

3. Nitrogen usually was determined by the micro-Kjeldahl method. The hydroxylamines were reduced to ammonia by digestion with glucose in the presence of  $K_2SO_4$ - $CuSO_4$  catalyst.

**Acknowledgment.**—This research was conducted under Contract AF 23(616)-8 with the

United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command.

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## Low Temperature Oxidation of Solid Ferrous Sulfate Heptahydrate with Oxygen in the Presence of Solid Calcium Hydroxide

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RECEIVED OCTOBER 10, 1957

The purpose of the present work was to study the oxidation of solid ferrous sulfate heptahydrate by oxygen in the presence of solid calcium hydroxide. An induction period preceded the oxidation. The amount of oxidation was directly proportional to the amount of calcium hydroxide present in the mixture. The rate of oxidation was increased by the presence of calcium chloride, and by the presence of excess calcium hydroxide. The induction period was decreased by a decrease in particle size of the ferrous sulfate, by addition of calcium chloride, and by shaking the mixture. It is suggested that the induction period consisted of a double decomposition reaction which was favored by the absorption of moisture on the solid calcium compound.

### Introduction

Solutions of ferrous sulfate vary greatly in rate of oxidation depending on the  $pH$  of the medium.<sup>1,2</sup> Oxidation does not become significant until the  $pH$  is raised to the point where ferrous hydroxide begins to precipitate.<sup>3</sup>

The above behavior suggested to us the study of the oxidation of solid ferrous sulfate with oxygen in the presence of solid calcium hydroxide. Preliminary experiments conducted at room temperature revealed that ferrous sulfate monohydrate was not oxidized under these conditions unless the system was humid. The heptahydrate was oxidized by dry oxygen, on the other hand, and the reaction could be followed quantitatively by determining the residual ferrous iron in the mixture. The reaction was studied at room temperature at an oxygen pressure slightly greater than atmospheric using as variables the calcium hydroxide-ferrous sulfate heptahydrate ratio, agitation of the reaction mixture, particle size of ferrous sulfate, excess of reactants, and presence of calcium chloride.

**Reagents.**—Mallinckrodt ferrous sulfate granulated Analytical Reagent, Baker and Adamson Quality Calcium Hydroxide Powder (Lot No. Fa70) and C. P. Baker Analyzed anhydrous calcium chloride powder (12 mesh and finer) were employed as reagents. The ferrous sulfate and calcium chloride were ground and screened with Tyler's Standard Screens to obtain size fractionation. This operation was performed using a Ro-Tap Testing Sieve Shaker. The amount of sieved calcium chloride to be used in a given run was weighed approximately. It then was dried by heating at  $325^\circ$  for 12 hours and stored in a desiccator.<sup>4,5</sup> The preliminary weighing minimized handling of the dried material and its exposure to atmospheric moisture.

**Apparatus and Experimental Technique.**—Figure 1 is a diagram of the apparatus. A 250-ml. filtering flask (dried in an oven at  $110^\circ$ ) was used as reaction vessel A. This flask was clamped to a high-frequency vibrator B used to obtain a thorough and uniform mixing of the reactants. The oxygen from a gas cylinder was admitted at C and on passing through the system was dried by magnesium per-

chlorate contained in towers D and E, and in drying tube F before entering the reaction vessel. The oxygen outlet was protected from atmospheric moisture by its immersion in dibutyl *o*-phthalate contained in graduated cylinder G. The reservoir H permitted an even distribution of the oxygen among six outlets at position I (only one is illustrated). Each outlet was supplied with a stopcock so that any number of samples up to a maximum of six could be oxidized at the same time. In case of simultaneous runs, regulation of the pinchcock attached to each outlet at position J permitted equalization of the oxygen pressure in the reaction vessels. This was shown by similar rates of bubbling through equal heights of the organic liquid.

The weighed reactants were added one at a time to the reaction vessel. A rapid stream of oxygen was passed through the system until the last reactant was added. This procedure assured the removal of any moisture in the system as well as a quick displacement of the air by the oxygen shortly after stoppering the flask.

If the mixture to be oxidized consisted of three substances, the vibrator was turned on for five minutes after the addition of the second reactant in order to obtain good mixing. In all cases the ferrous sulfate was added last. As soon as it was added the mixture was shaken for a certain time, the time depending on the particular mixture. Also, at this time the oxygen pressure was decreased by regulating the valve on the tank until it was only slightly higher than atmospheric pressure, so that no bubbling occurred. In this manner any water expelled from the hydrated salt remained in the system and was not removed as would have been the case had the stream of dry oxygen been continued. The level of the liquid within the outlet tube was kept constant during the oxidation in order to maintain the same oxygen pressure during the process. This was done by adjusting the valve on the tank since any change in the adjustment of the pinchcocks would result in different oxygen pressures in the reaction vessels with the possibility of reducing it greatly in any one vessel. At the end of the oxidation treatment of one sample, the reaction vessel could be removed from the apparatus after closing the stopcock on the particular line without disturbing the oxidation being carried out in other reaction vessels.

**Analytical Procedures.**—The course of the oxidation of solid ferrous sulfate heptahydrate with oxygen was followed by determining quantitatively the residual ferrous iron in the reaction mixture. The mixtures were warmed gently with an excess of standard 0.5 *N* potassium dichromate solution which was 3.4 *N* in hydrochloric acid. The excess dichromate was titrated electrometrically with standard ferrous sulfate using a Serfass Electron Ray Titration Assembly with polarized platinum electrodes. It was shown that no oxidation occurred in the air during the dissolving of the samples and that substitution of sulfuric acid for hydrochloric acid did not affect the results. The latter acid was used, however, because the mixtures dissolved more readily in it.

Approximately 700 samples were analyzed during the

(1) J. Cornog and A. Hershberger, *Proc. Iowa Acad. Sci.*, **36**, 264 (1929).

(2) O. Lievin and J. Herman, *Comb. rend.*, **200**, 1474 (1935).

(3) J. Herman, *ibid.*, **202**, 419 (1936).

(4) W. D. Cooke, Ph.D. Thesis University of Pennsylvania, Philadelphia, 1949.

(5) J. F. Hazel, W. M. McNabb and W. D. Cooke, *THIS JOURNAL*, **75**, 1552 (1953).

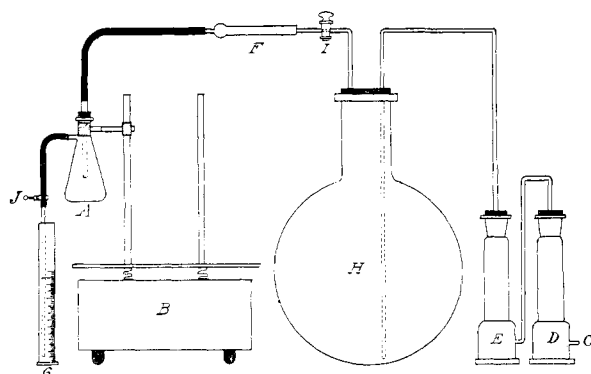


Fig. 1.—Apparatus for oxidation.

course of the study. All analyses were carried out with solutions of the same concentration using equal volumes and equal dilutions both in the analysis and in the standardization. In order to prevent the electrodes from becoming sluggish, they were cleaned after each 10 or 15 titrations by immersing in concentrated nitric acid and then by thorough rinsing with distilled water.

**Description of the Reaction.**—The color changes which occur when a stoichiometric mixture of finely powdered ferrous sulfate heptahydrate and calcium hydroxide is shaken are striking. For solid reactants of particle size less than 0.074 mm., the mixture is white with an almost imperceptible green tint due to the presence of the ferrous salt. On shaking, the mixture slowly acquires a cream shade. This is the induction period during which a small amount of oxidation (less than one per cent.) occurs. The end of the induction period is marked by the color of the mixture suddenly changing to a deep green, and heat and moisture being released. Shaking of the mixture is stopped to prevent clumping.

The green color was attributed to the products formed in an exchange reaction since a precipitate of similar color was obtained when solutions of ferrous sulfate and calcium hydroxide were mixed. Visual evidence of oxidation was indicated by the appearance of brownish colored particles shortly after the deepening of the color. A red color developed within two to four minutes. Analysis of mixtures during the green color stage were not reproducible, and values of from 3 to 30% oxidation were obtained. The variation in results was considered to be due to the rapid oxidation reaction which accompanied the double decomposition reaction.

**Method of Study.**—The time of oxidation reaction to occur was measured from the time of the appearance of the green color since the amount of oxidation during the induction period was small. All studies of the oxidation of ferrous sulfate were made at room temperature (28–30°) and at an oxygen pressure of 9 mm. in excess of atmospheric pressure. A four hour period was found sufficient to yield the maximum oxidation possible in any system.

**Calcium Hydroxide–Ferrous Sulfate Ratio.**—The degree of oxidation varied directly with the molar ratio of calcium hydroxide to ferrous sulfate heptahydrate as shown by the results in Fig. 2. The solid curve was calculated on the assumption that ferrous hydroxide was an intermediate product. The experimental results, obtained with particles less than 0.074 mm. and a four hour oxidation period, are represented by circles in this figure. Complete oxidation occurred when the solid reactants were present in equimolar amounts. Excess calcium hydroxide also promoted complete oxidation.

**Method of Expressing Results.**—In reporting the effect of other variables on the reaction, the results are expressed as percentage reaction, where this term refers to the percentage ratio between the observed degree of oxidation and the degree of

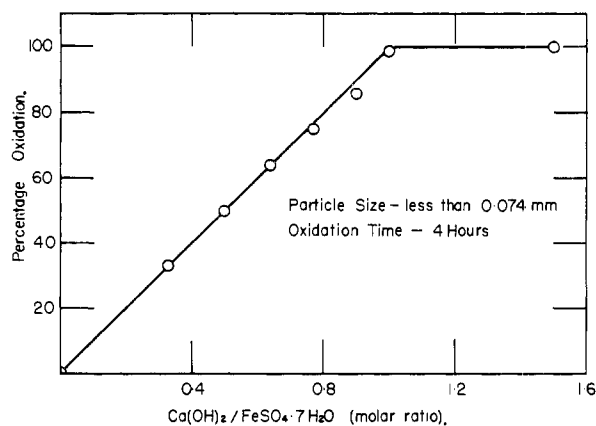


Fig. 2.—Variation of oxidation with calcium hydroxide.

oxidation possible as determined by the ratio of the reactants.

**Particle Size.**—The effect of particle size was studied only with reference to the ferrous sulfate. The calcium hydroxide used in all experiments consisted of a fine powder with a particle size smaller than 0.074 mm. Two particle sizes of ferrous sulfate were investigated: (1) less than 0.074 mm.; (2) 0.074 to 0.147 mm. The results obtained with equimolar mixtures of the reactants are given in Fig. 3. There was no difference in the rate of

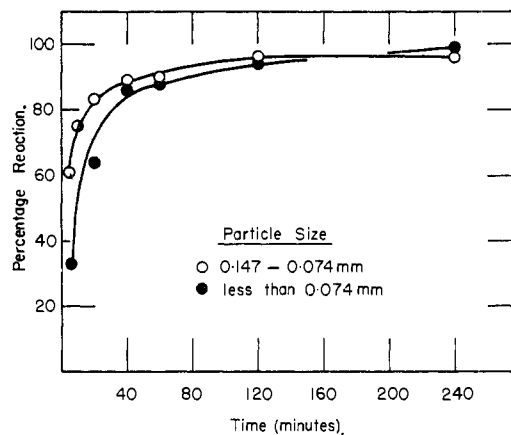


Fig. 3.—Effect of particle size on the oxidation reaction.

oxidation when the two different size particles were used. The time required for the green color to appear, marking the end of the induction period, did depend on particle size, however. The induction period had a mean value of eight minutes for particles less than 0.074 mm. and a mean value of 30 minutes for particles in the range 0.074–0.147 mm.

**Effect of Excess Reactants.**—Mixtures with a twofold excess of both ferrous sulfate heptahydrate and calcium hydroxide were studied. The results of this variation in molar ratios are compared with the oxidation of stoichiometric mixtures in Fig. 4. The rate of reaction was very rapid when an excess of calcium hydroxide was present but was unaffected by an excess of ferrous sulfate. The induction period was increased by an excess of ferrous sulfate.

**Studies with Calcium Chloride.**—Addition of solid calcium chloride to the mixture decreased the induction period markedly. The mixtures be-

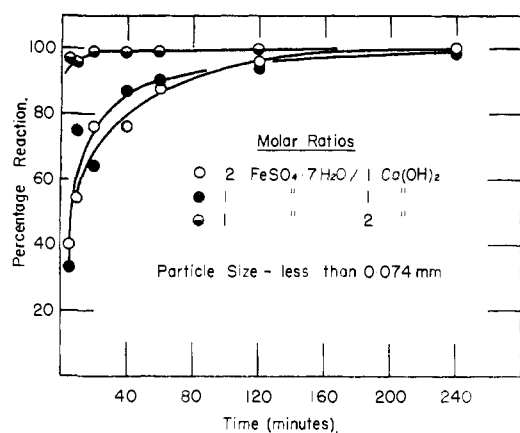


Fig. 4.—Effect of reactant ratio.

came quite moist under these conditions due to dehydration of the ferrous sulfate heptahydrate, and agitation could not be continued without serious clumping. The over-all yield was decreased when clumps were present because ferrous sulfate in the interior was excluded from contact with oxygen.

Subsequently, it was found that ferrous sulfate heptahydrate can be oxidized in the presence of calcium chloride alone under conditions similar to those prevailing in the reaction with calcium hydroxide. As in the case of calcium hydroxide, moisture was required for the oxidation to proceed and no reaction was obtained with ferrous sulfate monohydrate unless the mixture was exposed to atmospheric moisture for a long period. With the heptahydrate the degree of oxidation depended on the amount of calcium chloride in the mixture, and on the length of the oxidation treatment. The maximum oxidation obtained was of the order of 20%.

The effect of varying amounts of calcium chloride was studied with respect to the oxidation of ferrous sulfate alone as well as of different mixtures with calcium hydroxide. The results are plotted in Fig. 5.

### Discussion

The fact that the degree of oxidation varied directly with the molar ratio of calcium hydroxide to ferrous sulfate heptahydrate, Fig. 2, suggests that ferrous hydroxide was an intermediate product in the reaction. The deepening of the color, observed visually, may be attributed to the presence of two oxidation states of iron in the mixture, Fe(II)-Fe(III), while the completion of the reaction corresponded to complete conversion of the iron to Fe(III) as shown by analysis of the mixtures.

Since only the higher hydrate of ferrous sulfate,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , took part in the exchange reaction at room temperature, it was concluded that a supply of moisture was necessary for the reaction to occur. The moisture was provided by the dehydration of the heptahydrate, which starts losing water at  $20^\circ$ .<sup>6</sup> Langmuir showed that dehydration of a solid hydrated salt occurs at the boundary of the solid phases. A nucleus of the second phase must be present before the reaction can start.<sup>7</sup> Hume

(6) H. O. Hofman and W. Wanjukow, *Trans. Am. Inst. Mining Eng.*, **43**, 523 (1912).

(7) I. Langmuir, *THIS JOURNAL*, **38**, 2221 (1916).

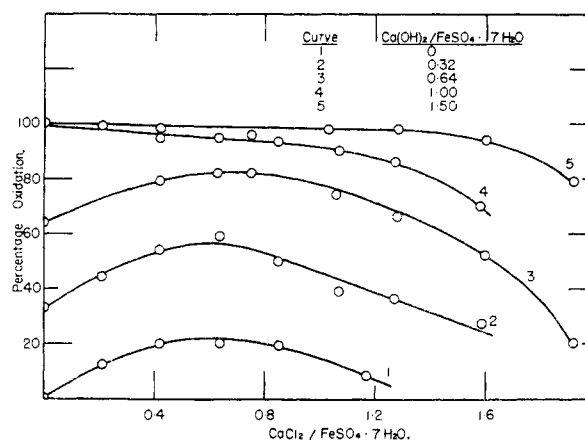


Fig. 5.—Effect of calcium chloride on the reaction.

and Colvin observed that nuclei usually originate on the edges and corners of crystals.<sup>8</sup> The treatment to which the hydrated salt was subjected to obtain size fractionation would be expected to favor the dehydration reaction on this basis.

The induction period which preceded the initiation of the reaction may be attributed to the slow process of dehydration until enough moisture accumulated in the system for the exchange reaction to occur. When the reaction mixtures were allowed to stand undisturbed the reaction started only after a period usually longer than an hour and in many cases it did not proceed. The initiation of the reaction was accelerated by shaking the mixtures. The continuous agitation provided better contact with the dry oxygen and facilitated the dehydration process. As soon as the reaction started, as indicated by deepening of the color, the shaking was stopped to prevent interference with the reaction by the formation of large aggregates. The dehydration was accelerated at this time by the exothermic nature of the reactions. The rapid rate of oxidation in the presence of excess  $\text{Ca}(\text{OH})_2$ , Fig. 4, may be attributed to the property of calcium hydroxide adsorbing moisture. The accompanying decrease in vapor pressure would tend to facilitate dehydration of the ferrous sulfate.

It was found, Fig. 5, that the degree of oxidation of ferrous sulfate heptahydrate increased with increasing amounts of calcium chloride. A maximum value was reached after which the over-all yield gradually decreased. In suggesting an explanation of these results it may be assumed that moisture was transferred from the hydrated ferrous sulfate to the calcium chloride. The water associated with the calcium chloride as a result of this process consisted of water of hydration and of adsorbed water. The latter provided a moist surface for contact with the ferrous sulfate. With increase in the amount of calcium chloride the amount of oxidation reached a maximum. The continued addition of calcium chloride resulted in more of the water being used for the formation of hydrates of calcium chloride leaving less water available for adsorption. As a result the oxidation decreased under these conditions.

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(8) J. Hume and J. Colvin, *Proc. Roy. Soc. (London)*, **A125**, 635 (1929).