The Kinetics of the Transition of Titanium Dioxide

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The kinetics of the transition of anatase to rutile have previously been investigated[1,2]. In these studies samples, after being heated, were analyzed by means of the X-ray diffraction method. The rate of the transition of compounds such as titanium dioxide, germanium dioxide and silica is complicated by the variation in the size of the particles, the temperature, the surrounding atmosphere and the presence of small amounts of impurity.

Attention should be paid to the values of the activation energy of the transition. It has been reported that the value of the activation energy of the transition was equal to that of the sublimation energy in some organic compounds[3,4] and in sulfur[5], while the value of a compound such as mercuric iodide was not equal to that of the sublimation energy[6]. It is, therefore, important to determine the value of the activation energy in the transition of titanium dioxide as correctly as possible and to compare it with other thermodynamic values.

Meanwhile, it has been proved that there is a large difference between the dielectric constants of anatase and rutile; from this fact it was possible to analyze both elements in the mixture. We have measured the transition rate of anatase to rutile, analyzing their mixture by the dielectric constant method, and have obtained some interesting results to explain the transition process.

Experimental

In this study the raw materials of titanium dioxide (anatase) was prepared by the following procedure. Titanium tetrachloride was distilled after the impurities in it had been precipitated by letting hydrogen sulfide pass through it. The distillate was added, drop by drop, to a 50% sulfuric acid solution, and the mixture was heated to drive off hydrochloric acid until no Cl^- was detected. The solution thus obtained was diluted with distilled water and then hydrolyzed at 90~100°C. The precipitated gel was washed with distilled water, and then the product obtained was heated for five hours at 700°C in an electric furnace. Two kinds of samples, "a" and "b" were used in this study, both being prepared in the same manner. It was later proved that they have different rates of transition.

Zn, Mg, Pb, Fe, Al, V, Ca, Cu, Ga, Cr and Sn were not detected spectroscopically, while the lines of Si were faintly observed. According to the electron-microscopic observation, the crystal size of the raw materials was $0.09\sim1\ \mu$, while the crystal size of sample "a" was a little larger than that of sample "b". The pattern of rutile was not detected by the X-ray diffraction.

The dielectric constant of the mixture of anatase and rutile was measured by the method reported by Oehme[7]. The measuring equipment used was a DK Scope, type 59 (Yanagimoto Co., Ltd.). In the measurement of the dielectric constant of powder by the immersion method, it is necessary to eliminate completely the foams of air occluded in the powder. By using the coaxial cylindrical cells shown in Fig. 1, it is possible to measure the difference in capacity between liquid and powder suspension. 0.700 g. of the sample was accurately weighed and put into A in the figure. After pouring aceton into A and B until half the height of a bakelite cylinder was reached, the powder suspension in A cell was agitated carefully by a stainless steel wire until no bubble rose. By switching C on the respective side, the capacities of the A and B cells were compared with one other. From the difference in the readings on the scale, ΔS, it is possible to determine the proportion of rutile or anatase in powder. Figure 2 shows the calibration curve obtained in this work.

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[6] D. G. Fade and N. H. Hartshorne, ibid., **1938**, 1636.

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The X-ray diffraction patterns of the samples were obtained by the Geiger Counter X-ray Diffractometer, and the results were compared with those of the dielectric constant method.

The sample in the sintered alumina boat was placed in a quartz tube, which was then set in a platinum electric furnace equipped with a voltage transformer and a chromel-alumel thermocouple. The position where the sample was placed in the furnance was selected so as not to be affected by the temperature variation in the furnace. In any given run, the temperature fluctuation did not exceed ±2°C. The temperatures of the experiments were established within 3 min. after the boat had been put in the furnace.

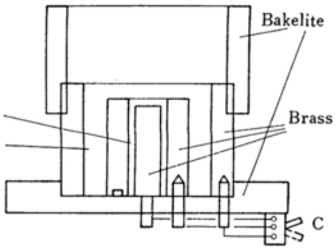

Fig. 1. Coaxial cylindrical cell for the analysis of the anatase-rutile mixture by means of the dielectric constant measurements.

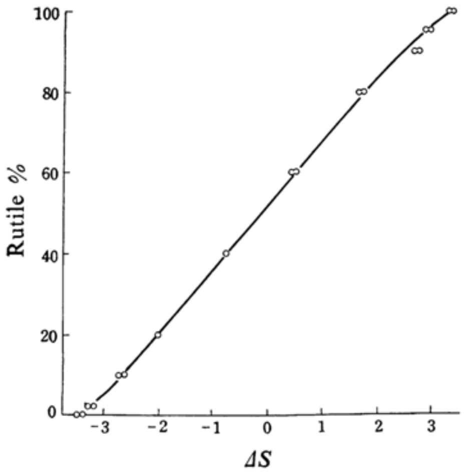

Fig. 2. Calibration curve for the analysis of the anatase-rutile mixture by means of the dielectric constant measurements.

The oxygen atmosphere was obtained from a bomb containing oxygen prepared electrolytically from distillated water. The oxygen was dried by letting it pass through sulfuric acid and calcium chloride. By using a u-type flow meter, the flow velocity of the oxygen was controlled.

Potassium chloride or lithium chloride was added to the samples in the form of solutions, and the mixtures were dried at 150°C before heating.

Experimental Results

The results of experiments on many samples, which were subjected to different heat treatments or surrounding atmospheres and which contained different additives, are sammarized in Figs. 3—6. Within the range of experimental uncertainty, no variation in the lattice parameter was encountered for any sample, and the diffraction patterns of anatase and rutile agreed fairly well, with respect to both the *d* values and the relative intensities, with those previously reported[8] by means of the

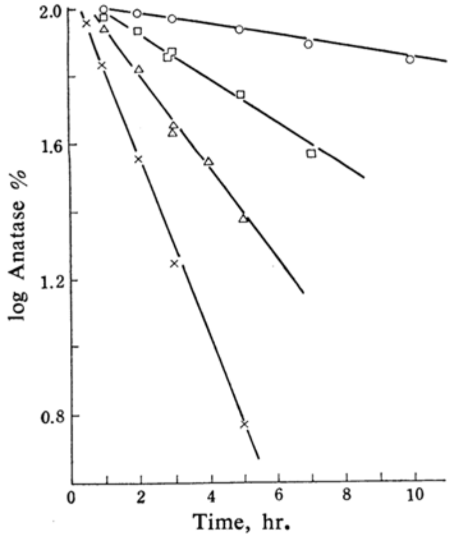

Fig. 3. First-order plots of the data in the sample "a" in air.

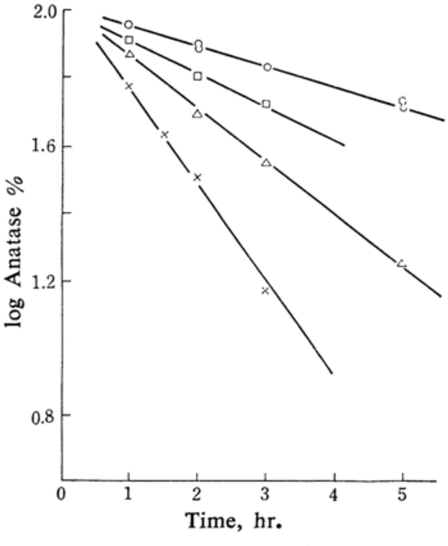

Fig. 4. First-order plots of the data in the sample "b" in air.

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[8] A. S. T. M. X-ray powder diffraction card.

X-ray diffraction method. No line broadening was encountered throughout the whole stage, nor was there any evidence for the existence of solid solutions, i. e., of disordered structures.

The color of most samples turned from white to yellowish as the transition proceeded, but the color of the sample with potassium chloride turned greyish.

Transition of Pure Titanium Dioxide in Air. —The transition from anatase to rutile modification was found to occur between 750 and 800°C in pure titanium dioxide in air. The rate of transition depends on the heating time and the temperature. Figures 3 and 4 show the transition of pure titanium dioxide in air, log(Anatase %) against time being illustrated. Fig. 3 shows the transition of "a", and Fig. 4, that of "b". These data were treated as previously reported by Czanderna, Rao and Honig[1] and by Rao[2]. In this study the data were plotted for the first-order equation; the data follow the first-order law fairly well for two kinds of samples, "a" and "b". However, there was a large difference between the rates of the transition of "a" and "b" as shown in Table I. In Table I the values of the rate constants, k, are shown for the transitions without and also with flux.

The activation energy was computed from the standard Arrenenius plot of $\log k$ against $1/T$ shown in Fig. 7. The deviation of each plot from the straight line is within the range of experimental error. The values of the activation energy thus obtained were 110 and 116 kcal./mol. for "a" and "b" respectively.

Attention should be paid to the fact that the values of activation energy do not differ significantly between "a", and "b" even

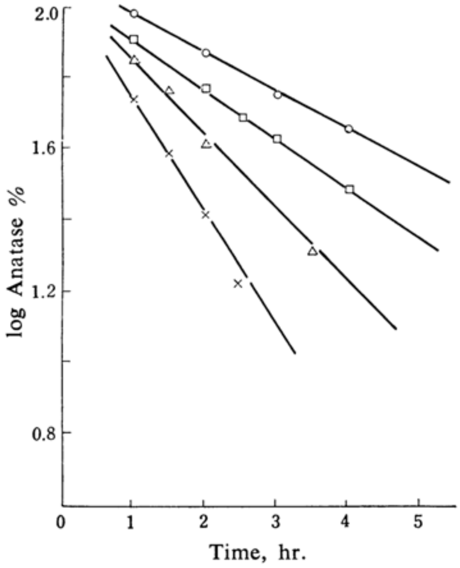

Fig. 5. First-order plots of the data in the sample "b" in O_2.

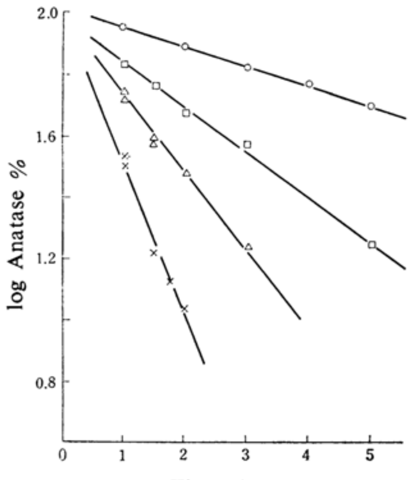

Fig. 6. First-order plots of the data in the sample "b" with LiCl in air.

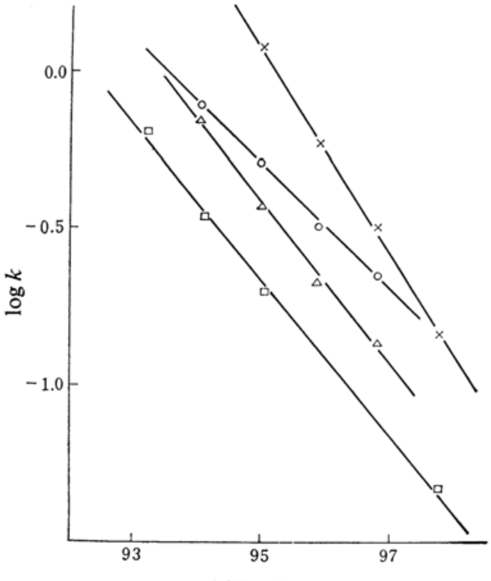

Fig. 7. Arrhenius plots of $\log k$ against $1/T$.

-□- a, air; -×- a, air, LiCl
-△- b, air; -○- b, O_2

TABLE I

Sample	Heating condition	Rate constant, $k \times 10^2$, hr^{-1}	
		780°C	790°C
a	Air	19.6	34.5
a	Air, LiCl	100.0	—
b	Air	36.5	69.2
b	O_2	51.8	78.1

though the difference in rates is large.

Transition of Pure Titanium Dioxide in an Oxygen Atmosphere.—Czanderna, Rao and Honig(1) reported that the transition was not significantly affected by the atmosphere. In this study, the "b" samples were heated in an oxygen atmosphere; the results obtained are shown in Fig. 5. The rate of transition was greater in an oxygen atmosphere than in air, as is shown in Table I. The deviations from the first-order rate law and the standard Arrhenius plot are very small. The value of activation energy estimated from Fig. 7 was 92 kcal./mol.

Transition of Titanium Dioxide with Flux.—The rate of transition with lithium chloride was determined with sample "a" in the same way as has been described above. Figure 6 illustrates the transition in air with 1% lithium chloride. The rate of transition in the presence of lithium chloride was greater than that without lithium chloride, as is shown in Table I, and the deviations from the first-order rate law and from the standard Arrhenius plot are small. The value of the activation energy estimated from Fig. 7 was 150 kcal./mol.

The transition with potassium chloride was very different from that with lithium chloride. We could not estimate rate constants because of the fluctuation of the data. The percentages of rutile in the samples after heating them till 800°C did not exceed 15%.

Discussion

A large number of polymorphic transitions of chemical compounds have been studied in recent years, and it has been pointed out that in those cases difficulties remain in obtaining reproducible data. These difficulties are perhaps, partly caused by the fluctuation in the behavior of the starting materials. In the present study attention was directed to the following items in order to obtain the starting material of titanium dioxide; (a) it was made as chemically pure as possible, (b) the crystal growth of anatase ended in it, and (c) it contained no rutile-type compound. Thus, it was possible in this study to obtain reproducible data for one sample. Nevertheless, different transition rates were found for two samples prepared by the same procedure, as was seen in the transition of pure titanium dioxide in air. This may be caused by the facts that the preparing conditions were not yet completely controlled and that the physicochemical behavior of the samples, for example, in the particle size and in the number of lattice defects differed; therefore, the frequency factors in the equation of transition rates were different.

The kinetics of the transition of anatase to rutile have been studied by Rao et al.(1,2), by means of the X-ray diffraction method. In the present study the transition rate was measured from the change in the dielectric constant of the samples. It might be suggested that the analysis of a mixture of anatase and rutile by the X-ray diffraction method, in which the heights of the diffraction peaks of the two components are compared, is accompanied by error when the crystal growth of anatase is incomplete. The analysis of the anatase-rutile mixture by the measurement of the dielectric constant, which has recently been described by Oehme(7), was tried in this study; it was proved that the analysis could also be successfully carried out in a sample which contains anatase below 10% or above 90%. The analysis of such a sample is known to be difficult to perform by the X-ray diffraction method.

The activation energy for the anatase-rutile transition in air was measured by Czanderna, Rao and Honig(1) as 110±10 or 90±10 kcal./mol., and later by Rao alone(2) as 80±10 kcal./mol. They empolyed as a starting material anatase obtained by precipitation from an ammoniacal solution of titanium after elimination of the impurities. However, in our study the value of this energy is calculated as 110 kcal./mol. or 116 kcal./mol. It is thought that this discrepancy is caused by the fact that Rao et al. dried their samples at a relatively low temperature (160°C). It is difficult to dehydrate completely the titania gel prepared by hydrolysis in an aqueous solution of titanium salt; furthermore, the crystal growth of anatase is incomplete in this case.

It was assumed by Czanderna et al. that atmosphere had no effect upon the anatase-rutile transition, but it was recognized in our experiment that the value of the activation energy of this transition is somewhat larger in air than in oxygen.

As for the effect of the flux, it is probable that the lithium or potassium atom may enter into the lattice of titanium dioxide, and/or that flux may react with titanium dioxide to form a titanate of lithium or potassium. It was proved by flame photometric analysis that the lithium or potassium ion was not found in the washing liquid obtained by the cold or hot washing of the samples which had been heated with flux. However, it was found that the lithium or potassium ion was present in that solution which had been obtained by dissolving the samples in sulfuric acid. On the other hand, it was impossible to recognize the change in the lattice constant by means of X-ray diffraction analysis. Also, there was no abnormal change in the dielectric constant of the samples. It might be necessary to carry out accurate measurements in order to clarify the atomic behavior of the flux.

The rate of tranision has been theoretically treated by Avrami[9], and his equation has been applied to explain the phenomena in the transition of several materials. However, in the transition of titanium dioxide, it has been proposed that treatment by Avrami's equation may provide only a formal account of the conversion process. The results obtained in our experiments fit fairly to the first-order rate law, the deviations from the straight line being found not to exceed the range of experimental error. The induction period might exist in the case of the transition of sample "a" in air, but it was impossible to clarify this phenomena because of the fluctuation of the analytical process. The data fluctuate when the conversion takes place only in a small amount of anatase or rutile, especially below 2%.

It might be worth comparing the values of the activation energy in the transition with those of the thermodynamical properties. It has been reported that the activation energy is equal to the energy of sublimation, e. g., in the transition of sulfur[5], *o*-nitroaniline[3] and azoxybenzene, but not in mercuric iodide[6]. Meanwhile, de Boer[10] has proposed that the transition of the tridymite form of silicon dioxide into the cristobalite form would resemble that of wurtzite into zinc-blende. He has assumed that it might be neccessary to break the links between the Si- and O-atoms before SiO_4 tetrahedra can be shifted and that after such shifts the Si-O links might be re-established; consequently, such a transition might not proceed easily.

It might be assumed that the transition would be accompanied by the rupture of the bond in such compounds as AB_2, e. g., in silica, germanium dioxide, or titanium dioxide, and that the bond energy would be nearly equal to the activation energy. In the quartz-tridymite transition of silica, it has been reported that the activation energy is 96 kcal./mol., while the bond energy of Si–O is calculated to be 89.3 kcal./mol. by Pauling[11] and 101 kcal./mol. by Huggins[12]. Furthermore, it will be reported that the activation energy is about 100 kcal./mol. in the hexagonal-tetragonal transition of germanium dioxide[13], while the bond energy of Ge–O was reported to be 104 kcal./mol. as calculated from Huggins' data[12], It was impossible to find the bond energy of Ti–O, but, with the assumption that the bond energy would be obtained by dividing the heat of formation[14] by the number of bonds per stoichiometric molecule of such compounds as titanium dioxide, it is possible to establish the bond energy of Ti–O as 109 kcal./mol., which value is nearly equal to the activation energy of the anatase-rutile transition. Such an assumption might also explain the transition in mercuric iodide. It might be necessary, however, to carry out an investigation into the transition in compounds similar to titanium dioxide in order to prove the above idea.

Summary

The kinetics of the transition of anatase to rutile have been studied in the temperature range 750∼800°C by means of dielectric constant measurements. The kinetic data can be fitted reasonably well by the first order equation. The transition rate is significantly affected by the heating atmosphere and the flux, and the values of the activation energy show a significantly large difference in these cases. In an air or oxygen atmosphere the value of the activation energy in the transition of pure titanium dioxide is 110 or 116 kcal./mol. and 90 kcal./mol. respectively. When 1% of lithium chloride is added to the titanium dioxide, the value of the activation energy of the transition is 150 kcal./mol.

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