

The solubility of the hexacoordinated form with three waters per salt molecule seems to be a maximum, similar to the case of cobaltous nitrate in *t*-butyl alcohol.¹ Therefore, the reduction of the water activity and concentration of the liquid phase, from the composition at which the solid changes from trihydrate to dihydrate, results in reduction of the concentration of cobalt chloride, in essence by eliminating $\text{CoCl}_2 \cdot 3\text{H}_2\text{O}$ from solution, to give the observed extrapolation. At some critical water activity, the equilibrium swings strongly to the side of the 4-coördinate condition, and $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ in the tetrahedral form¹⁷ apparently is more soluble than the trihydrated six-coördinate form, the cobalt chloride concentration increasing along a line extrapolating to $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ as the water activity is reduced.

The data seem to indicate that between the dihydrate and an anhydrous solid phase there occurs a solid with one molecule of water per molecule of salt. The data do not enable one to determine with certainty whether this is the normal monohydrate of cobaltous chloride, already known, or whether the solid might be a monohydrate-monoacetate. A similar uncertainty exists with the anhydrous solid—the data do not differentiate between unsolvated, monoacetate or diacetate material. An experimental impediment to resolution of the difficulty is the manner in which anhydrous CoCl_2 apparently imbibes acetone. Bell, Rowlands, Bamford, Thomas and Jones¹⁸ claim to have isolated $\text{CoCl}_2 \cdot \text{CH}_3\text{COCH}_3$, and report that it decomposes to

(18) W. R. G. Bell, C. B. Rowlands, I. J. Bamford, W. G. Thomas and W. J. Jones, *J. Chem. Soc.*, 1927 (1930).

CoCl_2 at 19.5°. If this report is correct, the anhydrous solid in our ternary system at 25° must be CoCl_2 , and the acetone retention of the solid must be due to the relatively powdery nature of the anhydrous material in contrast to the finely crystalline solids obtained at other positions in the phase diagram.

Experimental

General procedures and analytical methods have been described elsewhere.¹

Cobaltous Chloride.—The commercial chemically pure hexahydrate was used as stock material. The dihydrate was prepared from this by desiccation over concentrated sulfuric acid, under reduced pressure, for one week. The anhydrous salt was prepared by heating the dihydrate in an atmosphere of hydrogen chloride, and the composition was confirmed by analyses for cobalt and for water. A sample of monohydrate was prepared by long desiccation over concentrated sulfuric acid under reduced pressure.

Acetone.—The commercial pure liquid, free of substances reducing permanganate, was equilibrated with anhydrous potassium carbonate for 48 hours, and distilled with precautions to exclude water. The material so prepared gave final water analyses of 0.2–0.3% of water by weight, and treatment with calcium hydride, alumina, CuSO_4 , CaCl_2 or Na_2SO_4 gave no improvement. Although the pyridine-rich modification¹⁹ of the Karl Fischer reagent was used in the water analyses, it was possible that the residual quarter per cent. of water might be an analytical artefact, due to inadequate suppression of the ketone effect in the Karl Fischer titration. Our suspicion that a small water content of the order indicated might actually exist in well-dried acetone received some support from conductimetric experiments of others,^{20,21} but cannot be considered proven.

(19) D. M. Smith, W. M. D. Bryant and J. Mitchell, Jr., *THIS JOURNAL*, **61**, 2407 (1939).

(20) A. Lannung, *Z. physik. Chem.*, **A161**, 255, 269 (1932).

(21) K. J. Mysels, *J. Phys. Colloid Chem.*, **61**, 708 (1947).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WISCONSIN]

The Effect of Silica Gel Upon the Decomposition of Hydrogen Peroxide¹

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A study of the thermal decomposition of hydrogen peroxide in basic silica gels, formed by the addition of sodium silicate to sulfuric acid, shows that the formation of the gel has no effect upon the stability of H_2O_2 at room temperature. The existence of reaction chains during the thermal decomposition in the gel is indicated by a wall effect and during photochemical decomposition by quantum yields which are appreciably greater than one. The kinetics of the decomposition of H_2O_2 in the presence of the chloride-chlorine couple is the same in silica sol and gel. The quantum yield for photochemical decomposition in the neighborhood of λ 3650 is of the same order of magnitude in silica gel and sol. On the basis of these experimental findings it is concluded that the apparent correlation observed by Fells and Firth (for sols containing HCl) and by the present author (for sols containing H_2SO_4) between the end of an induction period for the decomposition of H_2O_2 and the gelation of the sol is not determined by the physico-chemical changes associated with gelation.

I. Introduction

The best known examples of chemical reactions in gelatinous media are concerned with studies of the Liesegang phenomenon.³ The formation of

(1) The work described in this article was performed in 1942 at the suggestion of Professor Farrington Daniels. The study of a chain reaction in silica gel appeared to be of interest in connection with work on reaction kinetics in gelatinous propellants. Publication has been delayed because of the pressure of other work. The author takes pleasure in expressing his appreciation to Professor Daniels for helpful advice throughout the course of the work.

(2) California Institute of Technology, Pasadena, California.

(3) Wo. Ostwald, *Kolloid-Z. Zsigmondy Festschrift*, **36**, 380 (1925); J. Alexander, "Colloid Chemistry," Vol. I, The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1926, pp. 783–807.

crystals in gels has been studied by Holmes.⁴ Fells and Firth⁵ used hydrogen peroxide to produce gas bubbles in silica gels and substantiated earlier findings by Hatschek⁶ who had described and studied the formation of lenticular gas bubbles in gels in contrast to the spherical bubbles observed in liquids. Fells and Firth reported that the change from spherical to lenticular bubbles occurred gradually as the sol set to a gel, an observation which is in agreement with every other physico-

(4) H. N. Holmes, *J. Phys. Chem.*, **21**, 709 (1916).

(5) H. A. Fells and J. B. Firth, *Proc. Roy. Soc. (London)*, **114A**, 517 (1927).

(6) E. Hatschek, *Kolloid-Z.*, **15**, 226 (1914).

chemical test relating to gelation. Limited experimental studies on the kinetics of thermal decomposition of hydrogen peroxide led Fells and Firth to the conclusion that "hydrogen peroxide is not decomposed until a viscosity is reached in the sol approaching very closely to the formation of a firm gel." The apparent stability of hydrogen peroxide before gelation was attributed to formation of acid sols of the type $\text{SiO}_2 \cdot x\text{H}_2\text{O} \cdot y\text{H}_2\text{O}_2$, which decomposed during the polymerization process accompanying gelation. The formation of compounds of the type $\text{SiO}_2 \cdot x\text{H}_2\text{O} \cdot y\text{H}_2\text{O}_2$ had been reported earlier by Komarovskii.⁷

Without the temporary formation of stable peroxy-silicic acids, or the production of active catalytic centers as the result of gelation, it is not to be expected that the rate of thermal decomposition of hydrogen peroxide should be noticeably different in the sol before gelation and in the gel after setting, since the molecular and ionic mobilities are known to remain practically constant.⁸ The experimental evidence accumulated as the result of investigations of the thermal and photochemical decomposition of hydrogen peroxide in silicic acid gels during the present studies indicates that the formation of the gel has no noticeable specific effect on the kinetics of decomposition of H_2O_2 .

Extensive literature exists on the decomposition of H_2O_2 in non-gelatinous media. The thermal decomposition of H_2O_2 in the presence of inhibitors and dust shows an induction period followed by a unimolecular rate of decomposition, whereas no induction period is observed in the absence of inhibitors.⁹ When all impurities are removed, then the reaction is of zero order and exceedingly slow in glass vessels^{9,10} and also of zero order in silica containers above a limiting concentration of H_2O_2 .¹⁰ A considerable amount of work has been done on the decomposition of H_2O_2 in the presence of bromide, chloride, iodide and iodate ions. The mechanism of these reactions has been clarified, particularly through the work of Bray and Livingston and their collaborators.¹¹ The photolysis of hydrogen peroxide solutions has also been studied extensively, especially by Kornfeld,¹² F. O. Rice and his collaborators,^{13,14} Allmand and Style,¹⁵ and Heidt.¹⁶ Discussion of the photochemical decomposition of H_2O_2 may also be found in popular textbooks on photochemistry.^{17,18} Some of the results re-

ported by various investigators on the thermal, halide-catalyzed and photochemical decomposition of H_2O_2 in solutions have been repeated for the decomposition in silica gel and are described in the following sections.

II. Experimental Procedures and Results

Since the object of the present investigations was the determination of a possible specific effect of gelation on the kinetics of decomposition, the experiments were designed to afford a direct comparison between decomposition rates in the sol before gelation and in the same mixture during and after gelation.

A. Determination of H_2O_2 Concentration.—The precise quantitative determination of hydrogen peroxide in sols and gels offers considerable experimental difficulty. The procedures tested included (1) the addition of excess permanganate followed by titration with ferrous sulfate, and (2) iodimetric determination in the usual manner. A somewhat better defined end-point was obtained occasionally with the second procedure which was therefore employed for most of the quantitative determinations of H_2O_2 in sols and gels containing HCl. The first procedure was usually followed for mixtures containing H_2SO_4 with good results. Checks between solutions, sols and gels were obtained which indicated a precision of about 2%. The procedure followed for iodimetric titrations of gels is outlined briefly in the following paragraph.

The gel (approximately 25 cc. contained in a 250-cc. erlenmeyer flask) was broken up with a broad stirring rod until a viscous paste was obtained; 20 cc. of 4 *N* sulfuric acid was added and the erlenmeyer flask was then swirled vigorously. Four drops of neutral ammonium molybdate and 1 to 1.5 g. of KI were next introduced. The mixture was again shaken vigorously and allowed to stand for a few minutes. Finally sodium thiosulfate solution was added and the end-point determined with starch indicator in the usual manner. Special care was taken to break up the gel by vigorous shaking in order to minimize the time required for complete titration.

B. Decomposition of H_2O_2 in the Presence of the Chloride-Chlorine Couple.—The experimental studies of Livingston and Bray¹⁹ indicate as the over-all result a first-order decomposition of hydrogen peroxide in solutions containing chloride ions. Some experimental tests were therefore designed to demonstrate the occurrence of a first order decomposition reaction in acid sols during and after gelation.

A mixture which set to a gel almost instantly was prepared from 25 cc. of a solution containing 100 cc. of 40° Be sodium silicate, 300 cc. of H_2O , a few cc. of H_2O_2 and one cc. of concentrated HCl. The logarithm of the number of cc. of thiosulfate solution required for titration proved to be proportional to the time passed since preparation of the sol, thus substantiating the occurrence of first-order decomposition of H_2O_2 in the presence of the chloride-chlorine couple.¹⁹

In a second series of experiments 80 cc. of H_2O , 80 cc. of a solution containing 600 cc. of concentrated HCl and 400 cc. of H_2O , 120 cc. of a solution containing 64 cc. of 40° Be sodium silicate, and 300 cc. of H_2O , were added to a few cc. of Merck superoxol, giving a sol which required nearly 7 hours before a rigid gel was formed. The reaction flasks for these tests had been thoroughly cleaned with hot dichromate solu-

Mechanism of Chemical Reactions, Prentice-Hall, Inc., New York, N. Y., 1946.

(19) R. S. Livingston and W. C. Bray, *THIS JOURNAL*, **47**, 2069 (1925); *ibid.*, **48**, 405 (1926).

(7) A. Komarovskii, *Chem. Ztg.*, **38**, 121 (1914).

(8) See, for example, H. B. Weiser, "Colloid Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1935.

(9) F. O. Rice and O. M. Reiff, *J. Phys. Chem.*, **31**, 1352 (1927). Studies of inhibitor action have been made by K. J. J. and H. N. Aiyee, *THIS JOURNAL*, **55**, 575 (1933), and D. Richter, *J. Chem. Soc.*, 1219 (1934).

(10) B. H. Williams, *Trans. Faraday Soc.*, **24**, 245 (1928).

(11) W. C. Bray, *Chem. Revs.*, **10**, 161 (1932).

(12) G. Kornfeld, *Z. Wiss. Phot.*, **21**, 66 (1921).

(13) F. O. Rice and M. L. Kilpatrick, *J. Phys. Chem.*, **31**, 1507 (1927).

(14) H. C. Urey, L. H. Dawsey and F. O. Rice, *THIS JOURNAL*, **51**, 1371 (1929).

(15) J. A. Allmand and D. W. G. Style, *J. Chem. Soc.*, 596, 606 (1930).

(16) L. J. Heidt, *THIS JOURNAL*, **54**, 2840 (1930).

(17) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Cases," Reinhold Publishing Corp., New York, N. Y., 1941.

(18) G. K. Rollefson and M. B. Burton, "Photochemistry and the

tion before use. Representative results are shown in Fig. 1. Reference to Fig. 1 shows not only the occurrence of a first-order rate of decomposition, but indicates also that the rate constant for the decomposition of H_2O_2 in sol and gel is the same.

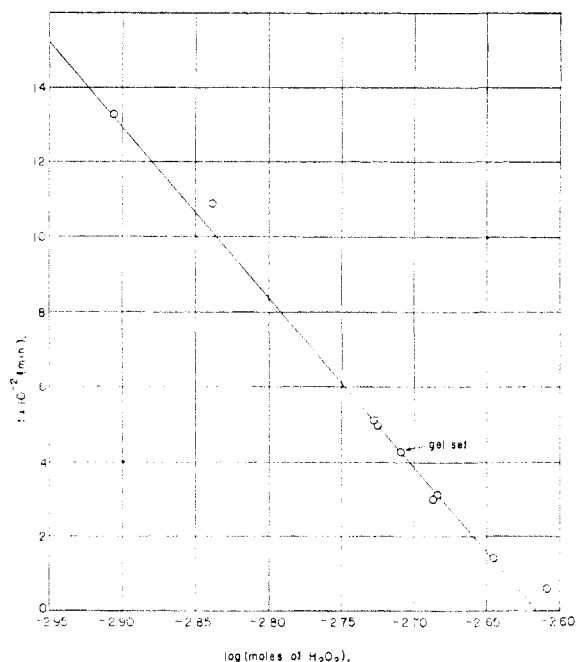


Fig. 1.—Thermal decomposition of hydrogen peroxide at 25° in acidic sodium silicate sol and gel containing hydrogen chloride.

The rate of H_2O_2 decomposition in basic mixtures, in which the pH changes appreciably during gelation,²⁰ also

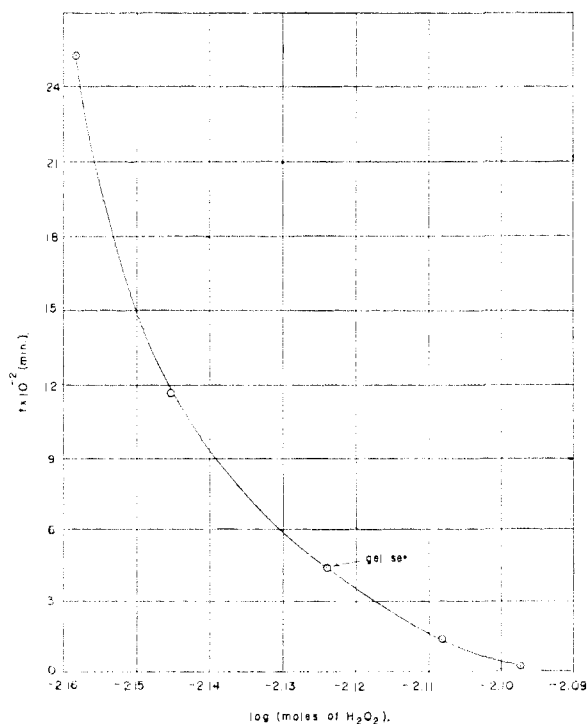


Fig. 2.—Thermal decomposition of hydrogen peroxide at 25° in basic sodium silicate sol and gel containing hydrogen chloride.

(20) C. B. Hurd and A. J. Marotta, *ibid.*, **62**, 2767 (1940).

showed no discontinuity in the specific reaction rate. Representative results are shown in Fig. 2. The first-order rate law does not appear to be obeyed in either the sol or the gel in this case.

C. Thermal Decomposition of H_2O_2 in Silica Sols and Silicic Acid Gels Containing H_2SO_4 .

The thermal decomposition of H_2O_2 in slightly basic sols and gels containing H_2SO_4 yields results similar to those reported by other investigators^{9,10} for solutions containing H_2O_2 . Representative data are shown in Fig. 3.

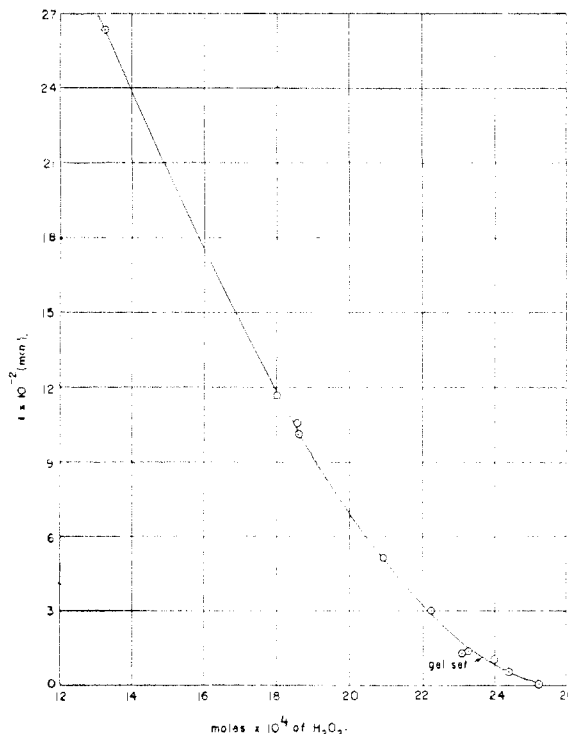


Fig. 3.—Thermal decomposition of hydrogen peroxide at 24.6° in basic sodium silicate sol and gel containing sulfuric acid.

Since it is well known that hydrogen peroxide is stable for long periods of time in strongly acid media, such very acid mixtures may serve to test any possible catalytic effects which may be induced by the formation of a gel. Again the results were wholly negative, since some strongly acid sols (pH less than 3), which formed a rigid gel after about 24 hours, showed no measurable H_2O_2 decomposition over a period of several days.

If slightly acid, neutral or very weakly alkaline mixtures are prepared and allowed to gel, a zero order decomposition may occur after an initial induction period of varying length during which the H_2O_2 is seemingly stable. These results are similar to those reported by Fells and Firth⁵ for sols containing HCl , except that the end of the induction period was not correlated with any obvious physical change in the sol. The end of the induction period occurred at any time between the preparation of the sol and long after the formation of a firm gel. The length of the induction period may be dependent, among other factors, on the pH changes which occur during gelation and which may be relatively large for nearly neutral gels.²⁰ An experimental study of the correlation between pH and the length

of the induction period was not made, since it seemed highly probable that factors other than a pH change were also involved in determining the length of the induction period which is followed by a zero order decomposition mechanism.^{9,10} The possibility of the formation of peroxy sulfates of titanium, which may be present in sodium silicate, should also not be overlooked. The stability of these peroxy compounds is very sensitive to the pH and may enter into the over-all picture. Evidence for the presence of titanium complexes is provided by the development of a characteristic yellow color when acid solutions of commercial sodium silicate are added to H_2O_2 solutions.

On the basis of these results, it appears that the observations of Fells and Firth⁵ must have been dependent upon the existence of a highly selective set of conditions involving low concentration of H_2O_2 and possibly neutral gels containing some titanium. Whatever the ultimate dependence of the length of the induction period on H_2O_2 concentration, pH , foreign ions, adsorption and stabilization on silica sol, etc., may be, it seems unlikely on the basis of the variation of the length of the induction period observed, that there is a definite correlation between the physical changes associated with gelation and the stability of H_2O_2 , as suggested by Fells and Firth.

D. Wall Effect During the Thermal Decomposition of H_2O_2 in Gels.—An investigation of the thermal decomposition of H_2O_2 in silicic acid gels in various types of containers revealed the presence of a wall effect.

E. Photochemical Decomposition of H_2O_2 in Silica Sol and Silicic Acid Gel.—The quantum yields of the photochemical decomposition of H_2O_2 were determined by use of a uranyl oxalate actinometer in the usual manner.^{17,21}

An H-6 mercury vapor lamp served as light source and the light was rendered parallel by the use of a quartz lens. A Corning light filter No. 536 was interposed between the light source and the reaction cell, which was made of brass and consisted of four accurately machined compartments, each 1 in. wide, 1 in. long, and 2.5 in. deep. The cell was painted with glyptal black and coated with paraffin before use. The compartment windows were made from thin

glass slides which transmitted more than 90% of the incident light for the wave length region near 3650 Å., as ascertained by measurements on a spectrophotometer. The actinometer solution was prepared by mixing equal volumes of 0.080 molar solution of oxalic acid with 0.020 molar uranyl nitrate. For representative tests a basic silica sol containing H_2O_2 was prepared, which set to a gel in 3 to 6 hours. The quantum yields were determined by exposures of 50-minutes duration for the sol before setting to a gel and for the gel some time after setting. Appropriate corrections for the dark reaction were made in each case by separate analyses of control samples protected from light.

Two representative results of the study of the photochemical decomposition of H_2O_2 in silica sol and silicic acid gel led to the following numerical values. Quantum yield for sample A before gelation = 5.0, and after gelation = 6.9; quantum yield for sample B before gelation = 6.5, and after gelation = 10.7. Reference to these experimental data indicates considerable scatter of experimental results. Nevertheless, it appears safe to conclude that chain reactions occur and that the quantum yields in sol and gel are of the same order of magnitude. Measurement of the quantum yield as a function of H_2O_2 concentration seemed to indicate that the quantum yield increases with increasing H_2O_2 concentration. Similar results have been reported previously for solutions of H_2O_2 .¹⁶

III. Conclusions

The occurrence of a definite wall effect during the thermal decomposition of H_2O_2 in silica gel as well as photochemical decomposition with quantum yields appreciably greater than unity establishes the existence of reaction chains during the thermal and photochemical decomposition. Because of the existence of a wall effect, the sol and gel probably do not act as strong catalysts for the decomposition of H_2O_2 , since it would be expected that catalytic effects by the silica sol or gel would mask the occurrence of a wall effect.

The results relating to the photochemical decomposition, to the wall effect, to the thermal decomposition in the presence of the chloride-chlorine couple, and to the thermal decomposition in sulfuric acid gels and sols are all similar to the results obtained on liquid solutions. It may therefore be concluded that the type of correlation obtained between the end of an induction period and the formation of a rigid gel, reported by Fells and Firth,⁵ is not to be expected as a rule and is rather dependent upon the existence of a special set of circumstances related to the concentration of H_2O_2 , the pH , etc.

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(21) W. G. Leighton and G. S. Forbes, *ibid.*, **52**, 3139 (1930); F. P. Brackett, Jr., and G. S. Forbes, *ibid.*, **55**, 4459 (1933); G. S. Forbes and L. J. Heidt, *ibid.*, **56**, 2363 (1934).