Studies on the Reactions between Oxides in Solid State at Higher Temperatures. IV.[1] The Reaction between Calcium Oxide and Stannic Oxide.[2]

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Introduction. In the system calcium oxide and stannic oxide, there exists calcium metastannate ($CaO \cdot SnO_2$), and it has been reported that the compound has a cubic perovskite structure with a lattice constant of $a=3.92$Å.[3] Zulkowski[4] reported that he obtained $2CaO \cdot SnO_2$. Tamaru and Andô[5] found that the solid reaction of this system was remarkably accelerated by the traces of reducing agents and they studied the mechanism of which in detail. They reported that, while in vacuum only a slight reaction was observed at 900°, in a reducing condition it proceeded smoothly even at still lower temperatures; that the end product of the reaction with a mixture of excess calcium oxide was $2CaO \cdot SnO_2$; and that the compound was soluble in dilute hydrochloric acid (1:1). Besides, Tamaru and Sakurai[6] obtained $CaO \cdot SnO_2$ by the oxidation of $CaO \cdot SnO$ when an excess of stannous oxide was present.

The present paper deals with the solid reaction of this system in a current of dry oxygen. The experimental procedure was almost the same as in the previous reports.[1][7][8]

(1) III, *This Bulletin*, **17** (1942), 64.
(2) Published in Japanese in *J. Chem. Soc. Japan*, **62** (1941), 199.
(3) V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad. i Oslo*, I, **1926**, No. 2; *Chem. Zentr.*, **1926**, II, 1390.
(4) K. Zulkowski, *Chem. Ind.*, **24** (1901), 422; *Chem. Zentr.*, **1901**, II, 564.
(5) S. Tamaru and N. Andô, *Z. anorg. allgem. Chem.*, **184** (1929), 385; **195** (1931), 309; *J. Chem. Soc. Japan*, **52** (1931), 36, 107.
(6) S. Tamaru and H. Sakurai, *Z. anorg. allgem. Chem.*, **195** (1931), 24; *J. Chem. Soc. Japan*, **52** (1931), 120.
(7) *This Bulletin*, **16** (1941), 428.
(8) *This Bulletin*, **16** (1941), 455.

I. Reaction Products at 1300°. Mixtures of various proportions of $CaCO_3$ and SnO_2 were heated at 1300° for 10 hours, and the amounts of free CaO and those of CaO and SnO_2 soluble in 4N HCl were determined. Some of the reaction products began to melt already at 1400°. The results of the experiment with the densities of the products are given in Table 1.

Table 1. Reaction products at 1300°.

Mixing ratio		Density	Free CaO (%)	Soluble in 4N HCl		
CaO (%)	CaO : SnO_2			CaO (%)	SnO_2 (%)	CaO/SnO_2
100	—	3.205				
69.07	6 : 1	3.816	45.99	—	—	—
52.75	3 : 1	4.359	17.77	35.02	47.30	1.99
42.67	2 : 1	4.727	0.00	42.05	57.51	1.96
35.82	3 : 2	5.058	0.00	—	—	—
27.13	1 : 1	5.608	0.00	26.31	67.50	1.05
15.69	1 : 2	6.192	0.00	15.04	40.81	0.99
0	—	6.981				

Table 2. X-ray data of CaO·SnO_2.

Intensity	sin θ* (obs.)	hkl	sin θ* (calc.)
vw	0.225	β 100	0.223
m	246	100	246
w	314	β 011	315_5
vst	347_5	011	348
w	446	β 200	446
st	492_5	200	492
w	543_5	120	543_5
w	551	β 112	550_5
m	598_5	121	598
st	608	112	607_5
w	689	220	691
m	696_5	022	696
vw	706	β 301	706
w	735	221	734_5
vw	745	212	742
st	778_5	310	777
		301	779_5
vw	839	β 312	838
vw	843	β 213	842
w	885_5	320	883
vw	906_5	β 004	905_5
m	914	231	913
		132	915
st	922	312	923
w	928	213	928
$a = 3.93$ Å, $b = 3.99$ Å, $c = 3.87$ Å.			

* For K_α and K_β lines of iron.

Table 3. Interference lines of 2CaO·SnO_2.

Intensity	sin θ*
vw	0.179_5
m	197
m	343
vst	356_5
w	447_5
vw	461
st	492
w	548_5
m	595_5
st	606_5
w	624
w	660
st	688
vw	737
m	836
vw	853
vw	862_5
w	911
w	919
w	932_5
vw	941
w	947_5
m	971
w	977
w	982

* Anticathode: Fe.

As more CaO than necessary to form $2CaO \cdot SnO_2$ remains in free state, and excess SnO_2 over $CaO \cdot SnO_2$ is insoluble in 4 N HCl, it is admitted that the two stannates, calcium orthostannate ($2CaO \cdot SnO_2$), and metastannate ($CaO \cdot SnO_2$) are formed in this reaction, and both of them are soluble in 4N HCl.

From the corresponding mixtures, the two stannates were obtained almost in pure state. As the products were dissolved equally well in 1N HCl, it was difficult to determine the amounts of $2CaO \cdot SnO_2$ and $CaO \cdot SnO_2$ separately.

In the X-ray patterns of the reaction products, too, no indication of the existence of other addition compounds could be obtained, and it seemed that no appreciable amounts of solid solutions were formed in this system. As shown in Table 2, although the principal lines of $CaO \cdot SnO_2$ can be interpreted from the lattice constant, a=3.92Å, which has hitherto been given,(3) the values, a=3.93Å, b=3.99Å and c=3.87Å, must be given as correct. It has already been known that some crystals of the perovskite type is transformed from the cubic into the rhombic structure.(9)(10) While the crystal structure of $2CaO \cdot SnO_2$ is not certain, as seen from the interference lines given in Table 3, so far is obvious that the compound has a different structure from that of $CaO \cdot SnO_2$.

II. Course of the reaction between 900° and 1200°. The course of the reaction was followed analytically with mixtures of CaO and SnO_2, corresponding to $CaO:SnO_2=2:1$ and 1:1, in the range between 900° and 1200°. The preparations were ignited at 1200° before use. The results are given in Tables 4 and 5. The reaction begins to take place at about 900°, which agrees with the result of Tamaru and Andô,(5) and it proceeds smoothly with increasing reaction temperature.

With a mixture of $CaO:SnO_2=1:1$, when the reaction proceeded moderately, the ratio of CaO to SnO_2, which was soluble in 4N HCl, respectively, was nearly equal to 1; so it was obvious that the final product

Table 4. Course of the reaction with a mixture of $CaO:SnO_2=1:1$ (CaO = 27.13%).

Reaction temperature	Time (hrs.)	Free CaO (%)	Soluble in 4N HCl		
			CaO (%)*	SnO_2 (%)	CaO/SnO_2
900°	10	26.76	0.37	—	—
950°	1	26.56	0.57	4.36	0.36
	3	25.96	1.17	6.60	0.48
	6	24.40	2.73	8.86	0.83
	10	23.90	3.23	10.58	0.82
1000°	0.5	25.50	1.63	4.66	0.94
	1	—	—	6.16	—
	3	22.76	4.37	12.18	0.96
	6	21.06	6.07	16.58	0.98
	10	19.90	7.23	19.36	1.00

* Calculated.

(9) *Cf.* J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 52, London (1927).
(10) S. S. Cole and H. Espenschied, *J. Phys. Chem.*, **41** (1937), 445.

Table 4.—(*Concluded*)

Reaction temperature	Time (hrs.)	Free CaO (%)	Soluble in 4 N HCl		
			CaO (%)*	SnO_2 (%)	CaO/SnO_2
1100°	0.5	20.26	6.87	17.80	1.04
	1	16.76	10.37	24.80	1.12
	3	12.30	14.83	33.70	1.18
	6	10.56	16.57	37.70	1.18
	10	10.30	16.83	38.06	1.19
1200°	0.5	10.90	16.23	38.06	1.15
	1	8.86	18.27	43.10	1.14
	3	6.60	20.53	48.20	1.14
	6	5.56	21.57	50.84	1.14
	10	5.10	22.03	51.82	1.14

* Calculated.

Table 5. Course of the reaction with a mixture of $CaO:SnO_2 = 2:1$ ($CaO = 41.75\%$).

Reaction temperature	Time (hrs.)	Free CaO (%)	Soluble in 4 N HCl		
			CaO (%)*	SnO_2 (%)	CaO/SnO_2
900°	10	41.66	0.09	—	—
1000°	0.5	40.50	1.25	4.20	0.79
	1	40.16	1.59	5.70	0.82
	3	38.30	3.45	9.16	1.01
	6	36.38	5.37	14.18	1.02
	10	35.30	6.45	16.72	1.04
1100°	0.5	35.20	6.55	17.01	1.03
	1	31.70	10.05	23.40	1.15
	3	25.10	16.65	30.14	1.48
	6	21.56	20.19	33.72	1.61
	10	20.50	21.25	34.08	1.68
1200°	0.5	23.50	18.25	32.54	1.57
	1	21.36	20.39	35.62	1.60
	3	17.40	24.35	41.26	1.65
	6	16.00	25.75	42.98	1.68
	10	15.10	26.65	43.60	1.71

* Calculated.

in this case was $CaO \cdot SnO_2$. However, at the early stage of the reaction, the ratio was smaller than 1, and, as neither interference lines of a new compound nor deviations of the positions of $CaO \cdot SnO_2$-lines were observed in the X-ray photographs, it could be regarded, just as in the case of the reaction between MgO and SnO_2,[1] that the excess of SnO_2 existed in an amorphous state. With a mixture of $CaO:SnO_2=2:1$, as the reaction proceeded, the composition of the product tended gradually toward $2CaO \cdot SnO_2$. An example of this tendency is shown graphically in Figure 1.[11]

(11) Calculated by assuming $CaO \cdot SnO_2$ and $2CaO \cdot SnO_2$ are formed in their normal compositions.

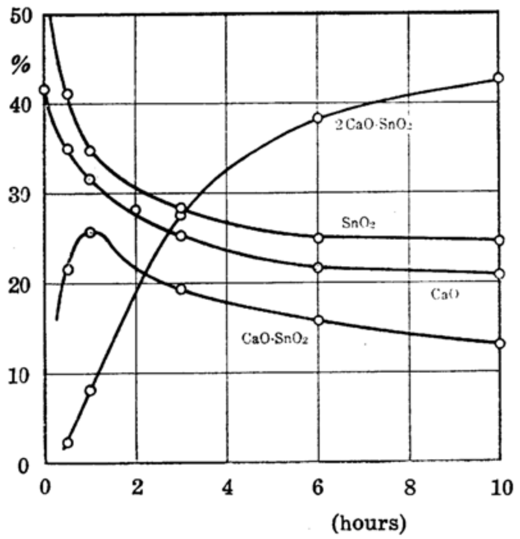

Fig. 1. $CaO:SnO_2 = 2:1$, 1100°.

Without passing dry oxygen, the reaction proceeded at 900° already with a moderate rate, but the course of the reaction was the same as before.

III. Discussion of the results. As it is clear from the above experiments, two stable addition compounds, $2CaO \cdot SnO_2$ and $CaO \cdot SnO_2$, are formed by the solid reaction between CaO and SnO_2, and there exist no appreciable solid solutions in this system. In this reaction $CaO \cdot SnO_2$ is formed at first, whatever the mixing ratio of the components may be, and, when an excess of CaO is present, $2CaO \cdot SnO_2$ is formed gradually by the further reaction between $CaO \cdot SnO_2$, thus previously formed, and the excess of CaO. The formation of a small amount of $2CaO \cdot SnO_2$ is also recognized with a mixture of CaO:SnO=1:1; however, it is probable that the compound is formed locally where CaO exists in excess. The course of the reaction is similar to that of the reaction between MgO and TiO_2,[7] in which the first reaction product, $MgO \cdot 2TiO_2$, is the richest in the acid component, and $MgO \cdot TiO_2$ and $2MgO \cdot TiO_2$ are formed by the further reactions.

It is considered that, at lower temperatures, the amorphous solid solution, which is formed at the contact surface of the two components, reaches to a measureable amount, and SnO_2 in this state is soluble in 4N HCl; so that, at the beginning of the reaction, the ratio of soluble CaO to soluble SnO_2 becomes apparently smaller than 1. When the amorphous product reaches to a certain amount, $CaO \cdot SnO_2$ crystallizes out easily. Although the amount of the amorphous product is not so large, the tendency is the same as in the reaction between MgO and SnO_2.[1]

In their experiment on the reaction between CaO and SnO_2, Tamaru and Andô[5] have considered that soluble SnO_2[12] exists as $2CaO \cdot SnO_2$. It is true that $2CaO \cdot SnO_2$ is the final reaction product in this reaction with a mixture of an excess of CaO; however, as it is obvious from the present experiment, $CaO \cdot SnO_2$ is formed at first and it is also soluble in dilute hydrochloric acid. Therefore, it must be considered also in their experiment that soluble SnO_2 exists as the two stannates, $CaO \cdot SnO_2$ and $2CaO \cdot SnO_2$. Further, although they have considered only the formation of $2CaO \cdot SnO_2$ in their discussion of the mechanism of the reaction, it must be admitted naturally that $CaO \cdot SnO_2$ is formed at first.

Finally, the relation,[7]

(12) In their experiment, soluble SnO_2 means that which is soluble in a dilute hydrochloric acid of 1:1.

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

for the amount of combined CaO holds fairly well from the beginning of the reaction, and, in the present reaction, neither a rapid initial reaction nor an induction period exists. It is considered that the reaction is also controlled by the diffusion of the two components through the reaction product, and, with a mixture of $CaO \cdot SnO_2=1:1$, the energy of activation between 950° and 1200° is calculated as Q=85 Kilocalories per mole.[13]

While the value is far greater than those of the other reactions previously studied,[7][8] it is a little smaller than that of the reaction between MgO and SnO_2[1]. On the other hand, the energy of activation of the reaction between CaO and TiO_2[8] is also slightly smaller than that of the reaction between MgO and TiO_2.[7] Thus, whether the acidic component is TiO_2 or SnO_2, the energy of activation of the reaction with CaO as the basic component is a little smaller than that of the reaction with MgO. While it has been studied in detail by Hedvall and others[14] that CaO is more reactive than MgO in the exchange reactions between certain salts and oxides in solid state, the same tendency is obtained in the addition reactions between the oxides.

Summary.

(1) It has been confirmed that two stannates, $2CaO \cdot SnO_2$ and $CaO \cdot SnO_2$, are formed by the solid reaction between the components, and both of them are soluble in 4N HCl. The crystal structure of $CaO \cdot SnO_2$, which has been considered as cubic, should correctly be assigned as rhombic with a unit cell size of a=3.93Å, b=3.99Å and c=3.87Å.

(2) The reaction begins to take place at about 900°. The reaction product exists at first in an amorphous state; when the amount of which has reached a certain value, the reaction proceeds smoothly, forming $CaO \cdot SnO_2$. $2CaO \cdot SnO_2$ is formed gradually when an excess of CaO is present.

(3) It has been considered that the reaction is controlled by the diffusion of the components through the reaction product, and the energy of activation of $CaO \cdot SnO_2$ formation has been calculated as 85 Kilocalories per mole.

(4) Whether the acidic component is TiO_2 or SnO_2, the energy of activation of the reaction with CaO has been found to be a little smaller than that of the reaction with MgO.

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(13) From the amounts of combined SnO_2, the value of Q=82 Kilocalories was obtained approximately.
(14) *Cf.* J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 67, Leipzig (1938).