Studies on the Reactions between Oxides in Solid State at Higher Temperatures. VI.(1) Discussion of the Reaction Mechanism with a Special Reference to the Effect of Particle Size on the Reactions.

By Yasuo TANAKA.

(Received January 7, 1942.)

Introduction. In the present series of investigations, the author has studied several examples of the addition reactions between so-called basic and acidic oxides in the solid state at relatively high temperatures. The experiments have been carried out with the mixtures of two components, consisting of fine powders. The method of investigations was as follows: after the addition compounds, formed by the solid reactions, had been confirmed, the courses of the reactions were followed analytically by the difference of solubility of the components as well as that of the reaction products, and the results were checked by means of the X-ray method. Since the course of the reaction between MgO and TiO_2 had been proved to be the same under various experimental conditions, the other reactions were studied only with the pressed bodies of the powder mixtures. As these reactions take place only at high temperatures, it is difficult to follow the course of reaction quantitatively by the so-called Tubandt's method,(2) which determines the exchanged amount at the contact plane of the two solid substances after the reaction and which has been applied for the reactions between metals or between certain salts.

As for reaction between solid substances, it has been considered in the first report(3) that an amorphous layer of the mixture of the components is formed at first at their contact surface; that a new reaction product crystallizes out easily from this mixture, so long as the reaction temperature is sufficiently high; and that the later reaction proceeds by the diffusion of the components through this crystalline layer.(4) If the surface reaction takes place rapidly enough, comparing with diffusion, the step that determines the rate of the whole reaction lies in the diffusion process, and many solid reactions have been regarded to be controlled by this process.(5)

The mechanisms of the present reactions had been discussed to some extent in the first report as well as in the others, and it was estimated that the rates of these reactions were also determined chiefly by the dif-

---

(1) V, *this Bulletin*, **17** (1942), 186.

(2) *Cf.* C. Tubandt, "Handbuch der Experimentalphysik," Bd. XII, 1. Teil, Leipzig (1932).

(3) I, this Bulletin, **16** (1941), 428.

(4) *Cf.*, for instance, W. Jost, "Diffusion und chemische Reaktion in festen Stoffen," 39, 180, etc., Dresden and Leipzig (1937).

(5) *Cf.* G. F. Hüttig, *Z. angew. Chem.*, **49** (1936), 882; W. Jander, *Z. angew. Chem.*, **49** (1936), 879; J. A. Hedvall, "Reaktionsfähigkeit fester Stoffe," 146, etc., Leipzig (1938).

fusion process. However, these reactions were proved to have their own characteristics, and it was expected that there existed something different in their reaction mechanisms.

The present paper aims at dealing with the mechanism of these reactions in more detail, by studying theoretically as well as experimentally the effect of the particle size of each of the components on the reactions.(6) Further, the mechanism of sintering due to the solid reactions is discussed.

I. Types of Reactions. The main characteristics of the reactions studied are summarized in Table 1. Though each of the characteristics has been explained on separate occasions, some of them will be repeated here.

Table 1. Main Characteristics of the Reactions in the Present Investigations.

Reaction system	Addition compound	Solid solution range	Compound or solid solution formed at first	" Reaction temperature " (°C)	Initial reaction	Heat of** activation Kcal./mole
$MgO-TiO_2$(3)	$2MgO\cdot TiO_2$ $MgO\cdot TiO_2$ $MgO\cdot 2TiO_2$	–	$MgO\cdot 2TiO_2$	725(10)	rapid	36
$CaO-TiO_2$(7)	$CaO\cdot TiO_2$	$3CaO\cdot 2TiO_2$ $\sim CaO\cdot TiO_2$* $(+TiO_2)$	$CaO\cdot TiO_2$* $(+TiO_2)$	675(10)	rapid	30.3
$MgO-Al_2O_3$(1)	$MgO\cdot Al_2O_3$	$MgO\cdot Al_2O_3$ $\sim MgO\cdot 2Al_2O_3$	$MgO\cdot Al_2O_3$	<800	rapid	41.1
$MgO-SnO_2$(8)	$2MgO\cdot SnO_2$	–	–	950	slow	100
$CaO-SnO_2$(9)	$2CaO\cdot SnO_2$ $CaO\cdot SnO_2$	–	$CaO\cdot SnO_2$	900	no	85

* Contains a slight excess of TiO_2.
** Of the formation of the first reaction product.

When a reaction is controlled by diffusion, there exists approximately a relation,(11)

$$d\xi/dt = k'/\xi \qquad \text{or} \qquad \xi^2 = 2k't + \text{const.}, \qquad (1)$$

where ξ is the thickness of the reaction product and t, the reaction time. If the reaction, with powder mixtures, is assumed to proceed uniformly on the particles of a spherical substance with a radius of r,

---

(6) It may not be amiss to mention here that the author's purpose is not to present in this paper unique and quantitative discussions, but rather to offer some suggestive mechanisms of the reactions which are consonant to the experimental results obtained.

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

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

(9) IV, this Bulletin, **17** (1942), 70.

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

(11) H. Braune, *Z. physik. Chem.*, **110** (1924), 147; W. Jost, *loc. cit.*, 15, 30.

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

hold between ξ and x, the reaction amount per unit substance at a given time.(12) Therefore, we obtain

$$\{1-\sqrt[3]{1-x}\}^2 = \frac{2k'}{r^2}t\,, \tag{2}$$

or

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

The rates of the main parts of these reactions were expressed by this equation, and accordingly it was pointed out, as above mentioned, that they were controlled by diffusion.

However, in the three systems, MgO–TiO_2, CaO–TiO_2 and MgO–Al_2O_3, the reaction proceeded within a half an hour from the commencement of the reaction, more rapidly than the rate expressed by equation (3); the reaction between MgO and SnO_2 proceeded slowly at first, especially at lower temperatures, namely, rather an induction period was observed in this case; while in the reaction between CaO and SnO_2, the above equation was held from the beginning.

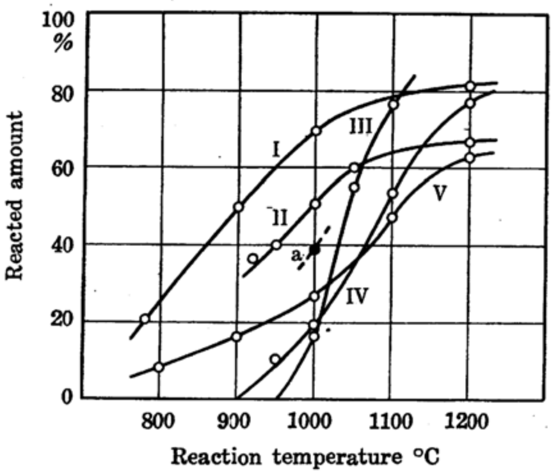

Fig. 1. Reacted amounts at various temperatures.

Curve I: The amount at a half an hour with a mixture, $MgO : TiO_2 = 1 : 2$, calculated from unreacted TiO_2.(3) (13)

Curves II–V: The amounts at three hours, respectively, with the mixtures, $CaO : TiO_2 = 1 : 1$, calculated from free CaO;(7) $MgO : SnO_2 = 2 : 1$(8) and $CaO : SnO_2 = 1 : 1$,(9) calculated from soluble SnO_2; and $MgO : Al_2O_3 = 1 : 1$, calculated from free MgO.(1)

Further, when the energy of activation, Q, of the diffusion process was calculated from the temperature coefficient of the velocity constant according to

$$k = Ae^{-Q/RT}\,, \tag{4}$$

it was found that the values for the three former reactions lay approximately between 30 and 40 Kilocalories per mole, while those for the last two were 100 and 85 Kilocalories, respectively. Thus the energies of activation of the last two reactions were twice to three times greater than those of the former ones.

The effect of temperature on these reactions can also be seen dis-

---

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

(13) As the preparations were used without heat treatment in this experiment, the reaction took place very easily. Under similar conditions as in the other reactions, the reacted amount at 3 hours falls on the point a.

tinctly from the reaction amounts at a certain reaction time given in Figure 1. The reaction takes place moderately already at as low as 800° in the systems, $MgO–TiO_2$, $CaO–TiO_2$ and $MgO–Al_2O_3$, while the reaction temperature,(10) or the temperature at which the first evidence of the reaction is observed, of the systems $MgO–SnO_2$ and $CaO–SnO_2$, lies at 950° and 900°, respectively; nevertheless, the increase of the reaction rate with the temperature is very remarkable in the latter two reactions.

From these facts, the reactions studied here can be classified into two types: (1) the reactions of the three systems, $MgO–TiO_2$, $CaO–TiO_2$ and $MgO–Al_2O_3$, in which a rapid initial reaction and a small energy of activation are observed, and (2) those of the systems, $MgO–SnO_2$ and $CaO–SnO_2$, which have an induction period rather than a rapid initial reaction and a large energy of activation. It is easily expected that there should exist a certain relationship in the differences of the initial states of these reactions and their energies of activation.

II. Considerations on the Initial States of the Reactions. Surface Diffusion and Inner Diffusion. The initial states of these reactions will be considered at first. It is true, as has been stated in the first report,(3) that the reaction heat is one of the causes for a rapid initial reaction, but an induction period can not be explained from this consideration. The difference in the initial states may be interpreted as follows:

Although the relation (3) is derived approximately by assuming that a reaction with powder mixture proceeds uniformly on a spherical substance, the experimental conditions do not strictly correspond to the assumption, because the particles of the components are by no means in contact with each other completely at the commencement of the reaction, however fine the preparations may be. The reaction begins only at the contact points of the components, and therefore, it takes place but slightly at the beginning. As the reaction proceeds, the product is formed from these contact points in the particles of both components. At the same time, however, the product tends to diminish its own surface area, because the crystals of the product at this stage are not yet fully developed, or in a state of disorder and have a large surface energy;(5) a diminution of the surface area results in the increase of the interface of the components, and consequently the reaction rate increases gradually.

Now we shall consider a mixture of components, A and B, consisting of spherical particles in which all particles of A are surrounded completely by B, e.g., a mixture with a large excess of B. The total surface of A is covered more rapidly with the reaction product than that of B; and after the thickness of the product on A becomes approximately uniform, a further reaction proceeds with a constant rate. Then equation (3) becomes valid for A, or generally, for the component of which surface area is smaller.(14) Thus an induction period should be observed at the beginning of the reaction. Assuming that a volume change due to the reaction is to be neglected and that the product is formed in both component particles with nearly equal quantities, the course of reaction is represented schematically in Figure 2 as t_1, τ and t_2.

---

(14) The total surface area of a given component in an unit reaction mixture will be frequently denoted simply as "surface area".

The present investigations have been carried out with the mixtures, compositions of which are corresponding to, or not too far from those of the reaction products. With these mixtures, if the particles of both components are assumed to be of equal size, about a half of the particles which surround each particle of a given component consists of its own; therefore, it should require a longer time before the particles are covered completely with the reaction product and the reaction begins to proceed uniformly. However, if the particles consist of different sizes, as it occurs practically, they will be in contact with each other more closely, and a uniform reaction may be observed comparatively readily. This condition is especially well satisfied in the present experiments, because they have been carried out with the pressed bodies. In these instances, equation (3) would be approximately applicable for both of the components.

So far it has been considered that the diffusion takes place only through the reaction product; however, it occurs also in another way, namely, one of the components can migrate on the surface of the reaction product as well as that of the other component. These two kinds of diffusion may be termed as the inner diffusion and the surface diffusion. It has been known that in metals the surface diffusion takes place more readily than the inner diffusion.⁽¹⁵⁾ Moreover, there are many instances of the solid reactions between oxides which take place smoothly in the temperature range still lower than that of the present experiments, and they have been regarded to proceed chiefly by the surface diffusion at these temperatures.⁽¹⁶⁾

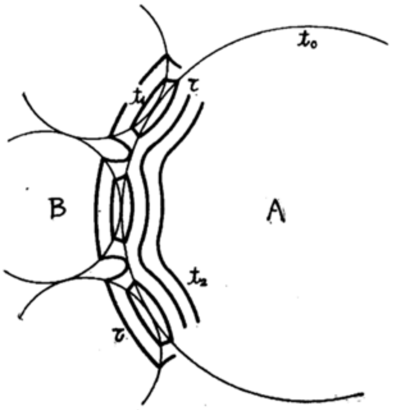

Fig. 2. Course of the reaction without surface diffusion (model).

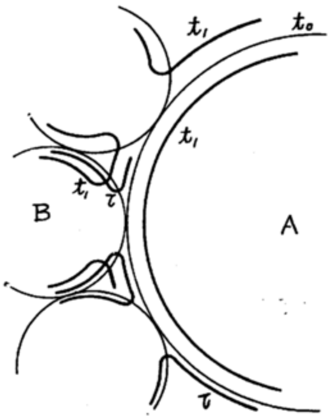

Fig. 3. Course of the reaction with a rapid surface diffusion (model).

Therefore, let us consider a reaction in which the component B migrates on the reaction product, and, further, on A far more readily than it suffers the inner diffusion. When the components consist of very fine powders, as have been used in the present experiments, the reaction

---

(15) I. Langmuir, *Chem. Rev.*, **13** (1933), 147; *J. Franklin Inst.*, **217** (1934), 543.

(16) J. A. Hedvall and G. Cohn, *Kolloid* Z., **88** (1939), 224.

proceeds considerably at its early stage of the reaction owing to the surface diffusion. After the surface of A is covered completely by B, the inner diffusion proceeds uniformly on A; and, as the step that determines the rate lies also in the inner diffusion, equation (3) holds for A, or the diffused component.(17) In this case, therefore, a rapid initial reaction should be obtained. (It is considered that the part of a particle of A which is not surrounded by B, and even a particle which is not at all in contact with B, is covered gradually by B.) The course is shown schematically in Figure 3. In this case, the size of A particles increases with the reaction, while that of B decreases and disapppears finally.

According to the above considerations, a rapid initial reaction rate, found in the reactions of the three systems, MgO–TiO_2, CaO–TiO_2 and MgO–Al_2O_3, may be explained as to be due to the rapid surface diffusion; and the induction period of the reaction between MgO and SnO_2, as the absence of the distinct surface diffusion. There may exist such an intermediate case in which the surface diffusion takes place slowly and compensates the induction period of the inner diffusion, and equation (3) holds apparently from the beginning of the reaction. The reaction between CaO and SnO_2 is probably an example of this case.

III. Discussions on the Effect of Particle Size of the Components on the Reactions. The relation between the surface phenomenon and the inner diffusion can be more distinctly understood when the effect of particle size of the components on the reactions is considered.(18)

There exists the relation (2) between the reaction amount and the particle size, and, by the reaction between $BaCO_3$ and SiO_2 with a mixture of $BaCO_3:SiO_2=1:10$, Jander(12) has proved experimentally the validity of the relation by changing the particle size of $BaCO_3$.(19) However, as it is discussed in the last section, equations (2) and (3) should hold for the component with a smaller surface area when only the inner diffusion occurs, and for the diffused component when the rapid surface diffusion takes place; and there exists a rapid or a slow initial reaction period before these relations become applicable.

We shall discuss the effect of particle size on these reactions, taking the different cases into consideration. The radii of the two components are denoted as r_A and r_B, and for convenience, let r_B be constant, $r_{B\,0}$.

§ 1. *The Case in which no Surface Diffusion exists.* The following two instances will be discussed.

(*a*) The particles of A are surrounded completely by those of B:—In the normal reaction period(20) equation (2) holds for A. In the

---

(17) In this paper, "diffused" component means the component into which the other diffuses. The component that diffuses into the other will be referred to as the "diffusing" component. In Fig. 3, A is the "diffused", while B is the "diffusing" component.

(18) When we consider a powder mixture of the two components with a definite composition, their total surface areas are inversely proportional to their particle sizes.

(19) The existence of a slight induction period, which he explained in a different way from that of this paper, was observed in his experiment.

(20) The period in which the reaction proceeds owing to the inner diffusion according to equations (2) and (3) will be mentioned as the normal reaction period.

region where the reaction does not proceed too far, since the relation between the reaction amount and the thickness of the product can be expressed approximately by

$$x = 3\xi/r_A \, ,$$

equation (2) becomes

$$x^2 = \frac{k''}{{r_A}^2}t \, . \tag{5}$$

Let τ be the initial reaction period, x_τ be the reaction amount produced in this period, and the reaction time from the commencement of the reaction be denoted as t, then we obtain from (5)

$$x = \frac{k}{r_A}\sqrt{t-\tau}+x_\tau \, . \tag{6}$$

In the induction period, ξ also increases according to the relation (1), while x changes with ξ and can be expressed as

$$x = \frac{1}{r_A}\int k(\xi)d\xi \, , \tag{7}$$

or

$$x = \frac{1}{r_A}\int k(t)dt \, . \tag{8}$$

However, since r_B is constant, as seen from Figure 2, it is admitted that the reaction amount per one particle of A increases with ξ, or with t nearly in the same way, unless r_A is not very small; namely, in (7) and (8), $k(\xi)$ and $k(t)$ may be assumed to be independent of the particle size of A. Then τ becomes also constant, and we have

$$x_\tau = \frac{k_\tau}{r_A}\sqrt{\tau} \, ,$$

and equation (6) becomes

$$x = \frac{k}{r_A}\sqrt{t-\tau}+\frac{k_\tau}{r_A}\sqrt{\tau} \, . \tag{9}$$

Therefore, the whole course of the reaction is expressed approximately by (8) and (9), and, throughout the induction and the normal reaction periods, there exists a relation,

$$x = K/r_A \, , \tag{10}$$

between x and r_A. In other words, the reaction amount at any reaction time should be inversely proportional to the particle size of the component A.

(*b*) Equal amounts of A and B exist:—⁽²¹⁾ When $r_A \gg r_{B\,0}$, since A becomes surrounded completely by B, the conditions in (a) are satisfied and equation (10) holds for A. Similarly, when $r_A \ll r_{B\,0}$, the same relationship holds for B, and in this case x is constant whatever r_A may be, because r_B is constant. With a medium sized particle of A, for instance, $r_A = r_{B\,0}$, as it is discussed in the last section, the particles of the two components are in contact with about a half of their own component; therefore, the reaction amount in the induction period is smaller than that which is discussed in (*a*), and it takes a longer time until the induction period is completed.

In this case, therefore, the curve in which x is plotted against $1/r_A$ at a certain reaction time changes gradually from $x = K/r_A$ to $x = \text{const.}$ in the neighbourhood of $r_A = r_{B\,0}$.

§ 2. *The Case in which remarkable Surface Diffusion occurs.*

(a) B diffuses on A, which is surrounded completely by B:—If we neglect the reaction amount due to the inner diffusion in the initial reaction period, the condition becomes just as discussed in § 1 (*a*), although the reaction amount in the initial stage is, of course, very much and this period is completed rapidly. Therefore, the course of reaction is expressed approximately by (8) and (9), and the relation (10) holds at any reaction time.

(*b*) Equal amounts of A and B exist:—When B diffuses on A, the above relations hold approximately, whatever the relation between r_A and r_B may be. Similarly, when A diffuses on B, equation (10) holds for B, and x becomes constant, whatever r_A may be. However, when r_A and r_B differ too much far and the surface area of the diffused component is far larger than that of the diffusing component, it needs a longer time until the total surface of the former is covered completely, and therefore the reaction amount at a certain reaction time, especially at the beginning of the reaction, is smaller than what is discussed above. In an extreme case, no normal reaction period is attained.

IV. Results of the Experiments on the Effect of Particle Size.

The above discussions seem to have proved experimentally for the reactions of the systems, MgO–SnO_2, MgO–Al_2O_3 and CaO–TiO_2; the details of which are described in the experimental part (sections VII–IX). The experiments have been carried out with the mixtures corresponding to the addition compounds.

The results of the experiment on the reaction between MgO and SnO_2 correspond to the case of § 1 of the last section; therefore, it is concluded that the reaction proceeds, as it is expected, mainly by the inner diffusion. However, a slight tendency of diffusion of MgO on the surface of SnO_2 is also observed.

As for the reaction between MgO and Al_2O_3, it is concluded that Al_2O_3 diffuses rapidly on MgO at first, and a further reaction takes place uniformly on the surface of MgO. In the last report,⁽¹⁾ it was found

---

(21) The argument is carried out for the equal volume amounts of the components, but it is valid to a first approximation for equi-molar mixtures or for the mixtures corresponding to the addition compounds.

that this reaction proceeded more readily with the mixtures containing the excess of MgO than with the other mixtures. As the particles used at that occasion were very fine and could be regarded as nearly of equal size, the total surface of MgO per unit mixture became larger when MgO existed in excess. Since Al_2O_3 diffuses on the surface of MgO, it is understood that the reaction proceeds rapidly in this condition.

By the reaction between CaO and TiO_2, it is considered that CaO diffuses on TiO_2, while at the same time the inner diffusion takes place comparatively readily; and indeed, as it is clear from the experiment in the second report,⁽⁷⁾ the reaction amount in the initial stage of this reaction is not so much as compared with those of the reactions, MgO–Al_2O_3 and MgO–TiO_2. It is of some interest to note that Al_2O_3, the acidic component, migrates on MgO in the reaction between MgO and Al_2O_3, while the basic component, CaO, diffuses on TiO_2 in this reaction.

In analogy to these experiments, it is admitted that the other two reactions, MgO–TiO_2 and CaO–SnO_2, proceed, respectively, as discussed in section II; and the component which migrates on the surface of the other may be regarded as MgO and CaO, respectively.

The technical importance of the effect of particle size on the reactions will be mentioned here. The solid reaction in which the surface diffusion takes place rapidly, for instance, the reaction between MgO and Al_2O_3, proceeds more readily when the diffused component is very fine; therefore, in order to obtain a certain addition compound with ease, we should endeavour to pulverize the diffused component as fine as possible rather than *vice versa*. This is particularly well understood from Figure 6 (in section VIII), where the reaction proceeds more rapidly when MgO, the diffused component, (and Al_2O_3, not necessarily) is very fine. When no distinct surface diffusion exists, it is desirable that both of the components are pulverized equally well, because the reaction rate is then controlled by the particle size of the component with a smaller surface area (or with a greater particle size); only when one of the components exists in a small quantity, this component should be fine.

V. Further Considerations on the Diffusion Mechanism. As it has been stated in the first report, Wagner⁽²²⁾ considered that the reactions in solid state proceed frequently by the exchange of the components in the form of ions (generally smaller metal ions), or by the "ionic diffusion", through the reaction product in which electrical neutrality is always preserved. He proved this point experimentally for the reaction between AgI and HgI_2⁽²³⁾ and supposed further that the analogous mechanism may hold for the formations of silicates and spinels,⁽²²⁾ but the experimental confirmations for the latter reactions are still lacking. On the contrary, Hedvall and Cohn⁽¹⁶⁾ stated that the diffusion in such a compound as silicates or spinels, the formation of which takes place smoothly already at so low temperatures that no distinct ionic conductivity is observed, could hardly be considered as ionic; and that these reactions proceed probably by the migration of the neutral atoms, or atom groups,

---

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

(23) E. Koch and C. Wagner, *Z. physik. Chem.*, B, **34** (1936), 317.

through the defect positions of the crystals, which exist owing to the incompleteness of the crystal growth,(24) or on the "inner surface" of the crystals. This mechanism may be mentioned as the "non-ionic diffusion". Thus, no conclusion has been given on the kinds of the elementary particles which migrate in these reaction products.

It is considered that the similar solid reactions can never be explained by a single mechanism; and, indeed, by studying the exchange reactions of certain wolframates and molybdates with a group of divalent metal oxides as well as their electric conductivities, Jander(25) has considered that some of these reactions proceed by the ionic diffusion while others by the migration of the neutral acid anhydride, i.e., WO_3 or MoO_3.

Also the two types of the reactions found in the present investigations will probably be due to the differences in the nature of the reaction products as well as in their diffusion mechanism, and the author would like to explain, at present, these differences as follows:

Although the ionic conductivities of these reaction products are not yet certain, it may be assumed that they are very small at the temperature as low as 800°. The three reactions, MgO–TiO_2, CaO–TiO_2 and MgO–Al_2O_3, are then to proceed, at least lower than 800° by the non-ionic migration of the components through the product. The surface diffusion in these instances may also be explained by a similar mechanism. On the other hand, for the other two reactions, MgO–SnO_2 and CaO–SnO_2, which begin to take place at 950° and 900° respectively, the interpretation of the ionic diffusion may be possible. It is considered, namely, that the crystals of these reaction products are (when once formed) well developed, and it is difficult for the neutral atoms, or atom groups, to diffuse through them; and that they begin to dissociate with the increasing temperature, and the ions thus produced become to be able to exchange with each other. In these systems, the possibility of the ionic surface diffusion might be expected at higher temperatures; however, as Hedvall has stated,(16) the exchange of ions at the surface of the ion crystals is hardly in question.

The energies of activation obtained in the latter two reactions may be regarded as that of the ionic diffusion. At higher temperatures, the ionic diffusion in the former three may also be possible; however, it is considered that the controlling steps are still the non-ionic diffusion, and that the energies of activation obtained, which are smaller than those of the latter ones, will be those of the non-ionic diffusion.

In this way, the differences in the energies of activation of the two types of the reactions as well as the existence of the surface diffusion in the former cases can well be interpreted. However, the final conclusion on this problem should be drawn only after more examples of similar reactions have been accumulated, and especially after the physical properties of the products have been made clearer.

VI. Sintering due to Solid Reactions. The phenomenon of sintering, i.e., a phenomenon in which a solid substance shrinks and reduces its porosity when it is heated within such a temperature range as it does

---

(24) At lower temperatures, the existence of the defect positions of this type is well understood.(16)

(25) W. Jander, *Z. anorg. allgem. Chem.*, **192** (1930), 295.

not melt completely,(26) has been utilized widely in the ceramic industry. Of course, the formation of a liquid phase, owing to the low melting eutectics, is one of the causes of sintering; however, the phenomenon occurs also in pure solid state and it is especially remarkable when a solid reaction takes place. Hedvall(27) called the phenomenon as "Trockensinterung" and, indeed, "Trockensinterung" of metals has recently been developed into so-called powder metallurgy.(28)

For the use of refractories, which are exposed to high temperatures, it is desirable that the high melting substances are selected, and in the course of their manufacture, they should be sintered at relatively low temperatures without forming any liquid phase. Now magnesium oxide, which has a very high melting point and is well qualified as a basic refractory, sinters at a lower temperature than its melting point; and while it has been known that the existence of such oxides as Fe_2O_3 or Al_2O_3 is, probably owing to the formation of an addition compound, effective for its sintering, the author(29) has recently found further that the addition of a small quantity of TiO_2 is very effective in this connection. For instance, when the pressed bodies of the various mixtures of MaO and TiO_2 were ignited at 1400°, their porosities diminished as shown in Figure 4.(30)

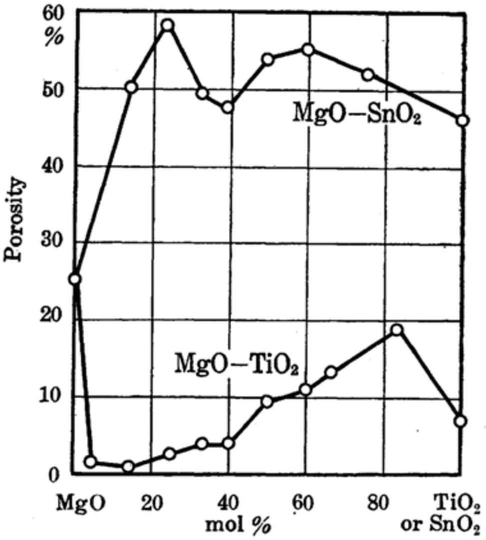

Fig. 4. Porosities of the ignition products at 1400° of the systems $MgO\text{-}TiO_2$ and $MgO\text{-}SnO_2$.(31)

In this system the sintering is particularly remarkable by the mixtures in which $2MgO \cdot TiO_2$ is formed. While MgO belongs to the cubic system, $2MgO \cdot TiO_2$ has also a cubic spinel structure; and it is easily expected that the spaces among the crystals become smaller when the particles of the same crystal system are packed most closely to each other than in the other cases. Fe_2O_3 and Al_2O_3, too, form with MgO addition compounds with the spinel structure.

However, the addition of SnO_2 (which belongs, as well as TiO_2, to the fourth group of the periodic system and also forms with MgO the

---

(26) While the meaning of sintering is not certain, it is defined here as above.

(27) J. A. Hedvall, *loc. cit.*, 81.

(28) *Cf.*, for instance, W. D. Jones, "Principles of Powder Metallurgy," London (1937); W. Seith, "Diffusion in Metallen," Berlin (1939).

(29) Y. Tanaka, *J. Soc. Chem. Ind. Japan*, **42** (1939), 387, 202B; 390, 204B; Y. Tanaka and T. Takagi, *J. Soc. Chem. Ind. Japan*, **42** (1939), 874, 405B.

(30) *J. Chem. Soc. Japan*, **60** (1939), 212.

(31) Let W be the weight of a porous solid substance, V be its total volume and s, its specific gravity, then the porosity, P, is calculated from

$$P = \frac{s - W/V}{s} \times 100\% \ .$$

spinel type compound, $2MgO\cdot SnO_2$) is not effective at all for the sintering of MgO; the porosities of this system at 1400° are also given in Figure 4.(32) (33) Therefore, it is easily conceivable that sintering, due to the solid reaction, depends not only on the structure of the addition compound but also on the reaction mechanism.

As for the above two systems, the following discussions may be given. Namely, by the reaction between MgO and TiO_2, MgO migrates on the surface of TiO_2 and, as seen from Figure 3, the particles of MgO are deformed and their sizes decrease gradually. Therefore, the total body shrinks and, furthermore, it is considered that the crystal growth of MgO is accelerated by the stress due to its deformation; thus the body sinters by the reaction. On the other hand, by the reaction between MgO and SnO_2, the surface diffusion occurs but slightly and the reaction takes place chiefly in the neighbourhood of the contact points of the components, and especially, as shown in Figure 2, if it is assumed that the components exchange each other with nearly equal quantities,(34) the particle sizes of the two components are unchanged; therefore, the vacant spaces remain as before and no sintering should be observed. The reaction between MgO and Al_2O_3 belongs to the former case, and the body sinters actually.

The author would like to point out, further, that the existence or non-existence of the surface diffusion and the phenomenon of sintering may play an important rôle in manufacturing mixed catalysts.

Experiments on the Effect of Particle Size.

VII. The Reaction between Magnesium Oxide and Stannic Oxide. The effect of particle size of the components on the reaction between MgO and SnO_2, where no distinct surface diffusion has been considered to take place, was studied at first. With a mixture corresponding to the addition compound, $MgO:SnO_2=2:1$, the particle size of one of the components was kept constant, as 150 to 200 meshes to the inch, and that of the other component was changed.

Although it was difficult to obtain coarse particles from commercial preparations of MgO and SnO_2 (and of other oxides also) which were very fine powders, this was achieved by the following method: as the preparations were hardened moderately when they were kneaded with some water, dried and heated at 1200° to 1300°, they were crushed carefully and passed through different sieves. Although these particles consisted by no means of single crystals and were different in shape, they were assumed to be spherical, and their "mean radii" were estimated approximately as given in the second column of Table 2.

The amounts of free MgO and those of SnO_2, soluble in 4N HCl, of the reaction products at 1100° are given in Table 2. The reaction proceeded slowly within a half an hour and after 3 or 6 hours it seemed to have proceeded normally. The reacted amounts were calculated from the percentage of soluble SnO_2 based on the theoretical value of total SnO_2 though it contained, as it was stated in the third report,(8) some amorphous SnO_2.(35)

---

(32) *J. Chem. Soc. Japan*, **61** (1940), 1023.

(33) As the sintering of TiO_2 and SnO_2 themselves are different from each other, the comparison is not strict; however, the tendency is obvious.

(34) When the reaction proceeds by the ionic diffusion, this condition is satisfied.

(35) Since mixing of the components containing coarse particles can hardly be executed completely homogeneous, to calculate the reacted amount from free MgO will introduce much uncertainty. Ideally, a total analysis should be made with each reaction product.

Table 2. Effect of Particle Size on the Reaction between Magnesium Oxide and Stannic Oxide.
$MgO:SnO_2=2:1$ ($SnO_2=65.14\%$), 1100°.

Particle size of MgO		Particle size of SnO_2	Free MgO	SnO_2 Soluble in 4 N HCl	Free MgO	SnO_2 Soluble in 4 N HCl	Free MgO	SnO_2 Soluble in 4 N HCl
Mesches' inch	Mean radius (mm)	Meshes/ inch	(%)	(%)	(%)	(%)	(%)	(%)
Reaction time (hrs.)			0.5		2		6	
32– 48	0.20	150–200	33.13	4.16	32.12	6.90	31.59	7.98
65–100	0.09	”	32.80	4.75	31.32	8.27	30.37	10.46
150–200	0.04_5	”	32.73	4.98	30.60	10.57	29.08	13.65
200–*	0.02_5	”	32.60	5.27	30.27	11.05	27.99	15.08
150–200	0.04_5	32– 48	33.86	2.60	33.53	3.52	32.48	5.38
”	”	65–100	33.33	3.93	31.77	8.79	30.81	10.02
”	”	200–*	32.46	5.68	29.96	11.13	27.68	16.70

---

* Pulverized with an agate motar as fine as possible.

As shown in Figure 5, the curves in which the reacted amounts are plotted against the reciprocals of the mean radii of MgO or SnO_2 particles at each reaction time turn out just as discussed in §1(*b*) of section III. However, the effect of the size of SnO_2 is a little greater than that of MgO which indicates that MgO migrates to some extent on the surface of SnO_2.

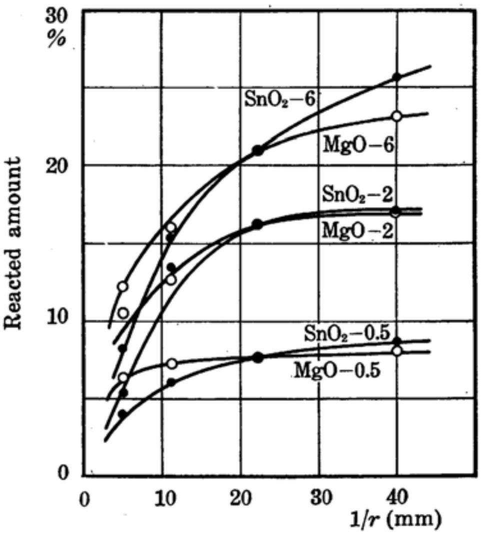

Fig. 5. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between MgO and SnO_2 at 1100°.

SnO_2-2 means, for instance, the reacted amounts at two hours with varying the particle size of SnO_2.

VIII. The Reaction between Magnesium Oxide and Aluminium Oxide. As in the above experiment, with a mixture of $MgO:Al_2O_3=1:1$, the effect of particle size on the reaction between MgO and Al_2O_3 was studied at 1200°. The reacted amounts were expressed by the percentage of combined to total MgO, which was, in case of the mixtures containing coarse particles, determined by total analysis.

The results are given in Table 3, and the relation between the reacted amounts and the reciprocals of the particle sizes are shown in Figure 6. Contrary to the results of the reaction between MgO and SnO_2, the effect of the particle size of MgO is far greater than that of Al_2O_3. Namely, when the particle size of Al_2O_3 is constant, the reacted amounts are nearly proportional to the reciprocals of the mean radii of MgO particles, or to the surface area of MgO; while the effect of the size of Al_2O_3 is not so remarkable unless its size is not very coarse. This agrees with the discussion of §2 of section III.

Table 3. Effect of Particle Size on the Reaction between Magnesium Oxide and Aluminium Oxide. $MgO:Al_2O_3=1:1$ ($MgO=28.34\%$), 1200°.

Particle size of MgO Meshes/inch	Particle size of Al_2O_3 Meshes/inch	Reacted amount (%)	
Reaction time (hrs.)		1	6
32– 48	150–200	4.30	5.19
65–100	"	8.29	10.59
150–200	"	17.78	24.45
200–*	"	26.60	38.99
150–200	32– 48	8.17	13.33
"	65–100	12.70	22.20
"	200–*	19.47	27.30

* Very fine.

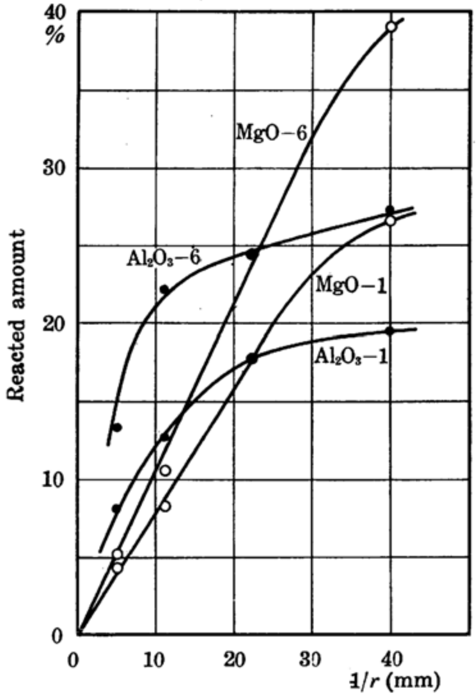

Fig. 6. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between MgO and Al_2O_3 at 1200°.

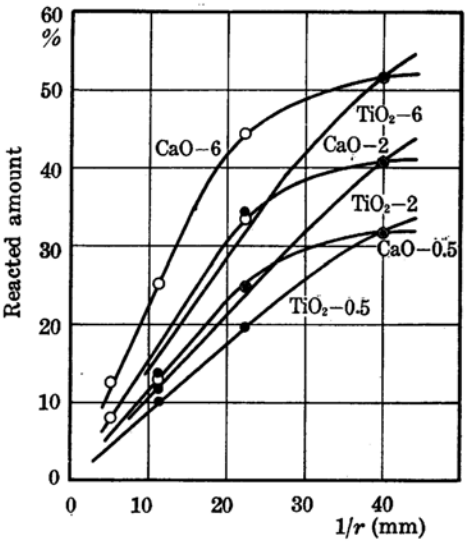

Fig. 7. Relations between the reacted amounts and the reciprocals of the mean radii of the components by the reaction between CaO and TiO_2 at 950°.

IX. The Reaction between Calcium Oxide and Titanium Oxide. The results of the experiment with a mixture of $CaO:TiO_2=1:1$ at 950° are shown in Table 4 and in Figure 7. The reacted amounts were calculated from the percentage of combined to total CaO.(36)

---

(36) As the combined CaO was calculated from free CaO, the existence of some uncertainty was unavoidable. Moreover, since one of the components was kept constantly to be very fine powders, smaller than 200 meshes to the inch, the results were not so clear.

Table 4. Effect of Particle Size on the Reaction between Calcium Oxide and Titanium Oxide.
$CaO:TiO_2=1:1$ ($CaO=41.24\%$), 950°.

Particle size of CaO Meshes/inch	Particle size of TiO_2 Meshes/inch	Reacted amount (%)		
Reaction time (hrs.)		0.5	2	6
32– 38	200–*	8.7	8.0	12.6
65–100	”	12.9	14.3	25.2
150–200	”	24.8	33.4	44.4
200–*	”	31.7	40.7	51.6
200–*	65–100	10.1	11.8	13.6
”	150–200	19.7	25.2	34.4

---

* Very fine.

Although the effect is not so distinct as in the reaction between MgO and Al_2O_3, it is obvious as far as that the effect of the particle size of TiO_2 is greater than that of CaO, and that a linear relationship between the reacted amounts and the reciprocals of the particle sizes holds approximately for the former. It seems that the inner diffusion takes place comparatively easily in this reaction.

Summary.

(1) The main characteristics of the solid reactions between the oxides, studied in the present investigations, have been summarized. These reactions can be classified into the following two types: (1) the reactions of the systems, $MgO–TiO_2$, $CaO–TiO_2$ and $MgO–Al_2O_3$, which have a rapid initial reaction period and a small energy of activation, and (2) those of the systems, $MgO–SnO_2$ and $CaO–SnO_2$, in which no rapid initial reaction and a large energy of activation are observed.

(2) The rapid initial reaction is probably due to the existence of a rapid surface diffusion, and when the reaction proceeds chiefly by the inner diffusion, no rapid initial part may be observed.

(3) The effect of the particle size of each of the components on these reactions has been discussed. In the reactions without distinct surface diffusion, the effect of the particle size of the component, of which total surface area is smaller, should be great, while that of the diffused component becomes remarkable when the sufrace diffusion takes place rapidly.

(4) For the three reactions, $MgO–SnO_2$, $MgO–Al_2O_3$ and $CaO–TiO_2$, the above discussions have been proved experimentally by changing the particle size of each of the components.

(5) Technical importance of the effect of particle size on solid reactions has been stated.

(6) Some further considerations on the diffusion mechanism have been given, and the difference in the energies of activation has been interpreted.

(7) Finally, the phenomenon of sintering due to solid reactions has been discussed. It is considered that the sintering occurs by the reactions in which a rapid surface diffusion takes place.

In conclusion, the author wishes to express his sincere thanks to Dr. R. Yoshimura for his interest, to Mr. K. Hirota for criticizing and discussing the problem willingly, and also to Dr. R. Negishi and to the other colleagues. He is also indebted to Messrs. S. Takasago and T. Sugawa for their assistances in the experiments.

Further the author takes this occasion to express his hearty gratitude to Prof. Y. Shibata of Tokyo Imperial University, to Prof. T. Marusawa, the former Director of the Central Laboratory, and to Dr. M. Sato, the present Director, for their keen interests and constant encouragement in carrying out the present series of investigations.

Department of Inorganic Chemistry, The Central Laboratory,
South Manchuria Railway Company, Dairen.