Studies on the Reactions between Oxides in Solid State at Higher Temperatures. III.⁽¹⁾ The Reaction between Magnesium Oxide and Stannic Oxide.⁽²⁾

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Introduction. In the system magnesium oxide and stannic oxide the existence of magnesium orthostannate ($2MgO \cdot SnO_2$), which has a cubic spinel structure with a unit cell size of $a=8.580$Å and a density of 4.738,⁽³⁾ has been known. The composition of the precipitate, obtained from a water solution of the two salts, has been considered as $MgSnO_3 \cdot nH_2O$.⁽⁴⁾ But there has been no report on the solid reaction between magnesium oxide and stannic oxide. The phase equilibrium of this system at high temperatures is also unknown.

The present paper deals with the solid reaction with pressed cylinders of the powder mixtures of magnesium oxide and stannic oxide. The experiments were carried out in a current of dry oxygen. Since the solid reaction involving stannic oxide is, as it has been studied by Tamaru and Andô,⁽⁵⁾ accelerated remarkably by the existence of a minute quantity of a reducing agent, this effect should carefully be excluded.

I. Reaction Products at 1400°. As done in the previous experiments,⁽¹⁾ mixtures of various proportions of MgO and SnO_2 were heated at 1400° for 10 hours. The densities of the reaction products were measured, and the amounts of free MgO and those of MgO and SnO_2 soluble in 4N hydrochloric acid were determined. The methods of determinations were the same as described in the first report. The results are given in Table 1. The products were studied further by the X-ray method. As there was no indication of melting in all the reaction products, the reaction was considered to have proceeded in solid state.

The density of each of the reaction products was always smaller than the theoretical value calculated as a mechanical mixture of the components, but no singular point could be observed in the relationship between the mixing ratios and the densities.

From the results of the solubility measurements, it was found that MgO in the reaction products dissolved always in 4N HCl completely, and that, while SnO_2 preparation heated at 1200° was practically insoluble

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(1) (a) I, *This Bulletin*, **16** (1941), 428.
(b) II, *This Bulletin*, **16** (1941), 455.

(2) The main part of this paper has been published in Japanese in *J. Chem. Soc. Japan*, **61** (1940), 1023.

(3) G. Natta, L. Passerini, *Atti. accad. Lincei*, Rend. [6], **9** (1929), 557; *Chem. Zentr.*, **1929**, II, 828.

(4) *Cf.* J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 419, London (1927).

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

Table 1. Reaction products at 1400°.

Mixing ratio		Density	Free MgO (%)	Soluble in 4 N HCl		
MgO (%)	$MgO:SnO_2$*			MgO (%)	SnO_2 (%)	MgO/SnO_2
100	—	3.493				
61.05	6 : 1	4.201	41.49	19.56	38.95	1.88
46.40	3 : 1	4.456	18.94	27.46	53.60	1.91
35.41	2 : 1	4.725	1.98	33.43	64.59	1.93
29.50	3 : 2	5.046	2.22	27.28	51.67	1.97
21.40	1 : 1	5.466	1.22	20.18	38.78	1.95
15.13	2 : 3	5.834	1.23	13.90	27.89	1.86
7.85	1 : 3	6.376	1.09	6.76	14.07	1.81
0	—	6.953				

* Approximately.

even in concentrated hydrochloric acid, SnO_2 in the reaction products became soluble in 4N HCl. As the molecular ratio of the amount of MgO to that of SnO_2, which was soluble in 4N HCl, respectively,⁽⁶⁾ was always nearly equal to 2, it was concluded that $2MgO \cdot SnO_2$ was the only addition compound formed in this condition. With a mixture of $MgO:SnO_2=2:1$, almost pure $2MgO \cdot SnO_2$ was obtained.

The results of the röntgenographic studies, too, agreed with these results. The lattice constant of $2MgO \cdot SnO_2$ was found to be $a=8.61$Å, and it seemed that no distinct solid solutions were formed in this system.

II. Course of the reaction between 900° and 1100°. Mixtures of $MgO:SnO_2=2:1$ and 1:1 were heated at a certain temperature in the range between 900° and 1100°, and the course of reaction was followed analytically. The preparations were ignited at about 1200° before use. The results are given in Tables 2 and 3. No reaction was practically observed at 900°, and the reaction temperature,⁽⁷⁾ or the temperature at which the reaction begins to take place, was found to be about 950°. This temperature was far higher than those of the reactions between MgO or CaO and TiO_2;⁽¹⁾ however, it was easily recognized that the reaction velocity increased more rapidly than in the latter reactions with the increasing reaction temperature.

As the combination ratio of MgO to SnO_2 was found to be smaller than the normal molecular ratio of $2MgO \cdot SnO_2$ in the temperature range studied here and especially at the beginning of the reaction, it was suspected that a compound such as $MgO \cdot SnO_2$ was formed at first. However, even in a mixture of $MgO:SnO_2=1:1$, the above ratio increased continuously toward 2 as the reaction proceeded, and, moreover, in the X-ray patterns of the reaction products in this period, only the inter-

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(6) Hereafter, this ratio will be mentioned as the combination ratio of MgO to SnO_2.

(7) G. Tammann, *Z. anorg. allgem. Chem.*, **149** (1925), 21.

Table 2. Course of the reaction with a mixture of $MgO:SnO_2 = 2:1$ ($MgO = 34.70\%$).

Reaction temperature	Time (hrs.)	Free MgO (%)	Soluble in 4N HCl		
			MgO (%)	SnO_2 (%)	MgO/SnO_2
900°	10	34.75	—	—	—
950°	10	34.19	0.64	2.51	0.95
1000°	0.5	33.86	0.71	2.29	1.16
	1	33.27	1.42	3.91	1.36
	3	30.05	4.83	10.68	1.69
	6	26.40	8.27	18.12	1.71
	10	22.71	12.14	25.37	1.79
1050°	0.5	28.09	6.56	15.15	1.61
	1	23.65	11.27	25.09	1.68
	3	18.30	16.79	35.92	1.75
	6	13.42	21.35	46.90	1.70
	10	12.20	22.97	48.48	1.77
1100°	0.5	20.72	14.24	33.19	1.60
	1	15.17	19.88	42.36	1.75
	3	11.78	23.07	50.04	1.72
	6	8.04	27.17	54.38	1.87
	10	8.09	26.30	54.26*	1.81

Table 3. Course of the reaction with a mixture of $MgO:SnO_2 = 1:1$ ($MgO = 21.11\%$).

Reaction temperature	Time (hrs.)	Free MgO (%)	Soluble in 4N HCl		
			MgO (%)	SnO_2 (%)	MgO/SnO_2
900°	10	20.83	—	—	—
950°	10	20.55	0.56	2.17	0.97
1000°	0.5	20.90	0.20	2.27	0.33
	1	20.09	1.00	4.29	0.88
	3	17.49	3.72	11.91	1.17
	6	15.73	5.54	14.11	1.47
	10	12.73	8.82	22.73	1.45
1050°	0.5	18.10	2.99	10.18	1.10
	1	15.10	6.18	16.10	1.43
	3	7.73	13.83	31.78	1.63
	6	5.94	15.47	34.49	1.68
	10	6.40	15.06	34.89	1.61
1100°	0.5	10.81	10.62	26.57	1.49
	1	8.47	13.05	32.65	1.49
	3	6.53	14.91	36.49	1.53
	6	5.18	16.31	37.08	1.64
	10	4.67	16.83	38.07	1.65

ference lines of the addition compound, $2MgO \cdot SnO_2$, were observed besides those of the uncombined MgO and SnO_2. Therefore, the formation of a new compound other than $2MgO \cdot SnO_2$ was not probable. As no deviations of the positions of $2MgO \cdot SnO_2$-lines were observed, the existence of a solid solution between $2MgO \cdot SnO_2$ and SnO_2, too, was hardly considered. The excess of SnO_2 existed perhaps in an amorphous state and was soluble in 4N HCl.(8)

III. Experiment in open air. As already mentioned, the above described experiments were carried out entirely in a current of dry oxygen. For comparison, the experiment in open air was made at 950° without passing dry oxygen. The change of free MgO is given in Table 4 which shows that the reaction takes place more rapidly than in the previous experiments. But the composition of the reaction products changed with the reaction as before; for instance, with a mixture of $MgO:SnO_2=1:1$, the combination ratio of MgO to SnO_2 was fuond to be 1.64 after 10 hours.

The rapid reaction rate in this experiment is probably due to the effect of the traces of reducing gases, which are inevitably contained in air, because the effect of reducing atmosphere on the reactivity of stannic oxide is, as it is previously stated,(5) very remarkable. The effect of water vapour may also be considered.(9)

Table 4. Experiment in open air at 950°.

Reaction time (hrs.)	Free MgO (%)	
	$MgO:SnO_2=2:1$	$MgO:SnO_2=1:1$
0.5	31.97	19.17
1	29.09	16.57
3	24.66	12.65
6	20.67	11.10
10	20.59	8.50

IV. Discussion of the results. In the present reaction, it must be noticed that, although $2MgO \cdot SnO_2$ is the only stable addition compound, the product formed at first seems to contain a large excess of stannic oxide, and as the reaction proceeds the product tends gradually to have the normal composition of $2MgO \cdot SnO_2$. This phenomenon may be explained as follows:

By a solid reaction, as it has been discussed in the first report,(1a) an amorphous layer of the mixture of the components is formed at first at their contact surface, and from which a new reaction product crystallizes out. The amorphous product may be regarded as a solid solution of the components. In the reaction between MgO and SnO_2, it is considered that the crystallization of the addition compound, $2MgO \cdot SnO_2$, is somewhat difficult, and at lower temperatures the amorphous solid solution reaches to a considerable amount. The crystal lattices of SnO_2 in this state are disturbed, and the oxide becomes soluble in dilute hydrochloric acid, and while MgO in this state exists probably as free MgO, namely, it is soluble in 20% ammonium chloride solution; therefore the combination ratio of MgO to SnO_2 becomes apparently smaller than 2. When the amount of the amorphous product reaches to a definite value, the

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(8) Formerly, the present author(2) has considered that, while the excess of SnO_2 exists forming a solid solution with $2MgO \cdot SnO_2$, the crystal structure of which is the same as that of pure $2MgO \cdot SnO_2$. But it seems more probable to consider the existence of an amorphous state.

(9) *Cf.* J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 157, 204, 221, etc., Leipzig (1938).

stable addition compound, $2MgO \cdot SnO_2$, begins to crystallize out smoothly. The later reaction proceeds by the diffusion of the two components through this crystalline layer, and, as the amount of $2MgO \cdot SnO_2$ increases, the above ratio tends gradually toward 2.

In the previous experiments,(1) it was considered that the stable addition compound crystallized out readily, and no particular attention was paid in the amorphous reaction product, although in the reaction between MgO and TiO_2,(1a) as it was discussed on that occasion, the tendency of its existence was observed at lower temperatures. (In the reaction between CaO and TiO_2,(1b) as only the amounts of free CaO were determined, the formation of the amorphous product was not certain.) As the temperature ranges in which the two reactions were studied were comparatively higher than their reaction temperatures, it was admitted that considerable amounts of the amorphous product did not exist in these experiments.

As it is already stated, the magnesium stannate obtained from a solution has been reported to have a composition of $MgSnO_3 \cdot nH_2O$.(4) On the other hand, it has been known that, in the system CoO and SnO_2, though the composition of the stannate obtained from a water solution is $CoC \cdot SnO_2$, no interference lines of the compound are found in the X-ray patterns, and that at higher temperatures it is easily decomposed into $2CoO \cdot SnO_2$ and SnO_2.(10)(11) In these systems, it seems that, while a metastannate hydrate ($MO \cdot SnO_2 \cdot nH_2O$) is obtained from a solution, it is decomposed into an amorphous mixtures on heating, and from which an anhydrous orthostannate ($2MO \cdot SnO_2$) is formed.

In the solid reaction between ZnO and TiO_2, Cole and Nelson(12) have reported that, while the reaction product obtained at first at lower temperatures had an apparent composition of $ZnTiO_3$, it was proved to be a solid solution between $ZnTiO_4$ and TiO_2; that the unit cell size of the solid solution, which had a cubic spinel structure, decreased with the content of TiO_2; and that the composition of the solid solution was altered as the reaction proceeded. Further, they stated that the formation of the solid solution, which dissociated into $ZnTiO_4$ and TiO_2 completely above 1050°, was reversible with temperature. This reaction resembles to the present reaction. However, while the excess of TiO_2 exists thereby as a solid solution with a definite crystal structure, the excess of SnO_3 exists as an amorphous state, or as an amorphous solid solution of the two components, in the present reaction. Besides, in the present case, the composition of the reaction product, obtained as low as 950° by the experiment in open air, too, tended gradually to $2MgO \cdot SnO_2$, and, moreover, it was proved that no decomposition of pure $2MgO \cdot SnO_2$ took place after 10 hour's tempering at 1100°. Therefore, the formation of the amorphous solid solution could hardly be regarded as reversible in these temperatures, and, as it is already mentioned, the formation of a solid solution with a definite crystal structure is also unlikely.

The existence of a solid solution has been observed in the system,

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(10) J. A. Hedvall, *Z. anorg. allgem. Chem.*, **92** (1915), 369.

(11) G. Natta and L. Passerini, *Gazz. chim. ital.*, **59** (1929), 620; *Chem. Zentr.*, **1930**, I, 128.

(12) S. S. Cole and W. K. Nelson, *J. Phys. Chem.*, **42** (1938), 245.

CaO and TiO_2, too.(1b) In this reaction, however, no distinct deviation of the composition of the reaction product was observed during the main part of the reaction, and it might be considered that, only with mixtures containing an excess of CaO, after the major part of TiO_2 reacted forming $CaO \cdot TiO_2$, a solid solution rich in CaO was obtained.

In the present reaction, although a considerable amount of the amorphous reaction product exists, as the later reaction is possible by the diffusion of the two components through the layer of the crystalline reaction product, it is expected that the rate determining step of the whole reaction lies also in this process; and indeed the relation,(13)

$$\left\{1-\sqrt[3]{1-x}\right\}^2 = 2kt\,,$$

holds approximately between 1000° and 1100°, and from which the apparent energy of activation is calculated roughly as $Q=100$ Kilocalories per mole.(14)

However, it must be mentioned that, while a rapid initial reaction has been found in the solid reactions between MgO or CaO and TiO_2,(1) the present reaction proceeds at the beginning of the reaction, especially at lower temperatures, more slowly than the rate expressed by the above equation, namely, there exists rather an induction period. Further, as it is already stated that the velocity of the present reaction increases rapidly with increasing reaction temperature, so the energy of activation, 100 Kilocalories per mole, is far greater than those of the reactions between MgO or CaO and TiO_2 and other reactions so far studied.(1a) The reaction temperature of this reaction is also very high. From these facts it is anticipated that the mechanism of the present reaction is somewhat different from those of the reactions previously studied.

Summary.

(1) It has been found that $2MgO \cdot SnO_2$ is the only stable addition compound which is formed by the solid reaction between MgO and SnO_2, and that the compound is soluble in 4N HCl.

(2) While the reaction in dry oxygen begins at about 950°, it takes place more readily in open air, probably, due to the effect of the traces of reducing gases contained in air.

(3) The reaction product seems to exist at first in an amorphous state, and, when the amount of which reaches to a certain value, $2MgO \cdot SnO_2$ becomes to crystallize out smoothly; the later reaction proceeds by the diffusion of the components through this crystalline layer.

(4) It has been considered that the main part of the reaction is controlled by the diffusion process, and the energy of activation of which has been estimated as about 100 Kilocalories per mole.

(5) An induction period has been observed at the beginning of the

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(13) These notations have been given in the first report.

(14) Calculated from the amounts of combined MgO with a mixture, $MgO:SnO_2 = 1:1$. Nearly equal value was obtained from the amounts of combined SnO_2, too.

reaction, and the energy of activation is very great when compared with those of the reactions hitherto studied.

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