configuration with the halogen–halogen axis perpendicular to the plane of the ring at its center has been excluded.[2]

A careful study of these systems, possibly along the lines of the molecular orbital approach suggested by Pimentel[9] appears very desirable.

[9] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

LOS ANGELES 24, CALIFORNIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Reaction between Ferric Sulfate and Calcium Chloride in the Solid State[1]

BY J. FRED HAZEL, WALLACE M. MCNABB AND WILLIAM D. COOKE[2]

RECEIVED DECEMBER 22, 1951

The reaction between solid ferric sulfate and calcium chloride to form ferric chloride and calcium sulfate has been studied with particular reference to the effects of temperature, particle size, reactant ratio and the presence of water and ferric chloride as catalysts. When the materials were strictly anhydrous the reaction was found to occur only above 300°. The addition of small amounts of ferric chloride or of water caused the reaction to be initiated at much lower temperatures. The reaction was slow between 80 and 90°. At 118° a yield of 22% was obtained in five minutes while a maximum conversion of 43% was found in one hour. The percentage reaction was 88% in five minutes at 225° and 96% for the same period at 340°. At low temperature the presence of an induction period indicated that the reaction was autocatalytic. The percentage conversion decreased rapidly with increase in particle size. Mixtures containing an excess of one of the reactants had higher rates of reaction and gave greater yields than stoichiometric mixtures. The reaction could not be reversed.

The reaction between solid calcium chloride and ferric sulfate to form ferric chloride and calcium sulfate has been studied quantitatively by taking advantage of the solubility of one of the products, ferric chloride, in ether. The effects of temperature, pressure, particle size and reactant ratio on the reaction have been investigated.

Experimental

Materials.—Baker C.P. ferric sulfate and calcium chloride were used in the experiments. Petrographic analysis of the ferric sulfate revealed that it contained between 1 and 2% ferric oxide. When heated in the air to 550° it showed evidence of decomposition. A decomposition pressure of 23 mm. at 553° has been reported for this compound.[3] In preliminary experiments it was found that ferric sulfate from two other sources contained ferric oxide to about the same extent.

Heat Source and Temperature Control.—The temperature at which the reaction was studied ranged from 82 to 340°. Temperature control up to 200° was realized by the use of boiling liquids.[4]

By means of a thermocouple inserted in the powder, it was found that the time required for the reaction mixture to be heated from 90°, the temperature at which the reaction begins, to 118° was 15 seconds. To reach 182°, 180 seconds were necessary.

An electric heater was used for temperature control above 200°.

To obtain rapid heating, an electrically heated brass block with a hole drilled to accommodate the reaction tube was used as a preheater. The temperature of the block was adjusted about 75° above the temperature at which the reaction was to be carried out. The reaction mixture was allowed to remain in the preheater long enough for the temperature to approach the desired value. It was then transferred to the heater. In this manner mixtures could be heated to the reaction temperature in about one minute.

Procedure.—The materials were screened with Tyler Standard Screens to obtain size fractionation. They were weighed out approximately in the desired ratio and dried at 325° for 12 hours.

The dried reactants were placed in screw-cap bottles and conveyed to a dry-box charged with phosphorus pentoxide. A positive pressure was maintained in the box with air which had been dried by passing through sulfuric acid, calcium chloride and magnesium perchlorate. The materials were screened again in the dry-box and then mixed. To obtain uniform mixing the container was placed for one-half hour on a high frequency vibrator which kept the material in a semi-suspended state.

The exact ratio of the two reactants was found by determining the percentage iron in the mixture. In some reactions, a small amount of water was added as a catalyst. To accomplish this a weighing bottle containing a known quantity of the mixture was opened while on a balance, and allowed to pick up the desired amount of water from the atmosphere. The material was remixed as described above.

Reactions were carried out with about 0.15 g. of mixture in 9-mm. Pyrex tubes. After being heated for the desired length of time the contents of the tube was transferred to a small vial, weighed and extracted with ether.

Method of Analysis.—Ferric chloride was extracted from the reaction mixture with anhydrous ethyl ether. The ether layer was evaporated and the iron determined by a method previously described.[5] From the amount of iron in the sample, the completeness of the reaction was calculated.

The reliability of the extraction process as a quantitative method for following the course of the reaction was tested. It was found that ferric chloride was completely extracted from synthetic reaction mixtures and that no iron was extracted from ferric sulfate. However, when a 250-mg. sample of reactants was extracted with anhydrous ether (0.01% water) a small amount of iron, 0.09 mg., was found in the extract. This value was reproducible and was considered to be the blank determination of the reagents used.

Experiments in Open Tubes.—In open tubes protected from moisture with reactants dried at 325° for 12 hours, reactions occurred only at temperatures greater than 300°. Small amounts of water caused the reaction to proceed at much lower temperatures. The reaction was also catalyzed by ferric chloride. A striking demonstration of this was obtained by heating a layer of the unreactive mixture in an open Petri dish at 250°. No reaction occurred until a few crystals of anhydrous ferric chloride were added. The reaction then proceeded rapidly with the formation of the ferric chloride being evidenced by the widening, dark circle spreading out from the spot at which the catalyst was added.

Autocatalytic effects in reactions between solids are not uncommon.[6] Another indication of the autocatalytic na-

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[1] Presented before the XIIth International Congress of Pure and Applied Chemistry, New York, N. Y., September 10-13, 1951.

[2] From a dissertation by William D. Cooke presented to the faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XIV, Longmans, Green and Co., London, 1935, p. 311.

[4] C. D. Hodgman, "Handbook of Chemistry and Physics," 28th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1944, p. 528.

[5] W. D. Cooke, J. F. Hazel and W. M. McNabb, *Anal. Chem.*, **21**, 643 (1949).

[6] A. Sieverts and H. Theberath, *Z. physik. Chem.*, **100**, 463 (1922); J. Kendall and F. J. Fuchs, THIS JOURNAL, **43**, 2017 (1921); C. N. Hinshelwood, *J. Chem. Soc.*, **119**, 721 (1921); H. S. Taylor, "A Treatise on Physical Chemistry," D. Van Nostrand, Co., Inc., New York, N. Y., 1925, p. 981.

ture of the present reaction was the existence of an induction period[7] before the rate of reaction became appreciable. Conversely, rapid removal of the catalyst formed by the reaction by means of a rapidly moving stream of preheated air, extended the induction period indefinitely. Hulett and Taylor[8] observed a similar type of behavior in a study of the decomposition of mercuric oxide.

In experiments conducted in open tubes in a quiet atmosphere it was found that the size of the sample as well as the temperature affected the loss of the catalyst. With 0.1% water as a catalyst and at 250° a reaction occurred in 15 minutes using a 1-g. sample whereas a 0.1-g. sample did not react. Further, in the case of 0.25-g. samples, reaction occurred at 156°, but not at 225 or 250°. At 300° and above, reaction was again possible. Thus, in those cases where accumulation of the catalyst was favored, as with the larger samples and at temperatures below 200°, the reaction took place. Above 300°, little catalyst was needed.

The above results clearly suggested the use of closed tubes for the reaction. Confirming this the following results were obtained: 1. A 0.1-g. reaction mixture containing 0.1% water, which would not react in an open tube, did react when the tube was sealed. 2. If a mixture was heated in an open tube, as in the above, and the tube then sealed, the reaction still would not occur. This indicated that the volatile catalyst was lost in the initial heating. 3. To eliminate the possibility of the sealed tube reactions being caused by an increase in pressure, a mixture as in no. 1 was placed in a sealed-off hypodermic syringe. In this fashion it was possible to prevent a build-up in pressure without allowing any volatile matter to escape. Reaction occurred which proved that the reactivity in sealed tubes was not caused by an increase in pressure.

Side Reactions.—The dissociation of ferric chloride into ferrous chloride and chlorine[9] was investigated. This reaction was found to consume 0.5% of the ferric chloride at high temperatures and 0.1% at lower temperatures.

At temperatures above 200°, the products of the reaction were colored by the presence of ferric oxide. At 340°, decomposition was appreciable and sulfur trioxide was found in the evolved gases. This was unexpected since the ferric sulfate used had been dried at 325° for 12 hours without noticeable coloration. Since the dissociation is reversible, the coloration caused by ferric oxide was decreased considerably when the reaction was carried out in sealed tubes. Under these conditions a yield of 97% was obtained. Hence, no more than 3% of the ferric sulfate could have been converted to ferric oxide. At lower temperatures, less than 3% was decomposed. Below 200°, a series of reactions in open and sealed tubes showed no difference in yield.

In the following the reactions above 200° were carried out in closed tubes.

Effect of Water on the Reaction.—The minimum amount of water required to initiate the reaction at 100, 156, 250 and 300° was determined to be 1.0, 0.7, 0.13 and 0%, respectively. Thus, the lowest temperature requiring no catalyst, 300°, corresponds roughly to the temperature, 306°, above which ferric chloride does not exist as a solid.[10]

The results in Table I show that there was a slight increase in the yield with increasing amounts of water at 250°. Stoichiometric mixtures were used. With mixtures containing 10 and 25% water, the amount of ferric chloride formed decreased to 80%.

TABLE I

VARIATION OF YIELD WITH AMOUNT OF WATER ADDED AT 250°

% H_2O	Percentage yield Min.: 5	15	30	60
0.07	0	0	0	0
.13	85	84	..	85
.5	87	83	87	87
1.0	83	83	80	84
2.0	85	86	86	86
5.0	86	93	94	96

The same effect was noted at lower temperatures. At 156°, a mixture containing 1% water gave a yield of 74% in one hour, as compared to 84% with 5% water.

Effect of Ferric Chloride on the Reaction.—To determine the amount of ferric chloride necessary to initiate the reaction, anhydrous reaction mixtures were prepared containing increasing amounts of ferric chloride. It was found that 0.07% was able to catalyze the reaction. This amount was found to be independent of the temperature and was sufficient to initiate reaction at 118, 200 and 250°.

As in the case of water, the yield was raised only slightly by increasing the amount of catalyst. The yields at 250° for mixtures containing 0.07 and 1.0% ferric chloride are shown in Table II.

TABLE II

VARIATION OF YIELD WITH AMOUNT OF FERRIC CHLORIDE AT 250°

$FeCl_3$, %	Percentage yield Min.: 5	15	30
0.04	0	0	0
0.07	87	87	88
1.0	93	92	92

The reactions catalyzed with ferric chloride gave inconsistent results. The mixtures containing water, however, were found to give reproducible reactions. This may have been caused by the fact that the addition of water gave a uniform distribution on the surface of the reactants. For this reason in all subsequent experiments, unless otherwise stated, the reactions were catalyzed by the addition of 1% water.

Induction Periods and Catalysts.—At low temperatures with mixtures containing 1% water as catalyst, a pronounced period of induction was noted. The reaction curves for runs at 105, 100 and 92° are shown in Fig. 1. It may be seen that addition of 1% ferric chloride decreased the induction period at 92°.

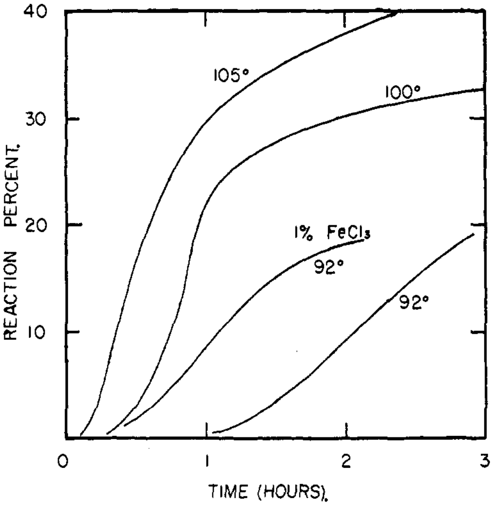

Fig. 1.—Low temperature induction periods.

Since ferric chloride and water both catalyze the reaction, the question arose as to whether or not water is only an indirect agent which forms ferric chloride. The addition of 10% water in the reaction mixture was found to cause the formation of 0.8% ferric chloride at room temperature as determined by ether extraction. Water cannot be added to the mixture without the formation of ferric chloride and hence it is difficult to prove experimentally whether it is able to catalyze the reaction directly.

Calcium sulfate and ferric oxide were tested but not found to alter the rate of reaction.

Temperature at which the Reaction Is Initiated.—Heating curves[11] were run for the reaction being studied but no definite breaks were found even when the rate of heating was as low as 3° per minute. This result shows that the heat of reaction is small, a fact in agreement with the theo-

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[7] S. Glasstone, "Textbook of Physical Chemistry," 2nd ed., D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1078.

[8] G. A. Hulett and G. B. Taylor, *J. Phys. Chem.*, **17**, 567 (1913).

[9] P. Fireman and E. G. Portner, *ibid.*, **8**, 500 (1904).

[10] Reference 3, p. 50.

[11] J. A. Hedvall, *Z. anorg. Chem.*, **96**, 67 (1916); **98**, 57 (1916).

retical value for the reaction calculated from the heats of formation, 2 kcal.

The problem also was approached directly by carrying out the reaction at closely spaced, low temperature intervals, 82, 92 and 100°. At 82°, reaction occurred but the rate was low and only 5% conversion was obtained in seven hours. At 92 and 100°, the yield was pronounced but the rate of reaction was still low (Fig. 1). From these data it was concluded that the reaction begins at an indefinite temperature between 80 and 90°.

Effect of Temperature on Reaction Rate and Yield.—The effect of temperature on the rate and completeness of the reaction was studied at temperatures ranging from 82 to 340°. The results are plotted in Figs. 2 and 3. The reactions were carried out using material smaller than 0.06 mm. mixed in stoichiometric ratios with 1% water present.

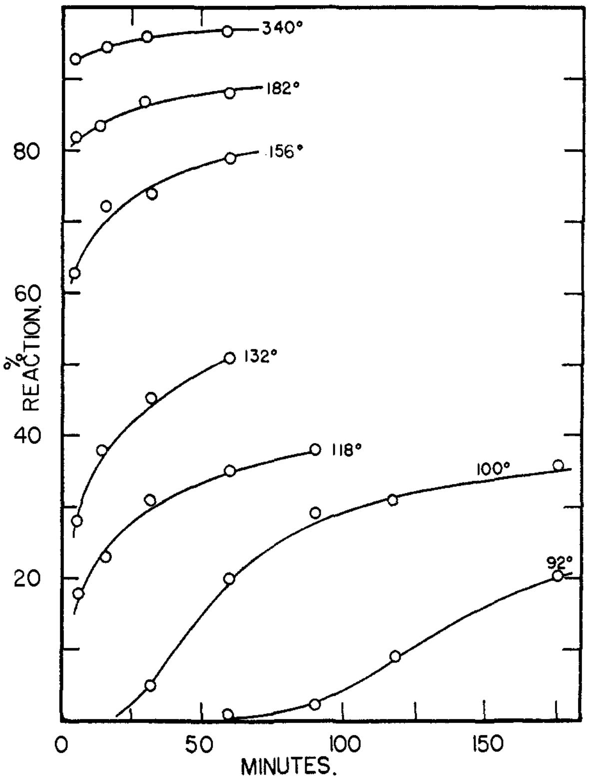

Fig. 2.—Effect of temperature on the reaction rate.

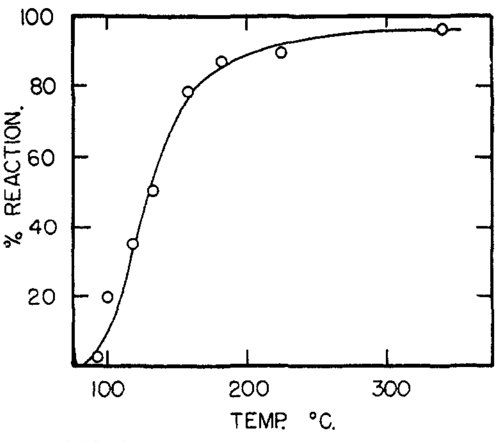

Fig. 3.—Yields in 60 minutes at different temperatures.

It can be seen from Fig. 2 that the period of induction decreased with increase in temperature. Above 200° the rate of reaction was so high that it could not be followed and maximum yield was obtained in less than five minutes. At 340°, the reaction was about 96% complete. Appreciable decomposition into ferric oxide occurred at this temperature and this lowered the percentage conversion.

Figure 3 shows the yield obtained in 60 minutes at different temperatures.

The Effect of Particle Size.—The reactants were graded according to particle size into six different groups as shown in Table III. Reactions were carried out at two different temperatures, 250 and 156°, for various lengths of time with 1% water present. The results obtained at 250° are shown in Table III. Figure 4 gives the results found at 156°.

Table III

Variation in Yield with Particle Size at 250°

Size, mm.	Percentage yield Min.:			
		15	30	60
0.42–0.25	0	0	0	0
.25– .18	31	85	93	97
.18– .15	40	80	94	94
.14– .07	50	80	85	90
.07– .06	85	83	85	88
<0.06	88	88	89	90

The data show that the difference in reactivity caused by particle size is more pronounced at the lower temperature and that only the smallest particles gave a high yield under these conditions.

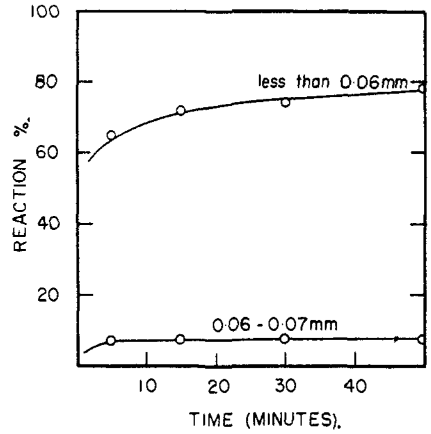

Fig. 4.—Effect of particle size at 156°.

At 250°, the reaction did not occur with the largest particles and it was not reproducible with 0.25–0.18 mm. material in the 5-minute and 15-minute runs. Wide variations were noticed in the latter case and in about one-third of the trials the reaction did not proceed. These results were correlated with the fact that the reaction begins at certain active centers. It could be observed that the process began at one or two points in the reaction mixture, and spread outwardly from these points. With the finer particles, the number of active centers was much larger as evidenced from the speckled appearance of the material in the beginning of the reaction.

Effect of Packing the Reactants.—The reactants were packed together by placing a small charge in a 9-mm. closed tube and applying pressure to the material by means of a snugly fitting brass rod. The magnitude of the pressure applied was controlled by means of a trip balance. Two thousand grams was placed on one pan of a balance. The tube containing the mixture was placed on the other pan and pressure applied until the two pans were level. Since the area of the brass plunger was 0.25 cm.^{2}, the pressure applied was 8000 g./cm.^{2}. The reaction mixture was not compressed all at once, but small portions were packed layer upon layer. The entire procedure was carried out in a moisture-free atmosphere.

The mixtures used were of stoichiometric composition with 1% water added as a catalyst. This material had a particle size of less than 0.06 mm. Yields of 87% and 89% were obtained at pressures of 4000 and 8000 g./cm.^{2}, respectively. When no pressure was applied, the yield was 74%. The above results indicate that pressing the reactants together increase the yield. In other studies of this effect, it has been found that the yields are raised, as a rule, by compression of the reactants.[12]

Effect of Excess Reactants.—The completeness of a solid phase reaction depends to a great extent on the surface area of the reaction interface. To increase this area, mixtures were prepared containing one of the reactants in excess of the stoichiometric ratio. The material used was less than 0.06 mm. in grain size, and 1% water was added as catalyst. Twofold and fourfold excesses of both ferric sulfate and calcium chloride were used. The experiments were carried out at 118°, and the results are plotted in Figs. 5 and 6.

Increasing the amount of one of the reactants increased the yield. It was noted that in the cases where a large excess of either ferric sulfate or calcium chloride was employed a period of induction was evident. This might be explained on the basis of a reaction beginning at active centers which are believed to be reactive, high energy, contact points between particles of the reactants.[13] If such is the case, when a large excess of one of the reactants is present the total number of contact points would be decreased. This would tend to decrease the initial rate of reaction.

Reversibility of the Reaction.—If the reaction is assumed to take place between pure solids, *i.e.*, without formation of solid solutions, thermodynamics would require that equilibrium would occur at only one temperature. The reaction would go to completion in the one direction above that critical value of the temperature and in the other direction below that temperature. If the heat of reaction is small, as in the present case, one might expect, in agreement with the observations of Tamman,[12] that the equilibrium temperature would not be high.

The fact that the reaction rate became zero well short of complete reaction, as shown in Fig. 2, suggests that equilibrium was met at all the temperatures studied and the effect of excess reactants in increasing the yield lends support to this possibility. The formation of solid solutions would permit the occurrence of equilibrium at any temperature since the chemical potentials of the solids would in such case no longer be constant.

Despite these indications, no reaction could be found to proceed in the reverse direction, that is

$$2FeCl_3 + 3CaSO_4 \longrightarrow Fe_2(SO_4)_3 + 3CaCl_2$$

Mixtures of ferric chloride and calcium sulfate when heated failed to consume any ferric chloride. Search for the temperature at which an equilibrium might be met was made over a small range. Two reactions were carried out at 250° for five minutes. One of these was analyzed and found to be 88% complete. The other sample was then placed in a bath at 118° for one hour. An analysis of this second reaction showed that the amount of ferric chloride was not decreased by heating at a lower temperature. The same procedure was carried out with a reaction mixture which had been heated 40 minutes at 156° and three hours at 118°; again, no decrease in the amount of ferric chloride was found.

The decrease in the reaction rate between solids to zero before completion has been explained as being due to the building up of a barrier of reaction products.[14]

Discussion

The mechanism of the reaction is uncertain particularly at temperatures below 300°. It is significant that a small percentage of water (or ferric chloride) had to be present in order to make the reaction possible at the lower temperatures. Although no liquid phases were noted under any conditions, liquid films may have been present on the solid surfaces. The films could have served as a vehicle for the reaction. Above 300° the presence of liquid films was less probable.

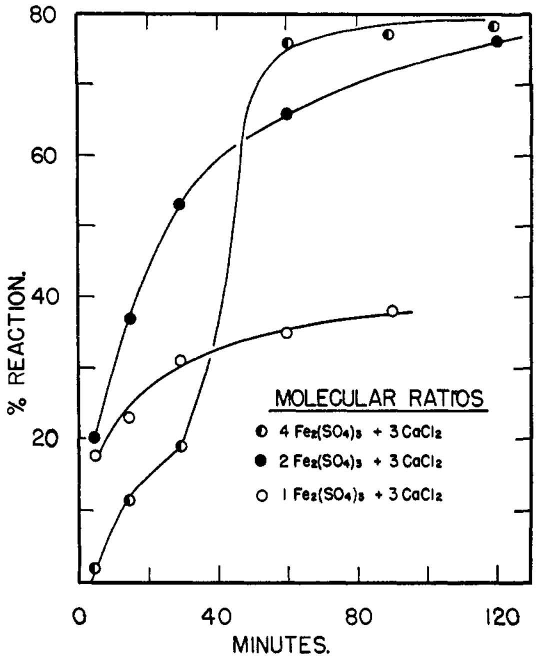

Fig. 5.—Effect of excess ferric sulfate on the reaction.

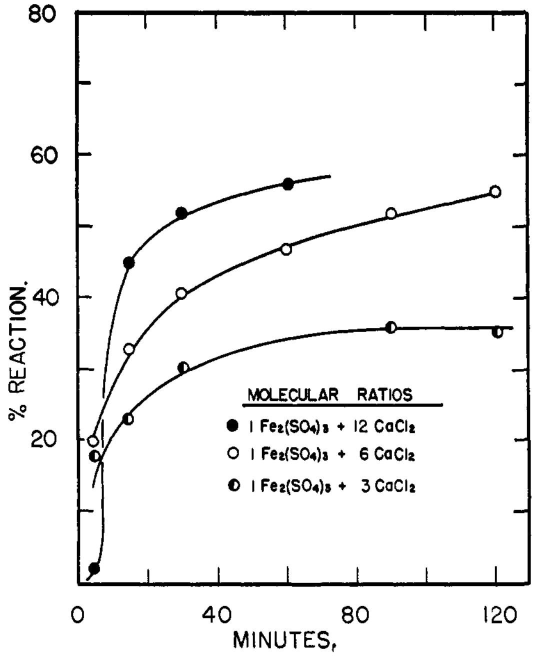

Fig. 6.—Effect of excess calcium chloride on the reaction.

The physical properties of the substances in the reaction are given in Table IV. In chemical interaction between solids, one of the reactants must be able to diffuse to the interface through one of the phases present. The high melting points of the reactants indicate that they do not form liquid phases through which diffusion could easily occur. Concerning the products of the reaction, calcium sulfate has a high melting point, while ferric chloride begins to sublime below 100°.[15] The phase diagram of ferric chloride[10] shows that it can exist as a liquid at low temperatures only under high pressure. For example, at 290°, or 16° below the melting point, a pressure of about 20 atmospheres is necessary to liquefy the solid material. The

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[12] G. Tammann, *Z. anorg. Chem.*, **149**, 21 (1925).

[13] C. H. Desch, "Chemistry of Solids," Cornell University Press, Ithaca, N. Y., 1934, p. 169.

[14] G. Cohn, *Chem. Revs.*, **42**, 528 (1948).

[15] T. Carnelley and W. C. Williams, *J. Chem. Soc.*, **37**, 125 (1880).

TABLE IV

PHYSICAL PROPERTIES OF SUBSTANCES IN THE REACTION

	M.p., °C.	Calcd. temp. of self-diffusion,[20] °C.	Ionic size, Å.[18] Cation	Ionic size, Å.[18] Anion	Crystal form
Ferric sulfate	Dec.[4]	At least 225	0.67	*ca.* 2.23	Rhombohedral-orthorhombic[19]
Ferric chloride	306[15]	30	0.67	1.81	Hexagonal[4]
Calcium chloride	772[5]	250	1.0	1.81	Cubic[4]
Calcium sulfate	1450[5]	590	1.0	*ca.* 2.23	Rhombic-monoclinic[4]

formation of a eutectic mixture involving ferric chloride could possibly give rise to a liquid phase.

Many reactions between solids proceed with high velocity because the crystals have a certain amount of disorder.[14] Diffusion of disordered ions is an exchange reaction which is capable of a transfer of ions over distances which are much greater than the mean free path. No data are available on the extent of crystalline defects in either ferric sulfate or calcium chloride but there is some evidence that ferric sulfate is the active constituent of the reaction mixture. Ferric sulfate will also react with sodium chloride,[16] a substance which has been prepared with almost a perfectly ordered lattice.[17]

A solid phase reaction can proceed at the temperature of self-diffusion of one of the reactants, or at a crystallographic transition point.[21] Self-diffusion is not appreciable in calcium chloride under 250° (Table IV), and the crystal has only one modification. Hence, diffusion in this substance cannot proceed below 250°. Diffusion would appear to be more probable in the ferric sulfate crystals which do exhibit two rather indefinite modifications.

Crystals of ferric sulfate exhibit an ideal situation for a high degree of Frenkel disorder.[14,22] The small size of the ferric ion and the large ionic radius of the sulfate ion (Table IV) are favorable for the removal of the cation to an interstitial position. It is suggested that the sulfate ion in ferric sulfate is tightly held in its lattice position while the ferric ion is free to migrate. Neither calcium ion nor chloride ion in calcium chloride has a high rate of diffusion since the temperature is well below the temperature of self-diffusion.

The supposition of rigidity of the sulfate lattice is strengthened by the fact that the particle size of the calcium sulfate formed in the reaction is approximately the same as the ferric sulfate involved. If large particles of ferric sulfate react, the calcium sulfate crystals are large, and if fine powders are used the product is finely divided. Ferric sulfate and calcium sulfate have been reported to exist in the form of rhombic crystals. Therefore, it is possible that the sulfate lattice is undisturbed and the ferric and calcium ions are exchanged.

(16) K. H. Oenicke, *Chem. Centr.*, [1] **11**, 447 (1840).

(17) R. M. Barrer, "Diffusion in and Through Solids," Cambridge University Press, New York, N. Y., 1941, p. 264.

(18) H. A. Lange, "Handbook of Chemistry," Handbook Publishing Company, Sandusky, Ohio, 1944.

(19) E. W. Posnjak and H. E. Merwin, THIS JOURNAL, **44**, 1965 (1922).

(20) G. Tammann and Q. A. Mansuri, *Z. anorg. Chem.*, **126**, 119 (1923).

(21) J. A. Hedvall, "Reacktionfahigkeit fester Stoffe," Barth, Leipzig, 1938, p. 128.

(22) J. Frenkel, *Z. Physik*, **35**, 652 (1926).

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WESTERN AUSTRALIA]

The Diffusion Coefficients of Calcium Chloride and Ammonium Chloride in Concentrated Aqueous Solutions at 25°

BY J. R. HALL,[1] B. F. WISHAW AND R. H. STOKES

RECEIVED AUGUST 20, 1952

A Goüy diffusiometer is described and measurements on calcium chloride and ammonium chloride solutions up to high concentrations at 25° are reported and discussed.

Introduction

The Goüy diffusiometer, as developed by Ogston and co-workers[2] and simultaneously by Kegeles, Gosting and Longsworth,[3] is probably the most accurate and convenient method for determining diffusion coefficients in solutions of moderate and high concentrations. Over its chief rival in this concentration range, the magnetically-stirred porous diaphragm cell,[4] it offers the advantages of being an absolute instead of a relative method, of somewhat greater intrinsic accuracy and of requiring shorter times for runs (though the latter advantage is somewhat offset by the time required for measuring the photographic records). In this Laboratory we have therefore transferred our program of diffusion studies in aqueous electrolytes to a Goüy instrument, and are now reserving the porous diaphragm cell for studies involving organic solvents and strongly colored solutions, for which optical methods employing a plastic diffusion cell are inapplicable.

The Goüy diffusiometer which we have built for this purpose combines some of the features of

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[1] The sections of this paper dealing with the construction of the apparatus and the measurements on calcium chloride are abstracted from a thesis presented by J. R. Hall in partial fulfillment of the requirements for the degree of Bachelor of Science with Honours in the University of Western Australia.

(2) C. A. Coulson, A. G. Ogston, *et al.*, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).

(3) G. Kegeles and L. J. Gosting, THIS JOURNAL, **69**, 2516 (1947); L. G. Longsworth, *ibid.*, **69**, 2510 (1947).

(4) R. H. Stokes, *ibid.*, **72**, 763 (1950).