[CONTRIBUTION FROM THE INSTITUTE FOR INORGANIC AND ANALYTICAL CHEMISTRY OF THE GERMAN INSTITUTE OF TECHNOLOGY]

The Changes of the Magnetic and Catalytic Properties during the Transformation of a Mixture of Calcium Oxide and Ferric Oxide into Calcium Ferrite[1]

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1. Purpose of the Investigation

If a stoichiometrical mixture of the oxides of a bivalent metal and of a trivalent metal is brought to higher temperatures, in many cases a crystalline compound will be formed according to the scheme $MeO + R_2O_3 \longrightarrow MeR_2O_4$. In several former communications it was shown[2] by us that *before* the formation of the crystallized addition compound very active intermediate substances are formed, *e. g.*, some with a very high catalytic effect, as high magnetic susceptibility and similar enhanced properties. From the magnetic, optic, x-ray spectroscopic, catalytic, and other properties, it could be concluded without doubt that these active intermediates are by no means mixtures of the starting materials ($MeO + R_2O_3$) with the crystallized end-products (MeR_2O_4) but that the reaction mixture or parts of it are present in specifically characterized compositions. In agreement with the theory of W. Jander,[3] the experimental results pointed to the conclusion that these active intermediates consist of comparatively thin films which envelop the starting material, thus leaving the kernel entirely unaffected. It was possible to obtain about 30% in the system CaO/Fe_2O_3, about 15% in the system SrO/Fe_2O_3, and about 10% in the system BaO/Fe_2O_3 of the total mixture in the form of this film. If the heating is continued further, crystals of the compound MeR_2O_4 begin to form in increasing quantities while the amount of starting material ($CaO + Fe_2O_3$) diminishes. With the onset of this crystallization, the activity of the substance decreases and the film has but little more to do with the building up of the system.

In view of the generality of this phenomenon and of the great significance of oxidic mix-catalyzers in industry, it seemed necessary to find an explanation of the nature of these carriers of the active properties and their changes with time by systematic investigations. For this purpose parts of a stoichiometrical mixture of calcium oxide (as calcium carbonate) and ferric oxide were brought to various temperatures (t_1); each substance thus prepared was tested for its magnetic properties, its catalytic effect at different temperatures (t_2) and other properties which might help to explain its nature. The results of the investigations and the conclusions reached are described in the following sections.

2. Experimental Arrangement and Nomenclature

The substances, after being prepared as described in the following section, were tested for their catalytic activity in the decomposition of nitrous oxide ($2N_2O \longrightarrow 2N_2 + O_2$) at different temperatures (t_2). Further their magnetic susceptibility, their "powder-density" (weight of 1 cc. of the finely ground powder after being shaken to a fairly compact mass), their color, and (in the experimental series II) their carbon dioxide content was determined. The catalytic activity in the formation of carbon dioxide ($2CO + O_2 \longrightarrow 2CO_2$) as well as x-ray data, which had been obtained by us in former similar experiments, were sometimes used for comparison.

The *catalytic activity* in the decomposition of nitrous oxide was measured with the same arrangement as has been described before.[4] In all the experiments mentioned here 577 cc. (c, measured at 20°) of nitrous oxide, always purified and dried in the same way, were led past the catalyzer per hour. The cross section of the catalysis tube was 1.54 sq. cm. In experiments with pure, unmixed calcium oxide, the sample weighed 0.208 g. (0.00371 mol calcium oxide) in those with pure, unmixed ferric oxide 0.59 g. (0.00371 mol ferric oxide), and in the mixed catalyzer, consisting of calcium oxide *and* ferric oxide 0.800 g. (0.00371 mol $CaO·Fe_2O_3$). In substances containing the calcium oxide partially or wholly bound to carbon dioxide, 0.800 g. was also weighed out each time; in these cases the number of moles is somewhat smaller (depending on the carbon

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(1) Active oxides, 81st communication.

(2) A summary of 18 treatises has been given by G. F. Hüttig, *Z. Elektrochem.*, **41**, 527 (1935).

(3) W. Jander and W. Scheele, *Z. anorg. allgem. Chem.*, **214**, 56 (1933); W. Jander, *Z. Angew Chem.*, **47**, 235 (1934).

(4) (a) Hüttig, Zinker and Kittel, *Z. Elektrochem.*, **40**, 307 (1934); (b) Hüttig, Novak-Schreiber and Kittel, *Z. physik. Chem.*, **A171**, 85 (1934); (c) Hüttig, Sieber and Kittel, *Acta physicochimica, U. R. S. S.*, **2**, 129 (1935).

dioxide content) than when carbon dioxide-free samples are used, and the measured catalytic activity is therefore not at once comparable with that of the carbon dioxide-free substances. The percentage of nitrous oxide which was decomposed by the catalyzer is represented by α, while t_2 is the temperature at which the catalysis was observed.

The *magnetic susceptibility* was measured *before* the substance had been used as catalyzer, employing two different field strengths (480 and 950 gauss) and an arrangement which has been applied and described in former investigations.[5] χ represents the "magnetic mass-susceptibility" (susceptibility referred to 1 g. of the substance) and ρ the "powder-density" (defined above).

The *color* of the samples (Ow) is designated according to the color chart (with 24 divisions) of Wilhelm Ostwald (Grosser Farbatlas; editor Unesma G. m. b. H., Leipzig). In our case the following were important:

4	5	6	7	8
reddish	reddish with brown tint	reddish-brown	reddish-purple	purple

The two added letters indicate the content of gray.

In samples where calcium carbonate was used as starting material, the *carbon dioxide content of the catalyzer* is given by the number of moles of carbon dioxide (n) which exist per 1 mole of calcium oxide; *e. g.*, $n = 0.33$ signifies that one-third of the total calcium is present as calcium carbonate.

3. Preparation of the Samples

Series I.—Starting materials: *calcium oxide* (Kahlbaum "pro analysi") was heated for two hours to 1050°; it then showed a $\rho = 0.957$ and $\chi = -0.58.10^{-6}$. The *ferric oxide* (Fe_2O_3) was prepared from an aqueous solution of ferric chloride by precipitation with ammonia[6] and ignition for two hours over the Bunsen burner of the ferric hydroxide formed. *Preparation of the parts of the system CaO/Fe_2O_3:* the calcium oxide and the ferric oxide were mixed in molar proportions ($1CaO:1Fe_2O_3$), pulverized in an agate mortar for one-half hour and pressed through a 10,000-mesh sieve; then they were mixed for two hours in a machine and afterward kept for six hours in a crucible at a temperature t_1 (see Table I). Every sample has been subjected to the complete temperature treatment of the substances prepared at lower temperatures. The samples were cooled from temperature t_1 to room temperature in a vacuum desiccator. After this, they were once more pressed through the same sieve and mixed for one hour; then they were ready for the investigation. Great care was taken to keep moisture and carbon dioxide away from the sample.

Series II.—Calcium carbonate (Schering and Kahlbaum, Berlin, D. A. B. 5; analysis 99.57% $CaCO_3$, 0.43% H_2O) was mixed with the same ferric oxide as in series I in molar proportions ($1CaCO_3:1Fe_2O_3$), then pulverized for one-half hour in an agate mortar and finally mixed for twelve hours with a machine. The further treatment was as in series I, only that instead of pressing it through a sieve, the mixture was pulverized in an agate mortar.

Series III.—These samples were prepared exactly as those of series II with the only difference that after preparing the stoichiometrical mixture ($1CaCO_3:1Fe_2O_3$) a further 3% of crystalline calcium ferrite ($CaFe_2O_4$) was admixed. The latter was identical with the product of series I after the sample had been heated to $t_1 = 1000°$.

Series IV.—In preparing the samples of this series, special care was taken that the heating, and therefore also the changes caused thereby, were the same in all layers of the sample. The preparation was the same as in series II; however, the heating was not done in a crucible but the mixture was made into a paste with purest methanol (puriss. free from acetone) and with that the middle portion of a porcelain tube, which fitted exactly in the center of an Heraeus furnace, was covered evenly with a layer 0.25 mm. thick. Within two hours the furnace was brought to a temperature of 120° while a stream of dry air was passed through it. After leaving it at that temperature for two hours, the passage of air was stopped, the oven heat-insulated and the temperature gradually brought to t_1 in five hours where it was held for $\tau = 6$ hours. Here the various samples do *not* have the same temperature treatment as the substances prepared at lower temperatures.

A number of preliminary experiments have shown that the treatment with methanol is without influence upon the products formed. A crucible was divided into 2 symmetrical parts by an exactly fitting plate of eternite. One-half was filled with the mixture without methanol, while the other half contained the paste prepared with methanol. The whole was then heated as has been described above. By repeating the experiments at different temperatures, t_1, a series of samples were prepared. In all cases the contents of both halves of the crucible showed identical magnetic properties, in particular also the temperature t_1, at which ferromagnetism at first becomes apparent, is the same.

The samples of series V were prepared exactly as those of series IV, with the only difference that the time of heating (τ) to temperature t_1 was not the same in the various samples, as is stated in Table I, column 1.

4. The Results Obtained

The observed catalytic activity in the decomposition of nitrous oxide is given for all samples in Fig. 1. In the lower left corner of each graph the number of the experimental series corresponding to one of the above described modes of preparation is given. The temperature (t_1) of prepara-

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(5) Hüttig and Kittel, *Z. anorg. allgem. Chem.*, **199**, 136 (1931).

(6) Hüttig and Garside, *ibid.*, **179**, 49 (1929).

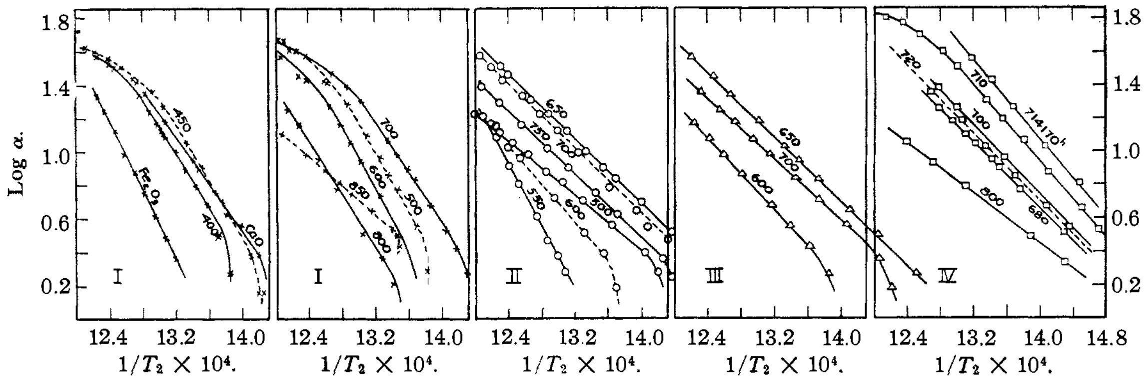

Fig. 1.

tion is given with each curve and identifies the various substances within a given series. The value $1/(t_2 + 273) = 1/T_2$ is plotted as abscissa, while the ordinates represent the corresponding value for $\log_{10} \alpha$. In the interval $\alpha = 2$ to 30%, the experimental results form a straight line on the graph. It is therefore possible to represent these results by the equation $\log_{10} \alpha = -(q'/T_2) + \log n'$, where q' and $\log n'$ are individual constants for each sample. If q (cal.) is set equal to $1.986 \times 2.303\ q'$, then q represents in the usual notation the "heat of activation," *i. e.*, a number which for a given sample must be the smaller, the more catalytically active any single active place, while n' represents a number which is proportional to the number of catalytically active places.

TABLE I

1	2	3	4	5	6	7	8	9
			$\chi \times 10^6$ gauss					
t_1, °C.	q, cal.	Log n'	480	950	Mean value	ρ	Color	γ, %
Series I: CaO, Fe_2O_3, CaO/Fe_2O_3								
	31640	10.233	−0.6	−0.6	−0.6	0.96		
	46280	13.746	37.4	37.5	37.4	2.56	7 pi	
20			30.1	30.0	30.1	1.08	7 le	
200			26.6	26.8	26.7	1.08	7 le	
300			29.7	29.9	29.8	1.36	7 ic	
400	38830	12.197	25.6	25.7	25.6	1.16	7 ic	
450	39198	12.427	28.7	28.7	28.7	1.51	6 ic	
500	39830	12.590	25.2	25.0	25.1	1.54	7 ng	
550			25.3	25.3	25.3	1.32	6–7 ng	
600	41060	12.628	29.5	29.6	29.5	1.14	6 ng	
700	36080	11.596	156.2	131.0		1.31	5 ng	
800	34600	10.230	395.5	300.2	ferro-	1.71	4 ng	
850	19210	6.172			magnetic			
900			443.3			2.11	5–6 pi	
1000			766.4			2.18	8 pl	
Series II: $CaCO_3$, Fe_2O_3, $CaCO_3/Fe_2O_3$								
At the 50-degree intervals from 450 to 750°, inclusive, the following fractions of carbon dioxide were evolved: 0.003, 0.019, 0.027, 0.062, 0.279, 0.961, and 1.00.								
20			21.5	21.5	21.5	1.58	7 le	φ
200			21.6	21.5	21.6	1.58	7 le	φ
300			21.5	21.4	21.5	1.58	7 le	φ
400			21.6	21.6	21.6	1.56	7 le	φ
450			22.0	21.9	21.9	1.58	6–7 le	1.0
500			22.2	22.2	22.2	1.59	6 le	1.97
550	41480	12.15	22.5	22.5	22.5	1.60	6 le	3.0
600	26390	8.19	23.3	23.5	23.4	1.61	5 ng	6.0
650	22090	7.44	29.9	29.9	29.9	1.46	5 ng	27.68
700	22500	7.52	87.2	80.4	ferro-	1.65	4 ng	
750	21450	7.06	133.9	116.6	magnetic	1.65	4 ng	
800	18750	6.16	117.7	103.2		1.93	4–5 ng	

TABLE I (*Concluded*)

Series III: $CaCO_3/Fe_2O_3$

At 700° the carbon dioxide fraction evolved was 1.00.

1	2	3	4	5	6	7	8	9
			$\chi \times 10^6$ gauss					
t_1, °C.	q, cal.	Log n'	480	950	Mean value	ρ	Color	γ, %
20			54.0	46.0		1.55	7 le	
			(21.5)	(21.5)				
600	24100	7.61	56.1	49.1		1.57	5 ng	
			(23.6)	(24.7)				
650	21950	7.43	99.6	94.5		1.51	4–5 ng	
			(68.5)	(71.5)				
700	20350	6.83	110.7	102.5		1.53	4 ng	
			(80.0)	(79.8)				
Series IV: $CaCO_3/Fe_2O_3$								
20			21.6	21.6	21.6	1.68	7 le	ϕ
400			21.6	21.5	21.6	1.61	7 le	ϕ
630			23.7	23.7	23.7	1.52	5 ng	7.0
680	22230	7.48	27.1	27.0	27.1	1.41	4–5 ng	18.0
690			27.8	27.8	27.8	1.44	4–5 ng	20.7
700	23460	7.92	28.2	28.2	28.2	1.41	4–5 ng	21.7
710	25800	8.84	32.2	32.1	32.2	1.39	4–5 ng	34.6
720	22870	7.71	119.1	112.7	ferro-	1.33	5 ng	
800	17290	5.74	132.2	121.4	magnetic	1.71	5 ng	
Series V: $CaCO_3/Fe_2O_3$								
6h at 717			30.9	29.9	ferro-magn.	1.48	5 ng	
12h at 714			33.0	33.2	33.1	1.30		38.0
70h at 714	26340	9.14	38.3	38.2	38.2	1.43	4 ie	54.8
336h at 714			39.8	39.6	39.7	1.38	4 ie	59.5

In Table I, columns 2 and 3, the values q and log n' for the various samples are given; the identity of the samples may be seen in columns 1. As the decomposition products of nitrous oxide have an influence upon the catalytic activity[7] and also other complications are possible, these figures may only be used for qualitative comparisons. In columns 4 to 6 are given the mass susceptibilities (χ) measured with field strengths of 480 and 950 gauss; in column 7 the powder densities (ρ), in column 8 the color. The amount of carbon dioxide given off by the sample during its preparation ($1-n$) is given as a footnote to series II and III. The significance of the figures given in column 9 (γ) is explained in section 5.

Series III (Table I) below the observed χ-values those susceptibilities appear in brackets which are found if the known magnetic effect of the added calcium ferrite is eliminated by calculation from the observed values.

In Figs. 2 and 3 the temperature of preparation (t_1) is always plotted as abscissa and perpendicularly to it some of the properties characterizing the substance. Points referring to samples of series I are always marked with x, those of series II with o, those of series III with Δ and those of series IV with □. In Fig. 2a the α-values of samples of series I for temperatures of catalysis (t_2) of 500°, 515 and 530° are drawn. For comparison also the catalytic activities, observed previously[8] with a similar set of experiments and measured by the reaction $2CO + O_2 \longrightarrow 2CO_2$ are here drawn as a dotted curve (the divisions of the ordinates are, however, not valid for this curve). Figure 3b gives curves for the α-values of series I (. . . curve), III (--- curve) and IV (-·- curve) for $t_2 = 530°$ and of series II (drawn out curve) for $t_2 = 500°$, 515 and 530°. In Fig. 2a, the $(1-n)$ values are given for series IIa. For the first 4 experimental series, the q-values are given in Figs. 2b and 3c, while the values for log n' of the same series are plotted in Figs. 2c and 3d. Figures 2d and 3e show the magnetic susceptibilities (χ); here in the case of series IV the calculated figures (in brackets in Table I) have been used. Figures 2e and 3f refer to the powder densities (ρ) and Figs. 2f and 3g give a graphical presentation of

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(7) Compare E. W. R. Steacie and J. W. McCubbin, *J. Chem. Phys.*, **2**, 585 (1934); G.-M. Schwab and H. Schultes, *Z. physik. Chem.*, **B25**, **411** (1934); and G.-M. Schwab and R. Staeger, *ibid.*, **B25**, 418 (1934).

(8) See footnote 4a, p. 311; and Kittel and Hüttig, *Z. anorg. allgem. Chem.*, **217**, 193 (1934).

the differences in color, the ordinates representing the number of the color chart. Figure 2g is based on previously obtained x-ray data[4a] (p. 311) curve A representing the estimated intensity of a line of the Debye photograph (characteristic of the oxide mixture) and curve B referring similarly to a line of the crystallized calcium ferrite.

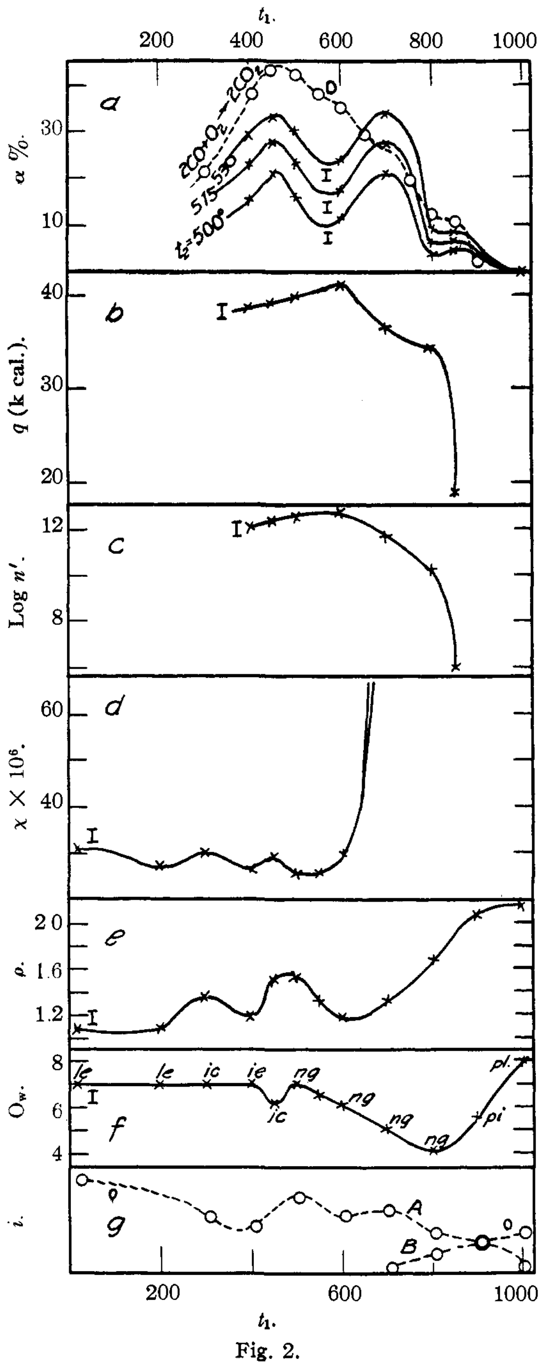

Fig. 2.

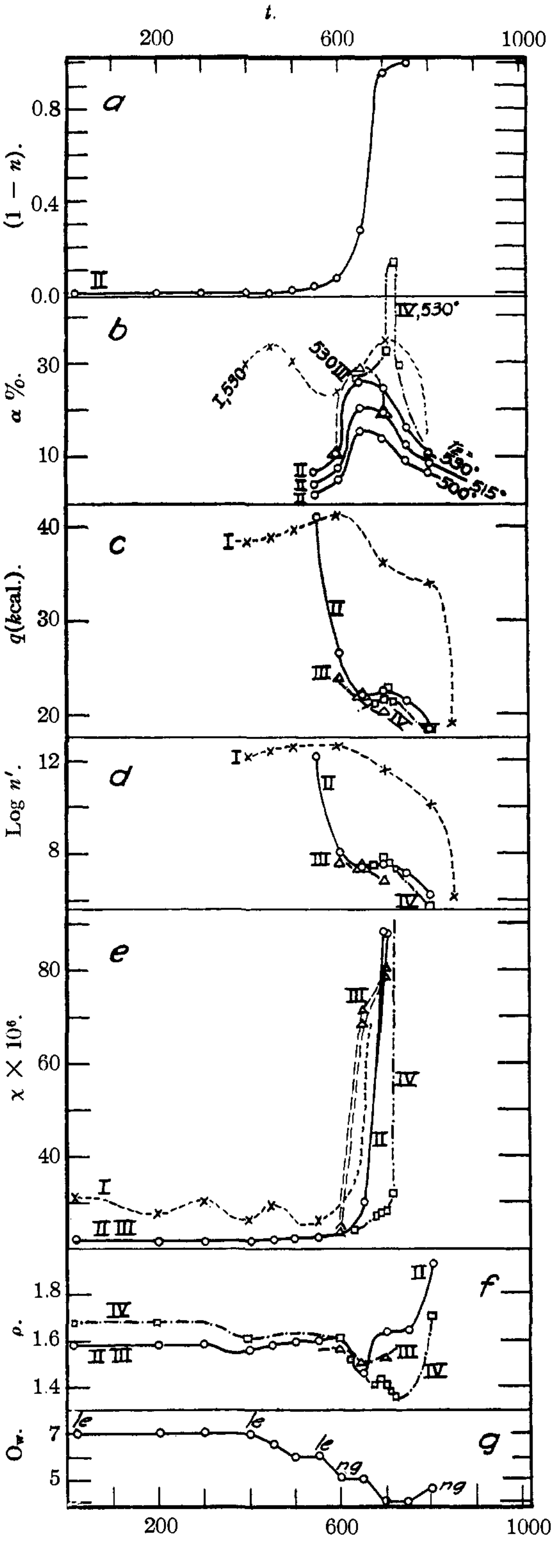

Fig. 3.

For an evaluation of the above catalytic data, the following results from ***preliminary experiments*** may also be mentioned.

No.	Sample	Amount used for catalysis, g.	Streaming velocity (c) cc./hr.	q, cal.	Log n′
1	CaO	0.800	577	31640	10.67
2	CaO	.208	577	31640	10.23
3	CaO (previously 12h at 1000°)	.800	577	31690	10.56
4	Fe_2O_3	.8000	577	46280	13.81
5	Fe_2O_3	.592	577	46280	13.75
6	Fe_2O_3	.592	200	49780	14.01

The starting substances were the same as described for experimental series I in Section 3.

5. Evaluation of Results

Let us consider first the series II, Table I. The mixture of calcium carbonate and ferric oxide, prepared at room temperature, does not change its properties if it is heated to t_1 = 400°. On heating further, a slight loss of carbon dioxide commences in the region from 400 to 450°; the original color 7 le changes toward 6 le and the paramagnetism here shows its first increase.[9]

All these changes take place in the temperature interval from 450 to 650°. At 650° the magnetic susceptibility which is independent of the field strength reaches a maximum with $\chi \times 10^6 = 29.9$; here also the catalytic activity in the decomposition of nitrous oxide reaches maximal values (Fig. 3b). About 28% of the total carbon dioxide content of the sample has been given off by that time and the color has changed to 5 ng. In the region from 650 to 700° ferromagnetism suddenly appears which becomes rapidly larger with increasing temperature of preparation, while simultaneously a decrease of the catalytic activity toward minimum values is observed.[10]

The carrier of the increased activity, as is observed to a greater degree with samples prepared between 400 and 650°, *cannot be the crystallized calcium ferrite*, because even the smallest quantities of calcium ferrite (cryst.) would induce strong ferromagnetic properties in the sample, and no paramagnetism could be observed with substances containing calcium ferrite; besides, no calcium ferrite in this region is determinable even by x-ray spectra (*cf.* Fig. 2g). The carrier of the increased activity must therefore be an intermediate between the original oxide mixture and the crystallized calcium ferrite; it must be a specifically characterized composition which *no longer* possesses the properties of the original mixture *nor yet* the properties of the crystallized calcium ferrite. With regard to the *quantity* of this "*active intermediate*" it could further be determined that it cannot, in general, be limited simply to a covering of the surface in a layer with a thickness of a few molecules. Such a thin covering by the active intermediate, though it would be sufficient to explain the changes of those properties which only depend upon the condition of the surface (*e. g.*, catalysis[11] or color), would never be able to explain the fundamental changes of those observed properties which represent a mean value of the condition of *all* molecules (*e. g.*, the magnetic susceptibility or the pycnometrically determined density).[12]

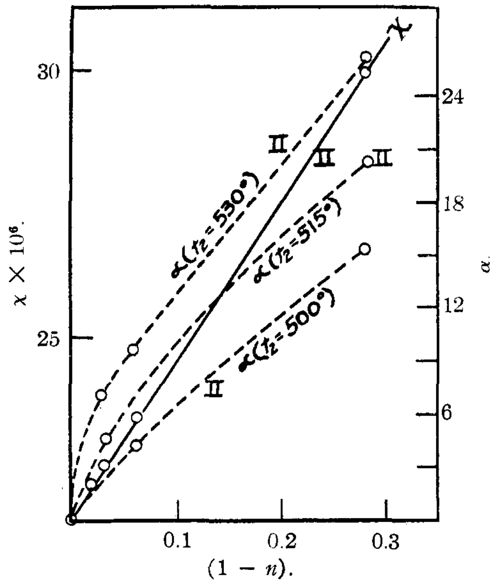

Fig. 4.

In the following way a numerical idea may be obtained from our experiments as to the percentage of the total sample (γ, *cf.* Table I) which is present in the "active intermediate" form. If the number of moles of carbon dioxide (1 − n) which have been given off by the sample per 1 mole of calcium carbonate during its preparation is plotted as abscissa, and the ordinates represent the magnetic susceptibility (χ), the relationships between χ and (1−n) as shown in Fig. 4 (drawn out curve) are obtained. It can be seen that a strict proportionality exists between the increase of susceptibility and the amount of carbon dioxide

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[9] Van Vleck, *Phys. Rev.*, **31**, 587 (1928); Freed and Kasper THIS JOURNAL, **52**, 4671 (1930).

[10] J. H. Chesters and C. W. Parmelee [*J. Am. Ceram. Soc.*, **17**, 50–59 (1934)] have observed the course of ferrite formation by means of dilatometrical measurements.

[11] H. S. Taylor, *Chem. Rev.*, **9**, 1–46 (1931); *Z. Elektrochem.*, **35**, 542 (1929).

[12] The pycnometrically determined densities will be dealt with in a future publication.

given off by the sample.[13] Because calcium oxide as well as calcium carbonate can only be diamagnetic, this probably means only[14] that each mole of calcium oxide, formed by the decomposition of calcium carbonate, at once forms the "active intermediate" with the ferric oxide and remains as such for some time. By extrapolating the straight line (Fig. 4) to the value $(1-n) = 1.0$ a value is obtained for $\chi \times 10^6 = 51.5$; *i. e.*, this susceptibility (*independent* of the field strength) should be observed if 100% of the sample were to exist in the "active intermediate" form; the increase in susceptibility $\chi \times 10^6$ of such a sample compared to that of the original mixture ($\chi \times 10^6 = 21.5$) amounts therefore to $51.5 - 21.5 = 30.0$.[15] By comparison of the actual increase obtained with different samples of this value, which corresponds to a 100% product, the percentage of "active intermediate" present in the different samples is obtained. This is given as $\gamma\%$ in column 9 of Table I. In series II, the sample which was prepared at 650° contains the largest quantity of the "active intermediate" (27.7%).

The "active intermediate," at least in a first approximation, represents a uniform substance. If this substance soon after its formation should undergo slow changes, perhaps by aging, the measurements should show a continuity of states, and such a proportionality as is evident from Fig. 4 would be unthinkable. Aside from the magnetic mass susceptibility $\chi = 51.5 \times 10^{-6}$, this intermediate form may also be characterized by the heat of activation in the nitrous oxide decomposition, which in our experimental arrangement is measured as $q = 20{,}000$ to $25{,}000$ cal. (*cf.* column 4 of the series II, III, and IV). Corresponding to the fact that the magnetic susceptibility of the ferric oxide, which is used as starting material, may have very different values depending upon the preparation, the magnetic susceptibility obtained for the pure active intermediate varies greatly with different starting substances. In the present case, the starting mixture $CaCO_3 + Fe_2O_3$ had $\chi = 21.5 \times 10^{-6}$, the active intermediate $\chi = 51.5 \times 10^{-6}$. In another series[13] the starting mixture had $\chi = 16.3 \times 10^{-6}$ and the active intermediate $\chi = 45.3 \times 10^{-6}$. In both cases, however, the *increase* is practically the same, *viz.*, about 30×10^{-6}.

If, as is demonstrated in Fig. 4 by the interrupted curves, $(1-n)$ is plotted as abscissa and the catalytic activity as ordinate (α), the α becomes larger with increasing $(1-n)$ and accordingly also with increasing χ, however, without having a direct proportionality. Compared to direct proportionality, the α-values slow up in their increase, and that to a greater degree the more "active intermediate" is formed. This means that a smaller portion of the active molecules formed (*cf.* also the log n'-values of column 5, Table I) is available for catalysis, if a more active intermediate is formed. This seems to us a proof that the active intermediates are formed primarily on the surface of the particles, from where further formation proceeds toward the interior of the particles, whereby the molecules are the less accessible for the molecules to be catalyzed the further away they are from the surface.

That in the series II the formation of a 100% "active intermediate" is not reached is due to the fact that the formation of the crystallized calcium ferrite from the active intermediate commences before the whole starting mixture has been transferred into the "active intermediate." If therefore a high content of the "active intermediate" is desired, it is necessary to prevent the premature formation of calcium ferrite, *i. e.*, to let the whole sample in all parts be transformed as uniformly as possible and to interrupt the process at the proper moment. Such conditions are fulfilled in the working method according to which the samples of series IV (see section 3) have been prepared. By this method it was possible to obtain products with a content of active intermediate (γ) as high as 35%. On the basis of experience gained from series IV, samples with even 60% of the active intermediate have been obtained in series V (*cf.* Table I). In the case of these products which contain practically no more carbon dioxide, one has to imagine that the proportionality between the carbon dioxide given off and the increase of susceptibility ceases if the last remaining portions of calcium carbonate have no ferric oxide sufficiently near them to combine to form the active intermediate; in this case the decomposition of calcium carbonate into calcium oxide and carbon dioxide could take place free from complications.

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(13) Kittel and Hüttig, *Z. anorg. allgem. Chem.*, **219**, 256 (1934).

(14) The absolute applicability of this reasoning is probably only then guaranteed, when experiments with mixtures in various proportions $CaCO_3$:Fe_2O_3 have also been made.

(15) See footnote 13, p. 262, where these "increases" for the system CaO/Fe_2O_3, SrO/Fe_2O_3 and BaO/Fe_2O_3 have been calculated, but erroneously have not been stated as increases but as total susceptibilities.

On the other hand, it seemed probable that a little addition of crystalline calcium ferrite (as was the case in series III) would hasten the formation of calcium ferrite. Our respective observations (Fig. 3e, curve III) make it probable that in such a case the "active intermediate" is formed already at a lower temperature, while this statement could not be made for the crystallized calcium ferrite. As the magnetic values which form the basis here are obtained by a complicated correction by calculation, the reliability of these statements is less than in the other observations.

If instead of a mixture of calcium carbonate and ferric oxide a stoichiometric mixture of calcium oxide and ferric oxide is used, as has been done in series I, an excess of calcium oxide is always present, and every calcium oxide molecule necessary for the reaction with ferric oxide does not have to be furnished by the primary decomposition of calcium carbonate. Accordingly portions of the starting material can *at first* proceed toward the formation of a more basic product.[16] Thus the fluctuations of the magnetic susceptibilities (Fig. 2d), as they appear with samples prepared at temperatures up to 600°, can be explained. The double maximum of the catalytic activity (Fig. 2a) could also have the same cause[4a] (pp. 308–309). The q and $\log n'$ values do not show similar double turning points (Figs. 2b and 2c).

Summary

1. Mixtures in stoichiometrical proportions $1CaO:1Fe_2O_3$ and $1CaCO_3:1Fe_2O_3$ were heated to various high temperatures under varying conditions.

2. Samples thus obtained were tested for their catalytic activity in the decomposition of nitrous oxide at various temperatures; further their magnetic susceptibility, their powder density, color, and carbon dioxide content were determined.

3. A detailed description of the preparation of the samples is given.

4. The results of the experiments are presented in figures and tables. For each sample the heat of activation (q) in cal. and a number n' is given which is proportional to the number of active centers in cases free from complications. Previously obtained results for the catalytic activity in the formation of carbon dioxide and x-ray data are used for comparison.

5. The following conclusions are drawn from the observations. The carrier of the increased activity is a specifically characterized "active intermediate" which no longer possesses the properties of the original mixture nor yet those of the crystallized calcium ferrite. A way to calculate the percentage of the "active intermediate" is given; the most active samples contain up to 60% of it. The "active intermediate" is a uniform substance with a susceptibility which is independent of the field strength and equal to $\chi = 51.5 \times 10^{-6}$, and with a heat of activation (in the decomposition of nitrous oxide from 20,000 to 25,000 cal. Its formation starts on the surface of the particles and proceeds toward their interior.

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[16] In the literature the compounds $CaO \cdot Fe_2O_3$ and $2CaO \cdot Fe_2O_3$ are given as definitely known calcium ferrites.