



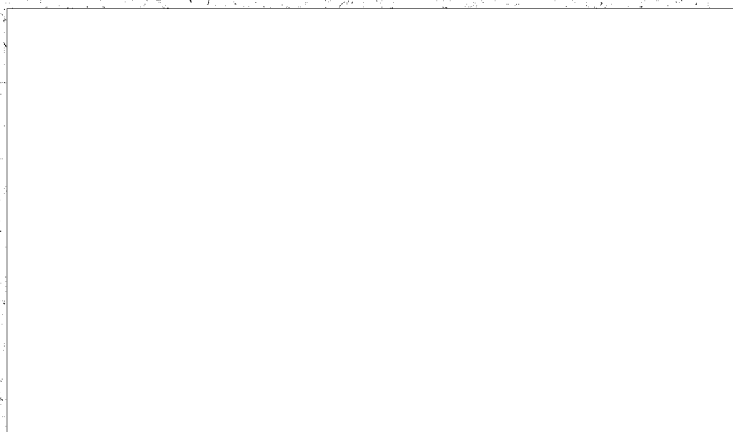
THE INFLUENCE OF THE GAS ATMOSPHERE AND  
COMPACTING PRESSURE ON REACTIONS  
IN THE SOLID STATE

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(From German)

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THE INFLUENCE OF THE GAS ATMOSPHERE AND COMPACTING  
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To examine the influence of foreign gases and possible contact effects on the reaction velocities of solids, an apparatus is described in which the progress of reactions with time in the solid state can be followed in specific gas atmospheres. This apparatus has been used to investigate the temperature dependence of a number of spinel reactions in nitrogen as well as the influence of the compacting pressure, the particle size, the degree of mixing of different foreign gases ( $O_2$ ,  $H_2$ ,  $CO_2$ ,  $SO_2$  and  $NH_3$ ) and vacuum on the reaction velocity.

The compacting pressure acts in three, clearly distinct different ways, which to some extent overlap. The particle size (of  $Al_2O_3$ ) in the system  $ZnO/Al_2O_3$  has practically no influence on the reaction velocity.  $O_2$  promotes the reaction  $MgO + Cr_2O_3$  very considerably, even in slight traces, which is explained by the intermediate formation of  $MgCrO_4$ . Whilst  $O_2$  has no effect in the system  $MgO/Al_2O_3$ , the reaction  $MgO + Fe_2O_3$  is markedly inhibited by  $O_2$ , for which the repression of the thermal dissociation of  $Fe_2O_3$  may be made responsible.  $H_2$  and  $NH_3$  exercise no influence in the system  $MgO/Al_2O_3$ . Whereas  $CO_2$  is without visible effect in the system  $MgO/Al_2O_3$ , this gas atmosphere in the system  $ZnO/Al_2O_3$  appreciably accelerates the reaction velocity.  $SO_2$  considerably promotes the reaction in the system  $MgO/Al_2O_3$ . No definite proof was obtained of any variation of the reaction velocity in a vacuum.

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In a large number of investigations, Hedvall (15-22), Forestier (8-14, 30, 31, 37), Huttig (24, 25), Fricke (4) and other authors (3, 38) have dealt with the problem of the influence exerted on reactions in the solid state by the compacting pressure and foreign gases. A reliable interpretation of the experimental results is obviously prevented by the difficulty of varying only one of the different possible experimental conditions at a time. As these relationships have not yet been adequately clarified, the present investigation is intended to provide a contribution towards this end.

The systems which have been selected for this are distinguished for their unmistakable chemical reactions and for the simple methods of determination.

These requirements are sufficiently closely satisfied by the spinel systems consisting of the components MgO, ZnO, and CdO, as well as  $\text{Cr}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ . All the systems obtained with these components have been investigated, with the exception of zinc ferrite and cadmium ferrite.

#### A. Starting substances and experimental method.

##### I. Starting substances.

###### 1. Magnesium oxide.

The basic magnesium carbonate p.a. of Merck was ignited tightly pressed in a crucible furnace at first for 1 hour at 500 - 600°C and then for 24 hours at 1100-1200°C. Examination for impurities showed the absence of detectable quantities of halogen, sulphate and heavy metals and less than 0.1% of sodium. Under the microscope with a magnification of 500 small, transparent, often regular crystals with a diameter of about 2 $\mu$  were to be seen.

###### 2. Zinc oxide.

Zinc oxide p.a. of Merck, when examined for impurities, showed substantially the same results as magnesium oxide. For sintering, the product was pressed tightly in a clay crucible and ignited for 8-10 hours at 1100°C, during which it sintered, its volume being reduced by about 1/4. Microscopic determination of particle size gave a mean diameter of 26 $\mu$ .

###### 3. Cadmium oxide.

Cadmium acetate p.a. of Merck was precipitated with ammonium carbonate; the  $\text{CdCO}_3$  was filtered, dried and slowly decomposed in a crucible furnace. The resulting CdO was ignited for 8 hours at 800°C, sintering together to form a chocolate brown core. A higher sintering temperature was not selected because of the appreciable evaporation of CdO which occurs at 900°C according to equation (14).

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For References, see end.

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4. Aluminium oxide.

Merck's Brockman aluminium oxide was used as starting material. In order to remove some alkali content, which it possesses according to manufacturer's statements, it was boiled for 1 hour with 2n hydrochloric acid with vigorous agitation, filtered at the pump, washed and dried. It was then sintered for 12-15 hours at 1100°C.

Under the microscope, all particle sizes between 5 and 100 $\mu$  were found in fairly uniform distribution.

5. Iron oxide.

"Fe O according to Brandt" was used as starting substance, and this<sup>2</sup> was ignited in a clay crucible for 10 hours at 1100°C. The colour changed from reddish brown to bluish gray; the product sintered to about 1/3 of its original volume to a solid core. After grinding in a mortar, black particles with a mean diameter of 4-7 $\mu$  were mostly to be seen when examined under the microscope.

6. Chromium oxide.

"Purest" chromium oxide of Merck was ignited for 10 hours at 1150°C in a current of purified nitrogen. Externally, no sintering was observed. The colour became somewhat darker. The mean particle size, determined under the microscope was about 2 $\mu$ .

## II. Preparation of the mixtures and compressed compacts.

1. Mixing.

Mixing of the substances, weighed out in the desired proportions, took place in a "Multimix" made by the firm of Braun. This apparatus was found to be extremely useful in the present work, and can be highly recommended wherever there is a need for mixing powders as intimately and homogeneously as possible. A certain, truly not very great disadvantage of the "Multimix", is its tendency to grind, which for some experiments cannot be disregarded.

2. Pressing.

Pressing of the compacts was effected in a hydraulic laboratory press. The cylindrical moulds used had a diameter of 11.0 mm., by means of which compacts up to pressures of 12.5 t/cm<sup>2</sup> could be made. On each pressing stroke, there was a waiting time of one minute to allow equilibrium to become established.

Since it was found in the first pressing experiments that the compacts usually broke in two when removed from the press, all the compacts were broken through the centre and were subjected to reaction as half compacts.

The weight of a compact was about 7-8 mval.

The compacting pressure is indicated in the individual reactions.

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III. Apparatus.

All the reactions were carried out in a Silit rod furnace (current 10 amp., power 2 kW). 4 Silit rods A (see Figure 1) were used as heating rods. The regulating thermocouple C which was in a porcelain tube D, was introduced into the furnace from the end, so that the free junction E was directly adjacent a Silit rod, the regulation of the temperature being thus as free from inertia as possible. The furnace temperature could be kept constant to  $\pm 5^{\circ}\text{C}$ . The hard porcelain heating tube B (internal diameter 30 mm, length 650 mm) was glazed at both ends to glass tubes F and G. The glazed-on tubes terminated at either end in a ground sleeve S 1 and S 2. The ground inner piece connected to S 1 carried a glass tube H (10 mm diameter) projecting into the ground joint and having glazed to it a porcelain tube I, which served for receiving the measuring thermocouple. The junction of this thermocouple lay in the middle of the heating tube somewhat above the centre. Between S 1 and the glazed joint was a shortened pressure gauge J and the gas inlet K provided with a cock. Figure 2 shows the ground - joint attachment for S 2. The porcelain tube L could be pushed in the guide support M, a piece of vacuum tubing N serving as gas seal. This porcelain tube L served to carry a 3 mm thick iron wire O, to the front end of which was rivetted a round scraper P, 12 mm in diameter. The gas seal between L and O was also provided by a piece of vacuum tubing. The glass wall U was fused as flat as possible to provide a good view into the interior of the tube.

IV. Gas purification.

Most of the experiments were carried out in an atmosphere of nitrogen. In some cases, ordinary commercial nitrogen containing 3-4% oxygen was used, in others a nitrogen purified from oxygen and having an oxygen content of less than  $10^{-2}\%$ .

Purification of the nitrogen was carried out by the method of Meyer and Ronge (32). For adsorbing any oil vapour which could interfere with the catalytic effect of the active copper, a vessel containing silica-gel was inserted between the bomb and the Meyer-Ronge tower (referred to in what follows as the M-R tower).

After the oxygen absorption, the gas passed through a washbottle containing concentrated sulphuric acid, which served at the same time as bubble counter; it then passed through a Fresenius drying tower containing silica-gel, and finally through a drying tower filled with alternate layers of phosphorus pentoxide and glass wool.

In reactions in a current of hydrogen, the gas was also purified in the manner described, whilst all the other gases entered the sulphuric acid bottle directly, but otherwise passed through the same drying process; only in the case of ammonia, drying was done by means of soda lime.

V. Carrying out the experiments.

The experiments were all carried out as follows: The compacts, broken in two in the middle, were placed with the fracture on the

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support (a 20 x 70 mm piece of asbestos card 6 mm thick) and then the support with the compacts was pushed just behind the glazed joint at R. The temperature at that point was 150-200°C, the substance being thereby freed from any superficial moisture. After closing the furnace, the ground joint attachment T was placed in position and the gas was passed through for about  $\frac{3}{4}$  to 1 hour, whereupon by means of the scraper, the support with the compacts was introduced into the hot zone of the furnace.

At the appropriate times, whilst observing through the glass window U, a compact could be drawn off the support and placed in the ground joint attachment T. After completion of the experiments, the ground joint attachment was removed and the compacts analysed by the method described in the next section.

It was in this way possible to allow the entire reaction to proceed to conclusion in a definite gas atmosphere.

#### VI. Analytical method.

In the analytical investigation of the compacts after the reaction for determining the percentage conversion it was important to determine, in addition to the acid-insoluble  $\text{Me}_2\text{O}_3^*$  and spinel, also the acid-soluble  $\text{MeO}^*$ . As preliminary experiments had shown that even highly ignited  $\text{MeO}$ , if powdered finely enough, dissolves quantitatively in 0.1 n-hydrochloric acid when heated on the water bath for half an hour, the following method was adopted for analysing the compacts:

A suitable weighing, containing about 3-4 Mval free  $\text{MeO}$ , was heated in a 300 ml Erlenmeyer flask for 30 minutes with 50 ml 0.1 n-hydrochloric acid on a well-boiling water bath, with frequent shaking. It was then filtered at once hot from the insoluble residue (spinel +  $\text{Me}_2\text{O}_3$ ) and the excess hydrochloric acid in the filtrate was titrated back with 0.1 n-sodium hydroxide.

To prove the accuracy of this method, 9 reaction determinations by this method were carried out on an intimate mixture of  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$ , which had been heated for 13 hours at 1100°C. A mean value of 68.2% was obtained with a maximum error of  $\pm 0.5\%$ .

This relatively large error must be accepted in this reaction determination. As shown by a few preliminary experiments, it is partly due to the fact that a certain uncontrollable quantity of acid is consumed by the spinel and by  $\text{Me}_2\text{O}_3$ . There is, furthermore, the possibility that some acid may be lost in digesting and filtering.

The content of  $\text{MeO}$  in the starting mixture, the so called "zero value" was therefore not calculated from the weighed quantity, but was titrated in the same way as the compacts after reaction.

An error in the reaction determination of  $\pm 0.5\%$  is furthermore substantially less than the reproducibility of the reaction, which is

\*  $\text{MeO}$  denotes the divalent oxide and  $\text{Me}_2\text{O}_3$  the trivalent oxide.

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generally not more than  $\pm 1\%$  and is often worse than  $2\%$ . The fluctuations are particularly high at the commencement of the reaction, where the scatter of the values is not infrequently about  $\pm 5\%$ . This is easily understood since at the commencement of a reaction, the spinel is in a very active state, so that it may be dissolved by the acid to some extent.

## B. Experimental results.

### I. Reaction $\text{MgO} + \text{Cr}_2\text{O}_3$ .

For making the mixture, the preparations of  $\text{MgO}$  and  $\text{Cr}_2\text{O}_3$  described above were mixed in stoichiometric proportions. The compacting pressure was  $3.13 \text{ t/cm}^2$ , except of course the experiments in B.I.4.

#### 1. Reaction in nitrogen atmosphere.

Figure 3 shows the values obtained plotted against time.

The hardness of the compacts increased very rapidly as the reaction proceeded; whereas the non-ignited compacts could be crushed very easily, this was possible only with difficulty for a conversion of  $80\%$ . The colour changed with progressing conversion from chrome green to grey green.

#### 2. Influence of the compacting pressure.

To determine the dependence of this reaction on the compacting pressure, compacts were pressed at different pressures and were exposed to the same temperature for the same times.

The experimental results are plotted in Figure 4. The values of Figure 4a, as well as curve 1 in Figure 4b, show the results of experiments in a nitrogen atmosphere, whilst curve 2 in Figure 4b shows the results of a reaction in a vacuum, carried out by degassing for one hour before the compacts were pushed into the hot furnace, so as to remove the last traces of air from the reaction chamber.

Curve 3 in Figure 4b shows the results of compacting pressure experiments with a fresh mixture, in which sintered  $\text{Cr}_2\text{O}_3$  was replaced by the unsintered oxide.

The reasons for making experiments 8 and 9 are explained in the discussion of the experimental results.

#### 3. Influence of oxygen.

The experiments in Figure 5 and curve 3 in Figure 6 were carried out in an atmosphere of nitrogen in the presence of  $3-4\%$  of oxygen. For this purpose, the commercial nitrogen was not first freed from oxygen in a M-R tower, but merely dried in the usual way and passed into the furnace. In the experiments shown in curves 4 and 5 of

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of Figure 6, this commercial oxygen was mixed at a T-piece in the desired proportions by volume with nitrogen from the M-R tower. In curves 1 and 2, a current of dried oxygen and a current of dried air were used, respectively, as gas atmosphere, the air being taken from a compressed air generator. In the bracketed values of curves 1 and 2, a loose powder mixture was used, not a compact. In all the other experiments, the compacts were pressed at  $3.13 \text{ t/cm}^2$ .

#### 4. Reaction in a vacuum.

The experiments in a vacuum had to be made with the pump running, since the frequent movement of the porcelain tube L and the wire O made it impossible to maintain the vacuum when the pump was stopped. Since leakage in of gas could occur at the most at the movable parts at L and O, any gas which might perhaps find its way into the apparatus could not come into contact with the compacts, since it would be drawn off at once at the pump connection Q. In addition, with this arrangement, any vapours from grease, e.g. on inserting the greased porcelain tube into the furnace, were pumped off at once.

The results of the reactions in a vacuum are shown in Figure 7.

With regard to the experiments in a vacuum it should also be remarked that sintering in a vacuum appears to proceed more slowly than in a nitrogen atmosphere. The hardness of the compacts after the reaction was much less than with corresponding compacts with the same conversion, but prepared in nitrogen. A quantitative statement cannot be made, since there was no micro-hardness tester available.

## II. Reaction $\text{ZnO} + \text{Cr}_2\text{O}_3$

### 1. Reaction in nitrogen atmosphere.

Weighings of  $\text{ZnO}$  and  $\text{Cr}_2\text{O}_3$  with the molar ratio 1 : 1 were mixed in the usual way and compacts were made under a pressure of  $2.5 \text{ t/cm}^2$ . The results of the experiments, all of which were made in a nitrogen atmosphere, are shown graphically in Figure 8.

The external appearance of the compacts after the reaction were the same for colour and hardness as in the system  $\text{MgO}/\text{Cr}_2\text{O}_3$ .

### 2. Influence of compacting pressure.

The results of the investigation into the effects of compacting pressure in the system  $\text{ZnO}/\text{Cr}_2\text{O}_3$  are shown in Figure 9, curve 2.



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### III. Reaction $\text{CdO} + \text{Cr}_2\text{O}_3$

#### 1. Reaction in nitrogen atmosphere.

In this system also, the molar ratio was 1 : 1. Compacts pressed at  $1.25 \text{ t/cm}^2$  were made from the mixture prepared in the "Multimix". Figure 10 shows the results of the investigation in an atmosphere of nitrogen.

As shown by the peculiar "negative" conversion values at the commencement of the reaction, the analytical method employed is too inaccurate for this system. This is due to the fact that the cadmium-chromium-spinel formed in the nascent state at a low temperatures is also dissolved by hydrochloric acid, so that a larger quantity of hydrochloric acid is used than corresponds to the zero value, thus giving the appearance of a negative conversion. In Figure 10, the probably real conversion values have been extrapolated with reference to the usual forms of the curves.

The colour of the final spinel is chromium-green with a yellowish tinge.

#### 2. Influence of compacting pressure.

The results of experiments carried out in the usual way for examining the effect of compacting pressure are shown in Figure 9, curve 4.

### IV. Reaction $\text{MgO} + \text{Al}_2\text{O}_3$

#### 1. Reaction in nitrogen atmosphere.

The mixture was prepared in the usual way. The compacting pressure was  $2.5 \text{ t/cm}^2$  in all cases. The  $\text{Al}_2\text{O}_3$  preparation employed was a sieve fraction with an average particle size of  $40\mu$ .

In this system, the determination of the conversion was modified by titrating the excess of hydrochloric acid directly in the suspension after the water bath treatment, without filtering from the solid residue. It is true that the colour change is not so easy to recognise in this suspension, but the resulting accuracy is perfectly adequate for the purpose of the determinations.

Figure 11 shows the results of the experiments in an atmosphere of nitrogen.

#### 2. Influence of compacting pressure.

As before, compacts compressed under different pressures were heated together with the loose powder mixture ( $p = 0 \text{ t/cm}^2$ ) at the same time to the same temperature. Figure 9 shows the results.

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3. Influence of oxygen.

It was of interest to see whether in the system  $\text{MgO}/\text{Al}_2\text{O}_3$ , which unlike the system  $\text{MgO}/\text{Cr}_2\text{O}_3$ , is chemically inert to oxygen, the oxygen content of the atmosphere exerted any effect on the reaction velocity. For this purpose, reactions were carried out in gas atmospheres of different oxygen contents; the results are shown in Figure 11.

4. Influence of hydrogen.

Since the system  $\text{MgO}/\text{Al}_2\text{O}_3$  was the only one of those investigated which is chemically inert to hydrogen at the reaction temperatures employed, it was possible in this case to ascertain whether the reaction proceeds at a different velocity in an atmosphere of hydrogen from that in a nitrogen atmosphere.

The results of these experiments are also shown in Figure 11.

5. Reaction in a vacuum.

Figure 11 also shows the results of experiments in a vacuum; the experimental conditions are given in B.I.4.

In these investigations, a striking observation was made: When the hot compacts were removed from the furnace and placed in the attachment T, the originally pure white compacts became dark blue grey in colour. To ascertain whether a different compound had been formed, this product which surrounded the compact in a thin layer 0.1-0.2 mm thick, was scraped off and an X-ray photograph was made of it. No lines other than those of  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{MgAl}_2\text{O}_4$  were found.

On ignition in the air, the blue grey colour disappeared, and a pure white product was obtained.

6. Influence of carbon dioxide.

Since the starting mixture of  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  and also the  $\text{Al}_2\text{O}_3$  sieve fraction of  $40\mu$  had been exhausted it was necessary to use a fresh mixture of  $75\mu$  was used. On account of the considerably different particle size of the corundum, the comparative value in a current of nitrogen had to be re-determined and is shown in Figure 12.

The results of experiments made with the same mixture in an atmosphere of carbon dioxide are also shown in Figure 12.

7. Influence of ammonia.

The ammonia gas used was taken from a bottle and was dried with soda lime and magnesium perchlorate. Before and after the reaction, the furnace had to be well washed out with nitrogen, since at the temperatures employed, ammonia is almost completely decomposed into nitrogen and hydrogen.

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Figure 12 shows the results of experiments carried out on the mixture described in the preceding section.

#### 8. Influence of sulphur dioxide.

The sulphur dioxide employed for this purpose was taken from a bottle and dried with sulphuric acid and  $P_2O_5$ .

After the reaction, the compacts were not so strongly sintered as in the previous reactions. Figure 12 shows the conversion values obtained.

### V. Reaction $ZnO + Al_2O_3$

#### 1. Reaction in nitrogen atmosphere.

In weighing the portions for this system, an  $Al_2O_3$  sieve fraction of the particle size  $40\mu$  was used. The compacting pressure was  $2.5 \text{ t/cm}^2$ . In this system, as in the system  $MgO/Al_2O_3$ , the titration was also carried out directly in the suspension without first filtering.

Figure 13 shows the results of the experiments carried out in an atmosphere of nitrogen.

#### 2. Influence of compacting pressure.

Curve 1 in Figure 9 shows the results of the experiments carried out in the usual way.

#### 3. Influence of carbon dioxide.

Figure 13 shows the results of experiments, in which the influence of carbon dioxide on the reaction velocity in this system was investigated. The gas atmosphere employed was a mixture of nitrogen with 1 %  $CO_2$  of pure  $CO_2$ .

#### 4. Influence of the particle size.

In order to investigate the influence of the particle size on the reaction velocity, a number of mixtures were made with  $Al_2O_3$  in different particle sizes measured under the microscope.

Figure 14 shows the results of these experiments. The figure indicates the particle size of the  $Al_2O_3$  for each mixture. The zinc oxide used was the same preparation as in the preceding experiments.

In this case, these substances could not be mixed in the "Multimix", because the particle sizes of the  $Al_2O_3$  might have been altered by the grinding action of the machine. To avoid this, the weighed portions, calculated in the molar proportion 1 : 1 were shaken in a glass-stoppered bottle for 8-10 hours on a shaking machine.

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In these experiments, the gas atmosphere was nitrogen; the compacting pressure was  $2.5 \text{ t/cm}^2$ . In all the experiments, the furnace temperature was  $1018^\circ\text{C}$ .

#### VI. The system $\text{CdO}/\text{Al}_2\text{O}_3$

The attempt to investigate the reaction velocity in the system  $\text{CdO}/\text{Al}_2\text{O}_3$  failed, since at the temperatures necessary for securing a reasonable conversion, the rate of evaporation of the cadmium oxide was of the same order as the rate of formation of the spinel. The experiments had to be abandoned for the time being without result.

#### VII. Reaction $\text{MgO} + \text{Fe}_2\text{O}_3$

In this system also, the molar ratio was 1 : 1; the substances were mixed as usual and compacts were made from this mixture under a pressure of  $2.5 \text{ t/cm}^2$ . The  $\text{Fe}_2\text{O}_3$  weighings were taken from a sieve fraction of the particle size  $15\mu$ .

Difficulties were encountered in the titration, since small quantities of the spinel or of the iron oxide activated by the reaction (about 1-2 mg, maximum 3 mg) were dissolved in the 0.1 n-hydrochloric acid on digesting the substance on the water bath; this interfered with the titration because before the change in colour of the methyl red was reached, the solution became deep yellow in colour, due to the separation of colloidal iron oxide hydroxide with increasing  $p_{\text{H}}$  value, this taking place to such an extent that the change in colour could no longer be detected. The titration was therefore modified as follows: After filtering, 2 ml of an approximately 1 molar citric acid solution was added to the solution, whereby the small amounts of iron were held in solution. In this case, in the presence of  $\text{Fe}^{+++}$  ions, the solution became strongly yellow in colour. Bromothymol blue was therefore used as indicator, since in this solution, its pronounced change from yellow through green to blue could be clearly recognised.

##### 1. Reaction in nitrogen atmosphere.

The hardness of the compacts increased very greatly as the reaction proceeded; for a conversion of about 30% it was already so great that the compacts could only be crushed in a steel mortar. The colour changed substantially concurrently with the conversion from the blue grey of the starting mixture to the red brown colour of the final spinel.

Figure 15 shows the results of these experiments.

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2. Influence of compacting pressure.

The compacts pressed under different pressures were heated in a nitrogen atmosphere together with the loose powder mixture. Figure 9, curve 3 shows the results of these experiments.

3. Influence of oxygen.

Figure 15 shows the results of the experiments in commercial nitrogen (3.5% O<sub>2</sub>), in air and in pure oxygen at two different temperatures.

C. Discussion of the experimental results.I. Temperature dependence of the investigated reactions in a nitrogen atmosphere.1. Fundamental considerations on the calculation of the reaction velocity constants with reference to the reaction MgO + Cr<sub>2</sub>O<sub>3</sub>.

The calculation of the reaction velocity constants (R.V.C) for determining the energy of activation according to Jander's equation

$$2.k.z/r^3 = \left(1 - \sqrt[3]{\frac{100 - U}{100}}\right)^3$$

is based on the assumption of a constant particle radius. Therefore, using for instance the results shown in Figure 3, we obtain values for k which are dependent upon time. Since the smaller grains at the commencement of the reaction react more rapidly and the larger grains are left behind, the particle size distribution varies and hence the calculated R.V.C., in the course of the reaction. Jagitsch (27) has already referred to this fact in detail.

If, nevertheless, we wish to obtain a survey of the order of magnitude of the energy of activation, the k values are plotted against 1/T for the same reaction period. In doing this, the time will be measured so that the preponderance of lattice diffusion over surface diffusion can be seen from the variation of conversion with time.

In Figure 16, the R.V.C.'s corresponding to z = 10000 sec. for the reaction MgO + Cr<sub>2</sub>O<sub>3</sub> have been plotted logarithmically against 1/T in the usual way, the values of Table 1 being taken into consideration. Except for t = 817°C, the values lie fairly well on a straight line; the discrepancy for 817°C is understandable since such small conversion amounts are produced substantially

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by surface diffusion and not by lattice diffusion, and according to Hüttig (26, p. 390) the activation energies have different values for the two kinds of diffusion.

From the straight lines of Figure 16 we obtain the following values for the constants of the Arrhenius equation:

$$k = 7.9 \times 10^{-4} \times e^{-64000/RT} \text{ (cm}^2\text{/sec.)}$$

### 2. Reaction velocity constants and Arrhenius constants.

Table 1 shows the reaction velocity constants calculated for different systems with reference to the experimental results of Chapter B according to the scheme given above.

The third column gives the microscopically measured mean particle size of both substances used for the calculations; the particle size of the MeO is in front of the oblique stroke and that of the Me<sub>2</sub>O is after the stroke. The constants themselves are shown in column 4, being expressed in the unit cm<sup>2</sup>/sec. x 10<sup>16</sup>. By plotting these values against the reciprocal of the absolute temperature in Figure 16, we obtain the Arrhenius straight line of the reaction concerned, the equation for which is shown in column 6.

As already stated, these numbers merely represent lower limit values. Whereas in the system MgO/Al<sub>2</sub>O<sub>3</sub> Tanaka (39) found an energy of activation of 41.1 kcal and hence a relatively good agreement with the value of 46.0 kcal found here, Bengtson and Jagitsch (2) in the system ZnO/Al<sub>2</sub>O<sub>3</sub> obtained 98 kcal, almost twice the value given here, although it should be borne in mind that in the case of the last authors, the experimental conditions were substantially different, since they did not use a powder mixture but two compacts pressed against each other.

### 3. Qualitative comparison of the reaction temperatures.

If we compare purely qualitatively the reaction temperatures necessary for obtaining the same conversion in different systems, it is possible even at this stage to draw some interesting conclusions.

The maximum reactivity observed was found in the system MgO/Fe<sub>2</sub>O<sub>3</sub>; then come the systems CdO/Cr<sub>2</sub>O<sub>3</sub>, ZnO/Cr<sub>2</sub>O<sub>3</sub>, ZnO/Al<sub>2</sub>O<sub>3</sub>, MgO/Cr<sub>2</sub>O<sub>3</sub> and finally MgO/Al<sub>2</sub>O<sub>3</sub> as system with the maximum reaction temperatures.

These differences in reaction temperatures may be explained partly by differences in melting point and partly by differences in particle size. Thus, the order of melting points is Fe<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub>; since, however, the particle size of Al<sub>2</sub>O<sub>3</sub> is twenty times that of Cr<sub>2</sub>O<sub>3</sub>, it is clear that this Al<sub>2</sub>O<sub>3</sub> preparation has a

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lower reactivity than the  $\text{Cr}_2\text{O}_3$ , and therefore comes after the latter in the above-mentioned order. If, furthermore, we take the vacuum reaction as standard reaction for  $\text{MgO}/\text{Cr}_2\text{O}_3$  as is proposed below (see C, II.2.a), the difference in the reaction temperatures is still less.

In the case of the divalent components, the order of reactivities is analogous to that of the melting points ( $\text{CaO}$ ,  $\text{ZnO}$ ,  $\text{MgO}$ ). Due to the considerable differences in melting points, the differences in particle size are not evident.

Accurate considerations concerning the necessary  $\alpha$  - temperatures for attaining the same conversion are not possible because definite statements regarding the inactive state of the starting components cannot be made, since they were pretreated at different  $\alpha$  - temperatures: on the other hand, it is doubtful to what extent the melting point values, obtained by different methods, can be correlated.

## II. Influence of gas atmosphere and vacuum.

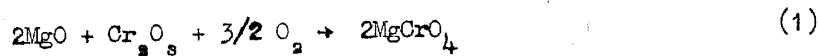
### 1. Influence of oxygen

#### (a) on the reaction $\text{MgO} + \text{Cr}_2\text{O}_3$ .

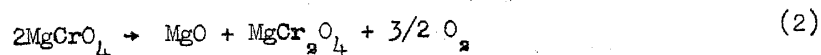
The experimental results (Figures 5 and 6) show a surprisingly considerable influence of the oxygen content of the atmosphere on the reaction velocity. Curves 4 and 5 of Figure 6 are most striking, where the conversion increased to more than double for an oxygen content of fractions of a percent. It is not surprising that this activating influence of the gas atmosphere has a stronger effect on a loose material than on compacts (see the bracketed measured points in curves 1 and 2).

It is very likely that this activating effect of oxygen on the reaction  $\text{MgO} + \text{Cr}_2\text{O}_3$  is due to the fact that in the presence of oxygen, an intermediate reaction can take place as previously indicated by Jander (29) for the system  $\text{ZnO}/\text{Cr}_2\text{O}_3$ .

According to this, intermediate magnesium chromate would be formed:



It may be assumed that this magnesium chromate is not stable at the temperatures employed and is immediately decomposed according to



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In the first place, this assumption is supported by the fact that the activation energy of this reaction in the presence of 3-4%  $O_2$  is only about  $1/3$  of the value in a pure nitrogen atmosphere (see Table 1 : 19900 cal).

Further experimental support for this assumption is provided by the fact that small amounts of chromate ions could be detected in the filtrates of these experiments by means of the diphenyl-carbazide reaction.

In order to lend further support to this reaction mechanism, the decomposition temperature of magnesium chromate had first to be determined and it had to be proved that its decomposition takes place according to equation (2), since no information on this point could be found in the literature.

$MgCrO_4$  was prepared by introducing  $MgO$  in small portions into a solution of 125 g  $CrO_3$  p.a. in 250 ml of water until the pH value was 6-7. This solution, filtered from slight impurities was evaporated under reduced pressure at  $60^\circ C$  to a dark red, syrupy liquid.

On cooling to 2 -  $3^\circ C$ , a thick, yellowish red crystalline mass separated out which was filtered off and washed with absolute alcohol and ether. The resulting product consisted of very beautiful lemon yellow crystals.

Analysis showed a  $CrO_4$  content of 43.95% for an Mg content of 9.20% (theoretically, for this Mg content the  $CrO_4$  content should be 43.86%). This composition corresponds with satisfactory accuracy to the formula  $MgCrO_4 \cdot 7H_2O$ , which according to Hill (23) should crystallise out below  $16^\circ C$ .

For determining the decomposition temperature, weighed portions of 2-3 g of this product were heated in a platinum crucible in the crucible furnace or in a porcelain boat in a tube furnace and the loss in weight at different temperatures was determined.

On heating in air, decomposition commences at  $350^\circ C$  although very slowly, a deepening of the colour towards orange being observable. At  $575^\circ C$  dissociation becomes more pronounced (colour commences to change towards green) and is practically complete at  $620^\circ C$ . The entire loss of weight is then 16.71 or 17.04% (theoretical loss of weight according to equation (2) is 15.86%).

In a current of nitrogen, decomposition is already quantitative at  $615^\circ C$ , the loss of weight is 16.95%.

In a current of oxygen, dissociation is already complete at  $630^\circ C$ ; the orange yellow colour persists, however, to  $625^\circ C$ , and the characteristic change of colour to grey-green the colour of spinel occurs only then. The total loss of weight is then 17.06%. Even at  $575^\circ C$  the weighable decomposition is very considerable.



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If the decomposition of  $\text{MgCrO}_4$  occurs according to equation (2) the  $\text{MgO}$  content of the ignited residue should be 17.33%. This was found to be 17.17%.

Thus, at temperatures of 600-620°C, magnesium chromate loses oxygen and decomposes into a mixture of  $\text{MgO}$  and magnesium chromite.

An attempt to obtain  $\text{MgCrO}_4$  in accordance with equation (1) below its dissociation temperature, as Vasenin (40) and Ford (5-7) were able to do in the system  $\text{CaO}/\text{Cr}_2\text{O}_3/\text{O}_2$  was unsuccessful, nor was it possible, in accordance with the reverse equation (2) to prepare magnesium chromate from magnesium chromite,  $\text{MgO}$  and oxygen. The chromate content of the products which had been heated for 12 hours in a current of oxygen at 550°C was not more than 0.1 - 0.2%.

It is, of course, not impossible that other compounds in the system  $\text{MgO}/\text{Cr}_2\text{O}_3/\text{O}_2$ , perhaps like those which Ford (5-7) found in his investigations in the system  $\text{CaO}/\text{Cr}_2\text{O}_3/\text{O}_2$ , or other valency stages of chromium, such as recently found by Scholder (35) exercise this activating function on the reaction in the presence of oxygen.

(b) on the reaction  $\text{MgO} + \text{Al}_2\text{O}_3$

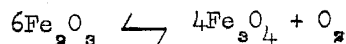
The values of Figure 11 fail to reveal any definite influence of oxygen on the reaction velocity; the observed deviations lie within the reproducibility of a reaction.

The rate of formation of  $\text{MgAl}_2\text{O}_4$  is accordingly unaffected by the oxygen of the atmosphere.

(c) on the reaction  $\text{MgO} + \text{Fe}_2\text{O}_3$

The values of Figure 15 show a distinct decrease in the reaction velocity due to the presence of oxygen, as compared with a pure nitrogen atmosphere. The extent of the inhibiting effect of the oxygen at 827°C is independent of the oxygen concentration, but at 865°C the inhibiting effect is more pronounced at higher oxygen contents.

An attempt to explain this fact led to the following consideration:- The equilibrium



is shifted in favour of  $\text{Fe}_2\text{O}_3$  in the presence of oxygen.

Simon and Schmidt (36) give 0.5 mm Hg as the equilibrium pressure of this system at 1150°C and 1.0 mm Hg for 1200°C; other figures in the literature are round about these values.

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The reaction temperatures employed are indeed much lower than these temperatures of a measurable dissociation, so that any appreciable thermal reduction can scarcely occur. It is, however, quite conceivable that a certain small number of high energy lattice particles split off oxygen in the surface in quantities which cannot be detected analytically and may be transformed into  $Fe_3O_4$ .

Since, on the other hand, the conversion  $Fe_2O_3 \rightarrow Fe_3O_4$  is accompanied by an extensive lattice transformation, and on the other hand the active molecules, which as regards energy are in a position for this, are situated at the important centres of the surface for reactivity, the surface of the  $Fe_2O_3$  preparation, in the absence of oxygen, may be thermally "reduced" and the  $Fe_2O_3$  may thereby be activated. In the presence of oxygen, this surface dissociation will be repressed and the reaction velocity thereby retarded.

According to Hüttig (25), changes in modification may become noticeable, even 100-200°C below the actual conversion point, through changes in the surface, and Anderson (1) also found such "primary" reactions or "surface" processes in the case of heterogeneous reactions.

## 2. Reactions in a vacuum.

### (b) Reaction $MgO + Cr_2O_3$

Figure 7 shows that the reaction  $MgO + Cr_2O_3$  proceeds much more slowly in a vacuum than in nitrogen.

It is not ruled out that traces of oxygen still possessed by the nitrogen purified by the M.R. Tower, and which according to the literature (32) are less than 10<sup>-4</sup>% bring about this increased conversion in nitrogen as compared with the reaction in a vacuum, and therefore the vacuum reaction must be regarded as the actual "standard" reaction, i.e. it proceeds without the influence of any foreign gases.

### (b) Reaction $MgO + Al_2O_3$

As shown by Figure 11, marked differences can be seen from the reaction in nitrogen, especially at the commencement, but these disappear in time. After 10 seconds, conversion is practically the same in both reactions.

Thus, in the system  $MgO/Al_2O_3$ , the reaction in a vacuum appears to proceed with the same velocity as in nitrogen. The inhibiting or promoting influences on the reaction velocity mentioned in the literature could not be confirmed for the systems investigated here and presumably are ascribable to the special features of the systems investigated.

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### 3. Influence of hydrogen on the reaction $MgO + Al_2O_3$

It will readily be seen from the results of Figure 11 that in principle the same applies here as for the experiments in a vacuum. Here again marked differences are to be observed, especially at the commencement of the reaction, but cannot be regarded definitely as real. Such irregularities occur quite frequently and are ascribable to the generally difficult reproducibility of reactions in the solid state.

In the reaction  $MgO + Al_2O_3$  a definite influence cannot be found in hydrogen as compared with the nitrogen reaction, nor was such influence expected.

### 4. Influence of carbon dioxide.

Although, as shown by Figure 12 carbon dioxide has no appreciable influence on the reaction velocity in the system  $MgO/Al_2O_3$  it does have in the system  $ZnO/Al_2O_3$ .

If 1%  $CO_2$  was added to the usual nitrogen atmosphere, the reaction velocity was practically the same as in a pure nitrogen atmosphere; in a pure  $CO_2$  atmosphere, however, a definitely higher reaction velocity can be observed.

This difference in behaviour is difficult to explain, since the increase in reactivity be the creation of fresh surfaces from an equilibrium situated on the side of  $MeC$  for a possible intermediate reaction

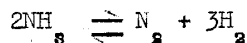


ought to be applicable for  $ZnO$  and for  $MgO$ .

Evidently, such loosening of the surface for the system  $MgO/Al_2O_3$  is not sufficient to influence the greater inertia of this system, to which reference has already been made, especially since, in this case, the  $Al_2O_3$  preparation employed had a considerably particle size.

### 5. Influence of ammonia on the reaction $MgO + Al_2O_3$

As shown by the values of Figure 12 an ammonia atmosphere does not exert any visible influence on the reaction  $MgO + Al_2O_3$ . This means that the establishment of the equilibrium



on the surface of the reaction mixture is without effect on the reaction velocity in this system.

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6. Influence of sulphur dioxide.

The values of Figure 12 show a definite reaction-promoting effect of sulphur dioxide on the reaction  $MgO + Al_2O_3$ .

There was the possibility that considerable amounts of  $MgSO_3$  were formed in the compacts, so that the  $MgO$  employed was no longer available for titration. Although this sulphite was very probably decomposed on digesting with hydrochloric acid, it is not certain whether the liberated  $SO_2$  was completely expelled on the water bath or consumed additional hydroxide in titration. Since, however, the  $SO_2$  content of a compact after the reaction was less than 1%, the strikingly high conversion values do not appear to have been produced by combined  $SO_2$  but are real. This phenomenon was not investigated further.

III. Influence of contact possibilities.1. Influence of compacting pressure.

If we compare the compacting pressure curves shown in Figures 4 and 9, the shape of the curves in the various systems is very different; certain uniform characteristic effects may, however, be observed and they appear to have a generally valid significance.

Considering first of all the compacting pressure dependency in the system  $MgO/Cr_2O_3$  (Figure 4), which was investigated more closely, it is found that the conversion at first remains constant with increasing compacting pressure between a pressure of 0 and 3 t/cm<sup>2</sup>, whence it increases substantially linearly to about 6.5 t/cm<sup>2</sup>; from that point there is only a slight increase until the maximum compacting pressure investigated.

The fact that the conversion remains constant up to a certain pressure and then suddenly increases permits of two possible interpretations:

(a) As has already been shown, this reaction may be increased considerably by traces of oxygen. There is now the possibility that the air enclosed in the compacts during the pressing operation, from a certain compacting pressure onwards, is no longer displaced from the compacts in washing out the reaction tube with nitrogen; the oxygen thus retained in the compacts would then be responsible for the increased conversion.

(b) From the known compacting pressure onward, a destruction of the grains of the substance occurs, thereby providing fresh surfaces of fission and fresh possibilities of reaction, causing the increased conversion.

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As shown by the results of an experiment carried out in a vacuum with the pump running (see Figure 4b, curve 2), the same compacting pressure dependency occurs in a vacuum as in nitrogen. The first of these two possibilities is thus eliminated.

To be able to support the second possible interpretation, it must be remembered that the hardness of the grains plays a considerable part. This hardness depends largely upon the nature of the pre-treatment and hence upon the sintering temperature. For this reason, it was of interest to repeat the experiments with a mixture of MgO and unsintered  $\text{Cr}_2\text{O}_3$ .

As shown by curve 3 in Figure 4b, there are two increases in the conversion by increased compacting pressure, at 0.75 and at 4 t/cm<sup>2</sup>. However, there is definitely no increase at 3 t/cm<sup>2</sup> as in the reactions with sintered chromic oxide.

On the assumption that the increase in the conversion due to increased compacting pressure results from the crushing of the  $\text{Cr}_2\text{O}_3$  particles, the unsintered  $\text{Cr}_2\text{O}_3$  appears to contain two groups of particles of different hardness, so that at a pressure of 0.75 or 4 t/cm<sup>2</sup> fresh possibilities of contact are provided which cause the increase in the conversion.

To avoid errors, it must be emphasised at this point that by "hardness" of the particles or grains we do not mean the hardness of the substance in the mineralogical sense - because this cannot of course be affected by sintering, but the hardness of a sintered grain, i.e. the mechanical ability to support stress possessed by the contact surfaces of the single crystals of which the particle is composed.

This effect that the conversion increases from a certain pressure due to the breaking up of the grains of substance, besides occurring in the system MgO/ $\text{Cr}_2\text{O}_3$  is also very pronounced in the system MgO/ $\text{Fe}_2\text{O}_3$  at a pressure of 5 t/cm<sup>2</sup> (see Figure 9, curve 3). In this latter system, apart from the "fracture effect", a second effect has been found responsible for the increase in the conversion: Between 0 and 3 t/cm<sup>2</sup> a considerable increase in conversion can be observed. It cannot be assumed that this slight pressure can already exercise a grain-crushing effect; on the contrary, in this case the pressure causes the particles to approach each other, that is to say, it results in a better contact of the grains, and so will be the cause of the increased conversion.

This effect will preferably occur at low pressures.

In the dependence upon compacting pressure in the system ZnO/ $\text{Cr}_2\text{O}_3$ , two different effects can clearly be observed. In addition to the increase in conversion caused by the compacting

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pressure, the drop in the conversion curve between the compacting pressure  $0t/cm^2$  and the compact with the lowest compacting pressure measured is remarkable. This confirms the phenomenon found by Fricke (4) and Forestier (10) and the reaction in the compact, particularly at low compacting pressures, may proceed more slowly in the compact than in the loose powder. Fricke explains this by the fact that, in the loose material, the points of growth can adjust themselves to each other more readily than in the pressed material. Perhaps this phenomenon may be explained better by stating that certain active corners and edges, which are situated in the surface of the grains and along which diffusion to the reaction partner can take place, become blocked in the compacting process so that they are not available for diffusion.

Apart from the system  $ZnO/Cr_2O_3$ , this phenomenon is also found to be very pronounced in the system  $ZnO/Al_2O_3$  and less pronounced in the systems  $CdO/Cr_2O_3$  and  $MgO/Al_2O_3$  (see Figure 9). Apart from such "blocking", the three last-mentioned systems do not appear to be affected in their reactivity by a variation in the compacting pressure.

Accordingly, three different effects are to be distinguished in the influence of the compacting pressure on reactions in the solid state, which probably overlap each other in their dependence upon the nature and structure of the grains.

(a) An increase in conversion, due to the purely geometrical approach of the particles.

(b) An increase in conversion, due to the crushing of individual substance grains at certain compacting pressures.

(c) A reduction in conversion by the blocking of possible favourable means of diffusion in the surface.

For a rational interpretation of the compacting pressure curves it would probably first be necessary to have statistically adequate experimental material, for which a satisfactory interpretation would be possible by systematically varying the experimental conditions and suitably selecting the components.

## 2. Influence of the particle size.

This influence was investigated only in the system  $ZnO/Al_2O_3$ . As Figure 14 shows, the conversion obtained for all the particle sizes of  $Al_2O_3$  employed is the same within the limits of error, although the latter vary by the factor of three. Any possible conclusion can therefore at present only refer to this special case.

However, this peculiar result at first appears to contradict all existing notions concerning the dependence of solid state reactions

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upon the particle size (27, 28 inter alia). It might possibly be explained according to Tanaka (39) by the fact that the  $Al_2O_3$  migrates on the ZnO or, in the case of the formation of a reaction layer, diffuses into the latter to the ZnO.

According to his experimental results, Tanaka considers this mechanism to be very likely. He believes that above all in reactions, whose character is strongly determined by surface diffusion, the particle size of the diffusing component is only of slight significance, whilst the particle size of the component on which the reaction product grows, affects the reaction velocity in the sense of Jander's formula (28).

Such an assumption of the diffusion of  $Al_2O_3$  to ZnO, however, is in direct contradiction with the results of Bengtson and Jagitsch (2), who found that the direction of migration was definitely in the opposite direction for the system ZnO/ $Al_2O_3$ .

Apart from the fact that all thermal data support the results of Bengtson and Jagitsch, the considerable difference in the particle sizes should be borne in mind in the present case. It may act upon the conversion like a variation in the mixing proportions of 1:1, depending upon the excess of the component whose direction of migration determines the reaction.

In conclusion, the influence of the mixing method employed on the conversion of the reactions herein described will be considered.

If we compare the values of Figure 13 with those of Figure 14, we find that in the former, the conversion values are substantially higher (for example about twice as high for 1000°C). The only difference in treatment of the two starting mixtures was that the preparation of the mixtures for Figure 13 took place in the "Multimix" and for Figure 4 on the shaking machine.

The objection that the higher conversion in Figure 13 was caused by a grain-crushing action of the Multimix is invalid, because the results of the above section have clearly shown that the particle size of the  $Al_2O_3$  is without influence on the reaction velocity; since, on the other hand, the particle size of the ZnO is only about 2 - 5% of that of the corundum, it is unlikely that its particle size has been materially altered by the Multimix treatment.

The reason for this difference probably resides in the fact that the individual ZnO grains readily agglomerate to form very small, loose spheres which persist in the mixing on the shaking machine, so that a homogeneous mixture is not obtained. These spheres, however, are not stable to the vigorous mixing action of the "Multimix" but are broken up into their constituents.

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For this reason, therefore, a much more homogeneous mixture can be produced in the "Multimix" than by mixing of moderate duration on the shaking machine, since it cannot be assumed that a mixture which after 10 hours is still at least 50% from being an ideal mixture, will have approached this degree of mixing to any considerable extent after say ten times as long. This shows the extent to which the results of solid state reactions depend upon the working conditions.

IV. Final remark.

The results obtained in the present work do not serve to simplify the by no means very simple picture of the reactivity of solida. It is shown that the course of solid state reactions may be influenced in very different ways. It is at present not possible satisfactorily to co-ordinate the observed facts with reasonable notions of the mechanisms of such reactions.

The possible interpretations proposed in the paper are to be supported by enlarging the experimental material .



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E. Summary.

1. It is intended to provide a contribution to the problem of the influence of foreign gases and contact possibilities on the reactivity of solid substances.

2. An apparatus is described, in which the course of solid state reactions with time can be followed in definite gas atmospheres.

3. A simple analytical method is given for determining the conversion in spinel reactions.

5. The temperature dependence of the reactions  $\text{MgO} + \text{Cr}_2\text{O}_3$ ,  $\text{ZnO} + \text{Cr}_2\text{O}_3$ ,  $\text{CdO} + \text{Cr}_2\text{O}_3$ ,  $\text{MgO} + \text{Al}_2\text{O}_3$ ,  $\text{ZnO} + \text{Al}_2\text{O}_3$  and  $\text{MgO} + \text{Fe}_2\text{O}_3$  has been investigated and the corresponding constants of the Arrhenius equation given.

5. In the action of the compacting pressure on the reaction velocity, three different effects are to be distinguished; in certain circumstances, these effects overlap; they were found definitely in the following systems:

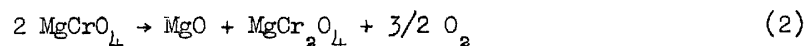
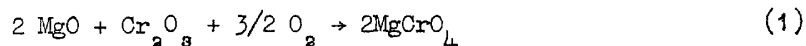
- (a)  $\text{MgO}/\text{Fe}_2\text{O}_3$
- (b)  $\text{MgO}/\text{Fe}_2\text{O}_3$  and  $\text{MgO}/\text{Cr}_2\text{O}_3$ ,
- (c)  $\text{NiO}/\text{Cr}_2\text{O}_3$  and  $\text{ZnO}/\text{Al}_2\text{O}_3$ .

The systems  $\text{MgO}/\text{Al}_2\text{O}_3$  and  $\text{CdO}/\text{Cr}_2\text{O}_3$  show little or no dependence of the conversion upon compacting pressure.

6. Whereas in the system  $\text{MgO}/\text{Al}_2\text{O}_3$  the particle size of the  $\text{Al}_2\text{O}_3$  has a distinct influence, in the system  $\text{ZnO}/\text{Al}_2\text{O}_3$  a variation of the particle size of the  $\text{Al}_2\text{O}_3$  by the factor 3 has no effect on the conversion obtained.

7. If the starting mixture is mixed in one case on the shaking machine and in the other case in the Multimix, there is a difference in the degree of mixing which, in the case of the latter method of mixing and in the system here investigated, results in a reactivity which is almost twice as great.

8. Oxygen promotes the reaction velocity in the system  $\text{MgO}/\text{Cr}_2\text{O}_3$  very greatly, so that oxygen contents of a few tenths of a percent can double the conversion. There probably occurs here an intermediate reaction of the type.



To confirm this, the decomposition temperature of  $\text{MgCrO}_4$  was determined; it is  $610 \pm 10^\circ\text{C}$ . In addition, it was shown by analysis of the solid decomposition product that the decomposition of

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$\text{MgCrO}_4$  takes place in accordance with equation (2)

In the absence of intermediate reactions which are influenced by  $\text{C}_2$ , the latter was found not to have any effect. Thus, for example, in the system  $\text{MgO}/\text{Al}_2\text{O}_3$  the reaction in oxygen proceeds at the same velocity as in nitrogen. On the other hand, oxygen exercises a definitely inhibiting effect on the reaction  $\text{MgO} + \text{Fe}_2\text{O}_3$  as compared with the same reaction in nitrogen. This is explained by the fact that in a nitrogen atmosphere, a surface thermal dissociation of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  may occur substantially below the actual dissociation temperature, whereby the  $\text{Fe}_2\text{O}_3$  is reactivated. This thermal dissociation is repressed by the presence of oxygen and the activating action of the nitrogen is cancelled.

9. In the temperature range investigated, hydrogen has no appreciable influence on the reaction  $\text{MgO} + \text{Al}_2\text{O}_3$ .

10. The same also applies for equilibrium mixtures of gases. In the system  $\text{MgO}/\text{Al}_2\text{O}_3$ , ammonia gas or the presence of the components  $\text{H}_2$  and  $\text{N}_2$  from the equilibrium  $2\text{NH}_3 \rightleftharpoons \text{N}_2 + 3\text{H}_2$  is without influence on the reaction velocity.

11. It was not possible to detect any influence by  $\text{CO}_2$  on the reaction velocity in the system  $\text{MgO}/\text{Al}_2\text{O}_3$ , whilst the reaction  $\text{ZnO} + \text{Al}_2\text{O}_3$  is distinctly accelerated by  $\text{CO}_2$ .

12. Gaseous  $\text{SO}_2$  increases the conversion in the system  $\text{MgO}/\text{Al}_2\text{O}_3$  to a considerable extent, an intermediate reaction participating in certain circumstances.

13. The reaction  $\text{MgO} + \text{Cr}_2\text{O}_3$  takes place in a vacuum ( $10^{-1}$  mm Hg with pump running) much more slowly than in nitrogen, it being not impossible that the traces of oxygen still present in the purified nitrogen are the cause of this increase in the conversion.

The reaction  $\text{MgO} + \text{Al}_2\text{O}_3$  has substantially the same velocity in a vacuum as in nitrogen.

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REFERENCES

- (1) J.S. Anderson, Discuss. Faraday Soc., 4 (1948) 163.
- (2) B. Bengtson and R. Jagitsch. Ark. Kem. Mineralog. Geol. 24A No. 18 (1947).
- (3) F.v. Bischoff. Z. anorg. allg. Chem. 250 (1942) 10.
- (4) R. Fricke and F. Blaschke. Z. anorg. allg. Chem. 251 (1943) 396.
- (5) W.F. Ford, W.J. Rees and J. White, Trans. Brit. Ceram. Soc., 48 (1949) 291.
- (6) W.F. Ford and W.J. Rees. Trans. Brit. Ceram. Soc. 47 (1948) 207.
- (7) W.F. Ford and J. White. Trans. Brit. Ceram. Soc. 48 (1949) 417.
- (8) H. Forestier and J.P. Kiehl. C.R. Acad. Sci., 229 (1949) 47.
- (9) H. Forestier and J.P. Kiehl. C.R. Acad. Sci., 229 (1949) 197.
- (10) H. Forestier, C. Haasser and J.L. Longuet. Bull. Soc. chim. France, 116 (1949) D 146.
- (11) H. Forestier and J.P. Kiehl. C.R. Acad. Sci., 230 (1950) 2288.
- (12) H. Forestier and J.P. Kiehl. C.R. Acad. Sci., 232 (1951) 1664.
- (13) Gmelin. Handbuch der anorg. Chemie, 27, Part B (1939) 47.
- (14) Gmelin. Handbuch der anorg. Chemie, 33 Part B (1924) 71.
- (15) I.A. Hedvall and K. Olsson. A. anorg. allg. Chem., 243 (1939) 237.
- (16) I.A. Hedvall and O. Runchagen. Z. Naturforsch. 28 (1940) 429.
- (17) I.A. Hedvall. Ing. Vetensk. Akad. Handl., (1942) 43.
- (18) I.A. Hedvall. Glastechn. Ber., 20 (1942) 34.
- (19) I.A. Hedvall and T. Günther. Z. anorg. allg. Chem., 251 (1943) 305.
- (20) I.A. Hedvall and A. Lundberg. Ark. Kem. Mineralog. Geol., 17 A, No. 12 (1944).
- (21) I.A. Hedvall. Silicates Ind., 16 (1951) 157.

-27-

REFERENCES (Contd).

- (22) I.A. Hedvall. Einführung in die Festkörperchemie, Brunswick, 1952.
- (23) A. Hill, G. Soth and J. Ricci. J. Amer. Chem. Soc. 62 (1940) 2131.
- (24) G.F. Hüttig and E. Kürschner. Z. Kolloidchem 81 (1937) 40.
- (25) G.F. Hüttig. Z. angew. Chem. 53 (1940) 35.
- (26) G.F. Hüttig in : Schwab, Handbuch der Katalyse, Springer, Vienna, 1943, Vol. 5.
- (27) R. Jagitsch. Chinia (Zurich) 1 (1947) 105.
- (28) W. Jander. Z. anorg. allg. Chem., 163 (1927) 1.
- (29) W. Jander and K.T. Weitendorf. Z. Elektrochem. angew. physik Chem. 41 (1935) 435.
- (30) J.P. Kiehl. C.R. Acad. Sc. 232 (1951) 1666.
- (31) J.P. Kiehl. C.R. Acad. Sc. 234 (1952) 943.
- (32) F.R. Meyer and G. Ronge. Z. angew. Chem. 52. (1939) 637.
- (33) M.S. Roberts and H.E. Mervin. Amer. J. Sc., (5) 21 (1931) 145.
- (34) R. Ruer and M. Nakamoto. Rec. Trav. chim. Pays-Bas. 42 (1923) 675.
- (35) R. Scholder. Z. Elektrochem. Ber. Bunsenges. physik. Chem., 56 (1952) 879.
- (36) A. Simon and Th. Schmidt. Z. Kolloidchem., Erg.-Bd., 36 (1925) 77.
- (37) P. Stahl. C.R. Acad. Sc., 232 (1951) 1669.
- (38) Y. Tanaka. Bull. Chem. Soc. Japan, 16 (1941) 428.
- (39) Y. Tanaka. Bull. Chem. Soc. Japan, 17 (1942) 229.
- (40) F.I. Vasenin. C.A. 42 (1948) 8594.

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TABLE 1.

Reaction velocity constants and Arrhenius equations of the systems dealt with in the present paper.

System	Conditions	Particle Size	Reaction velocity constant	t(°C)	Arrhenius equation: k =
MgO/Cr <sub>2</sub> O <sub>3</sub>	1:1, N <sub>2</sub>	2/2	4,2	817	7,9·10 <sup>-4</sup> ·e <sup>-64000/RT</sup> .
			15,7	915	
			74,0	997	
			592	1095	
			1970	1195	
MgO/Cr <sub>2</sub> O <sub>3</sub>	1:1, N <sub>2</sub> + 3,5% O <sub>2</sub>	2/2	246	817	2,4·10 <sup>-10</sup> ·e <sup>-19900/RT</sup>
			500	915	
			903	997	
MgO/Cr <sub>2</sub> O <sub>3</sub>	1:1 Vacuum	2/2	4,2	915	3,7·10 <sup>-3</sup> ·e <sup>-69000/RT</sup>
			46	995	
			317	1095	
ZnO/Cr <sub>2</sub> O <sub>3</sub>	1:1, N <sub>2</sub>	2,6/2	21	820	3,5·10 <sup>-4</sup> ·e <sup>-56000/RT</sup>
			162	905	
			426	950	
			818	990	
			1390	1030	
CdO/Cr <sub>2</sub> O <sub>3</sub>	1:1, N <sub>2</sub>	6/2	23,4	783	1,2·10 <sup>-4</sup> ·e <sup>-52000/RT</sup>
			130	865	
			290	910	
			1140	978	
MgO/Al <sub>2</sub> O <sub>3</sub>	1:1, N <sub>2</sub>	2/40	53	918	4,2·10 <sup>-6</sup> ·e <sup>-46000/RT</sup>
			780	1018	
			1440	1048	
			3310	1125	
			7860	1217	
ZnO/Al <sub>2</sub> O <sub>3</sub>	1:1, N <sub>2</sub>	2,6/40	110	835	9,1·10 <sup>-6</sup> ·e <sup>-45400/RT</sup>
			2860	900	
			13150	985	
			28400	1055	
MgO/Fe <sub>2</sub> O <sub>3</sub>	1:1, N <sub>2</sub>	2/15	45	783	1,3·10 <sup>-1</sup> ·e <sup>-61400/RT</sup>
			770	827	
			1920	865	
			8250	927	
			13200	1020	

(In these Figures, U = conversion and Z = Time)

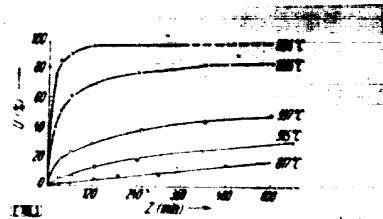
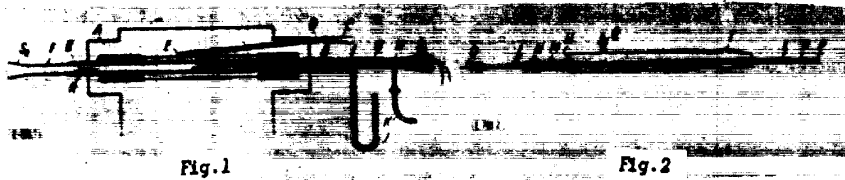


Fig. 3: MgO + Cr<sub>2</sub>O<sub>3</sub> 1:1; 3.13 t/cm<sup>2</sup>; N<sub>2</sub> atmosphere.

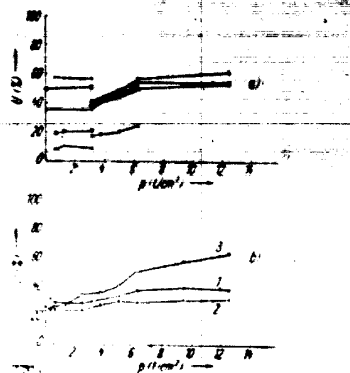


Fig. 4: MgO + Cr<sub>2</sub>O<sub>3</sub> 1:1; Compacting pressure dependence.  
(a) Reaction in N<sub>2</sub>  
(b) — x — = N<sub>2</sub>  
— + — = Vacuum  
— o — = Unsintered Cr<sub>2</sub>O<sub>3</sub>

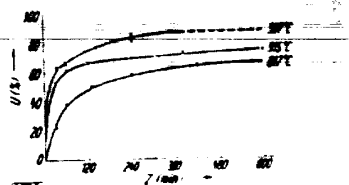


Fig. 5: MgO + Cr<sub>2</sub>O<sub>3</sub> 1:1; 3.13 t/cm<sup>2</sup>; N<sub>2</sub> + 3.5% O<sub>2</sub>

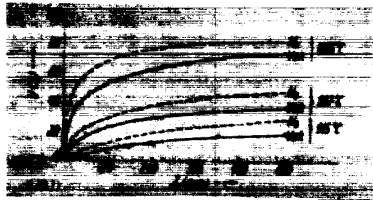


Fig. 7: MgO + Cr<sub>2</sub>O<sub>3</sub> 1:1; 3.13 t/cm<sup>2</sup>; Vacuum.



Fig. 6: MgO + Cr<sub>2</sub>O<sub>3</sub> 1:1; 3.13 t/cm<sup>2</sup>; t = 915°C; O<sub>2</sub> influence.



Fig. 8: ZnO + Cr<sub>2</sub>O<sub>3</sub> 1:1; 2.5 t/cm<sup>2</sup>; N<sub>2</sub> atmosphere.

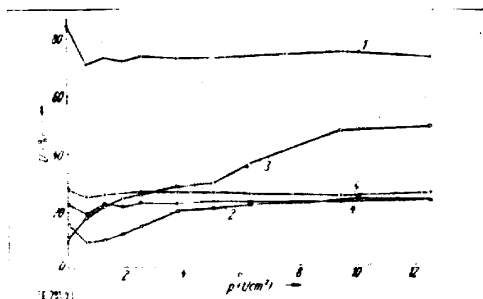


Fig. 9: ZnO + Cr<sub>2</sub>O<sub>3</sub>, CdO + Cr<sub>2</sub>O<sub>3</sub>, MgO + Al<sub>2</sub>O<sub>3</sub>,  
ZnO + Al<sub>2</sub>O<sub>3</sub>, MgO + Fe<sub>2</sub>O<sub>3</sub>;  
Compacting pressure dependence.  
1. — x — = ZnO + Al<sub>2</sub>O<sub>3</sub>  
2. — □ — = ZnO + Cr<sub>2</sub>O<sub>3</sub>  
3. — o — = MgO + Fe<sub>2</sub>O<sub>3</sub>  
4. — e — = CdO + Cr<sub>2</sub>O<sub>3</sub>  
5. — + — = MgO + Al<sub>2</sub>O<sub>3</sub>

Fig.10:  $\text{CaO} + \text{Cr}_2\text{O}_3$  1:1;  $1.25 \text{ t/cm}^2$ ;  
 $\text{N}_2$  atmosphere  
 - - - - Probably real values.

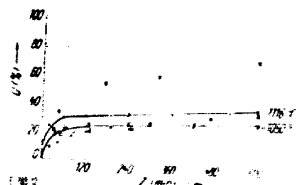


Fig.11:  $\text{MgO} + \text{Al}_2\text{O}_3$  1:1;  $2.5 \text{ t/cm}^2$ ;  
 $\text{N}_2$  atmosphere

Fig.12:  $\text{MgO} + \text{Al}_2\text{O}_3$  1:1;  $2.5 \text{ t/cm}^2$ ;  
 $\text{NH}_3$  and  $\text{SO}_2$

- =  $\text{N}_2 + 3.5\% \text{ O}_2$ ,  $1018^\circ\text{C}$
- ▲ =  $\text{N}_2 + 20\% \text{ O}_2$ ,  $1018^\circ\text{C}$
- =  $\text{O}_2$ ,  $1018^\circ\text{C}$
- v = vacuum,  $1018^\circ\text{C}$
- △ = vacuum,  $1105^\circ\text{C}$
- =  $\text{H}_2$ ,  $1018^\circ\text{C}$
- + =  $\text{H}_2$ ,  $1115^\circ\text{C}$
- =  $\text{H}_2$ ,  $1108^\circ\text{C}$
- x =  $\text{H}_2$ ,  $1212^\circ\text{C}$

- = reaction in  $\text{N}_2$
- x =  $\text{CO}_2$ ,  $1048^\circ\text{C}$
- + =  $\text{CO}_2$ ,  $1116^\circ\text{C}$
- =  $\text{NH}_3$ ,  $1048^\circ\text{C}$
- =  $\text{NH}_3$ ,  $1055^\circ\text{C}$
- ▲ =  $\text{SO}_2$ ,  $1016^\circ\text{C}$
- =  $\text{SO}_2$ ,  $1060^\circ\text{C}$

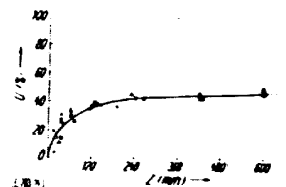
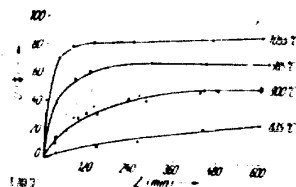


Fig.13:  $\text{ZnO} + \text{Al}_2\text{O}_3$  1:1;  $2.5 \text{ t/cm}^2$ ;  
 $\text{N}_2$  atmosphere and  $\text{CO}_2$  influence

Fig.14:  $\text{ZnO} + \text{Al}_2\text{O}_3$  1:1;  $2.5 \text{ t/cm}^2$ ;  $\text{N}_2$   
 Dependence upon particle size.

- = reaction in  $\text{N}_2$
- x = reaction in  $\text{N}_2 + 1\% \text{ CO}_2$ ,  $910^\circ\text{C}$
- = reaction in  $\text{CO}_2$ ,  $910^\circ\text{C}$ .

- ex =  $\text{Al}_2\text{O}_3$  particle size  $53 \mu$
- + =  $\text{Al}_2\text{O}_3$  particle size  $75 \mu$
- =  $\text{Al}_2\text{O}_3$  particle size  $125 \mu$
- △ =  $\text{Al}_2\text{O}_3$  particle size  $155 \mu$

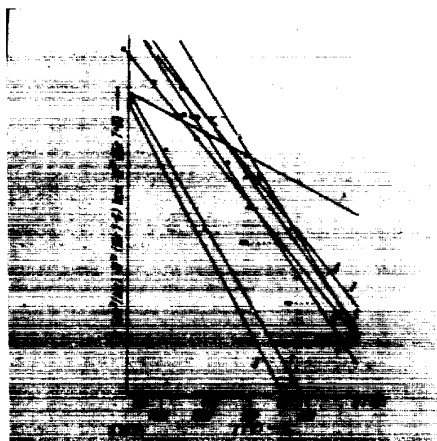


Fig.15:  $\text{MgO} + \text{Fe}_2\text{O}_3$  1:1;  $2.5 \text{ t/cm}^2$ ;  
 $\text{N}_2$  and  $\text{O}_2$  influence

Fig.16: Arrhenius straight lines for the  
 treated systems.

- = reaction in  $\text{N}_2$  atmosphere
- = reaction in  $\text{N}_2 + 3.5\% \text{ O}_2$ ,  $827^\circ\text{C}$
- = reaction in  $\text{N}_2 + 20\% \text{ O}_2$ ,  $827^\circ\text{C}$
- ▲ = reaction in  $\text{O}_2$  atmosphere,  $827^\circ\text{C}$
- ▼ = reaction in  $\text{N}_2 + 3.5\% \text{ O}_2$ ,  $865^\circ\text{C}$
- = reaction in  $\text{N}_2 + 20\% \text{ O}_2$ ,  $865^\circ\text{C}$

1. — x — =  $\text{MgO} + \text{Cr}_2\text{O}_3$ ,  $\text{N}_2$
2. — ○ — =  $\text{MgO} + \text{Cr}_2\text{O}_3$ ,  $\text{N}_2 + 3.5\% \text{ O}_2$
3. — + — =  $\text{MgO} + \text{Cr}_2\text{O}_3$ , vacuum
4. — ○ — =  $\text{ZnO} + \text{Cr}_2\text{O}_3$ ,  $\text{N}_2$
5. — △ — =  $\text{CaO} + \text{Cr}_2\text{O}_3$ ,  $\text{N}_2$
6. — □ — =  $\text{MgO} + \text{Al}_2\text{O}_3$ ,  $\text{N}_2$
7. — ○ — =  $\text{ZnO} + \text{Al}_2\text{O}_3$ ,  $\text{N}_2$
8. — □ — =  $\text{MgO} + \text{Fe}_2\text{O}_3$ ,  $\text{N}_2$