

Then

$$\frac{1}{n} = \frac{1}{2 \cdot 5 \cdot 10^{17}} + \frac{310}{10^{17}},$$

or

$$n = 3 \cdot 10^{14},$$

i.e., the atom concentration falls to 10^{-3} of its value, which is rather smaller than the effect produced by wall recombination.

These experiments were carried out in the Sir William Ramsay Laboratories, University College, London, in 1932, and we are glad to acknowledge our indebtedness to Professor F. G. Donnan, F.R.S., for the facilities extended to us. Our thanks are also due to Major F. A. Freeth, F.R.S., Mr. W. Rintoul, and Dr. E. H. Rodd for their interest in the work, and to Dr. O. L. Brady for his advice in the many analytical problems encountered.

The Catalytic Decomposition of Hydrogen Peroxide by Iron Salts*

By FRITZ HABER and JOSEPH WEISS, The Chemical Laboratories, The
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(Communicated by Sir William Pope, F.R.S.—Received May 1, 1934)

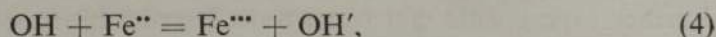
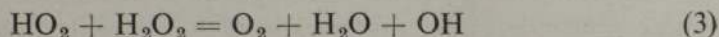
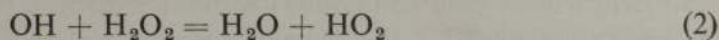
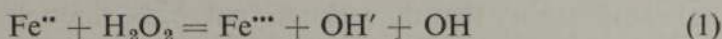
[*Note by Dr. O. H. Wansbrough-Jones*—Shortly before Professor Haber died, he gave the manuscript of this paper to Professor Sir William Pope. The final revision for the press had not been made and in its original form the paper was not suitable for publication in an English journal. Considerable alterations in the wording have accordingly been made ; but, since Professor Haber had considered carefully how he wished to present the results embodied in it, the form and sequence of the paper remain unmodified.

The paper is, further, a sequel to some communications in German periodicals which may not be familiar to its readers. In an attempt to make it more quickly understandable, while keeping it as far as possible as it was left by Professor Haber, the following summary has been added.

* The manuscript of this paper was handed to me for communication by Professor Haber a few days before his death ; I have to thank Dr. O. H. Wansbrough-Jones for editing it.—W. J. P.

The catalytic decomposition of hydrogen peroxide by both ferrous and ferric salts is shown by the authors to be both a chain and a radical reaction, involving in its stages the radicals OH and HO₂ and the anion HO'₂. Varying concentrations of the reactants alter the length of the chains, and favour alternative means of terminating them, giving rise to various reaction products. To obtain quantitative results it is assumed that, to a first approximation, the concentration of the radicals remains stationary, and on this basis equations are derived from which the ratios of the various reaction products under different conditions may be arrived at.

The main stages of the reactions are set out in four equations ((1)-(4)) :—



and inserting the appropriate reaction velocity constants, an equation (9') is obtained from which the ratio of the consumptions of hydrogen peroxide to ferrous ions may be expressed mathematically and to which experimental results adequately conform. More detailed consideration is then given to the effect of varying the acidity of the medium, and attention is called to the role played by the HO'₂ anion which enters into the reaction.

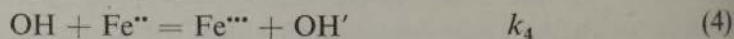
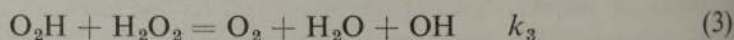
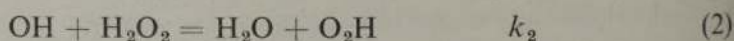
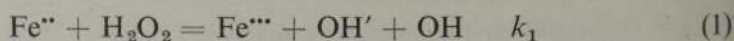
A large number of experiments are described and consideration of them shows that the main course of the reaction between H₂O₂ and Fe'' salts is described by the original equations ((1)-(4)), and that additional complications only come into being at the extreme ranges of the concentration ratios. To express their results the authors consistently use the value of the mean consumption ratio $\Delta\text{H}_2\text{O}_2/\Delta\text{Fe}''$ which they identify with the chain length, and study the variation of this ratio in different experimental conditions.

The effects of ferric salts are also described and largely elucidated. The effect of acidity is shown to be much more marked, and this is found to be due to the hydrogen peroxide no longer reacting as the uncharged molecule, as with ferrous salts, but rather as the ion HO'₂. The interplay between the reaction with ferrous and ferric salts is studied, and a remarkable result follows from an examination of the kinetic equations. By proper selection of the ratios of the concentrations of H₂O₂, Fe''' and Fe'' a sudden great increase in the rate of production of oxygen

may be predicted and has been found experimentally. The chain mechanism proposed gives a simple rationale for this curious effect.

Finally, the authors consider the implications of their work in more general terms. They have had to assume that either chain or radical reactions are possible within the system with which they deal and moreover that one type may be changed easily to the other by a small alteration in the conditions. This suggestion gives an adequate explanation of the facts, and may, in their view, be a much more general phenomenon.]

In a preliminary paper* we discussed shortly the catalytic decomposition of neutral solutions of hydrogen peroxide in the presence of ferrous salts, and we showed that our results were not explicable by the earlier theory that the reaction took place through the interaction of six-valent iron-oxygen compounds with the hydrogen peroxide, but could be easily understood if the decomposition was actually a chain reaction whose course depended on the ratio of the concentrations of the reactants. Further experiments which we now describe have confirmed this latter view, and we also show that this theory serves to explain the catalytic decomposition of hydrogen peroxide, both by ferrous and ferric salts, in all important respects. To describe the decomposition by ferrous salts in acid and neutral solution a system of four equations is required, of which two ((2) and (3)) are the original Haber-Willstätter equations, the first (1) describes the process by means of which the chains are initiated, and the last (4) that by means of which they are broken. For the catalysis by ferric salts only one additional equation is required. The first four equations are :—



By a neutral solution we mean one in which all the ferrous iron remains in solution while all ferric compounds have been precipitated. In the equations above Fe^{++} represents the total amount of dissolved bivalent iron, and if it be assumed that all the four processes are irreversible the rates of change of concentration of Fe^{++} , H_2O_2 , and the two radicals HO_2 and OH may be defined. Following the method of Bodenstein and Herzfeld $d(\text{OH})/dt$ and $d(\text{HO}_2)/dt$ are set equal to zero; that is to

* Haber and Weiss, 'Naturwiss.', vol. 20, p. 948 (1932).

say, the concentrations of HO_2 and OH become stationary, and the relation between the radical concentrations and the hydrogen peroxide concentration when only the ferrous iron is considered is expressed by the equations:—

$$(\text{OH}) = \frac{k_1}{k_4} (\text{H}_2\text{O}_2) \quad \text{and} \quad (\text{HO}_2) = \frac{k_1 k_2}{k_3 k_4} (\text{H}_2\text{O}_2).$$

Thus the concentrations of the radicals appear to be directly proportional to the concentration of the hydrogen peroxide which naturally decreases throughout the reaction, and this result is clearly at variance with the assumption of stationary concentrations for these radicals; moreover, they must initially be zero and become zero again at the end of the reaction, but their extremely small value makes the assumption of invariability a sufficiently good approximation to account for all the chemical facts.

The kinetic equations for those substances whose concentrations alter during the reaction by amounts that can be detected by chemical means are given by

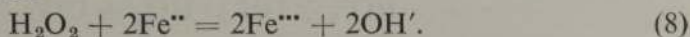
$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = k_1 (\text{Fe}^{**}) (\text{H}_2\text{O}_2) + 2 \frac{k_1 k_2}{k_4} (\text{H}_2\text{O}_2)^2 \quad (5)$$

$$\frac{d(\text{O}_2)}{dt} = \frac{k_1 k_2}{k_4} (\text{H}_2\text{O}_2)^2 \quad (6)$$

$$-\frac{d(\text{Fe}^{**})}{dt} = 2k_1 (\text{Fe}^{**}) (\text{H}_2\text{O}_2) \quad (7)$$

The fact is emphasized that the change in concentration of H_2O_2 cannot be represented by a simple equation of the first order.

In the simplest case it can be assumed that the concentration of hydrogen peroxide remains practically constant, so equation (7) may be integrated and the value of k_1 obtained, or its value may also be found from certain experiments in which the peroxide was decomposed without the liberation of oxygen. The latter reaction can be described simply by the stoichiometric relation



The situation is more complicated when, with varying concentrations of hydrogen peroxide, its consumption for each ferrous ion becomes greater than 0.5; (5) then must also be taken into account in addition to (7). Treating them as simultaneous differential equations, and dividing (5) by (7) we obtain the consumption ratios of the substances as

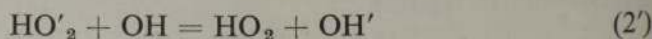
$$n = \frac{d(\text{H}_2\text{O}_2)}{d(\text{Fe}^{**})} = 0.5 + \frac{k_2}{k_4} \cdot \frac{(\text{H}_2\text{O}_2)}{(\text{Fe}^{**})} \quad (9)$$

This expression cannot generally be tested in its differential form, since only the mean consumption ratio \bar{n} can be measured experimentally. Thus

$$\bar{n} = \frac{\Delta(\text{H}_2\text{O}_2)}{\Delta(\text{Fe}^{**})} = \frac{\int_0^t \left[0.5 + \frac{k_2}{k_4} \cdot \frac{(\text{H}_2\text{O}_2)}{(\text{Fe}^{**})} \right] dt}{t}, \quad (9')$$

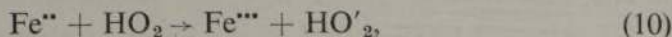
and this cannot be integrated in the general case, but this difficulty should be overcome in order that the quantity k_2/k_4 which, together with k_1 , determines the course of the reaction, may be evaluated. The quotient $d(\text{H}_2\text{O}_2)/d(\text{Fe}^{**})$ in (9) is clearly a measure of the length of the reaction chain in the interval of time under consideration, since this chain length is measured by the number of molecules of oxygen appearing for each ferrous ion lost. Its value will change with time, and will evidently have a lower limit at 0.5, which value is attained with relatively small $(\text{H}_2\text{O}_2)/(\text{Fe}^{**})$ ratios, so that (8) is applicable; but no upper limit is given by the above system of equations though there is a very low concentration of ferrous salts at which the system becomes incomplete owing to the inadequacy of the single chain-breaking mechanism (4) in describing all the phenomena which then occur.

The four irreversible velocity expressions contain no terms in H' or OH' , so that the reaction velocity is independent of the acidity of the solution, and further since neither (3) nor (4) contains these terms the chain length is similarly independent. This fact that k_1 does not vary with the acidity has been confirmed experimentally, and forms the feature discriminating between catalysis by ferrous and ferric salts, but experiments also show that the chain length is not completely independent of the acidity, as strictly according to the equations (1) to (4) it should be. It was at first thought that this might be due to the hydrogen peroxide in equation (2) appearing actually as the anion HO'_2 , but this supposition proved to be incorrect, for it was found that the equation



did not give the correct variation of chain length with acidity, giving actually for the ferrous catalysts a much more marked variation of chain length with acidity than was observed. Thus (2) as originally written must be taken as correct, and to account for this discrepancy we must assume that (4) is not sufficient as it stands, but must be modified to include the fact that the breaking of the chains is favoured by an increase in acidity, and does not itself give all the forms of chain breaking. With sufficiently small concentrations of ferrous iron, other processes whose

efficiencies depend on the p_{H} become important, and among the possible ones the following may first be considered



in which the anion HO'_2 is always present in the concentration given by the equation

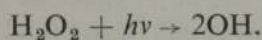


with the equilibrium constant*

$$k_{20^\circ\text{C}} = \frac{(\text{H}^+)(\text{HO}'_2)}{(\text{H}_2\text{O}_2)} = 1.2 \times 10^{-12}.$$

It would at first sight even seem possible to substitute this equation (10) for equation (4), but on closer examination it is found that the constant quantity 0.5 disappears from (9) and the important reaction (8) is no longer explained. Thus the process designated by (10) must be taking place as well as that of (4), and calculation on this basis shows that the constant 0.5 is retained and the explanation given above holds. Consequent on the introduction of the additional process (10) the consumption ratio n is no longer represented as a rigidly linear function of $(\text{H}_2\text{O}_2)/(\text{Fe}^{2+})$ but increases rather more slowly, especially in the region of small iron concentrations. Whether this actually occurs remains uncertain, for where the effect is expected to be marked the concentration of Fe^{2+} is so small that exact measurements can no longer be made. On the other hand, the introduction of (10) does not explain the variation of chain length with acidity, since on this formulation the chain length should remain completely independent; accordingly the introduction of (10) is presently to be avoided as an unnecessary complication, though it will be reconsidered in the second part of this paper.

That another chain breaking mechanism to supplement (4) is required is also clear from a consideration of the photochemical chains started by the formation of OH radicals†



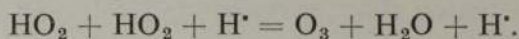
These chains come to an end (in the absence of dissolved iron) after forming chains of medium length, and there can be no doubt that their termination then arises from the reciprocal destruction of two radicals. The same process would occur in ferrous ion catalysis when the ferrous

* Joyner, 'Z. anorg. Chem.', vol. 77, p. 103 (1912).

† Urey, Dawson, and Rice, 'J. Amer. Chem. Soc.', vol. 51, p. 1371 (1929).

ion concentration was so small that chain breaking by (4) was relatively infrequent.

The experimental result that the photochemical decomposition of H_2O_2 proceeds more slowly as the acidity in the solution is increased* proves that this chain breaking process through the interaction of two radicals is favoured by the presence of H ion, and indeed the greater stability of acid solutions of hydrogen peroxide in the dark might well be attributed to the reciprocal removal of the two radicals under the influence of the low p_{H} . We think that the clearest example of such reciprocal action is to be found in the well-known formation of traces of ozone, whose presence is obvious from its smell, in the catalytic decomposition of H_2O_2 . In this case the radical HO_2 may be responsible, by undergoing the reaction



A quantitative proof of the breaking of the chains initiated by light through the interaction of two radicals is given by the fact that the velocity depends on the square root of the light intensity.† The unmistakable chain‡ character of the formation of oxygen from ozone and hydrogen peroxide falls into the same class,§ and the process



may start the chain. The effect of acid in decreasing the speed‡ of this reaction as well as of the decomposition of ozone in aqueous solution is probably a similar phenomenon.||

Returning now to our study of the catalysis by ferrous salts, it seems that the simplest application of equations (1) to (4) lies in the explanation of the fact that very different mean consumption ratios can be obtained by suitable mixing of dilute ferrous solutions with dilute solutions of hydrogen peroxide. For this purpose ferrous sulphate solution is allowed to run slowly from the horizontal outlet of a burette which is being rapidly rotated about a vertical axis, into a large quantity of hydrogen peroxide solution of known concentration. Thus 50 cc of ferrous solution are rapidly driven through the outlet into 2 litres of hydrogen peroxide solution and quickly distributed throughout the whole bulk. Sufficient time is then allowed to elapse before titrating the solution, so that no

* Kornfeld, 'Z. wiss. Photogr.,' vol. 21, p. 66 (1921).

† Allmand and Style, 'J. Chem. Soc.,' p. 596 (1930).

‡ Weiss (*in preparation*).

§ Rothmund and Burgstaller, 'Monatsh. Chem.,' vol. 34, p. 665 (1913).

|| Sennewald, 'Z. phys. Chem.,' A, vol. 164, p. 305 (1933).

further increase in this time produces any change in the observed composition, and the concentration of ferrous salt has been reduced to the limit of measurement. It is then strongly acidified to retard the decomposition of the unchanged hydrogen peroxide by the ferric iron now present and the residual hydrogen peroxide is finally estimated by titration with potassium permanganate, from which the average ratio \bar{n} of H_2O_2 decomposed by each Fe^{2+} can be evaluated. By this method we found that, contrary to the results of previous workers, a much higher value results for this ratio than that obtained when the solutions are mixed in a cruder manner, and further that the consumption ratio is far from attaining a value independent of the concentrations of either reactant.

TABLE I—CENTRIFUGAL EXPERIMENTS (IN NEUTRAL SOLUTION)

No.	$[\text{H}_2\text{O}_2]_0 \cdot 10^3$ mols/ltr.	$[\text{Fe}^{2+}]_0 \cdot 10^3$ mol/ltr. (entering solution)	$\bar{n} = \frac{\Delta\text{H}_2\text{O}_2}{\Delta\text{Fe}^{2+}}$
1	5.25	2.42	29.9
2	1.06	1.01	15.6
3	1.10	2.40	9.4
4	0.786	2.00	6.4
5	0.318	2.00	3.8
6	0.125	2.00	2.5

A different procedure, which had the advantage that the initial concentration ratio was better defined and that the rate of change could be determined for definite initial concentrations, gave important results. The second method was essentially this: one of the reacting solutions, normally the H_2O_2 , was propelled in known quantity per unit time, in the form of a rapidly flowing turbulent stream, from an opening through an air space of varying length into a receiver. Before reaching the exit, the flowing stream took up the second reactant, also in known quantity per unit time, from a second co-axial tube, and with sufficient turbulence mixing by this arrangement was practically instantaneous so that the initial concentrations ($t = 0$) could be deduced accurately from the experimental data. The liquid was left in the receiver until increasing the time had again no effect on the results, and the mean consumption ratio was again obtained as in the former centrifugal experiments, but now for well-defined initial concentrations of the reactants. Two methods of titration were required to obtain the amount of the chain reaction which had taken place from the moment of mixing to the final time; firstly the streaming liquid was allowed to flow directly into a known excess of

acid permanganate in the receiver so that the titration gave the sum of the H_2O_2 and Fe^{++} in the liquid, and secondly the permanganate was replaced by a strongly acid solution of the ferrous salt, by which means the unused H_2O_2 was rapidly destroyed according to (8). By this method the amount of reaction, according to the chain equations, which takes place in a time less than 1 second, may be found, but the time cannot be found with accuracy, though this difficulty can be overcome by varying the cross-sections of the turbulent stream. We have accordingly made two other series of experiments, "jet" experiments in which the liquid was forced from a glass jet of one square millimetre cross-section, and "pouring" experiments in which the liquid was poured all at once into a large funnel, and emerged from the opening into a wide vessel; in both series of experiments the second reactant was again added through a narrow coaxial tube.

In the "pouring" experiments, 1 litre of the liquid was collected in the receiver in, at most, 2 seconds, and the reaction was stopped after a measured time t by adding 1 litre of the inhibiting liquid, either acid permanganate or ferrous sulphate, and ensuring rapid mixing by mechanical stirring. If the concentrations are such that the reaction is slow, the uncertainty in the measurement of the time of the reaction is ± 1 second, and is negligible, as may be seen from the values of t shown in Table II.

From the "pouring" experiments, the velocity constant k_1 may be deduced immediately; from the "jet" experiments the reaction time may now be found, for the product $k_1 t$ is given accurately. The value of t found is of the order of $\frac{1}{2}$ second. From this we can obtain the initial value of the chain length in the jet experiments; that is, for concentration ratios not far removed from the initial concentration ratios at $t = 0$, and we thus obtain the three quantities, the velocity constant k_1 , the initial chain length, and finally the mean chain length throughout the complete reaction. The influence of temperature and acidity on these three quantities may also be determined separately.

Examining the results in more detail, we find in the "pouring" experiments that the consumption ratio is 0.5 as given by (8). The expression for the reaction velocity is then

$$-\frac{d(\text{H}_2\text{O}_2)}{dt} = -\frac{1}{2} \frac{d(\text{Fe}^{++})}{dt} = k_1 (\text{Fe}^{++}) (\text{H}_2\text{O}_2),$$

which may be integrated using the stoichiometrical relation (8) to give

$$k_1 = \frac{2.3}{(\text{H}_2\text{O}_2)_0 t} \log \frac{[\text{Fe}^{++}]_0 [(\text{H}_2\text{O}_2)_0 - x/2]}{[\text{H}_2\text{O}_2]_0 [(\text{Fe}^{++})_0 - x]},$$

where x is the amount of iron used up in the time t . Table II summarizes these "pouring" experiments; average values for the three temperatures employed are given at the foot of the table, and from these the energy of activation has been found to be 8500 ± 500 cal. In agreement with the theory, the results in the table show that the velocity constant does not vary appreciably with the acidity.

TABLE II—POURING EXPERIMENTS

No.	[H ₂ O ₂] ₀ 10 ⁴ mol./ltr.	[Fe ⁺⁺] · 10 ⁴ mol./ltr.	[H ⁺] · 10 ² equiv./ltr.	Temp. ° C	t sec.	Consump- tion ratio \bar{n}_0	k_1
1	5·21	34·2	0·186	19·7	14	0·5	25
2	5·00	32·5	4·46	20·2	13	0·5	25·3
3	6·95	35·0	0·186	19·7	13·5	0·5	24·2
4	6·83	34·3	1·86	19·7	13·7	0·5	24·2
5	5·35	33·4	0·186	19·7	15	0·5	21·3
6	5·25	23·0	1·84	20	15	0·5	21·6
7	7·08	52·8	0·186	20	9	0·5	25·1
8	11·07	8·82	9·34	21	15·5	0·5	23·3
9	0·97	10·7	18·7	21	16	0·5	20·5
10	5·00	20·5	4·46	46·5	13	0·5	63·7
11	5·11	21·5	4·45	44·5	13	0·5	64·5
12	5·11	21·5	0·187	44	13	0·5	60·0
13	3·60	12·4	0·465	46	13	0·5	65·1
14	6·02	57·7	0·186	6	29	0·5	12·1
15	6·02	57·7	4·45	6	29	0·5	12·3
16	6·07	24·6	1·86	6	27	0·5	9·4
17	6·07	24·6	8·5	6	34	0·5	10·5

$$k_1 (6^\circ \text{C}) = 11 ; k_1 (20^\circ \text{C}) = 23 ; k_1 (45^\circ \text{C}) = 63.$$

Table III gives the results of the "jet" experiments. Only the product $k_1 t$ can be obtained from this series, but its constancy is also a proof of the constancy of k_1 , since the method of experiment involves no considerable change in the time t in the different experiments. The reaction times are calculated from the values of k_1 which had been determined previously, and the mean consumption ratios \bar{n} which are also shown are seen to be definitely greater than the initial consumption ratios n_0 found from the much smaller times of flow in the "jet" experiments.

Equation (9) shows that when the consumption ratio differs at all from 0·5 the value of k_2/k_4 may be determined; and this can be done from both series of experiments. We have not used the integrated form of the expression (9'), since we are considering those reactions in which the ratio is not much removed from 0·5 when an average value can be

used without serious error. Table IV shows that \bar{n} and hence k_2/k_4 is smaller, for short initial chain lengths only, as the acidity increases, but the influence of the acidity is relatively small, certainly far removed from simple proportionality. As has been stated above, we believe this result to be the consequence of the reaction between two radicals, an additional process that becomes the more important the greater the chain length and the acidity.

TABLE III—JET EXPERIMENTS

	$[\text{H}_2\text{O}_2]_0 \cdot 10^4$ mols/ltr.	$[\text{Fe}^{++}]_0 \cdot 10^4$ mols/ltr.	$[\text{H}\cdot] \cdot 10^2$ equiv./ltr.	Temp. ° C	t sec	$k_1 \times t$	Initial con- sump- tion ratio n_0	Mean con- sump- tion ratio \bar{n}
1	130.0	15.90	1.51	20	0.44	10.2	0.5	2.02
2	126.0	23.43	0.94	20	0.52	11.9	0.5	2.23
3	80.70	20.15	56.0	20	0.56	12.9	0.5	0.63
4	83.85	19.80	15.5	20	0.54	12.4	0.5	0.75
5	87.00	21.30	15.1	20	0.50	11.3	0.5	0.77
6	98.15	26.38	6.24	7	0.45	5.0	0.5	0.87
7	101.75	25.64	3.14	41	0.43	28.7	0.5	1.57
8	92.70	21.57	3.07	17	0.50	10.7	0.5	1.26

TABLE IV

No.	$[\text{H}_2\text{O}_2]_0 \cdot 10$ mols/ltr.	$[\text{Fe}^{++}] \cdot 10^4$ mols/ltr.	$[\text{H}\cdot] \cdot 10^2$ equiv./ltr.	Temp. ° C	t sec	$\left(\frac{\Delta\text{H}_2\text{O}_2}{\Delta\text{Fe}^{++}}\right)_t$	$\frac{k_2}{k_4} \cdot 10^3$
1	67.5	16.9	0.47	20	4	0.68	2.8
2	65.6	15.2	0.47	20	4.8	0.66	2.3
3	20.65	13.6	0.47	20	12	0.60	2.7
4	11.20	8.82	0.47	21	14	0.56	3.7
5	10.97	10.7	0.19	21	15	0.56	3.7
6	55.0	17.2	4.46	20	4.8	0.555	1.2
7	21.2	10.0	4.46	20	12.2	0.565	1.7
8	82.85	21.7	0.15	20	0.5	0.625	3.0
9	98.75	16.2	$\sim 10^{-6}$ (neutral)	20	0.5	0.82	4.7
10	93.82	19.93	0.43	20	0.5	0.645	2.8
11	101.30	22.43	0.43	17	0.5	0.63	2.7

Nos. 1-7, jet experiments ; Nos. 8-11, pouring experiments.

Table V summarizes the results of experiments in which the time of observation has been extended so far that further increase had no effect. Pairs of comparable experiments with different acidities are shown

together, and while no exact quantitative evaluation of the part played by the reciprocal action of the radicals in shortening the chains can be made, the effect of increasing the acidity in shortening the chain is clearly seen.

TABLE V

No.	$[\text{H}_2\text{O}_2]_0 \cdot 10^3$ mols/ltr.	$[\text{FeSO}_4]_0 \cdot 10^4$ mols/ltr.	$[\text{H}^+] \cdot 10^2$ equiv/ltr.	$\frac{\Delta\text{H}_2\text{O}_2}{\Delta\text{Fe}^{2+}}$	Acidity ratio	Ratio of mean chain lengths
1	9.11	4.90	11.8	0.86	7.2	1.7
	8.90	5.00	85.0	0.50		
2	6.18	3.78	0.118	6.8	10	3.1
	6.32	3.65	1.18	2.2		
3	2.49	5.04	0.117	2.5	10	1.7
	2.47	5.05	1.17	1.5		
4	5.98	3.57	0.117	4.4	10	1.9
	6.82	3.39	1.18	2.3		
5	1.62	0.238	0.115	7.4	20	7.4
	1.61	0.243	2.31	1.0		
6	3.20	0.998	0.117	7.0	100	7.7
	3.15	0.990	11.7	0.9		
7	1.74	0.383	"neutral"	15.7	$\sim 10^4$	4.5
	1.72	0.268	0.57	3.5		

In Table VI are summarized a number of experimental results obtained at nearly constant p_{H} —a neutral solution. From these results it is possible to obtain an idea of the range of ferrous iron concentrations over which the mean chain length can be satisfactorily interpreted on the basis of equations (1) to (4), without taking the additional chain breaking mechan-

TABLE VI

No.	$[\text{H}_2\text{O}_2]_0 \cdot 10^3$ mols/ltr.	$[\text{FeSO}_4]_0 \cdot 10^4$ mols/ltr.	$v_0 \frac{[\text{H}_2\text{O}_2]_0}{[\text{Fe}^{2+}]_0}$	$\bar{n} = \frac{\Delta\text{H}_2\text{O}_2}{\Delta\text{Fe}^{2+}}$	f
1	10.1	0.384	262	23.5	$\sim 10^{-2}$
2	2.75	0.132	208	17.0	$\sim 10^{-2}$
3	2.81	0.138	203	16.3	$\sim 10^{-2}$
4	1.74	0.383	45	15.7	$\sim 10^{-2}$
5	3.00	1.08	28	14.7	$\sim 10^{-2}$
6	0.98	0.382	25	11.1	$\sim 10^{-2}$
7	0.72	0.340	21	6.8	$\sim 10^{-2}$
8	1.49	1.16	13	6.2	$\sim 10^{-2}$
9	0.48	0.333	15	5.7	$\sim 10^{-2}$
10	2.83	2.64	11	4.9	$\sim 10^{-2}$
11	4.68	4.81	10	4.3	$\sim 10^{-2}$
12	2.62	3.00	9	3.5	$\sim 10^{-2}$

isms into account. The ratio of the iron concentration after time t to the initial concentration may be denoted by f , so that

$$f = \frac{\text{Fe}_t}{\text{Fe}_0},$$

and from (7) it follows that

$$f = e^{-2k_1 (\text{H}_2\text{O}_2)_m t},$$

where $(\text{H}_2\text{O}_2)_m$ represents a mean value which does not differ seriously either from the initial value $(\text{H}_2\text{O}_2)_0$ or the final value $(\text{H}_2\text{O}_2)_t$, and is taken as constant from $t = 0$ to $t = t$. The differential equation (9') can then be integrated for constant values of H_2O_2 between the limits Fe_0 and Fe_t , and the integral evaluated with the aid of the values for k_2/k_4 which we had previously determined. For the mean consumption ratio we then obtain

$$\bar{n} = 0.5 + \frac{k_2}{k_4} \cdot \frac{1}{2k_1 \text{Fe}_0'' t} [e^{-2k_1 (\text{H}_2\text{O}_2)_m t} - 1].$$

From this expression the fraction f may be determined, and we find that in all experiments in Table VI it is nearly 1%. Thus until this region is reached equations (1) to (4) are adequate, and it is only during the final 1% of the iron consumption that the additional chain breaking mechanisms play any appreciable part.

CATALYSIS BY FERRIC SALTS

In the preceding part of this paper, a description of the catalytic decomposition of hydrogen peroxide by ferrous salts has been given, and we now wish to discuss the relation of this reaction to the catalytic decomposition by the aid of ferric salts. There are two possibilities to be considered. If some ferrous salt is formed as an intermediate during the ferric iron catalysis, the equations developed above must find their place in the full description of the ferric iron catalysis; since, in acid solution the only difference between the two cases will lie in the relative concentrations of the three reacting substances H_2O_2 , Fe'' and Fe''' . If, however, the ferric catalysis does not involve ferrous iron as an intermediary but rather proceeds through the iron being oxidized to a higher stage of valency, a new set of equations would have to be developed. The work of Bohanson and Robertson* might be interpreted as lending some support to this latter view, for their spectroscopic investigations of weakly acid solutions of ferric salts with hydrogen peroxide, in which some colour change is visible to the eye, were interpreted by them as

* 'J. Amer. Chem. Soc.,' vol. 45, p. 2493 (1923).

showing the spectrum of ferric acid. We do not, however, regard this result as convincing for the experimental material seems insufficient to prove conclusively that the spectrum was really ferric acid, and despite numerous experiments of our own we have been unable to satisfy ourselves on this point. We do not propose to describe these spectroscopic investigations in detail for the presence of ferrous salts in the ferric iron catalysis of hydrogen peroxide in acid solution has been established by Kuhn and Wassermann,* and we have been able to extend and confirm their most important results; and thus in our consideration of the ferric catalysis we start with the assumption that the iron is present alternately in the ferric and ferrous forms. The view sometimes expressed in the literature that the rate of decomposition is the same both for ferrous and ferric salts is false for the experiments on which it is based have been made in acid solution with the addition of small amounts of ferric or ferrous salts, and when ferrous salt is used it is transformed almost entirely into ferric at the very beginning of the reaction, and the resulting slow catalysis by the ferric salt is naturally the same as if ferric salt had been added at the beginning in place of the ferrous.

Most of the results of previous workers gave the velocities of decomposition of hydrogen peroxide in solutions in which its concentration ranged from 10^{-1} to 10^{-3} mol/litre, in the presence of 10^{-2} to 10^{-3} mol/litre of iron and with acid concentrations corresponding to 10^{-1} to 10^{-3} equivalents per litre of free sulphuric acid. The use of weaker acid solutions is inadvisable since special complications due to the ferric iron no longer being present mainly in the form of ferric ions will then arise. Instead, most of the iron is present in the form of imperfectly known iron complexes as indicated by the difference in the colour of the solution from the plain yellow characteristic of ferric solutions in the region of acidity mentioned above.

It has been found that the rate of consumption of H_2O_2 is monomolecular with respect to itself, directly proportional to the total amount of iron in solution, and inversely proportional to the equivalent concentration of the added acid. Table VII gives a number of our own results, together with those of previous workers,† for the velocity constants of decomposition of H_2O_2 calculated from the equation

$$-\frac{d(H_2O_2)}{dt} = K \frac{(Fe^{+++})}{[H^+]} [H_2O_2]. \quad (12)$$

* 'Liebigs Ann.,' vol. 503, p. 203 (1933).

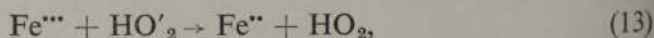
† v. Bertalan, 'Z. phys. Chem.,' vol. 95, p. 338 (1920); Spitalsky and Petin, *ibid.*, vol. 113, p. 161 (1924); Bohnsen and Robertson, *loc. cit.*

Fe⁺⁺⁺ represents the total amount of iron in solution expressed as mols/litre, and H⁺ is the equivalents per litre of added acid, in these experiments sulphuric.

TABLE VII

No.	[Fe ⁺⁺⁺] . 10 ³ mols/ltr.	[H ⁺] . 10 ³ equiv./ltr.	$\frac{[H^+]}{[Fe^{+++}]}$	$2k_{10}K \frac{[Fe^{+++}]}{[H^+]}$ 10 ³	$2k_{10} K . 10^3$
1	4.00	1.50	0.375	33.5	12.5
2	4.00	4.50	1.125	13.216	14.86
3	4.00	22.5	5.625	1.873	10.35
4	4.00	88.0	22.00	0.576	12.68
5	4.50	3.00	0.666	14.25	9.48
6	12.0	30.0	2.50	3.946	9.86
7	12.0	15.0	1.25	9.840	12.3
8	73.0	15.0	0.205	3.59	7.37
9	73.0	30.0	0.4105	26.5	10.88
10	73.0	150	2.055	7.48	15.35
				$2k_{10}K$ (mean from our own experiments)	$1.16 \cdot 10^{-4}$
				$2k_{10}K$ (v. Bertalan)	$1.17 \cdot 10^{-4}$
				$2k_{10}K$ (Spitalsky and Petin).....	$1.19 \cdot 10^{-4}$

The rate of reaction is inversely proportional to the acidity, and this is due to the fact that in contrast to the ferrous reaction the reactive state of the hydrogen peroxide is no longer H₂O₂ but is now the anion HO'₂, the concentration of which is related to that of the peroxide by (11). The variation with the total iron shows that in the stationary state only a small fraction of the iron is there as Fe⁺⁺; and this must be so since the velocity of reaction of the ferric ion with the peroxide anion is very small compared with the corresponding reaction of Fe⁺⁺ with H₂O₂. The primary process for the ferric ion is



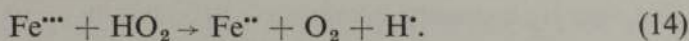
and the velocity constant in (13) is related to k in (12) by the relation $k = 2k_{13}K$. The factor 2 comes in from the fact that in the stationary state

$$-\frac{d(H_2O_2)}{dt} = +2\frac{d(O_2)}{dt}.$$

From our own and other workers' results we find that $k_{13} = 6.0 \times 10^7$ (secs. mol./litre) at 20° C.

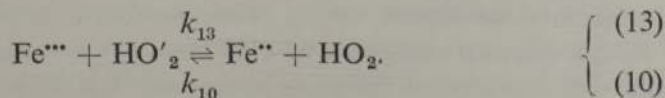
The temperature coefficient determined by different observers gives a heat of activation of about 21000 cal. of which 8600 cal. is due to the heat of dissociation of H₂O₂, and the remaining part to the reaction (13), including the heat of dissociation of the ferric salt.

The combination of equation (13) with the four equations used to describe the ferrous ion catalysis leads to a surprising result. The production of oxygen through the interaction of the radical HO_2 with H_2O_2 necessitated the introduction of a term containing the square of the concentration of the peroxide in the expression for $d(\text{H}_2\text{O}_2)/dt$; but (12) shows that in the ferric catalysis only a term in the first power of the peroxide is required. Thus in the latter case the production of oxygen cannot proceed as a chain reaction if the chains are to be of appreciable length, and the radical HO_2 which we have recognized as the characteristic chain carrier in the ferrous catalysis must be able to disappear in the ferric ion catalysis without initiating or continuing any reaction chains. This process is the following



When the speed of this reaction (14) is greater than that of reaction (3) the chain reaction simply changes over to a reaction of radicals not involving chains. This may be important in view of the simple illustration it affords of the ease with which a radical reaction may change to a chain reaction and *vice versa*; a very small variation of the conditions of the reaction being sufficient to effect this. In this reaction the rate of formation of oxygen, as given by the two equations (3) and (14), is evidently determined by two velocity constants, whose values lie sufficiently close together for either of the two reactions to predominate, the relative concentrations of H_2O_2 and Fe^{+++} being the determining factor. Generally (14) is the dominant reaction, but alterations are possible which favour (3) to such an extent that chains appear; increase of H_2O_2 and decrease of Fe^{+++} will cause this to happen, though there is a natural limit to the permissible decrease of Fe^{+++} determined by a minimal amount being necessary to initiate the chains.

There is yet another way in which the HO_2 may disappear while the ferric reaction proceeds, namely, the reaction (10) which was omitted in the previous discussion as probably being unnecessary but not false. It now becomes important, and we see at once that since it is the inverse of (13)



so long as reaction (10) proceeds with an appreciable velocity there will always be a certain amount of HO_2 which does not react according to (3) though it need not disappear according to the mechanism of (14). Examining this in further detail we see that if we wish to make reaction

(3) much the most important we must simultaneously keep the ferric ion concentration small in order to retard (14), and the H_2O_2 concentration large in order to favour (3), and also prevent the HO_2 from disappearing by means of reaction (10) with Fe^{2+} without the production of oxygen. These three conditions occurring together should give the most favourable conditions for the production of oxygen from a chain reaction in the ferric catalysis. The concentration of H_2O_2 should be 1 mol/litre or more, that of the ferric ion small, as might be given by a very slightly dissociated complex salt such as the acetate or succinate; and there should also be a substance present in solution that will combine with the ferrous ion and keep its concentration low; these three conditions will reproduce the experiments of Kuhn and Wassermann (*loc. cit.*) and will give rise to a greatly accelerated production of oxygen. The reaction chains will be very long, and their termination due not to reaction (4) but to the interaction of two radicals. In these circumstances the rate of production of oxygen increases by about 100 times, a phenomenon termed by its discoverers the "Katalasestoss" and believed by them to be fundamentally a new kinetic effect, but it seems that the explanation given above is satisfactory and their view less probable. It may be mentioned that their method of minimizing the amount of ferrous ion is not a new one; it consists in the addition of $\gamma\gamma'$ -dipyridyl, the action of which on mixtures of ferrous and ferric salts has been studied also by electrochemical methods by Friedheim and Michaelis.* This substance has been found to shift the potential so far to the side of the strong oxidizing materials that the development of the gaseous oxygen is a serious hindrance to the exact measurement of the electrode potential.

We have naturally tried to make a detailed analysis of the system obtained by combining all the relevant equations (1), (2), (3), (4), (10), (13), and (14), but the complicated expressions which result have proved to be of little value. The success attained previously in using the simple relationships (1) to (4) encouraged us to search for a simpler method of procedure, even at the risk of losing some of the completeness of the formulation. We have found that the (2), (3), (10), and (13) are adequate to explain the results, or, in other words, we make the assumption that the equilibrium expressed by (10) and (13) is readily established. Then the concentration of HO_2 can be derived with sufficient accuracy from the expression

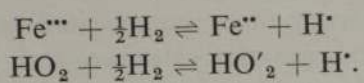
$$[HO_2] = \frac{k_{13}}{k_{10}} \cdot \frac{[Fe^{3+}]}{[Fe^{2+}]} [HO'_2],$$

* 'J. Biol. Chem.,' vol. 91, p. 343 (1931).

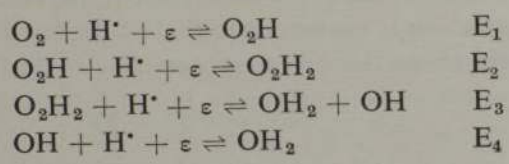
and the kinetic equation corresponding to (3) may then be transformed

$$\frac{d(O_2)}{dt} \sim k_3 \cdot \frac{k_{13}}{k_{10}} \frac{K}{[H^+]} \frac{[Fe^{III}]}{[Fe^{II}]} [H_2O_2]^2 \quad (15)$$

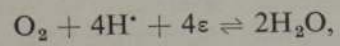
Kuhn and Wassermann found that the rate of production of oxygen is proportional to the square of the concentration of the H₂O₂ and was started by increasing hydrogen ion concentration ; both these results are explained at once by the above expression (15), and in addition the action of diminishing Fe^{II} concentration is clear. Of the constants in this expression, $k_{13}/k_{10} = K_A$ deserves closer attention ; k_{13} is known from our measurements to be $6 \cdot 10^7$, and it is probable that the reverse process which is in the exothermic direction will have no heat of activation and since also it is a simple transfer of charge it is likely that k_{10} will be about 10^{11} , the normal value for reactions taking place at every collision ; thus K_A will be about 10^{-3} . This result is of further interest, or we may express the reaction represented by (15) in the form



The first step will give the electrolytic potential of Fe^{III}/Fe^{II} (known to be + 0.75 volt) ; the second the electrolytic potential HO₂/HO'₂ for which no value has so far been available but which from the value of K_A is now seen to be about 0.58 volt. This value is certainly not very exact, but it suffices to furnish an estimate of the four reduction potentials which govern the electrolytic reduction of O₂ to H₂O.



The sum of $E_1 + E_2 + E_3 + E_4$ will give the free energy of the reaction



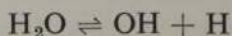
and so is numerically four times 1.23 volts. Now according to Lewis and Randall the sum $E_1 + E_2$ is equal to 1.36 volts, and from the value established above for the HO₂/HO'₂ potential and the known value of the dissociation constant of H₂O₂, the potential HO₂/H₂O₂ may be calculated. This sum $E_1 + E_2$ can be divided into the two parts

$$E_1 \sim 0.08 \text{ volt}$$

$$E_2 \sim 1.28 \text{ volts.}$$

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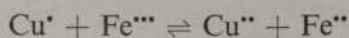
$E_3 + E_4$ can also be divided into its two parts, for the equilibrium constant of the reaction



is fully known thermodynamically. Thus $E_4 = 2.1$ volts and $E_3 \sim 1.46$ volts, all values being measured against the hydrogen electrode. The total energy of $\text{H} + \frac{1}{2}\text{H}_2 = \text{H}_2 + 50$ k. cal. is almost the same as for the reaction $\text{H} + \text{O}_2 = \text{HO}_2$. The great difference between this value and the much larger value for $\text{H} + \text{HO}_2 = \text{H}_2\text{O}_2$ is due to the fact that the double bond in the oxygen molecule must be opened to produce the first product HO_2 but is already open for the second step to proceed.

There are many other allied processes with a direct bearing on the explanations given above. Thus in our preliminary paper we have already discussed the catalysis by iodine ions, a subject on which we have made many experiments, and in this paper we have referred both to the photochemical catalysis and to the catalytic decomposition of H_2O_2 by ozone, but we do not wish to enter here upon a detailed consideration of these much more complicated processes. The points which we wish to stress are the existence and the importance of the radicals HO_2 and OH in the decomposition of hydrogen peroxide, and the easy change from the radical to the chain or from the chain to the radical reaction.

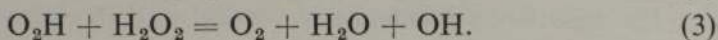
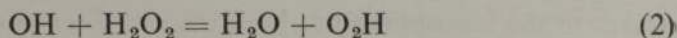
The promoting action of copper salts in the homogeneous decomposition of hydrogen peroxide in the presence of ferric salts has been studied by Bohanson and Robertson,* and we believe that their results are fully explicable in terms of the theory given above. We hold that the action of the cupric ion is analogous to that of the ferric. The promoting action then comes about through the reaction



The heterogeneous decomposition of hydrogen peroxide is closely connected to the homogeneous catalysis. We have found that according to the experimental conditions, polarization of a cathode of amalgamated platinum in sulphuric acid and hydrogen peroxide solutions may lead to the direct reduction of H_2O_2 without the production of any gas, the production of hydrogen alone, of oxygen and hydrogen simultaneously or of oxygen alone. In suitable conditions the last process may occur as a chain reaction, sixteen times as much oxygen being produced as the Faraday equivalent. We propose to discuss this in a later paper.

* 'J. Amer. Chem. Soc.,' vol. 45, p. 2512 (1923).

The single basic idea inherent in the foregoing theory is that the hydrogen peroxide molecule is never simultaneously attacked by two monovalent reagents, nor by a bivalent reagent, whether the material is oxidized to oxygen or reduced to water; instead there is monovalent change transforming the peroxide into one of the radicals HO_2 or OH . This is true of the chemical, photochemical, and electrochemical processes. These radicals may then produce oxygen or water in a second step, or they may take part in the chain reaction by further reaction with hydrogen peroxide to water and oxygen and reproduce themselves according to the equations



It may be that the easy change from radical to chain reactions, exemplified by this detailed study of the action of ferrous and ferric salts, will prove to be a result of more general value. The conception of chain reactions has influenced the general standpoint of chemists, and there now exists the danger of overlooking the main point that the progress of the reaction through the radicals is the primary process, and the formation of chains by these radicals an interesting but secondary phenomenon. The idea of the reaction progressing through radicals is less new than that of chain reactions, but it often seems that all its implications are not fully accepted. It may be worth emphasizing that the difficulties encountered in the interpretation of single steps in a reaction, whether a chain reaction or a radical reaction, become the less the more numerous the experimentally measurable relationships between the variable factors and the products of the reaction. The more various and complicated are the experimental changes which may be produced and studied in a reaction system the more certain is it that an explanation covering all of them will be actually correct. Thus in our work, the phenomenon of "Katalase-stoss" at first sight incompatible with our general knowledge of reactions, becomes finally the best piece of evidence in favour of the system of interactions which we have developed.
