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COLLEGE OF ENGINEERING

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Technical Report

THE KINETICS OF THE TRANSFORMATION OF QUARTZ TO TRIDYMITE IN THE PRESENCE OF OTHER OXIDES

Gerald I. Madden

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ABSTRACT

This investigation is concerned with the kinetics of the transformation of quartz to tridymite, two of the polymorphs of silica (SiO_2). The transformation was studied by heating quartz in the presence of other oxides in the temperature and composition range of tridymite stability. The systems studied were:

Na_2O-SiO_2
PbO -SiO_2
FeO -SiO_2
Cu_2O-SiO_2

The temperatures and compositions chosen for study were all in the tridymite plus liquid area of the equilibrium diagrams.

In the transformation process under consideration, the formation of cristobalite as an intermediate metastable phase in the tridymite stability range was reconfirmed. The most probable mechanism of transformation is by the solution of quartz into the liquid phase from which cristobalite is precipitated at a relatively rapid rate as a metastable phase. The more stable tridymite precipitates concurrently, but at a slower rate, eventually replacing both the quartz and the cristobalite.

The experimental procedure consisted of mixing reagent grade powders of the desired composition and pressing these mixtures into pellets. These samples were then placed on a sheet of platinum foil which in turn was placed in an alumina combustion boat. The samples were fired in a tube-type resistance furnace that was automatically controlled. Sample temperatures were measured with a platinum-platinum rhodium thermocouple. The samples were water-quenched and then subsequently prepared for either x-ray or metallographic quantitative analysis.

The results show the reaction proceeds slowly at temperatures near the upper range of tridymite stability. As the firing temperature is decreased the rate is increased until a maximum is reached. Below this point the rate again decreases. A semilogarithmic plot of time versus temperature gives a C-curve.

The rate of transformation has been shown to be dependent on the amount of liquid present and the type of oxide added to the original quartz. As the amount of liquid is increased the rate of transformation is increased. This finding is related to the increased surface area of the solid grains exposed to the liquid phase in samples containing more liquid. The rate of transformation is affected by the type of liquid as follows: Na_2O (fastest), PbO, FeO, Cu_2O (slowest).

The following empirical relationship has been developed to describe the kinetics of the transformation process:

$$R = Ke^{-C/T_i(abs)}[1470 - T_i]$$

where R is the transformation rate, K and C are constants and T_i is the temperature of interest.

Observations were also made on the grain growth kinetics of cristobalite in the Cu_2O-SiO_2 system.

In addition the lower temperature limit for the formation of cristobalite as a metastable phase in the transformation process was determined to be 880 ± 5° C.

CHAPTER I

INTRODUCTION

This investigation was undertaken to determine the effect of temperature and liquid composition on the rate of transformation of quartz to tridymite in the presence of other oxides. The results of this investigation could be of engineering importance because silica is encountered extensively in refractory materials and as a raw material in the glass industry.

The transformation of quartz to tridymite involves the formation of cristobalite as a metastable intermediate phase in the tridymite stability range. The systems studied were:

Na_2O-SiO_2
PbO-SiO_2
FeO-SiO_2
Cu_2O-SiO_2.

The results of the investigation are presented in the form of isothermal transformation diagrams. These diagrams can be used to determine the optimum firing times and temperatures in order to obtain given amounts of the desired phases in a fired product. In addition, an empirical relationship has been derived to describe the rate of the transformation.

Observations have also been made on the grain growth kinetics of the solid phases in the Cu_2O-SiO_2 system and on the lower temperature limit at which cristobalite occurs as a metastable phase.

CHAPTER II

REVIEW OF THE LITERATURE

In his book describing the properties of silica, Sosman[1] discussed in detail the meaningful investigations concerning silica polymorphs prior to 1927. Of the work done up to that time, the investigation of Fenner[2] provided the most extensive information on stable silica polymorphs. His results indicated that a given polymorph of silica can be transformed into another by a reconstructive transformation under the proper conditions. The quartz-to-tridymite transformation temperature was reported as 870° C, and the tridymite-to-cristobalite transformation temperature was reported to be 1470° C. Qualitative observations indicated very slow transformation kinetics for the reconstructive steps. It was also observed that under given conditions in the transformation processes, the most stable form of silica was not reached directly. This is an illustration of Ostwald's rule, which states: "In all reactions the most stable state is not straightway reached, but the next less stable, or that state which is the least stable of the possible states."[3] This rule does not always hold, as will be shown in the presentation of the results of the present investigation. The temperature stability relations of quartz, tridymite, and cristobalite, the polymorphs stable at ordinary pressures, are shown in Figure 1. These relations, proposed by Fenner, have been critically examined by various

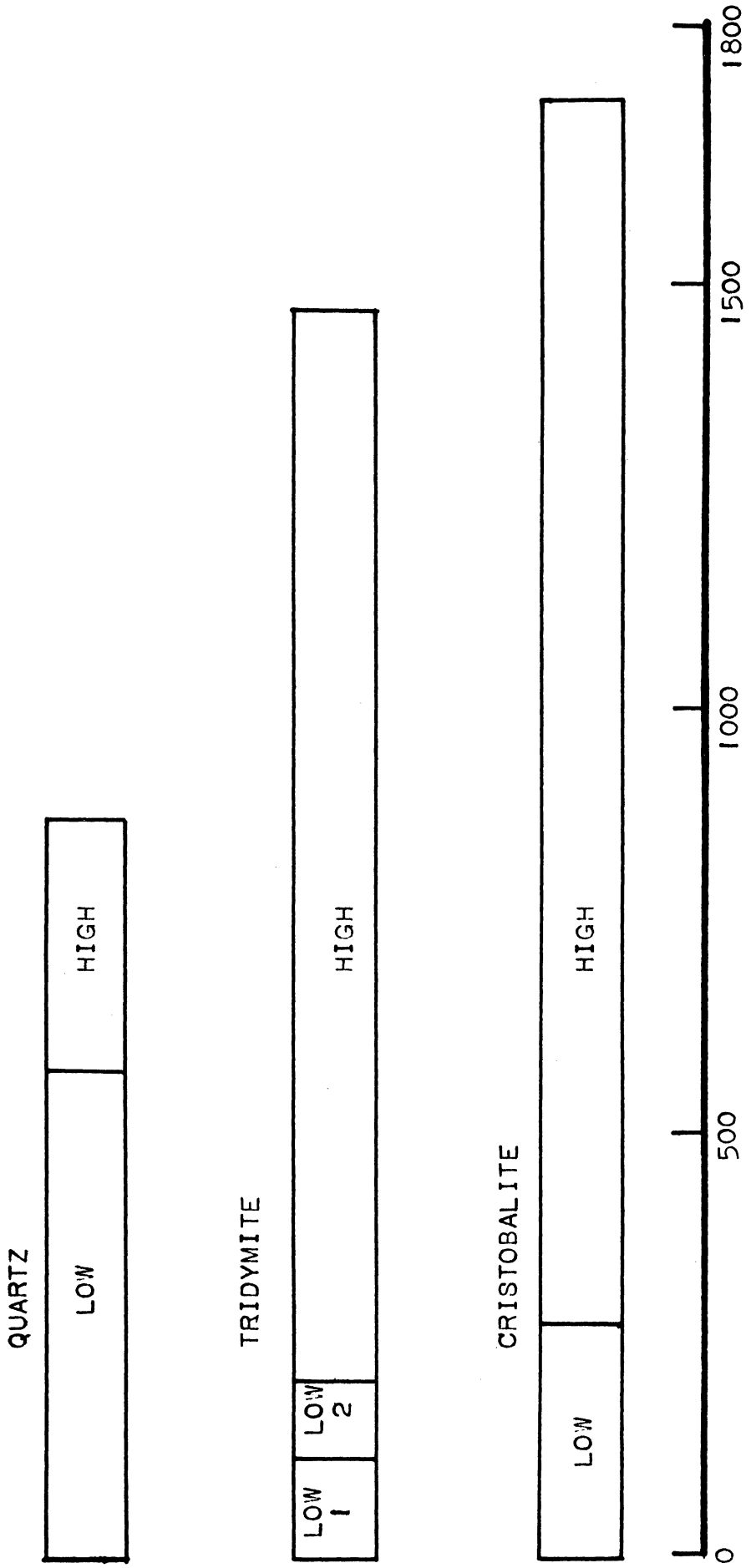


Figure 1. The stable SiO_2 polymorphs.

investigators since 1927. Criticism has been focused on the question of whether tridymite is really a stable polymorph of silica. A review of the available information on this question will be presented in the following section.

TRIDYMITE STABILITY

In a review of the work of Flörke,[4] Eitel[5] presents some of the arguments that indicate tridymite cannot be discussed in the equilibria relations of the one-component system SiO_2 as presented by Fenner. The low purity of the tridymite and cristobalite studied by Fenner has been put forth as a possible explanation of the anomalous behavior of the transformations of these two phases. The mineralizer used by Fenner was sodium tungstate; foreign ions were thus introduced into the structures. The low-to-high bond straightening transformations were observed to occur at various temperatures for tridymite and cristobalite.

The introduction of foreign ions into the structure of tridymite was postulated as a necessary step for its formation. Buerger[6] refers to tridymite as a "complex-stuffed" compound, having the chemical formula $NaCaAl_3Si_{15}O_{36}$. The foreign ions present in both tridymite and cristobalite cause structural defects which interrupt the regular stacking sequence of the SiO_4 tetrahedra, giving a superstructure of the type ABCAB:A'B'C'A'B', where the dotted line indicates the position of the disturbances and a 60° rotation. This combination of three- and two-layer structures is referred to as cristobalites if the three-layer sequences prevail,

but if the two-layer sequences prevail, the structures are called tridymites. Using this information Eitel and Flörke conclude that if fused mineralizers containing foreign cations are used for crystallization studies, the results of phase identification would not be valid for the true SiO_2 system, and Fenner's diagram would be erroneous. Tridymite would not appear in the SiO_2 system, and cristobalite would be accepted only in its idealized structural form.

Holmquist[6] made additional investigations to determine whether a foreign oxide must be present for the formation of tridymite. His results showed tridymite formed readily when quartz and alkali chlorides were heated in air but did not form at any temperature when quartz and sodium chloride were heated in an oxygen-free atmosphere. Because oxidation takes place and silicates are formed when alkali chlorides are heated with silica in air, it appeared alkali oxides were necessary for the formation of tridymite. He also found tridymite formed directly from quartz at lower temperatures, and cristobalite formed as an intermediate phase at higher temperatures. Interpretation of the data placed the quartz-cristobalite inversion temperature at 1025° C ± 25° and eliminated tridymite as a stable crystalline phase of pure silica. Tentative diagrams are given for the silica-rich end of binary silica-metal oxide systems, showing tridymite as a binary incongruently melting phase containing a small amount of metal oxide, and having a stability range that varies with the stabilizing oxide.

Another investigation of tridymite stability was carried out by D. Roy and R. Roy.[7] In the results of this work, evidence was presented for the existence of a polymorphic transformation between stable tridymite and stable cristobalite. Variations observed in the reconstructive transformation temperature of tridymite to cristobalite were said to be related to the crystalline solubility which gives varying degrees of stacking disorder in the polymorphs. When the reactions were carried out with fluxes having minor crystalline solubility, the transformation between stable tridymite and ordered cristobalite occurred reversibly at 1470° C within the limits of ±30°. No significant change in lattice spacing was observed in these cases. Changes in lattice spacings and reconstructive transformation temperatures took place when the same starting material was added to fluxes with components that were expected to go into solution with tridymite and cristobalite. These fluxes also changed the displacive transformation temperature of cristobalite. The authors thus felt tridymite was a stable pure form of silica.

A recent investigation by Rockett[8] included a review of the problem of tridymite stability. In this work tridymite was prepared in a sodium tungstate melt and then purified until the final composition showed the Na_2O content to be below the minimum (0.5%) claimed necessary for tridymite stability. This tridymite was then fired at temperatures between 890 and 1450° C for times ranging from 24 to 800 hours—no cristobalite formed. Firing above 1470° produced cristobalite. The author used these results to substantiate the diagram of Fenner showing

tridymite as a pure silica polymorph. Further discussion and reasoning by Rockett indicate the Fenner diagram can be retained as a basic tool in silica studies.

The investigations cited here are presented to show the existence of the problem of tridymite stability. The present investigation concerns silica in the presence of other oxides in amounts far above the purity limits discussed above. Therefore the controversy over tridymite stability is not directly related to the present work.

QUARTZ-TO-CRISTOBALITE TRANSFORMATION

Consideration of the quartz-to-cristobalite transformation in studies of the quartz-to-tridymite transformation is important because of the formation of cristobalite as a metastable phase in the tridymite stability range.

Chaklader and Roberts have studied the quartz-to-cristobalite reaction in the temperature range 1500° to 1650° C.[9] In this study natural quartz was used as the raw material and quantitative analysis of the experimental samples was performed, using a differential thermal analysis technique. In analysis of the samples no tridymite was observed, and the total amount of quartz and cristobalite was less than 100%. This finding led to the conclusion that an intermediate transition phase was occurring in the transformation process. A kinetic analysis of the reaction and evidence showing the transition phase to be a glassy phase with a specific gravity of 2.30 gm/cc was presented.

The effect of trace amounts of Al_2O_3 on the transformation of quartz to cristobalite has been studied by Chaklader.[10] Al_2O_3 was added to pure quartz in trace amounts and fired at 1500°, 1530°, and 1570° C. The addition of Al_2O_3 in increasing amounts showed first an increase and then a decrease in the rate of formation of cristobalite. A critical Al/Si ratio was proposed as having the maximum catalytic effect on the reaction. The reaction between the quartz and the Al_2O_3 was said to have proceeded in two steps: (1) nucleation on the quartz grains by the catalyst, and (2) propagation of a diffusion layer produced by the penetrating catalyst. A first-order reaction was indicated from the information obtained in the study.

An x-ray analysis of the quartz-to-cristobalite transformation has also been reported by Chaklader.[11] Samples of pure quartz were fired at 1560° C for various times up to 10 hours. The presence of a transition phase was again reported, and the speed of formation of cristobalite was studied. The cristobalite formed was thought to be of a highly ordered nature because of the lack of observation of line broadening effects. The kinetic analysis used in the other investigations reported by the author was used again. This analysis involved two first-order reactions, quartz transforming to the transition phase, and the transition phase transforming to cristobalite. Photomicrographic analysis was also undertaken to study the reaction. The results of this investigation were put forth as substantiating the previous investigations.

A geometric model based on the experimental findings presented above

has also been presented by Chaklader.[12] Once again the basic assumption in the model is that the transformation process involves two consecutive first-order reactions. Another assumption of importance is that the original quartz crystals are spheres, and that the transformation proceeds by the formation of spherical shells of the transition phase and the cristobalite. An analytical expression for the amount of cristobalite formed was derived. The validity of this expression was tested by firing quartz at 1550° C for various times. By using an x-ray technique the amounts of the phases present were determined. The author felt the results obtained verified use of the proposed model.

Another investigation of the quartz-cristobalite transformation was performed by Kuellmer and Poe.[13] This study involved analysis of single-crystal x-ray photographs to determine the validity of Chaklader's transformation model. A diffraction pattern obtained from a piece of quartz glass which was used as a source of amorphous SiO_2 showed two diffuse rings. To determine a lower limit of detection of an amorphous phase, a quartz fragment was coated with petroleum jelly, and a layer of quartz glass powder was then applied. The results showed that less than 3 wt % of the quartz-glass powder produced marked x-ray scattering. Quartz fragments were heated at 1481°, 1505°, and 1511° C, for various times and studied using single crystal techniques. No amorphous SiO_2 rings were observed which could be compared with the diffuse rings observed on photographs of the original amorphous SiO_2. The reconstructive quartz-to-cristobalite transformation was seen by the authors as quartz transforming

to quartz with a high dislocation density. This highly disordered quartz phase then transforms to disordered cristobalite, which in turn transforms to ordered cristobalite. They attribute the results obtained by Chaklader to experimental differences between the standard samples and the experimental samples used in the DTA and x-ray intensity measurements.

From the above discussion it is evident that there is some controversy over the mechanism involved in the transformation of quartz-to-cristobalite.

Earlier investigations on the quartz-to-cristobalite reconstructive transformation have been reviewed by Sosman.[14] He indicates that the rate of the transformation is strongly influenced by two factors: (1) the state of subdivision of the quartz, and (2) the temperature. Large homogeneous untwinned quartz crystals were shown to transform extremely slowly at a given temperature while the same quartz, finely divided, transformed rapidly at the same temperature. The formation of cristobalite at lower temperatures in the tridymite stability range was slower than at temperatures near the range of cristobalite stability. There was no evidence presented of a sudden rate increase at 1470° C, the tridymite-to-cristobalite inversion temperature. Conclusions drawn from the investigations cited indicate the usual logarithmic increase in the rate of a chemical reaction with increased temperature.

CRISTOBALITE-TO-TRIDYMITE TRANSFORMATION

Another important step under consideration in the present investi-

gation is the transformation of cristobalite to tridymite. Qualitative observations of other investigators have indicated that at a given temperature this transformation is much slower than that of quartz to cristobalite.[15] The speed was observed to be less at a temperature near the inversion point than at some lower temperature. In the course of the transformation of quartz to tridymite, in which cristobalite formed as an intermediate metastable phase, it was observed that a given fragment of quartz always transformed completely to cristobalite before any tridymite appeared. Fragments were observed that contained quartz and cristobalite or cristobalite and tridymite but none in which all three were present. Tridymite was observed to form either by direct transformation of cristobalite grains or by solution of cristobalite in a flux and reprecipitation as tridymite.

In studies concerned with the ordering of cristobalite, Hill and Roy[16] made observations on the transformation of cristobalite to tridymite. Highly ordered cristobalite containing small amounts of disordered cristobalite was heated at 928° C at a pressure of 3000 psi. The disordered cristobalite was transformed to tridymite, and the reaction proceeded by the transformation of the ordered cristobalite to tridymite. X-ray results indicated a decrease in cristobalite particle size after firing in the tridymite stability range. The authors concluded that the original Fenner diagram for stable silica equilibria was correct. The questionable parts were thought to be caused by metastable equilibrium problems in the system.

Hill and Roy[17] have also made silica structure studies on tridymite. The purpose of their work was to determine (1) whether tridymite could be formed without other ions such as Na^{+}, Ca^{+2}, Al^{+3}, H^{+}, etc., present, (2) whether tridymite could be identified in the presence of other SiO_2 phases, and (3) the stability relationship of tridymite to cristobalite. From the results obtained the authors concluded tridymite is indeed a pure phase of SiO_2. The reaction observed was: starting material → disordered cristobalite → tridymite, where the starting material was either quartz or silica gel in the presence of water.

Two different tridymites formed which can exist at room temperature and have considerably different crystal structures. The x-ray diffraction patterns of the tridymites show differences in intensities and line positions for the different tridymites, which are in turn distinct from the cristobalite reflections. Thus, the tridymite formed from cristobalite is said to be a pure SiO_2 polymorph.

KINETICS OF THE SILICA TRANSFORMATIONS

The reconstructive silica transformations have been described qualitatively as being sluggish. In contrast to the low-to-high displacive transformations which occur as soon as the temperature of transformation is reached, the reconstructive transformations occur in measurable time intervals.

In a study of the influence of iron oxide on the rate of quartz

inversion in lime and lime-clay bonded silica brick, Hugill and Rees[18] found the transformation of quartz to tridymite to be promoted by the presence of iron oxide. Qualitative observations of the extent of transformation were made on brick samples, and the amount of tridymite present after firing was related to the cross breaking strength, modulus of rupture, and the crushing strength of the brick. All three properties were observed to have higher values with increased tridymite content. Increasing the amount of iron oxide present in the brick promoted the formation of tridymite, but no quantitative information to describe the reaction rate was obtained.

Grimshaw, Hargreaves, and Roberts[19] studied the kinetics of the quartz transformation in the presence of various additives. The results showed that the reaction proceeds rapidly if the added oxide forms a liquid with silica at the firing temperature. When the transformation is a solid-state process, the reaction proceeds rapidly only in the immediate vicinity of the particles of catalyst; the catalytic effect decreases rapidly as a function of time. The catalysts used in the experiments were Fe_2O_3, which formed a liquid, and CaO, MgO, Al_2O_3, and TiO_2, which reacted in the solid state. The CaO addition had the greatest accelerating effect on the solid-state reaction, and the Al_2O_3 addition inhibited the reaction rate. The important factors in the transformation process were the presence of a liquid phase, the subdivision of the solid catalyst, and the type of oxide added. Analysis of the results was confined to the systems in which the reaction proceeded in the solid state.

A study of the effects of the addition of alkali oxides to quartz on the formation of tridymite was reported by de Keyser and Cypres.[20] Their results show that the addition of small quantities of alkali oxides completely changes the thermal evolution of quartz. Tridymite forms more rapidly in the presence of Na_2O and K_2O than in the presence of Li_2O at the same molar concentrations and temperatures. CaO additions were made to the three alkali oxide-silica systems to determine their effect on the speed of the transformation. The presence of CaO inhibited the quartz transformation, the inhibiting influence being more marked in the Na_2O- and K_2O-silica systems than in the Li_2O-silica system. The speed of the transformations without CaO present was explained on the basis of the amount of liquid formed in the respective systems. There is more liquid formed at the same molar concentrations and temperatures in the K_2O- and Na_2O-silica systems than in the Li_2O-silica system. The presence of CaO does not change the temperature at which a liquid forms in the Na_2O- and K_2O-silica systems, but it changes the viscosity of the liquid to a great extent. As the liquid phase becomes more viscous, the speed of transformation is reduced. In the case of the Li_2O-silica system the eutectic temperature is lowered, and the viscosity of the liquid phase is increased. The overall effect is not as marked as in the other two systems.

A study of the reaction rates of silica in the presence of other oxides at various temperatures has also been reported.[21] The purpose of the investigation was to determine the rate at which glass is formed

when silica is heated in the presence of another oxide. In the binary systems studied the speed of the reaction was found to be dependent on the added oxides: K_2O (greatest effect), Na_2O, B_2O_3, CaO, MgO (least effect). Studies of ternary systems gave similar results. The reaction rates were influenced by the amount and type of oxide added. The extent of reaction was measured by determining the amount of crystalline silica present after a given firing time. The results also show the reaction rate is influenced by the amount of liquid formed in the various systems studied.

CHAPTER III

EXPERIMENTAL PROCEDURE

The experimental procedure consisted of mixing reagent grade materials in the desired proportions and pressing the mixtures into pellet-size samples 0.4 in. in diameter and approximately 0.5 in. in height, firing the samples at various temperatures, and water quenching after firing. The samples were then prepared for either metallographic or x-ray examination to determine the extent of the reaction under consideration. The following aspects of the procedure will be described in detail:

(a) materials
(b) sample preparation
(c) firing procedure
(d) sample analysis
  point count analysis
  x-ray analysis

MATERIALS

Reagent grade oxides were used as raw materials except for Na_2O which was added as anhydrous sodium metasilicate. Analysis of the quartz is included in Appendix I. Since in the systems studied the oxide added to quartz was always in a relatively large amount—the lowest addition being 1.25 wt % Na_2O to give 10% liquid at the higher firing temperatures—additional purification of the quartz was unnecessary. The quartz powder was about 140 mesh. The other oxides were also powders.

The added oxide used in the FeO-SiO_2 system was Fe_2O_3. The Fe_2O_3-SiO_2 samples were fired in a 50 CO-50 CO_2 atmosphere, where the Fe_2O_3 was reduced to FeO.[22]

SAMPLE PREPARATION

The materials described above were weighed on an analytical balance and mixed in various amounts to give different liquid contents in the system studied.

In the iron oxide-silica, lead oxide-silica, and copper oxide-silica systems, additions of about 1% water were made to act as binders. The mixtures thus prepared were then pressed in a 0.4-in. diameter steel die at a pressure of 15,000 psi. The samples were then placed on a sheet of platinum foil, which was in turn placed in an alumina combustion boat. In the systems in which water was used the samples were dried before being fired.

FIRING PROCEDURE

The cylindrical samples described above were then fired in the Leco tube type resistance furnace illustrated in Appendix II. The furnace was heated by silicon carbide heating elements, and the temperature was automatically controlled by a Wheelco controller. The controller was actuated by a platinum-platinum 10% rhodium thermocouple placed between the furnace tubes. The sample temperature was measured separately by placing a platinum-platinum 10% rhodium thermocouple in the position the samples were in during firing. The accuracy of the temperature

readings obtained with this thermocouple was determined by checking with a thermocouple calibrated by the National Bureau of Standards. The temperatures measured were determined to be accurate to ±5° C, including the ±2° C variation possible in the NBS standard thermocouple.

After firing, the samples were water quenched to preserve the phases present at the firing temperature. The samples were then removed from the quench bath and dried prior to preparation for either metallographic or x-ray examination.

SAMPLE ANALYSIS

Two methods of sample analysis were used in this investigation, point counting on a reflected light sample for the Cu_2O-SiO_2 system and x-ray analysis of the PbO-, FeO-, and Na_2O-SiO_2 systems.

Point Count Analysis

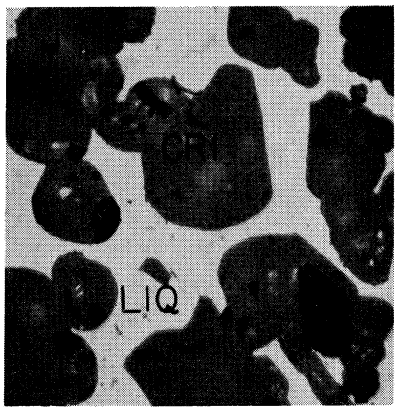
In the Cu_2O-SiO_2 system the difference in morphology of the solid phases and the differences in reflectivity between the solid and liquid phases made it possible to analyze the samples using a reflected light ceramographic technique. This involved mounting the samples in either a bakelite or a polyester resin and then impregnating them with a thermosetting resin to fill the pores present and prevent pulling out any of the phases during polishing. The polishing procedure consisted of polishing on 400 and 600 grit polishing wheels and then polishing with 8- and 1 μ diamond abrasives, respectively. The samples were then analyzed by a point-counting technique. Approximately 250 points were counted on

each sample, and the percentage of the solid phases present was determined by calculating the percentage of the points falling in that phase. The microstructures developed in this system are illustrated in Figure 2.

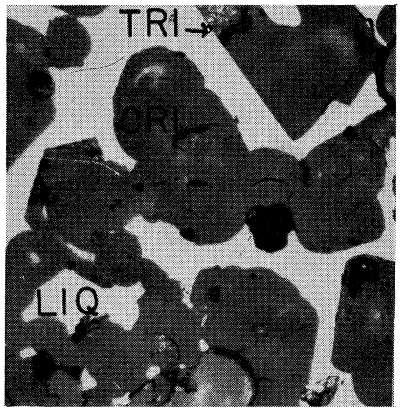
X-Ray Analysis

A quantitative x-ray technique was used to analyze the samples in the FeO-, PbO-, and Na_2O-SiO_2 systems. The method used was a modification of that of Holmquist, et al.,[23] which is similar to the technique described by Klug and Alexander.[24] This involves grinding the unknown sample into a powder of uniform mesh size and exposing the powder to x-rays in a recording diffractometer. The diffractometer trace is then analyzed by measuring the area under certain peaks and comparing the areas to standard curves prepared from known mixtures of tridymite and cristobalite. The standard deviation reported with this method is 3%.

The standard curves were prepared by mixing known quantities of cristobalite and tridymite which had been ground to approximately -325 mesh. The cristobalite was prepared by firing quartz in the presence of the added oxide at 1500° C for five hours. The tridymite was prepared by firing quartz in the presence of the added oxide for approximately two weeks. The long time is necessary to complete the reaction of the quartz-to-tridymite transformation. In preparing the standard materials it was necessary to have a different set for each composition studied in a given system. This was necessary because of the composition differences that would arise from the different liquid contents present in the samples.



a) 55 PERCENT LIQUID



b) 44 PERCENT LIQUID

Figure 2. Microstructures in the Cu_2O-SiO_2 system. Samples fired 4 hours at 1400°C. CRI-cristobalite, TRI-tridymite, LIQ-liquid. (250X)

After preparing the tridymite and critobalite as described above, mixtures were prepared containing 0, 25, 50, 75, and 100 wt % tridymite, with the balance being cristobalite. These mixtures were then run in a rotating sample holder on a Norelco Diffractometer using copper radiation. The tube was operated at 37 KV and 12 ma. The beam slit and detector slit were both 1°. The unit was equipped with a Geiger-Mueller detector. The recording instrument was made by Minneapolis-Honeywell.

The diffractometer traces obtained were then analyzed by measuring the area under the d = 4.31Å peak representing the amount of tridymite and the area under the d = 4.04Å peak representing the amount of cristobalite. The areas were measured with a compensating polar planimeter. Two standard curves could then be obtained from these data: the percent tridymite versus the area under the 4.31Å peak and the percent cristobalite versus the area under the 4.04Å peak. The type of curve obtained is illustrated in Figure 3.

The samples containing unknown amounts of tridymite and cristobalite were analyzed by running them under the same conditions as the standards. The areas under the peaks were measured and compared to the standard curves to determine the extent of the reaction of quartz transforming to tridymite. A semilogarithmic plot of time versus percent tridymite was prepared to determine the time to 50% transformation to tridymite. An illustration is given in Figure 4. The time to 50% tridymite was chosen to describe the reaction kinetics. This time was then plotted as a function of temperature at a constant liquid content to graphically illustrate the effect of the various parameters on the reaction.

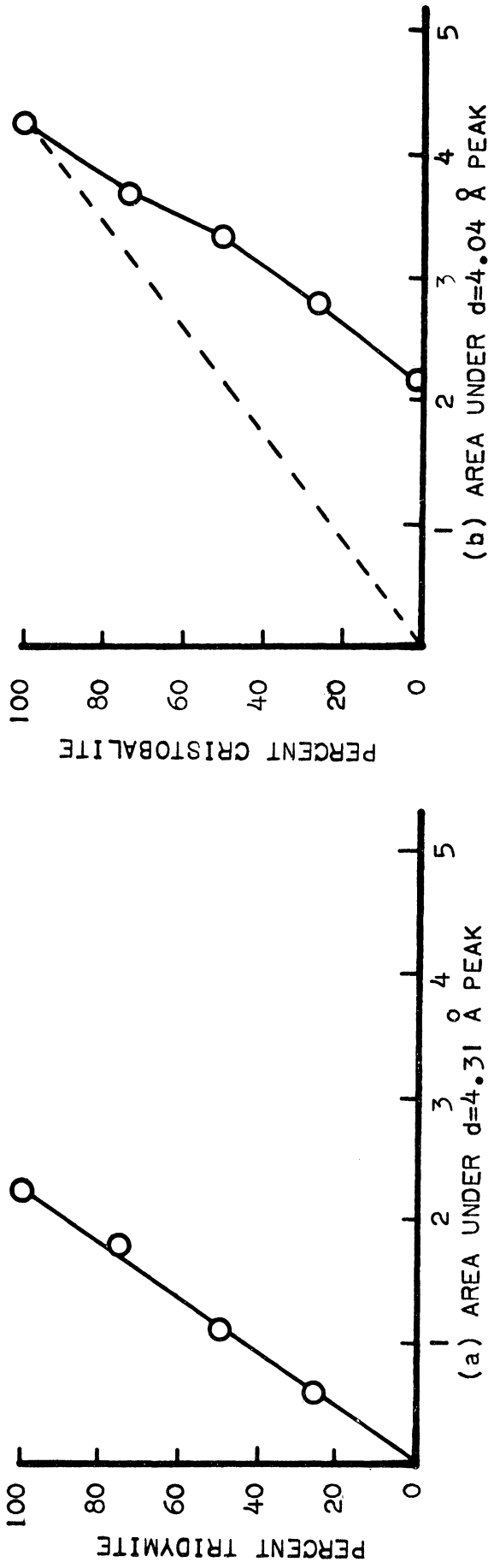


Figure 3. X-ray standard curves for the Na_2O-SiO_2 system. Samples contain 10% liquid.

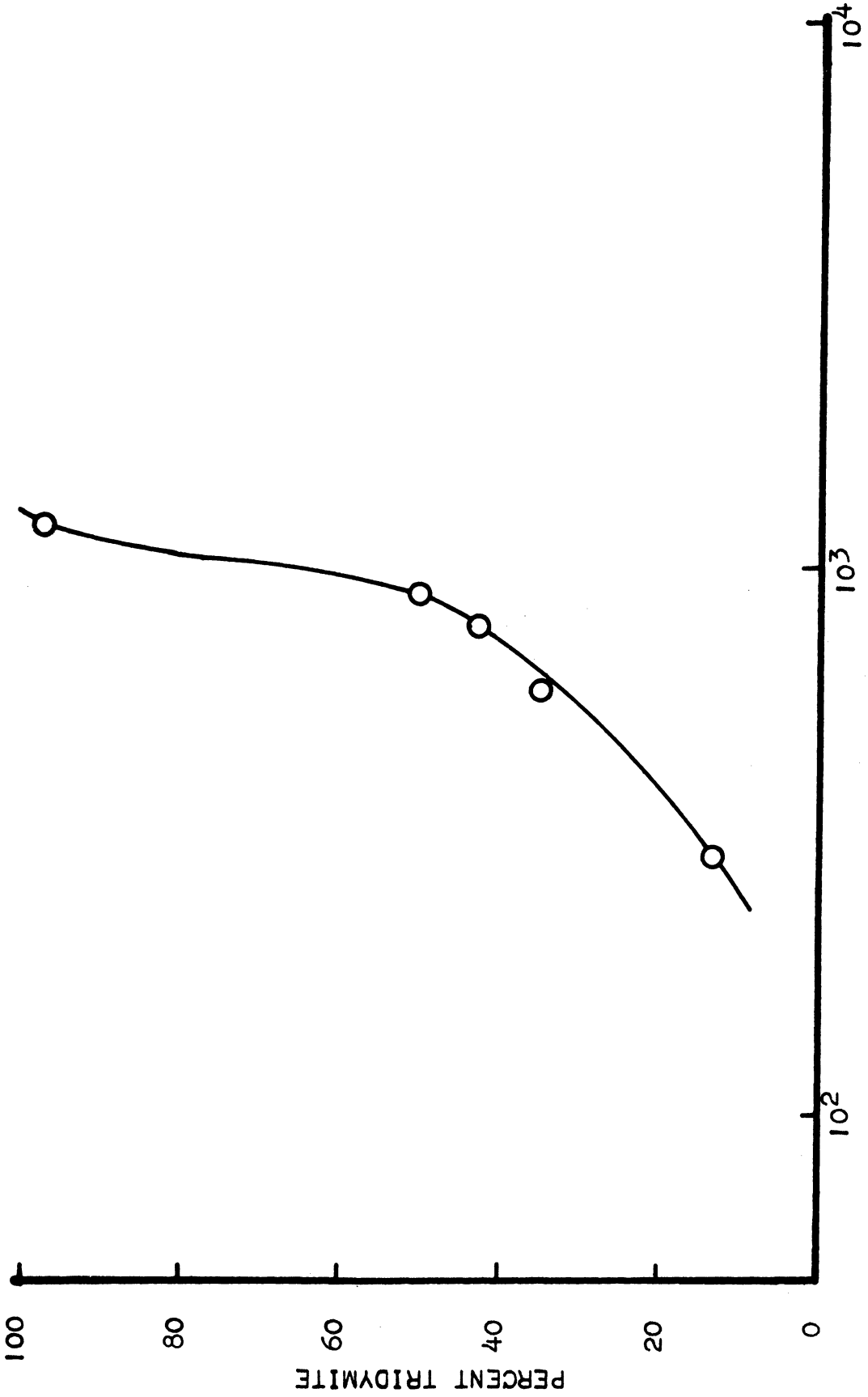


Figure 4. Firing time versus percent tridymite. Na_2O-SiO_2 samples containing 40% liquid, fired at 1250°C.

CHAPTER IV

EXPERIMENTAL RESULTS

This investigation is concerned with the time required for quartz to transform to tridymite in the presence of another oxide. When quartz is heated in the tridymite stability ranges, cristobalite can form as an intermediate metastable phase. Thus, when quartz is heated in the presence of another oxide at a temperature where the stable phases are tridymite and liquid, the most probable mechanism of transformation is by the solution of quartz into the liquid phase from which cristobalite is precipitated at a relatively rapid rate as a metastable phase. The more stable tridymite precipitates concurrently, but at a slower rate, eventually replacing both the quartz and the cristobalite.

The results obtained for the systems studied will be discussed separately. The liquid contents and liquid compositions for the four systems are presented in Appendix III.

SYSTEM: Cu_2O-SiO_2

The phase relationships for the system Cu_2O-SiO_2 are shown in Figure 5. This diagram was originally determined by Berezhnoi, et al.[25] and was modified slightly by Gadalla, et al.[26] In both of these investigations, at the oxidation potential of air the eutectic temperature was found to be the same, but Gadella redetermined the eutectic composition as 6% SiO_2 rather than 8% as had been reported by Berezhnoi. For the purposes of this investigation the slight reported difference is of

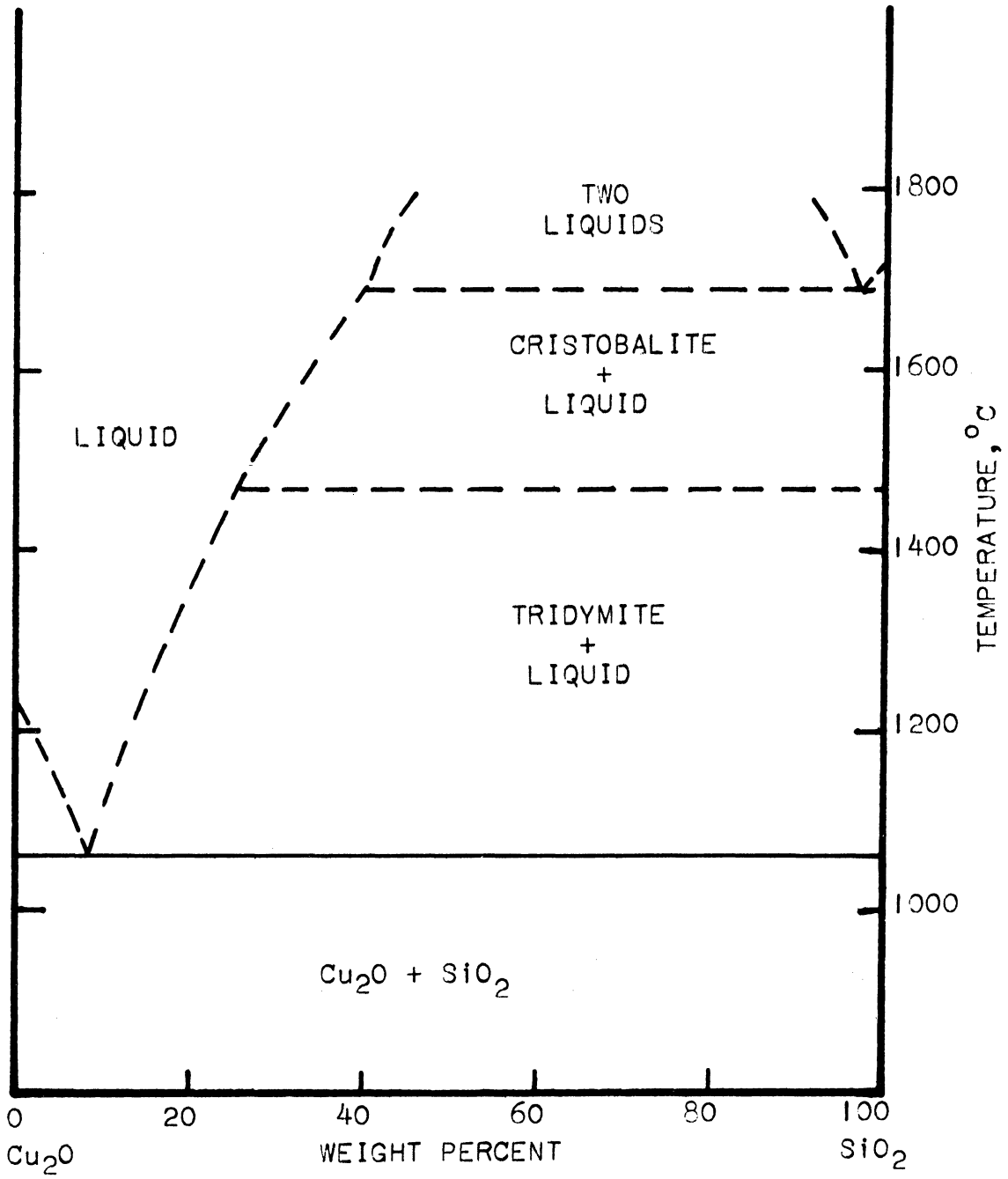


Figure 5. Phase relationships for the Cu_2O-SiO_2 system.[25]

no importance in either carrying out the experiments or interpreting the results.

The time for 50% transformation of the original quartz to tridymite is plotted semilogarithmically versus the temperature in Figure 6. This figure shows the typical C-curve that is developed. As the amount of liquid increased the rate of transformation increased.

The formation of tridymite from quartz as a function of temperature and composition proceeded at a rate which is represented by the curve shown in Figure 4. The initial rate was low; then it accelerated and finally decelerated when the reaction neared completion. Therefore, the time for 50% tridymite formation as determined by this method is a more accurate measure of the reaction than some point near the beginning or end of the process.

The effect of prefiring samples in the cristobalite stability range prior to firing in the tridymite stability range was also studied. The results are presented in Figure 7. This figure shows that at a given firing temperature for equal firing times the amount of tridymite formed in the prefired samples is greater than the amount formed in the non-prefired samples. This result would be expected since the quartz-to-cristobalite transformation does not have to take place in the prefired samples, even though this is not the rate limiting step, since there is always cristobalite available to transform to tridymite at the firing temperature.

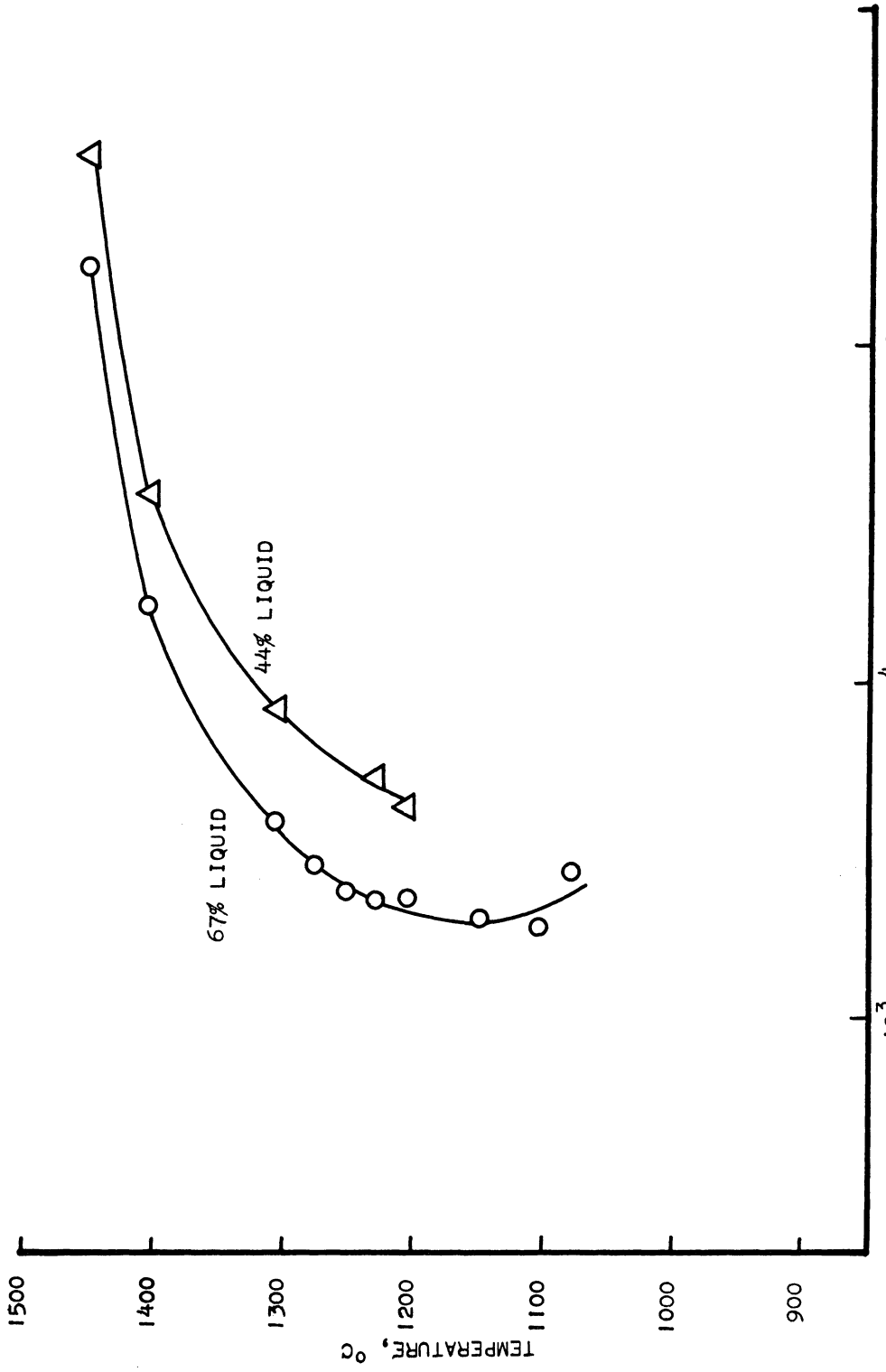


Figure 6. Isothermal transformation diagram for the Cu_2O-SiO_2 system.

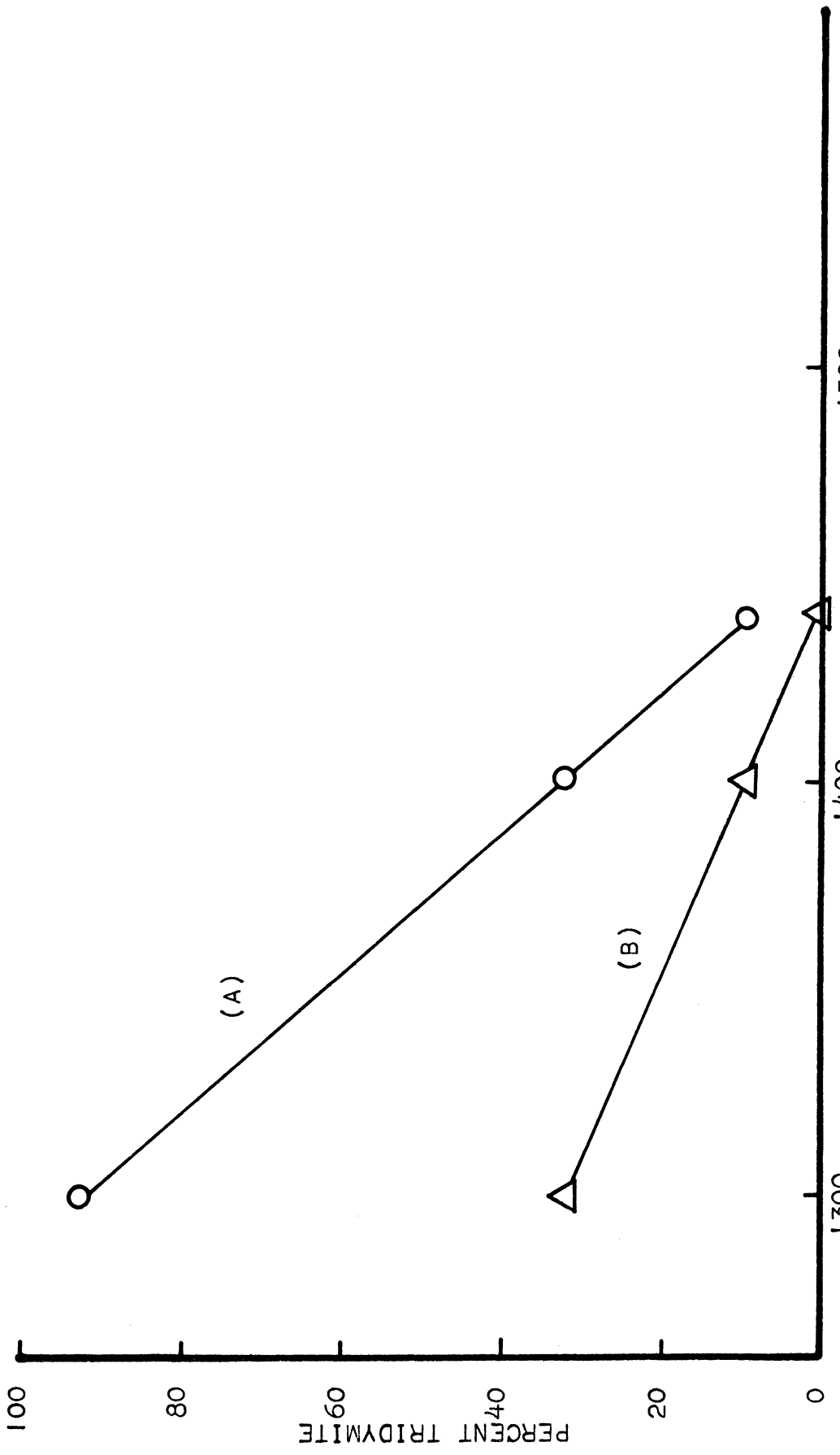


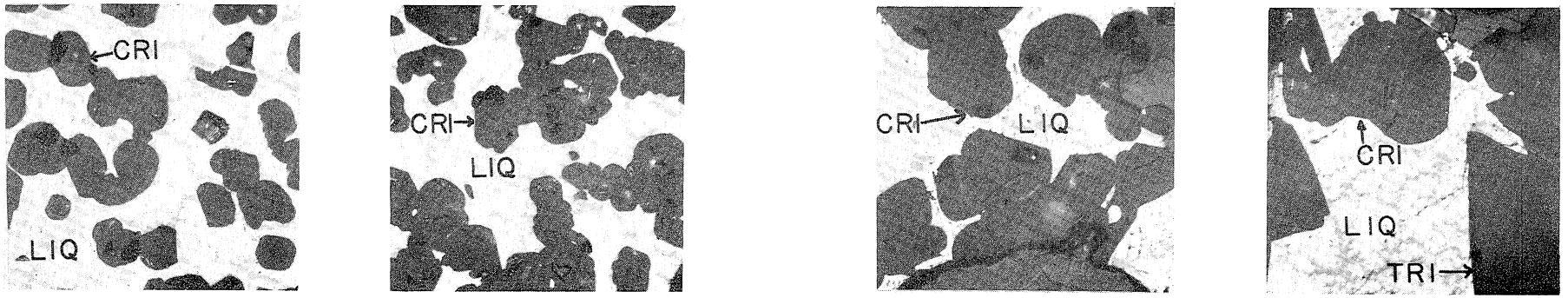
Figure 7. Comparison of transformation rates of prefired and non-prefired Cu_2O-SiO_2 samples containing 67% liquid. (A) Samples prefired at 1500° C, 4 hours; (B) samples not prefired.

Also of interest in the Cu_2O-SiO_2 system are the grain growth kinetics of the solid phases present, tridymite and cristobalite. Figure 8 shows the microstructures obtained by firing samples of the same composition for different times at the same temperature. The metastable cristobalite which transformed to tridymite also increased in grain size as the firing time was increased. This grain growth occurred by the solution-reprecipitation mechanism described by Burke in his discussion of grain growth of a solid in the presence of a liquid phase.[27] The effect of the amount of liquid present was also a factor in the grain growth kinetics in systems of this type.[28,29] The effect of the amount of liquid on the grain size of the cristobalite is shown in Figure 9. As the amount of liquid increased there was less growth of the cristobalite grains. This finding agrees with those in the investigations cited, which were concerned with refractory oxide solid materials other than silica.

SYSTEM: Na_2O-SiO_2

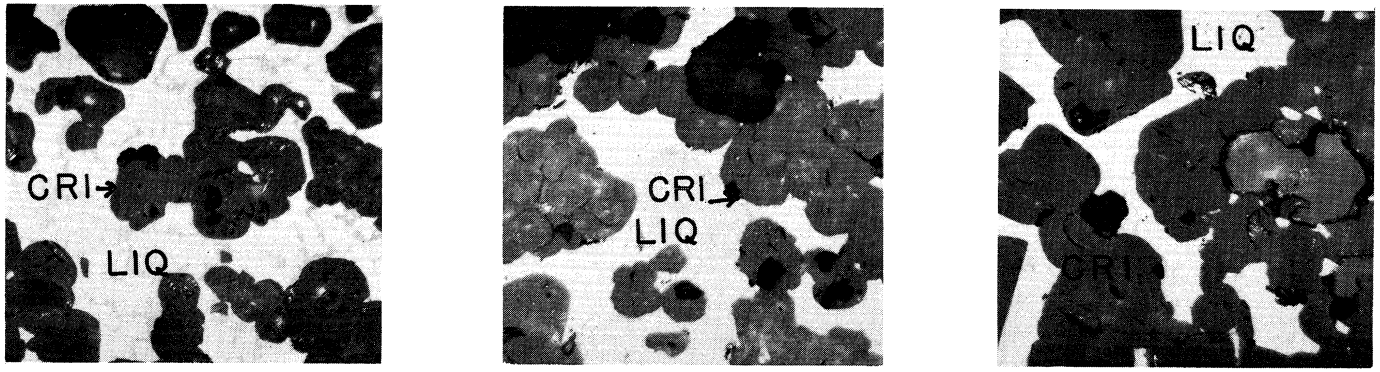
The phase relationships for the system Na_2O-SiO_2 are shown in Figure 10.[30] In this system the wide range of temperatures over which the two-phase tridymite-plus-liquid field exists provided the opportunity to study the quartz-to-tridymite transformation in the range 900° to 1450° C. The x-ray procedure described above was used in analyzing the samples to determine the extent of the transformation.

The isothermal transformation curves obtained in this system are



1	4	FIRING TIME (HOURS)	16	72
0.0176	0.0404	CRISTOBALITE GRAIN SIZE (mm.)	0.0432	0.0448

Figure 8. Variations in the metastable cristobalite grain size for Cu_2O-SiO_2 samples containing 67% liquid. Fired at 1400° C. CRI-cristobalite, TRI-tridymite, LIQ-liquid. (250X)



LIQUID CONTENT (PER CENT)	67	55	44
CRISTOBALITE GRAIN SIZE (mm.)	0.0404	0.0426	0.0477

Figure 9. Variations in the metastable cristobalite grain size for Cu_2O-SiO_2 samples. Fired at 1400°C for 4 hours. CRI-cristobalite, LIQ-liquid. (250X)

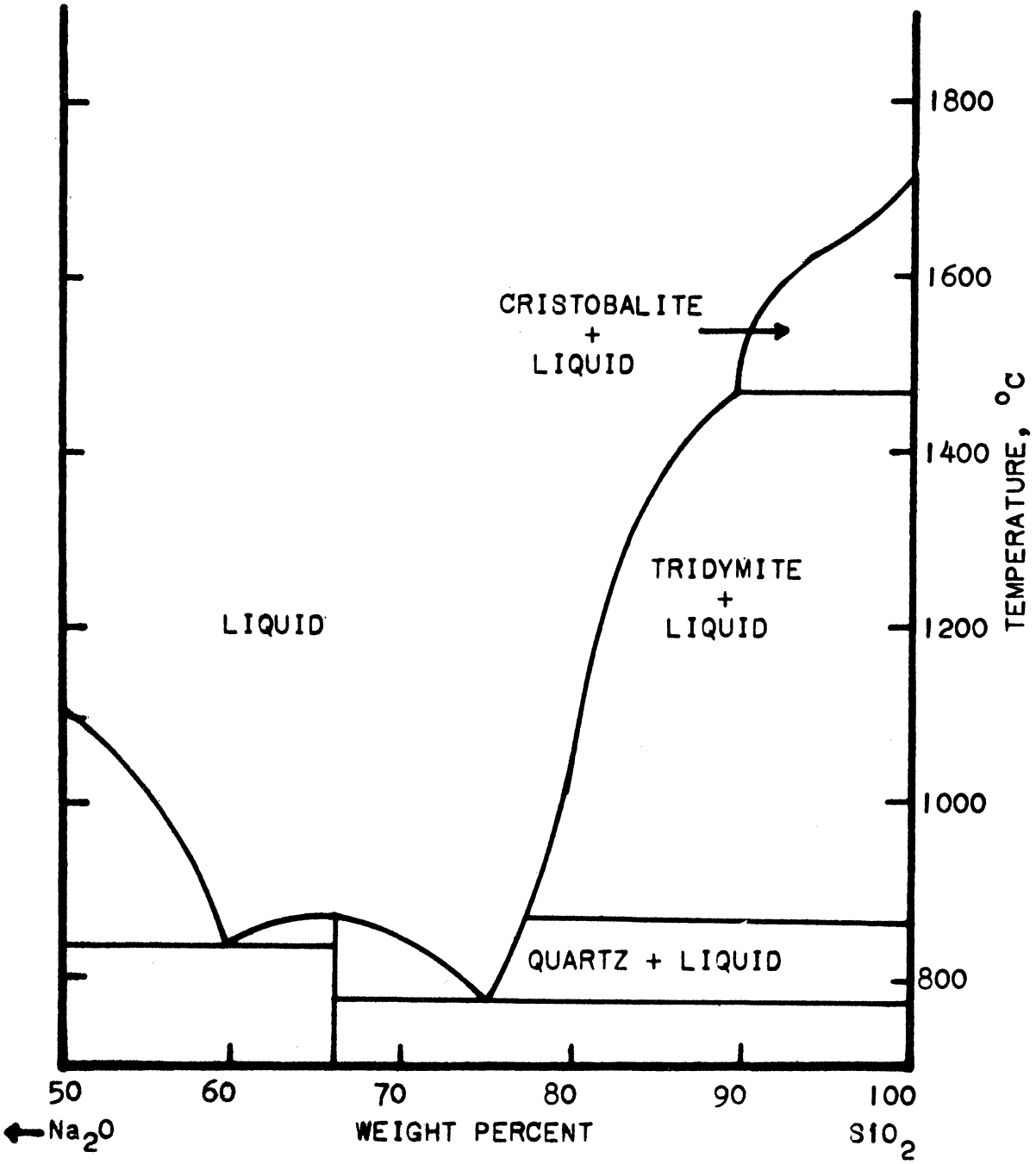


Figure 10. Phase relationships for the Na_2O-SiO_2 system.[30]

shown in Figure 11. As in the case of the Cu_2O-SiO_2 system, C-curves were obtained with higher liquid contents showing faster transformation rates.

Another point of interest in this system is related to the free energy-temperature relationships of the silica modifications. Mosesman and Pitzer have determined the free energy-temperature relations of the stable silica modifications.[31] Their data can be presented graphically as shown in Figure 12.[32] This figure shows the schematic representation of the thermodynamic relations of the silica polymorphs. A point of interest is the temperature at which the extension of the quartz line intersects the extension of the cristobalite line in Figure 12. Above this temperature, quartz should transform first to cristobalite before transforming to tridymite. This transformation process has been observed in this investigation as well as in other studies previously cited. Below this temperature, to the lower temperature limit of tridymite stability, quartz should transform directly to tridymite. Since the formation of cristobalite was observed at temperatures as low as 900° C, additional samples were run at smaller temperature intervals down to 860° C. The results obtained are shown in Table I. These results show that when tridymite is formed from quartz in the presence of Na_2O, the intersection of the extension of the quartz and cristobalite lines in figure 12 should occur at 880° ± 5° C. Thus, the transformation of quartz to tridymite in the presence of Na_2O occurs directly in the temperature range 867° to 880 ± 5° C.

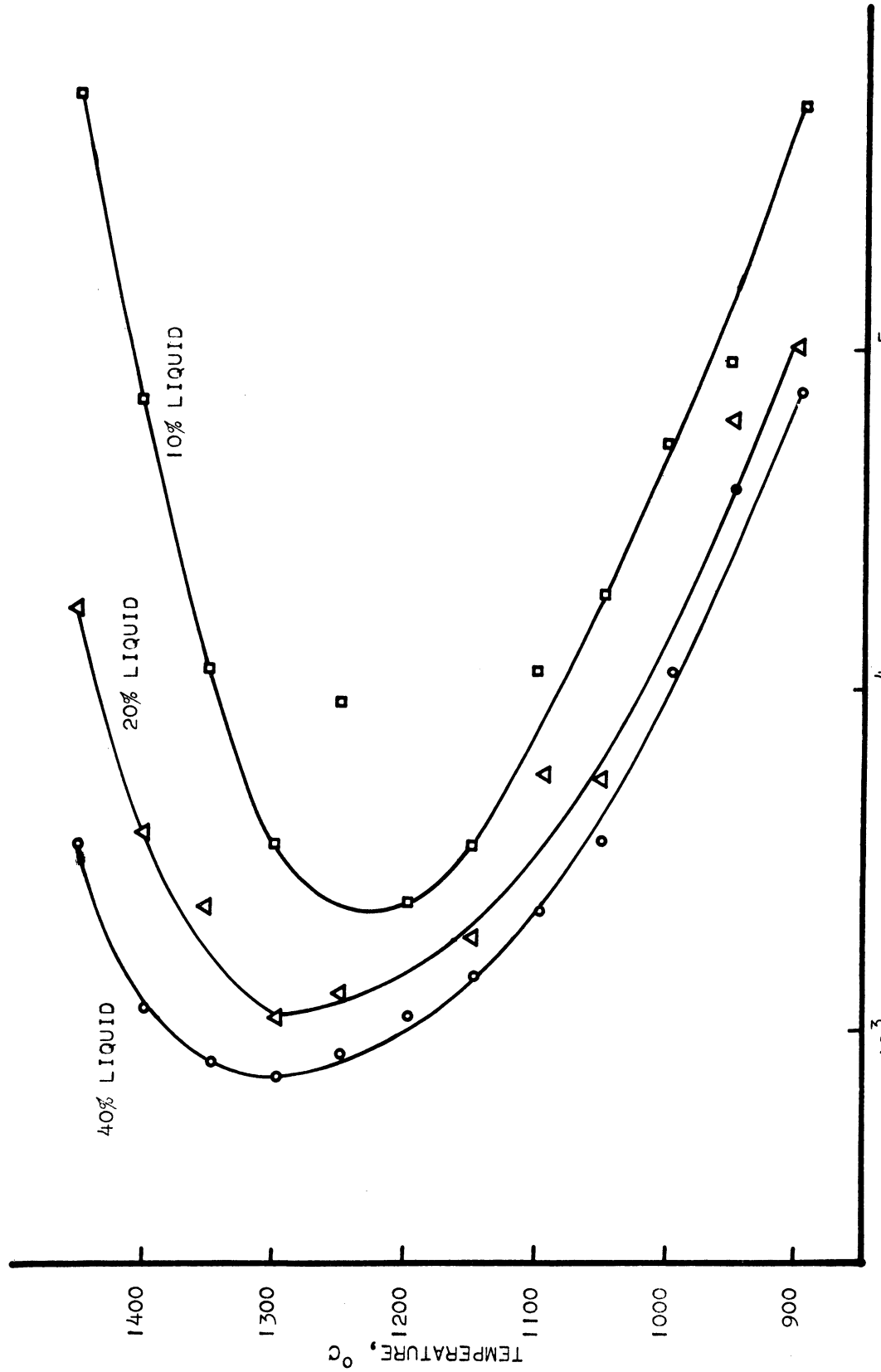


Figure 11. Isothermal transformation diagram for the Na_2O-SiO_2 system.

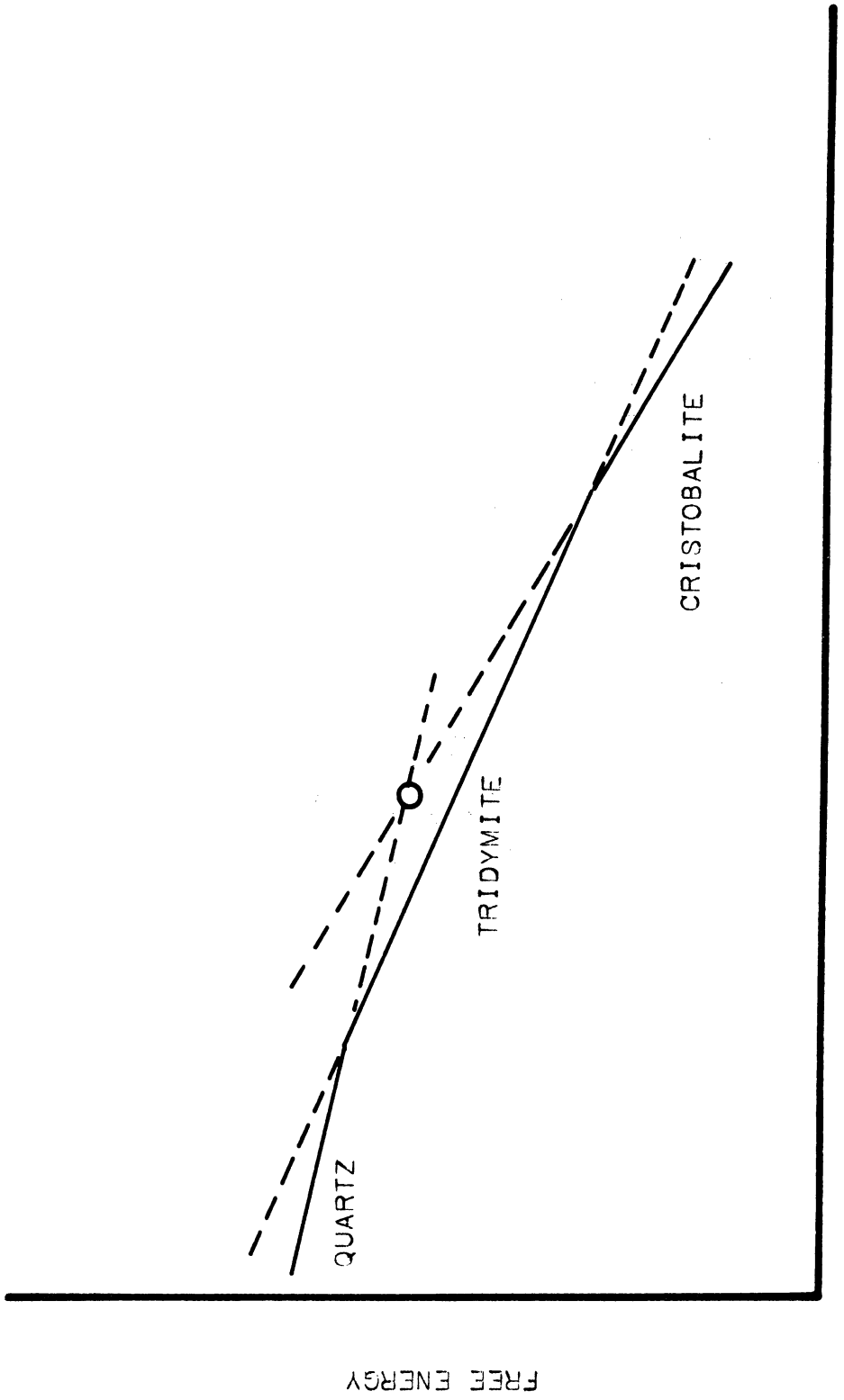


Figure 12. Schematic free energy versus temperature diagram of the stabile silica phases.[32]

TABLE I

SUMMARY OF THE EXPERIMENTAL DATA ON THE DIRECT TRANSFORMATION OF QUARTZ TO TRIDYMITE IN THE Na_2O-SiO_2 SYSTEM

Firing Temperature, °C	Firing Time, hr	Silica Polymorphs		
		Quartz	Cristobalite	Tridymite
900	46	X*	X	X
885	72	X	X	X
875	96	X	-	X
860	96	X	-	-

*X indicates the presence of the polymorph.

SYSTEM: FeO-SiO_2

The FeO-SiO_2 phase relationships are shown in Figure 13.[33] Once again the transformations show the typical C-curve illustrated in Figure 14. Sample analysis in this system was made by the x-ray technique. The amount of liquid is shown to have a decided influence on the rate of transformation, as was observed in the systems discussed previously. The samples containing higher amounts of liquid transformed faster than those with lower liquid contents.

SYSTEM: PbO-SiO_2

The phase relationships for the PbO-SiO_2 system are shown in Figure 15.[34] The quantitative x-ray technique was used to analyze the samples but with a variation from the method described above. The variation in-

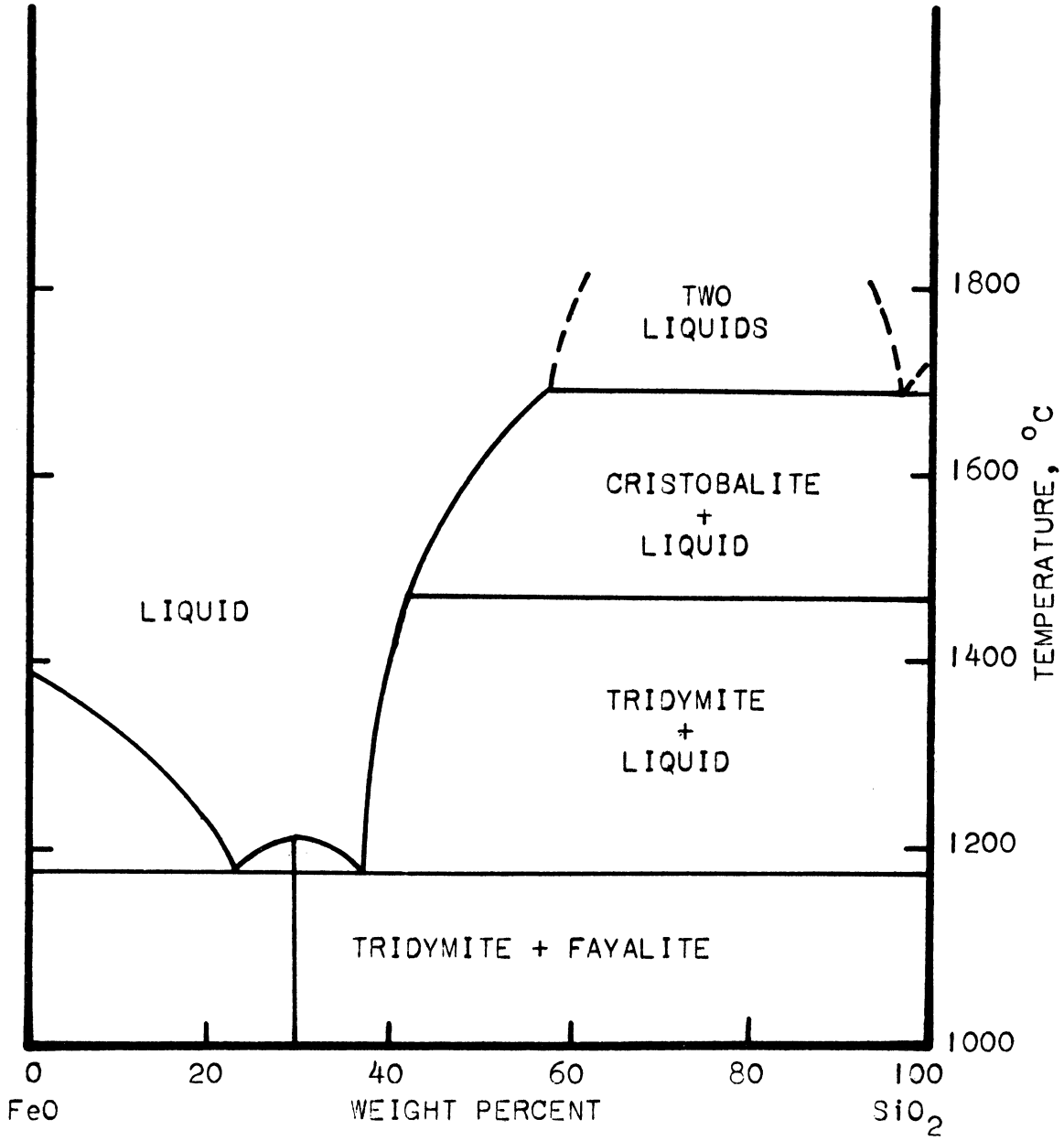


Figure 13. Phase relationships for the FeO-SiO_2 system.[33]

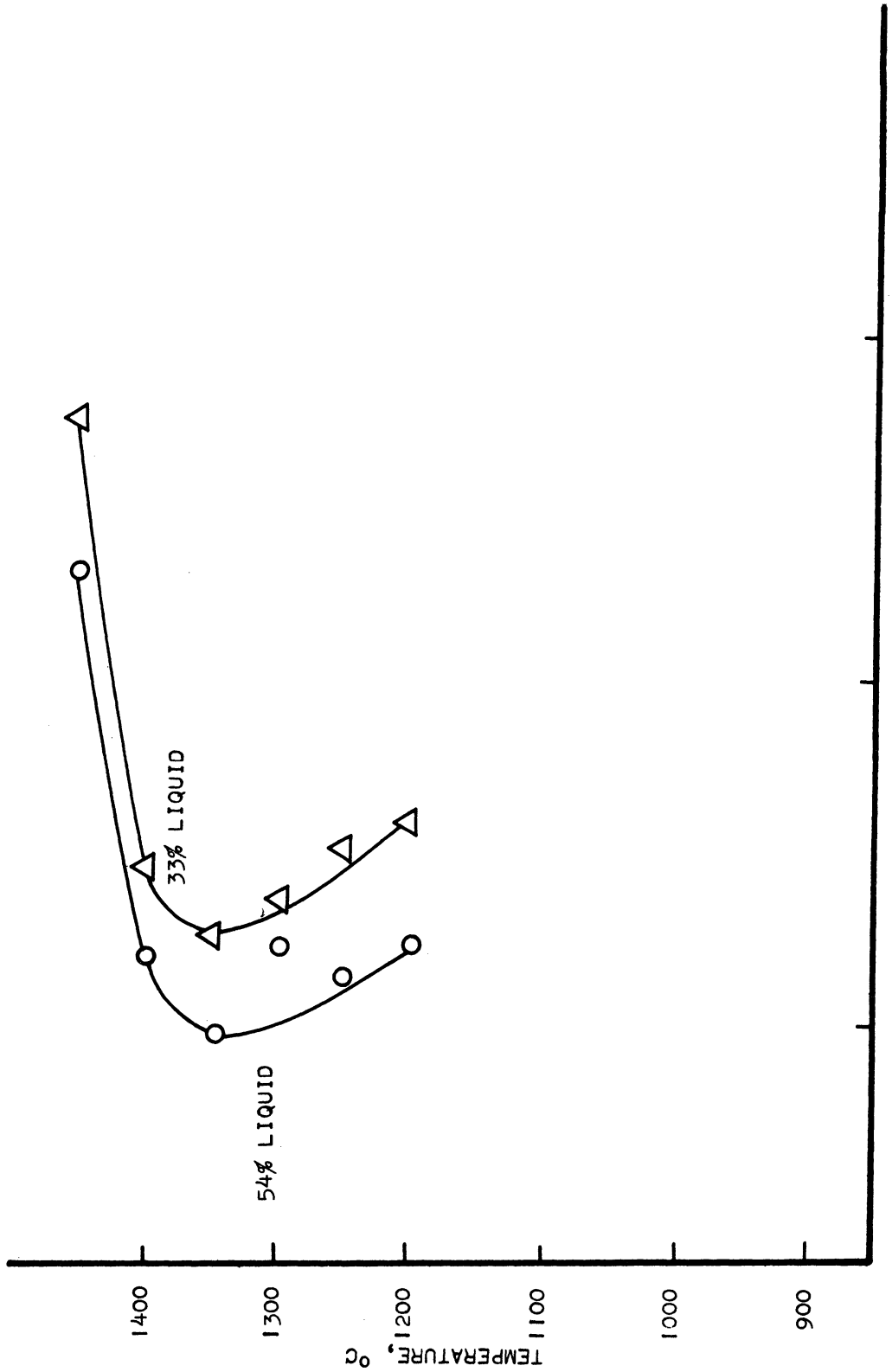


Figure 14. Isothermal transformation diagram for the $FeO-SiO_2$ system.

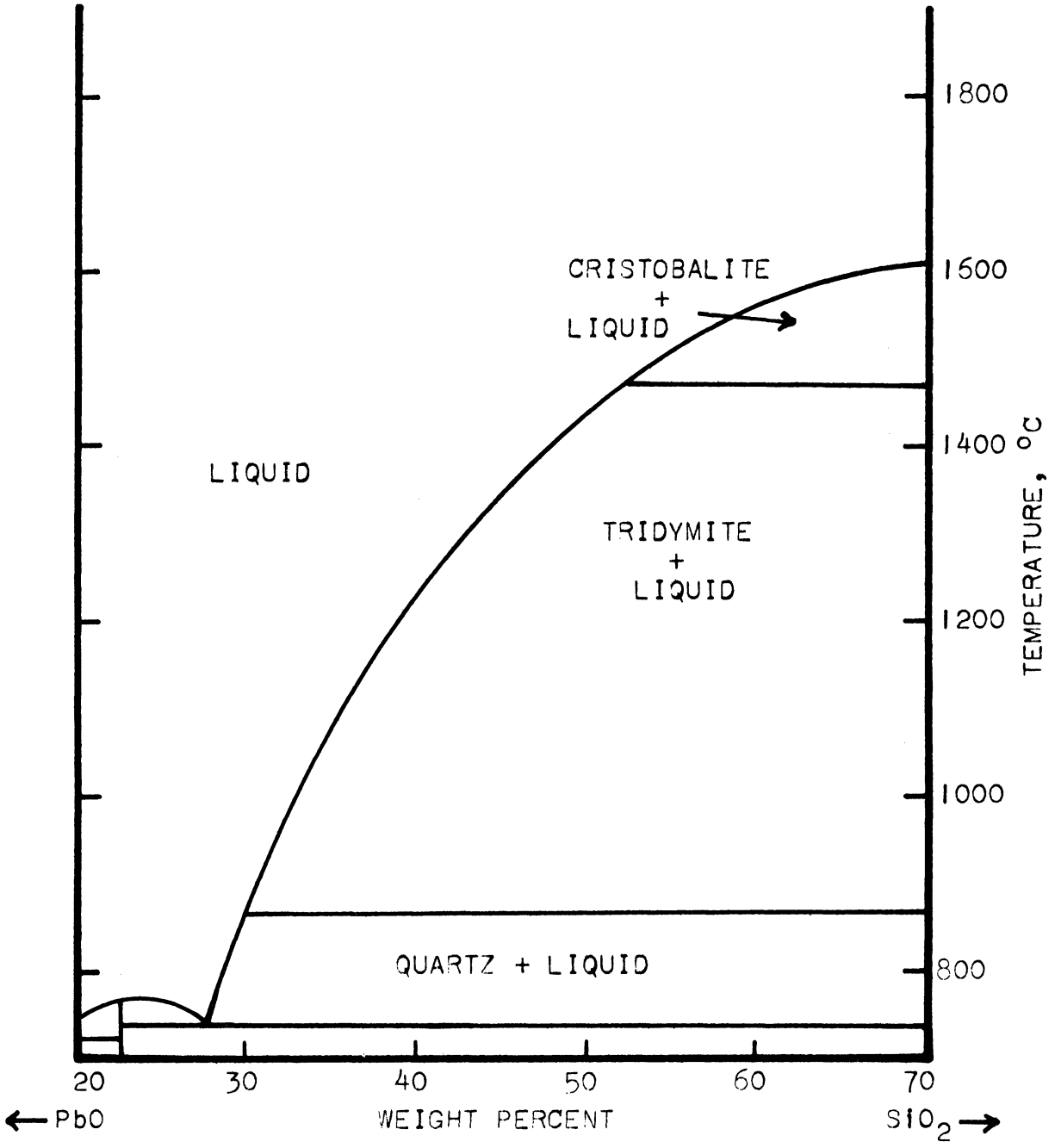


Figure 15. Phase relationships for the PbO-SiO_2 system.[34]

volved analyzing the d = 2.84 Å peak to determine the cristobalite content and the d = 3.34 Å peak to determine the quartz content. The percent tridymite was determined by subtracting the percent quartz plus cristobalite from 100. The results obtained in this system are shown in Figure 16. This figure shows behavior similar to that found in the other systems studied.

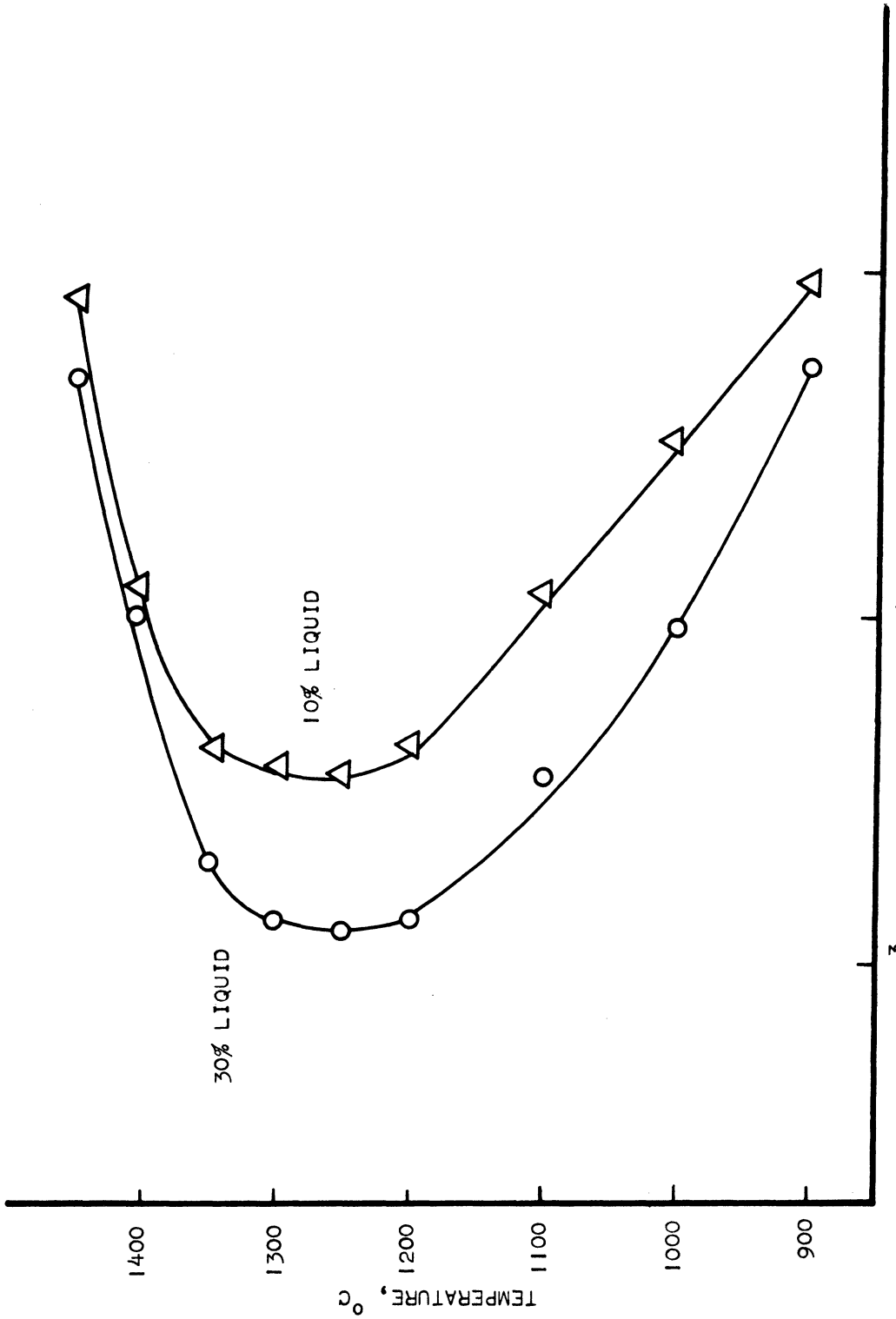


Figure 16. Isothermal transformation diagram for the PbO-SiO_2 system.

CHAPTER V

DISCUSSION OF RESULTS

The results obtained will be discussed in terms of a comparison of the systems studied and an analysis of the reaction.

COMPARISON OF SYSTEMS

From the results presented, there are several observations that can be made concerning the kinetics of the transformation of quartz to tridymite. The rate of the reaction is affected by the amount of liquid present and by the type of oxide that is added to the original quartz to form the flux. Inspection of the time-temperature-transformation curves presented shows that as the amount of liquid present is increased, the reaction time is decreased. Calculation of the boundary area per unit volume in the Cu_2O-SiO_2 system shows that increasing the liquid content increases the boundary area of the solid material that is exposed to the liquid phase. The following relationship was used to determine boundary area per unit volume:

$$B_V = 2N_L$$

where B_V is the boundary area per unit volume and N_L is the number of solid-liquid phase boundaries traversed by a random line.[35] The calculations are summarized in Table II. Thus, the increased rate of transformation at higher liquid contents is related to the increased area of

the solid phases exposed to the liquid phase. This increases the possibility for solution and reprecipitation of the transforming phases.

TABLE II

COMPARISON OF THE RELATIVE AREA-TO-VOLUME RATIO WITH THE AMOUNT OF LIQUID AND TRANSFORMATION RATE FOR THE Cu_2O-SiO_2 SYSTEM

Firing Temperature, °C	Amount of Liquid, %	Area-to-Volume Ratio, B_V	Time for 50% Transformation to Tridymite, sec
1440	44	104	360,000
	67	220	180,000
1300	44	92	8,100
	67	176	6,480
1250	44	84	4,860
	67	220	2,400

The curves presented also show that the rate of transformation decreases as a function of the added oxide in the following order: Na_2O (fastest), PbO, FeO, Cu_2O (slowest), when the amount of liquid is kept constant. At 1300° C and 30% liquid content, the times to 50% transformation to tridymite for the systems studied were found to be:

Na_2O	1000 sec
PbO	1400 sec
FeO	2000 sec
Cu_2O	9000 sec

In analyzing these results to determine the factors that might contribute to the variations observed, it was determined that the composition of the liquid phase present had an effect on the transformation kinetics

(Table III). When the liquid phase contained a higher concentration of SiO_2 the rate of transformation to tridymite increased. Since the concentration of the accompanying oxide was lower at the interface between the liquid and solid phases, there was less solute to move away from the interface, allowing for the more rapid crystallization of the tridymite from the liquid.

TABLE III

SUMMARY OF THE LIQUID COMPOSITION AND TRANSFORMATION RATE DATA FOR SAMPLES CONTAINING 30% LIQUID

System	Firing Temperature °C	Mole Percent Silica in the Liquid Phase	Time for 50% Transformation to Tridymite, sec
Na_2O-SiO_2	1000	79	12,000
	1200	82	1,200
	1400	86	1,800
PbO-SiO_2	1000	67	12,600
	1200	72	1,400
	1400	80	8,000
FeO-SiO_2	1200	42	3,840
	1400	46	3,000
Cu_2O-SiO_2	1200	25	7,200
	1400	34	60,000

Bockris, et al.[36] showed that as the mole percent silica in silica-metal oxide liquids is increased, the chain length of the discrete ions in the liquid increases. They also showed that the viscosity of the liquid increases as the silica content is increased. Since the quartz-

to-tridymite transformation proceeded at a faster rate at higher silica contents in the liquid, the liquid viscosity is not the controlling factor in the transformation.

In attempting to find other factors that could influence the rate of the transformation of quartz to tridymite, valence, ion size, and atomic weight and number of the added metallic element were investigated and found to give no correlation.

ANALYSIS OF THE REACTION

As discussed above, the reaction under consideration is complex and involves several steps. This includes the solution of quartz into the liquid phase and the precipitation of the metastable cristobalite phase. The more stable tridymite precipitates concurrently but at a slower rate, eventually replacing both the quartz and the cristobalite.

The experimental data show behavior similar to that observed in studies of the kinetics of devitrification and crystal growth in glass.[37,38] The rate of crystal growth in glass increases as the difference between the growth temperature and the liquidus temperature is increased. The growth rate reaches a maximum and then decreases in proportion to the reciprocal of the melt viscosity. This process has been described by the following empirical relationship:

$$U = \frac{(\text{constant})(T_o - T_i)}{\eta} , \qquad (1)$$

where $\underline{U}$ is the crystal growth rate, T_o is the liquidus temperature, T_i is the temperature at the growing interface, and η is the melt viscosity.

The relationship given in Eq. (1) was based on an empirical relationship between crystal growth rate and temperature for viscous liquids, originally presented by Preston[39] and given in Eq. (2):

$$U = Ke^{-C/T_i(abs)} (T_o - T_i) , \qquad (2)$$

where $\underline{K}$ and $\underline{C}$ are constants and $T_i(abs)$ equals $T_i + 273$. This empirical relationship is based on the combination of two assumptions Preston found experimentally justifiable for the temperature regions above and below T_m, the temperature at which the rate of crystal growth is at a maximum. In the temperature interval between T_m and the liquidus temperature, the rate of crystal growth was shown to be proportional to the difference between the liquidus temperature and the temperature at the growing interface. Preston considered this temperature difference to be the degree of supercooling and a measure of the force causing crystallization.

Below T_m the viscosity of the liquid, which increases rapidly as the temperature is decreased, is assumed to be responsible for the decrease in crystal growth rate despite the continual increase in the degree of supercooling. A semilogarithmic plot of crystal growth rate below T_m versus the reciprocal of the absolute temperature gives a linear relationship similar to the viscosity equation which is also an empirical relationship. The relationship shown by the semilogarithmic plot is:

$$U = - \frac{C}{T_i \text{ (abs)}} + B \ , \qquad (3)$$

where C is the slope of the line and B is a constant. Eq. (3) can be written:

$$U = Be^{-C/T_i \text{ (abs)}} \ , \qquad (4)$$

which is in the form of the well-known Arrhenius equation with C being an activation energy divided by the gas constant, R. To test the validity of the empirical relation given in Eq. (2), Preston obtained a value for C from a semilogarithmic plot of U versus the reciprocal of the absolute temperature. The value of U represented the rate of growth of devitrite ($Na_2O \cdot 3CaO \cdot 6SiO_2$) from a sheet glass composition. He then proceeded to plot the function $[e^{-C/T_i \text{ (abs)}}(T_o - T_i)]$ versus T_i obtaining a curve of the same shape as that obtained experimentally. The temperature at which the growth rate is at a maximum coincided with the experimental T_m. By considering the relation between the viscosity equation and the empirical equations developed, the relationship presented to describe the experimental curve obtained was:

$$U = K\left(\frac{1}{\eta}\right)^2 (T_o - T_i) \ . \qquad (5)$$

This equation is similar to Eq. (1) in which Swift shows the viscosity to the first power rather than the squared term in Eq. (5).

The relation between the process described above and the transformation of quartz to tridymite is readily apparent because polymorphic

transformations that require a change in coordination and diffusion of material show kinetics characteristic of nucleation and growth.

To determine the applicability of the type of analysis described above to the present investigation, the following empirical relationship was used:

$$R = Ke^{-C/T_i\ (abs)}(T_c - T_i) \qquad (6)$$

where R is the rate of transformation of quartz to tridymite at temperature T_i, T_c is the tridymite-cristobalite equilibrium temperature (1470° C), C is a constant that can be determined from the slope of the linear semilogarithmic plot of R versus the reciprocal of the absolute temperature, and K is a constant. It was found that semilogarithmic plots of R versus $1/T_i$ (abs) for values of T_i lower than T_m gave two different possible values for C because of a break in the curve as shown in Figure 17. The value of C was obtained from the lower temperature portion of the curve because this part of the curve best described the process taking place below T_m. Figure 17 was obtained from data in the Na_2O-SiO_2 system at 40% liquid concentration. The value for C obtained from this figure was then used in Eq. (6) to calculate $e^{-C/T_i\ (abs)}\ (1470 - T_i)$. These values were then plotted versus temperature as shown in Figure 18. This figure agrees with the experimental curve obtained for this composition and system, both in the shape of the curve and the temperature at which the rate becomes a maximum. Calculations were also made at the 20% liquid level in the Na_2O-SiO_2 system and the 30% liquid level in the

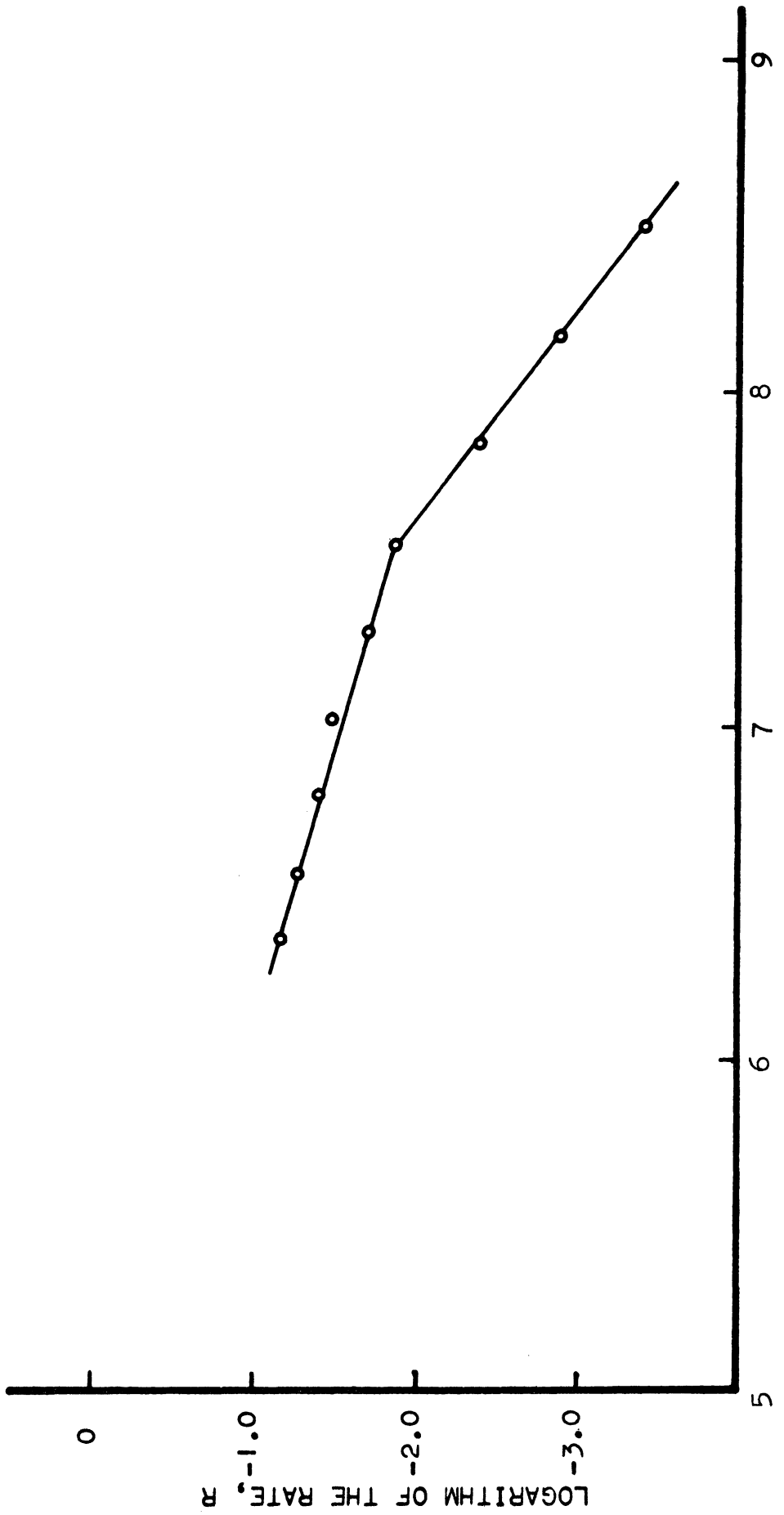


Figure 17. Logarithm of the rate, R, versus the reciprocal absolute temperature for Na_2O-SiO_2 samples containing 40% liquid.

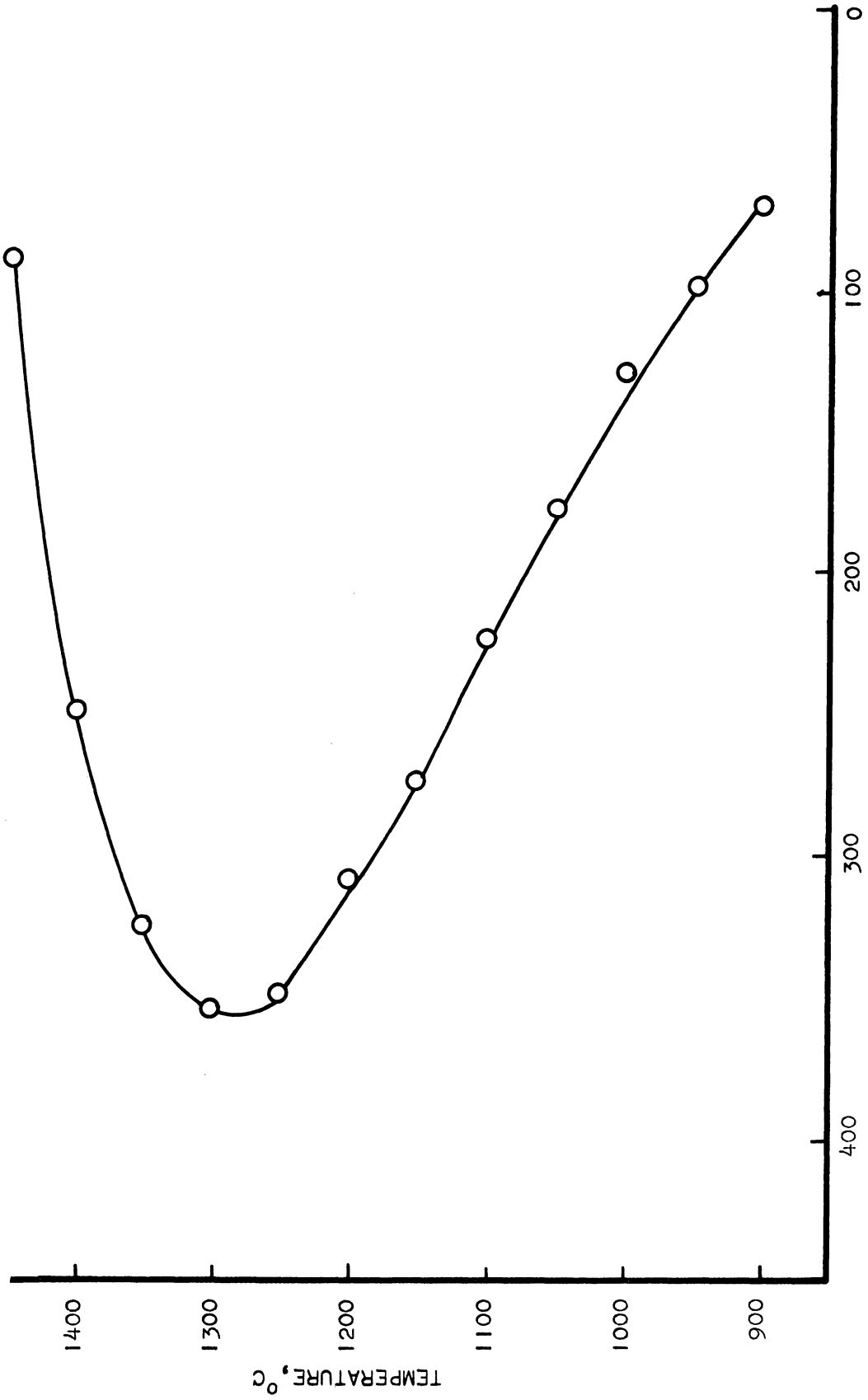


Figure 18. Calculated value of $e^{-C/T_i}(abs)$ $(1470 - T_i)$ versus temperature, °C for Na O-SiO_2 samples containing 40% liquid.

PbO-SiO_2 system. These results are also in agreement with the experimental findings. In the Cu_2O- and FeO-SiO_2 systems the semilogarithmic plots of temperature versus the calculated value of $e^{-C/T_i\ (abs)}(1470 - T_i)$ did not show the typical C-curve. In both these systems T_m occurs at a temperature close to the value of the lower temperature limit studied, and therefore it is possible that the value for $\underline{C}$ is inaccurate as obtained from a semilogarithmic plot of $\underline{R}$ versus the reciprocal of the absolute temperature. This inaccuracy could be the result of the fact that the portion of the curve near T_m is governed by both the supercooling effect in the upper temperature ranges and the nucleation effect at the lower temperatures.

Analysis of the results of this investigation shows that the rate of the transformation of quartz to tridymite can be determined by Eq. (6) if it is possible to determine an accurate value for $\underline{C}$.

CHAPTER VI

CONCLUSIONS

The following conclusions may be drawn from this investigation:

1. The rate of transformation of quartz to tridymite in the presence of other oxides is affected by the amount of liquid present at the firing temperature, the type of oxide added to the original quartz, and the temperature at which the transformation is taking place.

2. The kinetics of the transformation show the characteristics of a C-curve. The transformation proceeds slowly at temperatures near the upper temperature limit of tridymite stability (1470° C) and at temperatures near the eutectic temperature in the systems studied. The rate of transformation passes through a maximum as the temperature is varied in the tridymite stability range. The following empirical equation has been formulated to describe the rate of transformation:

$$R = Ke^{-C/T_i\,(abs)}\,[1470 - T_i]\,.$$

The validity of this relationship is dependent on the accuracy of the value obtained for the constant C. The part of the C-curve below T_m, the temperature at which the rate is a maximum, is taken into account by the factor $e^{-C/T_i(abs)}$. The part of the curve above T_m is related to the term $[1470 - T_i]$ where 1470 is the tridymite-cristobalite equilibrium temperature and T_i is the temperature at which the transformation is taking place. $T_i(abs)$ equals $T_i + 273$.

3. The rate of transformation of quartz to tridymite is related to the solubility of silica in the liquid phase. The transformation rate decreased in the following order: Na_2O (fastest), PbO, FeO, Cu_2O (slowest). The extent of solubility of silica in the liquid phase decreased in the same order. Decreasing the solubility of silica in the liquid decreased the rate of transformation.

4. The solid cristobalite grains which have formed as a metastable phase in the tridymite stability range, continue to increase in size even though the transformation of cristobalite to tridymite is taking place.

5. The lower temperature limit below which quartz transforms directly to tridymite in the Na_2O-SiO_2 system, without passing through the metastable cristobalite phase, has been determined to be in the range 875° to 885° C.

APPENDIX I

SILICA ANALYSIS

Analysis of the silica (α-quartz) used as the raw material in this investigation is as follows:

SiO_2	99.84 wt %
Al_2O_3	0.129 wt %
FeO	0.018 wt %
CaO	0.008 wt %
MgO	0.005 wt %

This analysis was supplied by the Fisher Scientific Company.

APPENDIX II

THE LABORATORY FURNACE

The furnace used in this investigation was Laboratory Equipment Corporation Model 2600. A detailed drawing of the furnace is shown in Figure 19. The furnace was heated by four Crusilite Type X silicon carbide heating elements with the following dimensions: (a) an effective heating length of 10 in., (b) a diameter of 3/4 in., and (c) an overall length of 25 in. The nominal resistance of the heating elements was about 1.8 ohm.

Power was supplied to the elements from a 5 KW auto transformer with single phase connection. A divided voltage control provided voltage independently to the upper and lower sets of elements in incremental steps of two volts. This control allowed for ease of maintenance of equal amperage for both sets of heating elements.

The furnace was equipped with Triangle H5 mullite tubes with the following dimensions: (a) 1-1/4 in. O.D., (b) 1 in. I.D., and (c) 30 in. overall length.

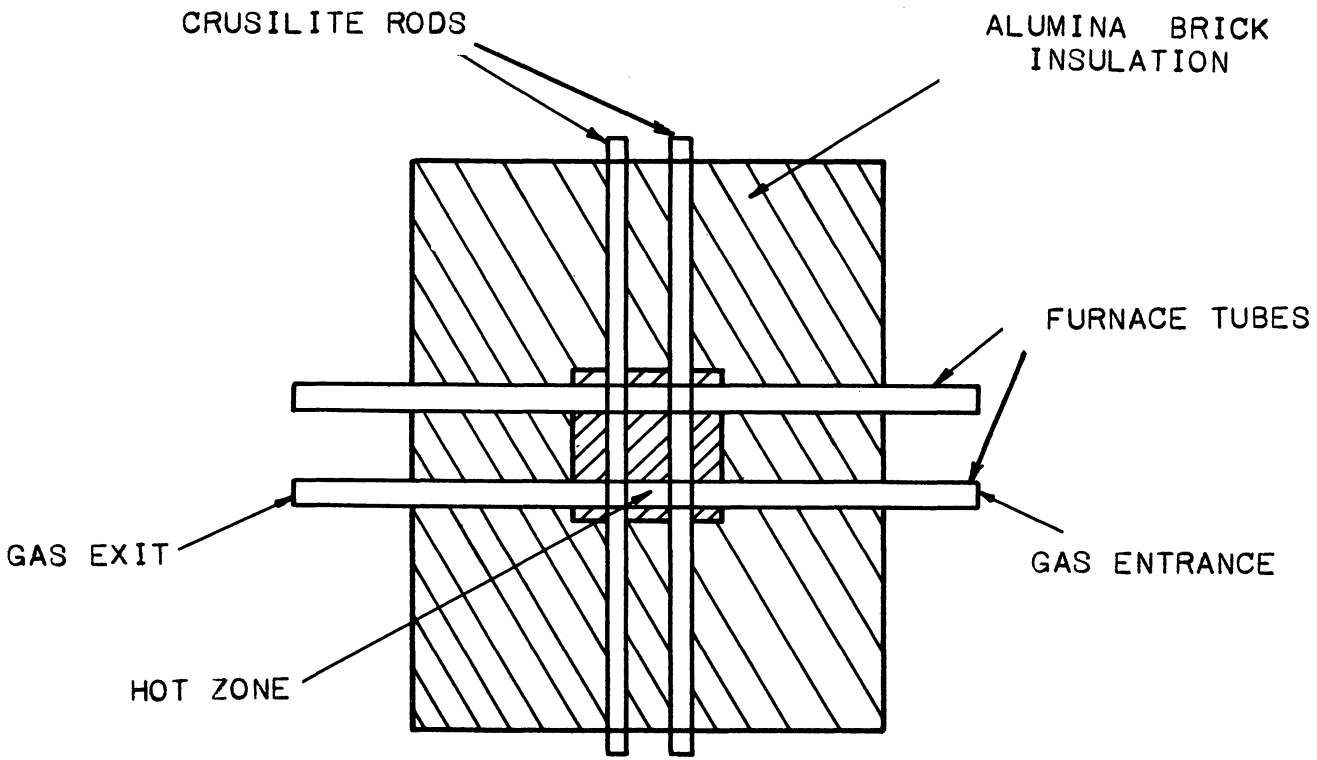


Figure 19. Scale drawing of the Laboratory Equipment Corporation furnace. 1/8" = 1".

APPENDIX III

LIQUID COMPOSITIONS AND AMOUNTS FOR THE SYSTEMS STUDIED

System	Amount of Liquid, %	Mole Percent Silica in the Liquid Phase				
		Temperature, °C				
		1000	1100	1200	1300	1400
Cu_2O-SiO_2	44, 67	--	21	25	29	34
Na_2O-SiO_2	10, 20, 30, 40	79	81	82	84	86
PbO-SiO_2	10, 30	67	69	72	76	80
FeO-SiO_2	33, 54	--	--	42	44	46

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