. Essential agreement with this value was obtained by Kargin (125) in measurements with a glass electrode on 0.1 and 0.5 molar distilled hydrogen peroxide, which led to the value $K = 1.55 \times 10^{-12}$ at 20°.

The determination of the dissociation constant of hydrogen peroxide has recently been repeated by Evans and Uri (126) with due regard for the effect of ionic strength. As a result of measurements with a glass electrode on hydrogen peroxide solutions up to 2 molar in concentration the dissociation constant for 20°C at zero ionic strength was found to be 1.78×10^{-12}, thus pK = 11.75. The measurements were also extended to other temperatures with the following results, at 15°C, $K = 1.39 \times 10^{-12}$; 20°, 1.78×10^{-12}; 25°, 2.24×10^{-12}; 30°, 3.55×10^{-12}. From these data the heat of dissociation may be calculated to be 8.2 kcal/mole. These *recommended* results are further established by the measurements of Everett and Minkoff (95), who compared the dissociation constant of hydrogen peroxide with those of various aryl and acyl hydroperoxides.

The conclusion is also reached that the glass electrode is entirely adequate for the measurement of pH in hydrogen peroxide solutions. For example, Reichert and Hull (127) compared the glass electrode and a number of colorimetric indicators as methods of determining pH up to concentrations of 30 wt. % and found relatively good agreement. In this course and in others (128)(129) are given typical pH - concentration curves for the titration of hydrogen peroxide containing acid or base. Wynne-Jones (130) has also demonstrated the adequacy of the glass electrode in hydrogen peroxide at even higher concentrations and has investigated the use of metanil yellow as an indicator. Actual values of pH obtained over the entire concentration range are shown in Fig. 6 of Chapter 9. This representation also illustrates the effect of carbon dioxide on the pH of hydrogen peroxide solutions, which, for example, causes the curve to fail to extrapolate to pH 7 at zero concentration. The presence of carbon dioxide may furthermore make it impossible to duplicate a pH titration curve by calculation, *e.g.*, the results of Reichert and Hull (127) by the methods outlined by Earl (129). On the other hand, it is seldom desirable to attempt calculation of pH according to the complicated equilibria in mixed acid solutions; even though the presence of carbon dioxide at ordinary atmospheric conditions may make a change of several tenths of a pH unit in the pH of hydrogen peroxide solution the precision of the usual measurements is seldom better than ±0.1 unit. Buffer systems have occasionally been used in experimental work with hydrogen peroxide, and their advantages may well be taken into consideration. Some question may arise in regard to the compatibility or resistance to degradation of buffers in such a reactive system, but no systematic study on which to base recommendations in this regard seems to be available.

The curves in Fig. 6 of Chapter 9 also illustrate the super-acid qualities of hydrogen peroxide at high concentration. It is evident that the hydrogen ion activity becomes very high as the solution approaches the anhydrous state. Evans and Uri have commented on this, suggesting that the equilibrium for:

$$H_3O_2^+ + H_2O = H_2O_2 + H_3O^+ \qquad (40)$$

must lie well to the right; they estimated the equilibrium constant to be about 10^3. Mitchell, Beck, and Wynne-Jones (131) have similarly shown how hydrogen peroxide is much less basic than water.

Reactions in Unusual Solvents

An understanding of the nature of the effects of solvation and other interactions in solution can be of considerable aid in determining the mechanism of reaction. A number of studies showing the effects of variation in nature of solvent have been reported, but only in a few of the more recent have these been interpreted satisfactorily.

Perhaps the least drastic change in solvent is afforded by substitution of part or all of the solvent water by heavy water, although this procedure does carry the drawback of introducing a change simultaneously in both solvent and solute because hydrogen exchange occurs rapidly. Such studies have shown that heterogeneous decomposition by platinum (132)(133), glass, and gold (134) is slowed by the presence of heavy water. Two reports (135)(136) assert that the homogeneous decomposition by iodide is also slowed, whereas in a third study (133) it was found without influence. The reduction of permanganate by hydrogen peroxide was found considerably slower in heavy water solution (136)(137), yet the catalysis of this reaction by manganous ion was more vigorous.

Methyl and ethyl alcohol have been investigated on a number of occasions for their effects on hydrogen peroxide reactions (138). For example, these substances have been found to inhibit catalytic decomposition by copper or manganese (139)(140). The reaction with ferrous ion was similarly suppressed (141), yet acetone and acetic acid showed considerably less effect. The effect may also depend markedly on concentration. In the case of iodide catalysis increasing proportions of methyl or ethyl alcohol or pyridine in the solvent steadily decreased the rate, with n-propyl alcohol, on the other hand, the rate showed a minimum with concentration (142). In contrast, isobutyl and amyl alcohols, glycerine, and ethylene glycol increased the rate of iodide catalysis, although Walton and Jones (143) pointed out that such solvents are still like water in a qualitative way. As a result of a study of sulfide oxidation in such solvents as ethyl and isopropyl alcohols, diisopropyl ether, acetonitrile, and proprionitrile, Overberger and Cummins (63) came to the conclusion that the oxidation was promoted in solvents capable of hydrogen bonding with hydrogen peroxide and that it is possible that water and alcohol may be equally effective in solvating hydrogen peroxide.

Other solvents investigated include acetone, which was shown to inhibit catalytic decomposition by platinum (144) and to suppress the thermal decomposition at 40° more than ethanol, dioxane, or tetrahydrofuran (74). Stoner and Dougherty (145) found the oxidation of disulfide acids by hydrogen peroxide to be acid catalyzed and as such to be accelerated by replacement of water by dioxane, which presumably offset hindering solvation effects. Ethyl ether was found to reduce the rate of decomposition on platinum (146), and the reaction between titanium tetrachloride and hydrogen peroxide in anhydrous ethyl acetate has been studied (147). 23% hydrogen peroxide in anhydrous hydrogen fluoride has recently been reported (148) to be an effective reaction medium for special purposes. Various other experiments might be reported here, but there is some hesitation in classifying them among unusual solvents, either because the proportions are so small or because more or less energetic reaction occurs directly with hydrogen peroxide. The subject has a special pertinence in regard to the stabilization of hydrogen peroxide, and further direction to studies which might be interpreted in terms of solvent effects may be found in Chapter 9.

REACTIONS WITH INORGANIC SUBSTANCES

In this section is given a brief exposition of the nature and character of the reactions of hydrogen peroxide with inorganic substances organized by the position of the elements of the periodic table according to the system used by Latimer (4). The closely related subject of decomposition processes is discussed in Chapter 8, and organic and biological reactions are dealt with in following sections. Much of the material presented comes from quite old or multiple sources, and no attempt has been made to give complete references to such older literature on this subject as is cited by Mellor (149) and Friend and Twiss (150). Some less comprehensive but more recent summaries of the inorganic reactions have been given by Bancroft and Murphy (20) and Stone (151). The reactions of hydrogen peroxide to form inorganic peroxides are discussed in Chapter 12. Although the material presented here comprises a review of a rather considerable body of available literature, it will be apparent that authoritative and comprehensive studies of these reactions are few.

In this discussion it should be recognized that reaction may be with either the anion portion of a molelcule, with the cation portion, or with both. Thus, fragmentary accounts of oxidation reactions of certain anions, e.g., that of sulfide or sulfite, have been oftentimes reported in the literature where the focus of attention was rather on some other part of the molecule. Consequently every instance of such reactions has not been cited. The action of hydrogen peroxide as a metal solvent via oxidizing action is also widespread, in fact, an acid solution of hydrogen peroxide rivals aqua regia in this regard. By proper choice of acid nearly all the metals can be dissolved, and several studies of the scope of this action are available (152). The oxidizing action of hydrogen peroxide is also of interest in corrosion, since it may be formed as an intermediate in the reaction of oxygen with various metals, as discussed in Chapter 2. Interesting aspects of this topic are the influence of hydrogen peroxide upon the form of oxide formed in corrosion (153) and upon the regularity of corrosion, e.g., it is reported (154) that zinc may be corroded to an especially smooth surface in the presence of hydrochloric acid. Other studies of general interest concern the effects of light and the magnetic field on hydrogen peroxide reactions. Dhar and Bhattacharya (155) found the absorption of light by certain reacting mixtures to be greater than that of the separate ingredients. Collins and Bryce (156) demonstrated that, as they expected, a magnetic field of 12,000 gauss had no effect on the rate of thermal decomposition of 1 to 3 wt.% hydrogen peroxide at 80°C.

All the reactions discussed are described for hydrogen peroxide in the liquid phase.Studies of reactions of hydrogen peroxide vapor have been limited to a few with carbon monoxide (62, 157), ozone (158), magnesium metal (159), and sodium potassium amalgam (160). Possible solid phase reactions have not been investigated at all.

Oxygen, Hydrogen

In aqueous acid solution an excess of hydrogen peroxide reacts with ozone according to the over-all equation:

$$H_2O_2 + O_3 = H_2O + 2O_2 \qquad (41)$$

With smaller proportions of hydrogen peroxide the ozone disappears more rapidly than the hydrogen peroxide. The essential features of this reaction were outlined by Rothmund and Burgstaller (161), and the kinetics over wide ranges of variables, effects of competitors and inhibitors, and other facts relating to the mechanism have been investigated by Taube and Bray (162). The reaction proceeds via free radical intermediates and has been regarded by some as essentially a catalysis of ozone decomposition by hydrogen peroxide.

The important question whether reaction occurs between hydrogen peroxide and hydrogen superoxide (perhydroxyl, HO_2) or the ion of its acid dissociation, O_2^-, has not yet been settled. George (163) concluded that reaction did not occur with either as a result of studies of potassium superoxide dispersed in hydrogen peroxide solution. The validity of this conclusion has been called into question (164) because the experiment dealt with a heterogeneous system, and mechanisms involving reaction of hydrogen peroxide and perhydroxyl, i.e., hydrogen superoxide, continue to be suggested. The supposition that perhydroxyl is a rather strong acid and that reaction is in fact with O_2^- ion is widely held. A somewhat unusual reaction which has been put forward concerns the disproportionation of potassium peroxide dihydroperoxidate into potassium superoxide and water (165). The course of reaction of hydrogen peroxide with either atomic hydrogen or atomic oxygen has been discussed by Geib (166).

The Halogens

Reactions of the halogens and their compounds with hydrogen peroxide may be listed among the most intensively studied in chemistry. The study of the rate and mechanism of a number of these reactions with chlorine, bromine and iodine has received repeated attention, yielding a reliable understanding of the processes involved. Two reviews are available which summarize this work; one by Bray (167) in 1932, provides direction to the earlier literature, and a more recent one by Baxendale (168) brings the subject up to date. The kinetic data available are summarized in the National Bureau of Standards Tables (3). Of particular importance in the discussion of the mechanism of these halogen reactions are two papers by Edwards (64,13) mentioned above.

The reactions with fluorine compounds do not parallel those of the other halogens. The oxidation of fluoride ion is thermodynamically unfavorable, and elemental fluorine brings about a decomposition and production of several products, not yet well characterized. The effect of hydrogen peroxide on various mixed fluorides was observed in an early study (169). Maass and Hatcher (170) found elemental chlorine and iodine to be not very soluble in anhydrous hydrogen peroxide, and observed that bromide and iodide were much more reactive than chloride with hydrogen peroxide. The effects of chloride and bromide in mixtures have also been studied (171).

Both elemental chlorine and its hydrolysis product, hypochlorite, are reduced to chloride ion by hydrogen peroxide (172). Chlorates are unaffected even at the boiling point in alkaline or neutral solution, but in acid hydrogen peroxide, chlorine and chlorine dioxide are produced (173). The hydrolysis of the chlorine dioxide is in turn, unaffected by the presence of hydrogen peroxide (174). Perchlorates are likewise unaffected, making perchloric acid of particular usefulness in adjusting the pH of hydrogen peroxide solutions.

The oxidation-reduction relationships of bromine with hydrogen peroxide are similar to those of chlorine, with the exception that bromate is reduced to bromide and elemental bromine. The most extensive halogen studies have been carried out with iodine compounds. References to the early literature are provided by Walton (175), and the extensive contributions of Abel (176) must be acknowledged. Morgan (177) has recently reviewed these reactions which are summarized by Table 4 taken from Bray and Liebhafsky (178). A dash indicates that substantially no reaction occurs.

Table 4

Reactions of Iodine with Hydrogen Peroxide

pH	Species			
	I^-	I_2	$I_2 + IO_3^-$	IO_3^-
13	—	$I_2 \rightarrow I^-$	$I_2 \rightarrow I^-$	—
5	$I^- \rightarrow I_2$	$I_2 \rightarrow I^-$	—	$IO_3^- \rightarrow I_2 + I^-$
1	$I^- \rightarrow I_2$	—	$I_2 \rightarrow IO_3^-$	$IO_3^- \rightarrow I_2$

Several studies of special aspects of iodine-hydrogen peroxide reactions may be mentioned. Rumpf (179) has reported a spectrographic study of the iodide reaction, and the pH changes occurring in the system with iodide and thiosulfate have been published (130). The oxidation of iodide forms the basis for a ''clock'' reaction (131). The reaction is catalyzed by the presence of iron, and several studies (132) have been made of this so-called ''Schönbein's Reaction.''

Sulfur, Selenium, Tellurium, and Polonium

Elemental sulfur is quite unreactive with hydrogen peroxide. With other valence states stepwise oxidation occurs, continuing, under suitable conditions, up to the hexavalent state in the form of sulfate or sulfur trioxide. Hydrogen sulfide in acid aqueous solution is oxidized but only to elemental sulfur. A recent study (133) has shown the rate of this reaction to be inversely proportional to about the 0.4 or 0.5 power of the hydrogen ion concentration and first order with respect to hydrogen peroxide concentration. In alkaline solution sulfate results (134). This reaction is catalyzed by iron, even to the extent that the purity of the solvent water used may be of considerable importance (135). The related reactions of the metallic sulfides have also been studied (134). Sulfite is readily oxidized to sulfate by hydrogen peroxide, and two tracer studies (51, 105), already discussed above, have increased considerably the understanding of this reaction. An interesting feature of the sulfite oxidation is the concurrent dimerization to form dithionate, $S_2O_6^=$, which occurs to some extent (186). Glasstone and Hickling (187) have contrasted this to the stoichiometric formation of dithionate in the electrolysis of sulfite. They attribute the electrolytic reaction also to the intermediate formation of hydrogen peroxide under the expecially favorable circumstances of high local concentration on the anode surface. Similar complications occur in the reaction by which hydrogen peroxide replaces the ''sulfide'' sulfur atom in thiosulfate, $S_2O_3^=$, with an oxygen atom to produce sulfate (51). In this case, apparently trithionate, $S_3O_6^=$, and tetrathionate, $S_4O_6^=$, may also be formed (188). Kinetically, the reaction has been reported (189) to be bimolecular, and the effects of various catalysts such as iodine and molybdate have been investigated (190).

It is of interest to compare and contrast the compounds of sulfur and oxygen, especially in regard to the insight this may provide into the mechanism of the reactions just discussed. Sulfur and oxygen are alike in having the same s^2p^4 outer electron structure, making their valence relationships similar. At the same time there is a considerable difference in their electronegativities and in their tendancies to hybridization. Another difference which may be of outstanding importance is the possibility which exists for sulfur to make use of *d* orbitals in sp^4d or sp^3d^2 hybrids, an energetically improbable situation for oxygen. To be considered in the light of these facts are the very short lifetime of the hydroxyl radical, OH, compared to the relative unreactiveness of the sulfhydryl radical, SH, the disproportionation under certain circumstances (191) of sulfur monoxide, SO, to form sulfur dioxide and elemental sulfur (analogous to ozone formation from molecular oxygen), and the apparently complete lack of *sp* hybridization in H_2S with a bond angle of 90°. Of particular importance is the question of the electron structure of sulfur in the hexavalent state, *i.e.*, whether six sp^3d^2 hybrid orbitals are present, thus involving the presence of π bonds in such a structure as sulfate. A number of references (192) discuss this topic and may be useful in considering the possibility that the ready oxidation of sulfur compounds by hydrogen peroxide is related to the ease with which it can cause the formation of these hybrid structures. In this respect Howard and Levitt (193) have commented on the fact that the presence of electron attracting groups on a sulfoxide or sulfide slowed the oxidation of these by peroxysulfate and hydrogen peroxide, respectively.

The reactions with hydrogen peroxide of the remaining members of the chalcogen family have received less attention. Selenites are readily oxidized by hydrogen peroxide to selenates (194), although reaction with selenious acid, H_2SeO_3, has been reported to be an exception. Elemental selenium is slowly oxidized to selenium dioxide (195), and it has also been reported to be converted to selenic acid, H_2SeO_4. Hydrogen selenide is rapidly attacked. Elemental tellurium dissolves in sufficiently concentrated hydrogen peroxide to yield telluric acid, H_2TeO_4 (196). This reaction occurs also if tellurium electrodes are acted on by an electric current in hydrogen peroxide solution, with evidence that hydrogen telluride may be an intermediate product (196). In general, tellurates result from hydrogen peroxide action, although telluric acid may be formed under suitable conditions (197). Tellurium dioxide is reported to be insoluble in hydrogen peroxide (67) although this implies that oxidation to telluric acid, corresponding to TeO_3, does not proceed *via* TeO_2, which by its insolubility would appear likely to interfere with further reaction. Elemental polonium has been reported (198) to dissolve in acid hydrogen peroxide.

Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth

Several sources (199) describe the course and kinetics of the reaction of hydrogen peroxide with nitrite. The end product is nitrate with peroxynitrous acid frequently mentioned as an intermediate. Nitrate is unreactive with hydrogen peroxide until high concentrations in acid are reached. Nitrate in neutral solution is essentially unreactive. Masson (200) found cyanate and carbonate to result from the reaction of cyanide with hydrogen peroxide; no oxygen appeared as long as excess cyanide was present. Schuster (201) reported thiocyanate to produce initially ammonia, then nitrate on reaction with hydrogen peroxide. Hydroxylamine, which bridges the gap structurally between hydrogen peroxide and hydrazine, was observed by Wurster (202) to be oxidized by hydrogen peroxide to nitrate.

The reaction in acid solution of hydrogen peroxide with hydrazine (203), N_2H_4, was reported in an early study by Browne (204) to produce hydrazoic acid, HN_3. More recently, Gordon (205) reported only molecular nitrogen and water to result from this reaction in aqueous solution. The rate of reaction was found to be greatest at pH 10 and no hydrazoic acid or ammonia could be detected among the products of reaction. Further recent work (47,206,207) has demonstrated the variations in the course of this reaction which can be brought about by changes of conditions. Of particular importance is the extraordinary sensitivity of the reaction to catalysis, and it has been suggested (47,206) that reaction does not proceed between hydrogen peroxide and hydrazine in dilute aqueous solution except as induced by catalysis. Similarly it has been observed (208) that these substances are even capable of coexistence for some time in the vapor state at 100°C. and a few mm.Hg. Admixture of concentrated hydrogen peroxide and hydrazine from common sources, however, will ordinarily result in explosion, although there may be an induction period of variable length, depending upon concentration, temperature, method of contacting, and presence of other species. Substances which in certain forms have been studied for their catalytic effect on this reaction are cobalt (205), titanium (47), iodide (206), copper (206, 139, 209, 210), and iron (139, 209). Molybdate and vanadate have been reported ineffective (209), and it was found (206) possible to inhibit the catalysis with a complexing agent. Interest in the reaction with hydrazine and hydrogen peroxide has also been stimulated by applications to propulsion systems.

The reaction between elemental phosphorus and hydrogen peroxide was described by Weyl (211) as producing phosphine, PH_3; and phosphoric acid. Phosphate is quite inert in hydrogen peroxide, and may be used as a stabilizing agent, as discussed in Chapter 9. Other valence states of phosphorus, *e.g.*, phosphorous acid, are converted (212) to phosphate. Elemental arsenic has been reported to be oxidized by hydrogen peroxide to arsenic acid, H_3AsO_4. Better understood is the oxidation of arsenite, $AsO_3^{\equiv}$, to arsenate, $AsO_4^{\equiv}$, which is quantitative (213). Metallic anitmony and its oxides are rather inert toward hydrogen peroxide, although the sulfide has been descirbed (214) as dissolving in ammoniacal hydrogen peroxide to form antimoniate. Some rather complicated effects on the crystallographic properties of antimony trioxide, Sb_2O_3, have been described (215). Moser (216) observed bismuth trioxide, Bi_2O_3, to be oxidized to bismuth tetroxide, Bi_2O_4, which could then in turn be reduced. In alkaline solution bismuth nitrate, $Bi(NO_3)_3$, has been found (217) to be converted to a yellow-brown bismuth hydroxide, $Bi(OH)_3$, plus a poorly characterized second component.

Carbon, Silicon, Germanium, Tin, Lead

Stoichiometric reaction of hydrogen peroxide with elemental carbon has not been observed, although the decomposition which occurs also entails some modification of the carbon surface. Rupp and Schlee (218) reported that hydrogen peroxide oxidized carbonate to formic acid and formaldehyde, but later (219) discovered this action to have been brought about by impurities present. Other than reports (220) of absorption and peroxide formation (221) no other instances of reaction of hydrogen peroxide with silicon compounds appear to have been reported. Germanium metal has been reported (222) to be etched by hydrogen peroxide. The inertness of metallic tin has been commented upon in the discussion of handling procedures in Chapter 4. In solution, stannous tin is converted to stannic (223), and the hydrous stannic oxide is quite inert as well as valuable as a stabilizer. The relative inertness of these elements is not shared by the last member of the group, lead, which is a very active decomposition catalyst. Solution of metallic lead occurs in acid hydrogen peroxide; on increasing the pH the oxides appear, with lead dioxide clearly the product under alkaline conditions (224).

Gallium, Indium, Thallium

In this group only the reactions of thallium appear to have been studied, it being reported that thallium metal is converted to thallous hydroxide, TlOH, and that thallous oxide, Tl_2O, is oxidized to thallic oxide, Tl_2O_3.

Zinc, Cadmium, Mercury

Zinc metal can be converted to zinc oxide, ZnO, by the action of hydrogen peroxide. It has also been reported (225) that hydrogen peroxide will cause zinc to dissolve in alkaline alcoholic solution. Another unusual effect was reported by Stone (151), who found that addition of hydrogen peroxide to sulfuric acid, in which amalgamated zinc was producing hydrogen, caused gas evolution to cease, then later begin again. A peroxide is readily formed from divalent zinc, an old report asserting that this reaction occurs explosively with the carbonate. Metallic mercury dissolves in acid hydrogen peroxide, oxides appearing when the pH is raised. No report of a cadmium reaction appears available.

Copper, Silver, Gold

Metallic copper may be dissolved in acid hydrogen peroxide. This has been studied from the standpoint of corrosion by Glauner and Glocker (226). Oxidation may also occur, to di-, tri-, and quadrivalent states, depending upon the conditions (227). Hydrogen peroxide in hydrochloric acid is reported to dissolve metallic gold, and oxides of gold are reduced by alkaline hydrogen peroxide (228). The effect of alloying gold on the rate of its attack by hydrogen peroxide-sodium chloride mixtures has also been studied (229). Elemental silver is similarly dissolved by acid hydrogen peroxide, oxidation being to the univalent state. Likewise in alkaline solution reduction to the metal occurs (230), although formation of the oxide has often been considered (231).

The action of hydrogen peroxide upon silver compounds brings into consideration effects encountered in photography. In alkaline solution hydrogen peroxide will develop a latent photographic image (232). Mees (233), in reviewing this subject, has commented, as the early investigators did, on the structural similarity of hydrogen peroxide to such a substance as hydroquinone in relation to photographic developing action. Also mentioned (233) is the reasonable conclusion that the active entity in the development by hydrogen peroxide is the perhydroxyl ion; however it would be of considerable general interest to establish this by the experimental technique developed by James (234). Hydrogen peroxide can also darken a photographic emulsion directly, an effect observed as early as 1842. Because this phenomenon is sensitive enough to respond to minute concentrations of hydrogen peroxide it has been used as a method of detecting traces of hydrogen peroxide, as described in Chapter 2. Of particular importance in establishing an understanding of this ''Russell Effect'' has been the discrediting of the idea, advanced even recently, that hydrogen peroxide exerts this action by emitting some mysterious radiation or radioactivity.

Nickel, Palladium, Platinum

Hydrogen peroxide acidified with hydrochloric or sulfuric acids, but not acetic, is capable of dissolving metallic nickel. No action of hydrogen peroxide on acid nickel sulfate was observed (235), although decomposition occurs on the nickel hydroxide formed in alkaline solution. Metallic platinum is quite resistant to attack by acid hydrogen peroxide (236). Effects of hydrogen peroxide on platinum such as passivation (237) and production (238) of platinum trioxide, PtO_3, in relation to electrolytic behavior, have been described. Bivalent platinum in complex compounds; *e.g.*, $(NH_4)_2 PtCl_4$, is oxidized (239) to the quadrivalent state, as in $(NH_4)_2 PtCl_4(OH)_2$.*

Cobalt, Rhodium, Iridium

The rate at which cobalt metal dissolves in hydrogen peroxide to produce cobaltous ion was reported (240) to be first order with respect to the difference between the momentary cobalt concentration in the solution and the saturation cobalt concentration, for the particular pH and hydrogen peroxide concentrations. At higher pH, cobaltous and later cobaltic oxides are produced. In ammoniacal solution hydrogen peroxide has been reported to produce a complex such as $[(NH_3)_5CoO_2Co(NH_3)_5]^{+5}$ containing both tri- and tetrapositive cobalt (241) (See Chapter 12).

Iron, Ruthenium, Osmium

Oxidation and reduction in the presence of hydrogen peroxide of the ferrous-ferric iron system has received intensive study in connection with the associated decomposition process. Ordinarily it is the oxidation of ferrous ion to the ferric state which is predominant in acid solution, with precipitation of the colloidal hydroxide at higher pH. The possibility of oxidation to other states has also been considered (242), and Evans, George, and Uri (243) studied the formation of a complex between perhydroxyl ion and ferric ion. Under suitable conditions the treatment of steel with hydrogen peroxide can yield a polished and corrosion-resistant surface (244). Interaction of hydrogen peroxide with a number of iron complex compounds has received study (245). Activation by light has been observed in certain of these reactions.

Manganese, Technetium, Rhenium

The chief attention in the reaction of hydrogen peroxide with manganese compounds has been centered on permanganate reduction which proceeds to manganous ion in acid, manganese dioxide in alkaline solution. The formula of the manganese dioxide so obtained is never found to correspond exactly to MnO_2, and several investigations of this aspect have been made (246). The reaction of hydrogen peroxide with permanganate is exceedingly fast, especially when catalyzed by the presence of manganous ion, nevertheless, kinetic measurements have been made (247). Mers, Stafford, and Waters (248) have discussed the mechanism of the reaction. Only one investigation (249) of rhenium appears to have been recorded, this showed solution of rhenium heptoxide, Re_2O_7, to occur in hydrogen peroxide.

Chromium, Molybdenum, Tungsten

With this group of elements there is begun consideration of those elements which readily form well-known peroxy acids. For a more adequate consideration of these compounds, reference should be made to Chapter 12.

Chromium metal is relatively inert in acidic or basic hydrogen peroxide, only a slow solution taking place. Aside from study of peroxychromates, most attention has been directed toward the reduction of chromic anhydride, CrO_3, by hydrogen peroxide to form trivalent chromium (250). Molybdenum in all valence states is similarly converted to a peroxide (251), and phosphomolybdate cannot be precipitated in the presence of hydrogen peroxide (252). Molybdenum sulfide reacts with hydrogen peroxide to form sulfate, barring the use of this substance as a lubricant in contact with hydrogen peroxide. Tungsten may be dissolved in hydrogen peroxide to form tungstic acid, H_2WO_4, and may be further converted to peroxytungstates.

Vanadium, Niobium, Tantalum

A number of stages have been postulated to occur in the reaction of meta-vanadate, VO_3^-, or vanadium pentoxide, V_2O_5, with hydrogen peroxide to the peroxy form (253). Niobium and tantalum affect each other's solubility in acid hydrogen peroxide; apparently they form colloidal solutions (254). The actual solubilities differ considerably, tantalic acid being only partially soluble whereas niobic acid is quite soluble in hydrogen peroxide. The metals also differ (255), tantalum being virtually inert in acid hydrogen peroxide.

Titanium, Zirconium, Hafnium

The yellow complex compound formed when a titanium salt is mixed with hydrogen peroxide is of considerable interest since this reaction is the basis of a highly specific method of analyzing for hydrogen peroxide, as recounted in Chapters 10 and 12. The reaction of hydrogen peroxide with titanous ion, Ti^{+++}, has been reported (47) to produce free hydroxyl radicals, and the further conversion to the peroxy state, TiO_3, occurs readily. An oxysulfate has also been described (256). Titanic hydroxide has also been reported to form a colloidal solution or gel in hydrogen peroxide (257). The formation of a titanium-fluoride complex ion may also be catalysed by hydrogen peroxide (258). Zirconium, either as the metal or as the sulfate appears to be quite inert in hydrogen peroxide (259).

Boron, Aluminum, Scandium, Yttrium

Colloidal elemental boron is converted to boric acid, H_3BO_3, by hydrogen peroxide (260) with no further action observed. Metallic aluminum is acted on to a very small extent by hydrogen peroxide to form aluminum hydroxide. The formation of an adherent layer of the hydroxide on the surface undoubtedly accounts for the outstanding inertness of aluminum as a storage container. It is nevertheless possible for corrosion to occur in the presence of other substances, notably chloride, and quite a number of studies of this topic have been reported (261). The role of the chloride has been suggested to be a loosening of the aluminum hydroxide film as well as increasing the electrical conductivity of the solutions. That electrolytic corrosion actually does occur has been demonstrated by Akimov and Oleshko (262) using colorimetric indicators.

Rare Earths and Actinides

Few of these elements have received attention with respect to their reactions with hydrogen peroxide. An oxide R_4O_9 is said to be characteristically produced from the rare earths and this appears to have been demonstrated for lanthanum and samarium. The reaction of ceric ion with hydrogen peroxide to produce cerous ion is quantitative and its use in an analytical procedure for hydrogen peroxide is discussed in Chapter 10. Among the actinides thorium has been observed to form an oxide Th_2O_7 (263), and uranium, besides forming a peruranic acid, is oxidized from the quadrivalent state to uranyl ion, UO_2^{++} (264).

The Alkaline Earths

Metallic magnesium is slowly dissolved by hydrogen peroxide to form the hydroxide; the other alkaline earth elements appear not to have been examined in this respect, but would be expected to behave similarly. The status of the system in solution is fixed by the equilibrium between peroxide, hydroxide, and hydrogen peroxide, e.g., as examined by Abegg (265) in the case of barium hydroxide (See also Chapter 3). Reports have been given of the reaction of radium halides on hydrogen peroxide which on examination prove to have dealt in fact with the effects of the radiation therefrom.

The Alkali Metals

Just as with water, the alkali metals react violently with hydrogen peroxide to produce hydrogen gas. In the case of sodium amalgam Baker and Parker (266) reported differences in the reactivity with various samples of water to be caused by the presence of hydrogen peroxide. The peroxides of these elements are described in Chapter 12.

REACTIONS OF HYDROGEN PEROXIDE IN ORGANIC CHEMISTRY

The greatest usefulness of hydrogen peroxide has been in the area of reactions with organic substances. For the most part the basic mechanisms of these reactions, such as in bleaching, have been little understood, but the combination in hydrogen peroxide of powerful oxidizing potential with efficiency and specificity of action as well as the fact that its reaction by-products are innoccuous has favored its use. More recently there has been an increase in its application to well-defined steps in organic synthesis, for example, epoxidation, hydroxylation, quinone formation, ring splitting, polymerization, and peroxidation. Such reactions are being used in the production of waxes, resins, polymeric materials, plasticizers, drugs and medicinals, insecticides, and many organic intermediates. It seems safe to say that such application and the study of the reactions involved is likely to undergo outstanding growth.

In many instances hydrogen peroxide forms an organic peroxide or a peroxy acid, either organic or inorganic, in the reaction mixture and it is this species rather than hydrogen peroxide as such which is the active agent. Such formation may come about naturally through the choice of a non-aqueous solvent or the specific peroxide may be deliberately chosen in order to attain an increased reaction rate or high degree of specificity. The reasons for the differences in behavior between the different peroxides were developed above in the general discussion of mechanism. Because of such differences in behavior it is of importance in interpreting the results reported in the use of ''hydrogen peroxide'' as a reagent to ascertain what peroxide structure was actually the true reactant. Frequently it is optional whether the peroxide is added as such or whether it is formed *in situ* from hydrogen peroxide, and in some instances the same results are attained with different peroxides. In most cases in which hydrogen peroxide is nominally listed as the reactant, but is in fact not, it will be found that the actual peroxide is one of the peroxy acids, either peroxyformic or peroxyacetic, less frequently one of the higher homologues or peroxybenzoic acid. Peroxy acids of some of the heavier metals, such as osmium or molybdenum are sometimes formed *in situ*. Sometimes a reaction is described as involving hydrogen peroxide when the actual reagent added is an organic peroxide; for example, tertiary butyl hydroperoxide and benzoyl peroxide are the commonest non-acyl or di-substituted peroxides so described. When peroxides other than those just mentioned are used, it is much less likely that the reaction will be attributed to hydrogen peroxide. To this list must be added those substances which form free radicals on reaction with hydrogen peroxide. Outstanding in this respect is the system hydrogen peroxide-ferrous iron, known as Fenton's reagent (267). At low hydrogen peroxide/ferrous ion concentration ratios this is an exceedingly active oxidizing system, and a survey of the types of organic substrates affected by it has been made by Merz and Waters (268).

These factors make the reactions of peroxy acids and other peroxy compounds of interest in an account of the organic reactions of hydrogen peroxide. The present discussion has been anticipated in this respect by the outstanding review by Swern (269) of peroxy acids, which contains 700 references to the literature. Other reviews of the organic reactions of hydrogen peroxide and peroxy acids have been published by Taylor (270), Johnson (271), Friess (272), Hudlicky (273), and Testa (274). A useful table summarizing representative reactions was presented by Shanley and Greenspan (275). The following is a brief guide to literature describing typical organic reactions of hydrogen peroxide.

Alkanes

The saturated paraffins are found (275) to be inert to the action of hydrogen peroxide, either concentrated or in the presence of metallic catalysts, although emulsions or mechanical dispersions in concentrated hydrogen peroxide can be detonated. Alkyl Grignard agents react to form alcohols (276).

Ethylenic Substances---Epoxidation and Hydroxylation

Compounds containing an unsaturated carbon to carbon bond, $RCH = CHR'$, can be converted to the expoxy or oxirane form $RCH\underset{O}{-}CHR'$, and further to the polyhydroxy or glycol form, $RCH(OH)CH(OH)R'$, through the action of various peroxides. The literature dealing with these reactions has been reviewed and discussion of the mechanism and experimental procedures, including lengthy tabulations of substances undergoing the reaction, has been given in two papers by Swern (269,277). Other less comprehensive reviews dealing largely with practical aspects are also available (278). This reaction is sometimes known as the Prileschajew reaction (279) and has been carried out with aliphatic aryl, alicyclic, and heterocyclic olefins, unsaturated fatty acids and esters, fats and oils, and unsaturated alcohols. Ordinarily hydrogen peroxide alone is ineffective, e.g., 1-pentene was unaffected by 90 wt. % hydrogen peroxide even in the presence of iron or vanadium (275). In order for reaction to proceed it is generally required that a peroxy acid be present to offer a more electronically unsymmetric peroxide group than that existing in hydrogen peroxide. Whether the reaction is readily stopped at the epoxide or whether it continues to the glycol depends on the conditions, gentler treatment being required to obtain the epoxide in high yield. Inorganic catalysts, which operate through a peroxy acid form, have also been developed for this purpose (280,67); that using osmium in *tert*-butyl hydroperoxide has been referred to as the Milas reagent. Peroxy acids are not effective in epoxidation of ketones and acids having a double bond $\alpha\beta$ to the carbonyl group. Here alkaline hydrogen peroxide does react, however (278). Study has also been made of the photochemical addition of hydrogen peroxide

(281)
to the double bond. Considering alicyclic substances in particular, a number of studies are available. Cyclohexane alone does not react (275). The hydroxylation of cyclohexanone and its conversion to adipic acid has been studied (282). Other work has been conducted with the terpenes, cadalene (283) and brasilein (284), the terpin, cineole (285), the terpene alcohol, sabinol (286), and an indene derivative (287).

Alcohols

Ethanol does not react with concentrated hydrogen peroxide (273) in the cold mixture although mixtures in certain concentration ranges can detonate with tremendous violence. In the presence of ferric ion, however, reaction proceeds to the formation of acetic acid (288) or even to carbon dioxide (275). Tertiary alkyl alcohols can be converted to alkyl hydroperoxides (70), and a number of products are obtained from tertiary aromatic alcohols (289). With the polyhydric alcohol, glycerol, formic acid is obtained directly with hydrogen peroxide, glyceric acid and glycollic acid being intermediates (290). In the presence of ferric ion glyceraldehyde is formed, and calcium carbonate favors formaldehyde and acid formation. The mechanism of these reactions with alcohols has been studied by Merz and Waters (291).

Carboxylic and Keto Acids, Aldehydes, and Ketones

The reaction of hydrogen peroxide with the simpler carboxylic acids is a frequently used route for the preparation of peroxy acids. Further oxidation can also occur (292); the longer chain acids being least susceptible to this. In the oxidation of the dicarboxylic acid, oxalic, acid conditions were found to promote the conversion to carbon dioxide, basic conditions to retard it (293). Mesoxalic acid behaves similarly (294). The presence of hydroxyl groups was found also to increase the rate of oxidation, e.g., in the series succinic, malic, and tartaric acid (295). The unsaturated fumaric and maleic acids have also been investigated (296). Oxidation of maleic anhydride with hydrogen peroxide is in use as a commercial method for tartaric acid manufacture (297). Reactions with keto acids, such as glyoxylic and acetoacetic, have been studied (298); mechanisms which may account for the observed base catalysis have also been discussed (299). Reactions of hydrogen peroxide with the dicarbonyl, glyoxal (300), the related glycollic acid (301), and triketones (302), and other ketones (303) have also been studied.

The aldehydes react directly with hydrogen peroxide to form hydroxy alkyl peroxides, $RCH(OH)OOH$ and $RCH(OH)OOCH(OH)R$, and these in turn react further to form acids and other products (304). The reaction is acid catalyzed (305), and the kinetics of the reactions with formaldehyde, acetaldehyde, and propionaldehyde have been studied (306). The product of oxidation of formaldehyde is formic acid, (307), but it is notable that under alkaline conditions molecular hydrogen is also a product (308). Urea-formaldehyde resins are also decomposed by hydrogen peroxide (309).

Organic Nitrogen Compounds

Primary amines, RNH_2, are vigorously decomposed by hydrogen peroxide, secondary amines, R_2NH, react energetically to form hydroxylamines, R_2NOH, and tertiary amines, R_3N, are sluggishly oxidized to amine oxides, R_3NO (275). In the presence of ascorbic acid and iron, nitrobenzene is similarly converted to nitrophenylhydroxylamine (310). Nitriles, RCN, are converted to amides, $RCONH_2$, by the action of hydrogen peroxide; the reactions of benzamide (74) and adiponitrile (311) in this fashion have been studied. Saponification of nitriles has also been reported (312). Amino acids react with hydrogen peroxide in the presence of ferric ion to produce keto acids (313). Azobenzene is readily converted to azoxybenzene (314), and coupling to form trisazoxy derivatives has also been reported. There has also been interest (315) in the bleaching of the triphenylmethane dye, malachite green. Of interest for their spectacular quality are the luminescent reactions of hydrogen peroxide with certain nitrogen compounds. Best known is that with luminol or 3-aminophthalohydrazide (316), which, when observed in the dark, shows light resembling that of the firefly. Huntress, Stanley, and Parker (317) have described in detail the conditions for carrying off this reaction in most efficient and showman-like fashion. Other luminescent reactions have been described with Butter Yellow (318), pyrogallol (319), and a number of other dyes (320). Luminescent reactions within organic compounds have also been reported (321).

Organic Sulfur Compounds

It is reported that hydrogen peroxide in a mixture of sodium sulfide and benzylchloride can produce mercaptans (322). Such compounds containing sulfhydryl groups, or mercaptans, can in turn be oxidized to disulfides, e.g., ethyl mercaptan, C_2H_5SH, is converted to diethyldisulfide, $C_2H_5SSC_2H_5$, although catalysis is generally required. An outstanding example of this is the conversion of cysteine to cystine (323); the tripeptide, glutathion, acts similarly (324). These disulfides, which may also be termed persulfides, can in turn be converted to products such as RSOSOR (325) (See discussion of wool below). Cystine is reported (326) to react to form taurine. Sulfides are oxidized to sulfoxides, e.g., dibenzyl sulfide, $(C_6H_5CH_2)_2S$, produces dibenzyl sulfoxide, $(C_6H_5CH_2)_2SO$; reports of the behavior in this fashion have been given of alkyl and chloroalkyl sulfides (327), aryl trityl sulfides (328), and an amino sulfide (329). Further oxidation to sulfones, R_2SO_2, can then occur.

Carbohydrates

In the absence of a catalyst the carbohydrates are relatively unreactive, although detonable mixtures can be formed. With iron as a catalyst there can occur a well-known reaction for the preparation of a lower aldose from the aldonic acid, e.g., d-arabonic acid, $CH_2OH(CHOH)_3COOH$, is converted to d-erythrose, $CH_2OH(CHOH)_2CHO$. Morrell and Crofts (330) reported extensive studies of carbohydrate oxidation; fructose (331) and l-rhamnose diacetate (332) have also been studied.

Aromatic Compounds

Benzene and toluene do not react with hydrogen peroxide in the absence of a catalyst. If an iron compound is added to the peroxide layer and the mixture stirred, oxidation to phenol takes place. If further reaction is allowed, deeper oxidation occurs with the formation of interesting dark-colored and colloidal substances (333). Bottomley and Blackman (334) suggested a possible relation of this reaction to the formation of peat and coal. In the presence of acetic acid other substituted benzenes are oxidized, e.g., aniline is converted to nitrobenzene and azoxybenzene, and benzaldehyde produces benzoic acid. The polynuclear hydrocarbons yield quinones; with further action, ring opening occurs, as in the oxidation of phenanthrene to diphenic acid. Naphthol is similarly converted to the quinone (335) and ring splitting also occurs, for example to give *o*-carboxycinnamic acid. Hydrogen peroxide does not aid in the sulfonation of naphthol (336). On the other hand, hydrogen peroxide does promote halogenation of a number of compounds (337), *e.g.*, *p*-benzoquinone provides chloranil.

Heterocyclic Compounds

Considerable attention has been paid to the reactions of hydrogen peroxide with heterocyclic compounds. Examples which may be mentioned are furfural (338), thiophene (339), nicotinic acid (340), thymine (341), pyrazine derivatives (342), piperazine (343), phenazines and quinoxalines (344), and uric acid (345). Many of these are of biological interest, and additional matter in this respect will be found below. The compound 8-hydroxyquinoline is also of concern in the stabilization of hydrogen peroxide. The reactions of a large number of alkaloids with hydrogen peroxide, have also been investigated, especially by Schaer (346) and by Fernandes and Pizzaroso (347). To these must be added studies on nicotine (348), narcotine (349) and colchicine (350).

Many studies of amorphous and polymeric organic substances and their interactions with hydrogen peroxide have been carried out. Much of this work holds interest in respect to the use or biological significance of hydrogen peroxide and is reported in the discussions of those topics. To these may be added studies of the effects on natural and synthetic rubbers (351), coal (352), and sphagnum moss (353).

ORGANIC PEROXIDES

The field of organic peroxides is so large that it demands separate treatment, and it has not been attempted to cover it in this monograph. Abundant evidence has been furnished to indicate the relationships of hydrogen peroxide to organic peroxides; this has entered the discussion particularly in the sections on nomenclature, formation, safety and handling, structure, reaction mechanism, and uses. Attention may be directed to a number of books and reviews which will give a competent entry to this subject. Reference has already been made to the content of the review by Swern (269) and the book by Tobolsky and Mesrobian (40). A convenient introduction to the field has been provided by Milas, Margulies, and Shanley (354). A very adequate treatment of preparative methods, valuable also in showing the use of hydrogen peroxide in forming organic peroxides and for emphasizing some of the dangers inherent in these substances, is given by Criegee (355). Several other reviews (356) have appeared recently and will be found useful for their varying content and approach.

HYDROGEN PEROXIDE IN BIOLOGICAL PROCESSES

It has been pointed out that an important consideration in the chemistry of hydrogen peroxide is its position as an oxidation-reduction intermediate between molecular oxygen and water. The utilization by living organisms of atmospheric oxygen to oxidize various nutrients to carbon dioxide and water as the means of providing energy makes this relationship of particular interest in the vital processes of biological oxidation. It is clear that hydrogen peroxide is a metabolite normally produced and destroyed by a wide variety of plants and animals, but only a beginning has been made in establishing the mechanisms, limitations, and importance of this aspect of biological oxidation. In addition to playing a part in the processes which provide energy to the organism, there are other processes, for example synthesis and detoxication, in which hydrogen peroxide participates. All these are normal and perhaps indispensable activities occurring in living tissue, in which hydrogen peroxide takes part at extremely low concentrations. To consideration of these must be added concern about the effects on life processes when hydrogen peroxide becomes present at abnormally high concentration, either through malfunction of the organism or through deliberate or accidental exposure. Since hydrogen peroxide is normally present in nature only in minute proportions, the latter situation arises only during manufacture and use. In this division of the chapter all these aspects of hydrogen peroxide chemistry are discussed, an exception being that the discussion of the mechanism of catalytic decomposition by enzymes has been placed in Chapter 8. These are subjects having a large and somewhat diffuse literature; fortunately this is offset to some degree by the availability of a number of excellent reviews. For these reasons this discussion should not be depended upon for complete direction to the literature.

Biological Oxidation

In simplified fashion the process whereby energy is gained to carry out the life processes is regarded as a controlled oxidation whereby a substrate is converted by oxygen into water and carbon dioxide. This occurs in steps dealing with a few atoms of the substrate at a time in near-neutral, water solution at temperatures regarded as low by the chemist, the catalysis for the steps being supplied by biological catalysts or enzymes. From the standpoint of interest in hydrogen peroxide there are three kinds of reactions to be considered. These are the steps in which hydrogen peroxide is formed, those in which it acts as an oxidant, and those in which it is catalytically decomposed. A brief outline of the manner in which it is presently believed these steps occur may be given as follows.

The first step in the oxidation of substrate is usually a dehydrogenation. In this reaction an enzyme, termed a dehydrogenase* and usually active with only one specific substance or class of substances, activates two hydrogen atoms of the substrate in such a way that they are easily transferred to an acceptor molecule. Such loss of hydrogen is equivalent to oxidation of the substrate; for example, lactic acid, $CH_3CHOHCOOH$, may be converted to pyruvic acid, $CH_3COCOOH$. A number of substances can act as acceptors for the hydrogen removed from the substrate; frequently these acceptors are referred to as carriers, since they occupy a place in a chain of steps through which hydrogen is carried to its final reaction with oxygen to form water. The distinction of importance here is whether the molecule which accepts the hydrogen from the substrate is molecular oxygen or some other substance. If it is molecular oxygen, the result of the hydrogen transfer is the formation of hydrogen peroxide and the enzyme catalyzing the transfer is termed an aerobic dehydrogenase. The dehydrogenases which catalyze the transfer of hydrogen to acceptors or carriers other than molecular oxygen are termed anaerobic dehydrogenases.

Subsequent steps in the oxidation of the substrate may involve decarboxylation, hydration, and further dehydrogenation. In the decarboxylation a carboxyl group is removed to form carbon dioxide, this action being mediated by a carboxylase. The hydration step may also require intervention of an enzyme, a hydrase. Other steps of importance

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*The terminology of enzymes is still developing, and a consistent usage has not yet been established; certain of these dehydrogenases may be found to be called oxidases, for example. The problem of nomenclature in this field has recently been approached by Hoffmann-Ostenhof (357). According to his scheme all the enzymes of interest here are oxidoreductases.

in this chain of substrate degradation are regulated by enzymes termed oxidases. These enzymes activate molecular oxygen, enabling it to oxidize specific substrates without any action on the part of a dehydrogenase or of hydrogen carriers. Water is the result of oxidase action and hydrogen peroxide formation has not been detected.

A parallel to the action of the oxidases is found in the class of enzymes called peroxidases. These enzymes have been found in plants, milk, and blood and activate hydrogen peroxide to permit it to take part in the oxidation process. It appears that the substrates attacked in this fashion are certain phenols and aromatic amines. There are, however, a number of biologically important compounds in these classes which do not appear to be affected by peroxidase, and rather little is known regarding the importance of this action of hydrogen peroxide in the over-all oxidation scheme. The products of the peroxidase action are the oxidized substrate and water; no molecular oxygen is produced. Because of this characteristic, any stoichiometric reaction of hydrogen peroxide proceeding in this manner and therefore not resulting in oxygen generation can be referred to as''peroxidatic'', and the term is sometimes used in non-biological systems. In textile treatment, for example, it is desirable and economical for the action of hydrogen peroxide to be peroxidatic, confined to effective bleaching, and not wasted through catalytic decomposition.

The task of catalytically decomposing hydrogen peroxide and thereby eliminating it can be carried out in biological systems by an enzyme called catalase. This enzyme appears to occur in all plants and animals, excepting only a few microörganisms, and one of its purposes seems to be to prevent the accumulation of hydrogen peroxide to a toxic level. Catalase is outstandingly effective in this process, being active at very low hydrogen peroxide concentrations and capable of carrying out the decomposition at a rate far exceeding that of most of the other known catalysts. This decomposing action is sometimes called ''catalatic'' a term which is intended to be distinguished from and contrasted with peroxidatic action. It is possible that confusion on this score may arise in the future, since it has now been shown that catalase may also activate hydrogen peroxide to oxidize certain alcohols to aldehydes. This has been referred to as a coupled oxidation as well as peroxidatic action. The importance of this function of catalase is not yet established, but some investigators are of the opinion that it may be of equal or greater significance than the essentially wasteful, catalytic scavenging action of the enzyme.

The processes outlined above and others associated with them are discussed in detail by standard sources, for example, the textbook by West and Todd (358), or the reports on respiratory enzymes edited by Lardy (359). From the standpoint of studying the rôle of hydrogen peroxide there are two aspects which limit the material available and the interest in it. Hydrogen peroxide is a simple structure, universally encountered in biological systems; this robs it of interest as a unique metabolite playing a special part in cell chemistry. At the same time it is questioned whether the rôle of hydrogen peroxide is really a vital one, that is, whether it is involved as a link in the main current of steps in biological oxidation. No decision about this appears possible now, but a discussion (360) of it has brought out the fact that the main current of events may be surrounded by a protective system of checks and balances which permit the vital steps to be carried out without interruption; hydrogen peroxide may play a part in both the main and subsidiary functions. It should also be pointed out that the questions regarding the formation and reaction of hydrogen peroxide in biological oxidation were of considerable importance in much earlier investigation and theory which preceded the establishment of the scheme outlined above. Outstanding in this earlier work were the contradictory theories of Warburg and Wieland. Warburg proceeded through the development of the concept of oxygen activation, visualizing reaction of molecular oxygen and enzyme-bound iron as the primary act in respiration. This viewpoint, best appreciated from a book of Warburg's (361), precludes the formation of hydrogen peroxide through acceptance of hydrogen by oxygen. The opposing theory built up by Wieland emphasizes the activation of hydrogen and consequently the formation of hydrogen peroxide through action of oxygen as an acceptor. This theory emphasizing the dehydrogenation has also been treated in a book by its author (362). The current opinion provides a rôle for both kinds of action in biological oxidation. These and other earlier theories of oxidation are reviewed by Oppenheimer and Stern (363).

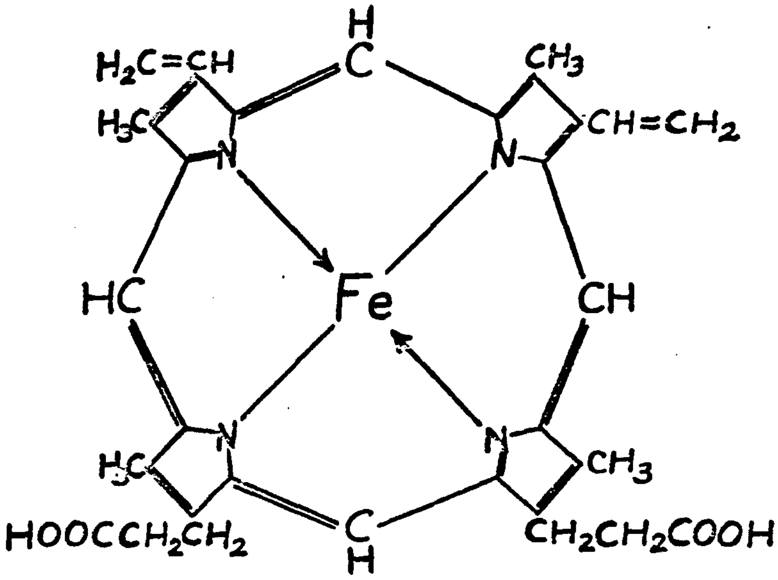
It is worth noting that much of the thinking about biological oxidation has been developed with reference to a number of ''model reactions,'' that is, *in vitro* systems having one or more properties similar to that believed to be possessed by a living system, *e.g.*, iron present and capable of catalyzing a reaction of a type considered to occur in an organism. Such comparisons have been useful in guiding and developing biological investigation, but cannot be depended on completely. For example, Dakin (364) in 1911 pointed out on the one hand that hydrogen peroxide alone among the oxidizing agents was capable of bringing about the same types of reactions controlled by enzymes and that this suggested a rôle for it in biological systems. On the other hand Dakin cautioned against acceptance too readily of the idea that catalase might also participate in the oxidation scheme. As mentioned in the discussion above, this old idea has only recently received additional experimental support warranting further consideration.

The Nature of Hemoprotein Enzymes

The structure of the enzymes which are of concern in the biochemical reaction or decomposition of hydrogen peroxide is relatively well understood and provides considerable insight into their mode of action. Useful introductions to the nature of all enzymes have been presented by Sumner and Somers (365) and Laidler (366). However, for the purpose of understanding the interactions of hydrogen peroxide with enzymes, only a few of the essentials and nomenclature dealing with a group of enzymes and related compounds known as hemoproteins need be discussed. Catalase and peroxidase are the enzymes of chief concern. These are made up of a protein bearing an active, or prosthetic group typified as an iron protoporphyrin. These enzymes are closely similar to the oxygen-carrying component of the red blood cells, hemoglobin, and the related oxygen-storing constituent of muscle, myoglobin. There is less comparison of these substances with some enzymes, *e.g.*, the proteolytic enzymes of digestion, which, although of complicated protein structure, do not bear a heavy metal porphyrin as prosthetic group and frequently exist in the organism in the form of precursors requiring activation to become effective as enzymes.

Although broadly similar, these four hemoproteins of interest in respect to the biochemistry of hydrogen peroxide, catalase, peroxidase, hemoglobin, and myoglobin, differ significantly from one another, thus accounting for their different actions with hydrogen peroxide either in the organism or under experimental conditions. These differences are found in the molecular weight, in the relative proportions of the constituent amino acids making up the protein part of the molecule, and in the number and accessibility of the iron protoporphyrin groups attached to the protein. These differences are discussed in detail by George (367); of special importance is the fact that catalase and hemoglobin carry four protoporphyrin groups per molecule, whereas peroxidase and myoglobin carry only one.

The structural formula of the iron protoporphyrin termed heme is shown as follows:



THE IRON PROTOPORPHYRIN, HEME

This structure is related (368) to that of chlorophyll, in which the coordinated metal is magnesium, and also to that of the phthalocyanines. As indicated, the central iron atom lies in the plane of the 16 member porphyrin ring, and is held to the pyrrole nitrogen atoms by four of the six available valences, leaving two to complete the octahedral complex, these being above and below the plane of the page in the model indicated above. In addition there must be considered the oxidation state of the iron; when it is in the ferrous state as pictured, the protoporphyrin is termed heme, or more clearly ferroheme. When the iron is in the ferric state the porphyrin is termed ferriheme or more specifically hemin or hematin if it is wished to designate specifically a coordinated anion present. With heme in free solution, not bound to any protein, it is presumed that two water molecules are coordinated in the fifth and sixth valence positions of the iron. George (367) represents this ferroheme as: $H_2O.Fe_p{\cdot}H_2O$. Upon oxidation this becomes $H_2O{\cdot}Fe_p{\cdot}H_2O$ with one positive charge. This ferriheme may coordinate chloride ion thus: $H_2O{\cdot}Fe_p{\cdot}Cl$, and it is then termed hemin; with hydroxyl ion coordinated: $H_2O{\cdot}Fe_p{\cdot}OH$, the ferriheme is hematin, although these terms may be used less specifically only to indicate the presence of ferric iron. Other molecules may be coordinated as well, the instance of hydrogen peroxide being, of course, of particular interest. Coordination of nitrogenous bases, *e.g.*, pyridine, with ferroheme occurs readily, giving hemochromogens, $B{\cdot}Fe_p{\cdot}B$; such a combination with ferriheme, $B{\cdot}Fe_p{\cdot}B$, is termed parahematin.

When such an iron protoporphyrin is attached to a specific protein, the enzyme proper is formed. The mode of attachment appears to be through one of the iron valencies and additionally through interaction of the protein with the two propionic acid groups of the protoporphyrin. In the case of catalase, four ferriheme or hemin groups are attached to a protein molecule of such size that the total iron content is about 0.1% by weight Fe (369). Catalase from different sources or species, *e.g.*, bacterial, liver, or red blood cells, may show different activities. The source of these differences is not yet entirely clear, but it may involve differences in accessibility of the hemin groups or the replacement of one or more hemin groups by biliverdin, an open ring derivative of heme (370). The ferrihemes of catalase are not easily reduced to ferroheme; in fact it is only recently that it has been found possible to do this without destruction of the enzyme. The enzyme peroxidase is similarly formed by linkage of ferriheme to a protein. A very apparent difference lies in the fact that only one ferriheme group is present per molecule. The protein molecule is also smaller and possesses the property of combining with a manganese protoporphyrin without loss of peroxidatic activity. Peroxidase is further distinguished by being less susceptible to inactivation by heat than catalase.

The hemoprotein enzymes catalase and peroxidase are often compared with hemoglobin and myoglobin in regard to behavior toward hydrogen peroxide. Although such study is instructive, it is not clear that the interaction of hemoglobin or myoglobin with hydrogen peroxide in the organism is ordinarily significant. These two substances are formed through the union of a protein termed globin with the reduced iron protoporphyrin, ferroheme (370). Hemoglobin bears four ferroheme groups and myoglobin bears one per molecule. The important physiological function of these substances is to coordinate molecular oxygen. In this way hemoglobin functions as the agent for transporting oxygen from the lungs to the tissues. This may be represented in the following way:

$$\underset{\text{Hemoglobin}}{Gb\cdot Fe_p\cdot H_2O} + O_2 = \underset{\text{Oxyhemoglobin}}{Gb\cdot Fe_p\cdot O_2} + H_2O \qquad (42)$$

The ferroheme of both hemoglobin and myoglobin can be oxidized to ferriheme, for example by peroxides, to give methemoglobin and metmyoglobin, respectively. Both of these substances, but not their reduced forms, possess the property of decomposing and directing peroxidatic activity of hydrogen peroxide to a small degree.

This brief introduction does not exhaust the list of hemoproteins. Other enzymes, such as certain of the oxidases and those termed cytochromes appear to have similar or related structures, but they have not yet been as well characterized, and few studies of their interaction with hydrogen peroxide have been made. The matter to be emphasized by this description of hemoprotein structure is the possibility which exists for hydrogen peroxide to occupy one of the coordination positions on the central iron atom of the iron protoporphyrin group. As Rawlinson (371) pointed out, the iron atom in these hemoproteins has been demonstrated to be the site of activity, the protein and protoporphyrin parts of the molecule performing the function of conditioning the iron to play this role, frequently in highly specific fashion, in a medium where simpler iron compounds would be totally inert or unspecific. It is this union of hydrogen peroxide with the iron which activates the hydrogen peroxide, making it susceptible to decomposition or reaction with other molecules. The problem of understanding the mechanism of hydrogen peroxide-enzyme reactions is thus largely one of elucidating the nature and fate of these complexes. These processes may be compared with those occurring with other substances which join with enzymes, *e.g.*, carbon monoxide, and especially other oxygen compounds related to hydrogen peroxide, molecular oxygen, hydroxyl ion, and water.

Reactions with Hemoproteins

In living systems the source of hydrogen peroxide is the reduction of molecular oxygen by aerobic dehydrogenases. An early reliable study which established this was by Thurlow (372), and more recent work by Keilin and Hartree (373) and Kenten and Mann (374) has extended our understanding of biological formation. Of particular interest is the isotopic tracer study on glucose oxidase (in fact a dehydrogenase) made by Bentley and Neuberger (103). This enzyme has received particular attention in regard to hydrogen peroxide formation (see Chapter 2), and this tracer work establishes that the oxygen in the hydrogen peroxide formed is derived solely from molecular oxygen and does not exchange with solvent water. Once formed in a living system hydrogen peroxide reacts or decomposes, and Chance (375) estimated that the steady state concentration of hydrogen peroxide maintained in this way in liver is a few micromolar. Considering that this minute concentration exists in the near-neutral pH of the tissue fluids, it must be concluded that the hydrogen peroxide is virtually undissociated and must react initially in this form.

One approach to the problem of establishing the nature of the interactions of hydrogen peroxide and hemoproteins lies in the study of the free iron protoporphyrin group in one or another of its oxidation states or complexes. This approach has been taken, for example, by Haurowitz (376) and Kikuchi (377) and the facts have been reviewed by Haurowitz (378) and George (367). It is found that free hematin, $H_2O\cdot Fe_p.OH$, forms a complex which may be represented as $H_2O_2\cdot Fe_p\cdot OH$; whereas heme, $H_2O\cdot Fe_p\cdot H_2O$, does not form such a complex. Similarly the parahematins react with hydrogen peroxide, but the hemochromogens do not. For example, the pyridine parahematin, $(Py \cdot Fe_p \cdot Py)^+Cl^-$, can be substituted successively with one and then two hydrogen peroxide molecules; with the hemochromogens attack on the porphyrin occurs.

The complexes formed by hydrogen peroxide with the hemoproteins have been studied more extensively, at first by visual spectroscopy and more recently by special rapid spectrophotometric techniques. All these complexes are so labile that they have not been isolated. Both peroxidase and catalase have been found to form three complexes; methemoglobin and metmyoglobin form only one complex. These are distinguishable according to their colors, and both Chance (375) and George (367) have described the differences in their reviews of this subject. Chance characterizes these complexes as primary, secondary, etc., according to the character of their spectra. It is certain of these complexes which take part in the enzymic action, and much effort has been devoted to understanding their respective roles. Chance (375) has pointed out that primary complexes occur only with the enzymically active hemoproteins and not with the catalytically inactive hemoglobin and myoglobin. There are also differences in the equilibrium constants of formation and dissociation for the two types of complexes. Also related to the mechanism of catalysis by these enzymes is the fact that the primary complexes are, relatively speaking, stable in the absence of excess hydrogen peroxide. This permits titration of the hemoproteins with hydrogen peroxide by special techniques, and such studies have shown that one hydrogen peroxide molecule is bound per iron atom. The course of these reactions and the form of the resulting complexes is not yet certain. Chance (375) and George (367) point out the effects of pH and foreign ions on the process and discuss some of the possibilities. For example, it is not clear in each case whether the hydrogen peroxide exists in the complex as the undissociated molecule or as the perhydroxyl ion, O_2H^-. Thus, three pathways to complex formation with the hemoprotein may be visualized:

$$Fe_p \cdot H_2O + H_2O_2 = Fe_p \cdot H_2O_2 + H_2O \qquad (43)$$

$$Fe_p \cdot OH + H_2O_2 = Fe_p \cdot OOH + H_2O \qquad (44)$$

$$Fe_p \cdot H_2O + H_2O_2 = Fe_p \cdot OOH^- + H^+ + H_2O \qquad (45)$$

Chance suggests that the enzymically active complex may be the one with the perhydroxyl ion.

Whatever the form of the active complex, it appears that the course of its reaction with a substrate occurs according to the following steps:

$$\text{Enzyme} + H_2O_2 = \text{Enzyme}.H_2O_2 \qquad (46)$$

$$\text{Enzyme}\cdot H_2O_2 + \text{Substrate} = \text{Enzyme} + \text{Products} \qquad (47)$$

In this simplified viewpoint all the enzymic actions are peroxidatic, the catalatic action being a special case in which a second molecule of hydrogen peroxide is the substrate.

Peroxidatic Enzyme Action

The action of peroxidase was first observed in 1863 by Schönbein (379), and the enzyme was named by Linossier (380) in 1898. It occurs widely in plant tissues as well as in milk and blood, but its presence in most animal tissues is not yet certain although evidence for it has been advanced. Besides activating hydrogen peroxide, peroxidase can also function with certain other peroxides. The rôle of peroxidase in biological processes has not yet been established with certainty, but considerable research has been devoted to determining the nature of its actions and an indication of the scope of this work may be given here. Elliot (381) investigated in 1932 the reactions with hydrogen peroxide catalyzed by peroxidase and listed tryptophan, tyrosine, a number of phenols (but not resorcinol), several diamines, nitrite, and iodide as undergoing reaction. Some of these, e.g., iodide (382), had been previously studied, but the work included considerable controversy. More recently studies have been made of the peroxidase action on thiols (383) (thiourea and dithiouracil), ascorbic acid (384), heteroauxin (385), diphtheria and tetanus toxins (386), aromatic amines (387), manganese compounds (388), and amino acids and proteins (389). Most of the work reported in these sources has been aimed at determining the biological significance of peroxidase. For example, Randall (383) reviews suggestions that it may participate in thyroxine synthesis, and Kenten and Mann (388) have given evidence for a rôle in the function of manganese as an essential micronutrient of plants. The work of Sizer (389) has added cystine and cysteine to the list of amino acids acted upon and has demonstrated the high degree of selectivity of peroxidase action on the biological activity of such proteins as hormones, toxins, antibodies, enzymes, fibrinogen, casein, and globulin. It was suggested that peroxidase may exert a regulatory action on such proteins. Balls and Hale (390) have shown that peroxidatic action is responsible for the annoying formation of brown pigment on freshly cut apple surfaces and have discussed means for suppressing this action.

The enzyme catalase also exerts peroxidatic action, although its outstanding capacity as a decomposition catalyst had long obscured and diverted interest from this property. According to the scheme of reactions (46) and (47), this peroxidatic action is quite understandable, but there remain marked differences in the character of the peroxidatic actions of catalase and peroxidase. In the studies of this action of catalase (373) it has been observed to depend on a continuous supply of hydrogen peroxide, such as generated by a dehydrogenase. There are also differences in substrate specificity. Catalase exerts peroxidase activity on primary and secondary alcohols and on nitrite. The rate of such reaction has been shown (391) to vary with alcohol chain length. Peroxidase, on the other hand, reacts with a wide variety of substances, as noted above. Thus there seems to be no group for which peroxidase is specific, whereas catalase in all its reactions reacts only with the hydroxyl group as in ROHCH, $HNO(OH)_2$, or H_2O_2; substitution of the hydrogen prevents catalase action. Thus the catalase-hydrogen peroxide complex can react with hydrogen peroxide or an alkyl hydroperoxide, but not with a disubstituted hydrogen peroxide (375). There are also differences in the kinetic order of the peroxidatic action of catalase and peroxidase. Chance (375) suggests that small concentrations of hydrogen peroxide may be regularly disposed of by the peroxidatic action of catalase and larger concentrations may bring into play the catalatic action. It has also been found (292) that when both catalase and peroxidase are present in a plant extract the catalatic action is suppressed until substrate oxidation is complete. It has also been pointed out that peroxidase is primarily a plant enzyme, catalase an animal enzyme, and the primary rôles of the two enzymes may be similar in the two kingdoms. Other substances, e.g., certain aldehydes (393), carotene (394), and ascorbic acid (395), have been reported to exhibit peroxidase-like activity.

Physiological Action of Hydrogen Peroxide

A substantial amount of work has been conducted with the aim of learning the effects of hydrogen peroxide on biologically significant substances or processes. These studies vary considerably in thoroughness and method of approach. Some are frankly model systems with the advantage of clearly specified conditions, but sometimes of doubtful pertinence to living systems. Others are based on organic substances or in vivo studies, being more realistic, but uncertain in regard to the influence of side-reactions and enzymes. Colonies of bacteria are frequently chosen for such studies and in such a system uncertainties may be introduced by the variation in hydrogen peroxide concentration during different growth stages, caused by differences in the partial pressure of oxygen present (396), or influenced by a growth factor (397).

The action of hydrogen peroxide on a number of typical carbohydrates was studied by Payne and Foster (398). The products were oxygen, hydrogen, carbon dioxide, carbon monoxide, formic and other acids, and aldehydes. The hydrogen, derived from formaldehyde, was a characteristic product. Pectic substances, other polysaccharides, and glycosides are also degenerated by hydrogen peroxide (399). These processes are affected by the presence of alkali (400), iron and copper (401), and ascorbic acid (402). A study (403) of various sugars as bacterial nutrients showed them to vary in their influence on hydrogen peroxide formation. The related substances, riboflavin (404) and streptomycin (405) also influence formation of or are affected by hydrogen peroxide.

The effect of hydrogen peroxide on fats has been little studied from the standpoint of biological processes. Fats and oils are relatively resistant and most studies (406) have been carried out with concentrated hydrogen peroxide or in the presence of heavy metal catalysts.

The most extensive studies of the effects of hydrogen peroxide on substances of biological interest have been made with proteins. The nature of such effects can vary considerably. More or less drastic treatment with hydrogen peroxide on albumin, gelatin, or tissue extracts can produce some aggregation (407), gelation (408), or even degradation to ammonia, ketones, and aldehydes (409). Less drastic treatment produces more subtle effects suggestive of actual physiological action. Studies of this kind have been made of effects on fibrin and fibrinogen (410)(the blood clot former), and globulin (411) (of importance in immune reactions), and myosin (412)(a muscle protein required for contraction); the studies of peroxidase actions on proteins by Sizer (389) are also of interest here. A certain degree of specificity appears to exist at this level of reaction; for example, it has been observed (413) that treatment of casein with hydrogen peroxide deprives it of the food value only of the methionine and tryptophan contained. These protein reactions appear to be of particular importance in relation to enzymes, many of which are affected. Studies of sperm survival (414), snake venom attenuation (415), intermediates in nitrogen fixation processes (416), and inactivation of bacterial and yeast dehydrogenase (417, 418), of papain (418, 419), of phosphatase (420), and of fig protease (421) as affected by hydrogen peroxide have been recorded. In most cases (not including urease and hexokinase (418)) there is interference with enzyme activity, and it is interesting in this respect to note a report (422) of the stimulation of catalase formation in a mold on treatment with hydrogen peroxide. Other protein materials which are deteriorated by hydrogen peroxide are hormones of the hypophysis (423) and red blood cells. This latter hemolysis of erythrocytes has been long known; only recently has it been observed (424) that α-tocopherol, or vitamin E, has a significant effect on this process.

Of particular interest in respect to the interactions of hydrogen peroxide and proteins is consideration of the effects on hair, wool and skin. All these substances are composed of protein materials, which although of varying amino acid composition, are quite similar. On the whole it must be said that these substances are relatively resistant to hydrogen peroxide, permitting its controlled use, as for bleaching of wool and hair or in the oxidation of previously applied dyes. Attack of these substances nevertheless does occur and the severity is dependent on time of contact, temperature, concentration, pH, and presence of heavy metal ions. It is apparent that the part of these proteins most susceptible to reaction with hydrogen peroxide is the disulfide bond, RSSR, carried by the amino acid, cystine. This fact assumes particular importance because the structure of cystine endows it with a special rôle in cross linking the long chain amino acid polymers which make up the protein. Attack at other bonds, such as that between carbon and nitrogen in the peptide link, RCONHR, or at salt or ester linkages, appears also to occur, but this is less vigorous and has received less study. Attention has been directed chiefly toward investigation of wool, and the chemical and physical results of hydrogen peroxide treatment under different conditions have been described (425, 426). Practical considerations of such treatment are discussed in Chapter 11. The widespread cosmetic use of hydrogen peroxide makes its action on human hair of special interest. Here again the attack is centered on cystine, being even more intense if anything, since human hair is outstandingly rich in this amino acid. Stoves (427) has presented experimental work and a review on this subject, pointing out the many-fold increase in severity of attack by hydrogen peroxide as pH is increased and how this impairs the setting properties of the hair. Stoves represented the disulfide attack as producing RSH and RSOH groups, and Coffart (428) reported hydrogen peroxide to combine reversibly with sulfhydryl groups formed in the skin, Smith and Harris (426) had earlier suggested steps of oxygen addition as in RSOSR, RSOSOR, RSO_2SOR, etc. Attack of the hair is catalyzed by certain metals, such as may remain from previous treatment, e.g., dyeing. Welwart (429) has reported charring of the hair and scalp burns caused by application of hydrogen peroxide in the presence of copper. On the other hand, when hydrogen peroxide is used to oxidize hair dyes, there is little damage to the hair since the dyes are preferentially attacked (427).

The use of hydrogen peroxide to bleach the hair is concerned with the decolorization of the pigment, melanin. Melanin is a high molecular weight derivative of tyrosine, and it may be of significance in regard to the superior effectiveness of hydrogen peroxide in bleaching melanin that tyrosine has been shown to be one of the few amino acids readily attacked by hydrogen peroxide. The failure of a parallel bleaching of the melanin in skin to occur is caused by the fact that hydrogen peroxide does not penetrate to the deeper layer of skin containing the pigment. Along with the bleaching of the hair, there is of course a certain amount of weakening and deterioration as discussed above; other possible contributing factors, such as action on natural oils or plasticizing fractions of the hair appear not to have been studied.

The experimenter seldom notices significant effects of hydrogen peroxide on taste and smell. As with water there is no flavor apparent, however, hydrogen peroxide does induce a sensation of astringency, sometimes described as ''metallic.'' An effervescence similar to that of soda water occurs as the hydrogen peroxide decomposes, giving a prickling sensation. At high concentration all these effects in the mouth are heightened to the point of painfulness, to say nothing of the hazard of burns, and such contact, as in the use of a pipette, is to be avoided. The prolonged use of lower concentrations in the mouth for medicinal purposes may lead to a condition of the tongue described as ''hairy;'' fortunately this is reversible and shortly disappears. It is difficult to characterize the smell of hydrogen peroxide. In fact, it is probably to be questioned whether it affects the olfactory cells or merely stimulates the general nerves of the nasal mucous membrane. Concentrated hydrogen peroxide manifests little odor unless occasion is deliberately taken to inhale near the surface of the liquid in a container or unless it should be spilled extensively. The sensation perceived is then reminiscent of ozone or of the halogens. The latter case is of interest in respect to the chemical characterization of hydrogen peroxide as a pseudohalogen. If circumstances arise to cause the dispersion of considerable hydrogen peroxide in the air, as in a mist, there ensues after a short time considerable irritation. Prolonged breathing in such an atmosphere induces gasping such as is encountered with ammonia or sulfur dioxide. This is accompanied by a sharp, burning sensation in the nasal passages on inhalation and exhalation.

Toxicity Studies

It is fortunate that such a reactive substance as hydrogen peroxide bears a minimal toxicity hazard; as recounted in Chapter 4, the outstanding dangers to be guarded against are spillage on the clothing and the possible resulting fire, and the potential destructiveness of uncontrolled decomposition of concentrated material. As far as direct chemical effects are concerned the organism is admirably adapted to withstand treatment with hydrogen peroxide, the skin being relative inert, and the tissue fluids having an efficient means for decomposing hydrogen peroxide encountered internally. There is little or none of the denaturation, solution, or charring encountered with other primary irritants. This is not to be taken to mean that hydrogen peroxide can be handled without concern, however, and the principles of safe handling, outlined in Chapter 4, should be adhered to strictly. In this section the results of some studies to establish the nature and limits of toxic effects of hydrogen peroxide will be reported. Because such effects are rarely to be encountered in practice, these studies are based largely on animal experimentation in the laboratory. An instance of the occurrence of asthma and eczema among workers in an Italian manufacturing plant, for example, was traced to sensitivity to ammonium peroxysulfate, and was not caused by hydrogen peroxide (430).

The toxicity of hydrogen peroxide to lower forms of life is familiar and has been much investigated; references to such work are given in the discussion of medical uses in Chapter 11. One characteristic of interest is the fact that a threshold concentration appears to exist, below which there is no effect. Tests (431) on yeast at pH 5.5 with peroxyacetic, peroxyphthalic, and peroxymaleic acids and hydrogen peroxide showed each to have a characteristic threshold, hydrogen peroxide having the highest and in addition, permitting the highest survival upon increasing concentration above the threshold. A similar effect was observed with fingerling trout (432). With higher forms of life such a result is also observed, but the much greater differentiation of function requires the effect to be specified clearly. Animal experiments have been divided according to tests on surfaces, such as skin and cornea, tests to show the effect of breathing the vapor or an aerosol, and studies of internal application. With rabbits it was observed (433) that application of 90 wt.% hydrogen peroxide to the shaved skin allowed absorption and caused death by gas embolism. However, there was a marked species variation in this respect. Cats, guinea pigs, rats, pigs, and dogs were much less susceptible in this manner and showed a correspondingly greater reaction on the skin at the site of application. Other factors are the greater susceptibility of the rabbit to embolism and differences in catalase content of the skin. In a study of the effect on human skin (434) the differences between the effect of 90 wt.% hydrogen peroxide on the palms and fingertips and on skin elsewhere were described. On the palms and fingertips the keratin is thick and nerve endings abundant. Here a thin smear of concentrated hydrogen peroxide causes strong prickling and formation of opaque white patches. Under the fingernails this is exceedingly painful. The whiteness is apparently brought about by refraction in the gas formed by decomposition under the first layer of skin and retained by the thickness of this layer here. More intense treatment may cause reddening and appearance of papules possibly followed by thickening. On other skin areas where the keratin is thinner, irritation occurs, but with less itching and the white appearance is confined to a few areas at the base of hairs. There is no evidence of penetration deeper than the first layer of skin, or stratum corneum, and all these effects disappear without trace. More severe effects have been observed on contact of the cornea of rabbits with hydrogen peroxide (433, 435). Amounts near one cc. of 90 wt.% hydrogen peroxide produced (433) effects like that on skin which were reversible. Greater amounts, near 3 cc, produced permanent opacity of the cornea. These results indicate a real need for concern that any hydrogen peroxide introduced into the eye be promptly washed out with water. Tests of the inhalation toxicity of hydrogen peroxide aerosols have been conducted (433, 436, 437) on mice, rats, dogs, and rabbits and include extensive records of blood and urine analysis on dogs undergoing such exposure (437). Such exposure causes burns of nose and paws, corneal damage, and pulmonary congestion. The corneal damage in rats was observed to follow an insidious course, developing slowly after exposure in the survivors of doses lethal to some animals. Dogs showed chronic irritation on exposure to 7 ppm. hydrogen peroxide for six months, and it was believed (437) that a concentration of 4 ppm. could be borne by men for long periods without effect. In these experiments there is difficulty in determining the dispersed concentration, since the hydrogen peroxide so readily condenses and decomposes. The effects of intravenous injection have been studied with several species (433,438).

In sublethal doses liver catalase and blood methemoglobin levels are affected. The dose of 90 wt.% hydrogen peroxide found lethal to 50% of injected rabbits was 0.015 cc/kg body weight. It has been observed (439) that this decreases with decreasing concentration, *e.g.*, to 0.003 cc/kg for 4 wt. %. The reason for this increasing toxicity of more dilute material appears to be that the dilute hydrogen peroxide penetrates the system more deeply before decomposing and blocking circulation. Concentrated material tends to be more completely decomposed at the site of injection. An instance has been reported (440) of the death of a person caused by inadvertant injection of hydrogen peroxide. Another gross effect to be observed on the internal application of hydrogen peroxide is necrosis of muscles so exposed (441). Ingestion of dilute hydrogen peroxide has been found without effect; more concentrated solutions cause irritation and bleeding and exposure to the danger of rupture from violent gas evolution.

There has also been much interest in the physiological effects of hydrogen peroxide at the molecular level. It has been found that hydrogen peroxide can induce mutation, and a number of references (442) describe the conditions and nature of this effect. This has sometimes been referred to as a radiomimetic effect and is of special interest in connection with the formation of hydrogen peroxide in living systems by ionizing radiation as discussed in Chapter 2. The mechanism of such mutagenic action has by no means been established with certainty, and several viewpoints and opinions are of interest. The mutation processes are closely related to carcinogenesis, and it has been pointed out by Jensen (Ref. 443, p.159) that there must be distinguished tumor genesis and tumor growth; factors of importance in one may not be so in the other. The mutagenic action of hydrogen peroxide also varies according to the accessibility of the cell nuclei to it (Ref. 443, p.116). Possible variation in catalase content throughout the cell may likewise influence the process. Schneider (Ref. 359, p.273) reports catalase to be nearly absent in the cell nucleus and to exist in soluble form in the cytoplasm; opinions differ on this, however, (443). It has nevertheless been established (444) that catalase is resistant to x-radiation.

A logical synthesis of the facts that x-rays both affect tumors and generate hydrogen peroxide is the idea that hydrogen peroxide might be of benefit in treatment of cancer. Tests of this have been made (Ref. 443, p. 149, 445) and are continuing, but so far no positive results have been noted. It is possible that the peroxide formed by radiation is an organic peroxide or hydrogen peroxide in the form of an addition compound, and the possibility has been suggested (Ref. 443, p. 149) that these elude decomposition by catalase. Much of the current opinion seems to be inclined to the idea that the effects of radiation are to be ascribed to free radicals formed and not to hydrogen peroxide as such which can also result from interaction of these free radicals (418). This does not alter the fact that hydrogen peroxide by itself is capable of causing mutation under suitable circumstances, but as Gray (446) pointed out, in spite of the similarity between this process and that initiated by radiation, it is true that x-rays break chromosomes along their entire length, whereas chemical action breaks them only at one bond. The chain length in processes involving radicals may also be of importance (Ref. 443, p. 159). Few other untoward effects of hydrogen peroxide at the molecular level have been suggested or investigated. A rôle in virus formation has been reported (447), and it has been suggested to play a part in anemia (448). Brain tissue has been demonstrated (449) to be readily poisoned by hydrogen peroxide, yet the injection of hydrogen peroxide into the whites of eggs did not impair the development of the embryo (450).

APPENDIX

Use and Significance of Electrode Potentials

For those not familiar with electrode potentials the following brief exposition of their use and significance with particular reference to hydrogen peroxide may be useful. By convention (4) these half-cell reactions are written with the electrons on the right, the reduced form of the substance on the left, and the potentials are counted above or below that of hydrogen, those reactions for which the reduced form is a better reducing agent than molecular hydrogen being given positive values. The electrode potential values designated E^0 refer to the potential which would be observed in solutions containing reactants and products all at unit activity. Gaseous substances are measured in atmospheres, solutes in molal units. Thus the values of E^0 for reactions (6) and (10) would refer to reaction of hydrogen peroxide at a concentration of approximately one molal and at pH = 0; values of E^0 for reactions (3) and (12) refer to pH = 14.

Given a list of such half-cell reactions and their potentials it is possible at inspection to determine whether it is favorable for a particular reaction to proceed to a marked degree. There is a tendency for the reduced form of a substance to be oxidized if the potential for its half-cell reaction is more positive than the half-cell reaction of the oxidant. In other words, reversal, <u>i.e.</u>, procedure from right to left, of any half-cell reaction, as written according to the above convention, will cause any reaction of more positive potential to proceed as written, <u>i.e.</u>, go left to right.

As an example of the oxidizing power of hydrogen peroxide it is seen that the potential of

$$2H_2O = H_2O_2 + 2H^+ + 2e^-, \quad E^0 = -1.76 \text{ v.}$$

is quite adequate to cause the oxidation

$$2H_2O + Pb^{++} = PbO_2 + 4H^+ + 2e^-, \quad E^0 = -1.46 \text{ v.}$$

That is, the reaction

$$H_2O_2 + Pb^{++} = PbO_2 + 2H^+, \quad E^0 = +0.30 \text{ v.}$$

may proceed from left to right as shown, with considerable potential available for the conversion of plumbous ion to lead dioxide. In the scheme of chemistry lead dioxide is generally thought of as a reasonably powerful oxidizing agent itself, and the fact that hydrogen peroxide possesses the capability of producing it from its reduced form illustrates the oxidizing power of hydrogen peroxide. There are, in fact, only a few oxidants which exceed hydrogen peroxide in oxidizing potential.

To illustrate the reducing action of hydrogen peroxide, the potential of

$$Cl^- = 1/2\,Cl_2 + e^-, \quad E^0 = -1.34\text{ v.}$$

is sufficiently less positive than the potential of

$$H_2O_2 = 2H^+ + O_2 + 2e^-, \quad E^0 = -0.67\text{ v.}$$

.to insure that the reaction

$$H_2O_2 + Cl_2 = 2H^+ + 2Cl^- + O_2$$

will proceed.

On the other hand, the potential of the half-cell reaction

$$2F^- = F_2 + 2e^-, \quad E^0 = -2.65\text{ v.}$$

is sufficiently negative that the oxidation of fluoride ion according to the reaction

$$H_2O_2 + 2F^- + 2H^+ = 2H_2O + F_2$$

cannot proceed appreciably. Similarly, the reversal of the reaction

$$Fe = Fe^{++} + 2e^-, \quad E^0 = +0.44\text{ v.}$$

will not permit the reaction

$$H_2O_2 + Fe^{++} = Fe + 2H^+ + O_2,$$

that is, hydrogen peroxide is not a sufficiently strong reducing agent to convert any considerable amount of ferrous ion into metallic iron.

The conflict between the convention established, which requires the writing of each half-cell reaction in a particular direction, and the tendency to think in terms of hydrogen peroxide as a reactant, that is, always appearing on the left of an equation, may make for confusion initially. Thus it may seem artificial to write as above,

$$2H_2O = H_2O_2 + 2H^+ + 2e^-, \quad E^0 = -1.76 \text{ v.}$$

instead of

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O, \quad E^0 = +1.76 \text{ v.}$$

However, if the conventional procedure is followed no uncertainties will arise regarding the significance of the sign and magnitude of the electrode potential for a reaction. This protocol will also be found to aid in maintaining a consistent attitude toward the direction of a particular reaction. For example, the emphasis, but not the procedure, is changed in thinking of water as a reducing agent or of oxygen as an oxidant instead of hydrogen peroxide as in the reactions given above. These inverted attitudes of course come under the categories of formation of hydrogen peroxide or of its rôle as an intermediate in the conversion of oxygen to water or vice versa. Both these topics are considered more fully in Chapters 2 and 3.

The examples given above show how half-cell reactions may be added to yield a complete reaction. In this procedure the potentials may also be added to give the potential for the complete reaction, that is, the potential which would be realized if an electric cell were constructed in which the reaction occurred. It is to be emphasized that this potential refers to a reversible cell operating as written. If certain of the steps in the reaction are not reversible the potential will be different. Or the proposed reaction may not occur because of an impossible intermediate reaction.

Half-cell reactions may also be combined to give a third half-cell reaction. This is illustrated by the procedure in which the hydrogen peroxide-water couple is obtained from the known values for the hydrogen peroxide-oxygen couple and the water-oxygen couple, <u>viz.</u>

$$\begin{array}{lcll} 2H_2O & = & 4H^+ + O_2 + 4e^- & E^\circ = -1.23\text{ v.} \\ H_2O_2 & = & 2H^+ + O_2 + 2e^- & E^\circ = -0.69\text{ v.} \\ \hline 2H_2O & = & H_2O_2 + 2H^+ + 2e^- & E^\circ = -1.76 \end{array}$$

The procedure for calculating

$$E^\circ,\ \left[4(-1.23) - 2(-0.69)\right]/2 = -1.76\text{v.}$$

illustrates that volt-equivalents must always be added when half-cell potentials are combined in any way.

The electrode potentials can of course be converted into free energy values through the relation $\Delta F^\circ : -n\mathcal{F}E^\circ$, $\mathcal{F}$ having the value 23,060 cal/volt-equivalent. The free energy may then in turn be used to calculate the equilibrium constant for the reaction: $\Delta F^\circ = -RT \ln K$, or at 25°C, $\Delta F^\circ = -1364.3 \log K$. For example, the potential for the oxidation of plumbous ion by hydrogen peroxide was given above as 0.30 volts. The free energy change for this reaction is then $\Delta F^\circ = -(2)(23060)(0.30) = -13,840$ cal. This result also might have been obtained directly from a tabulation of free energies of formation. The equilibrium constant is then calculated as K = antilog $(-13,840/-1364.3) = 1.4 \times 10^{10}$. Thus if the difference between concentrations and activities may be ignored, the concentrations in a hydrogen peroxide solution in contact with lead dioxide stand in the relation $(H^+)^2/(H_2O_2)(Pb^{++}) = K = 1.4 \times 10^{10}$. At unit pH then in a one molal hydrogen peroxide solution (about 3 wt.%) lead dioxide will appear after the concentration of plumbous ion has been raised [illegible] 7×10^{-11} molal — provided the reaction goes at all. At [illegible] the plumbous ion concentration which will support [illegible] ertion of lead dioxide becomes even more minute.

[illegible] detailed discussion of the use and significance of elec[illegible] eral, as well as numerical values, is given

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CHAPTER EIGHT

DECOMPOSITION PROCESSES

The readiness with which hydrogen peroxide may be decomposed into water and molecular oxygen is a characteristic which has been familiar since the discovery of this substance. It is a property both useful and troublesome and one brought about in many ways. It has been studied long and intensively, yet the understanding of it is even now relatively limited in many respects. In Chapter 7 the characteristics of hydrogen peroxide which determine its thermodynamic and mechanistic behavior are discussed. The processes under discussion in this chapter are governed by the same principles, but for the most part the understanding of decomposition is less advanced. There are several factors which contribute to this state of affairs. Decomposition processes are alike in that they all deal with the net reaction,

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (1)$$

which clearly includes both oxidation and reduction of hydrogen peroxide. Many of the pathways whereby this process is accomplished are believed to involve chain reactions. In the case of heterogeneous catalysis the manner whereby the action of the catalyst is exerted is understood only in a qualitative way. Although these bars to the development of satisfactory mechanisms for decomposition processes exist, the description of decomposition processes at a less sophisticated level can be given more completely. The development of a survey of this kind including direction to the literature is the purpose of this chapter. The problem of hydrogen peroxide stability is basically that of minimizing decomposition processes; this subject is treated separately in Chapter 9 because of its great practical importance and because the rates of decomposition of concern there are of a quite different order of magnitude. The use of decomposition processes for the generation of oxygen or power is considered in Chapter 11. The subject of hydrogen peroxide decomposition as a whole has never been reviewed adequately. In a few instances there exist outstanding reviews of limited aspects and these are mentioned in the appropriate sections below.

VAPOR PHASE DECOMPOSITION

It is only relatively recently that some understanding has been gained of the facts regarding vapor phase decomposition, particularly in regard to explosive decomposition. In this section the experimental work and theories dealing with decomposition of the vapor are reviewed. Experimental methods for generating hydrogen peroxide vapor are discussed in Chapter 4. Decomposition of the vapor initiated by radiation is discussed briefly on page 153.

Experimental

The vapor-phase decomposition of hydrogen peroxide was first investigated in 1923 by Hauser (1), who observed decomposition on a number of surfaces of various types, and by Hinshelwood and Prichard (2), who reported in a brief study that the decomposition in glass bulbs at 75°C. was a first order surface reaction. Elder and Rideal (3) in 1927 reported that the reaction came to an end when about 20% of the hydrogen peroxide vapor in their quartz vessel was decomposed, although complete decomposition was obtained after heating the quartz bulb to about 300-400°C. However, Kistiakowsky and Rosenberg (4) in 1937 reported complete decomposition on quartz, and no other observation has been reported in which abrupt cessation short of complete reaction was noted. Giguère (5) has made the plausible suggestion that Elder and Rideal were actually measuring the vapor decomposition in the connecting tubes to their vessel, while the actual rate in the quartz vessel itself was negligible.

The above studies are primarily of historical interest. More recent studies (5, 6, 7, 8) have now established that at temperatures up to about 400°C. and partial pressures of hydrogen peroxide of a few millimeters of mercury, the reaction is completely heterogeneous even in vessels made of the most inert surfaces studied, such as Pyrex. At temperatures in the region of 470 to 540°C. and at partial pressures of 1 to 2 millimeters of mercury (total pressure of one atmosphere) there is evidence that at least a part of the decomposition is homogeneous in glass vessels which have been treated with boric acid to reduce the activity of the surface (9). Very recent studies (10) at partial pressures of several millimeters of mercury (total pressure of one atmosphere) in a ''Pyrex'' glass flow apparatus at temperatures of 120 to 490°C. showed an abrupt change from heterogeneous to homogeneous decomposition at 425°C. At atmospheric pressure vapor containing 26 mole per cent or more hydrogen peroxide (198 mm.Hg partial pressure H_2O_2), the remainder being an inert gas, may be exploded by contact with a catalytic or hot surface (11), thus demonstrating that at sufficiently high concentrations, a completely homogeneous reaction can be propagated. The partial pressure of hydrogen peroxide in the limiting explosive composition decreases as the total pressure is decreased becoming for example, 22 mm. Hg at a total pressure of 40 mm, the lowest pressure studied. (The explosive characteristics of hydrogen peroxide vapor are also discussed in Chapter 4.)

The rate of the heterogeneous vapor-phase decomposition is characterized by an extraordinary sensitivity to slight changes in the physical nature of the reaction vessel surface, as well as its chemical composition. Because of this, it is not surprising that considerable variation has been found between the results reported by different workers on the magnitudes of the reaction rate, activation energy, or the effect of water vapor or other gases on the reaction. Salient observations of recent workers are summarized below.

Kondrat'eva and Kondrat'ev (7) passed moist air containing 0.01 to 0.4 mm. Hg of hydrogen peroxide through a ''molybdenum glass'' tube at temperatures from room temperature up to 175°C. They reported the reaction under these conditions to be second order with an activation energy of 8.5 kcal/mole. Rinsing the reaction vessel with potassium chloride or copper nitrate solutions activated the surface to the point that considerable decomposition of hydrogen peroxide vapor was observed at room temperature.

Mackenzie and Ritchie (8) studied the decomposition by a manometric method in silica vessels at 80°C, covering a three-fold variation in partial pressure range with the initial total pressures varying from 0.6 to 1.2mm. Hg. The procedure involved evacuation of the reaction vessel, followed by introduction of hydrogen peroxide by vaporization from a quantity of highly concentrated liquid. The rate of reaction was followed by the pressure rise. They reported water vapor to have a pronounced retarding effect. High ratios of oxygen or nitrogen partial pressure to that of hydrogen peroxide also resulted in somewhat slower rates, which may well have been caused by these gases reducing the rate of diffusion of hydrogen peroxide to the vessel surface. From these studies the decomposition rate was formulated by Mackenzie and Ritchie as second order with respect to hydrogen peroxide, with a term to account for the retarding effect of water vapor.

In a similar type of apparatus, Baker and Ouellet (6) used vapor containing initially about 70-75% hydrogen peroxide, the remainder being water vapor, at pressures of 10 to 20 mm. Hg and at temperatures from 70° to 200°C. They found the reaction to be first order up to least 80% decomposition, at temperatures up to about 140°C. Above 140°C. in their apparatus, the reaction was of irregular order, and the temperature coefficient was very small. Studies in the temperature range of 80° to 130°C. showed that the decomposition rate was slower in fused Pyrex than in ordinary Pyrex, and faster in lime soda glass than in either Pyrex vessel. The rate increased with surface-to-volume ratio, but adventitious variations between vessels of supposedly the same nature caused a several-fold variation in rate. Apparent activation energies for different Pyrex surfaces varied between 13.4 and 19.0 kcal/g mole. Addition of small quantities of air, oxygen, carbon dioxide, or water vapor did not change the reaction rate.

In a continuation of the above work and in a similar apparatus, Giguère (5) made very careful and extensive observations of the effect of surface treatment on the reaction rate, at total pressures of about 5 mm.Hg, the vapor being produced by evaporation, with some fractionation, of 95 - 99% hydrogen peroxide. In each case described below, the reaction was studied in a 1 liter spherical reaction vessel, and the first order rate expression was formulated in terms of the partial pressure of the hydrogen peroxide. The variation in activity of different surfaces is indicated in Table 1. To have a unified basis for comparison, for each case there is quoted the approximate temperature at which the first order rate constant (sec^{-1}) equals 10^3, as interpolated from Giguère's data, and also the apparent activation energy he reported.

It is seen that fusing a Pyrex surface was found to reduce greatly its activity, but treatment with hot chromic acid destroyed the inertness. Possibly tiny amounts of chromium oxides, which are catalytically active, are left on the glass surface, although it is known that chromic acid treatment also substantially increases the surface area of glass, which could also cause an increased rate of decomposition per unit of superficial area. (It has been found in other work that chromic acid treatment produces a glass surface which is more active than that produced by other cleaning methods. The activity persists even after numerous washings.) Re-fusing restored the surface to nearly the same low activity and the effect of these alternate treatments on activity could be repeated at least a few times. Washing with hot water or etching with hydrofluoric acid increased the activity and coating the glass surface with a salt resulted in a surface which was substantially more active than that produced by any of the other treatments. Temperature extrapolation indicates that the salt-coated Pyrex vessel gave a rate of decomposition about 10^5 times that in the fused Pyrex vessel. Two similar soda-lime vessels of the same make, given identical treatments, gave several-fold different reaction rates. Transparent silica vessels of two different makes were greatly different in their activity. Fused glass was found to become more active on aging until it reached a kind of equilibrium state. The activating effects of washing with hot water or acid are generally attributed to a selective solution of the more soluble

Table 1

Activity of Some Surfaces in Causing Hydrogen Peroxide Vapor Decomposition, from Giguère (5)

Surface	Approximate temperature at which k (sec.$^{-1}$) equals 10^3, °C	Activation Energy, kcal/mole
1. Pyrex vessel (III)	140	12.6
2. Vessel III fused	240	18.7
3. Vessel III cleaned with hot chromic acid	125	7.8
4. Vessel III, fused again	210	15.8
5. Vessel III, washed with hot water	157	16.1
6. Vessel III, coated with trisodium phosphate	65	21.6
7. Vessel III, etched with hydrofluoric acid	170	8.4
8. Soda-lime vessel (V)	100	11.4
9. Soda-lime vessel (VI) (superficially identical with V)	60	10.5
10. Transparent silica vessel (Vitreosil) (VII)	125	12.2
11. Vessel VII, fused	150	11.6
12. Transparent silica vessel (Amersil) (VIII)	70	10.3
13. Pyrex flask coated with tin surface (IX)	70	13
14. Pyrex flask coated with aluminum surface (X)	90	12

components of the glass, leaving a spongelike structure. After coating vessels with pure tin or aluminum mirrors deposited by an evaporation method, rates comparable to silica and soft glass vessels were obtained. However, Giguère points out that such metal surfaces may have far different activities than those formed in other ways on massive metal. It is seen that the most inert surface was obtained by fusing Pyrex glass. The greater activity of the silica surface over Pyrex is probably caused by its having more porous surface. In a two-liter Pyrex vessel of low activity, the temperature coefficient corresponded to an apparent activation energy of 7.5 to 8.0 kcal/mole at all temperatures up to 420°C., the highest studied, indicating that no homogeneous reaction apparently occurred.

There was no consistent correlation between the apparent energy of activation and the reaction velocity. Giguère attributes this lack of correlation to a variation in the number of adsorbed molecules, related to factor A in the modified Arrhenius equation $k = Ae^{-(E-\lambda)/RT}$, where E is the true energy of activation and λ the energy of adsorption of the reactant. Giguère (5), Baker and Ouellet (6), Mackenzie and Ritchie (8), and Tamres and Frost (12) have all observed adsorption of vapor to occur upon its introduction into the reaction vessel under some circumstances, as evidenced by an initial decrease in pressure or induction period followed by the expected pressure increase due to decomposition. Various other tests have confirmed that at least a part of the vapor adsorbed was hydrogen peroxide. In the studies by Giguère on silica, the phenomenon was observed at temperatures up to 175°C. The adsorption could presumably still occur at much higher temperatures, even if not detectable in the particular apparatus used. As would be expected, the phenomenon is more pronounced, the closer the partial pressure of hydrogen peroxide approaches the vapor pressure which would exist above the condensed phase. For example, at room temperature and initial vapor pressure of 0.5-0.7 mm.Hg and using highly concentrated hydrogen peroxide vapor, Tamres and Frost (12) found about three times as much hydrogen peroxide to be adsorbed as was present in the vapor phase, in a vessel packed with soft glass wool. The amount of adsorption occurring will also vary substantially with changes in the character of the surface. Thus Giguère found that his ''induction period'' did not occur in a silica vessel if it had been fused. Presumably the fusing sealed up the pore structure of the surface, thus greatly reducing the area available for adsorption, as well as possibly changing the character of the surface.

The patents of Cook (13) disclose that a coating of boric acid or various combinations of boric acid, borates, and certain oxides on the surface of reaction vessels retards the rate of decomposition, particularly if the coating is fused at a temperature of 300°C or higher. It is believed that the effect is due largely to the presence of boric acid or boric oxide as well as to the smooth surface provided by the fusing process.

McLane (9) reported that coating a Pyrex vessel with boric acid followed by fusing in a furnace at 500-520°C overnight gave a far lower rate of decomposition than was obtained in uncoated Pyrex, confirming Cook's work, and he also found that it was possible to obtain consistent results with different vessels or with the same vessel upon cleaning and recoating by this method. In such vessels, McLane studied the decomposition of hydrogen peroxide vapor at partial pressures of 1 to 2 mm. Hg in the presence of one atmosphere of oxygen or nitrogen, using a flow system and temperatures of 470-540°C. Two series of vessels were used, one series having a surface to volume ratio of about 7 cm^{-1}, the other about 3 cm^{-1}. The reaction rate was found to follow a first-order relation, and the rate constants in the vessels of higher surface-volume ratio were generally from about 0 to 50% higher than those in the lower surface-volume ratio vessels. The reaction rates were about 30% greater in nitrogen than in oxygen. The apparent activation energies were 40 kcal/mole in the vessels with surface-volume ratio of 7 cm^{-1} for both nitrogen and oxygen, and 50 kcal/mole in the 3 cm^{-1} vessels, in the presence of nitrogen. Insufficient data on oxygen were collected in the latter vessels to calculate an activation energy. On the basis of the effect of surface-volume ratio, and the magnitude of the activation energy, it was concluded that probably a portion of the reaction occurred in the homogeneous gas phase.

The results of a brief study by Harris (14) are consistent with the information reported from other sources. Harris bubbled a stream of nitrogen at one atmosphere through about 65% aqueous hydrogen peroxide held at 52°C and then passed the gas through a heated quartz reaction tube. The fraction of peroxide decomposed was quite variable and was increased by coating the tube with potassium chloride, adding mercury, or packing the tube. In the clean unpacked, experimental vessel, the half life was about 0.5 seconds at 505-525°C; this compares fairly closely with half lives of 0.7 and 0.9 seconds reported by McLane for hydrogen peroxide in the presence of nitrogen and oxygen respectively, with the use of vessels at 521°C coated with boric acid. Considering the large variations observed in the activities of various surfaces, this surprisingly good agreement in the reaction rates reported separately by McLane and Harris at this temperature level is consistent with the conclusion that a substantial portion of the reaction was homogeneous in both cases.

Very recent studies by Stein (10) show clear evidence of a transition from heterogeneous to homogeneous reaction as the temperature is raised. A vapor mixture of water and hydrogen peroxide was passed at one atm. through carefully cleaned ''Pyrex'' glass tubes in a flow apparatus, the partial pressure of the hydrogen peroxide being several mm. Hg, and the rate of decomposition was determined from analyses of the inlet and exit gases under steady-state conditions. The reaction rate was found to be first order in the heterogeneous range and second order in the homogeneous range. Figure 1 shows the observed rates of decomposition as a function of temperature, as expressed for a partial pressure of 0.02 atm. The abrupt shift from heterogeneous to homogeneous reaction at about 425°C. is very evident. Further evidence of the shift in mechanism is shown by the fact that two different reaction tubes showed substantial differences in reactivity in the lower temperature region but more in the high temperature region.

Additional studies on the decomposition of hydrogen peroxide vapor, which are rather difficult to interpret, have been reported

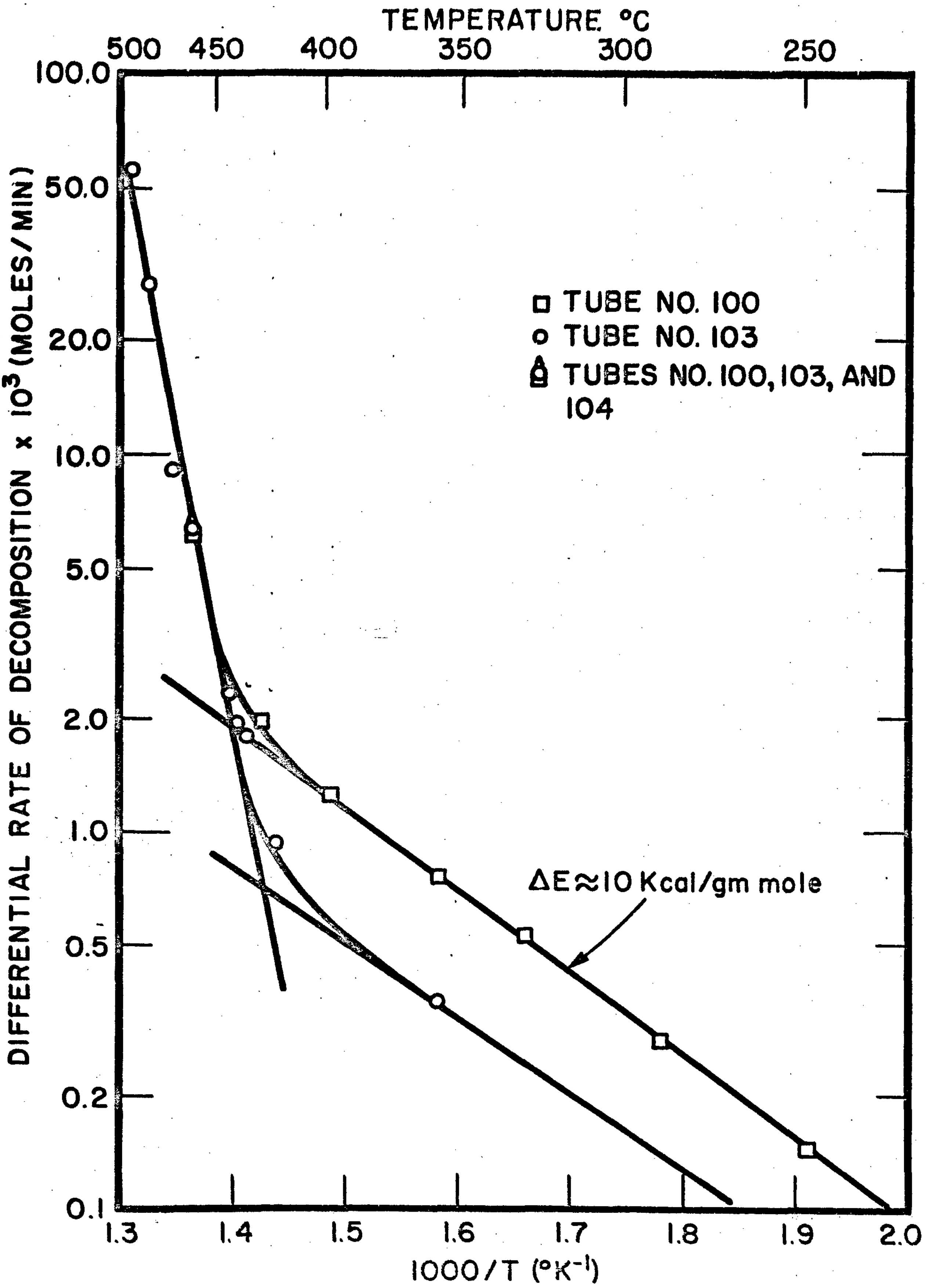

FIG. 1 – EFFECT OF TEMPERATURE ON THE DECOMPOSITION OF HYDROGEN PEROXIDE VAPOR. ($p_{H_2O_2}$ = 0.02 ATM.)

by Mizuwatari and Nagai (15) and Suito (16). The very few studies reported on photochemical decomposition of the vapor are summarized on p. 153 .

If a concentrated aqueous hydrogen peroxide solution is heated to a temperature at which the vapor produced lies within the explosive composition range (see Chapter 4), it is possible to ignite the vapor and produce a continuously-propagating flame. For example, on heating a vessel containing concentrated hydrogen peroxide to a temperature near the boiling point, the vapor can be ignited by a spark, hot wire, or catalytically-active surface, or even may become ignited from the vessel wall itself. Once ignited, heat transferred downward from the flame causes continuous vaporization of the liquid, and the flame will continue to ''burn'' quite evenly without supply of any external heat as long as concentrated liquid hydrogen peroxide is available. Flames of this type have been observed by Hart (17) at total pressures of 20 mm Hg or higher and they have also been observed at atmospheric pressure in studies in other laboratories. This phenomenon is a striking one to observe. For instance, if a beaker of 90 wt.% hydrogen peroxide is placed on a hot-plate the liquid becomes frothy and throws out mist and steam as boiling ensues. When ignition of the vapor occurs the mist instantly disappears, the surface of liquid becomes quiescent, frothing ceases, and the volume of liquid diminishes at a very high rate.

The ignition limits of vapor mixture of hydrogen peroxide and water at atmospheric and sub-atmospheric pressure are presented in Chapter 4. Figures 2 and 3 show the effect, at ②00 mm. Hg total pressure, of varying the nature and concentration of the inert gas present (18). Substitution of helium, nitrogen, or oxygen for a portion of the water vapor has no effect on the ignition limit, whereas carbon dioxide has some dampening effect. The interpretation of these data is uncertain since the role of the inert gas may be through its heat capacity, which affects the adiabatic reaction temperature, through its thermal conductivity, which affects the rate of heat dissipation from the reaction zone, in its effect on the rate at which free radicals formed in the reaction can dissipate by molecular diffusion, or in its

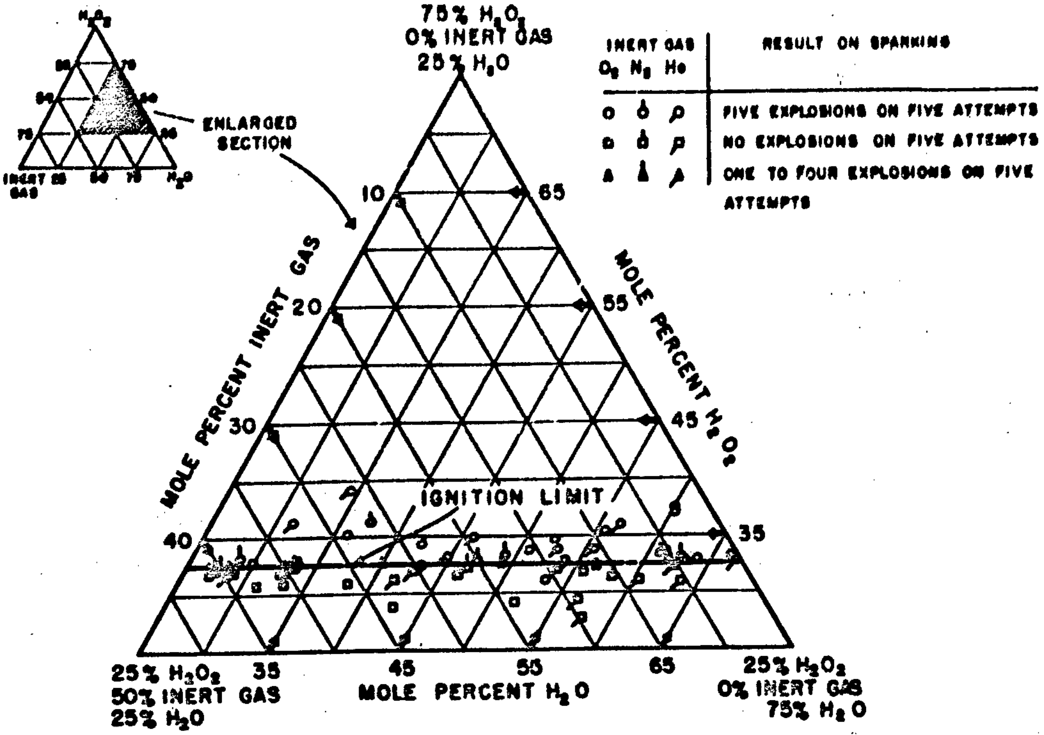

FIG. 2 — IGNITION LIMIT IN MIXTURES OF HYDROGEN PEROXIDE — WATER VAPOR — AND AN INERT GAS — TOTAL PRESSURE, 200 mm MERCURY.

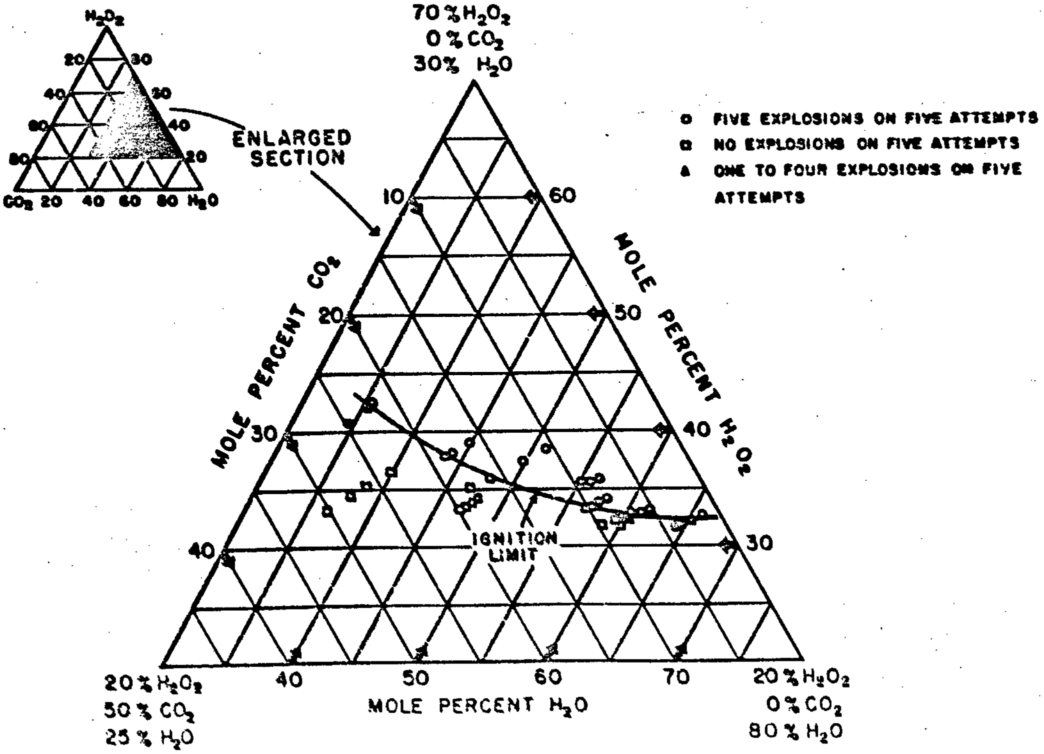

FIG. 3 — IGNITION LIMIT IN THE SYSTEM — HYDROGEN PEROXIDE — WATER VAPOR — CARBON DIOXIDE — TOTAL PRESSURE, 200 mm MERCURY

effectiveness in transferring energy in three-body collisions. The heat capacity effect is probably the most important. The adiabatic reaction temperature of the limiting ignition composition for the system hydrogen peroxide-water is, for example, 780°C. at one atmosphere pressure and 880°C. at 200 mm Hg total pressure-values that are much lower than those encountered in most fuel-oxidant systems.

Mechanism

In many cases it has been found that the relative activities of various surfaces in causing decomposition in the vapor phase is about the same as that observed in the liquid phase. Thus in both phases, Pyrex glass is more inert than soda glass, and acidic surfaces tend to be more inert than basic surfaces. With both phases, treatment with either chromic acid or hydrofluoric acid increases surface activity. Roiter and Gaukman (19) reported the same conclusion with catalytically active surfaces; they stated that the rate of decomposition increased in the order: lead dioxide, manganese dioxide, platinum and the relative activities of these three surfaces, as measured by them, were about the same in the liquid as in the vapor phase. These various observations suggest that the heterogeneous decomposition mechanism is the same in both phases under some experimental conditions. The amounts of adsorption reported to occur in vapor phase decomposition correspond in several cases to an adsorbed layer many molecules thick, which could behave in many ways like a liquid. This analogy must be pursued with caution, however. The amount of hydrogen peroxide adsorbed must decrease with increased temperature, probably with accompanying changes in the mechanism. Also liquid phase decompositions may frequently involve solution of ions into the bulk of the solution, thereby contributing a possibly unsuspected reaction to the observations made.

The mechanism of the homogeneous gas-phase decomposition can be inferred from energy considerations. The initial step, rupture of the hydrogen peroxide molecule, can only occur in two possible ways -- rupture of the O-O bond to form two OH radicals or rupture of an O-H bond to form an HO_2 radical and an H atom. The first of these possibilities requires 52 kcal per mole as compared to 90 kcal. per mole for the splitting of an O-H bond and would therefore appear to be far more probable. This initiating step is supported by the work of Urey, Dawsey, and Rice (20) who studied the emission spectrum of hydrogen peroxide when it was streamed rapidly through a cool discharge tube. They found water bands caused by OH radicals but no molecular or atomic hydrogen.

The energy changes for all possible chain carrying steps involving the species that may be present in this system may be calculated from the values and sources cited in Chapter 5. All possible branching mechanisms are accompanied by unfavorable, i.e., endothermic, energy changes and therefore the homogeneous reaction is probably propagated through the gas by unbranched chains. The only straight-chain mechanism involving exothermic reactions initiated by the activated OH radicals from the initial step is

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad (2)$$

$$HO_2 + H_2O_2 \longrightarrow OH + H_2O + O_2 \qquad (3)$$

These reactions involving free radicals probably proceed with little or no activation energy.

The chain-consuming steps are one or more of the reactions

$$2OH + M \longrightarrow H_2O_2 + M \qquad (4)$$

$$2HO_2 + M \longrightarrow H_2O_2 + O_2 + M \qquad (5)$$

$$OH + HO_2 + M \longrightarrow H_2O + O_2 + M \qquad (6)$$

the wall, inert gas, or hydrogen peroxide molecules acting as the third body. In the case of gas-phase flames and explosions, the heat generated by the over-all reaction is presumably sufficient to cause the liberation of further OH radicals from H_2O_2 molecules and thus bring about a propagating reaction which is essentially thermal in nature.

The above mechanism is consistent with observations made on on the ignition limits of hydrogen peroxide vapors, discussed above and in Chapter 4. The fact that the partial pressure of hydrogen peroxide at the ignition limit increases steadily with the partial pressure of the inert gases present also suggests an explosion which is essentially thermal rather than branched-chain in nature.

If hydorgen peroxide vapor is flowed past an active catalyst surface, the possible rate of decomposition on the surface can be much greater than the rate of transport of hydrogen peroxide to the surface, thus producing a situation where the actual observed rate of reaction is limited by the rate of diffusion of matter. In such a case a further increase in catalyst activity causes no change in the measured rate of reaction. The decomposition rates of hydrogen peroxide vapor have been studied on passage through a cylindrical tube, the wall of which was a very active catalyst, and also through a bed of catalyst spheres (21). It was shown that such a system is diffusion-controlled and the rates of decomposition observed agreed closely with those predicted from correlations of mass transfer data obtained from non-reacting systems. In such a diffusion-controlled reaction, the surface of the solid reaches a temperature substantially above that of the bulk of the gas flowing past it, and this temperature can be estimated by considering the characteristics of the simultaneous heat and mass transfer between the bulk of the gas and the solid.

DECOMPOSITION BY RADIATION

The reactions induced by radiation are commonly divided into two groups, photochemical processes, which are usually caused by ultraviolet radiation, and radiochemical processes, which proceed from the absorption of higher energy radiation such as x and γ radiation and that consisting of particles such as protons and α and β radiation. The latter group of processes is characterized by the appearance of ionization. Reference should also be made to the discussion on formation of hydrogen peroxide by radiation processes in Chapter 2.

Photochemical Processes

There is a large number of fragmentary and qualitative reports in the early literature of the decomposition of hydrogen peroxide by light and the effects of various solutes on the observations made. Systematic investigations began in about 1910 but correlation of the data of various investigators is rendered difficult by the fact that earlier workers frequently have not specified the values of variables later found to be of importance in determining quantum yields. Chief among these are intensity and frequency of radiation, pH, the nature of foreign materials such as commercial inhibitors in the solutions, the nature of the container walls, and correction for the concurrent dark reaction. The extreme sensitivity of the decomposition rate to trace impurities has been a particular source of difficulty; reproducible results on either the thermal or photochemical decomposition can be obtained only with the most meticulous experimental techniques.

The following recent experiment (22) illustrates the magnitude of the photochemical decomposition rate which may be observed. Ten c.c. of 90 wt.% aqueous hydrogen peroxide, free from inhibitors, was exposed at 25°C in a quartz container to radiation from a 100-watt mercury vapor lamp rated as emitting 2.2 watts of radiation in the near ultraviolet, 3200-3800 Å. The resulting hydrogen peroxide decomposition rate was 0.25 per cent per hour, which was about 70-fold that observed in the absence of radiation under otherwise the same conditions.

The absorption of ultraviolet radiation by hydrogen peroxide is discussed in Chapter 5. The spectrum consists of a continuum without structure, extending from about 3800 Å to beyond 2000 Å. The extinction coefficient is substantially independent of concentration below 50 wt.% hydrogen peroxide, although Beer's law is not strictly obeyed. Similarly, the extinction coefficients for aqueous solutions and for mixtures of hydrogen peroxide vapor with air, compared at the same values of concentration times path length, appear to be essentially the same.

Experimental Results. There is now general agreement that in dilute to moderate concentrations (about 0.2M) and at moderate intensities of absorbed radiation (below about 10^{17} quanta/ℓ sec.) the rate of decomposition (moles per liter per second) is directly proportional to the concentration of hydrogen peroxide and to the square root of the intensity (23, 24, 25, 26). At higher concentrations and moderate radiation intensities, there has been considerable disagreement. Thus, according to Qureshi and Rahman (27), the quantum yield becomes independent of concentration at concentrations of from 0.3 to 0.9M; and in the work of Allmand and Style (23), the observed effect of concentration varied, depending upon whether the concentration was reduced by adding distilled water or by allowing decomposition to proceed under radiation. However, in recent and very careful work, Dainton and Rowbottom (26) indicated that for intensities up to about 10^{17} quanta/l. sec. and concentrations up to 20 molar, the rate is still directly proportional to the hydrogen peroxide concentration and to the square root of the intensity, and the discrepancies of the earlier work may well be attributed to the presence of traces of inhibitors or impurities in the hydrogen peroxide used.

At very low radiation intensities and concentrations below 0.1-0.5 M, there are also some early reports that the yield tends to become independent of radiation intensity (23, 24, 28). At very high radiation intensities (above about 3×10^{17} quanta/l. sec.), Lea (25) has reported that the quantum yield becomes independent of concentration from 0.01 to at least 0.04M. Heidt (29), working at intensities of 5 to 12×10^{17} quanta/l. sec., concluded that there was a tendency for the quantum yield to increase with concentration from 1.8 to 4.2M. However, the increase is barely significant, considering the reproducibility of the data, and, in any case, is far less than linear.

Hydrogen peroxide is not affected by exposure to light of wave length greater than about 3800 Å. It has absorption bands in the infra-red, but is not decomposed by light of these frequencies. Data on the effect of wave length in the ultraviolet region on the decomposition are inconclusive. Henri and Wurmser (28) reported a 25 per cent decrease in quantum yield as the wave length was increased from 2080 to 2800 Å at concentrations of 0.02-0.05 M and radiation intensities in the neighborhood of 10^{17} quanta/l. sec.; Allmand and Style (23) reported a 100% increase in yield as the wave length was increased from 2750 to 3650 Å at concentrations of 0.5 - 11.5M and intensities in the same range.

TABLE 2

EFFECT OF WAVELENGTH ON TEMPERATURE COEFFICIENT OF RATE OF PHOTOCHEMICAL DECOMPOSITION

Wavelength, Å	Temperature Coefficient*, a	Temperature Range, °C	Reference
3650	1.42	2-22	(1)
3650	1.50	21-45	(22)**
Full mercury light	1.43	—	(2)
" " "	1.38 and 1.41	—	(39)
3130	1.32	10-30	(19)
3070	1.38	2-22	(1)
2750	1.28	2-22	(1)
2600	1.15	2-22	(1)

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* $(T_2-T_1)\log \underline{a} = 10\log(k_2/k_1)$

** not corrected for thermal decomposition

Temperature coefficients of the decomposition rate caused by radiation of various wave lengths are listed in Table 2. There appears to be a tendency toward decrease of temperature coefficient with decreasing wave length. These values compare with an experimentally measured coefficient of somewhat greater than 2 for thermal decomposition in the absence of radiation (see Chapter 9).

The effects of a wide variety of inorganic acids, bases, and salts on the rate of photochemical decomposition have been reported (28, 30, 31). The ranges of radiation intensities used were not specified, but they are almost certainly below 10^{17} quanta/l. sec. At these intensities, addition to the solution of strong inorganic acids causes marked inhibition, which, however, appears to approach a limiting value as the acid concentration is increased. Since the extinction coefficient is not altered appreciably by the presence of the acids (28, 30), this effect represents a true inhibition and not merely action as a radiation screen. Kornfeld (24), in reporting this effect for sulfuric acid, concluded on theoretical grounds that the rate in strong acid at moderate radiation intensities should approach 33% of that in neutral solution. According to Lea (25), at very high radiation intensities (above about 3×10^{17} quanta/l. sec.) and at hydrogen peroxide concentrations of 0.02-0.05*M*, the quantum yield becomes independent of pH in the range 1-6. This behavior at high radiation intensities is corroborated by Heidt (29), who reported only a minor effect of sulfuric acid up to a concentration of 4.1 *M*, when working at an intensity of about 5×10^{17} quanta/l. sec. and hydrogen peroxide concentrations of about 4 *M*.

Strong bases are far more effective inhibitors than acids. Their presence also results in a marked increase in the extinction coefficient (28, 29). It is notable that, in the absence of radiation, bases produce the opposite effect and strongly accelerate decomposition (see Chapter 9). Consequently, measurements of decomposition by radiation in the presence of bases becomes difficult because of the large correction for the dark reaction.

Alkali and alkaline-earth salts of strong acids (excepting halides) are without effect. Conflicting results are reported on the effect of halides. According to Matthews and Curtis (31), they exert only a slight inhibiting action; however, Anderson and Taylor (30) report marked inhibition, which becomes less marked in the presence of salts having a cation common to the halide salt. Hunt and Taube (32) reported bromide and chloride to be without effect.

Anderson and Taylor (30) have reported the effect of a large number of organic compounds on the photochemical decomposition at wave lengths of 2000, 2650, 2930, and 3050 Å. They have compared the inhibitive action at various wave lengths with absorptivity of each compound at each wave length and find parallel behavior--high absorptivity corresponding to high inhibitive activity--for acids, esters, amides, ketones, benzene, and alkaloids. Alcohols inhibit more than would be expected from their absorptivity. Amines show no correlation and may act in a different manner because of their basic nature. All these compounds are less effective when used as a light screen than when added directly to the hydrogen peroxide. From this, Anderson and Taylor concluded that these organic inhibitors influence the mechanism of decomposition, in addition to acting as radiation absorbers. Matthews and Curtis (31) also investigated several organic additives in mixed light of wave length above 2500 Å.

The frequently erratic results of single investigators and poor quantitative agreement between results from different sources indicate that quantum yields are markedly affected by adventitious impurities. The particular sensitivity to pH has been noted previously. According to Henri and Wurmser (28), as little as 2 p.p.m. of sodium hydroxide reduces the rate to 60 per cent of its normal value. The influence of alkali leached from glassware, of traces of ammonia in distilled water, or of atmospheric carbon dioxide may thus be significant. Tian (33) reports that rates are affected appreciably by the purity of the distilled water used for dilution, as measured by conductivity. Kornfeld (24) states that a consistent effect of variables could be obtained in tests on a given shipment of a certain commercial hydrogen peroxide, but that quantitative yields differed markedly between different shipments. Rice and Kilpatrick (34) report that the rate of photochemical decomposition is directly proportional to the concentration of dust particles, as measured by light scattering. It is evident that, as with studies on the stability of hydrogen peroxide, extreme care in purification and handling is necessary to obtain consistent results. For example, a description of the elaborate precautions taken in recent work is given by Dainton and Rowbottom (26).

Few studies of the photochemical decomposition of the vapor have been made. Some fragmentary studies have been reported (12, 35); the most recent and complete is that of Volman (36), in which hydrogen peroxide vapor initially at a partial pressure of 1.23 mm Hg (0.39 mm Hg of water vapor pressure also present) was illuminated with 2537 Å radiation. The quantum yield was found to be 1.7 ± 0.4, independent of the hydrogen peroxide pressure, and independent of temperature over the range of 25-50°C. No hydrogen was found in the products, and addition of oxygen or nitrogen did not affect the rate.

Mechanism. Reported quantum yields vary from approximately one up to several hundred. In agreement with experiment, long chains would be expected with low intensity radiation and high hydrogen peroxide concentrations. As the light intensity is increased, the chain length will decrease and a number of experimenters have reported values of the ''limiting quantum yield'' obtained at the highest intensity, in which chain reactions are presumably minimized or eliminated. The adventitious effects of impurities are also minimized under such conditions. The lowest quantum yields reported by various workers are given in Table 3.

The initial photochemical act has been assumed by recent investigators to be

$$H_2O_2 + h\nu \longrightarrow 2OH \qquad (7)$$

In support of this, Urey, Dawsey, and Rice (20) present data to show that the emission spectrum of hydrogen peroxide vapor, when streamed rapidly through a cool discharge tube, is predominantly that of the water bands—known from independent data to be due to hydroxyl radicals. Similarly, they state that when hydrogen peroxide is irradiated at wave lengths of 2025-2138 Å, the water bands appear in fluorescence.

TABLE 3

LIMITING QUANTUM YIELDS REPORTED FOR PHOTOCHEMICAL DECOMPOSITION

Reference	Wavelength, Å	H_2O_2 concentration, molarity	Limiting Quantum Yield
Lea (25)	2537	10^{-2}	1.39 ± 0.11
Heidt (29)	3130	1.7 - 4.5	1.7± 0.4
Hunt and Taube (32)	2537	0.02 - 0.2	0.98 ± 0.05 at 25°C 0.76 ± 0.05 at 0°C
Volman (36)	2537	10^{-4}	1.7 ± 0.4
Dainton and Rowbottom (26)	2537	0.1	1.9 ± 0.1

Lea (25) quotes, as confirmation for this initial reaction, the fact that hydrogen peroxide is a photosensitiser for the polymerization of vinyl compounds just as the electron transfer reaction,

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH + OH^- \qquad (8)$$

which is also a source of hydroxyl radicals, is a thermal sensitiser. Von Elbe (37) states that, if the initial reaction formed $H_2O + O$ as products, no reaction with hydrogen or with carbon monoxide would be expected, as oxygen atoms react with hydrogen peroxide much faster than with hydrogen or with carbon monoxide. From the fact that reaction between hydrogen peroxide and each of these two gases does in fact occur under radiation, he concludes that the initial reaction is not that forming monatomic oxygen but probably that represented by Equation (7). The only conflicting evidence comes from the recent studies of Hunt and Taube (32) who carried out the photochemical decomposition with relatively high absorbed intensities, using O^{18}-enriched water, together with the hydrogen peroxide. The oxygen formed was found to originate completely from the hydrogen peroxide. However, the fractionation effects observed seemed to be incompatible with the postualte that OH radicals are the only net products of the initial dissociation. These authors suggested that the primary act was instead

$$H_2O_2 + h\nu \longrightarrow H_2O + O \qquad (9)$$

followed by

$$O + H_2O_2 \longrightarrow OH + HO_2 \qquad (10)$$

They also suggested the possibility that reaction (7) occurred initially, followed by reaction in the solvent cage to form H_2O and O, thus

$$2\ OH \longrightarrow H_2O + O \qquad (11)$$

For the chain propagation Haber and Willstätter (38) have postulated the reactions

$$OH + H_2O_2 \longrightarrow H_2O + HO_2 \qquad (12)$$

$$HO_2 + H_2O_2 \longrightarrow H_2O + O_2 + OH \qquad (13)$$

as the chain propagation mechanism, following reaction (7). From schemes involving these reactions, Weiss (39) has correlated the kinetic behaviour of the system hydrogen peroxide-ozone, and many have done the same for the system hydrogen peroxide-iron salts. Lea (25) reports that quantum yields at high radiation intensities are consistent with the assumption of reactions (12) and (13) as the chain mechanism. Kornfeld (24) correlated the kinetics of photochemical decomposition of hydrogen peroxide in neutral and acidic solutions by assuming that reaction (13) takes place through the ion O_2^- formed by dissociation; i.e.,

$$HO_2 \longrightarrow H^+ + O_2^- \qquad (14)$$

$$O_2^- + H_2O_2 \longrightarrow O_2 + OH^- + OH \qquad (15)$$

The chain termination reactions most generally postulated are one or both of the following:

$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (16)$$

$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad (17)$$

By applying the reaction system (7), (9), (14), (15), and (17), Kornfeld (24) has derived kinetic equations predicting that, over wide ranges where the chains are of appreciable length, the quantum yield should vary as the first power of the hydrogen peroxide concentration, as the inverse square root of the radiation intensity, and inversely with concentration of hydrogen ion. These predictions are substantiated by the bulk of available data in the neutral and acid ranges. However, Kornfeld's scheme predicts an increase in the quantum yield with addition of base, whereas strong retardation has been reported from many sources. It appears that in the basic region other absorption processes, associated with the high absorptivity of basic peroxide solutions, may be significant.

The rate equations derived by Kornfeld permit calculation of the apparent activation energy of the photochemical reaction (as measured by the change in quantum yield with temperature) from the activation energies of the individual reactions. Kondrat'ev (40) has calculated the activation energies of the individual reactions from theoretical considerations, and predicts an apparent activation energy of 5.5 kcal. This corresponds to a temperature coefficient of about 1.4, which is within the range of reported values (see Table 2). Kondrat'ev, however, does not give details of his calculations or values of activation energies for the individual reactions.

Lea (25) reasoned that according to this reaction scheme, the photolysis should lose the characteristics of a chain reaction at sufficiently high radiation intensities and low concentrations of hydrogen peroxide. Under these conditions the kinetic equations predict that the quantum yield should be independent of intensity and hydrogen peroxide concentration. In agreement, he found that at intensities above 3×10^{17} quanta/l. x sec., the quantum yield was 1.39, independent of radiation intensity, of peroxide concentration between 0.010 and 0.034 *M*, and of pH between 1 and 6.

The fact that the quantum yield was independent of pH at these high intensities is taken to indicate that here reaction (13) proceeded as written, and not through the ionic mechanism (14 + 15) proposed by Kornfeld. Haber and Weiss (41) also have pointed out that the inhibitory effect of acid at lower radiation intensities may be due to acceleration of a termination reaction by hydrogen ion, instead of to Kornfeld's ionic mechanism represented by (14 + 15). Further discussion of the mechanisms involved and comparisons of the mechanisms of photolysis and radiolysis of hydrogen peroxide solutions may be obtained from the recent papers by Dainton and Rowbottom (26) and by Weiss (42).

Decomposition by Ionizing Radiation

The phenomena observed under bombardment by ionizing radiation are more difficult to interpret than those occurring under ultraviolet radiation. Not only are ionized particles involved in addition to those found in photolysis, but since free radicals are produced along the tracks of the fast particles, they may be distributed non-uniformly throughout the solution. Consequently rates of diffusion and other complicating effects may become important. Most radiochemical decomposition studies have been made with x-ray or γ radiation. In dilute aqueous solutions, with which most of the studies are concerned, the primary act will be decomposition of water into H and OH, some of which in turn will immediately form H_2 and H_2O_2 (see Chapter 2). If the conditions in the radiolysis are such that the chain carriers are relatively uniformly distributed, as would occur for example with high dosage rates and relatively long-lived radicals, then the reactions following the primary act would be expected to be similar to those occurring in photochemical decomposition. The only additional chain carrying reactions would be those proceeding from the H atoms

$$H + H_2O_2 \longrightarrow OH + H_2O \qquad (18)$$

and

$$H + O_2 \longrightarrow HO_2 \qquad (19)$$

With uniform distribution of radicals, the mathematical formulation of the dependancy of the radiolysis rate on hydrogen peroxide concentration and dose rate becomes the same as in the photolysis, e.g., for conditions in which long chains are formed, the moles of hydrogen peroxide decomposed per unit time should be proportional to the hydrogen peroxide concentration and to the square root of the radiation intensity (total radiation absorbed per unit volume and per unit time). The square root relationship of the radiation intensity is experimentally confirmed by several investigators (26, 43, 44, 45) using x-ray radiation or Co^{60} γ radiation. At high concentrations, the reaction rate has also been found to be approximately proportional to the hydrogen peroxide concentration (46) but at lower concentrations the rate is instead proportional to the half power of the hydrogen peroxide concentration (44, 45) or even independent of the concentration (47). Nevertheless, all these results are consistent with the expectation that the reaction chains would become short or non-existent as the concentration is lowered. The mathematical relationships would be more complex when short chains are involved. However, the half-power concentration relationship has also been found recently for concentrations as high as one molar by Hart and Matheson (43) and a chain reaction terminated by a third order reaction such as

$$2HO_2 + H_2O_2 \longrightarrow 2H_2O_2 + O_2 \qquad (20)$$

was postulated by them in order to explain these results.

Studies have also been reported (45, 47, 48, 49, 50) of the effect under x-ray and γ radiation of various solutes added to the hydrogen peroxide solutions and particularly of the role of hydrogen, since it is one of the primary products formed from the decomposition products of water. The decomposition of aqueous hydrogen peroxide solutions by β and γ rays from radium has been studied by Kailan (48) and that by γ radiation and neutrons has been investigated by Hopwood (5). Recent studies by Ebert and Boag (52) on the formation and decomposition of hydrogen peroxide showed marked differences between the results obtained with 1 Mev electrons and 1.2 Mev x-rays on the one hand and lower energy (200 kv) x-rays on the other. This field is in a rapid stage of development and a much clearer picture of the processes occurring under radiation bombardment should develop in the near future. Recent summaries of the state of knowledge in this area have been made by Dainton and Rowbottom (26) and Weiss (42, 53). See also the discussion in Chapter 2 on formation of hydrogen peroxide under radiation.

ELECTROLYTIC DECOMPOSITION

Aqueous solutions of hydrogen peroxide may be electrolyzed to yield molecular hydrogen and oxygen; at high current densities the over-all process is

$$H_2O_2 \longrightarrow H_2 + O_2 \qquad (21)$$

As the current density is decreased the yield of hydrogen becomes less than that indicated by reaction (21), ultimately becoming nil. In all cases, however, oxygen is liberated quantitatively in the proportion, one mole of oxygen for two Faradays of electricity. These facts were established by a number of workers (54, 55), beginning with Thenard. The underlying reasons for the changing proportion of hydrogen produced at the cathode have not been investigated. Weiss (56) observed that hydrogen, a mixture of hydrogen and oxygen, or oxygen alone was given off at the cathode, according to the conditions of current density and hydrogen peroxide concentration. Albareda (57) concluded, as earlier workers had, that this was to be explained by the concurrent catalytic decomposition. Tanatar (55) assumed reaction of hydrogen and hydrogen peroxide to produce two moles of water. Hydrogen peroxide has been observed (58) to affect the overvoltage of hydrogen.

The reaction at the anode whereby oxygen is released has received more intensive study (59, 60, 61). Hickling and Wilson (59) determined the current-voltage curves for hydrogen peroxide solutions in contact with a number of electrode materials. In a 0.01 M hydrogen peroxide solution current flow began at approximately 0.1 volts. A plateau then appeared in the current-voltage curve, the height of which is dependent on concentration and stirring. Hickling and Wilson concluded that the anode process in alkaline solution is:

$$HO_2^- = O_2 + H^+ + 2e^- \qquad (22)$$

In acid or neutral solution and with all electrodes except platinum the main process appeared to occur at a potential at which electrolysis of the supporting electrolyte began to occur. The conclusion therefore seemed warranted that the hydrogen peroxide decomposition under these conditions depends on interaction with some intermediate involved in the ordinary anodic evolution of oxygen, very likely hydroxyl radical. Further study and comment on mechanisms of anodic decomposition of hydrogen peroxide has been provided by Rius and Ocon (60) and Krasil'shchikov, Volchkova, and Antonova (61). The latter authors have provided an equation relating overvoltage with pH and hydrogen peroxide concentration.

These considerations are of course also of concern in polarography (62), whether hydrogen peroxide is present initially or formed through reduction of oxygen (63). Of particular interest is the oxygen induced decomposition of hydrogen peroxide (64) which has been suggested to proceed through a tack by superoxide ion. In the presence of certain metal ions the polarographic reduction of hydrogen peroxide is likewise catalysed (65).

DECOMPOSITION IN THE LIQUID PHASE BY INORGANIC CATALYSTS

Although there exists a large body of literature dealing with the catalytic decomposition of liquid hydrogen peroxide, a great part of it finds present value only as a descriptive guide. This is caused partly by the inherent difficulty of the subject and the slowness with which an understanding of catalysis in general has been developed. To an even greater extent, however, the advance of knowledge about hydrogen peroxide decomposition has been hindered by inadequate scope and dependability of experiment. In many cases it is only possible to say that catalysis takes place and observations have not been made or are questionable in regard to the effects of concentration, pH, temperature, the presence of impurities or additional components, and the state of the catalyst. These are of course the data required in any kinetic study, and it is only in the systems which have received scrupulous attention that adequate mechanistic descriptions can be offered. A factor of particular importance here is the effect of traces of extraneous materials in the hydrogen peroxide, such as adventitious impurities or those from the manufacturing process or deliberately added stabilizers. Much work has been carried out with hydrogen peroxide of questionable purity, particularly in earlier investigations reported in the literature.

Catalysis by the halogens, platinum, iron, and enzymes has probably received the greatest attention. Some other elements have been investigated briefly or not at all. Figure 4 summarizes

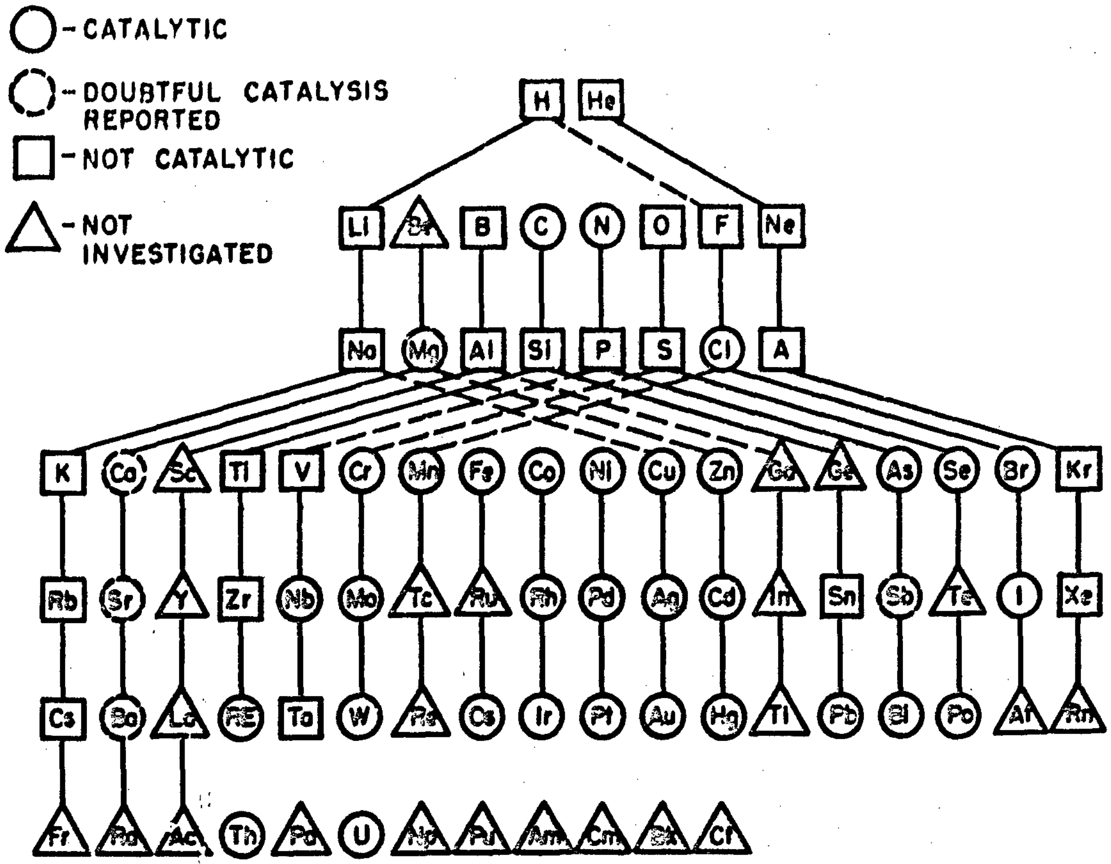

FIG. 4 - THE PERIODIC TABLE, SHOWING ELEMENTS (OR THEIR COMPOUNDS) REPORTED TO CATALYZE THE DECOMPOSITION OF HYDROGEN PEROXIDE

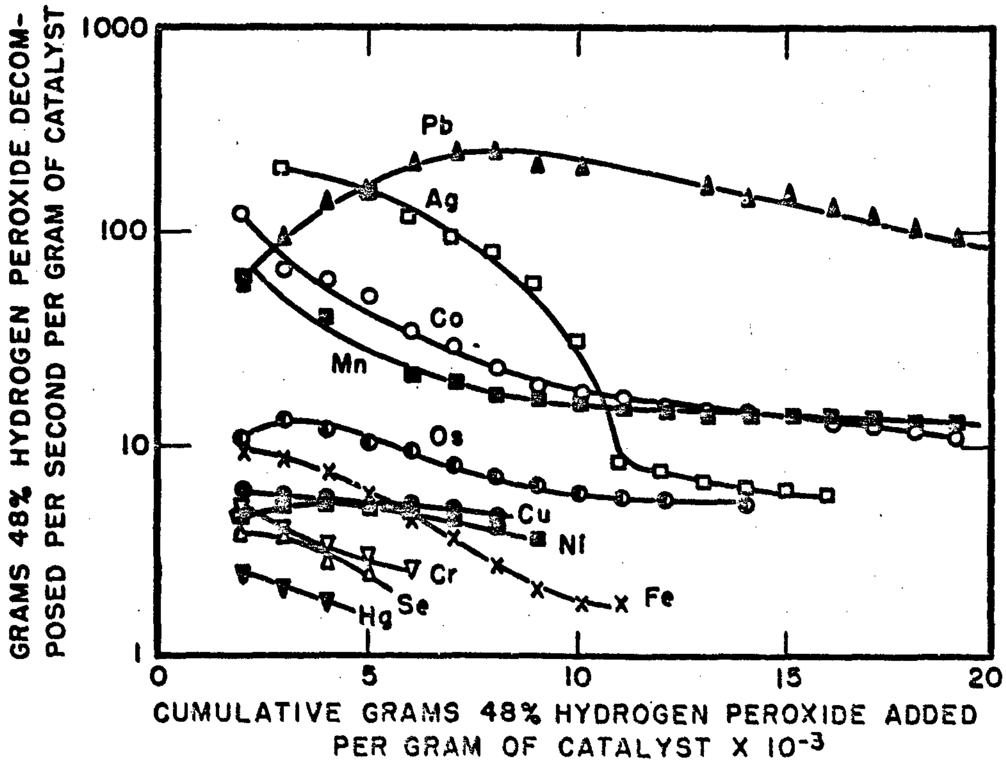

FIG. 5 - RELATIVE CATALYTIC ACTIVITY OF SOME METAL HYDROXIDES (FORMED FROM 0.0118g. METAL + 10cc. 4N NaOH).

the state of knowledge with regard to the occurrence of catalytic decomposition of hydrogen peroxide.* It is apparent that catalysis is encountered with many substances, including the heavy and transition metals, which show high catalytic activity in many other systems. Some caution should be exercized in interpreting Figure 4. The facts presented have been taken in some cases from literature reports which are doubtful, and the conciseness of the figure does not permit many pertinent qualifications which are discussed below in considering the individual elements. Entries in Figure 4 may be non-equivalent because of the relative reliability of the reports depended on, the variations in form of catalyst, whether homogeneous or heterogeneous, element or compound, compared at similar pH, etc., and especially, the differences and variability in the rate of catalysis. The range of decomposition rates is quite large. For example, under similar conditions metallic antimony is nearly inert, whereas osmium and lead can induce the decomposition at rates described as explosive. Gradations of activity among related elements are observed, as in the series zinc, cadmium, and mercury. More abrupt is the change from stabilizer to active catalyst in going from tin to lead.

In the following discussion a few general comments are given on the characteristics of homogeneous and heterogeneous decomposition. Following this there is presented a survey of the literature on catalytic decomposition arranged according to the position of the elements in the periodic table, using the system adopted by Latimer (66). The subjects of periodic decomposition, promotion, inhibition and poisoning are then briefly considered. There are several charateristics of the catalytic mechanisms which are exhibited in common by several elements, *e.g.*, the solubility product criterion for initiation of catalysis. It has been attempted to discuss a typical example of such a characteristic in full for at least one instance. As general references and introductions to the subject of catalysis there may be recommended the book by Schwab, Taylor, and Spence (67), the monograph by Berkman, Morrell, and Egloff (68), and the series of volumes edited by Emmett (69). Comparison of the decomposition processes of hydrogen peroxide with those of other peroxides has been made only

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*The indication on Fig. 4 that an element is not catalytic should not be interpreted to mean that it can be used as a material of construction; see Chapter 4.

in a few instances, e.g., with barium peroxide (70) and tetralin hydroperoxide (71). Some reasons for fundamental differences in this respect are discussed in Chapter 7. The experimental techniques for studying hydrogen peroxide decomposition are not particularly unique, although some special procedures have been described (72).

Homogeneous Catalysis

Homogeneous catalysts are those substances which exert a catalytic effect while present in true molecular solution. Such catalysis of hydrogen peroxide has been excellently reviewed recently by Baxendale (73), and this review should be consulted for more extensive comments of a general nature and for description of the homogeneous catalyses which occur with the halogens, iron, copper, permanganate, chromium, molybdenum, and tungsten. Baxendale points out that two general theories have been advanced to account for the mechanisms of homogeneous catalysis. One postulates the formation of highly reactive intermediates, usually peroxides, formed from hydrogen peroxide and catalyst which subsequently decompose to yield anew the catalyst. The second theory proposes the alternate oxidation and reduction of the catalyst in a sequence:

$$\text{Reduced catalyst} + H_2O_2 \longrightarrow \text{Oxidized catalyst} + H_2O \qquad (23)$$

$$\text{Oxidized catalyst} + H_2O_2 \longrightarrow \text{Reduced catalyst} + O_2 \qquad (24)$$

The net result of such a cycle is just the decomposition of hydrogen peroxide as in reaction (1). This theory finds particular support in the fact pointed out by many, e.g., Haïssinsky (74), that many of the most active catalysts are elements which may assume several valence states. It should be noted that although an oxidation-reduction scheme such as reactions (23) and (24) indicate may be calculated to be thermodynamically favorable, one or both of the reactions may not occur, as McAlpine (75) has shown for several hydrogen peroxide reactions.

All the homogeneous catalyses (and many heterogeneous ones) can be accounted for qualitatively by one of these two schemes, although the ultimate mechanisms are undoubtedly more intricate.

Thus Baxendale classifies catalyses proceeding by free radical chain mechanisms as cyclic oxidation and reduction, and an emphasis on the role of perhydroxyl ion (76) is similarly only the assumption of increased detail. Some other mechanistic schemes, especially those involving tautomeric forms of hydrogen peroxide, are no longer admissible. Another aspect is the so-called ''thermal decomposition,'' that is, the decomposition occurring in purified hydrogen peroxide, particularly at elevated temperatures. As the work of Rice and Reiff (77), Livingston (78), and the discussion in Chapter 9 demonstrates, this thermal decomposition is to be ascribed largely to heterogeneous catalysis by the containing vessel or by suspended matter. Although long chains involving a repetition of homogeneous processes may possibly be involved under some conditions, initiation of the chains is by walls or traces of impurity. Even with the purest hydrogen peroxide studied and at elevated temperatures, the decomposition observed in the liquid phase is not a homogeneous autodecomposition process of the hydrogen peroxide itself.

The relationships between homogeneous and heterogeneous catalysis have received little attention, largely because elements which give rise to both modes of catalysis have not been studied over the entire range of variables such as pH and concentration which determine the state of the catalyst. Iron provides an illustration of a catalyst with which the transition from homogeneous to heterogeneous mechanism can be observed. In acid solution reaction is purely homogeneous. If the pH is increased, however, colloidal material may begin to appear and a concurrent change in rate may occur, as illustrated in Fig. 9 of Chapter 9. At even higher pH, gross precipitation may be observed together with further kinetic changes. Other changes in physical form, such as supporting the catalyst, sintering it, or changing its crystal structure, can of course also greatly affect the rate observed. With the exception of some uncertainty at the pH where colloidal matter is first being formed there exists no doubt regarding the transition from homogeneous to heterogeneous decomposition as pH is increased. However, there is considerable doubt about the nature of the transition in mechanism. In some instances both modes of decomposition can be accounted for qualitatively by the same mechanism, e.g., cyclic oxidation and reduction. At the same time complexing or precipitation of the catalyst as colloid or solid may determine the fraction of the gross amount of catalyst present that is actually available for reaction, thereby affecting the decomposition rate observed. Such a circumstance is encountered in polymerization catalysis with peroxides (79). Or, in purely heterogeneous catalysis, the degree of dispersion of the solid will affect the rate observed by its effect on the surface exposed to the medium. In contrast there is the distinct possibility that the change in going from a homogeneous system to a heterogeneous one may change the fundamental character of the reaction undergone by the hydrogen peroxide, i.e., from an ionic to radical mechanism. Possibly there may be a relatively gentle gradation from one to the other as conditions are altered. In distinguishing between homogeneous and heterogeneous catalysis there must be considered the possible contribution to the former of adsorption from solution. Thus, argentous silver, which is non-catalytic when dispersed homogeneously, is easily adsorbed by glass (80). In the adsorbed state it may be rendered catalytic, either by overt reduction or perhaps only through polarization (81). Similarly the later use of the glass surface in contact with a more alkaline solution may activate adsorbed silver. This is particularly noticeable on the surface of a glass electrode.

Heterogeneous Catalysis

Progress in predicting or determining the mechanism of the decomposition of hydrogen peroxide by heterogeneous catalysts has been disappointingly slow and lags well behind the understanding of homogeneous catalysis. This position is not unique to hydrogen peroxide, but is common in most instances of heterogeneous catalysis. The study of hydrogen peroxide decomposition is of particular interest in this field because of the many effective catalysts which will carry out this one net process. Even though the number of ways in which the hydrogen peroxide molecule itself can be initially disrupted is limited, the subsequent courses of the catalytic mechanisms must include considerable variety. Additional complexity is introduced by the variety of possible forms of the solid, such as colloids, amorphous precipitates, crystals, and supported substances.

The present state of understanding of heterogeneous catalysis in general is well presented in the series of volumes edited by Emmett (69). Fundamental aspects of the nature of solids are dealt with by Seitz (82), Shockley (83), and Gomer and Smith (84). The major factors to be considered in relating catalysis to electron structure are recounted by Dowden (85). A somewhat less comprehensive, but useful concept is that of the polarization of atoms in solid surfaces presented by Weyl (81, 84). All these general considerations stress the outstanding importance which the process of chemisorption of hydrogen peroxide onto the catalyst surface must play. As Wheeler (84) points out in concise manner, this step involves the relatively drastic electronic rearrangement involved in electron sharing or transfer. Following the concept of Boudart (84), the surface may be visualized as acting either as a reservoir of particles or as an agent to loosen or dissociate hydrogen peroxide into fragments held at one or more sites on the surface. These fragments may react subsequently with molecules impinging from the surrounding fluid. Concurrently there will occur processes (strictly to be considered as homogeneous) which are propagated into the bulk of the fluid or take place in the film of fluid near the surface. Both physical and chemical rate processes may cause the state and concentrations of substances in this film to differ significantly from that in the bulk of the fluid or at the surface of the solid.

There are several viewpoints and general characteristics of the heterogeneous catalysis of hydrogen peroxide which may be pointed out. An early comprehensive study of the many factors affecting the performance of a catalyst for the decomposition of hydrogen peroxide was made by Bredig and von Berneck (86). Since decomposition of hydrogen peroxide occurs under conditions extremely far from equilibrium, it might be expected that oxygen pressure would be without effect on the course of the reaction, as these authors noted. Althoughthis is true for homogeneous catalysis, in heterogeneous reactions, other phenomena of importance to the reaction mechanism occur which are markedly affected by the oxygen pressure. Thus Roiter (87) found the rate of decomposition on platinum foil to be increased by reduction in pressure, presumably because adsorbed gas was removed from the catalyst surface. Others have studied the effects of salts (88), variation of solvent (89), light (90), and the magnetic field (91) on hydrogen peroxide catalysis. Much concern has been directed toward the problems of irreproducibility and variability of activity related to changes in particle size, total surface, and specific activity. Although the importance of these factors has been long recognized, progress has been hampered by inadequate experimental techniques for evaluating pertinent factors. More recently the introduction of procedures for determining microstructure by electron microscopy and surface area measurement (92) or by magnetic susceptibility measurements (93) has improved this position, but totally adequate means for characterising the factors responsible for activity are not yet at hand. For example, Schwab (94) has noted that if the rate of a catalytic process is formulated in terms of the Arrhenius equation, $k = A \exp(-E/RT)$, then the activation energy term, E, is a characteristic of the system and the coefficient A is determined by factors which introduce all the accidental fluctuations and irreproducibilities which make the acquisition of consistent data so difficult. An example involving hydrogen peroxide which seems to be well accounted for in this manner is evidently to be found in the vapor decomposition experiments (10) reported in Figure 1. Thus the parallel curves there, which deal with the heterogeneous regime, provide evidence of similar activation energies but of differing values of A introduced by adventitious variations in the surfaces of different glass tubes.

As the foregoing discussion of homogeneous catalysis indicated, there is often a striking change in catalytic activity in proceeding from a homogeneous system through systems with solid in various states of dispersion and activity. Several factors contribute to this behavior, and numerous instances occur in which no homogeneous catalysis takes place. In a relatively early attempt, Madinaveitia and Aguirreche (95) studied the effect of the addition of coagulant upon the rate of decomposition of hydrogen peroxide on a gold sol. To explain the maximum in rate observed it was noted that ionically dispersed gold was without catalytic effect and that macroscopic fragments of metal were also relatively inert. Thus both the presence of a solid and a high degree of dispersion were deemed necessary for effective catalysis. Other studies have shown that several elements with which catalysis is not observed when the system is completely homogeneous, e.g., silver, manganese, lead, and cobalt, do not begin to catalyze the decomposition of hydrogen peroxide until a certain solubility product has been exceeded. At higher concentrations, the metal or its hydroxide forms a solid phase, the presence of which seems to be required even though a cyclic oxidation-reduction scheme might be thermodynamically favorable in the absence of a solid. Once formed, the rate of decomposition on such a surface may be directly proportional to the surface area developed. This was demonstrated for the case of manganese dioxide by Parker, Cohen, and Smith (96), who made precise surface area measurements by means of a nitrogen adsorption technique. Because of this characteristic solubility product requirement it is important to note the amphoteric properties of many, or perhaps all metals. Wright and Rideal (97), for example, concluded that solid catalysts might be expected to be most active at the iso-electric point of the solid in question. Fair experimental agreement with this hypothesis was found. These characteristics are somewhat superficial and, as emphasized above, the more fundamental role of the surface, either in regulating concentration or in providing reaction pathways of reduced activation energy, must be determined before the mechanism can be described adequately. There is no indication that any universal mechanism (98) is applicable.

The important subject of electron transfer between heterogeneous catalyst and substrate has only begun to be considered in the case of hydrogen peroxide. Weiss (56) appears to have been first to suggest such action. He proposed that the rate controlling step in the decomposition of hydrogen peroxide by metals may be

$$H_2O_2 + \text{metal electron} \longrightarrow OH^- + OH \qquad (25)$$

It was pointed out that such action on copper-nickel alloys should be regulated by composition, being most rapid in the copper-rich region and falling to lower levels of activity as increasing proportions of nickel cause the d electron band to empty. Weiss emphasized that this behavior was to be imagined of importance only if the acidity of the solution were such that no corrosive attack occurred and only in the absence of an oxide film thick enough to prevent electron transfer. The catalytic activity of a series of alloys of lead-cadmium, tin-bismuth, and antimony-bismuth composition was measured by Kapustinskii and Shmelev (99). The effectiveness of these in decomposing hydrogen peroxide was correlated with the melting point diagram, and therefore the composition, of the alloy system. The activity was observed to occur at the phase boundaries. Dowden and Reynolds (100) experimented with foils of copper-nickel alloys. The foils were given an acid pretreatment, showed no sign of oxide layer, and were tested in dilute, neutral hydrogen peroxide at 20° to 80°C. Over the investigated range of 70 to 100% copper the decomposition rate was found to diminish with decreasing copper content in accordance with the hypothesis mentioned above. There was found to be a linear relation between frequency factor and activation energy, analagous to that shown for a homogeneous electron transfer process in Figure 3 of Chapter 7. The result with the alloys is to be contrasted with the homogeneous instance, however, in that with the alloys the substrate is the same and it is the catalyst that is varied. Arguments were developed by Dowden and Reynolds to show that this action could not be accounted for on the basis of an intermediate oxide film formation. It has been stated by Schwab (84, 101), however, that primary oxidation of the catalyst followed by fast oxygen desorption could also account for such behavior. This conclusion was related to experimental work with iron spinels and several alloy systems. Further comments on the role of electron transfer in the heterogeneous catalysis have been made by Leach (102).

From both the practical and theoretical standpoints it is of interest to compare the effectiveness of various heterogeneous catalysts, although it is difficult to devise a means for demonstrating the effects of wide ranges of important variables. A qualitative survey of this kind was made by Kastle and Clarke (103), and a similar one (104) is presented in Fig. 5. The data shown were obtained by measuring the time required to decompose successive 10 c.c. portions of 48 wt.% hydrogen peroxide added to a solution containing 0.0118 g. of the metal in question, added as the nitrate. Initially, 10 c.c. portions of hydrogen peroxide, the metal salt solution, and 4 N sodium hydroxide were mixed to precipitate the metal hydroxide. The decomposition was carried out in a large flask maintained at 95° to 100°C and surmounted by a reflux condenser which permitted less than 10% of the water vapor produced to escape. Although no quantitative conclusions can be reached, this comparison shows the extreme variation in decomposition rate and effects of dilution and aging encountered.

Acid and Alkali

The figures presented in Chapter 9 to illustrate the discussion of the effects of pH on the stability of pure hydrogen peroxide show the magnitude of the changes in decomposition rate which can be induced by alteration of the hydrogen ion concentration. It is clear that the addition of either acid or alkali to uncontaminated hydrogen peroxide solutions increase the decomposition rate. In the case of acids, the most reliable basis for this conclusion is found in the work of Roth and Shanley (105), who studied phosphoric, perchloric, hydrofluoric, and sulfuric acids and found the rise in decomposition rate with decreasing pH to be independent of the nature of the acid anion, possibly excepting phosphate. Since the acids were equivalent in effect and perchloric and hydrofluoric acids do not form peroxy acids it was concluded that the change in hydrogen ion alone was responsible. There are systems, however, in which the acid anion participates. An outstanding example is nitric acid. Hatcher and MacLauchlan (106) have described the violent decomposition of concentrated hydrogen peroxide which can occur when nitric acid is added in a proportion of about 50% or more. The decomposition is surface catalyzed and is characterized by an induction period, the appearance of brown fumes, and the production of an ozone-like odor. Although it has been suggested that the mechanism of this decomposition involves peroxy acid formation, this has not been established. Forbes (107) has pointed out that when a reductant is added to colorless nitric acid little happens until yellow nitrogen dioxide appears.

More attention has been paid to the increased decomposition brought about by addition of alkali to hydrogen peroxide, although the mechanism is no better understood. Doyle (108) observed the decomposition of 5 wt.% hydrogen peroxide at 70°C over the pH range 5.3 to 9.3. The rate expression was first order with respect to hydrogen peroxide concentration over the entire pH range in accordance with the finding of Bürki and Schaaf (109). A plot of the value of the logarithms of these reaction rate constants as a function of pH showed two straight lines intersecting at pH 8.7. This transition was remarkably abrupt, the slope being 0.2 below pH 8.7 and 2.6 at higher pH; these are the non-integral inverse orders, 0.2 and 2.6, of the hydrogen ion concentration. Although the scope of these experiments is not extensive, it appears that a change in rate controlling mechanism occurs at pH 8.7; that at lower pH perhaps being heterogeneous and that at higher pH being homogeneous. It can be tentatively concluded that the order with respect to hydrogen ion concentration is actually -2 at the higher pH's if the contribution of the first mechanism is subtracted and the precision of the work is considered. The transition is also in accord with Slater's observation (110) that changes in magnitude of decomposition rate occur between pH5 and 6 and between pH 8 and 9. Other reports have asserted that with further addition of alkali to hydrogen peroxide a maximum (111) or minimum (112) in decomposition rate is reached.

No completely acceptable mechanistic explanation of the acid or alkali induced decomposition is available, chiefly because of the lack of reliable kinetic data. Assurance that adventitious impurities are absent is particularly important (110, 113). A role for perhydroxyl ion has been cited often in discussion of the base catalyzed decomposition; for example, Abel (114) suggested the mechanism to be

$$H_2O_2 + HO_2^- \longrightarrow H_2O + O_2 + OH^- \qquad (26)$$

In the acid catalysis the peroxonium ion, $H_3O_2^+$, may well play a role. Further precise experimentation should permit understanding of the mechanisms, probably as an example of specific acid-base catalysis in which the decomposition rate can be expressed as the sum of two or three kinetic formulations of species dependency.

Oxygen, Hydrogen

Radicals such as hydroxyl and perhydroxyl appear to be of considerable importance in hydrogen decomposition processes, but their appearance as intermediates makes the discussion of them more appropriate in connection with the elements below. It is in the study of the homogeneous decomposition by iron that the most extensive consideration of these species has been developed.

The Halogens

With the exception of fluorine, the halogens catalyze the decomposition of hydrogen peroxide by a homogeneous cyclic oxidation-reduction mechanism which can be represented as follows:

$$H_2O_2 + 2X^- + 2H^+ \longrightarrow X_2 + 2H_2O \quad (27)$$

$$H_2O_2 + X_2 \longrightarrow 2X^- + 2H^+ + O_2 \quad (28)$$

This system has received extensive study, leaving no doubt that the net process proceeds as above. Furthermore, the individual reactions have been studied separately, and the kinetics established in terms of concentration dependence, reaction rate constants, frequency factors, and activation energies (73, 115, 116), and upon the basis of this knowledge the rate of the catalysis may be predicted for a given set of conditions. It is obvious that the rates of the two reactions must be equal if one form of the catalyst is not to become exhausted. Thus when the initial composition differs from this ''steady state'', there occurs net oxidation or reduction, whichever is appropriate, until the steady state concentrations of the two species, halide and halogen, are reached.

The subject of halogen catalysis has been very adequately reviewed (73, 117). Although the kinetics of the net reactions set out above are readily treated mathematically (118), the actual mechanism is undoubtedly more complex. Baxendale (73) has discussed the details of the kinetics and proposed mechanisms, which Edwards (116) has shown to have the characteristics of reactions to be understood according to the principles of general acid-base catalysis. Free radical routes have been suggested to occur (119), but these have been rejected (73, 120). The large body of experimental work dealing with both individual reactions and the over-all decomposition and upon which these conclusions are based are as follows: chlorine (121), bromine (122), and iodine (123). Iodine has received the greatest attention, including investigation of salt effects (124), the effect of iodine present in a non-homogeneous phase (125), and solvent effects as mentioned in Chapter 7. To a lesser extent these aspects have been investigated with chlorine and bromine. This is also true for the less well understood catalysis by iodate (126), which appears to proceed according to the scheme:

$$5H_2O_2 + 2IO_3^- + 2H^+ \longrightarrow I_2 + 6H_2O + 5O_2 \qquad (29)$$

$$5H_2O_2 + I_2 \longrightarrow 2IO_3^- + 4H_2O + 2H^+ \qquad (30)$$

This system exhibits an interesting periodicity. The effect of light upon the catalytic decomposition induced by bromine and iodine has also been investigated (127).

Sulfur, Selenium, Tellurium, Polonium

Sulfur does not catalyze the decomposition of hydrogen peroxide. Selenium decomposes hydrogen peroxide (128) by a cyclical oxidation-reduction process between selenate, $SeO_4^=$, and selenite, $SeO_3^=$, not involving the doubtful (128) peroxyselenate reported by Worsley and Baker (129). Bonét-Maury and Lefort (130) observed polonium to catalytically decompose hydrogen peroxide at a catalyst concentration below that at which platinum gave a measurable rate.

Nitrogen, Phosphorus, Arsenic, Antimony, Bismuth

With the exception of the action of nitric acid discussed above no catalytic decomposition involving nitrogen or phosphorus has been reported. In the course of their unsuccessful attempt to prepare peroxyarsenates Levi and Ghiron (131) found arsenates to be catalytic. Antimony has been listed (132) among substances found to be catalysts, but the effect is certainly a weak one if it occurs at all. The catalysis reported to occur with bismuth or bismuth oxide (133,134) seems more certain, but has been commented upon only qualitatively.

Carbon, Silicon, Germanium, Tin, Lead

The various forms of carbon, such as graphite and charcoals from diverse sources, provide heterogeneous catalysts for hydrogen peroxide decomposition that have a number of interesting characteristics. The activity of carbon varies considerably according to the source (135), and further change in activity may be brought about by special treatment. The effect of the addition of salts and of gelatin upon the catalytic activity of sugar charcoal was examined by Fowler and Walton (136); others have studied the influence of temperature, grain size, hydrogen ion concentration, radiation (137), concentration of hydrogen peroxide, and the chemical character of the carbon surface. The absorptivity of the surface (138) appears to be the most important characteristic that can be described at present, but the effect is not directly proportional to absorptivity. Surface treatments such as heating and nitrogen treatment (139) alter activity markedly. A pure sugar charcoal, shaken with a solution of hydrogen peroxide caused only a slight evolution of oxygen; but this action of sugar charcoal could be much increased if the charcoal was heated in a vacuum at 600°. Charcoal obtained from cellulose and rice starch and dried at 100° gave the strongest action; that obtained from dextrin, inulin and wheat starch showed weaker action; hardly any action was noted with charcoal from dextrose, lactose, maltose, or potato starch. Crude boneblack or blood charcoal decomposed hydrogen peroxide only slowly unless these forms of charcoal were heated first <u>in vacuo</u> from 600° to 900°.

Brinkmann (160) concluded that the activity of carbon increased with the number of basic surface-active groups, which could be estimated by the ability to adsorb hydrochloric acid and decreased with increasing number of acidic surface-active groups, estimated by sorption of sodium hydroxide. As a measure of the catalytic activity, the time required for the activity to drop to half its former value was measured under definite conditions. In this way small changes in the surface condition of the active carbon could be disclosed and evaluated. A direct connection, however, with the adsorptive capacity of the carbon apparently does not exist -- active forms of carbon with high adsorptive capacity may show only a very small catalytic activity towards hydrogen peroxide, while poor adsorptive capacity may accompany strong decomposing effects.

As to the mechanism of the decomposition of hydrogen peroxide by active carbon, the hypothesis was proposed by Brinkmann that at first an exchange reaction takes place between an -OH group on the carbon surface and an -OOH ion in the solution. The perhydroxyl ion thus activated by being added on suffers either self-decomposition, or reacts with a hydrogen peroxide molecule, reforming a hydroxyl ion.

It was found that active carbon which bore on the surface essentially only acidic groups (after being subjected to an oxidizing treatment), in spite of high adsorptive capacity showed no measurable catalytic activity toward hydrogen peroxide in neutral solution, when care was taken that all groups were present in the hydrogen form (as in -COOH groups). But when the acid group is converted by alkali over into the -COONa salt-grouping, there appears catalytic activity toward hydrogen peroxide, which, however, is very small compared to that of an active carbon with basic groups attached.

In judging the magnitude of the catalytic activity of active carbon upon the decomposition of hydrogen peroxide, Brinkmann pointed out that in the rapid evolution of gas from the surface of the carbon, only a small fraction of the available basic groups are involved, namely, those located in a thin, outer zone; whereas those groups which cover the inner surface in the pores of the carbon do not come into contact with the molecules or ions of the hydrogen peroxide, due to the marked interference with diffusion in the pores caused by the evolution of the oxygen. That this relationship is actually of controlling importance can be seen in the pronounced dependence of the decomposition rate upon the grain size of the carbon. The latter must be held within narrow limits if an accurate comparison of catalytic activity is to be based on such measurements.

Certain kinds of active carbon can be used in galvanic cells in place of manganese dioxide. It is known empirically that a relationship exists between the ability of a substance to decompose hydrogen peroxide and its electromotive activity, and use of this fact has been made in selecting types of active carbon for galvanic elements.

Silica was reported to be a good catalyst by Lemoine (141), but later work (142, 143, 144) has not supported this view. Fells and Firth (142) observed that no decomposition of hydrogen peroxide occurred in a silicate solution until gelation commenced, suggesting that the appearance of the colloidal or solid phase is required to initiate activity. However, Penner (144) concluded that the decomposition proceeded uniformly in both the solution and the gel and was induced by impurities or the container surface. Observations have also been made on the form of the bubbles generated in the silica gel (142) and upon photochemical decomposition in the system (144).

Germanium appears not to have been investigated for its possible action as a catalyst for hydrogen peroxide decomposition. Tin is quite clearly non-catalytic as the discussion in Chapters 4 and 9 indicates. The report (134) that a yellow precipitate of tin was slightly catalytic seems certain to have been based upon the observation of an impure sample.

Lead provides one of the most active heterogeneous catalysts. Qualitative features of this catalysis have been reported (134, 145, 146), namely, that divalent lead in acid hydrogen peroxide is without effect, alkaline conditions which produce lead dioxide being required to bring about the decomposition. A study (147) of the mechanism of this catalysis warranted the conclusion that it can be described as an oxidation-reduction cycle between divalent lead, $Pb(OH)_2$, and red lead oxide, Pb_3O_4. Under conditions where catalytic activity is high both of these are present as solid phases; in very basic solution higher oxides are formed. Thus, the characteristics of the various pH ranges are as follows. Lead nitrate dissolves in hydrogen peroxide to give clear, stable solutions. If alkali is added, a whitish yellow precipitate forms and moderate activity may be observed. With further addition of alkali the precipitate changes to an orange-red form and the decomposition becomes violent. The amount of alkali required to reach this catalysis point was found to be inversely proportional to the amount of dissolved lead, with an additional, uncertain effect of aging. The quantity of pyrophosphate required to stop the catalysis was roughly equivalent to that required for formation of lead pyrophosphate, $Pb_2P_2O_7$. The catalytic activity reaches a maximum at an alkali concentration near 0.2N; above this the lead becomes increasingly soluble as plumbite and plumbate and the catalytic activity diminishes. An unsuccessful attempt (147) was made to demonstrate the cyclic oxidation-reduction of lead by radioactive tracer techniques, but this approach was barred by the finding that even in the absence of hydrogen peroxide, exchange occurs between plumbous ion and lead dioxide in nitric acid (in agreement with the literature (148, 149)) and between plumbite and plumbate in basic solution (in disagreement (149)).

The operation of this action on metallic lead is quite striking. When polished lead, which is free from oxide coating, is immersed in hydrogen peroxide the activity is low. A white precipitate gradually forms and after accumulation converts to red lead oxide with consequent violent catalysis. If the lead metal is immersed briefly and then withdrawn, the small quantity of liquid clinging to the metal remains quiescent for a short time and is then suddenly thrown off the surface by violent decomposition as the metal acquires a coating of red lead oxide, Pb_3O_4. Solution of the lead occurs in this process, and this is undoubtedly connected with the observations that hydrogen peroxide destroys the passivity of lead (150) but does not affect the growth of dendrites on it (151). Practical lead catalysts for hydrogen peroxide decomposition have been described (152).

Gallium, Indium, Thallium

The elements gallium, indium, and thallium appear not to have been investigated with respect to possible catalytic action on hydrogen peroxide.

Zinc, Cadmium, Mercury

Zinc exhibits the unusual capability of acting both as a catalyst and as a stabilizer. As mentioned in Chapter 9, zinc in solution in 90 wt. % hydrogen peroxide exerts a stabilizing effect. It was observed (153) that this effect diminished as the concentration of the hydrogen peroxide was reduced and that in solutions of less than 40 wt.% hydrogen peroxide the zinc acted as a decomposition catalyst. This catalytic action was also observed (154) in mixture with other catalysts.

Metallic zinc was observed to decompose hydrogen peroxide with the evolution of hydrogen and oxygen by Weiss (56). No mechanism has been offered in explanation of the ambivalent action of zinc. The effect of cadmium has been investigated only in dilute solution and has been characterized as weakly catalytic (134,154) or as ineffective (155).

In contrast, mercury is clearly catalytic, and in addition, exhibits the interesting property of inducing the catalysis in a periodic fashion. A number of workers (132, 156), led by Bredig, have described this phenomenon, which is reproducible only under fairly exact conditions. Scott and Sorenson (157) described four distinct regimes of pH in which different actions of hydrogen peroxide upon metallic mercury were observed. In extremely acid solution, below pH of 0.5, the mercury remains bright and there is virtually no catalysis, but solution of mercury takes place. In the pH range between 1 and 4 mercuric oxide is formed on the surface of the mercury and both mercurous and mercuric ions are found to occur in solution, their concentration increasing with time. The concentration of mercuric ion was far in excess of the equilibrium value for $Hg^{++} + Hg = Hg_2^{++}$. Below pH 2.5 the quantity of oxide formed was voluminous and thrown into the bulk of the solution, although occasionally a bright surface on the mercury was maintained at a pH as high as 2.0. The periodic catalysis was observed in the pH range between 4.0 and 6.5, although Bredig and Stark (158) found it to be most prolonged at a pH of 7. This catalysis is characterized by a period of quiescence when the surface of the mercury is covered by a thin golden brown film followed by a period of activity upon a clear, bright mercury surface. This cycling, which is disturbed by stirring, may persist for a short time while precipitate is thrown off into solution at lower pH. Ernst (159) observed an induction period before cycling began, and the earlier workers have investigated the effects of additives, temperature, and polarization upon this behavior.

In the pH range above 8, the decomposition is continuous and rapid on a bright mercury surface and dissolved mercury is present at a concentration of less than 10^{-7} moles/ℓ. In keeping with these observations mercurous and mercuric ions and oxides of mercury are found to be reduced to metallic mercury in basic solution, mercurous oxide is oxidized to mercuric in the pH range of 1 to 4, and below pH of 1 the oxides are dissolved.

The mechanism of the mercury catalysis is not clear, although there appears to exist a basis for consideration of a cyclic oxidation-reduction between metallic mercury and mercuric oxide such as suggested by Quartaroli (134). The periodic feature is most readily explained as a balance between physical and chemical rate processes, the result of local depletion of hydrogen ion caused by the dissolving of mercuric oxide in the film adjacent to the mercury surface and the subsequent diffusion of hydrogen ion in from the bulk of solution. Experiments to establish the nature of the concentration gradients near the surface would be useful in clarifying the mechanism. It is also of interest to compare the catalysis by mercury with that of the noble metals. In the case of mercury there is a transition from a set of conditions in which the mercury obviously undergoes valence changes either necessary or concurrent to the catalysis to conditions in which no effect on the mercury is evident, just as, for example, bright platinum is itself apparently unaffected by the catalysis.

Copper, Silver, Gold

Copper acts both as a homogeneous and as a heterogeneous catalyst. In these respects copper is very similar to iron, although less active, and it has received far less study. The opinion seems well-founded that the catalysis by the two elements proceeds by much the same mechanism (73). Thus in the homogeneous catalysis there is an alternation between the cuprous and cupric states. Kinetic data and discussion of the reasons for the relative slowness of the copper catalysis have been published (160, 161). Sulfonamides inhibit the catalysis (162). The catalysis by copper in complex form, as with ammonia, amines, and citrate, has received study of considerable precision and detail (163). The results indicate that the decomposition rates encountered may be greater than with colloidal copper hydroxide. Several suggestions regarding mechanism for these complexes, including copper peroxide formation as a step, have been put forward, but none is unequivocal. Copper has also received attention as a promoter or a co-catalyst, especially with iron (161,164), but also with tungsten and molybdenum (154, 165, 166), manganese (167), and cobalt or nickel (168).

The heterogeneous catalysis by copper (134, 168, 169, 170) exhibits the same interesting maximum in rate as pH is increased that is observed with iron. This action for copper has been clearly described by Rudel and Haring (146) and Spitalski, Petin, and Konovalova (171). Thus with 0.4 mg. of cupric ion per liter, 30% hydrogen peroxide was observed to be colorless below pH 3.8 and grass green above pH 4.4. Between these two pH values a yellow turbidity due to copper hydroxide, $Cu(OH)_2$, was observed, and it was in this range that the decomposition rate maxima occurred. Metallic copper itself has not been observed to be particularly active, although it is sufficiently so to bar its use as a material of construction for contact with hydrogen peroxide.

In this group of elements silver is the outstandingly active one. Dissolved argentous silver is not noticeably catalytic, in fact, 90 wt.% hydrogen peroxide can be saturated with silver nitrate without effect. Similarly the metal and silver oxide, Ag_2O, in small proportions are soluble, and are thereby rendered non-catalytic. In the presence of a little alkali, however, this tolerance is markedly reduced, and the addition of argentous ion, metal, or oxide quickly produces a precipitate which initiates decomposition. There is considerable literature (170, 172) dealing with this catalysis. Various theories that the catalyst proper is the metal, the oxide, or a peroxide have been advanced, but the mechanism has not yet been established. Wiegel (173) hypothesized that the continuing catalytic decomposition occurred when the solubility product for argentous hydroperoxide, AgO_2H, was reached. He then proposed an oxidation-reduction cycle between the metal and the hydroperoxide. Weiss (56) interpreted Wiegel's work to show that reaction between argentous ion and perhydroxyl ion on silver metal produced the perhydroxyl radical, resulting in a chain reaction. McIntosh (174) observed that the rate of decomposition on silver exhibited a maximum as the alkali concentration was increased. There is also evidence that alternate solution and redeposition of the precipitate occurs, since silver sols become more coarse (173) in carrying out the catalysis. Similarly, a mirror may be plated out on the container wall during catalysis under appropriate conditions.

Recent studies (175) have established, in agreement with Wiegel, that the precipitate formed is metallic silver, and that argentous ion is present in solution. Both filtration and addition of chloride cause the catalysis to stop.

The relative proportions of argentous silver and alkali required to initiate catalysis have also been determined. In Fig. 6 is shown the silver nitrate concentration required to initiate catalysis in dilute hydrogen peroxide containing varying proportions of alkali. This ''catalysis point'' represents the condition at which catalysis can just be observed in the solution by careful inspection. No precipitate is discernable. With continued addition of silver a solid phase appears, and the conditions at which this less precise observation of these amorphous, white or light gray particles is made are shown in Fig. 7. It is apparent that this ''precipitation point'' is observed under conditions parallel to those of the catalysis point and that Wiegel's observations of the criterion for initiation of catalysis are confirmed. Concurrent observations of the decomposition rate (175) showed the rate to rise after becoming measureable, to reach a maximum, and then to decline to a constant value as the concentration of alkali increased. The rate was first order with respect to hydrogen peroxide concentration in the region where no solid phase was visible and became zero order when the precipitate appeared. This action is shown for 90 wt.% hydrogen peroxide in Fig. 8.

In considering a mechanism to account for these observations with silver it is interesting to note that conditions are favorable for oxidation and reduction between metal and argentous ion over the entire pH range studied, yet the metal is not stable until the criteria of Figs. 6 and 7 are met. The shape of the curves in these figures suggests that the criterion is the establishment of a solubility product. This cannot be argentous hydroxide, AgOH, however, since the product $(Ag^{+})(OH^{-})$ never exceeded 10^{-11}, well short of the accepted value (176) of 4×10^{-8}. Consideration of the solubility product for argentic hydroxide, $Ag(OH)_2$, appears warranted, on the other hand, since the product $(Ag^{++})(OH^{-})^2$ averaged 10^{-28} in these

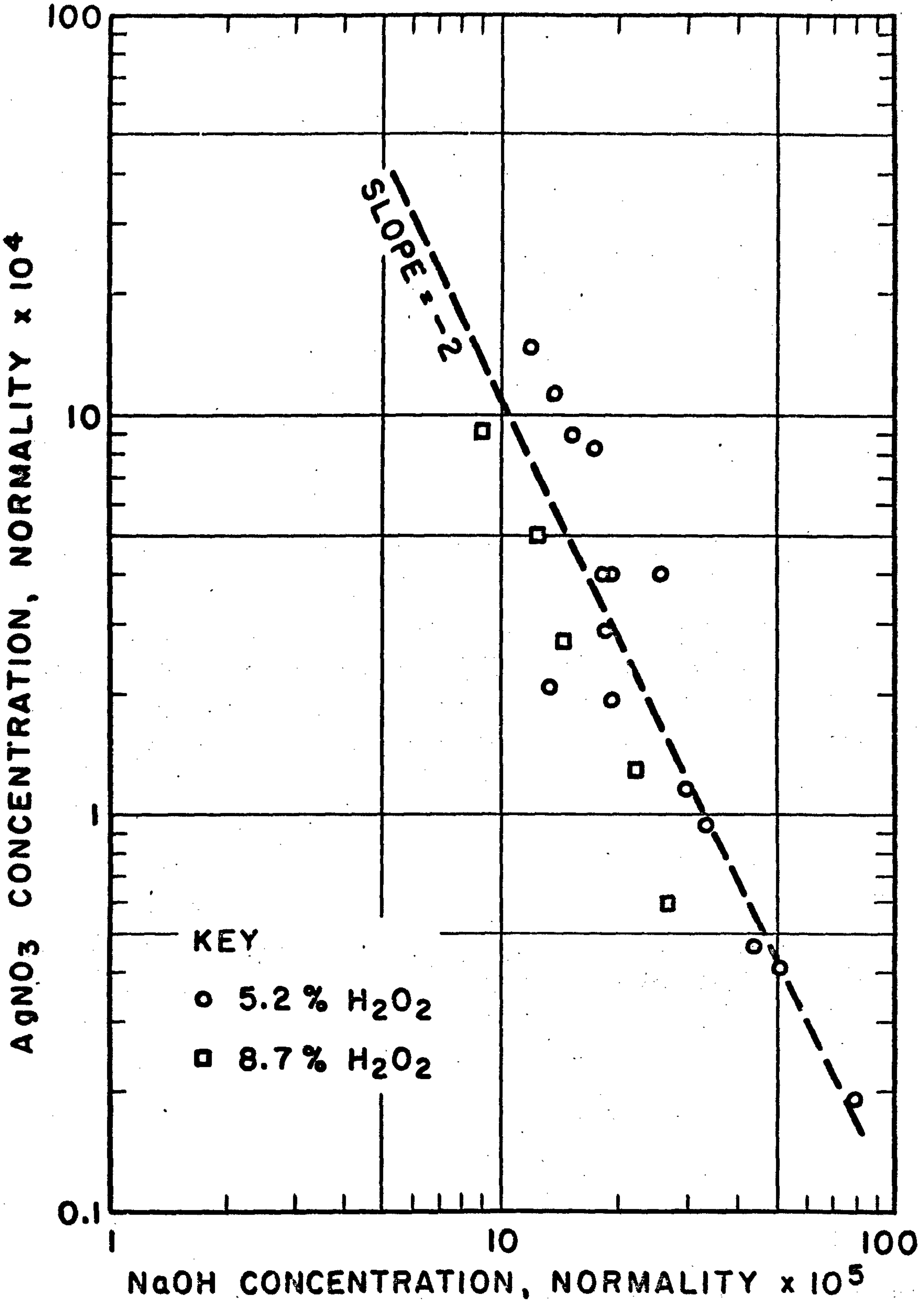

FIG. 6 – CONCENTRATIONS OF ARGENTOUS SILVER AND ALKALI REQUIRED TO INITIATE CATALYSIS IN 5.2 AND 8.7 WT. % HYDROGEN PEROXIDE

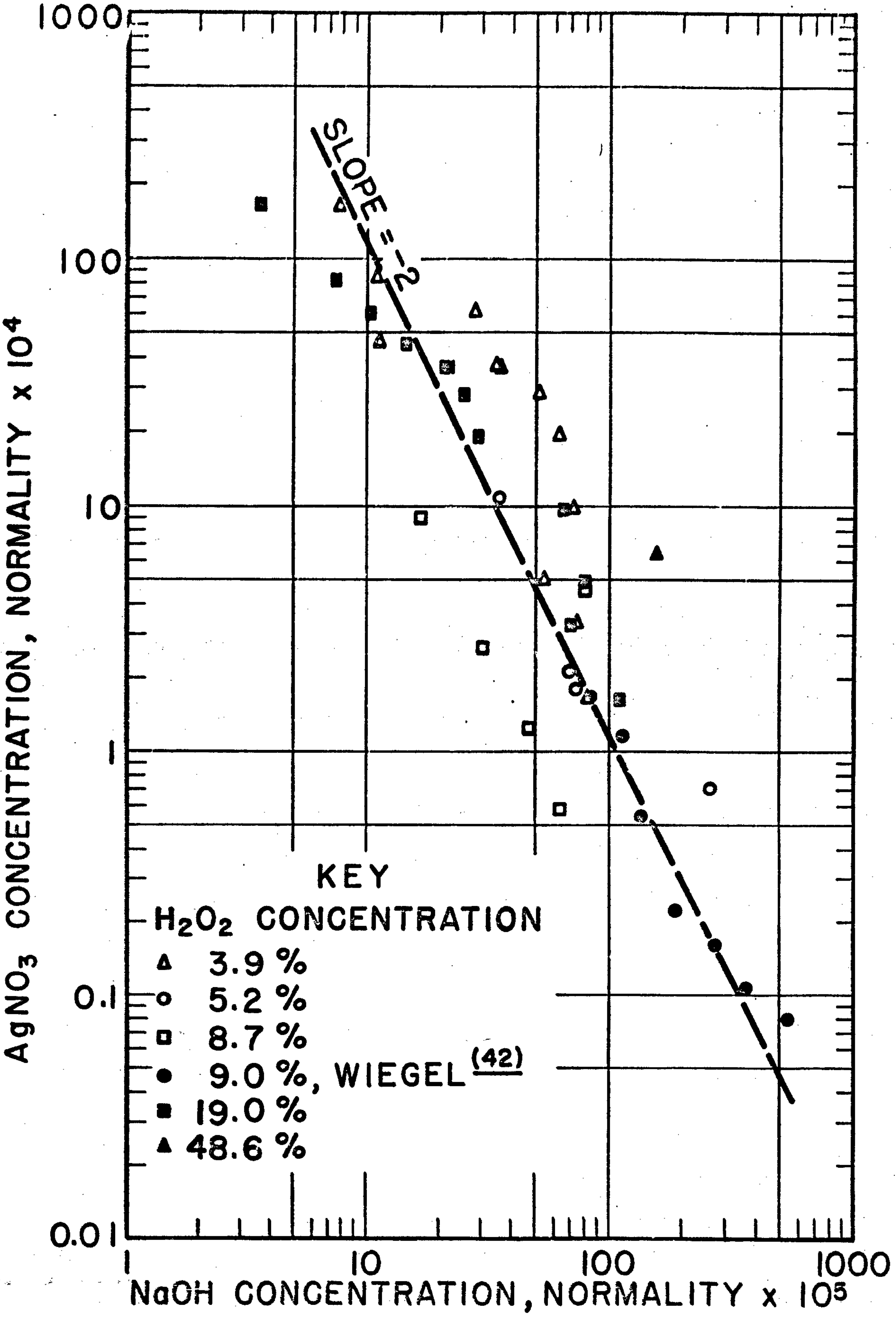

FIG. 7 - CONCENTRATIONS OF ARGENTOUS SILVER AND ALKALI REQUIRED TO FORM PRECIPITATE IN HYDROGEN PEROXIDE

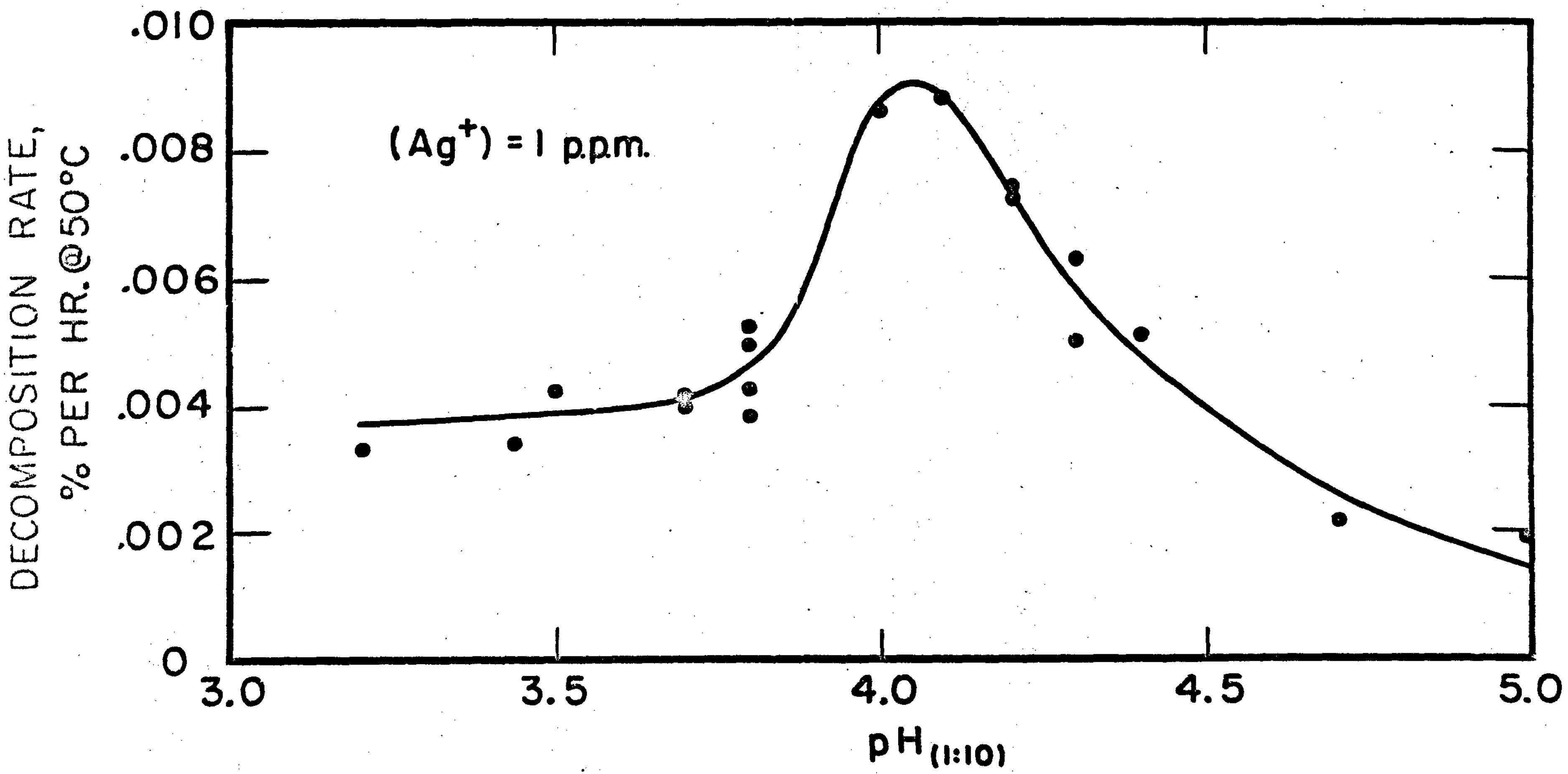

FIG. 8 — EFFECT OF DISSOLVED SILVER ON DECOMPOSITION RATE OF 90% HYDROGEN PEROXIDE

experiments, and this solubility product was estimated to be 10^{-32}. Measurable concentrations of argentic silver would not be expected to be formed by hydrogen peroxide except at high acidity (177), but reaction with argentic silver is known (178) to be vigorous. In spite of this agreement and the obvious slope of -2 in Fig. 6 and 7 it can be shown that the slope should be -1 for solubility products involving argentous or argentic (II or III) hydroxide or argentous hydroperoxide. The apparent lack of involvement of argentous ion and the necessity for metallic silver to be present suggests an oxidation-reduction cycle between metal and the argentic state, but this and the other mechanisms suggested remain speculative.

Gold provides a heterogeneous catalysis typical of the noble metals such as platinum, palladium, etc. A gold sol formed either *in situ* by reduction of auric chloride (179) or externally by the arc method (180) provides a catalyst which becomes increasingly active with increasing alkali concentration. The features of this catalysis, including the effects of salts and poisons, have been described excellently by Bredig and Reinders (180). Further investigations have been made of the effects of methods of preparation of gold sols and the temperature coefficients observed (181) and the degree of dispersion of the sols (95, 182).

Nickel, Palladium, Platinum

Nickel exerts virtually no catalytic effect in acid solutions of hydrogen peroxide, and shows only a mild catalysis when colloidal nickel hydroxide, $Ni(OH)_2$, is precipitated by the addition of alkali (75, 183). The action of mixtures of nickel oxide, Ni_3O_4, with other oxides (168) and supported nickel sulfate (184) have been studied with respect to their catalytic activity toward hydrogen peroxide. In the case of the supported nickel only silica gel among a number of supporting substances was found to activate catalysis to any degree. This action was observed to exhibit a maximum as the proportion of nickel on the silica was increased.

Palladium appears to behave much as platinum does, the features of catalysis by palladium specifically having been reported by Bredig and Fortner (185). The mechanism of both catalyses has been suggested (56) to involve electron transfer from the metal, and the activity of both metals has been reported (186) to exhibit a maximum with time of contact. A difference between the two appears to be engendered by the high absorptivity of palladium for hydrogen gas. In the hydrogenated state the palladium becomes a more active catalyst (185), and it is of interest to contrast this action with the report (187) that hydrogenated palladium can also bring about the formation of hydrogen peroxide from oxygen. A further distinction is found in the observation (188) that palladium black is no more active as a catalyst for hydrogen peroxide decomposition than the massive metal.

Platinum has received the greatest attention among the noble metal catalysts for hydrogen peroxide decomposition. In their lengthy study of this catalyst Bredig and von Berneck (86) characterized it as an "inorganic ferment", and it has often been referred to in this fashion to denote a resemblance of its action to that of enzymes. Platinum has been studied chiefly in the colloidal state or as platinum black; in these forms it is ordinarily highly active, whereas bright sheet platinum apparently is a considerably less active catalyst. The catalysis on platinum has generally been found (189,190) to be first order with respect to hydrogen peroxide concentration, but second order kinetics have also been reported (191). The presence of alkali increases the activity of platinum and acid inhibits it (86,190,192). Tartar and Schaffer (192) concluded that under acid conditions both hydrogen ion and the acid anion exert an effect, but that in basic solution the promotion is due to hydroxyl ion alone. They also concluded from studies of platinum protected by gelatin that the presence of acid or alkali affects both the catalytic process and the protection by the gelatin. Other treatments such as aging of the catalyst (193), heating (194,195), electrical polarization (196) or x-radiation (197) also affect the activity. Although heat treatment was found to decrease the activity of platinum, the ratio of the decomposition rates at two temperatures was unaffected by this treatment (194). The relationship of the potentials assumed by platinum in hydrogen peroxide (198) to the mechanism of decomposition has not been adequately explained (see also the discussion of standard electrode potentials in Chapter 5). The effect of the degree of dispersion on activity has been disputed. Sieverts and Brüning (190) found platinum black to be intermediate in activity between the colloidal and massive metal, but other (188) have concluded that the activities of the smooth metal and of platinum black are the same on an equal surface area basis. Alloying platinum with 10% iridium, rhodium, palladium, ruthenium, or osmium was found (199) to produce a series of hydrogen peroxide decomposition catalysts the activity of which decreased in the order cited. Substitution of water with other solvents also affects the decomposition rate on platinum, as discussed in Chapter 7.

A number of observations have been made of the effects upon platinum of various inhibitors and poisons. These include mercury and lead (200), carbon monoxide (201), triazo ion (202), cyanide (203)(disputed (204)), protective colloids (205), and many other salts (203, 206, 207) and non-electrolytes (203,207). In the case of poisoning by mercury, Maxted and Lewis (208) observed the decrease in activity to be proportional to the amount of mercury added up to a certain point. Kubokawa (209) found this relationship to be a linear logarithmic one. Salts exhibit differing effects as inhibitors for platinum. Heath and Walton (206) found aluminum, thorium, sodium, nitrate, sulfate, and fluoride ions without effect, whereas chloride, nitrite, and cyanide acted as poisons. Hexaplatinate, $Pt(OH)_6^=$, was observed neither to catalyze the decomposition nor to affect the action of platinum. Neilson and Brown (207) concluded upon the basis of a study of the effects of various sodium salts and chlorides that cations inhibit the decomposition of hydrogen peroxide by platinum and that anions accelerate its action.

Several mechanisms such as a cyclic oxidation-reduction involving platinum oxides, formation of atomic oxygen, reciprocal depolarization of atomic hydrogen and hydroxyl radical (210), and electron transfer (56) have been suggested to account for the catalysis of hydrogen peroxide decomposition by platinum. Rockstroh (211) recently reviewed this subject and concluded that the active form of platinum is the metal and that it provides a site for reaction rather than entering into an oxidation-reduction scheme. This is in accord with the much earlier conclusion reached by MacInnes (212), who scouted the intermediate oxide theory and emphasized the importance of adsorption. In this respect it is reported (190) that platinum dioxide is reduced by hydrogen peroxide and platinum monoxide in unaffected. There seems to be no doubt that the observed rate of decomposition on an active platinum surface is limited by the rate of diffusion of hydrogen peroxide to the catalyst surface (211,213) (See also the discussion of the coefficient of diffusion in Chapter 5). Further insight is provided by the study by Pennycuick (214) of the nature of colloidal platinum. It was concluded that the hydrophobic sol produced in an oxygen-containing system is negatively charged, with both metal and dioxide present on the surface of the particles and hexaplatinate ion present in the lyosphere surrounding the particles. Boiling or aging causes hexaplatinate to pass into the bulk of the solution and leads to coagulation. In a nitrogen or hydrogen atmosphere no oxide or platinate is present, the system being stabilized by the distribution of hydrogen and hydroxyl ions. This description appears to be in accord with the conclusion that the metal is the active entity. Thus, sols formed in a nitrogen or hydrogen atmosphere are several-fold more active than those produced under oxygen (215), and exposure of a sol formed under oxygen to a low partial pressure of oxygen increases its activity (87,216) (although greatly increased oxygen pressure is without effect (217)). The ineffectiveness of increased proportions of hexaplatinate has been noted above. The conclusion that substances such as chloride and cyanide owe their effectiveness as poisons to their ability to form complexes with platinum also appears to be consistent with this viewpoint. It seems likely that the metal itself functions by electron transfer to the hydrogen peroxide.

Cobalt, Rhodium, Iridium

In the metallic state cobalt exhibits a peculiar effect of passivity, that is, on being immersed in hydrogen peroxide the metal acquires an oxide coating and a mild catalysis ensues, but this behavior may be succeeded unpredictably by a state of enormously enhanced activity. At the exhaustion of the initial hydrogen peroxide and addition of more, however, the former slow rate of decomposition is resumed. A qualitative study of this phenomenon (218) revealed no correlation between appearance of the metal surface, electrode potential, pH, temperature, or time of immersion and the onset of the rapid catalysis. It appeared that the effect of high activity could be induced only in concentrated hydrogen peroxide, and that it was associated with large changes in electrode potential, generally toward more cathodic values.

Cobaltous ion does not exert a notable catalytic effect in hydrogen peroxide solution, but upon the addition of alkali, cobaltic hydroxide is precipitated and decomposition occurs (219). Tryhorn and Jessop (220) found the activity of this catalyst to vary considerably, and the mode of its action is not yet clear, although the following characteristics have been observed (218). Figure 9 provides a comparison of the pH-titration curves to be observed with a solution of cobaltous ion in the presence and absence of hydrogen peroxide. (The relative displacement along the abscissa is without significance, since a certain amount of free acid was initially present in these experiments.) The results indicate that in the presence of hydrogen peroxide direct oxidation to the cobaltic state and precipitation of cobaltic hydroxide occurs before conditions for the precipitation of cobaltous hydroxide are reached. Other experiments (218) showed that the concentration of cobalt required to initiate catalysis is inversely proportional to the alkali concentration, the criterion for catalysis thus being the attainment of a solubility product. At alkali concentrations below about 6N all precipitated cobalt is in the trivalent state, all soluble cobalt divalent. Some solution of trivalent cobalt occurs at more basic conditions. Pyrophosphate, carbonate, sulfide, and arsenate are ineffective as inhibitors of this catalysis, and the ultraviolet absorption spectrum of alkaline solutions containing cobaltous ion and cobaltic hydroxide is not affected by the addition of hydrogen peroxide. Radioactive tracer studies (221) showed that no exchange occurs between cobaltous

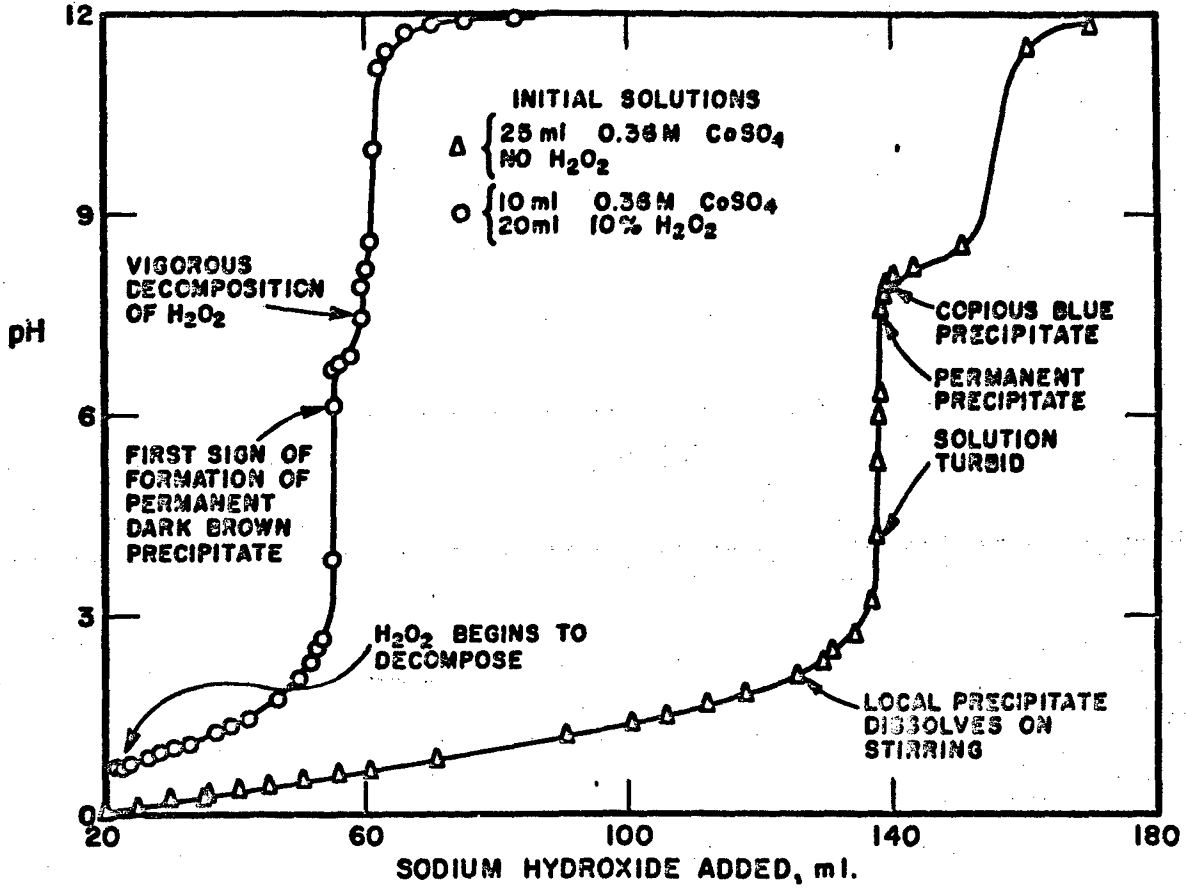

FIG. 9 COMPARISON OF TITRATIONS OF COBALT SULFATE WITH ALKALI IN THE PRESENCE AND ABSENCE OF HYDROGEN PEROXIDE

ion and cobaltic hydroxide either in the presence or absence of hydrogen peroxide. These facts appear to rule out an oxidation-reduction cycle as the mechanism of catalysis. A free radical mechanism remains for consideration, however. This has been suggested to explain the catalytic decomposition of ozone (222) and cumene hydroperoxide (223) by cobalt. Furthermore, a study (224) of the oxidation of water to oxygen by cobaltic ion revealed that this reaction can induce vinyl polymerization, and it was postulated the hydroxyl radicals are formed by electron transfer from hydroxyl ion to cobaltic ion, the latter perhaps being present as a dimeric aqueous complex. Other complexes of cobalt such as with ammonia and citrate also exert a catalytic effect on hydrogen peroxide (225). Supported cobalt (184,226) is also catalytic, and instances of promotion of hydrogen peroxide catalysts by cobalt have been reported (168,227).

Rhodium and iridium have received little attention in regard to their action as hydrogen peroxide decomposition catalysts. Rhodium black is only briefly reported to be more active than the massive metal (188). More informative studieshave revealed that the decomposition of hydrogen peroxide on iridium sols is kinetically first order in hydrogen peroxide concentration (217,228). Although the action of iridium is apparently quite similar to that of platinum, *e.g.*, in being inhibited by sulfide, mercury, and cyanide, Brossa (228) found that iridium is distinguished by the fact that alkali does not affect it, whereas acid enhances its action.

Iron, Ruthenium, Osmium

The homogeneous catalysis of hydrogen peroxide decomposition by iron has received extensive and skilled attention. Consequently a fairly detailed description is available in this instance, although many questions remain unanswered. The discussion below includes reference to the following aspects of this catalysis: the decomposition of hydrogen peroxide accompanying the oxidation of ferrous ion to the ferric state, the mechanism of the homogeneous decomposition mediated by ferric ion, the inhibition and promotion of the latter, decomposition brought about by iron in complex form, and heterogeneous iron catalysis. Several reviews (73,229,230,231,232) deal with this subject (excepting the heterogeneous catalysis); those by Baxendale (73), Medalia and Kolthoff (229), and Uri (230) are to be recommended especially.

The earlier investigations of the catalysis by iron (233, 234,235,236,237,238,239) have been concerned with both the catalysis accompanying the oxidation of ferrous ion and that due to ferric ion, however, the former has attracted particular interest because of its relation to the oxidizing powers of the ferrous ion-hydrogen peroxide mixture termed Fenton's reagent (229). Ferrous ion is oxidized by hydrogen peroxide according to the stoichiometry: $2Fe^{++} + H_2O_2 + 2H^+ \longrightarrow 2Fe^{+++} + 2H_2O$ (31)

This reaction is quantitative if ferrous ion is in excess, but decomposition of hydrogen peroxide and the evolution of oxygen occurs along with the oxidation of ferrous ion if hydrogen peroxide is present in excess. In addition to establishing these facts Mummery (234) also found that the initial liberation of oxygen in the latter instance occurred at an exceedingly rapid rate. This subsided to a much lower value as ferric ion became the dominant form of iron and catalysis due to it ensued. Haber and Weiss(240) defined for this phenomenon the consumption ratio, $\Delta(H_2O_2)/\Delta(Fe^{++})$. It is apparent that the value of this ratio will be 0.5 if reaction (31) proceeds quantitatively, and larger values will result if catalytic decomposition of hydrogen peroxide accompanies the oxidation of ferrous ion. There has been disagreement in regard to the limiting value which this ratio may assume, but it now seems well established by the work of Barb, Baxendale, George, and Hargrave (161) that this ratio does reach a limit determined by the reaction conditions and does not increase to the large values reported previously (240).

Several mechanisms have been put forward to account for the decomposition of hydrogen peroxide accompanying the ferrous ion oxidation. The formation of ferrate, FeO_4^{++}, as an intermediate was postulated by Bohnson and Robertson (235) on the basis of spectroscopic studies. The coloration they observed, however, is now attributed to the presence of impurities. A higher oxide of iron, such as Fe_2O_5, has been suggested to take part (237). Various kinds of complexes of iron and hydrogen peroxide have also been put forward. Bray and Gorin (238) proposed a mechanism involving ferryl ion, FeO^{++}. The presently-accepted mechanism, however, is one in which intermediate roles are assumed by the free radicals hydroxyl and perhydroxyl. Such a mechanism was first suggested by Haber and Weiss (240) following an earlier suggestion of Haber and Willstätter (241). Aside from its value to establish the mechanism of this catalysis this theory marks a significant advance in the understanding of reaction mechanisms generally. The mechanism involves the following set of reactions:

$$Fe^{++} + H_2O_2 \longrightarrow Fe^{+++} + OH + OH^- \qquad (32)$$

$$Fe^{++} + OH \longrightarrow Fe^{+++} + OH^- \qquad (33)$$

$$H_2O_2 + OH \longrightarrow O_2H + H_2O \qquad (34)$$

$$Fe^{++} + O_2H \longrightarrow Fe^{+++} + O_2H^- \qquad (35)$$

$$Fe^{+++} + O_2H \longrightarrow Fe^{++} + H^+ + O_2 \qquad (36)$$

This has been established by the work of Barb, Baxendale, George, and Hargrave (161) which should be consulted for the extensive experimental justification. This differs from the scheme originally suggested by Haber and Weiss (240) in that they proposed the reaction

$$H_2O_2 + O_2H \longrightarrow OH + H_2O + O_2 \qquad (37)$$

to occur instead of reactions (35) and (36). It can be seen that the oxygen is generated by the occurrence of reaction (36), and the competition of ferrous ion and hydrogen peroxide for hydroxyl radical determines the extent to which reaction (36) may take place.

The catalysis of hydrogen peroxide decomposition brought about by ferric iron proceeds similarly (161), the series of reactions involved being initiated by

$$Fe^{+++} + O_2H^- \longrightarrow Fe^{++} + O_2H \qquad (38)$$

and followed by reactions (32, (34), (35), and (36). This scheme is consistent with the kinetic expression $-d(H_2O_2)/d\theta = k(Fe^{+++})(H_2O_2)/(H^+)$ observed at high values of the concentration ratio, $(H_2O_2)/(Fe^{+++})$. It likewise accounts for the relation $-d(H_2O_2)/d\theta = k'(H_2O_2)^{3/2}(Fe^{+++})/[(H^+) + K]$ * observed at very low ratios and the still different kinetic expression found for intermediate concentration ratios. This mechanism also differs from the one suggested by Haber and Weiss (240); further experimental work (242,243) and discussion (244,245) pertinent to the kinetics and mechanism have been furnished by Andersen and Christiansen (242), Onat and Parts (243), Weiss (244), and Abel (245). In the light of the considerable number of studies of the initiation of polymerization by the iron-hydrogen peroxide system (246) there seems little doubt that free radical mechanisms are operative in these catalyses. Many questions remain, however. For example, the participation of ferrous ion in the ferric ion catalysis has not been firmly established (73), although the evidence (247) for it is reasonable. A complex, $[Fe(O_2H)]^{++}$, of the ferric ion and the perhydroxyl ion has been demonstrated (248) to occur, but it is not clear to what extent it participates directly in the above schemes. The more recent discussions of mechanism have also favored a role for the superoxide ion, O_2^-, as the actual reactant rather than the perhydroxyl radical from which it would be formed (249,250). Perhaps of greatest interest is the revival of consideration of higher valent iron as an intermediate. Medalia and Kolthoff (229) pointed out that the ferryl ion of Bray and Gorin may exhibit many of the attributes of the hydroxyl radical and might thus play a part in the above schemes. Cahill and Taube (251) have also suggested that quadrivalent iron may be an intermediate; they further propose that the two-electron step which produces it may occur side by side with a one-electron transfer, thus providing roles for both ferric ion and the state of higher valence.

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* K represents the ferric ion hydrolysis constant.

Studies of the oxidation of ferrous ion by hydrogen peroxide have yielded values for the frequency factor and activation energy (161, 252) and heat of reaction (253).

The effects of various anions such as nitrate (254), fluoride (161,250,255), chloride (161,256), sulfate (256), citrate (257), phosphate (255,258), and acetate (255) upon the catalytic decomposition of hydrogen peroxide by iron salts have been investigated. Effects of both promotion and inhibition were observed with varying citrate concentrations, whereas the effect of chloride was found to change from inhibition to inertness depending upon the ferric ion concentration. Others such as fluoride, phosphate, and acetate are observed to act as inhibitors, just as acetanilide (259) does. Representative data showing the effects of such inhibitors as phosphate and stannate are presented in Chapter 9. Other additives are outstanding as promoters for this catalysis, and the action of copper (161,164), molybdenum (260), mixed molybdenum and tungsten (261), and tunsten alone (262) have been studied in this respect.

Iron in various complex forms also causes catalysis, although the reactions have not been investigated extensively enough to establish the mechanism. These catalyses are of particular interest, however, because of their relation to the enzyme catalase, another catalyst which contains iron in a complex form. Decomposition involving complexes with dipyridyl and phenanthroline (237,239,263) has received attention in connection with studies of the mechanism of catalysis by iron as ferrous or ferric ion. In reviewing the catalysis by complex iron, Baxendale (73) has pointed out that during the formation of these complexes in the presence of hydrogen peroxide there is a catalytic decomposition more rapid than that observed with ferric ion alone or subsequently with the complex alone. It was concluded that in this instance too, a free radical mechanism is operative. The decomposition brought about by cyanide complexes of iron (73,264) is of particular interest because of the effect of radiation upon it. Kistiakowsky (265) observed that the weak catalytic effect of a ferrocyanide-ferricyanide mixture was [illegible] enhanced by exposure to light, and that the [illegible] decomposition was [illegible] after illumination was discontinued. Srikantan and Rao (266) suggested a role in the mechanism of this catalysis for a complex into which a hydrogen peroxide molecule is substituted, and the extended study of Lal (267) has established the importance in the mechanism of the aqueous complex formed by hydrolysis of the cyanide. This work has also ruled out ferric hydroxide as the active entity. The actions of ferri-nitrosopentacyanide (268) and various metal-ferrocyanides (269) have also been studied.

The decomposition of hydrogen peroxide by heterogeneous iron catalysts has not yet received any study which permits much insight into the mechanisms involved. Ferric hydroxide is an active catalyst (236,270), and an example of its action when present in small amounts relative to the hydrogen peroxide is given in Chapter 9, as well as an interpretation of the results as a colloidal surface effect. Others have suggested that the true catalyst is ferric ion adsorbed on the colloid (271) or that an oxidation-reduction cycle takes place (272) and have compared the effectiveness of this catalyst with its degree of crystallinity (273). The catalytic activity of iron oxide, Fe_2O_3, appears to have been studied only from the standpoint of the effect of crystal structure (236,274). Other heterogeneous iron catalyst for hydrogen peroxide decomposition that have been investigated are blast furnace slag (275), pyrite (276), and spinels (84). In the latter instance Schwab, Roth, Grintzos, and Mavrakis (84) postulated that the activity of a magnesium ferrite is due to ferrous ions present as a consequent of disorder at tetrahedral lattice sites; a zinc ferrite, which does not contain such ferrous ions exhibits no activity. Heterogeneous catalysis by mixed iron-copper hydroxides (277) and supported iron (239,278)) has also been recorded.

Ruthenium appears not to have been investigated for its action as a hydrogen peroxide decomposition catalyst. Osmium in alkaline solution provides a catalyst of rather high activity.

Fritzman (279) found it possible to observe the catalysis of dilute hydrogen peroxide with concentrations of osmium tetroxide as low as 10^{-6} mole/liter. At a thousand-fold greater osmium concentration the rate of decomposition was independent of osmium concentration and first order with respect to hydrogen peroxide. A maximum in rate was observed as the alkali concentration was increased. Neas, Raymond, and Ewing (280) studied this catalyst at high alkali concentration $[(NaOH)/(OsO_4) = (400)]$ in an apparatus permitting extremely rapid mixing and found the rate of decomposition to be dependent upon the square of the osmium tetroxide concentration (at mixed conditions). In the presence of acetic acid or propionic acid the catalytic decomposition and acid oxidation, which is negligible without hydrogen peroxide, appear to go forward to parallel and independent fashion (281).

Manganese, Tecnetium, Rhenium

The catalysis of hydrogen peroxide decomposition provided by manganese is an active one which has been observed and reported often. Dissolved manganese in the manganous state is itself without effect (282), although it has been reported to promote other catalysts, for example, copper (283). It has also been claimed that a homogeneous catalysis of hydrogen peroxide decomposition can accompany the stoichiometric reduction of permanganate, referred to in Chapter 7. These studies, however, have been made at pH values substantially higher than those used in the common analytical procedure. Evidence for such a catalysis initiated by permanganate has been published by Fouinat (284) and Abel (285) and has been reviewed by Baxendale (73). The mechanism proposed to account for this is one involving free radical intermediates; such mechanisms have also been suggested for other reactions of permanganate (286). However, the possibility of formation of manganese dioxide in the reaction of permanganate with hydrogen peroxide is well-known (287), and it is possible that this in fact provides the catalyst. Furthermore, calculations made by the present authors with the data presented (284) indicate that the value of the product

$(Mn^{++})(OH^-)^2$ exceeded 10^{-14} in all the experiments cited in this reference in which complete decomposition of the hydrogen peroxide occurred. This is consistent with the mechanism involved in catalysis by manganese dioxide as discussed below. Others (288) have described experimental methods of following the extremely high rate of the permanganate reduction and subsequent catalysis by manganese dioxide.

The catalysis by manganese dioxide (96,289) appears to occur *via* an oxidation-reduction cycle. A study (282) of this revealed that when manganous ion or permanganate was added to very dilute hydrogen peroxide solutions of various alkalinities, no catalysis occurred until the solubility product for manganous hydroxide, approximately 10^{-14}, was reached. The logarithm of the value of the product, $(Mn^{++})(OH^-)^2$ that had to be exceeded before catalysis began, was an inverse linear function of the concentration of hydrogen peroxide. The concentration of pyrophosphate required to prevent this catalysis was proportional to the manganous ion concentration. Radioactive tracer experiments extablished that exchange occurred between manganous ion and colloidal manganese dioxide while the decomposition took place and the mechanism was therefore postulated to be:

$$MnO_2 + H_2O_2 + 2H^+ \longrightarrow Mn^{++} + 2H_2O + O_2 \qquad (39)$$

$$Mn^{++} + 2H_2O \longrightarrow Mn(OH)_2 + 2H^+ \qquad (40)$$

$$Mn(OH)_2 + H_2O_2 \longrightarrow MnO_2 + 2H_2O \qquad (41)$$

However the evidence regarding exchange in the absence of hydrogen peroxide (291) is conflicting, and since these tracer studies involved a step in which the solutions were boiled, they are not conclusive (284,290).

The metal apparently catalyzes the decomposition by the same mechanism. The potential assumed by metallic manganese bearing a coating of manganese dioxide has been measured in aqueous solutions of varying pH and manganous ion and hydrogen peroxide concentration (292). The results were compared with similar potentials with platinum and with theoretical potentials calculated by assuming various mechanisms for the catalytic decomposition of hydrogen peroxide. The observations were consistent with the assumption that the potential was controlled by the reaction for the reduction of manganese dioxide to manganous ion. Scholder and Kolb (293), on the other hand, have suggested that peroxymanganates may participate in the catalytic mechanism. Further work will be required before the state of the catalyst can be characterized satisfactorily. In particular it is known that the composition of manganese dioxide seldom corresponds exactly to the formula MnO_2 (294); furthermore the oxide having this exact composition is reported (294) to be a weak catalyst. It seems further that the activity of the several oxide forms (295) can be related to their depolarizing properties (296). Heat treatment likewise affects the activity of manganese dioxide toward hydrogen peroxide (297). Supported manganese catalysts (298) appear to offer systems more amenable to characterization. Mooi and Selwood (299) studied the decomposition of hydrogen peroxide on oxides of manganese supported by alumina and rutile by magnetic susceptibility techniques (93) and found that the activity could be correlated with the oxidation state of the catalyst. The activity was at a maximum when the oxidation state was between +3 and +4, and an oxidation-reduction cycle involving manganese dioxide and the oxide Mn_2O_3 was therefore suggested. Reasons for preferring this cycle over the cycle indicated in reactions (39) to (41) were given. A question in regard to the relative ease of nucleation and formation of the catalytic solid phase was also raised. This is pertinent to all the instances in which a heterogeneous catalyst is formed <u>in situ</u>. It seems reasonable that the prevalence of requirements for a solubility product to be attained before catalysis can proceed indicates this to be a common pathway for formation of the solid, <u>e.g.</u>, the dioxide is the active manganese catalyst, but although the equilibrium is favorable this solid cannot be formed directly from solution, prior precipitation of manganous hydroxide being required to provide a solid phase upon which the higher oxidation state of manganese can be stabilized. Mooi and Selwood also suggested that the detailed mechanism may involve an electron transfer process whereby hydroxyl radicals are generated.

No report is available in regard to the possible catalytic action of tecnetium or rhenium.

Chromium, Molybdenum, Tungsten

These three elements are of particular interest because the homogeneous catalysis of hydrogen peroxide decomposition which they cause provides good evidence of the operation of mechanisms involving peroxy compounds as intermediates. Baxendale (73) has reviewed the subject. The qualitative features of the homogeneous catalysis by chromate have been reported by many of the early workers; extended kinetic studies first being provided by Riesenfeld (300) and Spitalsky (301), and amplified since by others (302,303,304). The hexavalent state, either as chromate, $CrO_4^{=}$, or dichromate, Cr_2O_7, is the active one, although some reduction to the chromic state, Cr^{+++}, occurs in acid solution with hydrogen peroxide. The mechanisms postulated have agreed in that the chromate reacts with hydrogen peroxide to form a peroxychromate which then decomposes to yield molecular oxygen. Uncertainty remains in regard to the subsequent form of the chromium, whether it is reduced to chromic ion, then oxidized again to chromate (301) or whether the chromate is regenerated directly from the peroxychromate (303,304). However, it appears safe to conclude that an oxidation-reduction cycle involving peroxychromate occurs. Promotion of chromate, with cobalt (227), manganese (305,306), molybdenum (307), and copper, iron, and nickel (306) has been described; vanadium is reported to inhibit the system (308).

As a heterogeneous catalyst chromium is not particularly active. The metal yields only a feeble catalysis which is little affected by pH, oxide formation on the surface, or the presence of dissolved chromium. In concentrated hydrogen peroxide some solution of the metal may be observed; similar preferential solution of chromium from stainless steel can also occur. Colloidal chromic hydroxide (309) and supported chromium (299,310,311) have also been studied.

The homogeneous catalysis by molybdenum (312) seems to proceed through the formation and decomposition of the peroxymolybdates, $MoO_6^{=}$ and $MoO_8^{=}$, and possibly, $MoO_5^{=}$, which are formed in hydrogen peroxide solution from molybdate, $MoO_4^{=}$. No other valence state appears to be involved. The promotion of the molybdate catalysis by other metals has been studied by Uri (154) and especially by Bogdanov (260,261, 307,313,314).

Tungstate is a less active catalyst than molybdate (becoming virtually inert in acid), but appears also to act through the equivalent peroxy compounds, $WO_8^{=}$ and $WO_6^{=}$. The kinetics of the catalysis have been studied by Bogdanov (315). The promotion of this catalysis has also received attention (261,262,313,316). The catalysis of hydrogen peroxide decomposition by tungsten in the metallic state or as the carbide has been studied briefly (317); in this state the catalytic activity of tungsten is reported to decline repidly with time.

Vanadium, Niobium, Tantalum

Vanadate has been described as providing a homogeneous catalyst for hydrogen peroxide decomposition which operates through an oxidation-reduction cycle involving various peroxyvanadates (308,318,319). Vanadium supported on rutile or alumina was found to be inactive (299). Metallic niobium was reported to act as a slow catalyst, whereas tantalum is inert (320).

Titanium, Zirconium, Hafnium

No information is available regarding the extent, if any, to which titanium, zirconium, or hafnium act as catalysts for hydrogen peroxide decomposition.

Boron, Aluminum, Scandium, Yttrium

Borate with hydrogen peroxide enters into an equilibrium which provides stable peroxyborate. The inertness of aluminum metal and the stabilizing properties of the hydrous oxide are discussed in Chapters 4 and 9, and further evidence of its non-catalytic nature is available (141,321). Scandium and and yttrium apparently have not been investigated as hydrogen peroxide catalysts.

Rare Earths, Actinides

The oxides of cerium and thorium were briefly reported by Lemoine (141) to be moderately good catalysts for hydrogen peroxide decomposition. Further information on these series of elements is not available.

The Alkaline Earths

Although the alkaline earths have occasionally been included in lists of catalysts for hydrogen peroxide decomposition, it seems reasonable to conclude that these elements are not catalysts per se, but rather exert an effect through the alkalinity of certain of their solutions. Magnesium ion does in fact provide a stabilizing action under appropriate conditions.

The Alkali Metals

No catalytic action upon hydrogen peroxide decomposition is exerted by the alkali metals.

Soils, Waters, and Miscellaneous Agents

The action of various soils (322), fuller's earth (323), metallized bentonite (324), mineral waters (325), sea water (326), synthetic detergents (327), and alloys (99) as catalysts for the decomposition of hydrogen peroxide has been observed and studied. In the case of natural waters, iron and chloride appear to be the chief active components.

Periodic Catalysis

A noteworthy aspect of a number of the catalysts for hydrogen peroxide decomposition is the remarkable periodicity of action which they exhibit. The best known examples are iodate (126) and mercury (156), but the phenomenon also occurs with metallic iron and copper (328) and other examples have been reported in the monograph by Hedges and Myers (329).

It seems clear that periodicity arises when physical rate processes such as diffusion bring about periodic changesin the concentration of some chemical species taking part in the catalysis. It has been suggested that the phenomenon may be due to the alternate relief and establishment of supersaturation with oxygen in the solution. However, in the instance of iodate catalysis (126) it was found that it was necessary to eliminate supersaturation before the periodicity was revealed. A study of the decomposition of quite pure hydrogen peroxide (105) showed no difference between experiments with and without shaking as long as the unshaken apparatus was allowed to come to equilibrium with respect to supersaturation. A case in which supersaturation may play a role may be observed if concentrated hydrogen peroxide is spilled over an expanse of cement floor. Under such circumstances waves of increased rate of oxygen release sometimes periodically sweep across the surface of the actively decomposing liquid.

Promotion, Inhibition, and Poisoning

Attention has been directed in the foregoing discussion of the various elements to studies which have demonstrated the promotional effect often observed when mixtures are tested for their catalytic effect. By promotion is meant an increase in decomposition rate over and above the sum of the rates to be observed with the individual components of the catalyst mixture. A well-known example encountered in homogeneous catalysis is that observed with mixtures of copper and iron (161,164); this is discussed further in Chapter 9. A number of other examples and a discussion of the phenomenon have been given by Berkman, Morrell, and Egloff (ref. 68, p. 414). Promotion is not confined to homogeneous catalysts, however, and may also be observed with co-precipitated metal hydroxides. This is shown for the case of silver in Figure 10. The results (104) exhibited there were obtained by the same procedure described on page 171 and may

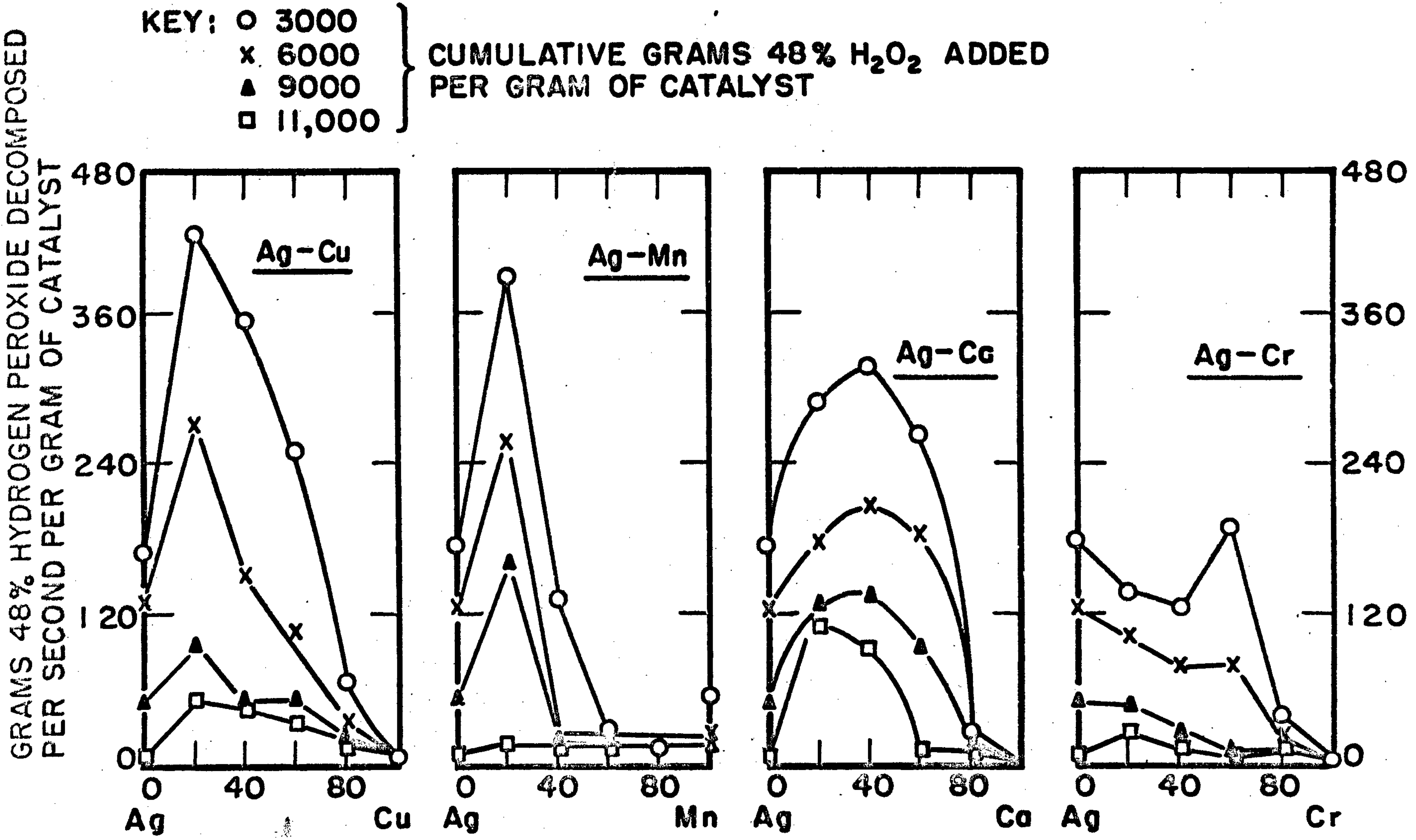

FIG. 10 — PROMOTION BY COPPER, MANGANESE, CALCIUM, AND CHROMIUM OF HYDROGEN PEROXIDE DECOMPOSITION BY SILVER (TOTAL WEIGHT OF METAL = 0.0118 g. IN 10 c.c. 4N NaOH)

be compared with Figure 5. These promotion studies indicate how the effect may vary with the dilution and age of the catalyst as successive portions of hydrogen peroxide are decomposed. It is also of interest to note the marked enhancement brought about by calcium hydroxide, which by itself has relatively little catalytic effect. Supporting a catalyst on an inert carrier may also promote its action; it may convert on otherwise inert material into a catalyst, or it may activate an ineffective valence form as in the case of argentous ion (81). The ease with which such promotion may come about through support by glass or silica (330) must be considered as a possible source of error in decomposition experiments. Other supported catalysts have been referred to in the discussion above. The kinetics observed on supported catalysts are often unusual (311).

Occasional mention has also been made in the above discussion of catalysts of substances which diminish or stop the decomposition of hydrogen peroxide, termed inhibitors or poisons. Practical application of such substances is made in stabilization as discussed in Chapter 9. A wide variety of substances act as poisons and a number have been mentioned above in connection with individual catalysts. Most of theose mentioned are inorganic, but many organic substances are strong inhibitors of such catalysts as silver and platinum (332). The mechanism of the poisoning action is frequently obscure, for example, two substances that separately are catalytic have been reported to be mutually inhibiting in mixture (333). Although early studies (86,334) competently describe the phenomena of poisoning qualitatively, it is only recently that an understanding based on electron structure has been approached. This subject in general is reviewed by Maxted (335).

ORGANIC AND BIOLOGICAL CATALYSTS

No simple organic substances of low molecular weight have been found to be true catalysts for hydrogen peroxide decomposition, and phthalocyanines (336) appear to be the only readily synthesized organic catalysts. Aside from these and the catalysis reported for colloidal cholesterol (337), the organic catalysts so far observed are all of biological origin. This applies also to such artificial hydrogen peroxide catalysts as iron-albumin mixtures (338) and hemin supported on charcoal (339) which have been likened to enzymes. And although many observations have been made with poorly defined biological catalysts as bacteria (340), yeasts (341), algae (342), and blood (343), the greatest attention has been centered on the enzyme, catalase.

The structure and biological function of catalase in relation to hydrogen peroxide and other hemoprotein enzymes is outlined in Chapter 7. The enzyme was named in 1901 by Loew (344), who studied the effects of pH, solvents, and salts on the action with hydrogen peroxide of crude extracts containing catalase. Later work (345) established the gross kinetics of the catalysis of hydrogen peroxide decomposition and the inactivation of the enzyme accompanying it. More recently it has been shown (346) how the interference of inactivation can be overcome by experimental methods much improved over the classical techniques. There is now a considerable body of information regarding the kinetics and mechanism of catalase action on hydrogen peroxide based on the work of Keilin and Hartree (347), Chance (348), George (349), Sizer and Beers (350), Theorell and Ehrenberg (351), and others (352). A number of inhibitors for the catalysis have been described (353). All these facts and the mechanisms held to account for them have been the subject of thorough recent reviews by Chance (346,354) and George (232). Two points of view are now current, one holding that the catalysis proceeds <u>via</u> the formation and decomposition of complex compounds of catalase and hydrogen peroxide (see reactions (46) and (47) in Chapter 7), the other considering that free radical intermediates are also involved. This was first suggested by Haber and Willstätter (241), has been discussed by several authors (102,355), and is championed in the review by George (232). An interesting suggestion in relation to this (232) is that the high activity for hydrogen peroxide decomposition which catalase exhibits is equivalent to that which it is estimated by extrapolation that ionic iron would provide were it not precipitated in alkaline solution. On the other hand preliminary reports (232) indicate that polymerization is not initiated by the catalase-hydrogen peroxide system, and a mechanism involving only the complex dissociation (354) appears to have greater currency at present.

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