Studies on the Reactions between Oxides in Solid State at Higher Temperatures. I. The Reaction between Magnesium Oxide and Titanium Oxide.*

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Introduction. From an early date, reactions in solid state, especially those between certain oxides at relatively high temperatures, have widely been used practically in the ceramic or the silicate industry, in the production of catalysts and pigments as well as in the various branches of chemical industry. Nevertheless, there have been a rather few scientific researches in this branch of chemistry. Although these reactions have recently become the object of a number of investigators, it is still desirable that more experimental results will be accumulated. The author has been studying for several years the addition reactions with the powder mixtures between a group of basic and of acidic oxides in the solid state, and the results will be published in a series of forthcoming papers.

By the reaction in solid state, the product is at first in an amorphous state, from which the new compound crystallizes out easily, when the reaction temperature is sufficiently high. At the lower temperature, the crystal growth is difficult, and this amorphous state is particularly active as a solid catalyst.(1) But the main object of the present series of investigation is not to discuss about this amorphous state. The experiments have been carried on in the temperature range so high that the reaction products may be considered to crystallize out comparatively easily. The present paper deals with the reaction between magnesium oxide and titanium oxide.

The reaction between magnesium oxide and titanium oxide was first studied by Hautefeuille.(2) He obtained magnesium ortho- and metatitanate ($2MgO{\cdot}TiO_2$ and $MgO{\cdot}TiO_2$) by fusing titanium oxide to-

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* A summarized translation of the papers published in Japanese in *J. Chem. Soc. Japan*, **59** (1938), 1412 (preliminary report); **60** (1939), 212, 314, 949.

(1) *Cf.*, for instance, J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 146, Leipzig (1938); G. F. Hüttig, *Z. angew. Chem.* **49** (1936), 882.

(2) P. Hautefeuille, *Ann. chim. phys.*, [4], **4** (1865), 169.

gether with magnesium chloride, and their densities were mentioned as 3.52 and 3.91, respectively. Wartenberg and Prophet(3) studied the fusion curve of the system magnesium oxide and titanium oxide and obtained two maxima, corresponding to the melting points of $2MgO \cdot TiO_2$ and $MgO \cdot 2TiO_2$ (dititanate). Büssem, Schusterius and Ungewiss(4) studied röntgenographically the reaction products between magnesium oxide and titanium oxide at 1460° and confirmed the existence of the three titanates, $2MgO \cdot TiO_2$, $MgO \cdot TiO_2$ and $MgO \cdot 2TiO_2$. Tammann(5) reported that the "reaction temperature" between magnesium oxide and titanium oxide in solid state was 725°. Jander(6) suggested that, in the solid reaction, $2MgO \cdot TiO_2$ was formed most easily among the three titanates. However, in studying the effect of titanium oxide on the sintering of magnesite, the present author(7) found that $MgO \cdot TiO_2$ was formed more readily than $2MgO \cdot TiO_2$ even in a mixture of $MgO : TiO_2 = 2 : 1$.

As it is a very interesting problem, which of the compounds is formed at first by a reaction between solid substances where two or more addition compounds can be present,(6)(8) the present experiment has been commenced mainly to make clear the order of formation of the three titanates in this reaction. In the meanwhile, Jander and Bunde(9) have studied the solid reaction of this system by the X-ray method and reported that $MgO \cdot TiO_2$ was formed at first, whatever the mixing ratio of the two components might be, and that, while $MgO \cdot 2TiO_2$ was formed comparatively easily, the formation of $2MgO \cdot TiO_2$ was very difficult. As for the fact that $2MgO \cdot TiO_2$ is difficult to be formed, the result of the following experiment agrees with that of Jander and Bunde, but as for the order of formation of $MgO \cdot TiO_2$ and $MgO \cdot 2TiO_2$, the conclusion of the two experiments are different.

Besides, it has been known that many solid reactions can be influenced by water vapour and other gases.(10) Especially, as studied throughly by Tamaru and Andô,(11) the reaction between calcium oxide and stannic oxide is accelerated remarkably by the traces of reducing gases due to the reduction of stannic oxide. As titanium oxide is comparatively easily reduced into lower oxides,(12) it is expected that a reducing atmosphere may also have an accelerating effect upon the present reaction, and the author has actually found this effect, qualitatively. However, this problem was not treated in the present research. The experiments were carried out in a current of dry air.

I. Reaction products at 1400°. In order to confirm the kinds of the addition compounds formed by the solid reaction between MgO and

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(3) H. v. Wartenberg and E. Prophet, *Z. anorg. allgem. Chem.*, **208** (1932), 369.

(4) W. Büssem, C. Schusterius and A. Ungewiss, *Ber. deut. keram. Ges.*, **18** (1937), 433.

(5) G. Tammann, *Z. anorg. allgem. Chem.*, **149** (1925), 68.

(6) W. Jander, *Z. Angew. Chem.*, **49** (1936), 879.

(7) *J. Soc. Chem. Ind., Japan*, **42** (1939), 387, 202B.

(8) W. Jander, *Z. Angew. Chem.*, **47** (1934), 235.

(9) W. Jander and K. Bunde, *Z. anorg. allgem. Chem.*, **239** (1938), 418.

(10) *Cf.* J. A. Hedvall, *loc. cit.*, 157, 204, 211 etc.

(11) S. Tamaru and N. Ando, *Z. anorg. allgem. Chem.*, **184** (1929), 385; **195** (1931), 309; *J. Chem. Soc. Japan*, **52** (1931), 36, 107.

(12) N. Nasu, *Science Repts. Tohoku Imp. Univ.* Ser. I, **25** (1936), 510; *J. Chem. Soc. Japan*, **56** (1935), 542, 659.

TiO_2 and to know their properties, uniform mixtures of various proportions of MgO and TiO_2 were pressed into small cylindrical bodies and heated at 1400° for 10 hours in a platinum boat; the densities of the reaction products were measured, they were studied by the X-ray method, and the compositions of them were determined analytically. As the lowest eutectic point of this system has been reported as 1625°(3), it might be sure that at 1400° the reaction proceeded in solid state without any formation of a liquid phase.

MgO used was the "Shika, extra pure", and TiO_2 was a "Kahlbaum" preparation; both of them were very fine powders. TiO_2 has three modifications, and it has been known that the preparation obtained from a solution is in anatase modification, and on heating, it changes irreversibly to rutile.(13) Their densities are 3.840 and 4.239, resepectively. The density of TiO_2 used here was 3.839, and it changed to 4.163 when heated at 1200° for 5 hours.

As shown in Table 1, the densities of the reaction products are always smaller than those of the mechanical mixtures of the corresponding composition, and as three singular points are found at $MgO:TiO_2=2:1$, 1:1 and 1:2, it is readily supposed that the three titanates corresponding to the above compositions are formed.

Table 1. Densities and compositions of the reaction products at 1400°. §

No. of sample	Mixing ratio $MgO:TiO_2$	Density	Composition (%)				
			MgO	$2MgO\cdot TiO_2$	$MgO\cdot TiO_2$	$MgO\cdot 2TiO_2$	TiO_2
1	—	3.493	100.0				
2	20 : 1	3.494	82.5	16.1	0.9	0.5	0.0
3	6 : 1	3.511	50.9	47.2	1.1	0.9	0.0
4	3 : 1	3.532	21.7	76.5	0.9	1.5	0.0
5	2 : 1	3.541	3.0	89.0	6.5	1.4	0.0
6	3 : 2	3.656	2.4	54.3	35.2	8.1	0.0
7	1 : 1	3.856	1.9	2.0	84.7	11.3	0.0
8	2 : 3	3.682	1.9	1.6	21.2	77.3	0.0
9	1 : 2	3.610	2.0	0.2	2.4	85.3	10.1
10	1 : 5	3.915	1.9	0.4	0.3	34.7	62.7
11	—	4.225					100.0

§ Mixing of the components and calculation of the compositions were carried out under the assumption that the two preparations were completely pure (ignition losses being considered).

This was confirmed by the X-ray method. At the same time, it was proved that in the reaction products TiO_2 was in the rutile modification. It seemed that there existed no appreciable amount of solid solutions between these compounds. The lattice constants of $2MgO\cdot TiO_2$, $MgO\cdot TiO_2$

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(13) *Cf.* J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 37, London (1927).

and TiO_2 are shown in Table 2, which are all in good agreement with the data hitherto given. The interference lines of $MgO{\cdot}2TiO_2$ are given in Table 3; the crystal structure of which is not certain.

Table 2. Lattice constants.

Crystal	Crystal form	Lattice constant	
		observed here	hitherto given
$2MgO{\cdot}TiO_2$	Cubic (Spinel str.)	$a = 8.42$Å	$a=8.41$Å ; (14) 8.413Å (4)
$MgO{\cdot}TiO_2$	Hexagonal (Rhombohedral)	$a = 5.46$Å, $\alpha = 55.0°$	$a=5.40$Å, $\alpha=55°1'$ (15) ; $a=5.54$Å, $\alpha=54°39'$ (16)
TiO_2 (Rutile)	Tetragonal	$a = 4.58$Å, $c = 2.95$Å	$a=4.58$Å, $c/a=0.66_1$ (17)

Table 3. Interference lines of $MgO{\cdot}2TiO_2$

Intensity §	$\sin\theta$ §§	Intensity §	$\sin\theta$ §§
w	0.195	vw	0.570
vw	0.248	w	0.582_5
st	0.276_5	m	0.628
vw	0.339	w	0.682
st	0.354	vw	0.737
w	0.401	w	0.771_5
w	0.437	w	0.781
m	0.495	vw	0.876
m	0.519_5		
w	0.556		

§ Roughly estimated as very strong, strong, medium, weak and very weak.

§§ For K_α and K_β lines of iron.

The determination of the compositions of the reaction products were carried out as follows:—To the finely pulverized sample was added 10 parts of a 20% ammonium chloride solution, and it was warmed on a water-bath for 40 minutes, while stirred constantly. The amount of MgO dissolved was regarded as free magnesium oxide. A 10% ammonium

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(14) Tom. F. W. Barth and E. Posnjak, *Z. Krist.*, **82** (1932), 325.

(15) Wm. H. Zachariasen, *Skrifter Norske Videnskaps-Akad. i Oslo*, **1**, (1928), 7; *Chem. Abstracts*, **23** (1929), 1790.

(16) T. Barth and E. Posnjak, *Z. Krist.*, **88** (1934), 265, 271.

(17) *Cf.* R. Glocker, "Materialprüfung mit Röntgenstrahlen," 2. Aufl., 240, Berlin (1936).

chloride solution, used by Büssem and coworkers,(4) was proved too dilute. By a similar treatment, it was proved that, $2MgO{\cdot}TiO_2$ was completely soluble in 4 N hydrochloric acid with a trace of $MgO{\cdot}TiO_2$, and that all the $MgO{\cdot}TiO_2$ with a small part of $MgO{\cdot}2TiO_2$ was dissolved in 12 N hydrochloric acid, while the major part of $MgO{\cdot}2TiO_2$ and free TiO_2 were insoluble even in concentrated hydrochloric acid. Therefore, by determining the solubility of each sample in these three reagents, it is possible to calculate the amounts of the three titanates formed and of free MgO and TiO_2. The results are also given in Table 1.

From these experiments it is obvious that three titanates,

Magnesium orthotitanate	$2MgO{\cdot}TiO_2$
Magnesium metatitanate	$MgO{\cdot}TiO_2$,
Magnesium dititanate	$MgO{\cdot}2TiO_2$,

are formed by the solid reaction between MgO and TiO_2 at 1400°; the purity of each of the three titanates obtained from the equivalent mixtures is 85–90%.

II. Course of the reaction between 780° and 1200°. The pressed cylinders of the mixtures corresponding to the three titanates, i.e., $MgO:TiO_2=1:2$, 1:1 and 2:1, and, as a case of excess MgO, a mixture of $MgO:TiO_2=6:1$ were heated at 1000° and 1200°, and in some instances at 780° and 900° also, for various durations of time; the course of reaction was followed by determining the compositions of the products analytically,* and the results were checked by the X-ray method.

The mixtures used for the reactions at 1000° and 1200° were heated previously to 600° to remove possible traces of hydroxide and carbonate of magnesium and kept in a desiccator; those used at 780° and 900° were treated at 400°, (because it was proved that at 600° the reaction might somewhat take place). The experiments were carried out in a platinum furnace fitted with a potentiometric temperature regulator. As already mentioned, a constant current of air, carefully dried with phosphorus pentoxide, was passed through the reaction tube during the experiments.

The compositions of the reaction products are given in Tables 4–7, and in some instances, they are graphically plotted in Figures 1–3. (In acid treatment, the solubilities of $MgO{\cdot}TiO_2$ and $MgO{\cdot}2TiO_2$ in 4 N and

Table 4. Course of the reaction, $MgO:TiO_2=1:2$.

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
780°	0.5	15.1	4.8	16.8	63.2
	1	14.0	6.9	18.8	60.2
	3	12.0	11.6	20.8	55.6
	6	10.9	11.6	26.3	51.2
900°	0.5	7.8	13.7	38.2	40.3
	1	6.8	14.6	41.7	36.9
	3	4.7	15.8	50.6	29.0
	6	4.0	11.9	60.0	24.0

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* There are only two or three instances of solid reaction whose courses have been studied analytically.

Table 4.—(*Concluded*)

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	$MgO\cdot TiO_2$	$MgO\cdot 2TiO_2$	TiO_2
1000°	0.5	5.4	4.8	65.5	24.3
	1	4.3	5.3	69.9	20.6
	3	3.3	9.2	68.0	19.4
	6	3.3	7.8	70.4	18.5
1200°	0.5	3.7	0.3	80.9	15.1
	1	3.4	0.6	82.3	13.7
	3	3.1	0.6	83.5	12.8
	6	2.9	0.5	84.9	11.7
	12	2.4	0.6	87.1	10.0

Table 5. Course of the reaction, $MgO : TiO_2 = 1 : 1$.

Reaction temperature	Time (hrs.)	Composition of the products (%)			
		MgO	$MgO\cdot TiO_2$	$MgO\cdot 2TiO_2$	TiO_2
780°	0.5	26.3	11.6	16.4	45.6
	1	25.3	13.7	18.4	42.6
	3	21.8	25.0	16.4	36.8
	6	19.3	33.1	15.4	32.2
900°	0.5	16.7	28.3	36.2	18.8
	1	12.2	43.5	33.3	11.0
	3	8.3	62.6	20.8	8.3
	6	7.4	65.8	20.3	6.6
1000°	0.5	10.4	36.5	53.2	0.0
	1	8.3	49.8	41.9	0.0
	3	4.8	71.1	24.1	0.0
	6	3.7	78.1	18.3	0.0
1200°	0.5	3.6	78.7	17.2	0.5
	1	3.7	80.2	14.3	1.8
	3	3.1	81.4	15.2	0.3
	6	2.8	83.5	13.8	0.0
	12	2.6	84.1	13.1	0.0

Table 6. Course of the reaction, $MgO : TiO_2 = 2 : 1$.

Reaction temperature	Time (hrs).	Composition of the products (%)				
		MgO	$2MgO\cdot TiO_2$	$MgO\cdot TiO_2$	$MgO\cdot 2TiO_2$	TiO_2
1000°	0.5	28.5	0.0	54.3	17.5	0.0
	1	27.5	0.0	61.1	11.4	0.0
	3	27.1	0.0	62.7	10.2	0.0
	6	26.0	4.0	60.5	9.5	0.0
1200°	0.5	22.1	15.9	57.2	4.4	0.4
	1	21.3	18.2	57.3	3.0	0.2
	3	15.7	39.4	42.3	2.6	0.0
	6	12.8	49.7	36.1	1.4	0.0
	12	11.6	54.7	32.2	1.5	0.0

Table 7. Course of the reaction, $MgO:TiO_2 = 6:1$.

Reaction temperature	Time (hrs.)	Composition of the products (%)				
		MgO	$2MgO\cdot TiO_2$	$MgO\cdot TiO_2$	$MgO\cdot 2TiO_2$	TiO_2
1000°	0.5	63.8	0.0	30.4	5.8	0.0
	1	63.1	0.0	35.0	2.0	0.0
	3	63.1	0.0	34.9	2.0	0.0
	6	62.4	2.0	34.6	1.0	0.0
1200°	0.5	51.4	45.8	1.8	1.0	0.0
	1	50.9	46.7	2.4	0.0	0.0
	3	51.1	46.1	2.4	0.4	0.0
	6	50.6	47.9	1.5	0.0	0.0
	12	50.4	48.7	0.9	0.0	0.0

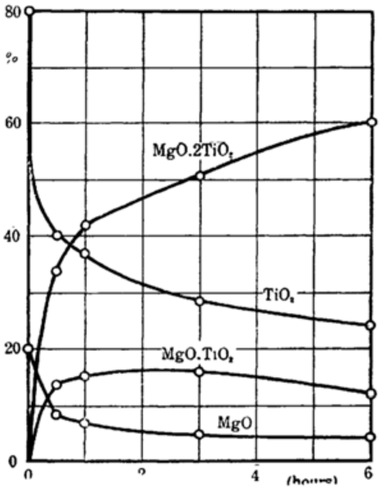

Fig. 1. Course of the reaction, $MgO:TiO_2 = 1:2$ at 900°.

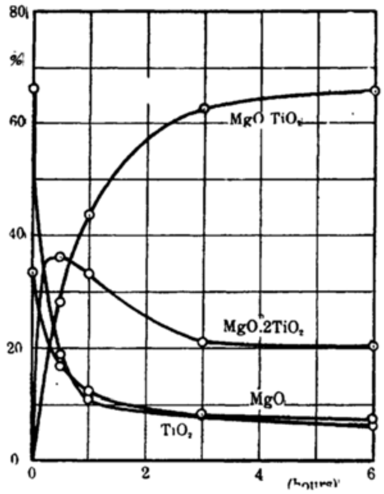

Fig. 2. Course of the reaction, $MgO:TiO_2 = 1:1$ at 900°.

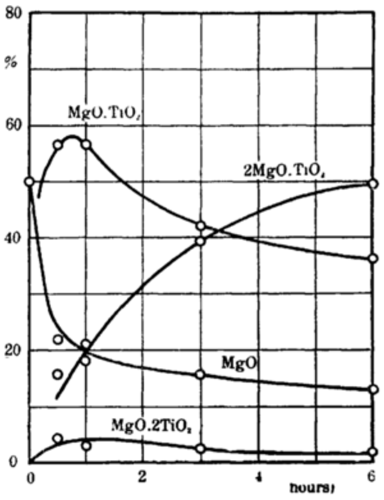

Fig. 3. Course of the reaction, $MgO:TiO_2 = 2:1$ at 1200°.

12 N HCl, respectively, were proved to increase with the decreasing reaction temperature. This might be attributed to the incompleteness of the crystal growth of the two titanates, i.e., to the existence of the amorphous reaction product, but the existence of the solid solutions might also be suspected.) With a mixture, $MgO:TiO_2=1:2$, it is obvious that the main reaction product is always $MgO\cdot 2TiO_2$; and it can be interpreted that some $MgO\cdot 2TiO_2$ accompanied is formed locally where MgO exists in excess, because the mixing of the components could never be completely homogeneous. In the case of $MgO:TiO_2=1:1$, while at the early stage

of the reaction there exists more $MgO{\cdot}2TiO_2$ than $MgO{\cdot}TiO_2$, the ratio of the two titanates is reversed as the reaction proceeds, and finally $MgO{\cdot}TiO_2$ becomes the main reaction product. So it may easily be recognized that the initial reaction product in this case is also $MgO{\cdot}2TiO_2$, and $MgO{\cdot}TiO_2$ is formed by the further reaction between $MgO{\cdot}2TiO_2$ thus obtained and the excess MgO. $2MgO{\cdot}TiO_2$ is never found in this mixture. This compound is very difficult to be formed, and in a stoichiometric mixture it is formed at 1200° at length, but the reaction is hardly completed at this temperature. With the mixtures of a large excess of MgO, e.g., $MgO:TiO_2=6:1$, the formation is easily completed at 1200°. The results of the röntgenographic studies agree with these results.

From these results it could be concluded that, by the reaction between MgO and TiO_2 in solid state, the first reaction product is $MgO{\cdot}2TiO_2$, whatever the mixing ratio of the two components might be; when an excess of MgO is present, $MgO{\cdot}TiO_2$ is formed gradually; and while $2MgO{\cdot}TiO_2$ is formed similarly, the velocity of its formation is very slow in the temperature range observed here. The reaction consists of the following three consecutive reactions:

$$MgO + 2TiO_2 \rightarrow MgO{\cdot}2TiO_2\,,$$
$$MgO{\cdot}2TiO_2 + MgO \rightarrow MgO{\cdot}TiO_2$$
$$MgO{\cdot}TiO_2 + MgO \rightarrow 2MgO{\cdot}TiO_2\,.$$

III. Influence of the experimental conditions on the course of reaction. The conclusion about the order of the formations of $MgO{\cdot}TiO_2$ and $MgO{\cdot}2TiO_2$ differs, as previously stated, in the above experiment and in the experiment of Jander and Bunde.(9) As this may be due to the difference in some of the experimental conditions, the experiments were repeated under various conditions.

(1) *The reaction in loose powder form with TiO_2 in rutile modification*:— In the experiment of Jander Bunde, TiO_2 was heated to 800° before use, and they stated that the preparation thus obtained was in rutile modification*, and the reaction was carried out with powder mix-

Table 8. Reaction in powder form with rutile.

Mixture	Reaction temperature	Time (hrs.)	Composition of the products (%)			
			MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
$MgO:TiO_2$ $=1:2$	1000°	0.5	15.7	0.0	21.8	62.5
		3	12.0	1.5	37.7	48.8
	1200°	1	5.1	0.0	74.4	20.4
$MgO:TiO_2$ $=1:1$	1000°	0.5	30.2	0.0	16.4	53.4
		3	28.5	0.9	23.3	47.2
	1200°	1	15.8	10.4	70.6	3.1

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* Although 915°, given by A. Schröder [*Z. Krist.*, **66** (1928), 493], may be regarded as the most probable transition temperature of anatase into rutile, under certain conditions rutile seems to be obtained already at as low as 800°.

tures in loose form. To compare with their experiment, the reaction experiment in loose powder form was made at 1000° and 1200° by using the TiO_2 preparation previously heated to 1200°, i.e., rutile. MgO, too, was used after the same heat treatment. The results are given in Table 8, which lead to a conclusion, more distinctly than the results in the last paragraph; that $MgO{\cdot}2TiO_2$ is the first reaction product. It goes without saying that the whole reaction proceeds slowly.

(2) *The reaction in loose powder form with anatase*:— The experiment in loose powder form with TiO_2 preparation used in the last paragraph, i.e., anatase, was also made. As shown in Table 9, although the reaction proceeds slowly, the course of the reaction is quite identical as before.

Table 9. Reaction in powder form with anatase, 1000°.

Mixture	Reaction time (hrs.)	Composition of the products (%)			
		MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
$MgO : TiO_2 = 1 : 2$	0.5	7.2	11.9	44.6	36.4
	3	4.4	8.6	63.9	23.2
$MgO : TiO_2 = 1 : 1$	0.5	13.5	19.4	67.1	0.0
	3	8.3	50.7	41.0	0.0

(3) *Influence of water vapour*:— It has been already cited that, in some instances, the influence of water vapour on the solid reaction is remarkable.(10) Although in the present experiment, this influence is always excluded carefully, Jander and Bunde touched nothing on this problem. Therefore, by way of precaution, an experiment to confirm this influence was carried out. A constant current of air was passed through a water reservoir at 98° and then into the reaction vessel; other experimental conditions were the same as in paragraph II. The results are given in Table 10; and it shows that, although the reaction seems to be slightly accelerated by the presence of water vapour, the course of the reaction in this case is also unchanged.

Table 10. Influence of water vapour, 1000°.

Mixture	Reaction time (hrs.)	Composition of the products (%)			
		MgO	$MgO{\cdot}TiO_2$	$MgO{\cdot}2TiO_2$	TiO_2
$MgO : TiO_2 = 1 : 2$	0.5	5.6	6.4	61.5	26.5
	3	3.0	8.7	70.4	17.9
$MgO : TiO_2 = 1 : 1$	0.5	8.2	50.7	41.1	0.0
	3	4.7	71.1	24.2	0.0

As seen from these experiments, the reaction proceeds, under various experimental conditions, in the same manner, and $MgO{\cdot}TiO_2$ could never be regarded as the first reaction product. Therefore, it can be concluded that, in general cases or—if it is permitted to use the word "normal experimental condition" as Jander(18) has previously used—under normal conditions, the course of the solid reaction between MgO and TiO_2 is as above mentioned, and even if $MgO \cdot TiO_2$ happens to be formed at first, it must be under special conditions.

IV. The reaction $MgO \cdot TiO_2 + TiO_2$ and $MgO \cdot 2TiO_2 + MgO$. The reactions between $MgO \cdot TiO_2$ and TiO_2, and $MgO \cdot 2TiO_2$ and MgO at 900° were studied further. The results of the experiments together with the purities of the two titanates used are shown in Tables 11 and 12.

Table 11. The reaction $MgO \cdot TiO_2 + TiO_2$ at 900°.

Reaction time (hrs.)	Composition (%)			
	MgO	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	TiO_2
(sample)	2.9	81.8	15.3	0.0
0	1.7	48.9	9.1	40.3
1	1.8	28.6	43.1	26.5
3	1.6	14.7	67.4	16.4
6	1.7	13.7	68·9	15.8

Table 12. The reaction $MgO \cdot 2TiO_2 + MgO$ at 900°.

Reaction time (hrs.)	Composition (%)			
	MgO	$MgO \cdot TiO_2$	$MgO \cdot 2TiO_2$	TiO_2
(sample)	2.1	0.3	88.8	8.8
0	18.5	0.2	74.0	7.3
1	14.7	17.0	64.9	3.4
3	12.4	27.1	59.5	1.0
6	12.2	28.3	58.5	1.0

The reaction between $MgO \cdot TiO_2$ and TiO_2 to form $MgO \cdot 2TiO_2$ proceeds more easily than the formation of $MgO \cdot TiO_2$ from $MgO \cdot 2TiO_2$ and MgO. From these facts, too, it is readily anticipated that $MgO \cdot 2TiO_2$ is the first reaction product by the solid reaction between MgO and TiO_2.

V. Mechanism of the reaction. In order that a reaction takes place actually between solid substances, it is necessary first of all that a part of the atoms (or atom groups) of the components is in a deviated position from the normal crystal lattice, i.e., in a state of disorder.(19)

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(18) W. Jander and E. Hoffmann, *Z. anorg. allgem. Chem.*, **218** (1934), 211.

(19) *Cf.* W. Jost, "Diffusion und chemische Reaktion in festen Stoffen," 39, Dresden and Leipzig (1937).

Then, at the contact surface of the two components, these atoms may exchange with each other, forming an amorphous layer of the mixture of them, and from which a new reaction product crystallizes out easily so long as the reaction temperature is high enough.(1)(6)

When a crystalline film of the reaction product is formed, further reaction is only possible by the diffusion of the two components through this film. Which of the components diffuses chiefly, depends on the nature of the reaction. By the reaction of silicate formation, it is believed that the basic oxide, e.g. MgO, diffuses(6)(18); by the spinel formation, Hild(20) has regarded that the basic oxide diffuses, while others(21) have considered *vice versa*. Wagner(22) has suggested that in ion crystals the smaller cation diffuses generally, and this supposition was proved for the reaction: $2AgI + HgI = Ag_2HgI_4$(23), where equivalent quantities of Ag^+ and Hg^{++} ions are exchanged in Ag_2HgI_4 phase, and Ag_2HgI_4 is formed newly at the two boundaries, AgI/Ag_2HgI_4 and Ag_2HgI_4/HgI_2. He has presented analogous interpretation for the formation of spinels and silicates.(22)

From these points of view, it may be admitted for the mechanism of the present reaction that, at the contact surface of magnesium oxide and titanium oxide, an amorphous layer of these mixtures is formed at first, the amount of which is not so much, within the temperature range observed here, from which the stable reaction product (in this case $MgO{\cdot}2TiO_2$) crystallizes out easily; and further reaction proceeds by the diffusion of the two components—probably in the form of Mg^{++} and Ti^{++++} ions—through this phase. Further discussions about the amorphous layer at the early stage of the reaction and the diffusion component are abridged here.*

As repeatedly stated, the first reaction product in this reaction is always $MgO{\cdot}2TiO_2$. About the problem which compound is formed at first by a reaction between solid substances in which many addition compounds can be formed, the relation is very complicated. For the formation of silicates, Jander(6)(18) has considered that the relative difficulty of the formation depends chiefly on the crystal structure of the addition compounds, namely, as the crystal structure of orthosilicates with tetrahedral SiO_4-group may be regarded as simple compared with the structure of metasilicates with long fibrous structure as -Si-O-Si-, the former crystallizes more readily from the amorphous layer and is formed at first. Contrary to Jander, Wagner(22) has considered that, as the diffusion in orthosilicates is easier than in metasilicates, even if both silicates are formed equally at the beginning of the reaction, metasilicate layer does not build up, and only the amount of orthosilicates increases; the relation is just as in the oxidation of metals where many oxide layers can be formed. At any rate, as it may be understood, the relative difficulty of

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(20) K. Hild, *Z. physik. Chem.*, A, **161** (1936), 317.

(21) W. Jander and W. Stamm, *Z. anorg. allgem. Chem.*, **199** (1931), 165; G. Hüttig and E. Zeidler, *Kolloid-Z.*, **75** (1936), 170.

(22) C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 309.

(23) E. Koch and C. Wagner, *ibid.*, **34** (1936), 317.

* Recently, W. Jander and G. Leuthner have studied about the amorphous reaction product between MgO and TiO_2. [*Z. anorg. allgem. Chem.*, **241** (1939), 57.]

diffusion in crystals also depends upon their crystal structures—for instance, the diffusion in orthosilicates with simple constitution is easier than in metasilicates with complicated fibrous structure—, crystals of simple structure can be found from either argument at the early stage of the reaction.

In the present case, although the crystal structure of $MgO{\cdot}2TiO_2$ is not certain, when it is permitted to assume that the crystal structure of $MgO{\cdot}2TiO_2$ is more simple than that of $MgO{\cdot}TiO_2$ and of $2MgO{\cdot}TiO_2$, it may be considered that $MgO{\cdot}2TiO_2$ crystallizes out most easily from the amorphous layer, and, even if other compounds are formed at the same time, they do not build up. Thus it is well interpreted that $MgO{\cdot}2TiO_2$ is the first reaction product. As the reaction proceeds and the thickness of $MgO{\cdot}2TiO_2$ layer increases, the diffusion in this layer becomes gradually difficult, and $MgO{\cdot}TiO_2$ begins to be formed at the contact surface of $MgO{\cdot}2TiO_2$ and MgO. $2MgO{\cdot}TiO_2$ is formed also in the same way, but with great difficulty.

By the solid reaction, if the diffusion process takes place slowly enough compared with the surface reaction, which is just so in most cases, the rate of the whole reaction is controlled only by the diffusion,(24) and there exists an approximate relation between the thickness of the reaction product (ξ) and the reaction time (t) :(25)

$$d\xi/dt = k'/\xi \qquad \text{or} \qquad \xi^2 = 2k't + C'.$$

By the reaction with powder mixtures, it is impossible to determine directly the thickness of the layer of the product, and it is the amount of the product formed, or of the components reacted (x) which can be measured; therefore, in order to apply the above relation to this case, the relation between them should be known. Jander(26) has derived the following relation, by assuming that the reaction proceeds uniformly on a spherical substance with a radius of r:

$$1-\sqrt[3]{1-x} = \xi/r,^*$$

and so

$$\{1-\sqrt[3]{1-x}\}^2 \doteq 2kt + C.$$

Although this relation holds strictly for a substance in a small amount, through which another substance in large excess diffuses, it can also be applied approximately, at least in the early stage of the reaction, to a mixture of any mixing ratio, and it has been proved for the reactions between barium carbonate and silica, etc.(26)(6)

It was tried to apply the relation to the result of the present experiment, and the relation between $\{1-\sqrt[3]{1-x}\}^2$ and the reaction time was plotted for the mixture corresponding to the first reaction product,

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(24) *Cf.* W. Jost, *loc. cit.*, 180.

(25) H. Braune, *Z. physik. Chem.*, **110** (1924), 147.

(26) W. Jander, *Z. anorg. allgem. Chem.*, **163** (1927), 1.

* x is expressed as the fraction of the original amount of the component.

i.e., $MgO:TiO_2=1:2$, in paragraph II. As the measured points fall on a straight line so long as the reaction temperature is not so high and the reaction proceeds not so far, it is recognized that the main part of the reaction is controlled by diffusion, but the line does not fall on the origin, showing that there exists a notable rapid initial reaction. It is natural that the above relation does not hold when the reaction proceeds too far.

For the rapid initial reaction, the following considerations may be given at present: as the reaction is exothermic,** at the beginning of the reaction, the true reaction temperature becomes inevitably higher than the furnace temperature, and, as the experiment has been carried out with pressed bodies of the mixtures of very fine powders, the surface reaction proceeds to a considerable amount. A similar initial reaction has been reported by Ward and Struthers(27) in the reaction between barium carbonate and ferric oxide.

The values of k for the diffusion process of $MgO{\cdot}2TiO_2$ formation can be roughly represented in terms of

$$k = A\ e^{-Q/RT},$$

or

$$k = 3.9\times10^4\ e^{-36{,}000/RT},$$

where Q may be regarded as the energy of activation in calories per mole of the diffusion.

As shown in Table 13, the value of Q is the same order as those which have been known in other solid reactions, and is also similar to those of the comparatively well studied diffusion processes between metals.(31)

Table 13. Energies of activation of the solid reactions.

Reaction	Mixing ratio	Product	Q (Kcal./mole)
$BaCO_3 + SiO_2$	1 : 10	Ba_2SiO_4 ?	50.2 (26), 40.7 (28)
,,	1 : 1	,,	42.6 (29)
$CaO + SiO_2$	1 : 1	Ca_2SiO_4	32.2 (29)
$BaCO_3 + Fe_2O_3$	1 : 1	$BaO{\cdot}Fe_2O_3$	25.0 (< 820°), 19.0 (> 820°) (27)
$BaCO_3 + WO_3$	1 : 10	$BaWO_4$	43.6 (30)
,,	1 : 1	,,	35.6 (29)
$MgO + TiO_2$	1 : 2	$MgO{\cdot}2TiO_2$	36.0

** When a reaction between solid substances takes place smoothly, it must be an exothermic one.

(27) R. Ward and J. D. Struthers, *J. Am. Chem. Soc.*, **59** (1937), 1849.

(28) W. Jander and E. Hoffman, *Z. anorg. allgem. Chem.*, **200** (1931), 245.

(29) W. Jander and W. Stamm, *ibid.*, **190** (1930), 65.

(30) W. Jander, *ibid.*, **166** (1927), 31.

(31) *Cf.* W. Jost, *loc. cit.*, 131.

Summary.

(1) It has been confirmed that three titanates, i.e., magnesium orthotitanate ($2MgO{\cdot}TiO_2$), metatitanate ($MgO{\cdot}TiO_2$) and dititanate ($MgO{\cdot}2TiO_2$), are formed by the solid reaction between MgO and TiO_2; $2MgO{\cdot}TiO_2$ is soluble in 4 N HCl and $MgO{\cdot}TiO_2$ in 12 N HCl, while $MgO{\cdot}2TiO_2$ is scarcely soluble even in 12 N HCl.

(2) By following the course of the reaction analytically, it has been found that the first reaction product is $MgO{\cdot}2TiO_2$, whatever the mixing ratio of the two components may be; $MgO{\cdot}TiO_2$ is formed gradually when an excess of MgO is present; and $2MgO{\cdot}TiO_2$ is formed similarly, but with difficulty.

(3) The reaction has been proved to proceed, under various experimental conditions, in the same manner, and $MgO{\cdot}TiO_2$ can never be regarded as the first reaction product.

(4) The reaction between $MgO{\cdot}TiO_2$ and TiO_2 to form $MgO{\cdot}2TiO_2$ has taken place more easily than the formation of $MgO{\cdot}TiO_2$ from $MgO{\cdot}2TiO_2$ and MgO.

(5) It has been concluded that, although there exists a notable rapid initial reaction, a further reaction is controlled by the diffusion of the two components through the reaction product. The energy of activation of the diffusion process of $MgO{\cdot}2TiO_2$ formation has been estimated to be 36.0 Kilocalories per mole.

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