

**209.** *The Retardation of Chemical Reactions. Part VII. The Reaction between Potassium Permanganate and Hydrogen Peroxide in Acid Solution.*

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THE attention of the senior author was drawn some years ago to the peculiarities of the reaction between potassium permanganate and hydrogen peroxide. During a preparation of the latter compound, he wished to test a distillate qualitatively for peroxide. Sulphuric acid and potassium permanganate were added, but the solution remained purple. Only after  $\frac{1}{2}$  hour did decolorisation take place. The same distillate, when diluted with water, decolorised potassium permanganate in acid solution almost instantaneously.

The fact that hydrogen peroxide, in fairly concentrated solution, apparently retards its own reaction with potassium permanganate was already known, and an attempt to elucidate the kinetics of the reaction had been made by Limanowski (*Rocz. Chem.*, 1932, **12**, 519, 638). He used Merck's perhydrol, redistilled it to free it from stabilisers, and followed the course of the reaction colorimetrically, using a green light filter which, being complementary to the red colour of potassium permanganate, increased the accuracy of the reading.

Using only figures for the middle portion of the reaction, and varying the concentrations of his reagents only within narrow limits ( $\text{KMnO}_4$  0.0005—0.0015;  $\text{H}_2\text{O}_2$  0.329—1.12;  $\text{H}_2\text{SO}_4$  0.0536—0.1072 g.-equiv./l.), he obtained fair agreement with the equation

$$dx/dt = k_1b(1 - x) + k_2ax(1 - x)$$

where  $x$  is the fraction of potassium permanganate decolorised (and also the relative concentration of manganous ions, believed to be formed almost instantaneously during the reduction of  $\text{MnO}_4'$ ), and  $a$  and  $b$  are the initial concentrations of potassium permanganate and hydrogen peroxide.

He found that increase in hydrogen-ion concentration reduced the velocity of the reaction, and was aware that manganous ions promoted the reaction and that hydrogen peroxide in high concentration had an inhibitory effect, which he attributed to the formation of complexes of the type  $\text{Mn}^{++}(\text{H}_2\text{O}_2)_4$ , which prevented manganous from interacting with permanganate ions. It is clear that Limanowski's velocity equation makes no provision for a diminution in  $dx/dt$  with rise in  $b$ , and that, although it may give fair agreement with experimental results over a narrow range, yet it cannot be valid for the reaction in general.

The reaction has been examined more recently by Riesenfeld (*Z. anorg. Chem.*, 1934, **218**, 257), most of whose experimental observations are in good agreement with those of similar experiments by the authors. Taking the time of complete decolorisation as a measure of the velocity of the reaction, he found that, when the concentrations of sulphuric acid and potassium permanganate were constant, and the concentration of hydrogen peroxide was increased gradually from extreme dilution, the velocity of the reaction first rose to a maximum when  $[\text{H}_2\text{O}_2]$  was about 0.005, then fell to a minimum when  $[\text{H}_2\text{O}_2]$  was about 0.5, and then rose slowly at still higher concentrations of hydrogen peroxide. (Concentrations throughout this paper are expressed as g.-equiv./l.) When he used other concentrations of permanganate and acid, the concentrations of hydrogen peroxide at which the velocity was a maximum and a minimum were practically unchanged. In all parts of the curve, an increase in the concentration of permanganate increased the reaction velocity. On the other hand, although an increase in acid concentration increased the velocity in the neighbourhood of the maximum, it retarded the reaction powerfully in the neighbourhood of the minimum.

To explain his results, Riesenfeld suggested that an equilibrium exists in aqueous solution:  $2\text{H}_2\text{O}_2 \rightleftharpoons \text{H}_4\text{O}_4$ . He assumed that at  $[\text{H}_2\text{O}_2] = 0.005$  the peroxide exists almost entirely in unassociated molecules, whereas at  $[\text{H}_2\text{O}_2] = 0.5$  only polymerised molecules are present. The rate of reaction of the polymerised molecules was considered to be very slow compared with that of the simple molecules. The retarding action of sulphuric

acid in the neighbourhood of the minimum velocity was attributed to a stabilising effect on the polymeric molecules.

To this explanation of the retardation at high peroxide concentrations three objections may be offered. (1) Sulphuric acid does not necessarily retard at minimum velocity, as will be clear from an examination of the results which follow. (2) The existence of  $H_4O_4$  is assumed *ad hoc*, and no evidence, such as might be derived from freezing-point determinations, is adduced for the existence of such molecules. (3) Although the *proportion* of polymerised molecules, in an equilibrium such as that postulated by Riesenfeld, would increase with concentration, the *actual number* of simple molecules would also increase in accordance with the equation  $[H_4O_4]/[H_2O_2]^2 = K$ . Such a hypothesis could not explain a diminution in reaction velocity with increase in concentration, unless a retarding rôle is assigned to  $H_4O_4$ , a possibility not envisaged by Riesenfeld.

#### EXPERIMENTAL.

The hydrogen peroxide was prepared from sodium peroxide and sulphuric acid by the method of Kilpatrick, Reiff, and Rice (*J. Amer. Chem. Soc.* 1926, 48, 3019), with modifications as recommended by Bailey (*Sci. Proc. Roy. Dublin Soc.* 1935, 21, 153). As a precaution against decomposition by dust particles at the surface, the pure peroxide solution thus obtained was filtered through three layers of Whatman No. 44 filter-paper into a Pyrex flask which had been washed repeatedly with distilled water similarly filtered (*idem, ibid.*).

Solutions of potassium permanganate were freshly prepared at frequent intervals from recrystallised salt, as comparatively slight decomposition with formation of manganous ions (which catalyse the reaction under investigation) would render the results valueless.

Riesenfeld used the time of complete decolorisation as a measure of the velocity of the reaction, but preliminary experiments showed that this was not legitimate, since in certain cases the time of decolorisation could be varied greatly by altering the rate of stirring (see later). This method of measurement also ruled out experiments with less than the stoichiometric proportion of hydrogen peroxide. To follow the whole course of an individual reaction by visual colorimetric comparison is possible when the concentrations are so chosen that the reaction is slow, but certainly not when it is complete in 10 or 15 seconds. It was decided therefore to follow the course of the reaction by means of a Lange photo-electric colorimeter. The lamp of the instrument was run off a 100-volt D.C. supply, free from serious fluctuations. The absorption of light by the permanganate solution was recorded continuously on the scale of the instrument, and a preliminary calibration enabled these readings to be converted into concentrations of permanganate. When a green filter was used, the absorption of light by the other substances present was negligible.

It was not found possible to use a constant-temperature room in connection with the 100-volt D.C. supply, but the variation in temperature in any one series of experiments did not exceed 1°. The mean temperatures of the different series are recorded in the appropriate places.

The course of each experiment having been followed from the time of mixing to complete decolorisation, the concentration of permanganate was plotted against time, and the curve produced backwards in order to give the initial velocity (manganous ions being then theoretically absent). As it was difficult to determine the exact slope of the curve at zero time, the velocity of reaction when  $82 \times 10^{-7}$  g.-equiv./l. of permanganate had been reduced was taken as the 'initial velocity.' In all series, this 'initial velocity,' rather than the time of total decolorisation, has been regarded as significant, and used in the curves given.

The chief practical difficulty is due to the fact that even the slightest decomposition of the permanganate solution (*e.g.*, by reducing agents in dust) is likely to produce some manganous ions, which are therefore almost certainly present in minute but variable concentration at the outset in all experiments. This difficulty has not been completely overcome, and inconsistencies, probably due to this source, have been observed between different series of experiments.

*Effect of Stirring on Reaction Velocity.*—This effect is illustrated by Fig. 1. Solutions *a*, *b*, and *c* all contained the same concentrations of hydrogen peroxide (0.098), sulphuric acid (0.05), and potassium permanganate (0.00057). The early parts of the three curves really coincide, but curves *b* and *c* have been displaced in the figure for clearness. The times of total decolorisation were :

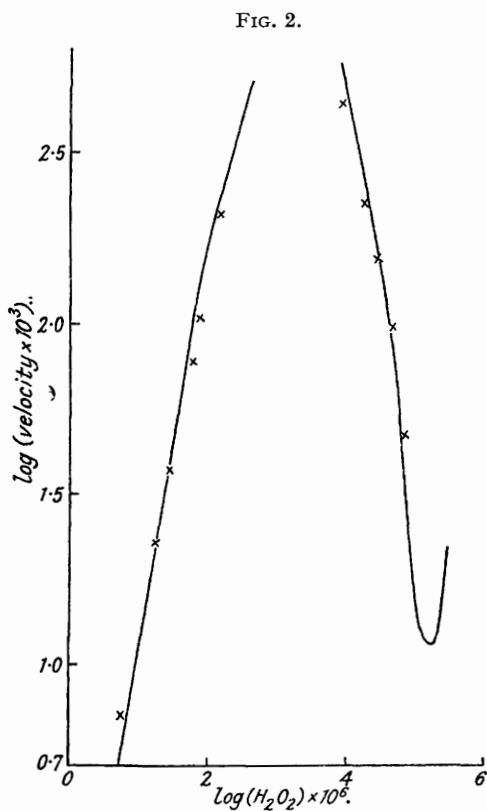
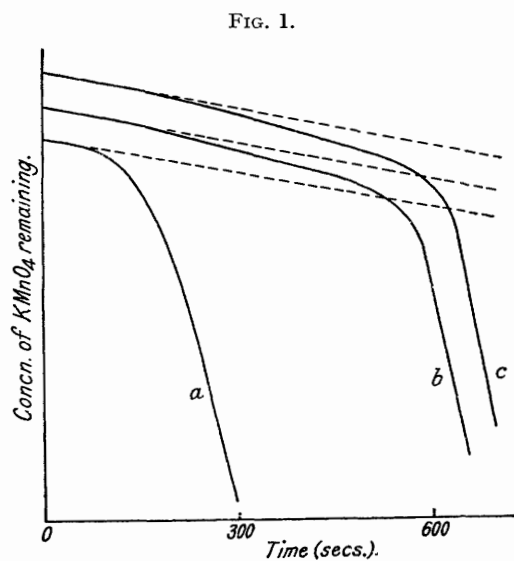
<i>a</i> (no stirring after initial mixing) .....	300 secs.
<i>b</i> (intermittent gentle stirring) .....	655 secs.
<i>c</i> (continuous vigorous stirring) .....	695 secs.

In Table I,  $S$  = speed of stirring (r.p.m.),  $T$  = time for complete decolorisation (secs.),  $[\text{KMnO}_4] = 0.0005$ ,  $[\text{H}_2\text{SO}_4] = 0.025$ .

TABLE I.

$[\text{H}_2\text{O}_2]$	0.0005.		0.00075.		0.00125.		0.0312.		0.044.		0.062.	
	$S.$	$T.$	$S.$	$T.$	$S.$	$T.$	$S.$	$T.$	$S.$	$T.$	$S.$	$T.$
	95	23.6	76	15.5	100	10.0	68	10.5	50	14.5	86	33.6
	143	24.8	93	15.9	120	10.8	107	10.8	78	14.0	109	33.0
	171	23.6	120	16.5	150	11.6	133	10.4	102	13.6	133	33.0
	198	23.2	150	17.0	200	12.6	150	10.1	143	15.7	158	40.6
	286	24.6	200	16.0	286	12.8	182	11.5	194	23.5	193	160
	400	25.2	273	16.6	400	12.0	264	17.8	222	21.5	214	240
	492	23.1	344	16.9			364	18.8	361	47.4	353	370
			392	15.4			476	25.3	458	60.8		

It will be seen that at low concentrations of hydrogen peroxide, the speed of stirring has little effect, but that at high concentrations its effect is very considerable. We are probably concerned here with the catalytic action of manganous ions. At low concentrations of peroxide, these



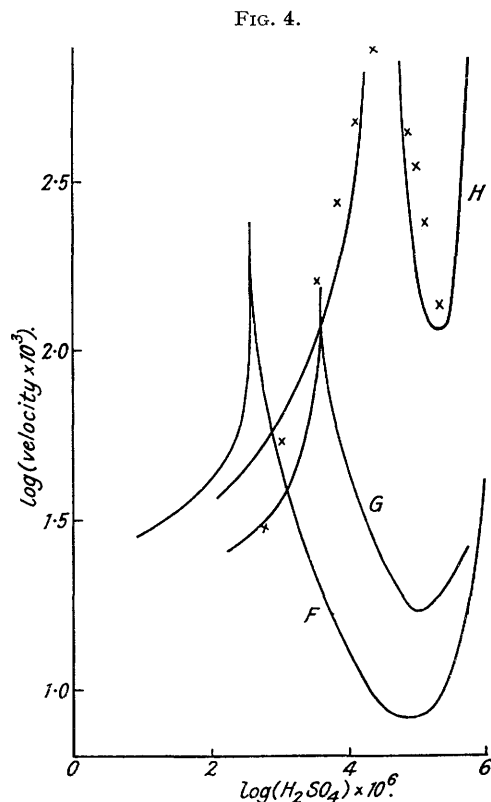
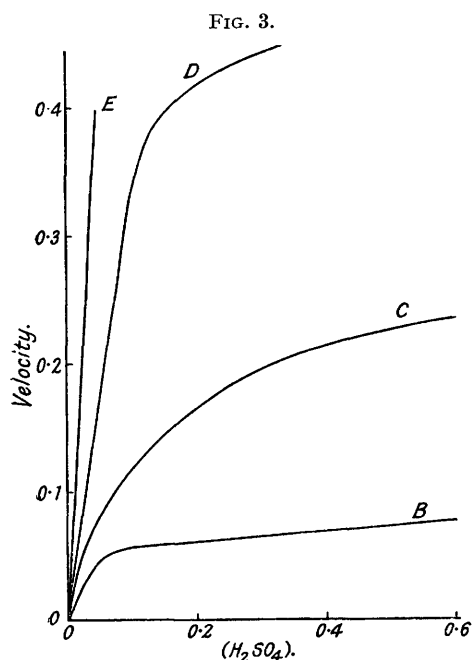
ions are very efficient catalysts, while at high concentrations they have comparatively little effect. In the latter case, their effect may be enhanced if they are allowed to accumulate locally, a theory supported by the streakiness often visible during the decolorisation of an unstirred solution. Stirring would prevent such local accumulation and thus retard the reaction. At peroxide concentrations in the neighbourhood of the velocity maximum, the later stages of decolorisation are in all events so rapid that changes due to local accumulation of catalyst would be obscured.

In all the experiments which follow, the reaction mixture was kept vigorously stirred except when readings were being taken.

*Series A* ( $15^\circ$ ):  $[\text{KMnO}_4] = 0.0005$ ;  $[\text{H}_2\text{SO}_4] = 0.025$ ;  $[\text{H}_2\text{O}_2]$  variable. A curve was obtained (Fig. 2) similar to that of Riesenfeld. The maximum and the minimum velocity were

at  $[\text{H}_2\text{O}_2] = \text{ca. } 0.005$  and  $0.16$  respectively. The velocities in the neighbourhood of the maximum were too great for the course of the reaction to be followed, even with the photoelectric colorimeter. The stoichiometric concentration of hydrogen peroxide is  $0.0005$ , which does not correspond with the maximum velocity. In Figs. 2 and 4, the logarithms of the velocity and of the concentration of hydrogen peroxide (or sulphuric acid) have been used for convenience in plotting.

Series B ( $16^\circ$ ), C ( $18^\circ$ ), D ( $15^\circ$ ), and E ( $19^\circ$ ):  $[\text{KMnO}_4] = 0.0005$ ;  $[\text{H}_2\text{O}_2] = 0.0000154$  (B),  $0.000028$  (C),  $0.00004$  (D),  $0.00075$  (E);  $[\text{H}_2\text{SO}_4]$  variable in all series. The concentrations of hydrogen peroxide in all these experiments were lower than that corresponding with the maximum velocity. It will be seen (Fig. 3) that increase in concentration of acid increases reaction



velocity in all four series, but that there is a tendency, especially noticeable in B and C, for the reaction velocity to become independent of the concentration of acid, when large amounts of the latter are added.

Series F ( $21^\circ$ ), G ( $15^\circ$ ), and H ( $16^\circ$ ):  $[\text{KMnO}_4] = 0.0005$ ;  $[\text{H}_2\text{O}_2] = 0.100$  (F),  $0.049$  (G),  $0.0285$  (H);  $[\text{H}_2\text{SO}_4]$  variable in all series. Here we are dealing with concentrations of hydrogen peroxide higher than that corresponding with the maximum velocity, and we find that variation in acid concentration yields a curve of entirely different type (Fig. 4) from those obtained in Series B, C, D, and E. Each curve shows a very sharp maximum, and a well-defined minimum.

Series I ( $18^\circ$ ), J ( $17^\circ$ ), and K ( $18^\circ$ ):  $[\text{H}_2\text{SO}_4] = 0.025$ ;  $[\text{H}_2\text{O}_2] = 0.042$  (I),  $0.065$  (J),  $0.00096$  (K);  $[\text{KMnO}_4]$  variable in all series. Whether the concentration of hydrogen peroxide is less (as in K) or greater (as in I and J) than that corresponding with the maximum velocity, the reaction velocity increases with permanganate concentration (Fig. 5).

Series L ( $15^\circ$ ). Limanowski's observation that moderate acceleration is produced by glass surfaces, at low concentrations of hydrogen peroxide and sulphuric acid, was confirmed. Using 100 c.c. of the reaction mixture,  $[\text{KMnO}_4] = 0.0005$ ,  $[\text{H}_2\text{SO}_4] = 0.025$ ,  $[\text{H}_2\text{O}_2] = 0.0005$  or  $0.00073$ , we observed increases in reaction velocity of 9 and 22% respectively, when 230 sq. cm. of glass surface, in the form of short glass rods, were introduced.

## DISCUSSION.

A satisfactory theory of the reaction must explain the following facts, a few of which were known before 1932, the remainder having been established by Limanowski, Riesenfeld, and the authors.

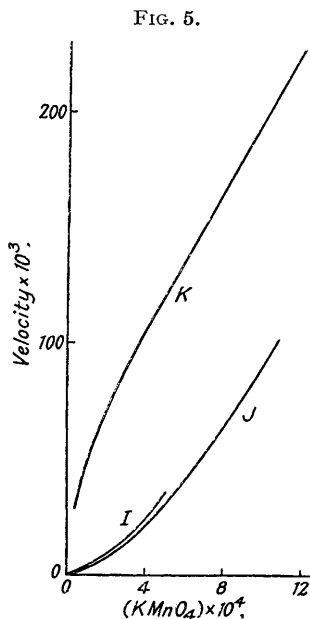
(i) When initial  $[\text{KMnO}_4]$  and  $[\text{H}_2\text{SO}_4]$  are constant, and initial  $[\text{H}_2\text{O}_2]$  is gradually increased, the reaction velocity increases to a maximum at  $[\text{H}_2\text{O}_2] = 0.005$ , falls to a minimum at  $[\text{H}_2\text{O}_2] = 0.16$ , and rises slowly at still higher  $[\text{H}_2\text{O}_2]$ .

(ii) When initial  $[\text{KMnO}_4]$  and  $[\text{H}_2\text{O}_2]$  are constant, and the latter low (less than 0.001), the velocity increases with increase in  $[\text{H}_2\text{SO}_4]$  and shows some tendency to become constant at high  $[\text{H}_2\text{SO}_4]$ .

(iii) When initial  $[\text{KMnO}_4]$  and  $[\text{H}_2\text{O}_2]$  are constant, and the latter high (greater than 0.02), the velocity rises to a maximum (the position of which varies with  $[\text{H}_2\text{O}_2]$ ) as  $[\text{H}_2\text{SO}_4]$  increases, then falls to a minimum, and finally rises again at high  $[\text{H}_2\text{SO}_4]$ .

(iv) Manganous ions catalyse the reaction powerfully at concentrations of hydrogen peroxide smaller than and up to that corresponding with maximum velocity, but have comparatively little effect at concentrations of hydrogen peroxide in the neighbourhood of the minimum velocity.

(v) The velocity increases with, but (at least at high peroxide concentrations) not in direct proportion to, permanganate concentration.



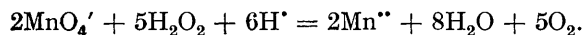
The theories of Limanowski and Riesenfeld are incapable of explaining all these facts, but we, too, are unable to advance a theory which is free from objections. It is difficult to formulate any single mechanism which will account for *both* maximum and minimum in the curve of Fig. 2 or in those of Fig. 4, and it seems probable that the rise in velocity at high  $[\text{H}_2\text{O}_2]$  is due to a secondary reaction, the velocity of which is negligibly small when  $[\text{H}_2\text{O}_2]$  is less than 0.1. One is tempted to suppose that the rise in velocity at high concentrations of acid (Fig. 4) must be attributed to the same secondary reaction. It will be noticed, however, that the concentrations of peroxide in curves G and H are less than that at which the secondary reaction has been assumed to

vanish, and no obvious explanation is forthcoming.

If we assume the intervention of a secondary reaction at  $[\text{H}_2\text{O}_2]$  greater than 0.1, we have still to account for a reaction, the velocity of which rises to a maximum at  $[\text{H}_2\text{O}_2] = 0.005$ , becomes negligibly small at  $[\text{H}_2\text{O}_2] = ca. 0.2$ , and is affected by changes in the concentration of acid, permanganate, and manganous ions as set forth above.

The curves of Figs. 2 and 4 bear some resemblance to those obtained for chain reactions which are explosive between certain limits of pressure and non-explosive outside them (see, *e.g.*, Fig. 2 of Thompson and Hinshelwood, *Proc. Roy. Soc.*, 1929, *A*, **122**, 610). It is possible, therefore, that we have to do with a chain reaction, but we believe that the explanation may lie in another direction.

Hydrogen peroxide is one of the few chemical compounds which are both reducing and oxidising agents. The ordinary reaction with potassium permanganate in acid solution may be considered as a reduction of the permanganate:



It is very unlikely that the reduction of  $\text{MnO}_4'$  to  $\text{Mn}^{**}$  really takes place in one step; if we suppose that it takes place in stages, the first stage may involve the production of an ion such as  $\text{MnO}_3'$ , which might be capable of being reoxidised to  $\text{MnO}_4'$  by a hydrogen peroxide molecule with sufficient energy. The likelihood of such reoxidation would increase with rise in  $[\text{H}_2\text{O}_2]$ .

A fair agreement with experiment may be obtained by using the empirical equation

$$v = k_1[\text{H}_2\text{O}_2][\text{H}_2\text{SO}_4][\text{KMnO}_4]/(k_2 + k_3[\text{H}_2\text{O}_2]^2[\text{H}_2\text{SO}_4]^2) \quad . \quad . \quad . \quad (1)$$

The term in the numerator represents the promotion of the reaction, while the terms in the denominator represent two types of retardation, the second, on our theory, being the reoxidation of the partially reduced permanganate by active hydrogen peroxide. Equation (1) reduces to

$$v = k_1[\text{H}_2\text{O}_2][\text{H}_2\text{SO}_4][\text{KMnO}_4]/k_2 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

at very low peroxide concentrations (Fig. 3, and the left-hand sides of the curves in Figs. 2 and 4), and to

$$v = k_1[\text{KMnO}_4]/k_3[\text{H}_2\text{O}_2][\text{H}_2\text{SO}_4] \quad . \quad . \quad . \quad . \quad . \quad (3)$$

at high peroxide concentrations, unless  $k_2$  also is large (the descending portions of the curves in Figs. 2 and 4).

Equation (1) ignores the catalytic effect of manganous ions. If, however, we suppose that the reaction represented by the term in the numerator, and the retardation represented by the second term in the denominator, are both catalysed by manganous ions, the effect of these ions will be great at low peroxide concentrations, and possibly very small at peroxide concentrations high enough for the second term in the denominator to become predominant.

Curves drawn with the aid of equation (1) can be made to correspond fairly closely with those of Figs. 1—5. For example, the crosses in Fig. 2 represent points obtained by giving  $k_1$ ,  $k_2$ , and  $k_3$  the values 1,  $10^{-8}$ , and 5 respectively, while in plotting those in Fig. 4 (curve H) the values 3.75,  $10^{-8}$ , and 2 were used.

The fact that different values must be assumed for the constants before the different curves can be reproduced may be due to slightly different concentrations of manganous ions initially present in the different series of experiments, but probably indicates that the equation requires modification.

We are unable to propose any detailed mechanism, to which exception might not properly be taken, for this very complicated reaction.

The authors' thanks are due to Mr. T. N. Richardson and Mr. C. W. Grove-White, who carried out some preliminary experiments on this reaction.