constants. For example, the difference between the two k's ranges from 2 to 19% as the fraction absorbed is changed from 0.81 to 0.99. Neither equation will hold over large variations in light intensity since the rate (Fig. 4) increases somewhat more rapidly than $I_{\text{abs.}}^{1/2}$. Plotting log k against $1/T$ (at $T = 450$°K. and greater) gives a straight line with a slope corresponding to an apparent activation energy of 5600 cal.

The behavior of isobutyraldehyde is definitely more complicated (Figs. 5 and 6) and no correlation of the experimental data with a rate equation has been made. It may be said, however, that the close proportionality between rate and light intensity indicates removal of chain carriers by some other process than recombination of radicals. Under comparable conditions the chain lengths of decomposition for both butyraldehydes lie between those reported by Leermakers[18] for acetaldehyde ($\Phi_d = 10$ to 20 at 180°) and valeraldehyde ($\Phi_d < 1$ at 180°).

It appears unwise, without more detailed knowledge of the intermediates involved, to attempt construction of any mechanism for the high temperature reactions. That this mechanism is far from simple is indicated not only by the behavior of isobutyraldehyde, but also by the fact that for *n*-butyraldehyde the high temperature quantum yield is definitely lower at λ 2654 than at λ 3130 (Table III), whereas if the process consisted simply of chains initiated by a dissociation of type B, the increase in importance of this dissociation at shorter wave lengths, as indicated by the low temperature experiments, would require a higher yield.

Summary

The photochemical behavior of *n*- and isobutyraldehydes in the vapor phase, both at ordinary and at elevated temperatures, has been investigated. The room temperature reactions are analogous to those of the lighter aldehydes, consisting of both polymerization and decomposition, the variations of which with wave length and pressure have been studied. Analyses of the reaction products at different wave lengths are used as a basis for assigning relative importance to different dissociation possibilities.

Chain photolyses are found for both aldehydes at elevated temperatures. That for *n*-butyraldehyde resembles the chain photolysis of acetaldehyde, while that for isobutyraldehyde differs sharply from acetaldehyde in kinetic character.

LOS ANGELES, CALIF. RECEIVED JULY 6, 1937

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[18] Leermakers, *Cold Spring Harbor Symposia on Quantitative Biology*, **3**, 49 (1936).

[CONTRIBUTION NO. 37 FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Reactions in the Solid State. I. The Reactions between Barium Carbonate and Ferric Oxide in the Presence of Oxygen[1]

BY ROLAND WARD AND JAMES D. STRUTHERS[2]

A number of reactions of commercial importance depend upon absorption of oxygen from the air by solid compounds or by the products of solid phase reactions. The preparation of peroxides of the alkali and alkaline earth elements, the reactions of the oxides of the transition elements with alkali and alkaline earth oxides, and the preparation of several contact catalysts are reactions of this type. These reactions have not been subject to thorough quantitative investigation. This paper records an attempt to determine the mechanism of the reaction between barium carbonate and ferric oxide in an atmosphere of oxygen at atmospheric pressure.

Historical.—The reaction between barium carbonate and ferric oxide has been studied by J. Guillissen,[3] who prepared barium ferrite by heating the reactants in air at 830°. In a later paper, J. Guillissen and P. J. van Rysselberghe[4] showed that an appreciable yield of barium ferrite was obtained by heating an equimolecular mixture of barium carbonate and ferric oxide at 720°. They do not state that the reaction was carried out in the presence of oxygen. L. Moser and H. Brock[5] report obtaining barium perferrite

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[1] Abstracted from a thesis submitted in partial fulfilment of the degree of Bachelor of Science at the Polytechnic Institute of Brooklyn.

[2] Recipient of Sigma Xi "Certificate in Commendation of Research," 1936.

[3] J. Guillissen, *Acad. roy. Belg., Classe sci.*, **5**, XIII, 233 (1927).

[4] J. Guillissen and P. J. van Rysselberghe, *Trans. Am. Electrochem. Soc.*, **59**, 95 (1931).

[5] L. Moser and H. Brock, *Ber.*, **42**, 4279 (1909).

by interaction of solids. They prepared the compound by heating a mixture of barium and iron hydroxides at 400° in a current of oxygen.

According to G. F. Hüttig, J. Funke and H. Kittel[6] an "active intermediate" compound is produced when calcium carbonate or calcium oxide is heated with ferric oxide. This compound is much more active catalytically than the crystalline calcium ferrite. The most active samples contain up to 80% of this intermediate. This so-called intermediate is possibly a perferrite.

We decided to study the reaction rates of barium carbonate with ferric oxide at various temperatures and to investigate the nature of the product obtained at each temperature.

Experimental

Preparation of the Reaction Mixture.—Barium carbonate (Merck reagent grade) which was found to be free from hydroxide[7] and ferric oxide (Baker Analyzed c. p. grade) were ground separately to fineness of 80–100 mesh, heated to 400° to remove adsorbed moisture and mixed in the stoichiometric proportion $BaCO_3$-Fe_2O_3 by quartering and grinding in a mortar until no white particles of the carbonate could be observed. The mixture was kept over phosphorus pentoxide for several days before use.

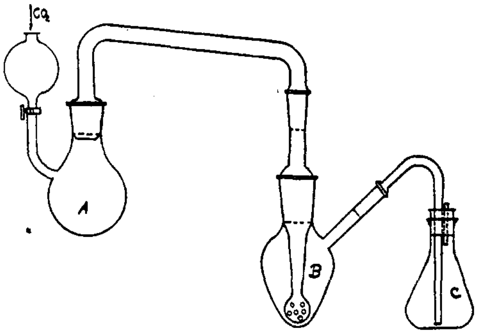

Fig. 1.—Chlorine evolution apparatus.

Procedure.—Four grams of the mixture was weighed into each of the combustion boats, preheated for thirty minutes in a tube furnace at 270°, at which temperature no reaction occurs. They were then introduced directly into a tube furnace maintained at constant temperature throughout each run. A steady stream of dry oxygen passed over the heated mixture served to oxidize the sample and also to sweep the carbon dioxide liberated in the reaction into absorption tubes containing "ascarite." The course of the reaction between the ferric oxide and the barium carbonate was followed by weighing the absorbed carbon dioxide at definite intervals of time. When the rate of evolution of carbon dioxide became negligibly small, the sample was removed from the furnace and analyzed. In these runs only the final amount of oxidation was determined. In one experiment three boats, each containing 4 g. of the mixture, were placed in the furnace, one of the boats being withdrawn after thirty minutes, another after sixty minutes, and the last one after three hundred and thirty minutes. In this case only was the rate of oxidation followed during the course of the reaction.

Analytical Methods. (a) Determination of the Amount of Ferric Oxide which Had Taken Part in the Reaction.—Ferric oxide which has been ignited is only slightly soluble in boiling 0.1 *N* hydrochloric acid, whereas the ferrites or perferrites produced in the reaction are completely dissolved. Hence, by determining the amount of soluble iron in a sample of the heated mixture, the extent to which the reaction had proceeded could be ascertained.

One-tenth gram of the reaction product was boiled for fifteen minutes with 100 ml. of 0.1 *N* hydrochloric acid. The precipitate was separated by filtration, washed with hot water, and the filtrate cooled. Sufficient hydrochloric acid was added to the filtrate to make the solution approximately 1 *N*, and the iron was reduced to the ferrous state by passing the solution through the silver reducer.[8] The ferrous iron was then titrated with 0.05 *M* ceric sulfate solution using ortho-ferrous phenanthroline as indicator.

(b) Estimation of the Amount of Oxidation.—Advantage was taken of the fact that the oxidized compounds formed in these reactions readily react with hydrochloric acid liberating chlorine. Figure 1 shows the apparatus used to determine the amount of chlorine liberated. The solid sample was placed in flask (A). Hydrochloric acid was introduced through the separatory funnel, and the chlorine liberated was swept into the receiving flask (B) containing a solution of potassium iodide acidified with hydrochloric acid. A second absorption flask (C) containing a similar solution received any chlorine which had not been absorbed in (B). The receiving flasks were cooled by immersion in an ice-bath. The iodine liberated in flasks (B) and (C) was titrated with 0.05 *N* sodium thiosulfate. It was found that the absorption in flask (B) was in all cases complete.

The amount of barium carbonate entering into the reaction could be determined readily from the carbon dioxide absorbed in the "ascarite" tubes. The dissociation of barium carbonate at the temperatures used in these experiments is negligible, and thus it is assumed that the evolved carbon dioxide gives a true measure of the reaction rate. In every case the final product was tested for the presence of barium peroxide. This compound was not produced in any of the reactions.

The analytical procedure described in (b) does not give any indication as to the composition of the oxidized product. It merely indicates the amount of oxidation which occurs during the reaction. It is impossible to say whether the valence number of iron in the oxidized product is IV or V.

Discussion of Results

A. The Nature of the Reaction Product.

—In measurement of the reaction rates it has been assumed tacitly that the rate of evolution of the carbon dioxide gives the rate at which the barium carbonate reacts with the ferric oxide. The fact

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[6] G. F. Hüttig, J. Funke and H. Kittel, This Journal, **57**, 2470 (1935).

[7] A. C. S. Committee on Analyt. Reagents, *Ind. Eng. Chem.*, **19**, 645 (1927).

[8] Bell Telephone Labs., Inc., Tentative Analytical Procedure No. 200264.

that no peroxide was detectable in any of the products lends some support to this assumption. It has also been assumed that the amount of iron rendered soluble in dilute hydrochloric acid gives the amount of ferric oxide which has reacted with the barium carbonate. It is nevertheless possible that dispersion of some of the ferric oxide in the reaction product may occur and that the ferric oxide in this form is soluble in the dilute acid. The mole ratios of iron to barium shown in Table I are calculated from the total carbon dioxide evolution and from the soluble iron. With the exception of the runs at 754° the ratios are reasonably consistent. The ratios show a slight decrease with rise in temperature. It is probable that, at the highest temperature, some independent decomposition of the barium carbonate occurs.

TABLE I

Temp., °C.	CO_2 evolved, g.	Oxygen combined, g.	Soluble Fe, g.	Mole ratio Fe/Ba
610	0.0278	None	0.0450	1.28
754	.2042	....	.3700	1.43
775	.2587	0.0331	.4080	1.25
808	.2849	.0373	.4320	1.18
835	.3741	.0554	.4510	1.20
880	.4169	.0557	.5060	1.21
970	.4735	.0118	.5500	0.92

If we assume that all of the ferric oxide rendered soluble enters into chemical combination the reaction may be represented by the equations

$$BaCO_3 + Fe_2O_3 \longrightarrow Ba(FeO_2)_2 + CO_2 \quad (1)$$

$$2BaCO_3 + Fe_2O_3 \longrightarrow Ba_2Fe_2O_5 + 2CO_2 \quad (2)$$

The decrease in the ratio may mean that at the higher temperatures equation (2) represents the reaction while at the lower temperatures reactions (1) and (2) proceed simultaneously.

Solid solution of the ferric oxide in the reaction product would lead to high values for the iron to barium ratio. In this case equation (2) may represent the reaction for all temperatures, the variation in ratio being accounted for by a change in the solid solution concentration. It is to be observed that there is no abrupt change in these ratios with change of temperature.

More recent experiments with barium carbonate and nickel oxide have shown that the rate at which the nickel becomes soluble is considerably greater than the rate of evolution of carbon dioxide, which in this case follows an entirely different mechanism.

The rate of oxidation was investigated in only one experiment with the ferric oxide–barium carbonate mixture. The results, shown in Table II, indicate that this reaction occurs subsequent to the formation of the ferrite. Further experiments with ferric oxide–barium hydroxide mixture have substantiated this. The variation in the oxidation with change in temperature is shown in Table I and presented graphically in Fig. 2. A maximum yield of the oxidized product is obtained between 835 and 880°. This temperature is considerably above that at which barium perferrite is reputed to decompose. Further experiments are in progress to determine the mechanism of the oxidation and the nature of the oxidized product. Since the oxidation process is a secondary one, and since the Fe/Ba ratio shows no abrupt change, it is probable that the reaction rate data can be used to gain some insight into the mechanism of the formation of barium ferrite. The initial chemical reaction between solid particles, usually too rapid for precise measurement, must occur at the contact points. This results in the formation of a layer of reaction product. Further reaction is only possible if one or both of the reactants diffuse through the film of reaction product. The rate-determining process in the reaction which results from diffusion may be either the rate of diffusion

TABLE II

$BaCO_3$–Fe_2O_3 MIXTURE, TEMPERATURE 728°

Time of heating, min.	CO_2 evolved, %	Perferrite in product, %
30	26.50	0.24
60	33.45	.98
330	48.20	6.78

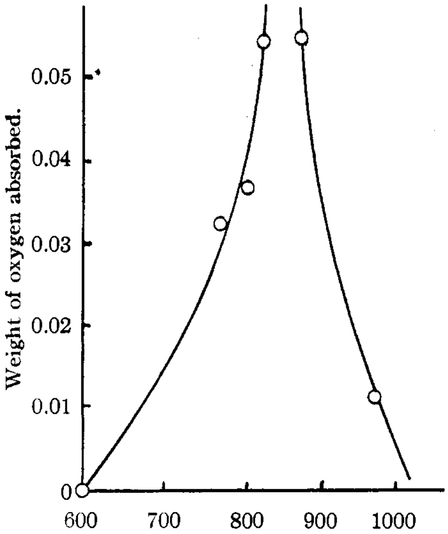

Fig. 2.

or the rate of activation of the reactants. Increase in temperature results in the acceleration of both processes but the acceleration in the diffusion process is slight compared with that of the chemical activation. In each case, however, the acceleration is fairly uniform provided there is no crystallographic transformation of either reactant. Considerable increase in reaction velocity is always observed at the temperature at which a physical transformation occurs in one of the reactants.[9] The theoretical treatment of diffusion-controlled reactions between solids has been developed by W. Jander and his co-workers.[10] The equation for the diffusion-controlled reaction is

$$Kt = \left\{1 - \sqrt[3]{\frac{100 - x}{100}}\right\}^2$$

where t is time, x is percentage reaction and K is a constant. The relation between the velocity of reaction and the temperature is expressed by the equation

$$K = Ce^{q/RT}$$

where T is the absolute temperature, R is the gas constant in calories, C is a constant from the physical state of the material and other undertermined factors, and q is the heat of activation for the process of diffusion.

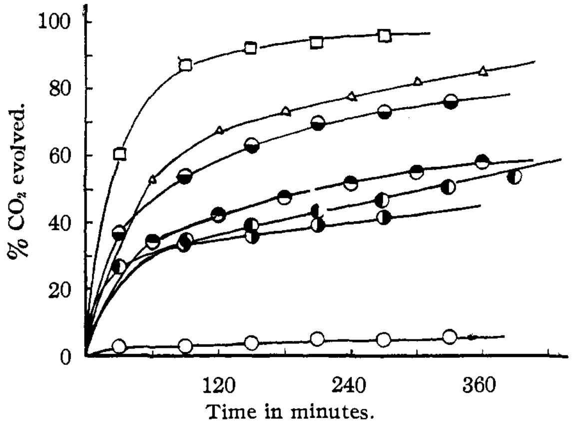

Fig. 3.—Percentage reaction *vs.* time for $BaCO_3$–Fe_2O_3 mixture. Temperatures: ○ 610°, ◑ 754°, ◐ 775°, ◓ 808°, ⊖ 835°, △ 880°, □ 970°.

Table III gives the data obtained for the $BaCO_3$–Fe_2O_3 system at temperatures ranging from 610 to 970°. The percentage reaction is assumed to be the same as the percentage of carbon dioxide evolved given in column 3, and the first figure in this column for each temperature shows the extent of the rapid initial reaction. The extent of the diffusion reaction is given by the difference between the initial and final reading in column 3 for any one temperature. The reaction at 610° is shown to be too limited for theoretical interpretation. In the other cases the diffusion reaction comprises from 15 to 40% of the reaction. Figure 3 summarizes these results. In Figs. 4 and 5 the plot of $\left\{1 - \sqrt[3]{\frac{100 - x}{100}}\right\}^2$ against t is shown, and the values of K, deduced from the slope of these curves, are given in Table III, column 5. Figure 6 gives the plot of log K against $1/T$. The break in this curve occurs in the neighborhood of the transition temperature of barium carbonate, while the two separate portions of the curve apparently are straight lines. From the slopes of these curves the values for q are 25,000 cal. below the transition point and 19,000 cal. above the transition point.

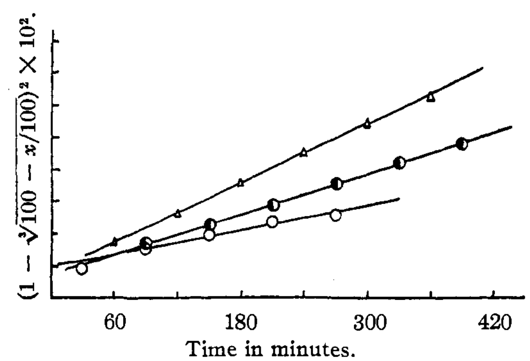

Fig. 4.—$(1 - \sqrt[3]{100 - x/100})^2$: $BaCO_3$–Fe_2O_3. Temperatures: ○ 754°, ◐ 775°, △ 808°.

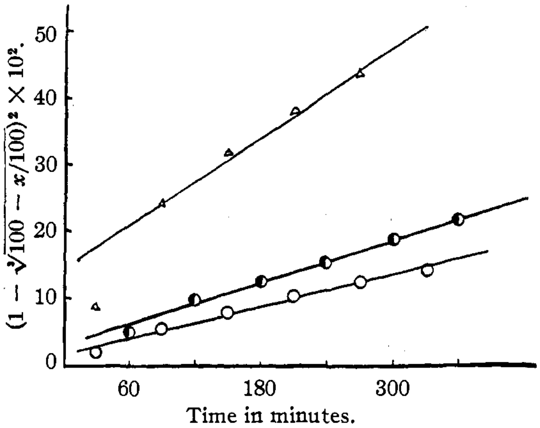

Fig. 5.—$(1 - \sqrt[3]{100 - x/100})^2$: $BaCO_3$–Fe_2O_3.

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(9) J. Arvid Hedvall, *Chem. Rev.*, **15**, 139 (1934).

(10) W. Jander, *Z. anorg. Chem.*, **163**, 1 (1927); **166**, 31 (1927); **168**, 113 (1928); **174**, 11 (1928); W. Jander and W. Stamm, **190**, 65, 397 (1930); **191**, 171 (1930). A more recent review is given by Jander in *Z. angew. Chem.*, **49**, 875 (1936).

TABLE III

$BaCO_3$–Fe_2O_3 MIXTURE AT VARIOUS TEMPERATURES

Temp., °C.	Time of heating, min. (t)	CO_2 evolved, %	$\left\{1-\sqrt[3]{\frac{100-x}{100}}\right\}^2 \times 10^{-2}$	$K \times 10^{-2}$
610	30	2.07		
	90	3.07		
	150	4.03		
	210	4.71		
	270	5.24		
	330	5.65		
754	30	25.77	0.894	0.245
	90	33.15	1.579	
	150	36.80	2.011	
	210	39.92	2.440	
	270	41.50	2.679	
775	30	26.58	0.96	0.318
	90	34.22	1.70	
	150	39.00	2.31	
	210	42.95	2.92	
	270	46.90	3.61	
	330	50.15	4.29	
	390	52.60	4.85	
808	60	34.55	1.74	0.469
	120	41.19	2.63	
	180	47.02	3.64	
	240	51.50	4.59	
	300	54.95	5.46	
	360	57.86	6.27	
835	30	37.15	2.06	1.162
	90	54.94	5.44	
	150	63.35	8.09	
	210	69.00	10.45	
	270	73.02	12.52	
	330	76.02	14.34	
880	60	52.7	4.88	1.502
	120	67.0	9.55	
	180	73.4	12.74	
	240	77.9	15.64	
	300	81.7	18.69	
	360	84.7	21.65	
970	30	65.50	8.92	3.335
	90	87.88	24.65	
	150	91.98	32.38	
	210	94.30	37.89	
	270	96.20	44.14	

While it is realized that the numerical values obtained from these plots are quite approximate, the authors believe that the following conclusions may be drawn. (1) The reaction subsequent to the first rapid reaction is controlled by diffusion of one of the reactants through the reaction product. (2) The energy of activation for this diffusion is greater below the transition point of barium carbonate. (3) The difference in energy of activation is directly connected with the heat of transition of the barium carbonate. With more precise measurements it may be possible to determine heats of transition by this method.

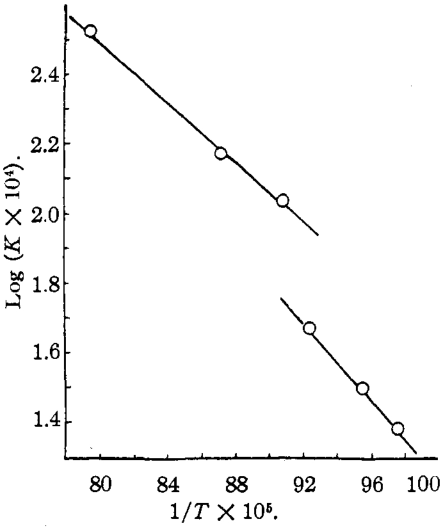

Fig. 6.—Log K *vs.* $1/T$: $BaCO_3$–Fe_2O_3.

Since crystallographic changes play such an important role in solid phase reactions it would be of interest to determine the mechanism by which the reaction is accelerated. The mechanism of crystallographic change has been investigated by Hume, Colvin, Topley and others.[11] From their experiments it was found that the process involves two steps: first the development of nuclei, and, second, the propagation of the interface through the crystal. The rate of propagation of the interface is constant at constant temperature. With the assumption that the particles are spherical of average radius r, and that nucleation occurs over the entire surface, the transformation may be represented by the equation

$$\alpha = (Kt)^3 - 3(Kt)^2 + 3Kt$$

where α is the fraction of substance transformed, K is a constant involving r and the rate of propagation of the interface, and t is time. It is possible that in a reaction between two solids the reaction rate may be controlled by the rate of transition of one of the reactants. In this case α would represent the fraction of the reactant undergoing transition which has taken part in the reaction.

Figure 7 gives a comparison of the reaction rate for the barium carbonate–ferric oxide mixture at temperatures above the transition point of barium carbonate with the theoretical transi-

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[11] J. Hume and J. Colvin, *Phil. Mag.*, [7] **8**, 589 (1929); Topley and Hume, *Proc. Roy. Soc.* (London), **A120**, 211 (1928).

tion curve calculated from Hume and Colvin's equation putting $K = 0.0025$. The two curves shown in Fig. 7, plotted from these data, are entirely different in type.

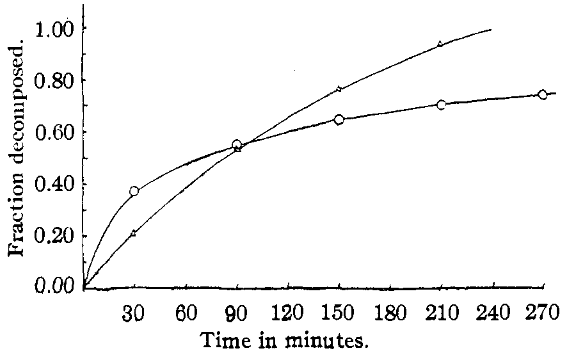

Fig. 7.—Fraction $BaCO_3$ decomposed: ○, experimental; △, theoretical ($K = 0.0025$).

Curves are shown in Fig. 8 plotted from data (Table IV) on the reaction between barium sulfate and alumina at temperatures above the transition γ alumina ⟶ corundum.[12] The theoretical curves are shown to be in fairly good agreement with the rate of reaction of the alumina. In this instance the reaction rate is controlled by the rate of transition of the alumina while with the barium carbonate–ferric oxide reaction the reaction remains under control of the diffusion process which is accelerated by the transition.

TABLE IV

Time, (t)	Fraction (α) Al_2O_3 soluble 1390°	1370°	α (calcd.) ($K = 0.0017$)	α (calcd.) ($K = 0.0013$)
60	0.190	0.358	0.290	0.216
120	.403	.524	.519	.399
180	.568	.706	.692	.551
240	.758	.829	.801	.674
420	.853	.990	.983	.907

It is suggested that the rate determining reaction is the transition rate only when the substance undergoing the transformation is not the diffusing substance.

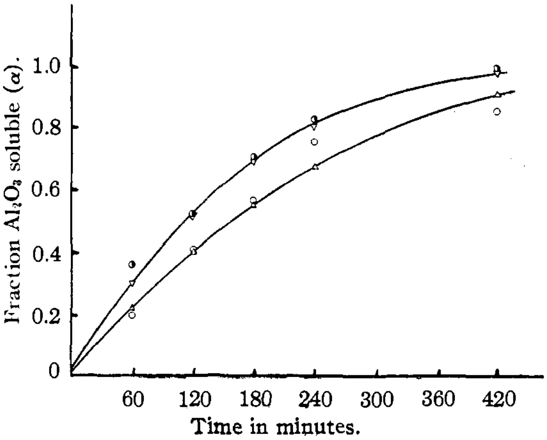

Fig. 8.—○, fraction Al_2O_3 soluble at 1390°; ◑, fraction Al_2O_3 soluble at 1370°; △, α ($K = 0.0013$); ▽, α ($K = 0.0018$).

Summary

The reaction between barium carbonate and ferric oxide in the presence of oxygen has been studied at temperatures ranging from 610 to 970°.

Reaction rates have been measured at 610, 754, 775, 808, 835, 880 and 970°. From these reaction rates the heat of activation (q) of the barium carbonate was calculated. The value for q below the transition temperature is 25,000 calories per mole and above the transition temperature is 19,000 calories per mole.

The mechanism is shown to be one of diffusion of barium carbonate through the reaction product.

A method is proposed for distinguishing between a reaction controlled by diffusion rate and one controlled by transition rate.

Oxidized compounds of iron are produced by the oxidation of the ferrites at temperatures above 700°. The most favorable temperature for their production lies between 835 and 880°. This is above the reported stability range of barium perferrite. No peroxide formation could be detected in any of the reaction products.

BROOKLYN, N. Y. RECEIVED APRIL 23, 1937

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[12] H. S. Booth and R. Ward, *J. Phys. Chem.*, **36**, 961 (1932).