Studies on the Reactions between Oxides in Solid State at Higher Temperatures. II.(1) The Reaction between Calcium Oxide and Titanium Oxide and the Photo-sensitivity of Calcium Titanate.(2)

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Introduction. As a second example of the reaction between oxides in solid state, the reaction with powder mixtures between calcium oxide and titanium oxide was studied, and, as it was found that the reaction products were photo-sensitive, some observations in this respect were also made.

It has been known from an early date that the mineral perovskite consists of calcium metatitanate ($CaO \cdot TiO_2$).(3) Ebelmen obtained the compound by fusing calcium carbonate and titanium oxide together with alkali carbonate, and there have been some reports on the synthesis of it by the use of fluxes.(3) However, about the reaction between calcium oxide and titanium oxide in solid state, there was only one research by Tammann,(4) in which he stated that the "reaction temperature" of this reaction was 675°.(5) By studying the fusion curve of

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

(2) A fuller communication has been published in Japanese in *J. Chem. Soc. Japan*, 61 (1940), 345.

(3) *Cf*. J. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, 52, London (1927).

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

(5) Quite recently, J. A. Hedvall and K. Andersson [*Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **38** (1941), 210] have reported their experiment on the solid reaction of this system, but the purpose of which was to compare the reactivity of the different preparations of TiO_2.

this system, Wartenberg and co-worker(6) supposed the existence of two other titanates besides $CaO \cdot TiO_2$, i.e., $2CaO \cdot TiO_2$ and $3CaO \cdot TiO_2$. The crystal structure of perovskite has been assigned as cubic, and the size of the unit cell has been given as a=3.795Å by Barth(7) and a=3.845Å by Levi and Natta,(8) but the latter authors reported that they could observe in their X-ray patterns some very faint lines which agreed with the size of the unit cell twice as great as the value above mentioned. Besides, natural perovskites have been reported in some instances as optically anisotropic. The density of natural perovskite lies between 4.037 and 3.974, and that of Ebelmen's preparation has been reported as 4.10.(3)

In the present research, the kinds of the addition compounds which exist in this system were confirmed at first, and then the course of reaction was followed analytically. As described in the first report, it was expected that reducing atmosphere might also have an accelerating effect upon this reaction. To prevent this effect, the experiments were carried out throughout in a current of dry oxygen.

I. Reaction products at 1350°. Uniform mixtures of various proportions of $CaCO_3$ and TiO_2 were pressed to small cylindrical bodies, and heated at 1350° for 10 hours.(9) The experimental procedure was almost the same as in the previous experiment. Both preparations used in the experiment were of Kahlbaum.(10) The densities of the reaction products were measured, and free CaO was determined by the method of Lerch and Bogue.(11) The results are given in Table 1.(12)

Table 1. Densities and free CaO of the reaction products at 1350°.

No. of sample	Mixing ratio $CaO : TiO_2$	Density	Free CaO (%)	$\frac{\text{Combined CaO}}{\text{Total TiO}_2}$
1	(CaO)	3.312		
2	6 : 1	3.492	60.73	1.49
3	3 : 1	3.620	36.20	1.38
4	2 : 1	3.721	17.86	1.39
5	3 : 2	3.907	3.69	1.39
6	1 : 1	4.056	0.00	1.00
7	1 : 2	4.086	0.00	(0.50)
8	(TiO)	4.233		

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(6) H. v. Wartenberg, H. J. Reusch and E. Saran, *Z. anorg. allgem. Chem.*, **230** (1937), 257.

(7) T. Barth, *Norsk geologik tidsskrift.*, **8** (1925), Sept.; *Chem. Zentr.*, **1926**, I, 11.

(8) G. Levi and G. Natta, *Rend. Acad. Lincei*, (1925), **39**; *Chem. Zentr.*, (1925), II, 2044.

(9) As it has been reported that the lowest eutectic point of this system is about 1450°, (6) it was considered that 1350° was the highest temperature at which the reaction might proceed with certainty in solid state.

(10) $CaCO_3$: Calciumkarbonat gefällt, zur Analyse; TiO_2: Titansäureanhydrid.

(11) W. Lerch and R. H. Bogue, *Ind. Eng. Chem.*, **18** (1926), 739.

(12) As CaO is very hygroscopic, the determination should be carried out immediately after ignition.

The densities of the reaction products were always smaller than the calculated values, assumed as mechanical mixtures, but no singular point could be observed in the relationship between the mixing ratios and the densities. The density of the sample⁽⁶⁾, i.e., $CaO:TiO_2=1:1$, was found to be 4.056, which agreed with the value given for $CaO{\cdot}TiO_2$.⁽³⁾

From the measurement of free CaO, too, it was anticipated that the sample (6) consisted of pure $CaO{\cdot}TiO_2$, because it contained no free CaO. By the mixtures with more CaO than this proportion, some free CaO was always found, but the molecular ratio of combined CaO to total TiO_2 became greater than 1, and in the sample (2) it reached approximately to a value of 1.5. Therefore, when it is assumed that the product consists of a pure compound, its empirical composition is to be $3CaO{\cdot}2TiO_2$. However, as the product of any mixing ratio did not dissolve completely even in concentrated hydrochloric acid, it was in vain to ascertain the kinds of titanates formed by the difference in solubility.

The reaction products were studied further by the X-ray method. The data of the sample (6) are given in Table 2. As no interference lines belonging to CaO and TiO_2 could be detected, it was evident that the product consisted of pure $CaO{\cdot}TiO_2$. The data indicate that the crystal is cubic with a lattice constant of $a=7.61_5$Å, but the principal

Table 2. X-ray tata of $CaO{\cdot}TiO_2$.

Intensity*	sin θ**	*hkl*	a (Å)
w	0.254	α 200	7.61
m	0.325_5	β 220	7.61
vw	0.346	β 300	7.60
vst	0.360	α 220	7.60
w	0.381_5	α 300	7.61
vw	0.422	α 311	7.61
w	0.440	α 222	7.62
w	0.460_5	β 400	7.61
vw	0.475	α 321	7.61
st	0.508	α 400	7.62
m	0.565	β 422	7.60
vw	0.583	α 421	7.60
vst	0.622	α 422	7.62
w	0.650	β 440	7.63
m	0.717	α 440	7.63
vw	0.730	β 620	7.59
st	0.802	α 620	7.63
vw	0.864	β 642	7.60
w	0.882	α 444	7.60
m	0.951	α 642	7.61
	mean		7.61_5

* Roughly estimated as very strong, strong, medium, weak and very weak. Very weak lines are omitted for the calculation of the lattice constant.

** For K_α and K_β lines of iron.

lines are explained with half the value obtained here, which confirms the observation of Levi and Natta.(8) (13)

By the sample (7), i.e., $CaO:TiO_2 = 1:2$, only the interference lines of perovskite and TiO_2 were observed, and by the samples with more CaO than the stoichiometric mixture of $CaO \cdot TiO_2$, too, no evidence was obtained which showed that any other addition compound than perovskite was formed.(14) But the positions of the interference lines of perovskite were slightly different from each other, and, as shown in Table 3, the lattice constant calculated from the main lines (as a half value) increased from 3.80Å to 3.83_5Å with increasing the ratio of combined CaO to total TiO_2 from less than 1 to about 1.5. Therefore, it was concluded that there existed a solid solution between CaO and TiO_2 —perovskite solid solution—, and the range of its existence spreads approximately from a slight excess of TiO_2 than $CaO \cdot TiO_2$ to a molecular ratio of $CaO:TiO_2 = 3:2$. $3CaO \cdot 2TiO_2$ may be regarded as a member of the solid solution, rather than a new addition compound. It is a well known fact that the addition compound between certain oxides can take up an excess of either of the components to form a solid solution; for instance, $MgO \cdot Al_2O_3$ forms a solid solution with excess Al_2O_3, and the range of its existence spreads from $MgO \cdot Al_2O_3$ to about $MgO \cdot 2Al_2O_3$.(15),(16)

Table 3. Lattice constants.

No. of sample	2	3	4	7
$\frac{\text{Combined CaO}}{\text{Total TiO}_2}$	1 49	1.38	1.39	(0.50)
hkl	Lattice constant (Å)			
α 110	3.84	3.82	3.81_5	3.79_5
α 200	3.80	3.79_5	3.81	3.80
α 211	3.84	3.83	3.82	3.80
α 220	3.85_5	3.84_5	3.83	3.81
α 310	3.83	3.82	3.81_5	3.81
α 321	3.83_5	3.83	3.82	3.80
mean	3.83_5	3.82_5	3.82	3.80

Further, by observing these results accurately, it is recognized that, while most of the interference lines of perovskite deviate and somewhat diffuse with the increase of the content of CaO, the position of 200 line

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(13) As for the crystals of the perovskite type, it has been reported that, for $PbZrO_3$, strictly speaking, a unit cell size of $a = 12.38 (= 3 \times 4.123)$ Å should be given. [A. Hoffmann, *Z. physik. Chem.*, B, **28** (1935), 65.]

(14) Besides CaO lines, some $Ca(OH)_2$ lines were detected.

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

(16) In these cases, whether the addition product of a simple molecular ratio, e.g., $MgO \cdot 2Al_2O_3$ or $3CaO \cdot 2TiO_3$, is really a member of the solid solution or an addition compound, can be decided rigorously only when the phase equilibrium in contact with the melt is made clear.

does not change within experimental errors. So it may be considered that perovskite solid solution deviates from the cubic structure gradually with the increase of the content of CaO; then it may also be explained that natural perovskites are sometimes optically anisotropic.

II. Fused products. To confirm the range of the existence of the perovskite solid solution and also of the possibility of the formations of $3CaO \cdot TiO_2$ and $2CaO \cdot TiO_2$, supposed by Wartenberg and coworkers,⁽⁶⁾ at still higher temperatures, the products obtained by the fusion of the components were studied.

Small sticks of the mixtures of $CaCO_3$ and TiO_2 corresponding to $CaO:TiO_2 = 3:1$, $2:1$ and $1:1$ were melted with oxy-acetylene flame and quenched in water; and then they were tempered at 1000° in a current of oxygen.⁽¹⁷⁾ Although it might be suspected that the components did not melt completely and also a part of the products was in glass state, the amounts of free CaO of these products were determined, which were, as shown in Table 4, nearly equal to those of the products of the corresponding mixtures at 1350°. The lattice constants of them were also almost the same as those obtained in the last paragraph.

Table 4. Free CaO of the fused products.

Mixing ratio $CaO:TiO_2$	Free CaO (%)	$\frac{\text{Combined CaO}}{\text{Total TiO}_2}$
3 : 1	36.63	1.38
2 : 1	17.15	1.41
1 : 1	0.00	1.00

With mixture $CaO:TiO_2 = 3:1$ and $2:1$, even by fusion, the ratio of CaO to TiO_2 in the solid solution could never reach to 1.5, the maximum values obtained with a mixture $CaO:TiO_2 = 6:1$ at 1350°. In order to reach this value, it seems necessary that a large excess of CaO must be present. From this experiment, too, the addition product, $3CaO \cdot 2TiO_2$, is more probably regarded as a member of the solid solution than a new compound, and, as the evidence of the formation of $3CaO \cdot TiO_2$ and $2CaO \cdot TiO_2$ could never be obtained in this experiment as well as in the products of the solid reaction, their existence could hardly be admitted at any temperature.

III. Course of the reaction. Mixtures of CaO and TiO_2, corresponding approximately to $CaO:TiO_2 = 1:1$ and $3:1$,⁽¹⁸⁾ were heated at a certain temperature in the range between 900° and 1200° for various durations of time, and the course of reaction was followed by determining

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(17) Perhaps, owing to the reduction of TiO_2, the fused products were slightly black in colour, which were naturally turned white by tempering.

(18) Owing to hygroscopicity of CaO, it was impossible to prepare mixtures of accurate composition. The content of CaO was determined analytically after heating.

free CaO. The sample of CaO used was a Merck preparation,(19) and was previously heated at 1100°; TiO_2 was used after the same heat treatment. Therefore, the crystals of the two preparations were evidently well developed compared with those of the preparations used in the first report (in paragraph II). As it has been ascertained in the previous paper that the reaction between MgO and TiO_2 in solid state proceeds in the same way under various experimental conditions, the present experiment was carried out only with pressed bodies. The results are given in Table 5.

Table 5. Free CaO (%) of the reaction products with a mixture CaO = 41.07%. ($CaO : TiO_2 = 1 : 1$).

Reaction time (hrs.)		0.5	1	3	6	10
Reaction temperature	920°	33.41	29.40	26.09	23.84	21.82
	950°	29.41	26.50	24.65	21.75	19.67
	1000°	24.97	22.83	20.38	17.77	—
	1050°	19.89	18.86	16.43	13.29	—
	1200°	16.84	15.73	13.73	12.91	—

Table 6. Free CaO (%) of the reaction products with a mixture CaO = 67.16%. ($CaO : TiO_2 = 3 : 1$).

Reaction time (hrs.)		0.5	1	3	6	10
Reaction temperature	920°	62.20	60.46	56.16	54.38	54.14
	1000°	57.64	56.14	54.46	53.45	—
	1200°	51.58	50.49	48.70	48.61	—

At 920° the reaction takes place already with a moderate rate, but it is never completed even at 1200°. By the reaction product with a mixture of $CaO : TiO_2 = 3 : 1$ at 1200° and 6 hours, the ratio of combined CaO to total TiO_2 becomes 0.81:1, which shows that a part of TiO_2 is also still in the free state.

X-ray photographs of some reaction products were taken. No other interference lines besides those belonging to perovskite, CaO (and $Ca(OH)_2$) and TiO_2 were detected. In all cases the lattice constant of perovskite was nearly equal to that of the sample (7) in the last paragraph, namely, the product might be considered to contain a slight excess of TiO_2 as solid solution, and the evidence of the formation of the solid solution with an excess of CaO was never found in the temperature range studied here.

IV. Mechanism of the reaction. The mechanism of the present reaction may be considered analogous to that of the reaction between

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(19) CaO aus Marmor, zur Analyse.

magnesium oxide and titanium oxide which has been discussed in the previous report.

By the solid reaction between magnesium oxide and titanium oxide, $MgO{\cdot}2TiO_2$ is formed most easily. In the present system, there exists only one addition compound, $CaO{\cdot}TiO_2$, but the compound has a range of solid solution, and at the beginning of the reaction the product is richest in titanium oxide, within the possible range of the solid solution, i.e., contains a slight excess of titanium oxide than the stoichiometric composition of $CaO{\cdot}TiO_2$. The tendency of the reaction product to be at first rich in titanium oxide is the same in the two reactions. It seems that, only with the mixtures containing an excess of calcium oxide, the solid solution rich in calcium oxide is formed, after the major part of titanium oxide has been reacted to form $CaO{\cdot}TiO_2$.

By plotting the relations between $\{1-\sqrt[3]{1-x}\}^2$ (20) and the reaction time for the mixture $CaO:TiO_2=1:1$,(21) it was proved that, although there was a rapid initial reaction, the later reaction was represented by the relation,(22)

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

between 920° and 1050°. (At 1200° the reaction had proceeded already too far within half an hour, so that the above relation did not hold.) The values of k thus obtained are expressed as,

$$k = 4.83\times 10^2 e^{-30,300/RT}\,.$$

The energy of activation of the diffusion process, $Q=30.3$ kilocalories per mole, is a little smaller than that of the formation of $MgO{\cdot}2TiO_2$, but it is the same order as those of the solid reactions hitherto known.(1) Thus it is concluded that the main part of the present reaction is also controlled by the diffusion of the two components through the layer of the reaction product.

The constant factor in the above equation, A, of the present experiment, $A=4.83\times 10^2$, is smaller than that of the formation of $MgO{\cdot}2TiO_2$ in the first report, $A=3.9\times 10^4$. This constant is related chiefly to the particle size of the components,(22) and, as already mentioned, the crystals of the preparations in the present experiment were well developed compared with those of the preparations used in the first report; therefore, the difference in A of the two experiments is easily understood.

V. Photo-sensitivity of calcium titanate. It was found that the reaction products kept in a glass tube turned to light red on the surface, and as the phenomenon was proved to be due to the action of light, some observations concerning this were carried out.

The results of the observations are summarized as follows:

(1) When the reaction products were left in the room, their surface turned to light red, and the colour change was more rapid when they were exposed to daylight, but the interior of the products remained white.

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(20) The notations have been given in the first report.

(21) Calculated from the amounts of combined CaO.

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

By the action of X-ray and ultra-violet ray, a colour change occurred also. When the products were kept in the dark soon after heating, the colouration did not occur, but the colour, once turned, hardly faded when the products were again placed in the dark.

(2) With different preparations used in the experiment (CaO: $CaCO_3$ of Kahlbauh or CaO of Merck; TiO_2: Kahlbaum or "Shika, extra pure") the change was observed equally well. But the phenomenon could not be observed by the magnesium titanates and also in the system zinc oxide and titanium oxide.

(3) Among the products obtained in the previous paragraphs, the products at 1200° were most sensitive, and those at 1350° were less sensitive; at 1350°, the samples (4) and (5) were comparatively sensitive, while pure $CaO{\cdot}TiO_2$ and especially the sample (7) coloured very faintly.

(4) In the presence of phosphorous pentoxide, even if the products were exposed to daylight for a long while, no colour change was observed. Therefore, it was obvious that the existence of moisture was necessary for the colouration.

(5) The coloured samples turned to white when they were heated to about 220°; the phenomenon was, namely, thermo-reversible.

As the colour change could not be observed by magnesium and zinc titanates, the penomenon may be assigned as characteristic for calcium titanate, but, perhaps, the minute impurities contained in the preparations may play an important rôle for the colouration. Further, as the traces of water is necessary for the colouration, it is supposed that some impurity decomposes water photo-chemically; the hydrogen formed thereby reduces TiO_2 to a lower oxide, the colour of which is red. However, the details of the mechanism is not yet clear.

The fact, that the products at 1200° are most sensitive, may easily be understood from the consideration that the titanate formed thereby is not yet crystallized well and is in a state of disorder, which is particularly reactive. At 1350°, the samples (4) and (5), which contain excess CaO as solid solution, are sensitive; it has been known that solid solutions turn readily into a state of disorder and are reactive in many respects.(23) On the other hand, the effect of the free CaO existing in these products may also be considered.

Recently, Williamson(24) has reported that some varieties of commercial TiO_2 and TiO_2 contaminated with iron showed reversible darkening in daylight. This is considered as a similar phenomenon obtained here, but the degree of colouration seems to be weaker than that of the present system.(25)

Summary.

(1) It has been ascertained that there exists only one addition compound, perovskite ($CaO{\cdot}TiO_2$), in the system CaO and TiO_2. As

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(23) *Cf.* J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 127, Leipzig (1938).

(24) W. O. Williamson, *Nature*, **140** (1937), 238; **143** (1939), 279.

(25) Afterwards, Williamson has reported his detailed observations in *Mineralog.* Mag., **25** (1940), 513. T. Ogawa [Reports of the 17th General Meeting, *Elect. Soc. Japan*, **1940** (3). 10] has also reported on the darkening of the ceramic bodies containing TiO_2.

for the unit cell size of pure perovskite, $a = 7.61_5$Å should be given as correct, which is twice as great as the value hitherto given.

(2) $CaO \cdot TiO_2$ has been proved to form a solid solution with the two components, the range of which spreads approximately from a slight excess of TiO_2 to $CaO:TiO_2 = 3:2$, and in which the lattice constant is enlarged and the crystal form deviates from cubic with the increase of the content of CaO.

(3) At the early stage of the solid reaction of this system, the product is richest in TiO_2 within the possible range of the solid solution; the solid solution rich in CaO may be formed gradually when an excess of CaO is present.

(4) It has been concluded that, although there exists a 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 has been calculated as 30.3 kilocalories per mole.

(5) It has been found that the reaction products turn light red by the action of light; some observations thereon have been made.

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