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

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Introduction. There exists only one addition compound, spinel ($MgO \cdot Al_2O_3$), in the system magnesium oxide and aluminium oxide. This compound belongs to the cubic system with a unit cell, consisting of 8 molecules of $MgO \cdot Al_2O_3$ and is able to contain an excess of aluminium oxide forming a solid solution. According to Hägg and Söderholm,(3) the lattice constant of pure $MgO \cdot Al_2O_3$ is $a = 8.056$Å, and at the Al_2O_3 the richest limit of the solid solution with α–Al_2O_3, which lies at about 67 mol % of Al_2O_3, or corresponds approximately to $MgO \cdot 2Al_2O_3$, and it decreases to $a = 7.968$Å.(4) They have stated further that the density of the solid solution is explained only under the assumption that the positions of the oxygen lattices are unchanged, and an excess of aluminium atoms exists by replacing the positions of the magnesium atoms and leaving a part of them unoccupied.

The solid reactions of the formation of $MgO \cdot Al_2O_3$ and those of the other spinel type compounds, especially those at lower temperatures, have been studied by many investigators.(5) However, there is no report in which the velocity of their formations has been followed quantitatively. Also the composition of the solid solution, formed at the first stage, is not certain. The present research is carried out with a view to make these two points clear and, further, to compare the results with those of the reactions in the previous papers.(6)(7)(8)(1) The experimental procedure was almost the same as before.

I. Reaction products at 1400°. Mixtures of MgO and Al_2O_3, corresponding to $MgO : Al_2O_3 = 2:1$, $1:1$ and $1:2$, were heated at 1400° for 10 hours; the amounts of free MgO of the products were determined and their X-ray photographs were taken. The results are given in Table 1.

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(1) IV, This Bulletin, **17** (1942), 70.

(2) The main part of this paper has been published in Japanese in *J. Chem. Soc. Japan*, **62** (1941), 477.

(3) G. Hägg and G. Söderholm, *Z. physik. Chem.*, B, **29** (1935), 88.

(4) The limit of solubility differs somewhat with the temperature. It differs also with the modifications of Al_2O_3, and the range of the unstable solid solution spreads to γ-Al_2O_3.

(5) For instance, W. Jander and W. Stamm, *Z. anorg. allgem. Chem.*, **199** (1931), 165; G. Hüttig and E. Zeidler, *Kolloid-Z.*, **75** (1936), 309; K. Hild, *Z. physik. Chem.*, A, **161** (1936), 317; W. Jander and H. Pfister, *Z. anorg. allgem. Chem.*, **239** (1938), 95.

(6) I, This Bulletin, **16** (1941), 428.

(7) II, This Bulletin, **16** (1941), 455.

(8) III, This Bulletin, **17** (1942), 64.

Since the reaction product, $MgO \cdot Al_2O_3$, as well as Al_2O_3, heated at higher temperatures (α–Al_2O_3), are insoluble even in concentrated acids, it is impossible to separate the reaction product from the unreacted Al_2O_3.

Table 1. Reaction products at 1400°.

Mixing ratio $MgO:Al_2O_3$	Free MgO (%)	Lattice constant of the spinel formed. (Å)
2:1	21.18	8.05_1
1:1	3.06	8.03_8
1:2	0.72	8.00_7

It was understood that, with a mixture of $MgO:Al_2O_3=2:1$, the reaction was completed forming pure $MgO \cdot Al_2O_3$, because the calculated amount of free MgO was 22.08%,(9) and the lattice constant of the spinel obtained coincided with that of pure spinel, given by Hägg and Söderholm.(3) With a mixture of $MgO:Al_2O_3=1:2$, the lattice constant of the spinel became considerably smaller, and the interference lines of α–Al_2O_3 were observed distinctly at the same time.

II. Course of the reaction between 800° and 1200°. The course of the reaction was followed by determining free MgO of the products, and some of the products were studied by the X-ray method. Preparations were ignited before use.

As shown in Table 2, the reaction took place already considerably at 800°, but it was never completed even at 1200°. The lattice constants of the spinels in these products agreed approximately with that of pure $MgO \cdot Al_2O_3$, and the positions of the interference lines of MgO and of α–Al_2O_3 were also unchanged.

Table 2. Free MgO (%) of the reaction products.

(1) $MgO:Al_2O_3 = 1:2$ ($MgO = 16.51\%$).

Reaction time (hrs.)		0.5	1	3	6	10
Reaction temperature (°C) ...	800	—	15.27	14.90	14.55	14.30
	900	—	13.43	13.08	12.19	11.30
	1000	12.96	10.94	10.00	8.85	8.35
	1100	7.38	6.60	5.73	5.29	—
	1200	4.85	4.17	3.56	3.08	2.95

(2) $MgO:Al_2O_3 = 1:1$ ($MgO = 28.34\%$).

Reaction time (hrs.)		0.5	1	3	6	10
Reaction temperature (°C) ...	800	—	26.49	26.03	25.81	25.28
	900	—	24.97	23.73	23.57	22.26
	1000	23.49	22.49	20.75	19.21	18.21
	1100	17.56	15.78	14.69	13.03	—
	1200	12.90	12.18	10.58	9.47	8.61

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(9) Although free MgO obtained is slightly smaller than this value, its smaller value cannot be avoided when the amount of which is practically too much.

Table 2.—(*Concluded*)

(3) $MgO:Al_2O_3 = 1:2$ ($MgO = 44.17\%$).

Reaction time (hrs.)		0.5	1	3	6	10
Reaction temperature (°C)	800	41.71	41.17	40.61	40.77	40.39
	900	39.98	39.40	38.40	37.87	37.21
	1000	36.66	36.14	34.95	34.56	—
	1100	31.61	29.89	28.16	27.20	—

III. Discussion of the results. It is obvious from the above experiments that pure $MgO \cdot Al_2O_3$, which is the richest in the basic component, MgO, within the possible range of the solid solution, is formed at the early stage of the reaction, whatever the mixing ratio of the components may be. It seems that, only with the mixtures containing an excess of Al_2O_3, the solid solution, rich in Al_2O_3, is formed after the greater part of MgO has been reacted to form $MgO \cdot Al_2O_3$. The tendency is quite reverse to that of the reaction between CaO and TiO_2,(7) in which the composition of the solid solution, formed at first, is the richest in the acid component. While the lattice constant of the spinel, obtained with a mixture of $MgO:Al_2O_3=1:1$ at 1400°, is a little smaller than that of pure $MgO \cdot Al_2O_3$, it is considered that, even in a stoichiometric mixture, the solid solution, rich in Al_2O_3, is formed locally where Al_2O_3 exists in excess toward the end of the reaction, leaving a part of MgO in free state.

As the lattice constant of the spinel, $a=8.00_7$Å, obtained with a mixture of $MgO \cdot Al_2O_3=1.2$ at 1400°, is 0.04_4Å smaller than that of pure $MgO \cdot Al_2O_3$, $a=8.05_1$Å, it is calculated that the spinel in this case contains approximately the excess of 8.5 mol % Al_2O_3, in forming a solid solution. Hägg and Söderholm(5) confirmed the limit of the solid solution by fusing the components. It is also expected, by the solid reaction, that a solid solution with more Al_2O_3 is obtained when the reaction proceeds further.

In the present reaction, there exists a rapid initial reaction just as in the reactions between MgO or CaO and TiO_2.(6)(7) A further reaction seems to be controlled by the diffusion of the components through the reaction product; the energy of activation of the process with a stoichiometric mixture is calculated as $Q=41.1$ Kilocalories per mole, and the value is nearly equal to those of the above two reactions.

Finally, when the influence of the mixing ratio of the components on the rate of the present reaction is considered, it is found that the reaction takes place more readily with a mixture of $MgO:Al_2O_3=2:1$, namely, when MgO exists in excess, than with the other mixtures. This cause will be discussed in the next paper.

Summary.

(1) It has been found that pure $MgO \cdot Al_2O_3$ is formed at first in this reaction, and the solid solution rich in Al_2O_3 is formed gradually when an excess of Al_2O_3 is present.

(2) Although there exists a rapid initial reaction, the later reaction is controlled by the diffusion process with an energy of activation of 41.1 Kilocalories per mole.

(3) The reaction proceeds more easily with the mixtures containing an excess of MgO than with the other mixtures.

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