

FROM THE TRANSACTIONS OF THE ELECTROCHEMICAL SOCIETY, Volume LIX,  
1931, being the Transactions of the Fifty-ninth General Meeting, at Birmingham,  
Ala., April 22, 24, 25, 1931.

541.1  
V359  
n°7

## STUDIES ON ZINC AND BARIUM FERRITES

By

JOSEPH GUILLISEN and P. J. VAN RYSSSELBERGHE

541.1  
V 359  
n°7

BRUXELLES - UNIVERSITE



## STUDIES ON ZINC AND BARIUM FERRITES.<sup>1</sup>

By JOSEPH GUILLISSEN<sup>2</sup> and PIERRE J. VAN RYSSELBERGHE.<sup>3</sup>

### ABSTRACT.

The formation of zinc ferrite by the direct addition of zinc and ferric oxides was studied at various temperatures between 580° and 660° C. During the first two or three hours of heating, the reaction obeys Tamman's logarithmic law on reactions between solid phases. An apparent equilibrium appears afterwards. At 580° C. the reaction takes place extremely slowly. It is found by thermal analysis that there is no evidence for the formation of a compound containing more zinc oxide than  $\text{ZnFe}_2\text{O}_4$ , at least not below 1,070° C. The solubility of zinc ferrite in normal and two-normal sulfuric acid is studied. A mixture of 7.5 per cent sulfur dioxide in air, passed on zinc ferrite heated at 450° C., decomposes it slowly and liberates the zinc as zinc sulfate.

The formation of barium ferrite resulting from the heating of a mixture of barium carbonate and ferric oxide was studied at 720° C. It also obeys Tamman's law. The apparent equilibrium towards which the reaction tends is destroyed when the mixture is stirred and heated again at the same temperature: the reaction goes on according to Tamman's law, the velocity of reaction being, however, considerably smaller than originally. The results are discussed and explained on the basis of diffusion.

### INTRODUCTION.

The temperatures at which various ferrites are formed by direct addition of the oxides or by reaction between ferric oxide and a carbonate have been determined by Guillissen<sup>4</sup> and by Guillissen and Richard<sup>5</sup> by means of thermal analysis: a sample of the mixture in

<sup>1</sup> Manuscript received January 2, 1931.

<sup>2</sup> Technical Director, Belgian Chemical Union, Brussels.

<sup>3</sup> Chemistry Department, Stanford University.

<sup>4</sup> Guillissen, Académie Royale de Belgique, Bull. Classe Sciences, 5 XIII, 233 (1927).

<sup>5</sup> Guillissen and Richard, *Ibid.*, 5 XIII, 238 (1927).

which a reaction is to be detected and a control sample are heated together in an electric furnace. A differential galvanometer, of the Lechatelier-Saladin type in the case of the investigations mentioned, is connected with the thermo-couples in such a way that its light spot moves in a plane whose co-ordinates are the temperature of the mixture and the difference of temperature between the mixture and the control.

As long as no reaction occurs, the light spot moves horizontally as the temperature gradually rises. When a reaction occurs the regular rise in the temperature of the mixture is interrupted and the light spot acquires, for a certain interval of temperature, a vertical co-ordinate. The

TABLE I.  
*Formation of Zinc Ferrite at 600° C.*

Time in hours	Weight of soluble Zn in 1 g. of mixture g.	Weight of Zn in Zn ferrite g.	Ratio Zn as ferrite Total Zn Per cent
0	0.2646	0.0000	0.0
1	0.1201	0.1445	54.6
2	0.0817	0.1829	69.1
3	0.0620	0.2026	76.5
4	0.0576	0.2070	78.2
5	0.0561	0.2085	78.8

break in the horizontal line indicates the temperature at which the reaction starts with an appreciable velocity.

This method does not however give the exact "starting point" of the reaction on account of the fact that the temperature is gradually increasing; a reaction could not be thus detected at a temperature at which it takes place extremely slowly. In many cases, and particularly in the formation of zinc ferrite, an exact determination of the minimum temperature at which a reaction may occur with finite velocity is of importance.

Ralston<sup>6</sup> gives for the minimum temperature of formation of zinc ferrite 730 to 750° C. Hamilton, Murray and MacIntosh<sup>7</sup> reported the minimum temperature to be 650° C. The results of Kato and Takei<sup>8</sup> show that the reaction takes place even at 600° C., 12 per cent of an equimolar mixture of zinc and ferric oxides being combined after 30 minutes and 38 per cent after 60 minutes.

<sup>6</sup> Ralston, "Electrolytic Deposition and Hydrometallurgy of Zinc," p. 25.

<sup>7</sup> Hamilton, Murray, MacIntosh: *Metall und Erz*, **15**, 1 (1918).

<sup>8</sup> Kato and Takei, *Trans. Amer. Electrochem. Soc.*, **57**, 297 (1930).



We studied the formation of zinc ferrite by following the progress of the reaction as a function of time at various constant temperatures. We found that the reaction takes place, though extremely slowly, even at 580° C. At temperatures higher than 600° C. the reaction takes place rather quickly, an apparent equilibrium being reached after a few hours. A section of this paper will be devoted to a discussion of this apparent equilibrium on the basis of the theory of diffusion. The course of the reaction below this apparent equilibrium follows Tamman's law<sup>9</sup> rather closely. Results obtained in a study of the formation of barium ferrite by the reaction  $\text{BaCO}_3 + \text{Fe}_2\text{O}_3 = \text{BaFe}_2\text{O}_4 + \text{CO}_2$  are also reported.

TABLE II.  
*Formation of Zinc Ferrite at 660° C.*

Time in hours	Weight of soluble Zn in 1 g. of mixture g.	Weight of Zn in Zn ferrite g.	Ratio Zn as ferrite Total Zn Per cent
0.00	0.2646	0.0000	0.0
0.25	0.1049	0.1597	60.3
0.50	0.0864	0.1782	67.4
0.75	0.0743	0.1903	72.0
1.00	0.0650	0.1996	75.4
2.00	0.0586	0.2060	78.0
3.00	0.0469	0.2177	82.1
4.00	0.0440	0.2196	82.9

#### THE FORMATION OF ZINC FERRITE.

*Apparatus.* The reactions were carried out in an electric oven consisting of a long quartz tube with a platinum heating coil. Its length was such that a constant temperature could be obtained on a length of about 20 cm. A mercury regulator, in series with the heating circuit, kept the temperature constant within about 10 or 20° C. at a temperature between 550° and 1,200° C. The temperatures were measured by means of a platinum-platinum rhodium couple. This couple was a part of the equipment of a differential Lechatelier-Saladin apparatus for thermal analysis.

Standardizing the couple by means of a few known melting points, we found that its accuracy was within  $\pm 10^\circ$  C. between 600° and 1,100° C. The materials to be studied were compressed in small nickel tubes or in small open porcelain containers and put in the central part of the oven which had previously been maintained at constant temperature for about half an hour.

<sup>9</sup> Tamman, *Zeit. angew. Chemie*, 39, 869 (1926).

*Chemicals.* Chemically pure, well dried ferric and zinc oxides were used. All our experiments were carried out with a mixture of constant composition, practically equimolar. One gram of the mixture contained 0.3293 g. ZnO or 0.2646 g. Zn. Both oxides were finely ground; the mixture did not leave any residue on a sieve having 60 meshes per inch (24 per cm.). The grain size was fairly uniform.

*Method of Analysis.* In order to determine the amount of ferrite formed, a sample of 1 gram was removed from the container, and shaken for half an hour in 10 cc. of an ammoniacal solution of ammonium chloride of the following composition: Concentrated  $\text{NH}_4\text{OH}$ , 500 g.;  $\text{NH}_4\text{Cl}$ , 170 g.; water, 500 g. ZnO is soluble in this solution, while zinc ferrite is not. We found that zinc oxide which has been

TABLE III.  
*Formation of Zinc Ferrite at 630° C.*

Time in hours	Weight of soluble Zn in 1 g. of mixture g.	Weight of Zn in Zn ferrite g.	Ratio Zn as ferrite Total Zn Per cent
0	0.2646	0.0000	0.0
1	0.0729	0.1917	72.5
2	0.0609	0.2037	77.0
3	0.0529	0.2117	80.0
4	0.0495	0.2151	81.3

heated for one hour at 800° C. is just as soluble as any sample of zinc oxide.

After half an hour the mixture is diluted and filtered. The zinc present in the filtrate is determined by titration. A standard solution of zinc chloride, obtained by dissolving pure zinc in hydrochloric acid, is titrated with a solution of sodium sulfide containing about 2 grams per liter, and the unknown solution is titrated at the same time. The end-points are determined by means of lead acetate paper. The amount of soluble zinc oxide present in the sample is deduced by comparison with the standard solution. This method is quick and gives satisfactory results. The amount of zinc ferrite formed corresponds to the weight of zinc oxide which has not been dissolved.

#### RESULTS.

*Formation of Zinc Ferrite at 600° C.* The variation in the percentage of zinc ferrite formed as a function of time is shown in Table I and Fig. 1, where the ratio, zinc combined as zinc ferrite : total zinc



is plotted against the time expressed in hours. The concentration becomes practically constant after 4 hours.

In Fig. 2 the ratio Zn in Zn ferrite : total Zn is plotted against the logarithm of the time. One sees that during the first three hours the variation is linear in agreement with Tamman's<sup>10</sup> law:

$$C = A \log t + B$$

in which C is the ratio Zn in Zn ferrite : total Zn, A and B are constants, and t is the time.

When the whole mixture was removed from the nickel tube after five hours of heating, reground and heated again at 600° C., the in-

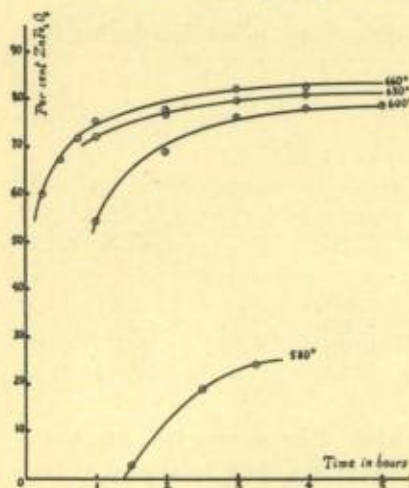


FIG. 1. Formation of Zinc Ferrite.

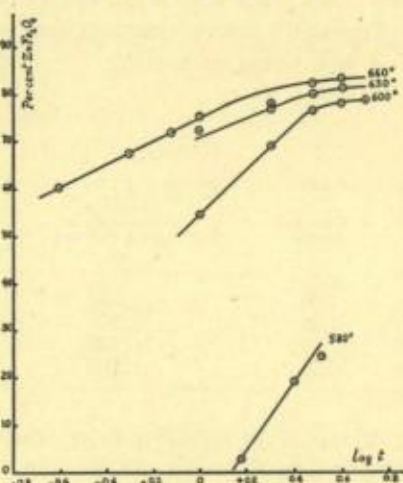


FIG. 2. Formation of Zinc Ferrite.

crease in the amount of ferrite was very slight. The mixture was then heated at 700° C. for 2.75 hours. The ratio Zn in Zn ferrite : total Zn went up to 86.4 per cent. Heating then for a few hours at 800° C. caused the ratio to become 93.3 per cent.

*Formation of Zinc Ferrite at 660° C.* The results are given in Table II and are plotted on Fig. 1 and Fig. 2. The maximum concentration of Zn ferrite is reached more rapidly than at 600° C.

*Formation of Zinc Ferrite at 630° C.* The results obtained at the intermediate temperature of 630° C. are given in Table III, and are plotted on Fig. 1 and Fig. 2. The curves are very close to those obtained at 660° C.

*Formation of Zinc Ferrite at 580° C.* We tried to detect a reaction at 580° C. As shown by the results of Table IV, and the curves of

<sup>10</sup> Tamman, *loc. cit.*

Fig. 1 and Fig. 2, the reaction becomes measurable after a little more than an hour of heating and tends towards an apparent equilibrium.

*Variation of the Maximum Concentration of Zinc Ferrite with Temperature.* Table V gives the maximum values of the ratio Zn in Zn ferrite : total Zn, at various temperatures, ranging from 600° C. to 890° C. Fig. 3 shows that this limiting ratio is a linear function of the temperature.

#### CONCLUSIONS.

Zinc ferrite begins to form by direct combination of zinc and ferric oxides at a temperature slightly below 600° C. At 630° C. the reaction takes place with a marked velocity.

Tamman's law on reactions between solid phases is verified during the first few hours of heating.

TABLE IV.  
*Formation of Zinc Ferrite at 580° C.*

Time in hours	Weight of soluble Zn in 1 g. of mixture g.	Weight of Zn in Zn ferrite g.	Ratio Zn as ferrite Total Zn Per cent
0.00	0.2646	0.0000	0.0
1.50	0.2570	0.0076	2.9
2.50	0.2140	0.0506	19.1
3.25	0.2000	0.0646	24.4

An apparent equilibrium is reached after 3 or 4 hours of reaction. By grinding the mass and heating it again at the same temperature the reaction is made to continue, but extremely slowly.

#### THE CHEMICAL PROPERTIES OF ZINC FERRITE.

##### *Non-existence of Ferrites More Basic than $\text{ZnFe}_2\text{O}_4$ .*

The existence of ferrites containing more zinc oxide than  $\text{ZnFe}_2\text{O}_4$  has been claimed.<sup>11</sup> Recent investigations by Swartz and Krauskorf<sup>12</sup> and Kato and Takei<sup>13</sup> have shown that such ferrites do not exist.

The method of thermal analysis with the Lechatelier-Saladin apparatus led us to the same conclusion. A mixture of zinc ferrite and of zinc and ferric oxides, the former oxide being in large excess, and a control sample of zinc oxide were heated together, very slowly, up to 1,070° C. The light spot moved regularly along a horizontal line and showed no evidence of reaction.

<sup>11</sup> Prost, *Métallurgie des métaux autres que le fer*, p. 44 (1926).

<sup>12</sup> Swartz and Krauskorf, *Am. Inst. Min. Met. Eng., Techn. Public. No. 40* (1928).

<sup>13</sup> Kato and Takei, *Trans. Am. Electrochem. Soc.*, **57**, 297 (1930).



*Solubility of Zinc Ferrite in N and 2 N H<sub>2</sub>SO<sub>4</sub>.*

The acid solutions used in the leaching of the products coming from the roasting furnaces contain from 40 to 100 g. of sulfuric acid, and are produced in the electrolysis of slightly acid solutions of zinc sulfate. Several samples of 0.5 or 1 g. of mixtures of zinc and ferric oxides and of zinc ferrite obtained in the course of the investigations reported in the preceding section were digested for a number of hours in 25 cc. of N or 2 N H<sub>2</sub>SO<sub>4</sub>, some with constant shaking, some with occasional shaking, and some without any stirring.

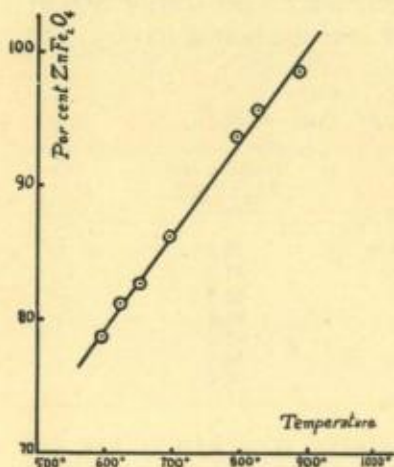


FIG. 3. Maximum Concentration of Zinc Ferrite.

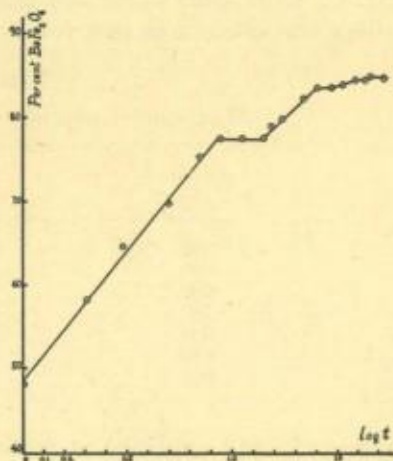


FIG. 4. Formation of Barium Ferrite at 720° C.

The dissolving process is in all cases extremely slow. The amount of zinc ferrite dissolved was deduced from analysis of the original mixture and of the residue after dissolution by the acid. The method of analysis was that described in the above section.

The *conclusions* are:

The dissolution is extremely slow.

The higher the temperature at which the ferrite has been formed, the slower the dissolution.

The solubility in 2 N H<sub>2</sub>SO<sub>4</sub> is about twice that in N H<sub>2</sub>SO<sub>4</sub>. After shaking for 1 hour a sample of 0.5 g. containing 96 per cent of zinc ferrite formed at 830° C. (the excess being zinc oxide and ferric oxide) in 25 cc. of N H<sub>2</sub>SO<sub>4</sub>, only 0.5 per cent of the ferrite was dissolved. When samples of the same ferrite mixture were digested with N H<sub>2</sub>SO<sub>4</sub>



and 2 N  $\text{H}_2\text{SO}_4$  for 50 hours without stirring, 6 and 12 per cent, respectively, of the ferrite was dissolved.

*Reaction Between Sulfur Dioxide and Zinc Ferrite.*

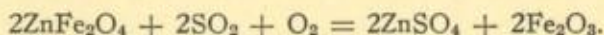
Ralston<sup>14</sup> claims that, between 400° and 500° C., a mixture of  $\text{SO}_2$  and air in concentrations such as those of the gases resulting from the roasting of zinc ores, decomposes zinc ferrite.

A mixture of zinc ferrite and of zinc and ferric oxides, obtained by heating at 660° C. an equimolar mixture of the oxides (per cent of  $\text{ZnO}$  combined as ferrite: 82.9) was heated in an electric oven to 450° C. A mixture of air and  $\text{SO}_2$  containing 7.5 per cent of  $\text{SO}_2$  by volume was allowed to pass for an hour over the heated ferrite. The

TABLE V.  
*Maximum Concentrations of Zinc Ferrite.*

Temperature ° C.	Maximum ratio Zn as ferrite Total Zn
600	78.8
630	81.3
660	82.9
700	86.4
800	93.9
830	95.9
890	98.8

amount of  $\text{ZnO}$  combined as ferrite decreased from 82.9 to 72.8 per cent. The  $\text{ZnO}$  was converted to zinc sulfate, probably according to the reaction:



This result confirms Ralston's statement, but shows that the reaction is too slow to be used with success in practice. More promising methods of getting rid of the zinc ferrite have been developed by Swartz and Krauskorf<sup>15</sup> and by Tainton.<sup>16</sup>

THE FORMATION OF BARIUM FERRITE.

Barium ferrite is formed by the reaction



The reaction was studied at an average temperature of 720° C. The experimental device was the same as that used in the study of the formation of zinc ferrite.

<sup>14</sup> Ralston, "Electrolytic Deposition and Hydrometallurgy of Zinc," p. 72.

<sup>15</sup> Swartz and Krauskorf, *loc. cit.*

<sup>16</sup> Tainton, *Trans. Am. Inst. Min. Met. Eng.*, 70, 486 (1924).

Chemically pure and well dried  $\text{BaCO}_3$  and  $\text{Fe}_2\text{O}_3$  were very finely ground and mixed. The equimolar mixture passed entirely through a sieve having 90 meshes per inch (36 per cm.). Thermal analysis with the Lechatelier-Saladin differential galvanometer indicated a reaction starting with an appreciable velocity between  $775^\circ$  and  $800^\circ$  C. The actual starting point of the reaction is certainly below this temperature.

TABLE VI.

*Formation of Barium Ferrite from  $\text{BaCO}_3$  and  $\text{Fe}_2\text{O}_3$  at  $720^\circ$  C.*

Time in hours	Loss of weight	Barium carbonate converted to ferrite Per cent
1	0.2106	48.29
2	0.2540	58.24
3	0.2815	64.55
5	0.3038	69.65
7	0.3277	75.13
9	0.3370	77.27
11	0.3370	77.27
13	0.3370	77.27
Stirred		
15	0.3436	78.79
17	0.3476	79.69
21	0.3578	82.06
25	0.3635	83.33
29	0.3635	83.33
Stirred		
33	0.3657	83.75
38	0.3674	84.26
42	0.3674	84.26
Stirred		
44.25	0.3691	84.61
52	0.3691	84.61

The course of the reaction was studied in detail at a temperature between  $715^\circ$  and  $725^\circ$  C. for a total time of 52 hours. After 13, 29, and 42 hours the mass was stirred, in order to renew the surfaces of contact between the grains. The results are given in Table VI and are plotted on Fig. 4. The amount of ferrite formed is deduced from the loss of weight of the mass, due to the evolution of  $\text{CO}_2$ . The original weight of the sample was 3.5426 g. The loss of weight corresponding to a complete transformation into ferrite would be 0.4361 g.<sup>17</sup>

One sees from Fig. 4 that Tamman's law is verified for each interval of time between two consecutive stirrings; the slope of the straight line is different for each interval.

<sup>17</sup> These results have already been published by one of us (J. G.) in a short monograph: Réactions Chimiques entre Phases Solides, Revue Universelle des Mines, 7 XVII, 253 (1928).



After 52 hours the mass was stirred again and ground more finely so as to pass entirely through a sieve with 150 mesh per inch or 60 per cm. The mass was then heated for 15 more hours at an average temperature of 720° C. A maximum percentage of 89.32 was reached after 8 hours.

#### DISCUSSION.

Spring and Roberts-Austen in their classical experiments have shown that Fick's law on diffusion applies to solids, and that diffusion is able to bring about chemical reaction.

Thanks to the methods of thermal analysis developed by Hedvall<sup>18</sup> and Tamman<sup>19</sup> reactions between solid phases have been studied in some detail. The temperatures at which reactions begin have been determined in many cases and the detailed study of a few typical reactions led Tamman to establish his logarithmic law. This law can logically be deduced by supposing that reaction results from the diffusion of the molecules of the two constituents into one another. On theoretical grounds it can be deduced as follows: The velocity of diffusion from a unit surface to a parallel unit surface at distance  $dl$  is given by Fick's law.

$$\frac{dx}{dt} = D \frac{dC}{dl} \quad (1)$$

in which  $dx$  is the amount of substance diffused,  $dC/dl$  is the concentration gradient and  $D$  the coefficient of diffusion.

If we suppose that  $dC/dl$  is inversely proportional to the time we obtain from (1):

$$\frac{dx}{dt} = \frac{b}{t} \quad (2)$$

in which  $b$  is a constant proportional to the coefficient of diffusion  $D$ ,  $dx$  is proportional to the amount of substance reacting, in our case proportional to the concentration of ferrite. Equation (2) is then the differential form of Tamman's law.

Integration of (2) gives:  $C = A \log t + B$ , in which  $A$  and  $B$  are constants. If diffusion is the main cause of chemical reaction between solid phases, the velocity of reaction will be larger the smaller the grains, since diffusion is then more rapid on account of the larger surface of the grains. Tamman showed this to be the case in his experiments on the formation of copper and lead tungstates and of cal-

<sup>18</sup> Hedvall, *Z. anorgan. Chem.*, 96, 64 (1916).

<sup>19</sup> Tamman, *loc. cit.*

cium molybdate. Our results for the formation of barium ferrite show that a reduction in the size of the grains permits the reaction to continue.

In many cases apparent equilibria have been noticed in reactions between solids. A real chemical equilibrium in such systems is thermodynamically impossible. An apparent equilibrium is due to the rate of diffusion of the original constituents into one another becoming extremely slow.

Our results in Table VI show that Tamman's law applies separately to intervals of time each of which corresponds to a different average composition and hence to a different coefficient of diffusion. It is evident that the proportions of original and resulting constituents directly influence the coefficient of diffusion.

Our results in Table V, which show that the limiting concentrations of zinc ferrite obtained at various temperatures with mixtures consisting of grains of constant size form a linear function of temperature, merely demonstrate that the coefficient of diffusion is itself a linear function of the temperature, a fact which it is logical to expect.

In Tamman's law, equation (3),  $A$  is proportional to the coefficient of diffusion, as shown by the derivation of that equation. Comparing the concentrations  $C$  obtained at various temperatures after constant times of heating we see that they are equal to a constant plus a term proportional to the coefficient of diffusion. Since, at least in the case of zinc ferrite, the limiting concentration is reached in approximately the same length of time at all temperatures, our deduction that the coefficient of diffusion of these mixtures is a linear function of the temperature is justified.

As a whole, our results lead to the general conclusion that diffusion is the main factor influencing chemical reactions between solid phases.

The importance of a clear understanding of the mechanism of reactions between solids cannot be sufficiently stressed. It is not the purpose of this paper to dwell on this subject. We will simply recall the importance of the problem of the formation of zinc ferrite in the hydro- and electrometallurgy of zinc. We hope that the preceding results and theoretical considerations will prove of some value in the practical handling of this problem.

*Department of Chemistry,  
Stanford Univ., Calif., December, 1930.*



## DISCUSSION.

LOUIS KAHLENBERG<sup>20</sup>: The composition of these ferrites is represented here as  $\text{ZnFe}_2\text{O}_4$ , magnetite with one atom of ferrous iron replaced by zinc (or barium). Are these compounds definitely established? What is the change in the magnetic properties by replacing a ferrous iron with zinc, on the one hand, and with barium, on the other hand, in case it is the magnetite formula to begin with?

P. J. VAN RYSELBERGHE: The answer to this question will be found in the paper by Kato and Takei<sup>21</sup>, which was presented to the Society last year, in which magnetic measurements are recorded.

E. M. BAKER<sup>22</sup>: On page 98 you state that all of the particles of zinc oxide and iron oxide would pass through a 60-mesh sieve. Were the particles closely sized or was there a possibility of fine material being present, so that the rapid rate of reaction in the early stages might possibly be attributed to fine particles reacting, first? The slower rate of reaction might then be due to the larger particles.

P. J. VAN RYSELBERGHE: As I remember, the particles were sized between two sieves. But they certainly were not absolutely uniform in size. There was a slight variation. However, the mixture was the same for all of the investigations.

E. M. BAKER: You did reject material which went through a somewhat finer sieve, so that the particles were all of the same order of magnitude?

P. J. VAN RYSELBERGHE: The same order of magnitude, yes. Referring to Table V and the linear relation between temperature and coefficient of diffusion, the behavior is analogous to that of the coefficient of diffusion of liquids (Ohlm's law). Thus our investigations have led to the detection of a new link between the properties of liquids and those of solids.

<sup>20</sup> Prof. of Chemistry, Univ. of Wisconsin, Madison, Wis.

<sup>21</sup> Trans. Am. Electrochem. Soc., 57, 297 (1930).

<sup>22</sup> Asst. Prof. of Chem. Engineering, Univ. of Michigan, Ann Arbor, Mich.