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Authors
Shannon, Robert D.
Pask, Joseph A.

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University of California

Ernest O. Lawrence
Radiation Laboratory

Berkeley, California

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UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

KINETICS OF THE ANATASE-RUTILE TRANSFORMATION

Robert D. Shannon and Joseph A. Pask

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I. INTRODUCTION

Titanium dioxide exists in three principal crystalline forms--anatase, brookite, and rutile. Anatase and rutile are synthesized commercially but brookite is found only in the form of natural single crystals. --- Brookite and anatase are both metastable forms and transform exothermally and irreversibly to rutile over a range of temperatures but usually at $\approx 750°$ C and $\approx 1000°$ C, respectively. The free energy of the anatase transformation must be negative at least above 400° C since the transformation has been found to proceed at that temperature in the presence of an alkali flux.[1] It is not known whether an equilibrium transformation temperature exists, however, since neither the heat of formation of anatase nor solubility data for the two crystalline forms, anatase and rutile, is known.

Barblan et al.[2] studied the crystallography and mechanism of the brookite-rutile transformation, while Rao et al.[3] determined the kinetics of the transformation. An oriented transformation was found which allowed Barblan et al.[2] to postulate a mechanism involving shifting of some of the titanium ions to new sites and a general rearrangement of the oxygen ions. The kinetic study indicated that the reaction was controlled in the initial stages by nucleation and in the latter stages by growth. The overall activation energy was 65 kcal/mole.[3]

The anatase-rutile transition is of greater interest to the ceramist than the brookite transition because of the use of anatase as a pigment and a raw material in ceramic systems. The crystallography of the anatase transformation was studied and a mechanism similar to the brookite transformation was derived.[4] The mechanism involves retention of the $\{112\}$ pseudo-close-packed planes in anatase and

rearrangement of the titanium and oxygen ions within the plane. A cooperative movement of the titanium and oxygen ions was proposed in which the majority of the titanium ions, in order to reach their new sites, break two of their original six Ti-O bonds.

The kinetics of transformation of synthetic anatase were determined by Sullivan and Cole[5] and Rao.[6] As in the transformation of brookite, the process was found to be a nucleation-growth phenomenon. The activation energy per mole varied from 80 kcal for pure TiO_2 to 110 kcal for relatively impure commercial TiO_2.

The rate of the anatase-rutile transformation is strongly dependent upon impurities.[7, 8, 9, 10, 11] The transformation temperature has been shown to vary from 400° to 1200° C, depending upon the method of synthesis, the atmosphere, and the presence of foreign ions, but the role these factors play in inhibiting or accelerating the transformation had not been explained. In this paper a critical literature survey and the results of experimental work on the effects of CuO and hydrogen- and vacuum-reducing atmospheres on the transformation are used to show that this role is primarily that of controlling the stoichiometry of the TiO_2.

The synthesis of TiO_2 is generally carried out by high temperature oxidation of gaseous halides[12, 13] or by precipitation from an aqueous solution.[14, 15] The conditions for precipitation of both anatase and rutile have been summarized by Nodop.[16] Iida and Ozaki[7] studied the effect of preparation method on the transformation and concluded that a major cause for differing transformation temperatures was the degree of crystallinity of the precipitate. Czanderna et al.[17] prepared some high purity anatase by precipitation from an ammonia solution. The

low temperature of transformation exhibited by this material could be attributed to the high purity of the TiO_2, although it might have been caused by the presence of the ammonia ion during precipitation. The latter explanation is supported by the work of Knoll and Kühnhold[10] who prepared, by precipitation from ammonia solutions, some anatase which transformed at 650° C.

It is generally found that if large quantities (> 5%) of the sulfate or phosphate ion are present, anatase is the predominant crystalline form. It was proposed by Reeves and Blouin[18] that the formation of soluble short chain linear polymers in the sulfate solutions leads to preference for the anatase structure. The precipitate has been found to be amorphous or of small particle size (less than 100Å) and has been found to contain as much as 9% SO_3.[5] Sullivan and Coleman[9] found that, upon heating, SO_3 is given off progressively up to the transformation region. They were unable to find any clear correlation between the rate of sulfur loss and transformation, although the removal of the last traces of sulfur did coincide with the beginning of the transformation. It appears that the sulfur atoms are effective in the formation of the anatase structure and, as will be shown later, that they help determine the stoichiometry of the TiO_2.

Conflicting data exist relating the effect of the atmosphere to the rate of transformation. Czanderna et al.[17] reported that the rate is unaffected when the transformation takes place in vacuum. Iida and Ozaki[7] found, however, that the rate was dependent upon the partial pressure of oxygen, becoming slower under greater partial pressures of oxygen.

The effects of additives have been studied by numerous investigators. These effects and some experimental results obtained in this investigation are summarized in Table I. The additives having the most pronounced inhibiting action are WO_3, and the chloride, sulfate, fluoride, and phosphate ions, in the order of increasing inhibiting effect. The additives which effectively accelerate the transformation are CuO, CoO, Li_2O, and Na_2O.

The most significant effects appear to be: (1) the accelerating action accompanying (a) the addition of CuO, CoO, and the alkali ions and (b) the presence of a reducing atmosphere, and (2) the inhibiting effect of the sulfate, phosphate, and fluoride ions. These effects suggested that the defect nature of TiO_2 may be responsible for the varying rates of transformation. The defect structure of TiO_2 and how it may affect the transformation are considered in the discussion.

Although much data exists on methods of preparation, on the effects of additives, and on the kinetics of transformation, no general understanding of the transformation has yet evolved.

This study was undertaken in order to ascertain more basic information about the mechanism of the transformation and the factors which control the rate of transformation. The kinetics of transformation of three commercial varieties of anatase were determined. This data provided rates and activation energies and a basis for studying the effects of impurities and atmospheres on the transformation. The effects of CuO and of vacuum- and hydrogen-reducing atmospheres on the rate of transformation were investigated by differential thermal analysis and by comparing rate curves obtained under the influence of CuO and atmospheres with those obtained in air from "pure" TiO_2.

II. EXPERIMENTAL

(1) Materials

Three commercial varieties of anatase were obtained. (1) Baker and Adamson reagent TiO_2, lot R163; (2) The Glidden Company, Zopaque SD, lot 1-K-1; and (3) The American Cyanamid Co., Unitane 0-110, lot 401887. Table II gives a summary of some of the properties of these materials, and Table III gives the results of spectrographic and chemical analyses.

(2) Procedures

For the kinetic runs, 400-500 mg samples were loosely packed in small platinum crucibles and heated in a tube furnace. A Pt-Pt-10% Rh thermocouple in contact with the platinum crucible was used to measure temperature. The time was measured from the instant the sample reached temperature, which was generally in the order of two minutes. The samples were air quenched after heat treatment. Material heated in platinum crucibles transformed at the same rate as that in alumina crucibles, showing that catalytic effects were absent.

To determine whether the transformation was being initiated at the surface of each grain and/or merely at the surface of the powdered mass, powder discs were compacted at 8,000 psi and partially transformed. Analysis of the crystalline content showed 31% rutile at the surface and 27% in the interior of the disc. This slight difference in amount of transformed anatase could probably be attributed to the pressure gradient in the disc, the higher pressures inducing more defects in the anatase. It was concluded from this data that the transformation was not beginning at the surface of the disc but at the surfaces of the individual grains. This conclusion was supported by the fact that the

transformed disc was not observed to crack at the surface. Since the transformation involves an eight percent shrinkage, severe cracking would be expected to occur in the transformed layer if the transformation were to proceed from the surface inward.

Sullivan and Cole[5] indicated that grain growth and sintering of anatase powder occur several hundred degrees below the transformation temperatures. Electron micrographs of the transformed R163 powder* showed that sintering occurs during the transformation. It is not clear what effect this sintering had on the kinetics of the reaction but certainly if extensive sintering had occurred before the surface of the grains were transformed, the decrease in area would have retarded the reaction rate at higher temperatures. Such an effect generally results in apparent activation energies which are lower than the true value.

In order to compare the transformation kinetics in hydrogen atmospheres with those in air and with 1% CuO additions, the R163 material was heated in mixtures of H_2-N_2. The samples were brought to reaction temperature in a vacuum of 2×10^{-4} mm Hg. These temperatures were below those at which the transformation could occur in air or vacuum. The reaction was timed from the point at which the hydrogen atmosphere was introduced and was carried out for 30 min for all samples at temperatures of 925 to 1025° C. The temperature was measured by a Pt-Pt-10% Rh thermocouple in contact with the platinum crucible. A liquid nitrogen cold trap was used to collect the water produced by the reduction reaction (a):

$$TiO_2 + xH_2 = TiO_{2-x} + xH_2O . \tag{a}$$
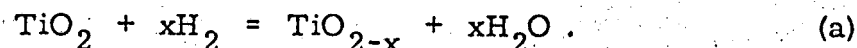
* The electron micrographs were prepared by the Glidden Company, Pigments and Color Division, Baltimore, Maryland.

Hydrogen-nitrogen atmospheres with 5%, 10%, and 20% H_2 were used. The samples were cooled with the furnace in the hydrogen-nitrogen mixtures.

Samples were also heated at 1017° C under vacuum (3×10^{-4} mm Hg obtained by an oil diffusion pump in conjunction with a liquid nitrogen cold trap). The specimens were first held in vacuum at 600° C for 30 min until they had outgassed; then, they were placed in the hot zone of the tube furnace for the desired amount of time and quenched.

The kinetics of transformation of the mixture R163 + 1% CuO were studied in the same way as for pure R163. The CuO was added by making a slurry with cupric nitrate solution, and drying slowly in an oven at 95° C. The nitrate had completely decomposed to CuO at 350° C.

Differential thermal analyses were obtained for mixtures containing 0.0 to 1.0% CuO and 30% CuO. The samples were also prepared by making a slurry with cupric nitrate solution.

The analysis of the anatase-rutile mixtures was performed according to a standard x-ray diffraction method using integrated peak heights and described fully in Klug and Alexander.[19] A rotating sample holder was used to minimize the possible orientation effects. It was not possible to avoid orientation of the long needle-like rutile crystals; thus, it was necessary to base the analysis on only the anatase content. The absence of orientation of the anatase was confirmed by agreement of the relative peak intensities with those given by the National Bureau of Standards.[20]

Diffuse reflectance spectra were obtained from the hydrogen-reduced specimens on a Cary 14 spectrophotometer to obtain a measure of the degree of reduction of the TiO_2.

Finally, diffusion couples of R163-CuO were prepared. Discs of 1 in. diam x 1/4 in. thick were pressed at 10,000 psi. The discs were immersed in CuO powder and reacted at 800 to 880° C, the temperature range over which the transformation of the CuO-TiO$_2$ mixtures could be expected to go to completion. The samples were then analyzed for copper content by x-ray fluorescence at varying distances from the CuO-TiO$_2$ interface. The analysis was made using a General Electric XRD-3 spectrometer equipped with a pulse-height discriminator. The intensity of the CuK$_\alpha$ peak at $2\theta = 45.2°$ was measured at the surface of the disc. This method yielded only approximate diffusion profiles since the depth of penetration by the x-ray beam was approximately 1 mm. Standard curves were prepared using mixtures of cupric nitrate and TiO$_2$ with the CuO content varying from 0.0 to 1.0%.

III. RESULTS AND DISCUSSION

(1) Kinetics of Transformation of Commercial Varieties of Anatase

Solid state reactions are characterized by two distinct processes-- nucleation of the new phase and the propagation of this new phase into the old. These reactions generally result in a sigmoid percent reaction-time (α-t) curve. The most intensely studied reactions of this type have been thermal decompositions, a broad survey of which has been made by Garner.[21] Probably an even simpler case of these reactions is the phase transformation, since nucleation and movement of the interface are not complicated by evolution of gaseous products as are decompositions and dehydrations.

The anatase-rutile transformation is characterized by the formation of a single new phase of differing volume and orientation. The transformation has been shown to begin sometimes at the surface of macroscopic

crystals and to progress toward the center.[4] Since a volume shrinkage
of approximately 8% occurs, a large strain energy must be overcome
for nucleation to take place. This strain energy will probably be the
largest contributing factor to the activation energy for nucleation, ΔG_1.
After stable nuclei have formed, they continue to grow with a different
activation energy for growth, ΔG_2. The relative magnitudes of these
two energies determine to some degree the shape of the α-t curve. If
we have $\Delta G_1 \gg \Delta G_2$, a long acceleratory period will result, assuming
of course, that the rate constant for nucleation, $K_1 \gg K_2$, the rate
constant for growth. If we have $\Delta G_2 \gg \Delta G_1$, nucleation is rapid and a
minimum acceleratory period results. In the case of the TiO_2 trans-
formation, the inflection point occurs at $\alpha = 0.5$, indicating an activation
energy for nucleation comparable to that for growth.

In a separate study it was indicated that in the later stages of
reaction the transformation might take place as an interface reaction.[4]
The possibility of the presence of the interface reaction and the fact
that commercial polycrystalline anatase exists in the shape of almost
spherical particles suggested the study of the kinetics of various
commercial powders. Ideally, the kinetics of the transformation should
be determined on single crystals but no large crystals of high purity or
quality were available.

Sullivan and Cole[5] studied colloidal titania produced by a commercial
process and concluded that the transformation was a first-order process
with an activation energy of 100 to 110 kcal. Rao[6] prepared highly
purified anatase and also found a first-order kinetic law but a lower
activation energy of 80 kcal. However, no attempts were made to
interpret their data in terms of the geometry of the crystals or to

suggest a mechanism. It is generally accepted that solid state reactions should not be considered apart from the geometry of the particles undergoing reaction and the type of nucleation which occurs.

Jacobs and Tompkins[22] have treated nucleation and growth in solid phases extensively using several laws for nucleation and considering the growth of one, two, and three-dimensional nuclei in both single crystals and polycrystalline aggregates. They reviewed the development of a series of expressions which have been used to explain the course of numerous reactions. In this study we used several of these expressions to analyze the reaction curves obtained for the three anatase samples, U-110, R163, and ZSD.

The acceleratory period was described reasonably well by an exponential law

$$\ln \alpha = K_1 t + c \tag{1}$$

where: α = percent transformation
K_1 = the rate constant
t = time

This law is based on the assumption of one-dimensional, linear, branching nuclei and a constant growth rate.

Three expressions described adequately the deceleratory period. The first of these and possibly the one to be anticipated on the basis of the size and shape of the crystals is the "contracting sphere" formula. The derivation supposes the eventual formation of an interface between reactant and product. This interface then moves from the surface inward in the form of a "contracting sphere". The expression is

$$(1 - \alpha)^{1/3} = K_2 t + c \tag{2}$$

Another law assuming random nucleation of particles according to an

exponential nucleation law and rapid surface growth of any particle

nucleated is

$$\ln (1 - \alpha) = K_3 t + c \tag{3}$$

Finally, the Avrami-Erofeyev equation which allows for overlapping of

nuclei is

$$\left[\ln (1 - \alpha) \right]^{1/3} = K_4 t + c \tag{4}$$

Figures 1-3 show typical sigmoid α - t curves for the U-110, R163,

and ZSD materials. The acceleratory period was described by the ex-

ponential law (1) and was valid from $\alpha = 0.0$ to $\alpha \simeq 0.50$. The decel-

eratory period was described reasonably well by expressions (2), (3),

and (4). The activation energy plots for each of these rate laws are

given in Fig. 4. Table IV shows a compilation of activation energies,

rate constants based on the Arrhenius relationship, and the region of

validity for each of the rate laws.

It does not appear possible to distinguish the correct rate law from

the expressions (2), (3), and (4) since the experimental points fit each

expression equally well. This is an inherent difficulty in studying

powder reactions,[21] particularly those in which the geometry of the

crystals is not certain and the particle size is not perfectly uniform.

However, the fact that the rate expressions give an ambiguous inter-

pretation of the mechanism does not prevent these rate curves from

being used as a basis for studying effects of other variables.

The DTA transformation temperatures taken as the maximum in

the exothermic peak and also shown in Table IV, differ for the three

materials and roughly correspond to the activation energies for growth.

This correlation suggests that DTA transformation temperatures might

be used to characterize the stability of different anatase samples. An attempt will be made to relate these differences in kinetics and DTA transformation temperatures to the nature and amount of impurities in the TiO_2 and thereby to the stoichiometry of the TiO_2.

(2) Transformation in Vacuum- and Hydrogen-reducing Atmospheres

It was shown in the introduction how an analysis of the effects of impurities led to the conclusion that the defect structure of TiO_2 might influence the rate of transformation. Unfortunately the defect nature of TiO_2 is not yet fully understood. There is considerable evidence for the formation of both titanium interstitials and oxygen vacancies. Weight loss data as a function of oxygen pressure[23] have been used to confirm the presence of oxygen vacancies while certain studies of the oxidation of titanium[24] and internal friction studies of vacuum-reduced rutile[25, 26] have led to the suggestion of a defect structure involving interstitial titanium ions. Electrical resistivity data[27, 28] have provided evidence for both the interstitial and vacancy mechanisms. An important factor seems to be the atmosphere in which the defects are formed. In hydrogen at all pressures[25, 29] and oxygen pressures greater than 10 mm Hg the presence of oxygen vacancies seems to be predominant.[30] At oxygen pressures less than 10 mm Hg[30] and in CO-CO_2 mixtures,[28] titanium interstitials have been found. At least two authors suggested that the defect structure for vacuum-reduced and hydrogen-reduced rutile are different,[25, 29] with the interstitial mechanism predominating in vacuum-reduced TiO_2 and the oxygen vacancy mechanism in hydrogen-reduced material.

One would expect the defect nature to strongly affect the chemical and physical properties of TiO_2. In the case of the anatase-rutile

transformation, on the basis of the proposed mechanism,[4] oxygen vacancies would tend to accelerate the collapse of the anatase structure while formation of interstitials would tend to preserve the structure of larger volume. If formation of oxygen vacancies is assumed to be the predominant mechanism in the reduction of rutile in H_2, then the accelerating effects of a hydrogen-reducing atmosphere would be explained. In addition, the accelerating effect of Cu^{+2} and Co^{+2} becomes understandable, if one assumes diffusion of ions whose valence is less than four and consequent substitution for Ti^{+4} ions with the formation of oxygen vacancies. Conversely, the presence of ions such as S^{+6} and P^{+5} substituting for Ti^{+4} would tend to reduce the number of vacancies and inhibit the transformation.

In Fig. 5 the percent transformation is plotted vs the temperature of transformation for samples heated for a constant time in air, in hydrogen and with 1% CuO additions. It is clear that the reaction is accelerated by the hydrogen atmospheres and the presence of the CuO. The degree of acceleration is proportional to the amount of hydrogen present in the atmospheres.

The samples heated in the H_2-N_2 atmospheres varied in color from light gray to a dark blue-gray, the dark color appearing in samples treated at the higher temperatures. The intensity of the color has been shown to be a measure of the reduction of the TiO_2.[31] Figures 6a and 6b show the effects of both transformation and reduction on the color of anatase R163. In Fig. 7 the difference in reflectance at 6500Å for non-reduced and reduced samples $(R_{Std.} - R_x)$ is plotted vs the percent transformation. The figure shows a direct proportionality between the degree of reduction of TiO_2 and the amount of anatase transformed.

The accelerating effect of hydrogen could reasonably be attributed to the formation of a second phase as well as to the presence of oxygen vacancies. Magnéli phases of composition Ti_nO_{2n-1} where n = 4, 5, 6, 7, 8, 9, or 10 have been shown to exist in rutile[32] and might be expected to also form in anatase. The precipitates of these lower oxide phases would probably form nucleation sites for rutile. Although no second phase was detected by x-ray analysis, the precipitation of such a phase would probably be in such small quantities as to be undetectable. Straumanis[31] showed a correlation between the color of reduced rutile and composition. He indicated that the second phase appeared only when the samples had attained a dark blue color. Recent data by Blumenthal and Whitmore[33] show the homogeneity region of rutile to be even narrower than that given by Straumanis. Cell measurements showed that the homo- geneity region of the rutile phase TiO_x extends from x = 2.000 to 1.991 instead of x = 2.000 to 1.983. At x = 1.991 the samples prepared by Straumanis were light gray in color. Thus, the presence of a second phase in our samples heated in H_2-N_2 mixtures appears almost certain. However, the presence of a second phase still does not rule out the presence of oxygen vacancies. From the evidence cited earlier it will be assumed that they are present and that the increase in rate of trans- formation in a hydrogen atmosphere is caused either by the formation of a second phase or by the presence of oxygen vacancies.

Figure 8 shows the results of runs in air and vacuum at 1017° C. The rate in vacuum follows that in air up to about 30% reaction and then begins to rapidly decrease. The defect mechanism proposed in vacuum is the formation of titanium interstitials. The reduction in rate of transformation observed in Fig. 8 strongly supports the interstitial

mechanism. We would expect interstitials to affect both nucleation and growth rates but the experimental data do not provide any information concerning this point. Such a case is not inconsistent with the fact that the retardation does not occur until 30% transformation. Since the formation of interstitials is probably also temperature activated, it might be assumed that the point at which the rate begins to decrease corresponds to the point at which the rate of formation of interstitials becomes measurable. On the other hand, it is also possible that interstitial formation inhibits the rate of growth more than the rate of nucleation in which case the early stages of the transformation would not be affected.

(3) Effects of CuO on the Transformation

Figure 9 shows the transformation curves for R163 + 1% CuO. Typical sigmoid curves resulted at greatly reduced temperatures. We analyzed these curves in the same manner as for pure R163 and obtained the rate constants and activation energies listed in Table IV. This analysis shows that the activation energy has increased by 50 kcal. It does not seem reasonable that the activation energy for the process should increase and the transformation temperature decrease. Since the process now involves (1) reaction between CuO and TiO_2 and (2) transformation, it is evident that the kinetic expression as developed earlier is no longer valid. Probably the activation energy as measured is for a combination of processes, involving transformation and diffusion of Cu^{+2} and oxygen vacancies into titania.

The DTA curves for mixtures of R163 and varying amounts of CuO show two features. First, Fig. 10 shows that the DTA transformation temperature progressively decreases from 1115° to 842°C with the

amount of added CuO. Beyond 1% there is no further decrease, which suggests that some sort of surface phenomenon is occurring in which the surface of the grains is gradually being covered by CuO. Approximate calculations show that with the assumption of a monomolecular layer of the oxide, 1% CuO would completely cover the surface.

Secondly, it can be seen from Fig. 11 that the temperature interval over which the reaction occurs decreased with the amount of CuO. This interval is generally an indication of the apparent activation energy for the process. Thus, it can be concluded that the apparent activation energy gradually increases with the amount of added CuO. The conclusion further supports the results with the R163-1% CuO mixtures in which the apparent activation energy was 175 kcal/mole.

The accelerating effect of the CuO might be caused by one or more of the following reactions: (1) a new TiO_2-CuO phase forming with possible enhancement of the nucléation rate, (2) oxidation of a cuprous compound formed during the decomposition of cupric nitrate, or (3) the formation of solid solution.

Taylor[34] found no evidence of any compound formation in mixtures of CuO and TiO_2 samples quenched from 1000° C. X-ray analyses of the mixtures of 1% and 30% CuO with R163 showed no traces of a second phase. This data, however, does not preclude the possibility of a high temperature phase similar to that present in the $CuO-Al_2O_3$[35] system, but it is unlikely that such a phase would decompose so rapidly on quenching as to completely prevent its detection.

The CuO was added in the form of $Cu(NO_3)_2 \cdot 3 H_2O$. The decomposition of the trihydrate has been found to go through several stages. The formation of an oxynitrate $Cu(NO_3)_2 \cdot 3 Cu(OH)_2$ was reported to

occur at 170° to 230° C with decomposition to CuO at 300° C.[36] Although the presence of Cu_2O was reported by Lecuir,[36] diffraction analysis performed in this laboratory on the samples of the trihydrate decomposed above 350° C showed no traces of any crystalline material other than CuO. Thus, the possibility of oxidation of a cuprous compound at the transformation temperatures seems remote.

No reference to formation of a solid solution of CuO in TiO_2 was found in the literature. To test the possibility that solid solutions were nevertheless formed, the diffusion couple was prepared. The diffusion profile is shown in Fig. 12, in which the Cu content and percent transformation are plotted as a function of the distance from the $CuO-TiO_2$ interface. Solid solution of Cu^{++} in TiO_2 at temperatures of 800-880° C occurs with the maximum concentration of copper apparently 0.2 to 0.3 wt. % or approximately 0.25 to 0.38 mole %. The formation of solid solution precedes the transformation and clearly causes the acceleration observed in Fig. 5. The mechanism through which the rate of transformation increases is, however, open to several interpretations. The copper ions dissolved in TiO_2 must occupy either (a) substitutional or (b) interstitial sites. Case (a) implies the formation of oxygen vacancies or an increase in titanium interstitials to preserve electrical neutrality while (b) implies a reduction in oxygen vacancy or titanium interstitial concentration. It would seem that only (a) with the formation of oxygen vacancies is likely to promote the transformation. Any increase in the number of interstitial ions should reduce the rate of transformation. Although (b) involves a decrease in titanium interstitials this decrease is more than compensated for by the copper interstitials. We concluded that solid solution of copper with the concomitant formation of oxygen

vacancies is the cause of the accelerated transformation although this conclusion was subject to the same consideration as the reduction of TiO_2 in hydrogen, namely, that formation of oxygen vacancies could lead to the formation of a second $Ti_n O_{2n-1}$ phase. The single phase region in rutile extends down to $TiO_{1.991}$ and we assumed that the single phase region in $Ti_{1-x} Cu_x O_{2-2x}$ extends to the same oxygen content. The maximum amount of copper dissolved corresponds to $Ti_{.996} Cu_{.004} O_{1.992}$; thus, formation of a second phase is possible.

A curious feature of the diffusion profile is the increase in copper concentration as the amount of anatase increases. This effect may indicate a higher solubility and/or diffusivity of Cu^{+2} in anatase which is not surprising in light of the more open anatase structure. A significant point is that diffusion is evidently proceeding against a positive concentration gradient. The existence of this solid solubility region points to the probable formation of oxygen vacancies at the level of 1.2×10^{21} vacancies per mole.

Ionic size is an important consideration in solid solution formation. Wells[37] lists the ionic radii of Ti^{+4} and Cu^+ as 0.68Å and 0.96Å, respectively, but fails to give a value of Cu^{+2}. An estimate of 0.57Å was made from nearest neighbor distances in a number of cupric compounds as listed in Table V. Thus, on the basis of ionic radius, the assumption of solid solubility appears valid. These data interpreted in conjunction with the rates in hydrogen and vacuum strongly suggest the formation of solid solution and the resulting oxygen vacancies as the most important factor in the accelerating effect of CuO.

(4) General Considerations on Impurity Effects

It is interesting to compare the DTA transformation temperatures

for the three samples of TiO_2 in light of the impurity contents shown in Table III. Assuming that only those impurity ions of the proper size could form solid solution (Al^{+3}, Mg^{+2}, Ca^{+2}, Fe^{+2}, Nb^{+5}, S^{+6}, and P^{+5}) and that ions of valence less than four increase the vacancy concentration, while those of valence greater than four reduce the vacancy concentration, it is possible to arrive at a speculative estimate of the change in vacancy content from the equilibrium value. No studies of the equilibrium concentration of vacancies in anatase have been made but Buessem and Butler[38] by assuming reaction (b) were able to determine the vacancy concentration in rutile by measuring the change in weight as a function of the oxygen pressure.

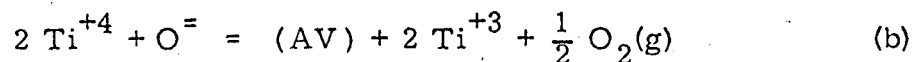$$2\ Ti^{+4} + O^= = (AV) + 2\ Ti^{+3} + \frac{1}{2}\ O_2(g) \qquad (b)$$

Table VI shows the equilibrium number of vacancies in rutile in the temperature range used for the study of U-110, ZSD, and R163, as calculated in the Appendix. The vacancy concentration in anatase would not be identical to that in rutile but because of similarities in bond strength and coordination should be of the same order of magnitude. Table VII shows the correlation between the change in vacancy concentration from the equilibrium value and the DTA transformation temperature. The change in vacancy concentration caused by the nature of the impurities is significant in comparison to the equilibrium value and should be expected to affect the transformation rate .

Although the data obtained in this study indicate that the nature of the impurities and the transformation environment control to a large degree the transformation temperature, it would also seem reasonable to expect the total impurity level to affect the transformation temperature and the activation energy. Table VIII shows that a high level of

impurities seems to raise the transformation temperature. The specimens prepared by both Rao[6] and Knoll and Kühnhold[10] in ammonia solutions transform in the range 600° to 700° C, while most TiO_2 precipitated from sulfate solutions transforms in the range 800° to 1000° C. The low temperature of transformation evidently arises from the purity of the TiO_2 or precipitation from the ammonia solutions. Rao's TiO_2 was spectroscopically pure, while Knoll and Kühnhold did not provide any indication of the purity of their material. It is not clear how precipitation from ammonia solutions might allow a low transformation temperature. Impurities entering into solid solution could easily occupy the large interstitial positions in the anatase structure and would, by stuffing the structure, tend to prevent the collapse of the structure. Besides stuffing the structure, substitutional cations of valence greater than four would tend to decrease the oxygen vacancy concentration. Thus, low impurity levels tend to favor a low transformation temperature and a low activation energy. However, even if the impurity level is low, the transformation temperature may still be high if the impurities are those which tend to reduce the vacancy concentration (e.g. anatase U-110).

Probably the variation in transformation rate among different samples of anatase is largely a result of a change in the activation energy. The activation energy can be thought of as arising from the strain energy developed during deformation of the oxygen close-packed structure and from the energy necessary to break the Ti-O bonds. The effect of the addition of impurities would be to increase the strain energy unless these impurities were such as to create oxygen vacancies. In the latter case one would expect the strain energy to be decreased. The presence

of the oxygen vacancies would also decrease the number of Ti-O bonds which must be broken. The effects of impurities can be summarized:

(a) Those impurities which enter interstitial positions or substitutional ions larger than Ti^{+4} increase the strain energy unless they reduce the number of Ti-O bonds which must be broken by creating anion vacancies.

(b) The impurities which form substitutional solid solution and create anion vacancies reduce the strain energy and the number of Ti-O bonds which must be ruptured.

When the transformation takes place in a reducing atmosphere or in contact with impurities which go into solid solution, the following processes may occur:

	Rate
1. Formation of vacancies at the surface	R_v
2. Nucleation of the rutile phase	R_{nucl}
3. Diffusion of the vacancies toward the interior of the crystal	R_d
4. Growth of the nucleated rutile crystals	R_g

Assuming that $R_v \gg R_d$ it is possible that the vacancies could accumulate at the surface and eventually nucleate micro-pores which would tend to reduce the activation energy for transformation or increase the number of possible sites of nucleation. Seitz[39] has stated that (a) vacancies will condense at spherical voids or inclusions in metals containing a volume of ~ 1000 lattice sites if $\frac{N_v}{N_{v_o}} \geq 2$, and (b) in a perfect crystal vacancies may condense to form voids if $\frac{N_v}{N_{v_o}} \geq 100$. ($N_v$ = number of vacancies present per cm^3; N_{v_o} = equilibrium number of vacancies per cm^3). If it is accepted that the rate of nucleation is increased by the

presence of vacancies, whether or not the rate of growth, R_g, is increased depends on R_d. The diffusion profile showed that the diffusion of Cu proceeded ahead of the transformation so that $R_d > R_g$. Such a condition should increase the rate of growth and this was observed.

If $R_v < R_d$ the vacancies would have diffused rapidly throughout the entire specimen, probably not nucleating voids at the surface. In this case such a radical change in the nucleation rate as was observed would not be expected.

A possible sequence of events in the CuO-or H_2-accelerated transformation is:

1. Vacancies form (with or without void formation) via diffusion of Cu^{++} or the reaction of H_2 with O. Precipitation of a second phase might be possible.

2. Rutile nucleates and vacancies diffuse toward the interior of the crystal. Rutile nucleation would be promoted by the formation of a second phase.

3. Rutile grows and diffusion of vacancies continues.

IV. SUMMARY

The transformation kinetics of three commercial TiO_2 powders were determined. Sigmoid transformation rate curves were obtained and these were interpreted in terms of a nucleation-growth process in which the activation energy for nucleation was comparable to that for growth. Several rate laws were successfully applied to the transformation-time curves but no clear interpretation of the mechanism could be derived from the rate laws. Activation energies for the three powders were 100, 115, and 190 kcal/mole.

The effects of impurities and of the transformation environment were described. In this study small amounts of CuO and a hydrogen atmosphere were found to accelerate the transformation while a vacuum of 3×10^{-4} mm Hg inhibited the transformation beyond $\alpha = 0.30$. CuO was found to go into solid solution with TiO_2 up to 0.2 to 0.3 wt. %. The suggested mechanism through which the rate changes occurred concerns changes in the TiO_2 defect concentration. It is proposed that:

1. The presence of a hydrogen atmosphere increases the vacancy concentration, thereby facilitating collapse of the anatase structure. However, the increased rate of transformation could also be attributed to the formation of a second Ti_nO_{2n-1} Magnéli phase precipitate. Precipitation of such a phase could provide nucleation centers for rutile.

2. Substitutional solid solution of CuO increases the oxygen vacancy concentration and acts in a similar manner to hydrogen. The dissolved CuO may bring about the formation of a second phase.

3. In a vacuum of 3×10^{-4} mm Hg interstitial titanium ions form, and through a "structure stuffing" effect, reduce the rate of transformation.

The overall effect of impurities appears to be twofold. First, the total impurity content affects the transformation through the "structure stuffing" effect. Large quantities of most impurities raise the transformation temperature, probably by increasing the activation energy. Secondly, the nature of the impurities appears to control the stoichiometry of the TiO_2. It is assumed that the oxygen vacancy defect

mechanism is operative. Ions of valence less than four and of small ionic radius which can substitutionally enter the structure, e.g., Cu^{++}, Co^{++}, or Li^{+}, would increase the oxygen vacancy concentration. This increase in vacancy concentration presumably reduces the strain energy which must be overcome before collapse of the structure can occur. Ions of valence greater than four, e.g., P^{+5} and S^{+6}, would correspondingly reduce the oxygen vacancy concentration and the rate of transformation. Similarly, substitution of two fluoride ions for an oxygen ion would reduce the number of oxygen vacancies and inhibit the transformation.

ACKNOWLEDGMENTS

APPENDIX

Calculation of Equilibrium Vacancy Concentration in Rutile

If we assume the following reaction

$$2Ti^{+4} + O^{=} \longrightarrow (AV) + 2Ti^{+3} + \tfrac{1}{2} O_2 \qquad (c)$$
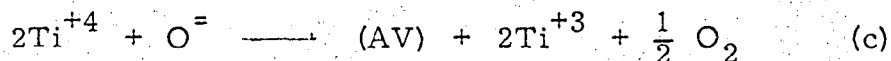
then,

$$K_{eq} = n_{AV} \cdot n_{Ti+3}^2 \cdot P_{O_2}^{\frac{1}{2}} = \exp \frac{-\Delta F^{\circ}}{RT} = \exp \frac{\Delta S}{R} \cdot \exp \frac{-\Delta H}{RT} \cdot$$

where K_{eq} = equilibrium constant for the reaction,

n_{AV} = mole fraction of anion vacancies,

n_{Ti+3} = mole fraction of Ti^{+3} ions,

P_{O_2} = oxygen pressure.

ΔF° = the change in Gibbs free energy for reaction (c)

ΔH° = the enthalpy change $= H_{AV} + 2H_{Ti+3} + \tfrac{1}{2} H_{O_2}$

ΔS = the entropy change

Experimentally[38] it is found that

$$\Delta S_{O_2}^{\circ} = 60 \text{ cal/}^{\circ}C \qquad \Delta H^{\circ} = 83,000 \pm 10 \text{ Kcal/mole,}$$

and if we assume

$$n_{Ti+3} = 2n_{AV} \; , \quad \text{then } K_{eq} = 4n_{AV}^3 \cdot P_{O_2}^{\frac{1}{2}} \; .$$

Letting $P_{O_2} = 0.2$ atm, the values of n_{AV} listed in Table VI were calculated at $T = 950^{\circ}$, 1000°, and 1050° C.

FOOTNOTES AND REFERENCES

This paper is based on a thesis submitted by Robert D. Shannon in partial fulfillment of the requirements for the degree of Doctor of Philosophy in engineering science, University of California, Berkeley, California, June 1964.

At the time this work was done the writers were, respectively, research assistant and professor of ceramic engineering, Department of Mineral Technology and Inorganic Materials Research Division, Lawrence Radiation Laboratory, University of California at Berkeley.

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TABLE I

Compilation of Data Concerning the Effect
of Impurities on Transformation of Anatase

Investigator	Additive	DTA T_{tr} °C	Remarks
Knoll and Kühnhold[10]	None	655	Impurities added during precipitation
	~0.1% NO_3^-	660	- - - - - - - - - - -
	0.1% Cl^-	735	Inhibited transformation
	0.1% $SO_4^=$	775	Inhibited transformation
	0.1% F^-	900	Inhibited transformation
Shannon[4]	None	1115	CuO added to the crystal-line anatase as a solution of the nitrate and in all cases served to inhibit the transformation.
	0.1% CuO	1113	
	0.2%	1091	
	0.3%	1047	
	0.4%	1003	
	0.6%	932	
	0.8%	872	
	1.0%	842	

TABLE I (cont.)

Investigator	Additive	DTA T_{tr} °C		Remarks
Flörke[11]		After 3 days at 850° C		Oxides added to crystalline anatase as nitrate solution
		%Anatase	% Rutile	
	5.0% Li_2O	0	100	Accelerator
	5.0% Na_2O	30	70	Accelerator
	5.0% K_2O	50	50	Accelerator
	5.0% CaO	90	10	---
	5.0% SrO	100	0	Inhibitor
	5.0% BaO	90	10	---
	None	80	20	---
		% Anatase	% Rutile	
Rao, Turner, and Honig[8]		1 hour at 708° C		Impurities added during precipitation.
	None	5	95	
	5.0 at.% Zn^{++}	24	76	Inhibitor
	5.0 at.% Cl^-	51	49	Inhibitor
		1 Hour at 870° C		
	5.0 at.% Al^{+3}	28	72	Inhibitor
	5.0 at.% $SO_4^=$	71	29	Inhibitor
	5.0 at.% $PO_4^{\equiv}$	100	0	Inhibitor

TABLE I (cont.)

Investigator	Additive	3 hours at 800° C		at 900° C		Remarks
		% Anatase	% Rutile	% Anatase	% Rutile	
Iida and Ozaki[7]						Impurities added to crystalline TiO_2 as solution of soluble salt
	None	100	0	18	82	
	1.0 mol.% Na_2O	100	0	86	14	Inhibitor
	1.0 mol.% CuO	0	100	0	100	Accelerator
	1.0 mol.% CoO	79	21	0	100	Accelerator
	1.0 mol.% NiO	97	3	0	100	Accelerator
	1.0 mol.% MnO_2	100	0	0	100	Accelerator
	1.0 mol.% Fe_2O_3	98	2	0	100	Accelerator
	1.0 mol.% Cr_2O_3	88	12	4	96	Accelerator
	1.0 mol.% MoO_3	84	16	20	80	Accelerator
	1.0 mol.% WO_3	100	0	85	15	Accelerator

		3 hours at 900° C	
			% Rutile
	Flowing O_2		52	The authors concluded that the transformation was inhibited by increased oxygen partial pressure.
	Flowing air		70	
	Flowing air		85	
	Vacuum		94	
	Flowing H_2		95	
	Static air		48	

Table II

Some Characteristics of Three Commercial Anatase Powders

Type	Percent TiO$_2$ [*]	Percent[**] anatase	Particle size	Method of preparation
B & A R163	99.0	99.0	-	-
Zopaque SD	97.3-99.2	100.0	0.05-0.25[***] microns	Hydrolysis of titanium sulfate solution
Unitane 0-110	99.4	99.7	0.25-0.30 microns	"

[*] The purity of the TiO$_2$ samples was determined by spectrographic and chemical analyses, Table III.

[**] The crystalline content was determined in this laboratory by x-ray analysis.

[***] A particle size distribution performed by The Glidden Company indicated that the ZSD titania had a mean diameter of 0.14 microns and that 85% of particles had diameter of 0.05 to 0.25 microns. Electron micrographs showed the particles to closely approximate spheres.

TABLE III

Spectrographic and Chemical Analyses of Three Anatase Powders

	R163		ZSD		U-110	
	Wt.%	Mole %	Wt.%	Mole %	Wt.%	Mole %
Spectrographic analyses of TiO$_2$ samples						
SiO$_2$	0.05*	0.067	0.04	0.053	0.075	0.100
Al$_2$O$_3$	0.20	0.157	0.35	0.274	-	-
MgO	0.09	0.179	0.09	0.179	0.005	0.010
CaO	0.035	0.050	0.017	0.024	0.003	0.004
FeO	-	-	0.025	0.028	-	-
SnO$_2$	-	-	0.01	0.015	-	-
Nb$_2$O$_5$	-	-	0.17	0.051	-	-
ZrO$_2$	-	-	-	-	0.08	-
BaO	-	-	-	-	0.001	-
PbO	0.005	-	0.006	-	-	-
Chemical analysis						
SO$_3$	0.018	0.018	0.014	0.014	0.075	0.075
P$_2$O$_5$	0.526	0.296	0.620	0.350	0.370	0.208

* These figures are the average of results obtained from two random samples of each of the indicated materials. The analyses were performed by American Spectrographic Laboratories, San Francisco, Calif.

TABLE IV

Kinetic Data for the Transformation of
U-110, R163, ZSD, and R163 + 1% CuO

Material	DTA Trans. Temp.	Expression	Region of Validity	E (Kcal)	$A(sec^{-1})$
U-110	1190° C	(1)	0.0 - 0.5	148	7.9×10^{20}
		(2)	0.5 - 0.9	186	6.2×10^{25}
		(3)	0.3 - 0.9	194	6.2×10^{27}
		(4)	0.3 - 1.0	204	4.1×10^{29}
R163	1115°	(1)	0.0 - 0.5	109	1.2×10^{15}
		(2)	0.45 - 0.90	94.6	1.1×10^{12}
		(3)	0.45 - 1.00	101	8.4×10^{13}
		(4)	0.70 - 1.00	108	3.1×10^{14}
ZSD	1138°	(1)	0.0 - 0.45	136	2.6×10^{19}
		(2)	0.40 - 0.95	113	6.7×10^{14}
		(3)	--	--	--
		(4)	0.70 - 0.95	116	2.4×10^{15}
R163 + 1% CuO	842°	(1)	0.0 - 0.60	154	4.7×10^{28}
		(2)	0.30 - 0.80	180	2.2×10^{33}
		(3)	0.30 - 0.90	170	8.5×10^{31}
		(4)	0.30 - 0.80	180	

TABLE V

Interionic Distances in Some Cupric Compounds

Compound	Distance* between Cu^{+2} and: (Å)		Ionic Radius (Å)
$CuCl_2$	4 Cl	2.30	0.58
$CuBr_2$	4 Br	2.40	0.48
$CuCl_2 \cdot 2 H_2O$	2 Cl	2.28	0.56
	2 O	1.93	0.61
$CuCsCl_3$	4 Cl	2.30	0.58
$K_2CuCl_4 \cdot 2 H_2O$	2 O	1.97	0.55
	2 Cl	2.32	0.60
CuF_2 (distorted rutile structure)	2 F	1.93	0.57
TiO_2 (rutile)	2 O	1.946	0.62

Average r_{Cu++} = 0.57 Å

* Interatomic distances taken from Wells.[37]

TABLE VI

Equilibrium Concentration of Vacancies in Rutile*
(from Buessem and Butler[38])

Temperature °C	K_{exp} (atm$^{1/2}$)	n_{AV} x 10^{-3}	N_{AV} (vacancies/mole) x 10^{21}
950	7.26×10^{-8}	3.4	2.1
1000	2.39×10^{-7}	5.1	3.1
1050	9.43×10^{-7}	8.1	4.8

* See appendix for calculations

TABLE VII

Transformation Temperature, Change in Vacancy Concentration, and Activation Energy for Various Samples of Anatase

Material	DTA T_{tr} °C	Change in vacancy concentration per mole from the equilibrium concentration x 10^{21}	Activation energy Kcal/mole
U-110	1190	-2.0	190
ZSD	1138	+1.8	115
R163	1115	+1.6	100
R163 + 1% CuO	842	+7.7	--

TABLE VIII

Transformation Characteristics of Anatase Preparations

Investigator	Sample	Approx. Percent TiO_2	DTA T_{tr} °C	Temp. of 50% reaction in 60 min	Activation energy Kcal/mole
Shannon	U-110	99.6	1190*	1080	190 ± 10
	ZSD	99.0	1138	1040	115 ± 10
	R 163	99.2	1115	1025	100 ± 10
	R163 + 1% CuO	98.2	842	782	
Rao[6]		99.9	~ 650 **	700	80 ± 10
Sullivan and Cole[5]		99.8	900 ***	790	105 ± 5
Sullivan and Coleman[9]	1	99.6	-	840	66
	2	99.6	-	850	85
	3	99.6	-	840	76
	4	99.6	-	975	41
Kuhnhold and Knoll[10]	Tetraethyl† ester	?	655	-	-
	NO_3		660	-	-
	Cl^-		735	-	-
	$SO_4^=$		775	-	-
	F^-		900	-	-

*   heating rate = 12° C/min   †Precipitated from ammonia solution with the presence of the
**   heating rate = 12.5° C/min   indicated ions. Analysis of the anhydrous precipitate showed
*** heating rate = 5° C/min   approximately 0.1% of the anions shown.

FIGURE CAPTIONS

Fig. 1. Percent transformation vs. time, anatase U-110.

Fig. 2. Percent transformation vs. time, anatase R163.

Fig. 3. Percent transformation vs. time, anatase ZSD.

Fig. 4. Activation energy plot, ln k vs. 1/T for the rate laws (1),

(2), (3), and (4) for anatase U-110.

Fig. 5. Percent transformation vs. temperature in H_2-N_2 mixtures

and for TiO_2-1% CuO, transformation time = 30 min,

anatase R163.

Fig. 6. a. Reflectance curves for TiO_2 R163, untransformed

and partially transformed in air. Curves show how

the transformation affects the color of TiO_2.

b. Reflectance curves for TiO_2 R163, untransformed

and partially transformed in 10%H_2-90%N_2 mixtures

for 30 min at various temperatures.

Fig. 7. Percent transformation vs. absorption at 6500 Å ($R_{std.}$ - R_x),

for samples of R163 heated in hydrogen-nitrogen mixtures.

Fig. 8. Percent transformation vs. time for R163 transformed in

air and vacuum (3 x 10^{-4} mm Hg) at 1017° C.

Fig. 9. Percent transformation vs. time for mixtures of R163 and 1% CuO.

Fig. 10. DTA transformation temperature vs. percent CuO in mixtures

of R163-CuO.

Fig. 11. DTA curves showing the exothermic peak caused by the

anatase-rutile transformation for various mixtures of R163-CuO.

Heating rate = 12° C/min.

Fig. 12. a. Percent copper vs. distance from the CuO-TiO_2 interface.

The sample was a pressed disc of R163 heated in CuO

powder for 6 hours at 880° C.

b. Percent anatase vs. distance from the CuO-TiO_2 interface.
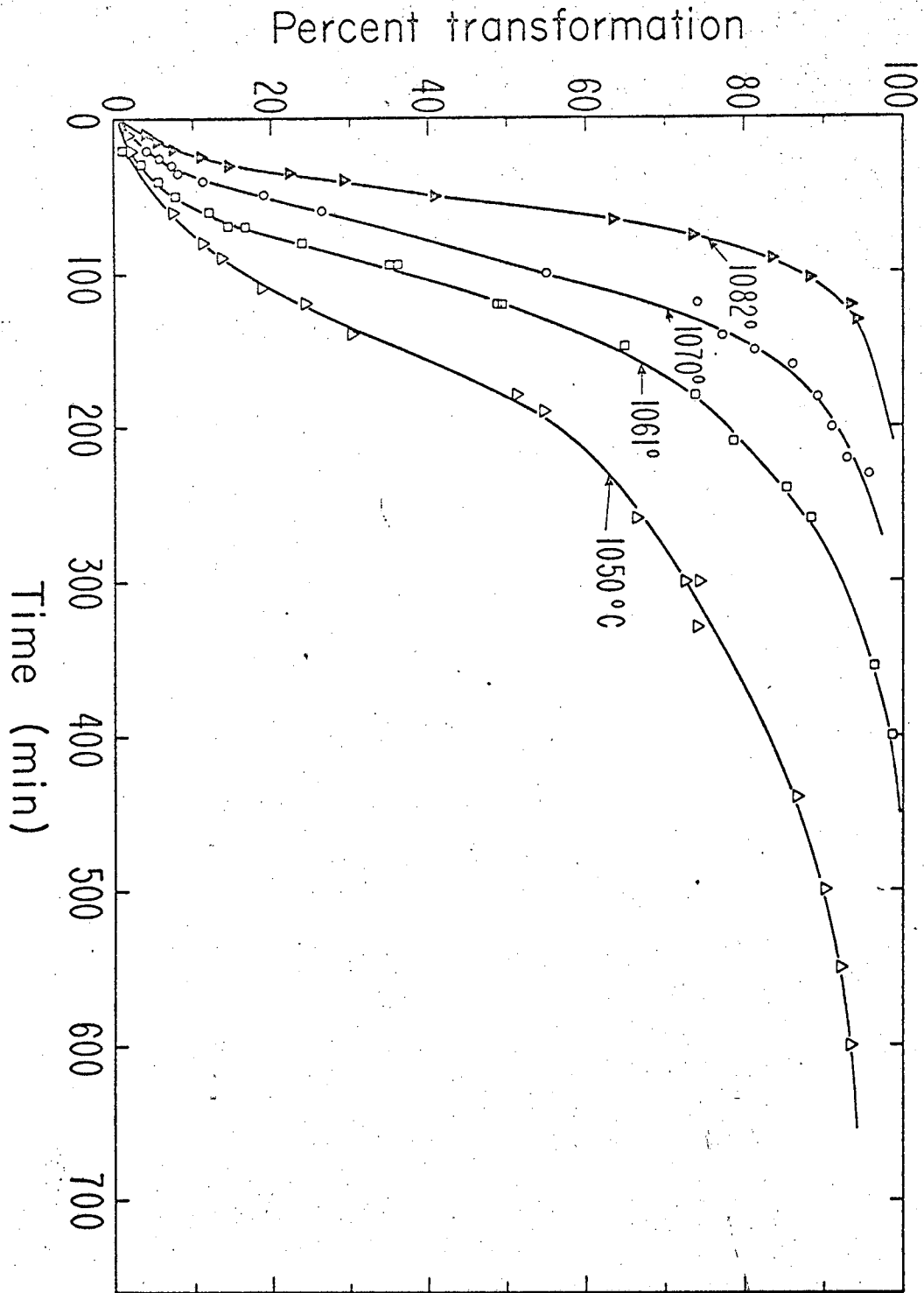
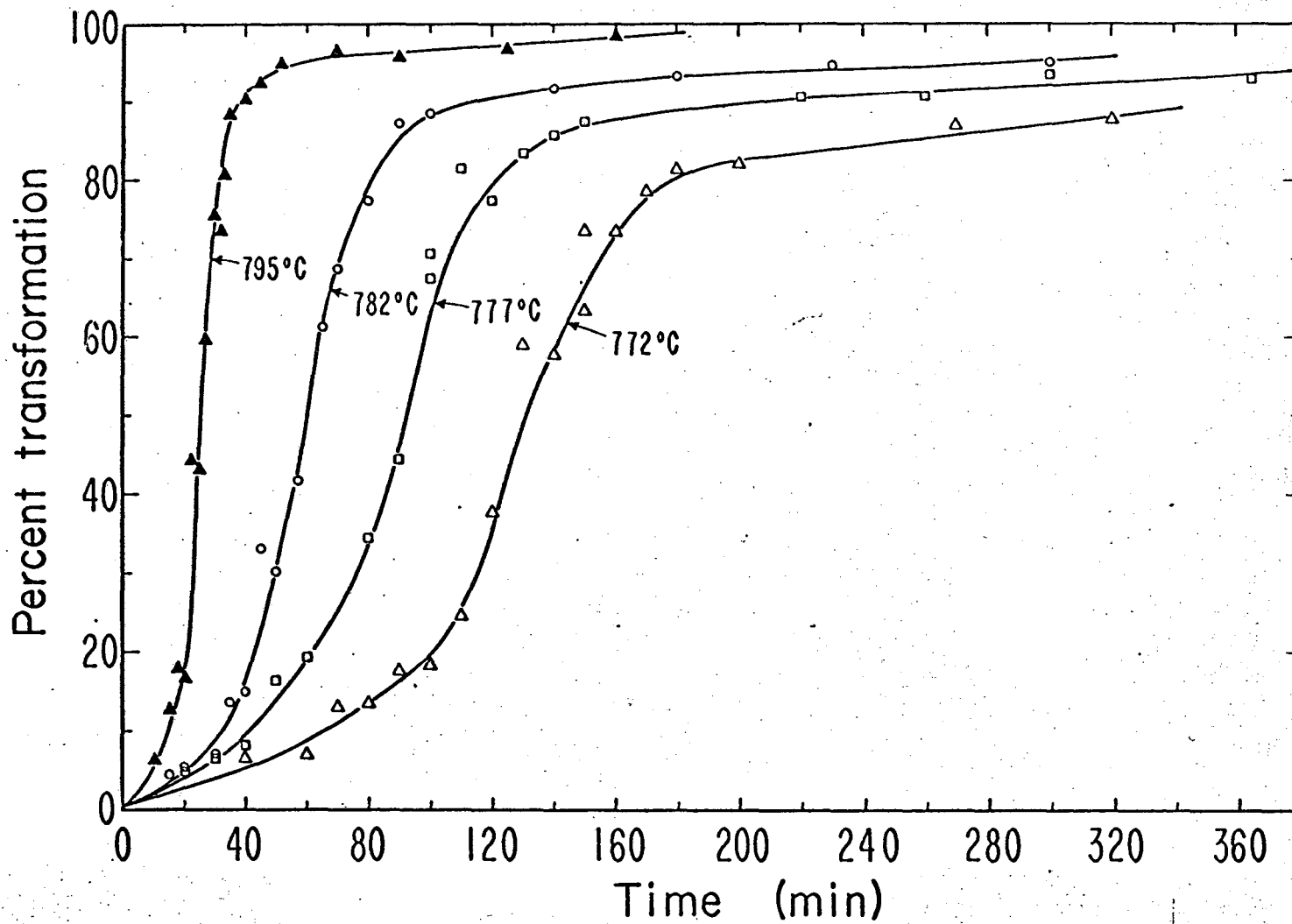Fig. 1.
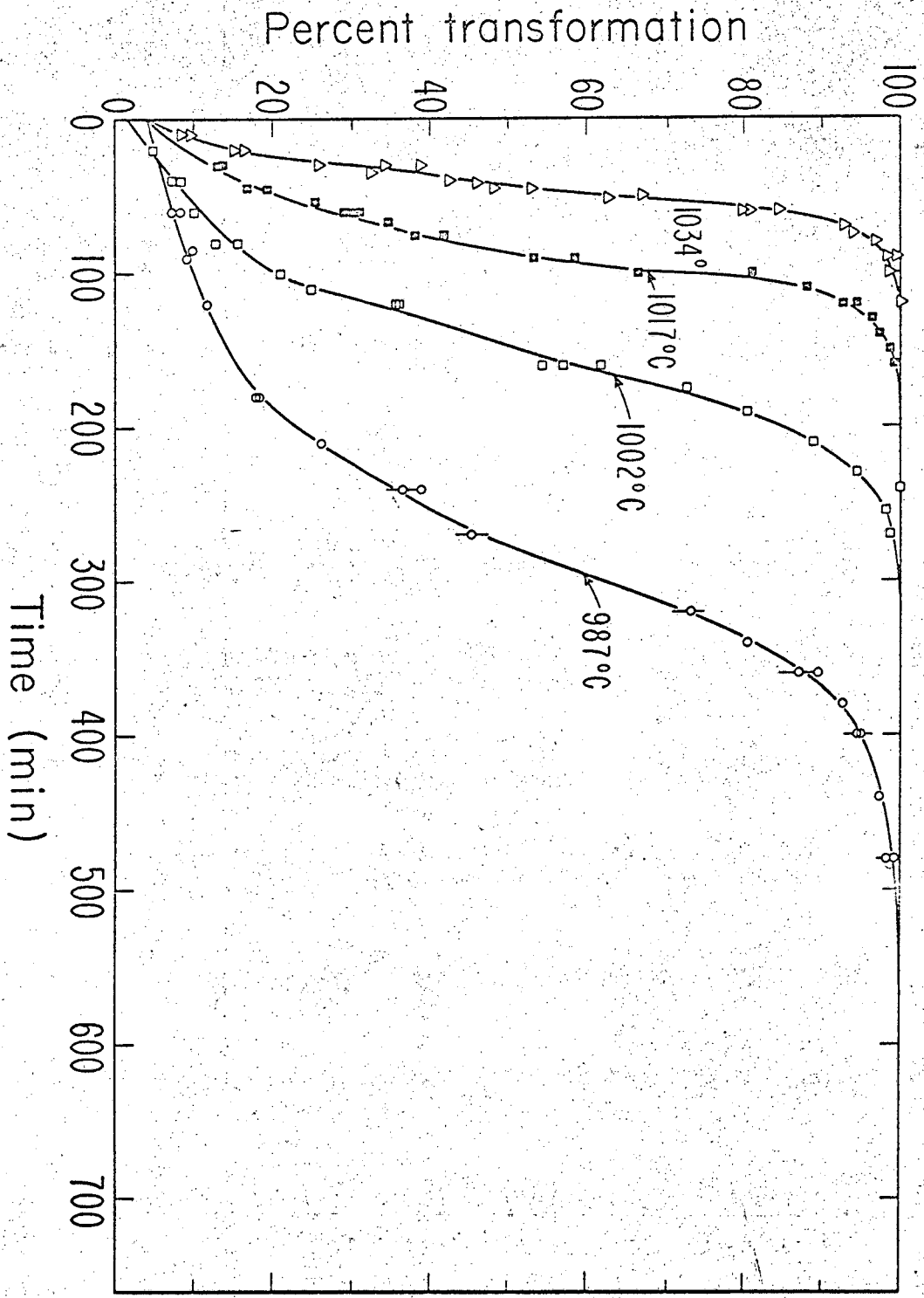
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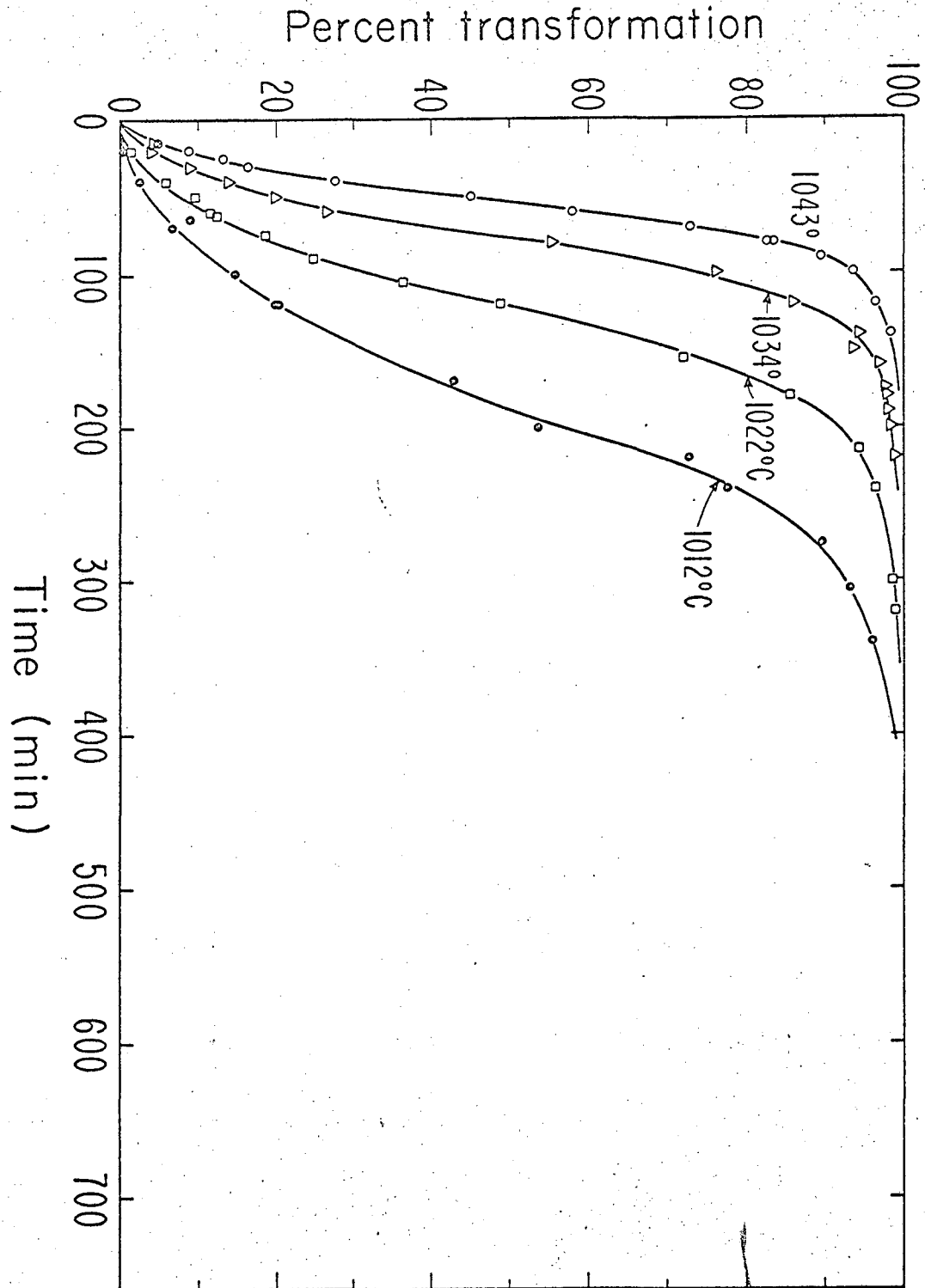
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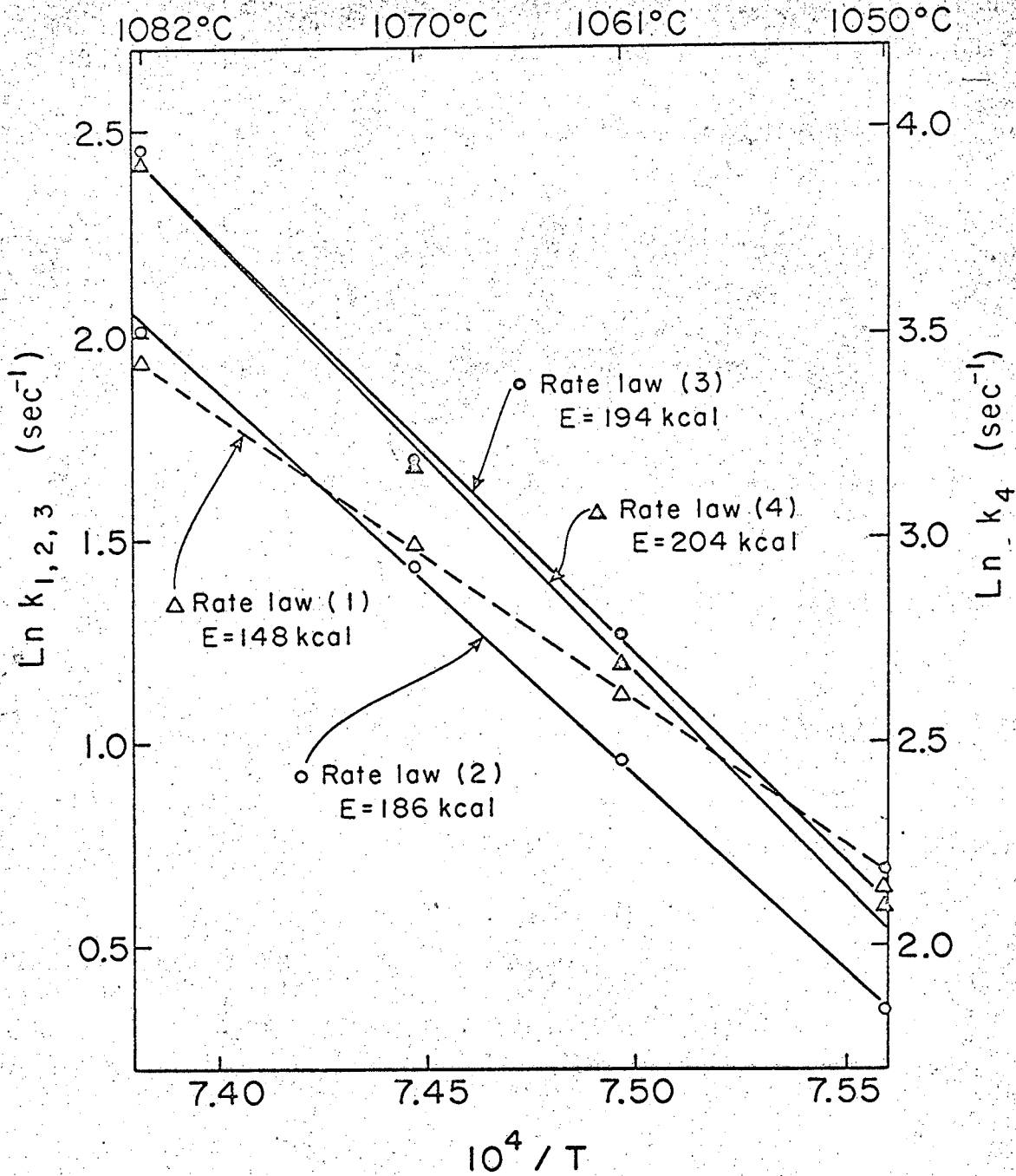
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MU-33965

Fig. 5.
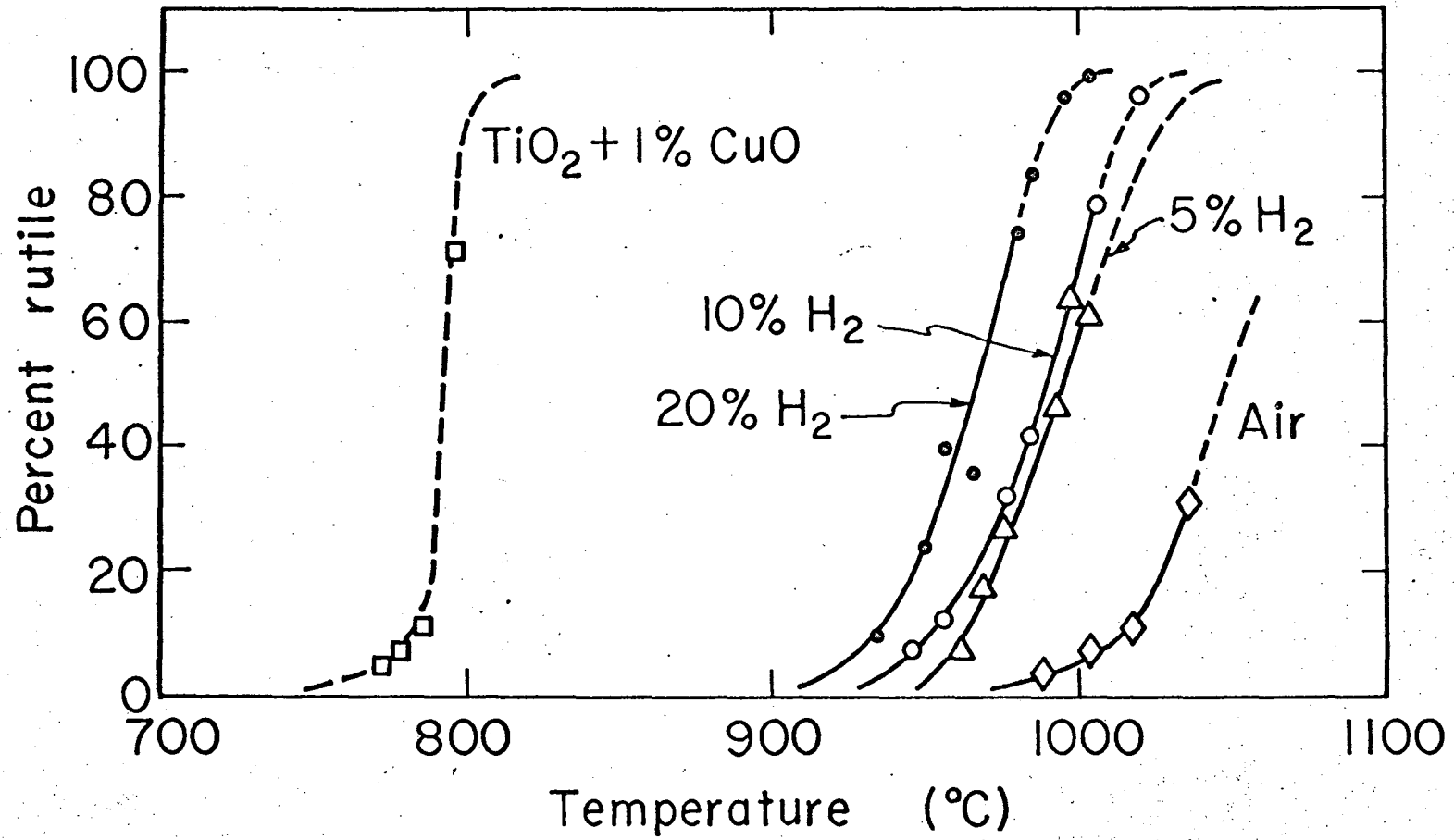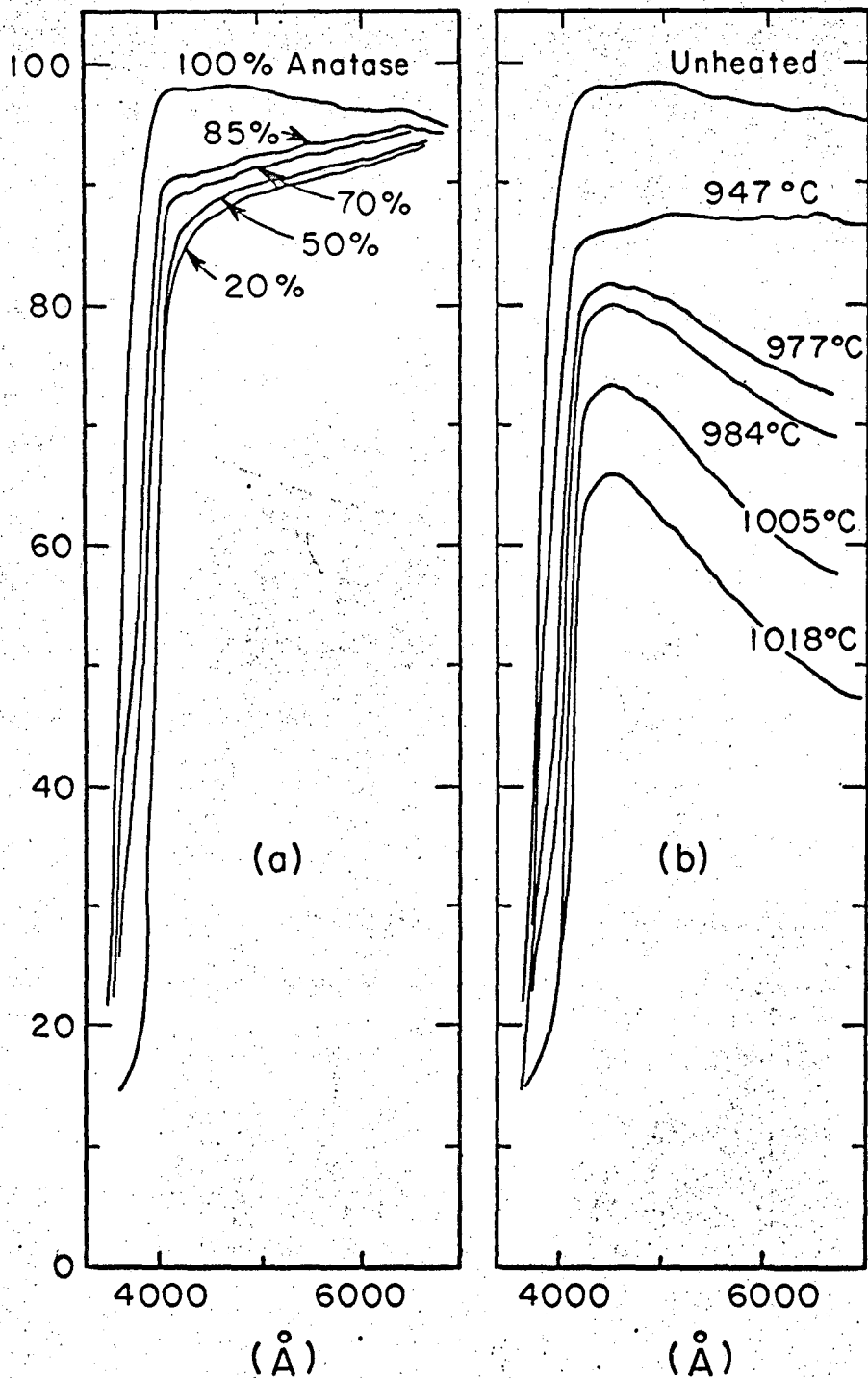
MU-33753

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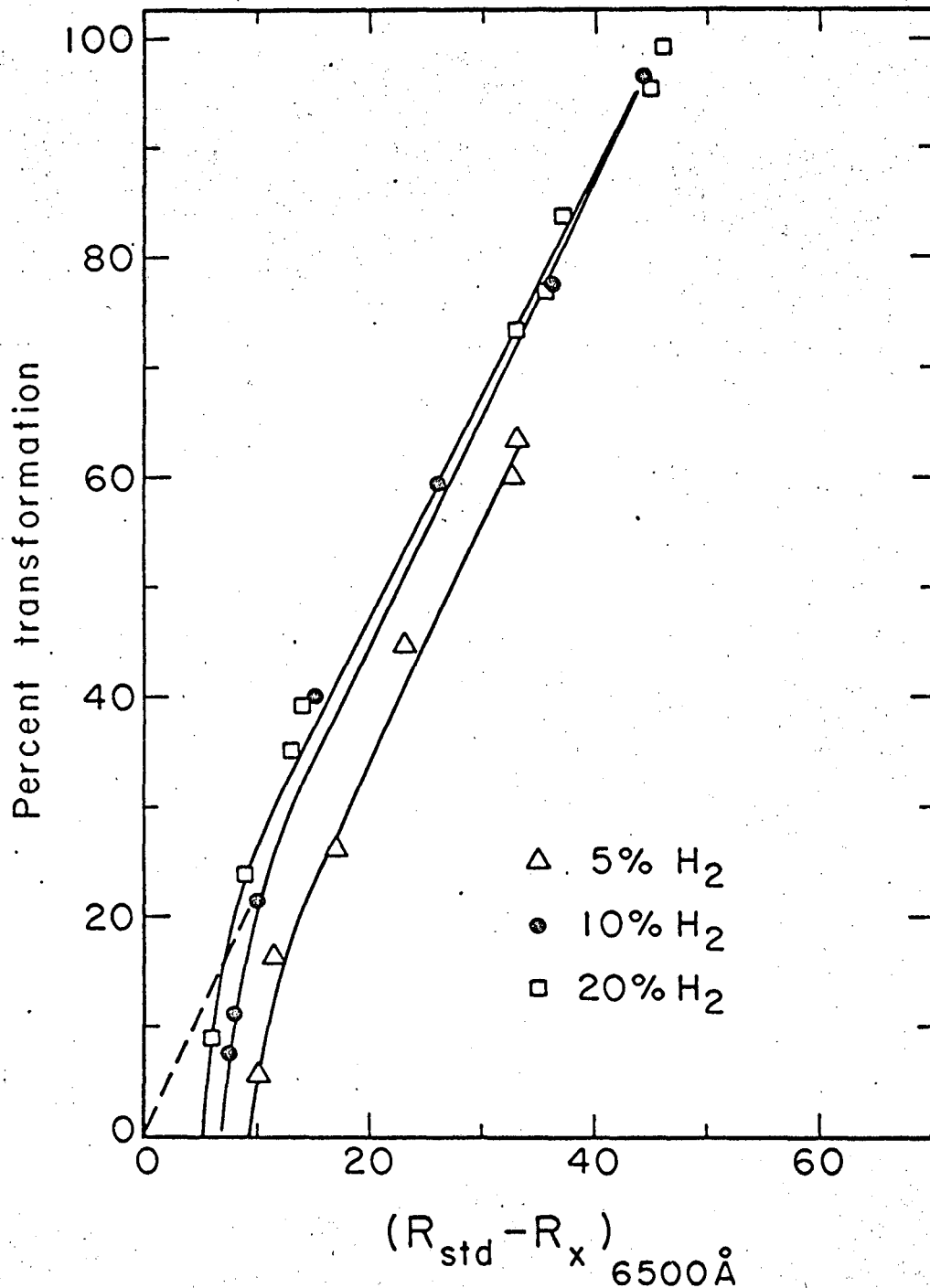
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Fig. 7.
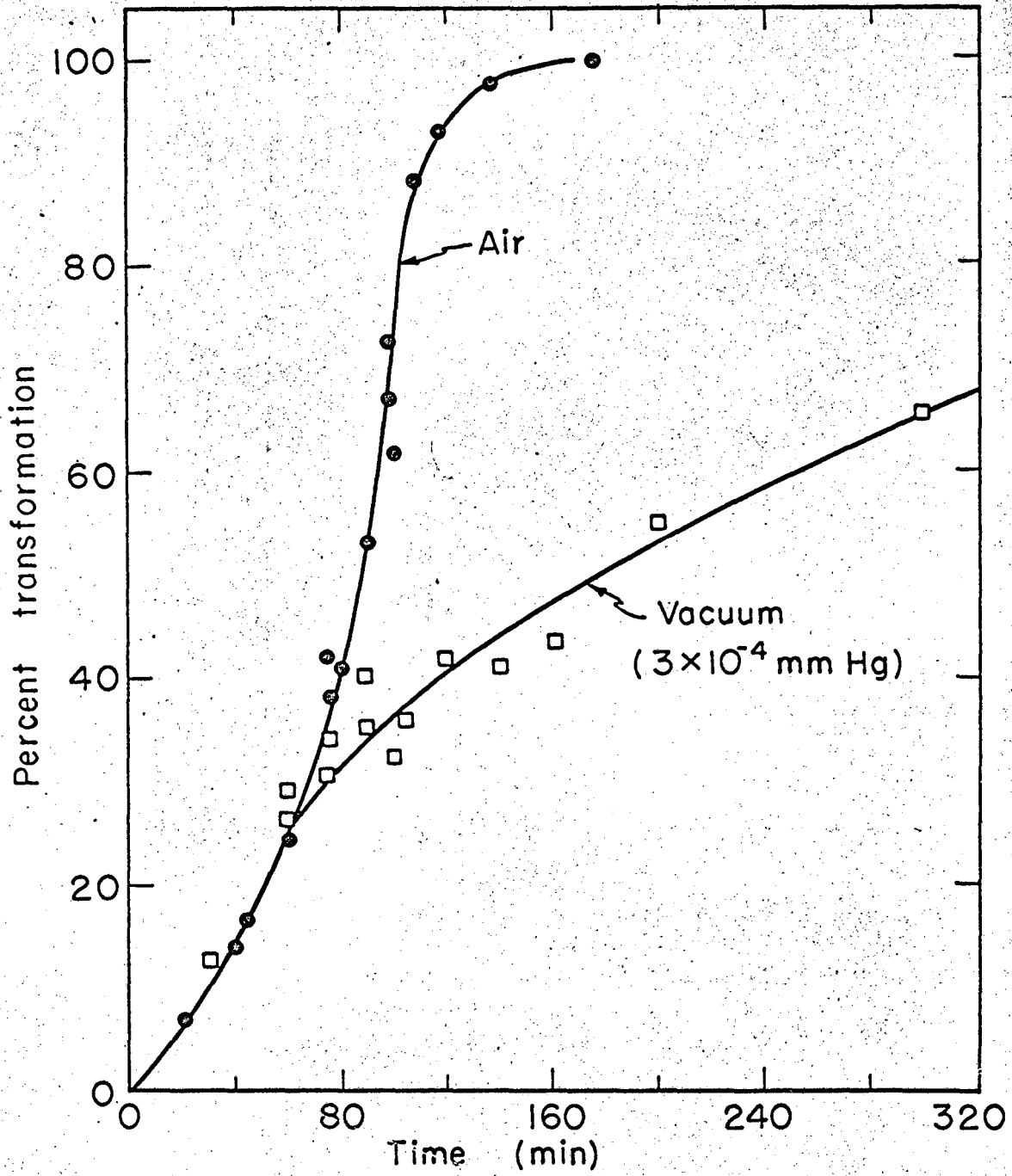
Fig. 8.

MU-33754

Fig. 9.

MU-33971

Fig. 10.

MU-33968
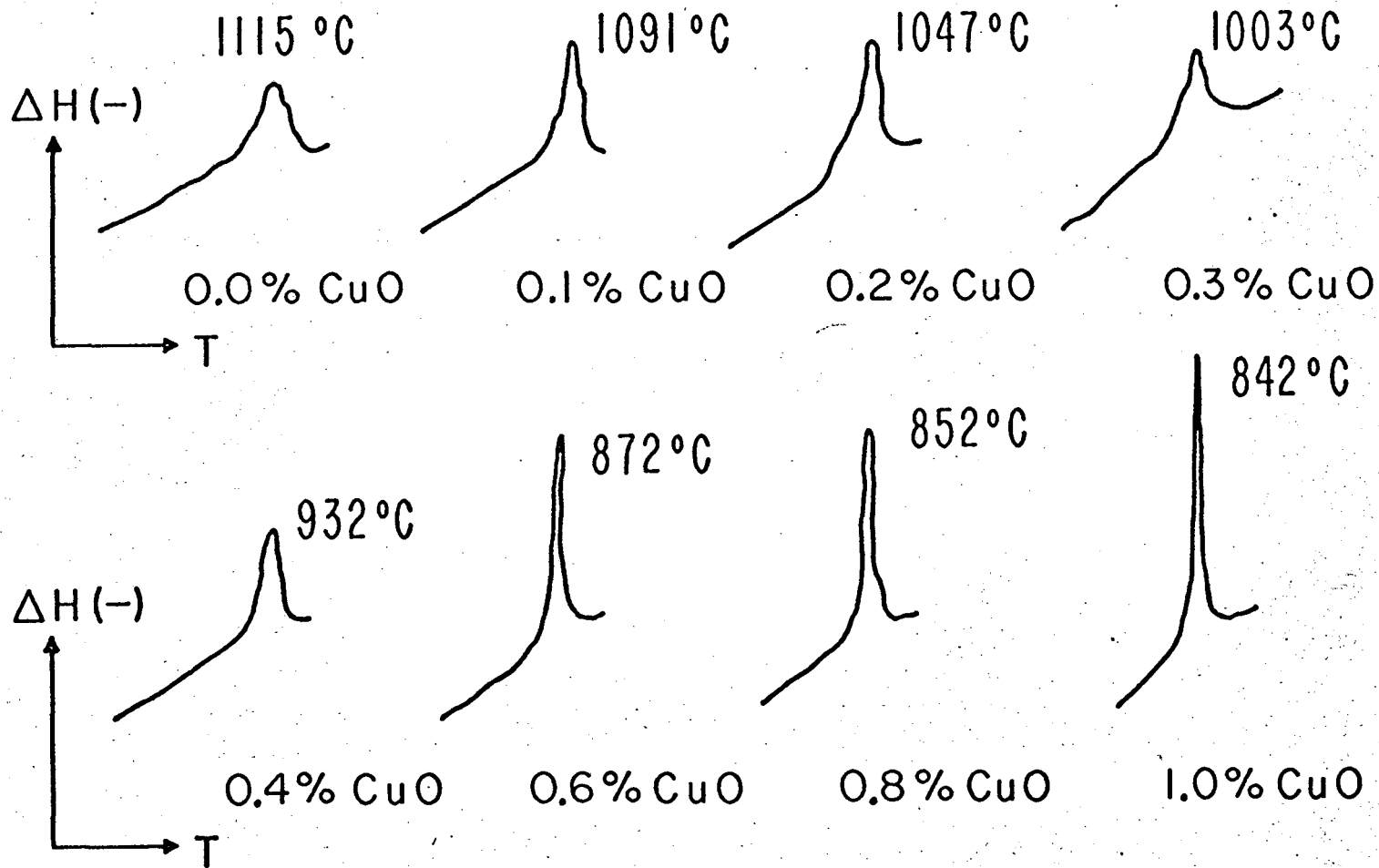
Fig. 11.

MU-33969

Fig. 12.

MU-33970