STUDY OF CRYSTALLIZATION OF GLASS

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY

SUPERVISION BY Howard Raymond Swift

ENTITLED Study of Crystallization of Glass

BE ACCEPTED* AS FULFILLING THIS PART OF THE REQUIREMENTS FOR

THE DEGREE OF Doctor of Philosophy in Engineering

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I. INTRODUCTION

A. Statement of the Problem

If a crystal is placed in a liquid which is supersaturated with respect to this material, the crystal will increase in size. It was the purpose of this investigation to add to the knowledge concerning the factors which influence the rate of growth of such a crystal.

The study was limited to crystal growth measurements in some soda-lime-silica glasses since these glasses are of a rather simple type, are of great commercial interest, and have rates of devitrification sufficiently low so that crystal development can be readily followed. The data may be of value in reaching a better understanding of the transition from the liquid to the glassy state.[1]

B. Applications

The development of crystals in glasses has attracted considerable attention since this process is usually undesirable. The manufacturers of large glass containers, plate glass, and hand-worked articles experience particular difficulty since the glass is held for long periods in the temperature range favorable for crystal growth. Devitrification is also frequently met in the manufacture of optical glass, since the physical properties are usually of primary importance and the devitrification tendencies secondary in selecting the composition.

In other ceramic fields, the problem of regulating the crystal growth is equally as important, since the nature, amount, and properties of the crystalline phases present quite frequently control the properties of the finished material. Some examples of crystal growth in ceramics are: the growth of interlocking crystals of mullite in porcelain to give maximum strength[2]; recrystallization and grain growth of refractory materials during manufacture and service[3]; the formation of crystals of proper size for maximum opacity in enamels[4] and in glasses[5]; the proper growth of colloidal colorants in glasses[6]; proper crystal development in adventurine glazes[7]; crystal development in special-purpose glazes[8]; crystal growth during the setting of plaster and cement.[9]

II. REVIEW OF LITERATURE

A. Factors Influencing Crystal Growth

The process of crystal growth involves primarily the following stages: (1) the establishment of such conditions of temperature and concentration that supersaturation exists in the system; (2) the arrangement of the components of the crystallizing phase to form crystal nuclei; (3) the migration of atoms, molecules, or groups to the nucleus; and (4) the attachment of such groups to the growing crystal.

The above process is complicated by numerous factors. Among these are: the dissolving of the nuclei and crystallites due to the high vapor pressure of small particles[10]; the local heating effects due to the release of energy in forming crystals[11]; the complexities arising from a variation of the affinity for atoms, molecules, and groups on different crystallographic faces[12]; presence of foreign materials adsorbing preferentially on different crystallographic faces[13]; movement of molecules over the surface of the growing crystal[14]; changes in the concentration as a result of crystallization[15]; action of local currents in the system[16]; decrease in volume of the system putting the material under tension[17]; coalescence of crystals[18]; modifications of crystals due to external forces[19]; modifications of the crystals due to the proximity of other growing crystals[20]; the unknown number of residual nuclei in the melt.[21]

B. Theories of Crystal Growth

In the explanation of a complex phenomenon, it is frequently necessary to make many assumptions idealizing the system neglecting the secondary factors. Such reasoning will give a fair insight of the complex phenomenon only if the complicating factors are of minor importance. The present theories of crystal growth are based on the idealized system and must suffer the limitations of the same.

Kossel[22] bases his theory of crystal growth on the energy released with the deposition of an ion upon different surface positions. His idealized crystal surface homogeneity has been criticized by Balarev[23] and his assumptions regarding the lack of adsorption and other secondary effects have been criticized by Kleber.[24] Balarev[25] points out that growth occurs, not only by the attachment of ions or molecules, but also by the attachment of crystals.

Stranski and Kaishev[26] consider the work of separation of component parts of the growing crystal in developing their theory of crystal growth. They assume among other things that the molecules go to positions of minimum energy on the crystal; that the surface has the same structure as the interior of the crystal; and that secondary effects are absent. These assumptions have been criticized.[23,24,25]

Roginskii and Todes[27] discuss the particle size distribution of the crystal phase with respect to the process of crystallization. Their work is based on many assumptions regarding the changes in crystal length, nucleation, and concentration with time and is not concerned primarily with the fundamental processes involved. No consideration is given to the possibility of different growth velocities in different crystallographic directions. Much of their theory is based on their fundamental postulate that the rate of linear growth is constant. Since many observations have been made to the contrary,[28] their results may be open to criticism.

Tammann[29] has given an excellent discussion of the effect of temperature on the rate of growth of crystals. His work is based on the over-all process of crystal growth without a consideration of the basic processes involved. His assumption that the melting point prevails at the boundary surface between a crystal and its melt during crystallization is only an approximation according to Masing.[11c]

Brandes[30] considers the vapor pressure and work of formation of a two-dimensional nucleus on different crystallographic faces in developing his theory of crystal growth. His idealized crystal structure and lack of consideration of adsorption effects limit his theory.

Other theories are based on considerations of growth of different crystallographic faces,[12e, 12f] and on a consideration of molecules evaporating from and condensing on different crystallographic faces.[14f, 31] Such theories suffer the same limitations as the above.

C. Devitrification of Glasses

The work that has been done on the devitrification of glasses may be divided into two major classifications: (a) determination of phase equilibrium relationships, and (b) observations of the rate of crystal growth in glasses.

The work of Morey and Bowen[32] is outstanding in regard to the determination of the phase equilibrium relationships which are of interest to the glass technologist. From the data which they present, the upper limit of crystal growth can be determined as well as the solubility of the precipitating phases at lower temperatures. No direct information concerning the rate of crystal growth can be obtained except the temperature at which the rate is equal to zero.

Zschimmer and Dietzel[33] measured the rate of growth of crystals at different temperatures in technical glasses and in soda-lime-silica glasses of varying composition. Mullensiefen and Zschimmer[34] measured the effect of alumina on the devitrification rate of several soda-lime-silica glasses, and Preston[35] studied the rate of crystal growth in a soda-lime-magnesia-silica glass.

The method employed by the previous investigators consisted of heating small samples of glass in a platinum container at different temperatures for varying lengths of time. Zschimmer, Dietzel, and Mullensiefen[33, 34] measured the thickness of the devitrified zone, while Preston[35] measured the radii of the spherulites present.

III. A STUDY OF THE RATE OF CRYSTAL GROWTH IN GLASSES

A. The Effect of Alumina on the Rate of Crystal Growth and Solution

1. Introduction

The effect of alumina in retarding devitrification of soda-lime glasses has been known since Schott found that the beneficial results obtained by the use of Thuringian sand were derived from the presence of alumina in the sand.[36] Morey[37] and Silverman [38,39] studied the effect of alumina on the liquidus temperature of some soda-lime-silica glasses and some soda-lime-magnesia-silica glasses. Mullensiefen and Zschimmer[34] studied the effect of replacing silica with alumina on the rate of crystal growth in some soda-lime-silica glasses.

It was the purpose of this phase of the investigation to extend the work of Mullensiefen and Zschimmer to include glasses of known viscosity and to trace the curves above the liquidus in measuring the rate of solution of the crystalline phases of these glasses.

2. Procedure

The compositions of the glasses studied are shown in Table I. The viscosity data of some glasses of similar composition were kindly furnished by the General Research Laboratory of the Owens-Illinois Glass Company.

Batches were prepared using C.P. chemicals, taking into consideration the small changes in composition experienced due to

Table I

Effect of Replacing Silica by Alumina on Some Physical Properties of Soda-Lime Glasses Used for Rate of Crystal Growth Measurements

Glass No.	A-0	A-2	A-4	A-6	A-8
Theoretical Composition					
SiO_2	71.0	69.0	67.0	65.0	63.0
Al_2O_3	0	2.0	4.0	6.0	8.0
CaO	12.0	12.0	12.0	12.0	12.0
Na_2O	17.0	17.0	17.0	17.0	17.0
Primary Phase[38]	D*	D*	W*	W*	W*

Temperature-Viscosity Relation (log n)[40]

Temperature (°C)	A-0	A-2	A-4	A-6	A-8
750	6.58	6.60	6.74	6.98	7.08
800	5.78	5.80	5.92	6.11	6.19
850	5.13	5.15	5.26	5.41	5.47
900	4.58	4.61	4.70	4.82	4.87
925	4.34	4.37	4.45	4.56	4.61
950	4.12	4.15	4.22	4.33	4.38
975	3.92	3.95	4.02	4.11	4.15
1000	3.72	3.76	3.82	3.91	3.95

D* - Devitrite

W* - Wollastonite

the volatilization of the soda. The glasses were melted in platinum, fined, air-cooled, ground in an agate mortar, and remelted. The resulting glasses were removed from the platinum crucibles and broken into fragments. Crystal growth measurements were made by two methods:

Method A. One-quarter inch samples of the glasses were placed on a flat piece of platinum-rhodium foil and heated in a Glo-Bar furnace at various temperatures for varying lengths of time. A chromel-alumel thermocouple was placed near the center of the sample holder.

The devitrified samples were sectioned for crystal length measurements. Devitrification practically always began at the edges with the crystals projecting inward, and the thickness of this devitrified zone was used as a measurement of the maximum crystal length.

Method B. For measurement of the rate of crystal growth near the liquidus and for measurement of the rate of solution of the crystals at temperatures above the liquidus, it was necessary to change the procedure. Samples of glass weighing approximately 0.04 grams were placed in platinum-rhodium holders similar to the one shown in Fig. 1.

This sample holder consisted of a small cup with a hole drilled in the bottom so that the sample could be examined by transmitted light. This holder was placed on the end of the Alundum thermocouple tube and held there by a platinum-rhodium sleeve which was so bent that a twist of the sleeve secured the

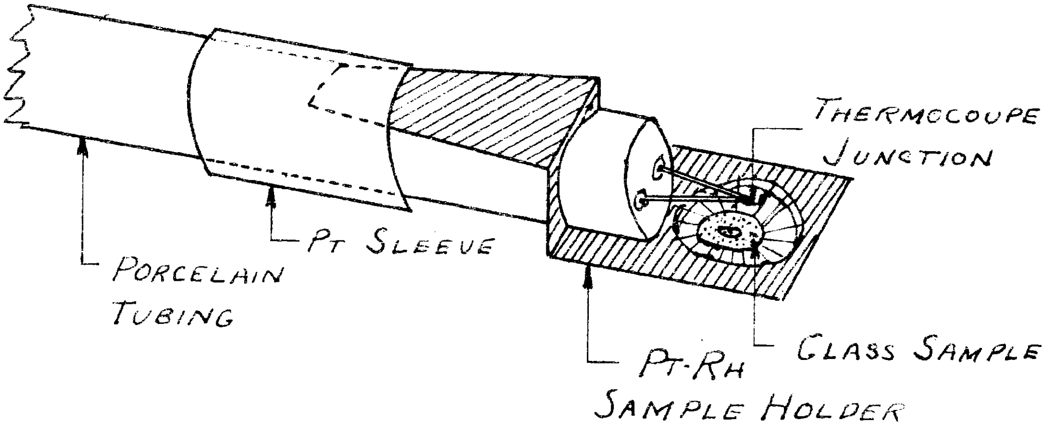


Fig. 1. Sample Holder Used for Study of Crystallization Rate

holder firmly in place. The platinum-platinum rhodium thermocouple was bent slightly so that the junction was as close as possible to the surface of the sample without touching it.

The glass was heated at approximately fifty degrees above the liquidus temperature in a platinum-wound gradient furnace to enable the sample to assume the shape of the holder. The sample was then moved so that its temperature was approximately thirty degrees below the liquidus temperature and crystals were allowed to form. The sample was then removed from the furnace, placed on a microscope stage, and the lengths of the crystals were measured, using transmitted light. Sketches were made of the crystals so that they could be relocated.

The sample was then placed in the cold end of the furnace, preheated for approximately one-half hour as the furnace was regaining thermal equilibrium, and slid into the hot zone. A type

K Leeds and Northrup potentiometer was used for the temperature measurements. By varying the position of the sample in the furnace and watching the deflections of the galvanometer, the temperature of the thermocouple was maintained within a degree or less of the desired temperature.

After a predetermined length of time, from two to sixty minutes, the sample was quickly removed and air-cooled. The crystal lengths were remeasured and the increase or decrease in size noted.

3. Results

In the base glass of this series, devitrite was found to be the primary phase (see Fig. 2). With the addition of 2% alumina, this was still the case (see Fig. 3). In the glass containing 4% alumina, wollastonite was the primary phase with devitrite crystals appearing at a lower temperature (see Figs. 4 and 5). The glass with 6% alumina also had wollastonite as the primary phase and devitrite as the secondary phase (see Fig. 6 and 7), while the glass with 8% alumina had wollastonite as the primary phase and cristobalite as the secondary phase (see Figs. 8, 9, and 10). The identification of the primary phases agreed with the work of Silverman.[38]

The effect of varying the time of devitrification on the lengths of crystals grown in glasses of varying alumina content is shown in Fig. 11; the changes in length with time at different temperatures is shown in Fig. 12. The slopes of these curves

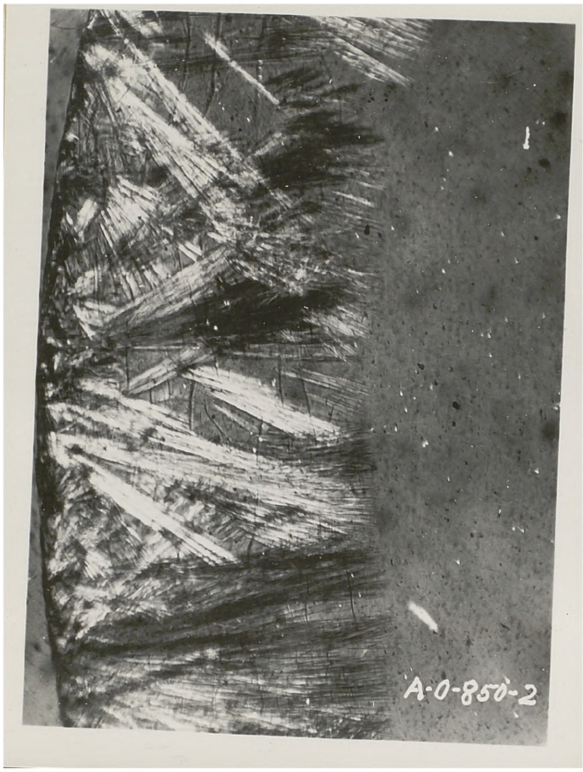


Fig. 2. Devitrite crystals in soda-lime glass with no alumina. Held at 850°C for 2 hours.
Crossed Nicols 75X

Fig. 3. Devitrite crystals in soda-lime glass with 2% alumina. Held at 1000°C for 4 hours.
Crossed Nicols 75X

Fig. 4. Devitrite crystals in soda-lime glass with 4% alumina. Heated at 900°C for 4 hours.
Uncrossed Nicols 75X

Fig. 5. Devitrite crystals inside and wollastonite crystals along edge of soda-lime glass with 4% alumina. Heated 2 hours at 1000°C.
Parallel Nicols 75X

Fig. 6. Devitrite crystals in soda-lime glass with 6% alumina. Heated 4 hours at 900°C.
Crossed Nicols. 75X

Fig. 7. Principally wollastonite and some devitrite in a soda-lime glass with 6% alumina. Heated 2 hours at 1000°C.
Parallel Nicols 75X

Fig. 8. Cristobalite crystals in soda-lime glass with 8% alumina. Heated 8 hours at 850°C. Trace of wollastonite along the edge.
Parallel Nicols 75X

Fig. 9. Cristobalite and wollastonite crystals in soda-lime glass with 8% alumina. Heated 4 hours at 900°C.
Crossed Nicols 75X

Fig. 10. Wollastonite crystals in soda-lime glass with 8% alumina. Heated 2 hours at 1000°C.
Parallel Nicols 75X

represent the gain in length per unit time or the rate of linear crystal growth.

The effect of temperature on the rate of crystal growth and rate of crystal solution in glasses with varying alumina content is shown in Fig. 13. The magnitude of the maximum rate of crystal growth, the temperature of maximum crystal growth, the liquidus temperature, and the nature of the phases precipitating are changed with the replacement of silica with alumina in these glasses.

Fig. 11

EFFECT OF ALUMINA ON CRYSTALLIZATION RATE OF SOME SODA-LIME GLASSES AT 850°C

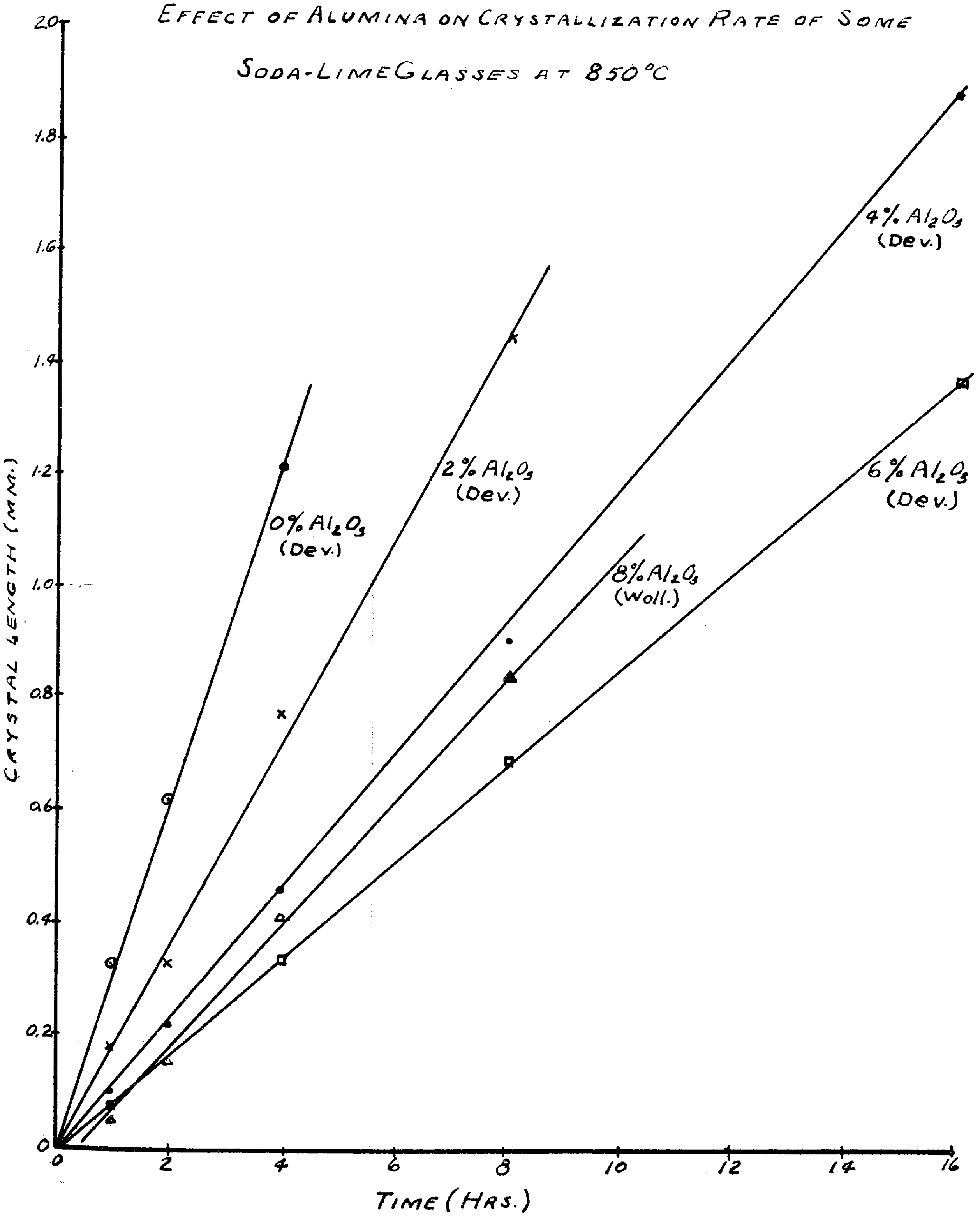


Fig. 12

EFFECT OF TEMPERATURE ON THE CRYSTALLIZATION OF DEVITRITE FROM A SODA-LIME GLASS WITH 4% Al_2O_3

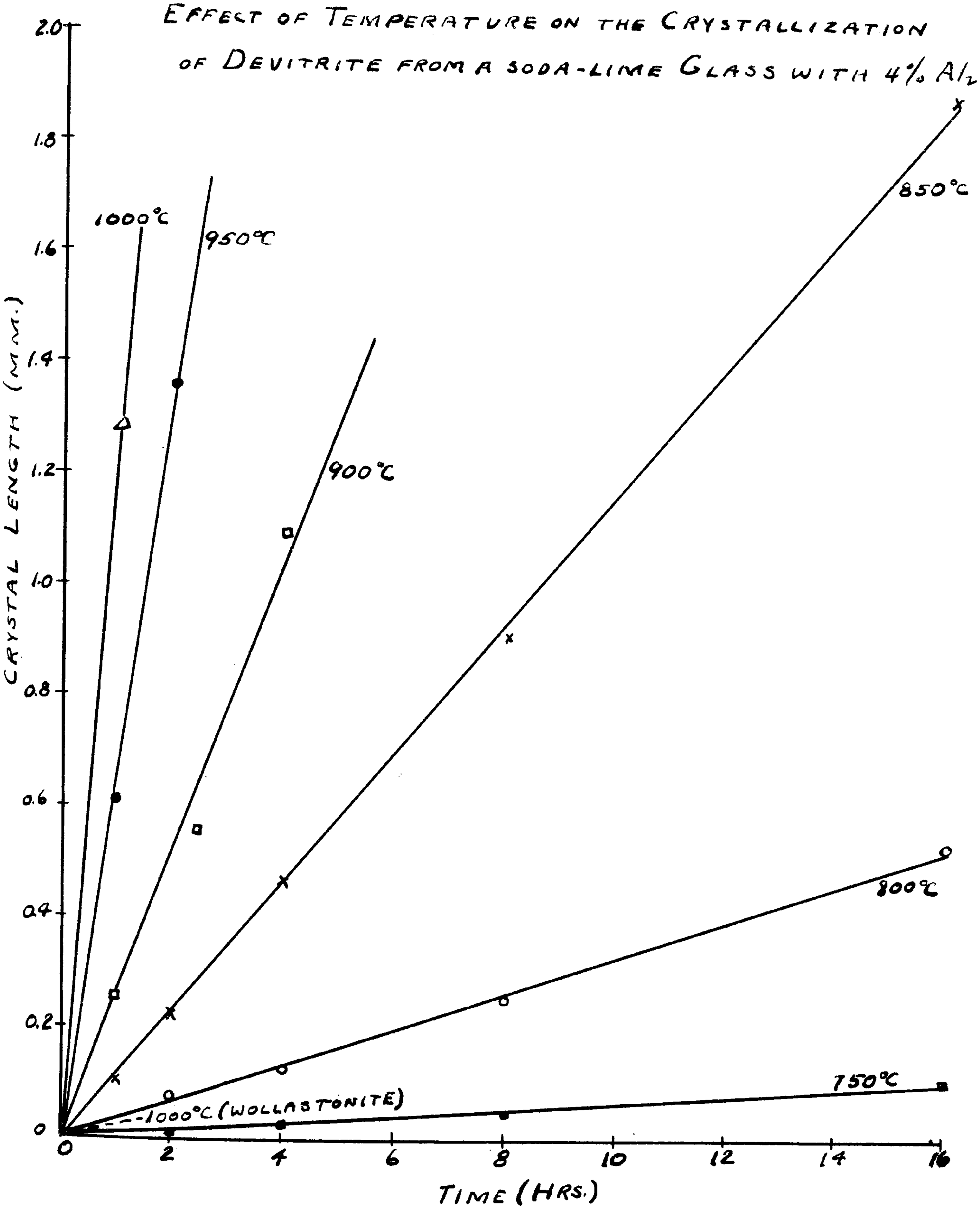
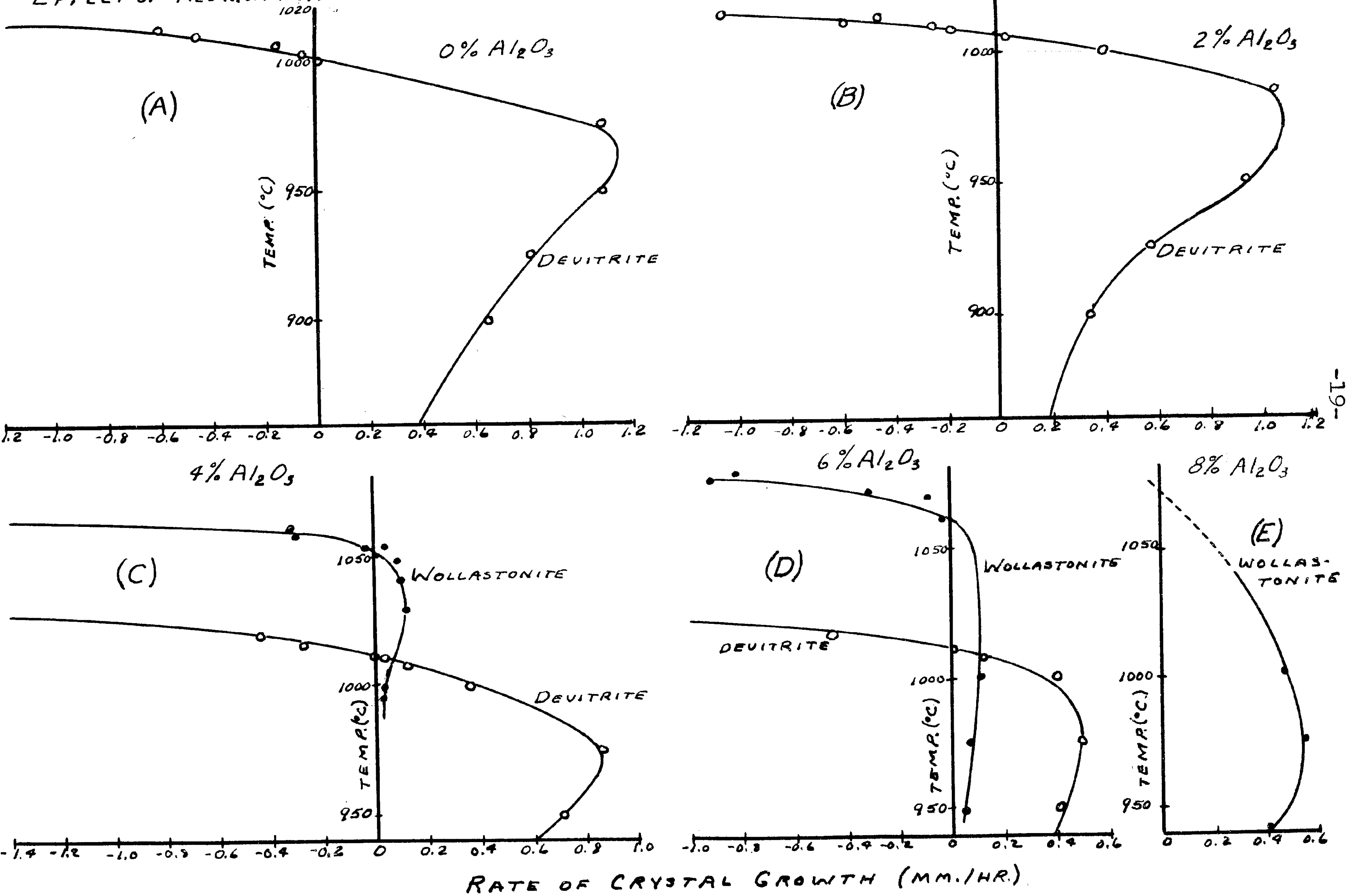


Fig. 13

EFFECT OF ALUMINA ON THE RATE OF CRYSTAL GROWTH AND SOLUTION RATE AT VARIOUS TEMP.'S



B. Effect of Magnesia on the Rate of Crystal Growth

1. Introduction

The effect of replacing lime with magnesia on the liquidus temperature of some soda-lime-silica glasses has been reported,[41,42] but with the exception of a brief note by Dietzel,[43] no definite data concerning the effect on the rate of growth are available. Dietzel indicated that the liquidus temperature and crystallization rate are lowered progressively with the replacement of lime with magnesia but offered no data.

It was the purpose of this phase of the investigation to determine the effect of replacing lime with magnesia on the rate of crystal growth of a series of soda-lime-silica glasses of known viscosity.

2. Procedure

The glasses used were furnished by the General Research Laboratory of the Owens-Illinois Glass Company. The compositions, liquidus, and viscosity-temperature data, shown in Table II, were published by the same laboratory.[42] The empirical equations for the viscosities, as indicated in Table II, were determined to facilitate interpolation.

3. Results

In the glass with no magnesia, cristobalite crystals occurred as the primary phase with devitrite crystals appearing at lower temperatures (see Fig. 14). The same phases appeared in the glasses with two and four percent magnesia replacing the lime (see

Table II

Effect of Replacing Lime by Magnesia on Some Physical Properties of Soda-Lime Glasses Used for Rate of Crystal Growth Measurements[42]

Glass No.	M-0	M-2	M-4	M-6	M-8	M-10
Composition						
SiO_2	73.5	73.7	73.9	73.7	73.3	73.5
Al_2O_3	0.3	0.2	0.2	0.2	0.2	0.2
CaO	10.0	8.1	6.1	4.1	2.4	0.3
MgO	0.2	2.0	4.0	6.0	8.0	9.9
Na_2O	15.8	15.7	15.6	15.7	15.8	15.9
Primary Phase	T*	T*	T*	T*	D*	B*
Liquidus (°C)	1004	996	968	921	910	1029

Viscosity-Temperature Relation

Log Viscosity						
7.65	707°C	705°C	704°C	710°C	721°C	738°C
7.00	741	741	738	746	757	774
6.00	802	804	804	816	821	843
5.00	882	891	891	907	907	932
4.00	993	1007	1010	1029	1029	1057
3.00	1152	1177	1182	1207	1213	1235
2.00	1399	1441	1457	1488	1527	1521

Constants in Empirical Equation: $\log n + \frac{a}{(°C-b)} - c$

a	3920	4000	4170	4460	3330	4420
b	280	260	238	224	318	256
c	1.51	1.35	1.37	1.54	0.66	1.52

T* - Tridymite
D* - Devitrite
B* - $Na_2O \cdot 2MgO \cdot 6SiO_2$

Fig. 14. Devitrite crystals in soda-lime glass with no magnesia. Heated 3 hours at 900°C. Trace of cristobalite also present.
Crossed Nicols 75X

Figs. 15 and 16). With the presence of six percent magnesia, diopside and devitrite were present with possibly some cristobalite (see Fig. 17). The glass having eight percent of the lime replaced with magnesia had diopside as the primary phase and a very faint trace of some crystals tentatively identified as devitrite as the secondary phase (see Fig. 18). The glass with ten percent magnesia had a sodium magnesium silicate ($Na_2O \cdot 2MgO \cdot 6SiO_2$) as the primary phase (see Fig. 19). The optical properties of this crystalline phase were checked with the data given by Botvinkin.[44]

The effect of replacing lime with magnesia on the rate of crystal formation at different temperatures is shown in Fig. 20. The liquidus temperature, temperature of maximum growth, rate of

Fig. 15. Devitrite crystals in soda-lime glass with 2% magnesia. Heated 3 hours at 900°C.
Crossed Nicols 75X

Fig. 16. Devitrite crystals in soda-lime glass with 4% magnesia. Heated 47 hours at 800°C.
Crossed Nicols 75X

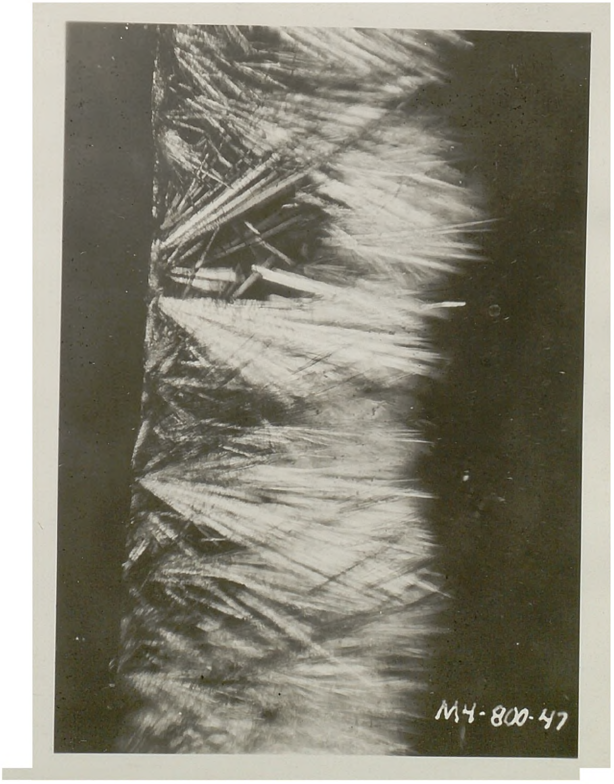


Fig. 17. Devitrite crystals with some diopside in soda-lime glass with 6% magnesia. Heated 40 hours at 860°C. Crossed Nicols 75X

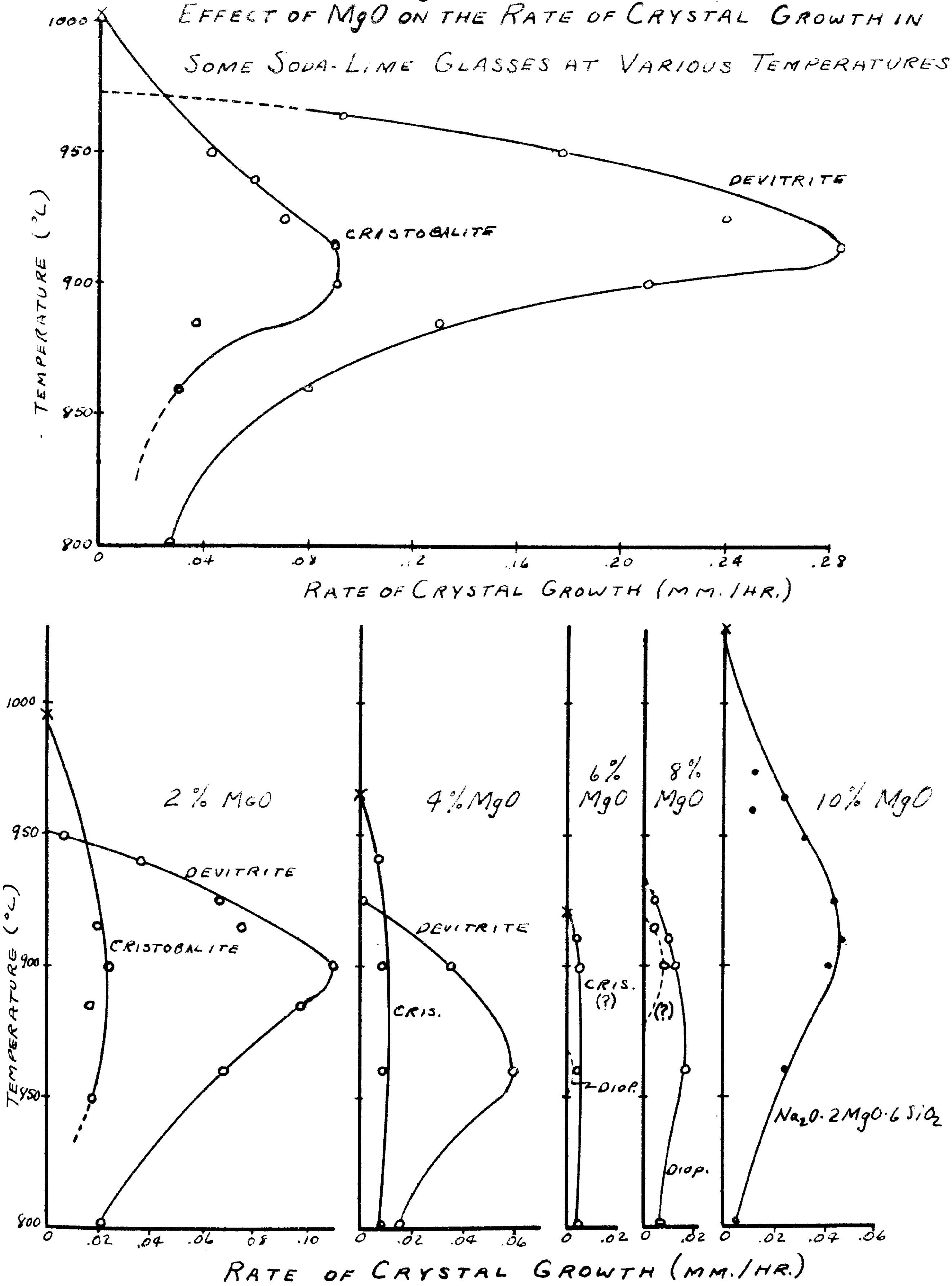
Fig. 18. Diopside crystals with devitrite (?) in soda-lime glass with 8% magnesia. Heated 16 hours at 900°C. Parallel Nicols 75X

Fig. 19. Crystals of $Na_2O \cdot 2MgO \cdot 6SiO_2$ in soda-lime glass with 10% magnesia. Heated 30 hours at 910°C.
Crossed Nicols 75X

maximum growth, and nature of the crystalline phases present are shifted with the substitution of magnesia for lime in these glasses.

Fig. 20

EFFECT OF MgO ON THE RATE OF CRYSTAL GROWTH IN SOME SODA-LIME GLASSES AT VARIOUS TEMPERATURES



C. Analysis of Data on Rate of Growth

1. Effect of viscosity and liquidus temperature

The preceding data indicate that changes in composition influenced the rate of growth considerably. These data may be explained qualitatively by considering the changes in the viscosity and liquidus temperature of these glasses.

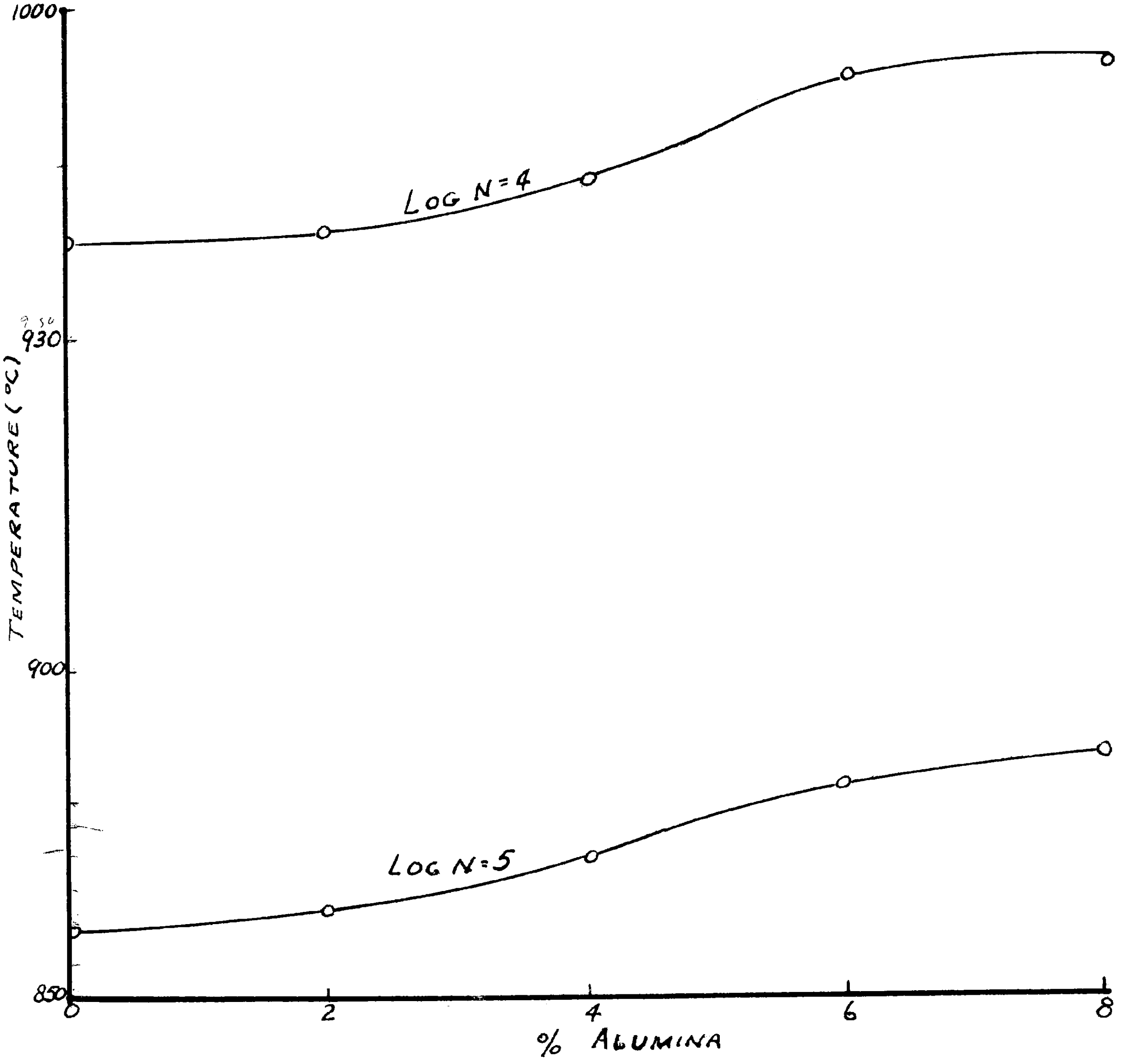
An increase in viscosity should decrease the rate of crystal growth, all other factors remaining constant. If the liquidus temperature is decreased in a given series of glasses, the rate of crystal growth should not only be decreased by the lower temperature of crystallization with the accompanying increase in viscosity and decrease in reaction rate but also by a decrease in the amount of material available for crystallization, since the composition of the glass differs more widely from the composition of the precipitating phase.

The replacement of silica with alumina in the soda-lime-silica glass studied gradually increases the viscosity, as is shown in Fig. 21. The temperature at which devitrite is in equilibrium with the melt is very gradually elevated as alumina is added, while the wollastonite liquidus is more rapidly elevated with the addition of alumina, as shown in Fig. 22.

The very slight increase of the devitrite liquidus should tend to increase the rate of crystal growth slightly, while the increased viscosity should lower the growth rate of devitrite substantially. The observed maximum rate of growth, as shown in Fig. 23, indicates that the viscosity played a dominant role in de-

Fig. 21

Effect of Al_2O_3 Substitution for SiO_2 on Viscosity of a Soda-Lime Glass*



* Data obtained through the courtesy of Owens-Illinois Glass Co.

Fig. 22

EFFECT OF ALUMINA ON THE LIQUIOUS TEMPERATURE FOR A SERIES OF SODA-LIME GLASSES

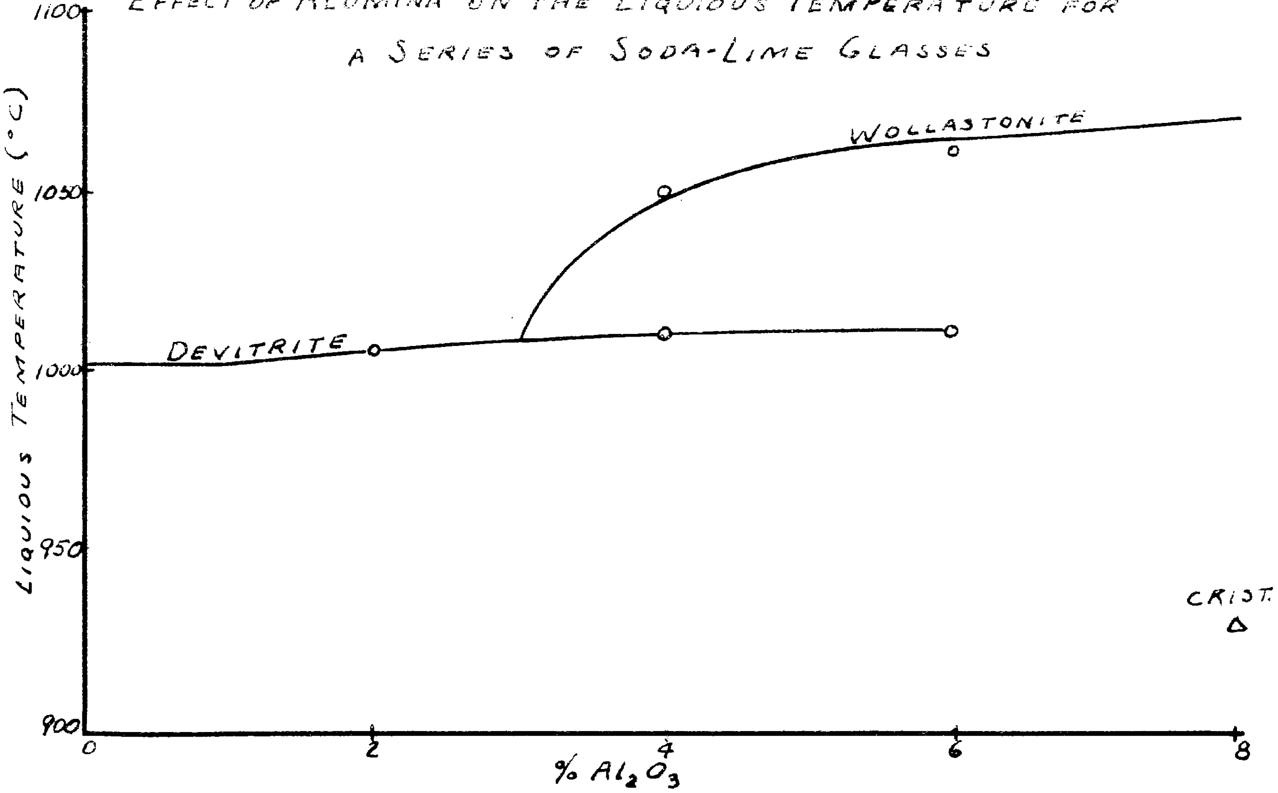
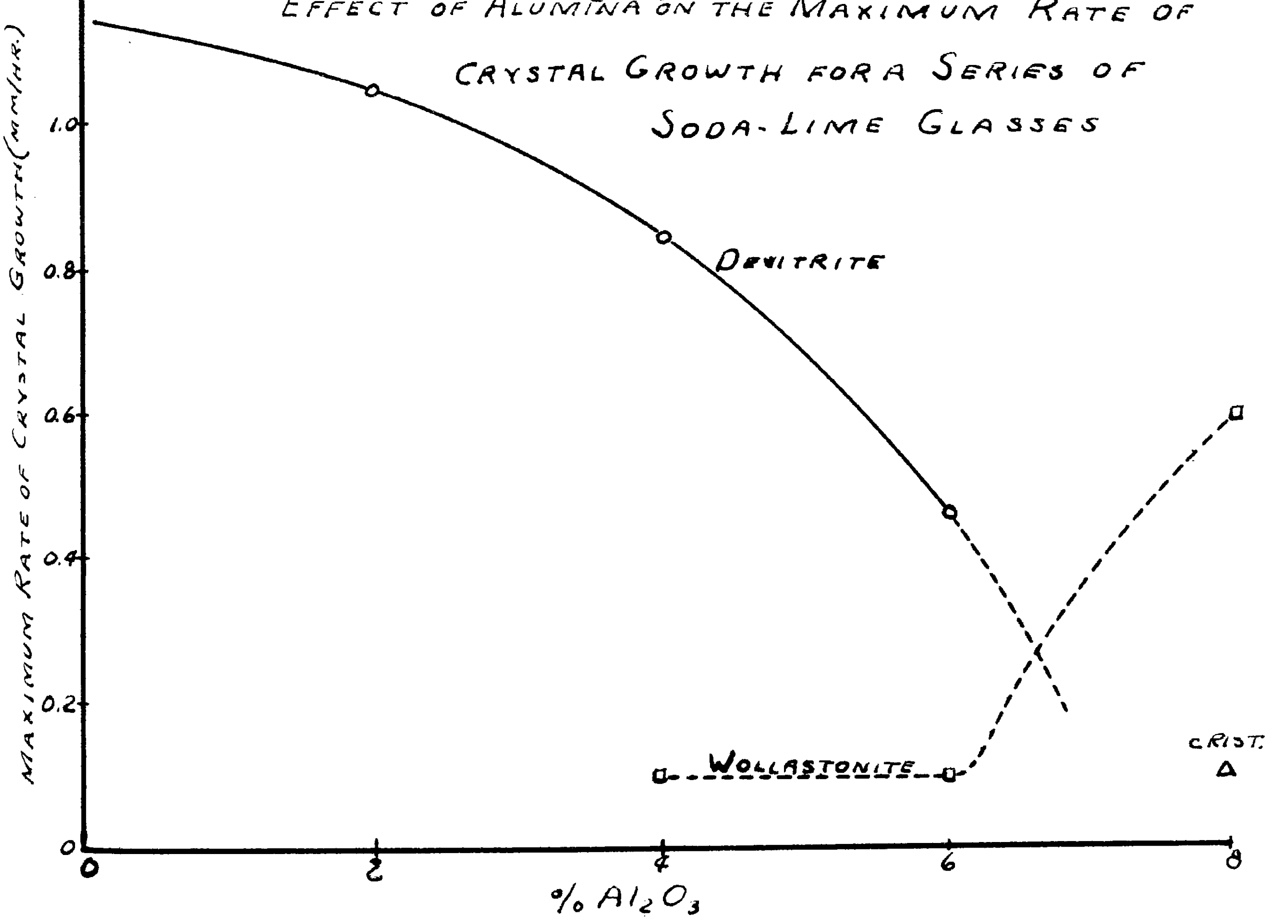


Fig. 23

EFFECT OF ALUMINA ON THE MAXIMUM RATE OF CRYSTAL GROWTH FOR A SERIES OF SODA-LIME GLASSES



creasing the rate.

It would be expected that the rate of wollastonite growth should be increased as alumina is added, since the liquidus temperature is elevated. The data obtained indicate that the increased viscosity was effective in stopping this rise up to a certain point, after which it was less effective (compare maximum rates of growth of wollastonite with four, six, and eight percent alumina in Fig. 23).

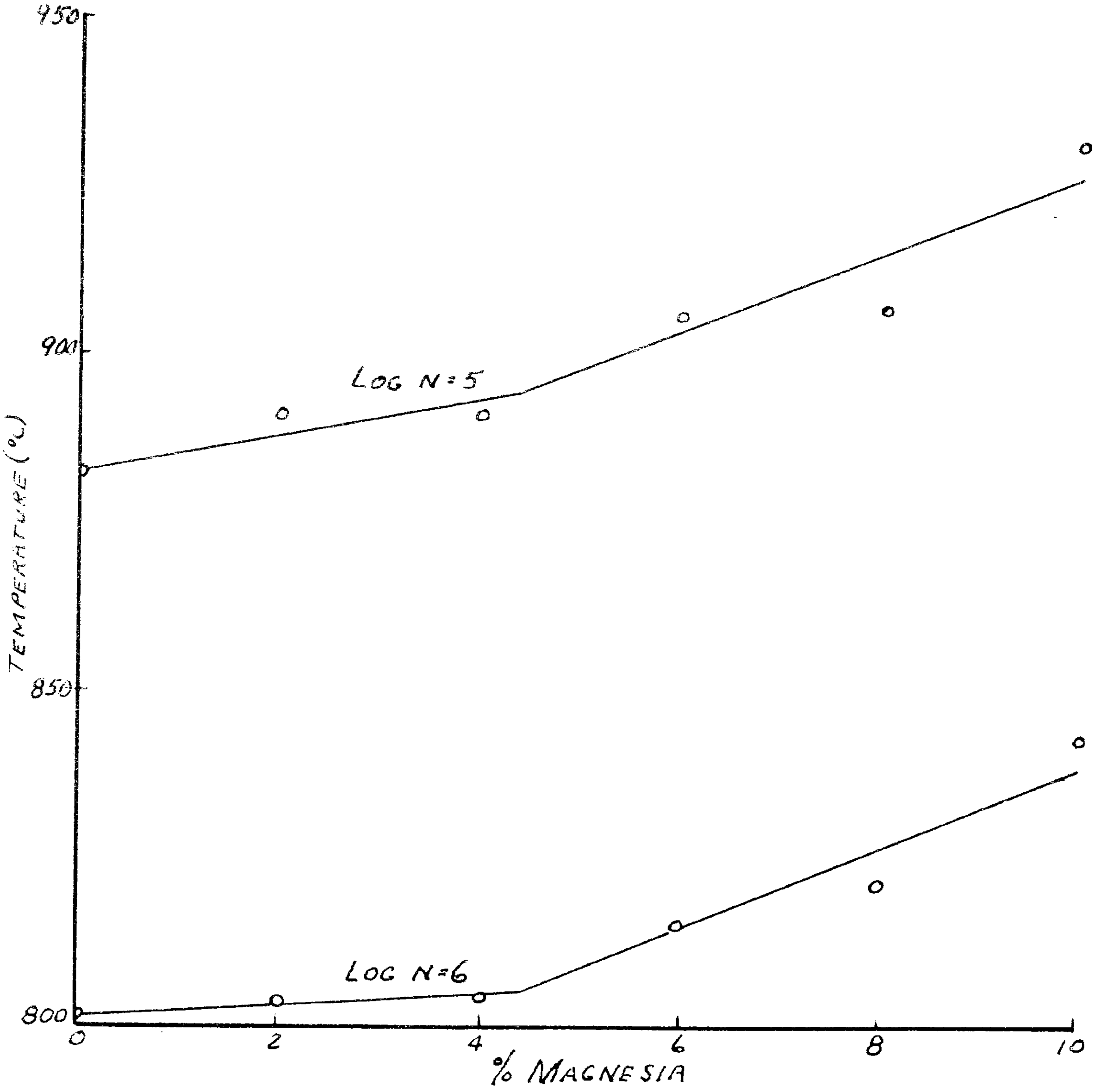
The replacement of lime with magnesia in the soda-lime-silica glasses increased the viscosity (see Fig. 24). The cristobalite liquidus and the temperature at which devitrite was in equilibrium with the melt were decreased progressively with the addition of magnesia, while the diopside liquidus was increased.

It would be expected that the increase in viscosity and decrease in liquidus temperature should both act towards decreasing the rate of growth of devitrite and cristobalite in these glasses. The very rapid decrease in rate of growth with the addition of magnesia is shown in Fig. 25.

The increased rate of growth of diopside with the replacement of lime with magnesia is explained similarly to the increased rate of growth of wollastonite with alumina in the preceding series. Evidently the increased viscosity is not sufficiently effective in decreasing the rate as the effects of increased liquidus temperature are in increasing the rate, and the rate is therefore increased with additions of magnesia.

Fig. 24

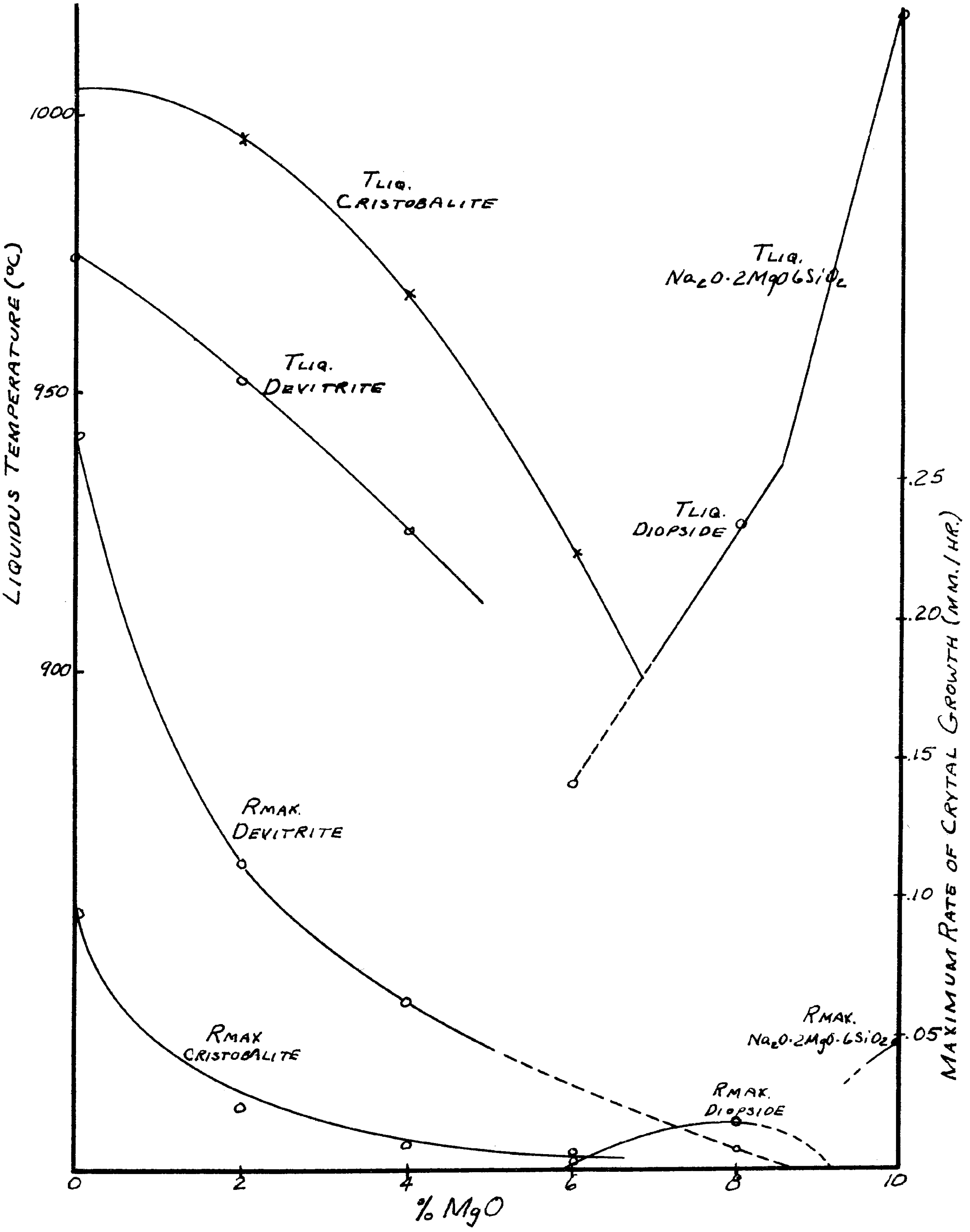
EFFECT OF MgO SUBSTITIONS FOR CaO ON VISCOSITY OF A SODA-LIME GLASS *



* BY OWENS-ILLINOIS GLASS COMPANY GENERAL RESEARCH LABORATORY

Fig. 25

EFFECT OF REPLACING LIME WITH MAGNESIA ON THE LIQUIDUS TEMPERATURE AND MAXIMUM RATE OF CRYSTAL GROWTH OF A SERIES OF SODA-LIME GLASSES



2. Effect of viscosity

There have been numerous attempts in the past to correlate viscosity with the rate of crystal growth.[45] Most of these data apply to the rate of crystal growth below the maximum, although Preston[46] offers an empirical relation that has some theoretical significance and gives the approximate shape of the rate-temperature curve.

It is possible to plot rate of growth against the logarithm of the viscosity as well as against the temperature, if the viscosity-temperature relation is known for the particular glass. Such a plot merely shifts the units of the ordinate in a regular manner. Since the logarithm of the viscosity is approximately a function of the reciprocal of the absolute temperature, the shift of the ordinate is not linear. Such curves reflect the dependence of the viscosity upon temperature.

The effect of viscosity on the rate of crystal growth and solution in some soda-lime-silica glasses varying in alumina content is shown in Fig. 26. The effect of viscosity on the rate of growth of cristobalite and devitrite in the soda-lime-silica glasses varying in magnesia content is shown in Figs. 27 and 28.

The fact that the maximum rates of growth, in Fig. 26, occur at approximately constant viscosity implies that the logarithm of the viscosity is increasing at about the same rate as the temperature of maximum crystal growth, in this particular series. If the viscosity is increasing more rapidly, the maxima are shifted as is shown in Figs. 27 and 28. The data have little

Fig. 26

VISCOSITY-CRYSTALLIZATION RATE RELATIONSHIP FOR A SERIES OF GLASSES VARYING IN ALUMINA CONTENT

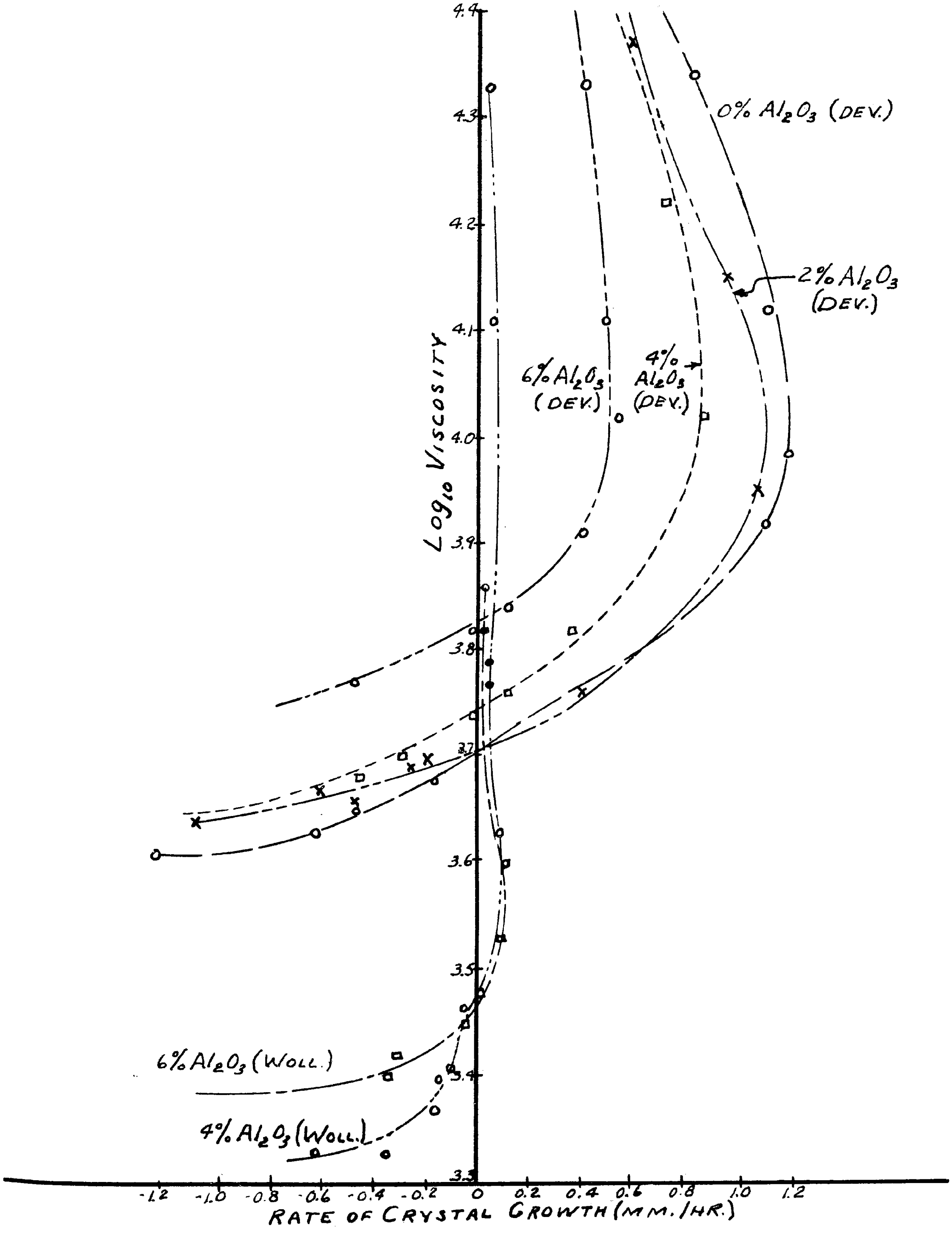


Fig. 27

EFFECT OF VISCOSITY ON THE LINEAR RATE OF GROWTH OF CRISTOBALITE IN SOME SODA-LIME GLASSES VARYING IN MAGNESIA CONTENT

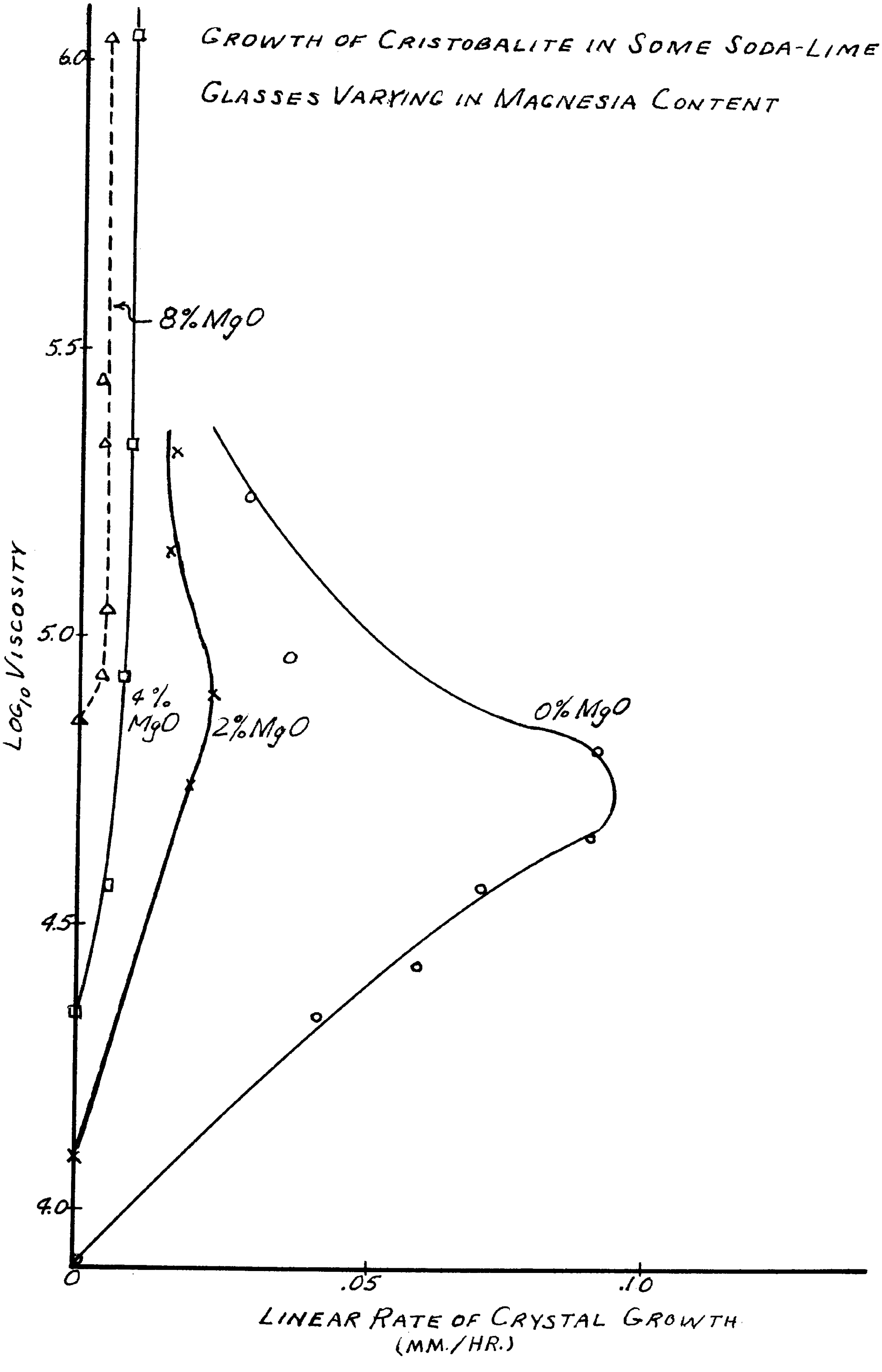
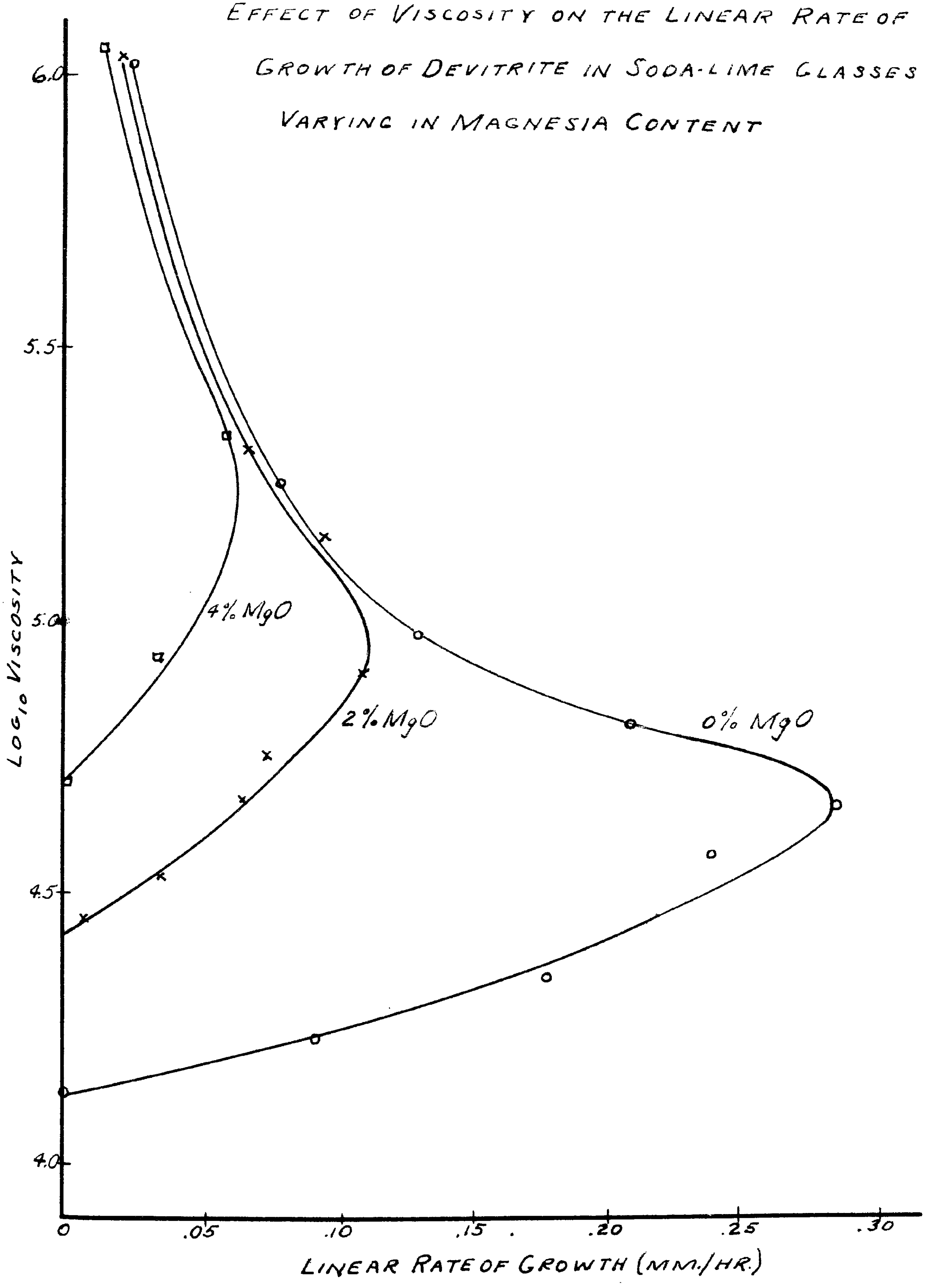


Fig. 28

EFFECT OF VISCOSITY ON THE LINEAR RATE OF GROWTH OF DEVITRITE IN SODA-LIME GLASSES VARYING IN MAGNESIA CONTENT



theoretical significance when considered alone, since other factors influencing crystal growth are neglected.

D. Analysis of Rate of Solution Data

The data indicate that the rate of growth-temperature curve is continuous with the rate of solution-temperature curve, if solution is considered to be negative growth. Tammann[29] indicated that such a relation would be expected, as shown in Fig. 29, but there has been no previous verification of such a relation.

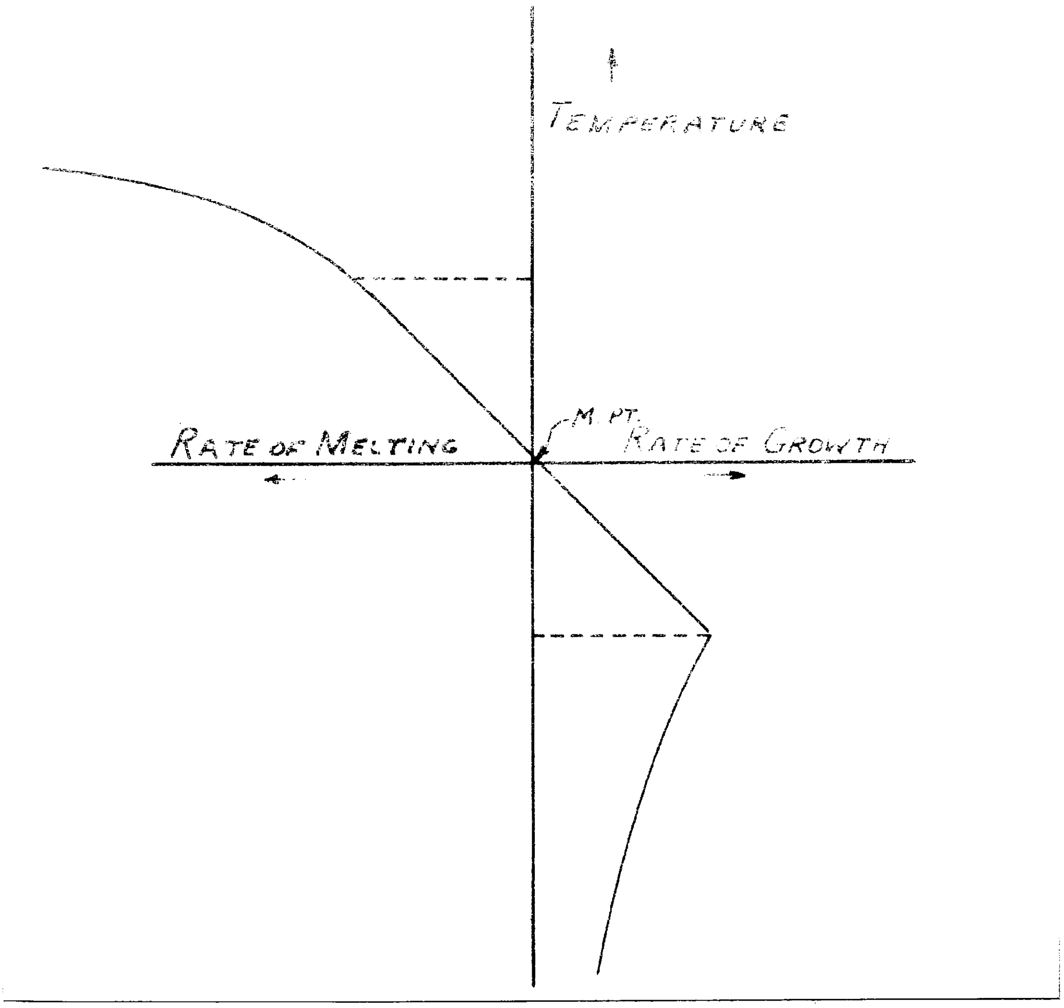


Fig. 29. Effect of Temperature on Rate of Growth and Rate of Solution of Crystals According to Tammann.

The effect of increasing the temperature above the liquidus on the rate of solution of devitrite and wollastonite in glasses of variable alumina content is shown in Fig. 30. The curves have the same general shape, although the slopes at the origin are influenced by the variation in alumina content.

The observed rates of solution were not linear with time but decreased as solution progressed. The reported rate was generally the rate of solution as about 20% of the crystal dissolved. When the solution was carried further, especially in the high alumina glasses, the rate of solution decreased with time.

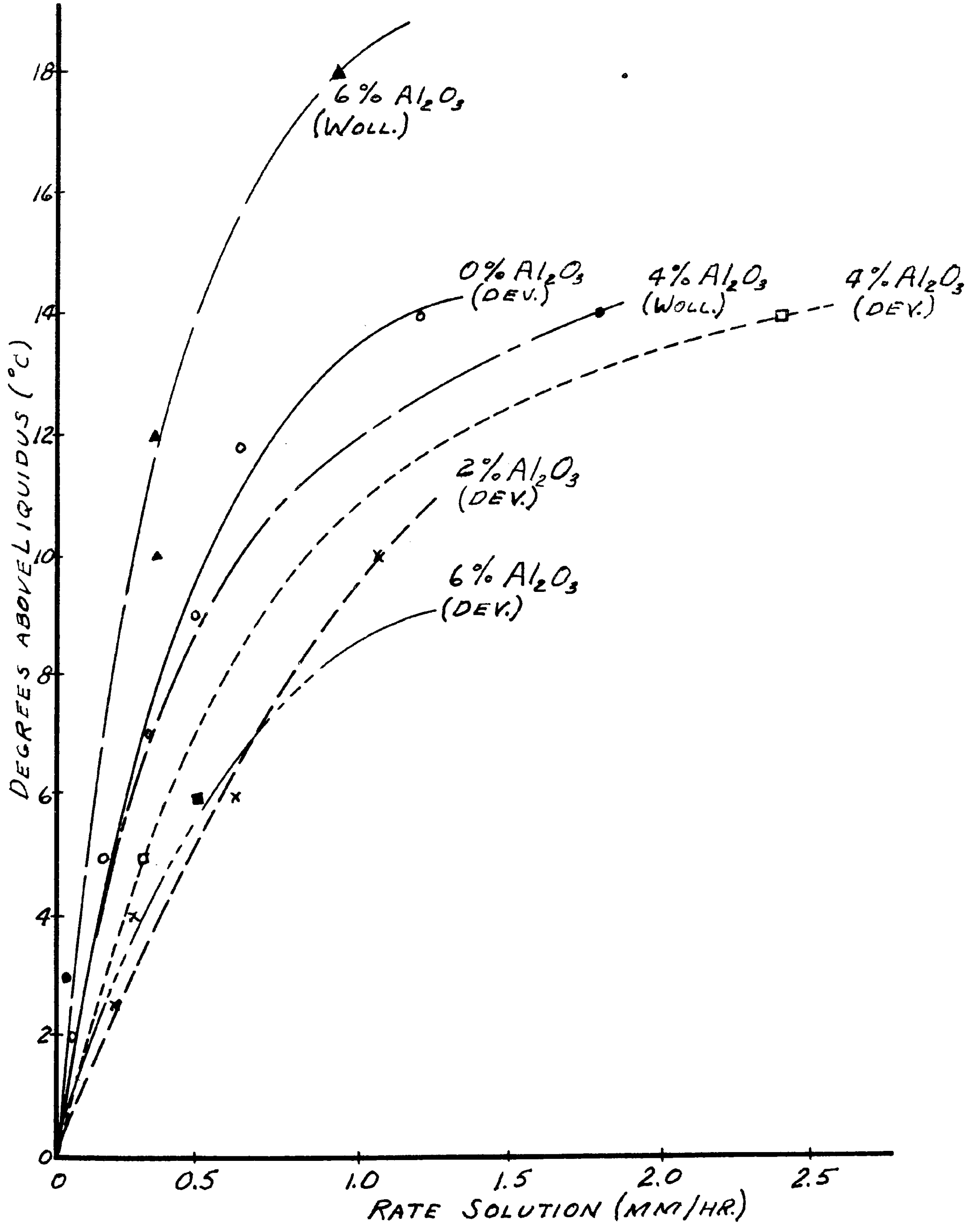
The analysis of the rate of solution data is complicated by a lack of knowledge concerning the factors which influence the solution rate and their relative importance. Undoubtedly the temperature and viscosity of the glass are of primary importance. The degree of saturation, the specific surface present, the crystal structure, the presence of local currents, and the gradient in composition of the glass from the crystal phase to the original glass must be considered.[47]

The increased rate of devitrite solution with the increase in alumina content may be due to the greater temperature of the liquidus which increases the reaction rate and offsets the greater viscosity. The decreased rate of wollastonite solution as alumina is increased may be due to the increased viscosity which offsets the effects caused by higher liquidus temperatures.

The data may have some commercial significance. It has been indicated that in a glass tank the temperature of the bottom

Fig. 30

THE INFLUENCE OF THE DEGREE OF SUPER-HEATING ON THE SOLUTION RATES OF DEVITRITE AND WOLLASTONITE IN SODA-LIME GLASSES VARYING IN ALUMINA



is far below the surface temperature and, in some cases, may be below the liquidus temperature of the glass. An extrapolation of the rate of solution data up to melting temperatures of the glass indicates that the rate is sufficiently high so that large crystals would dissolve in a very short time (one centimeter long crystals dissolve in approximately ten minutes at 1400°C).

IV. A STUDY OF SURFACE DEVITRIFICATION OF GLASSES

A. Introduction

It has been noted that devitrification almost invariably begins at the surface of glass. Brockbank[49] described devitrification as a surface phenomenon in 1913; Tabata[50] studied surface devitrification to a certain extent; Dietzel, Zschimmer, and Mullensiefen[33, 34] observed surface devitrification invariably; and in the preceding section, crystallization began on the surface with all samples.

Tabata[50] claims that surface devitrification is due to surface contraction caused by the surface tension of the glass; Sollner[51] claims that it is due to molecular orientation; Jackson[52] points out the importance of water vapor as does Germann.[53] Morey[54] claims that during the course of many experiments on devitrification, no case of surface crystallization was observed. Morey further states that surface devitrification, as is usually experienced, may be due to the inhomogeneity of the surface of the glass, loss of alkali or boric oxide, or to the fact that the surface first reaches the optimum temperature of crystallization.

It was the purpose of this phase of the investigation to study some of the factors influencing surface crystallization in order that the phenomenon may be more completely understood.

B. Procedure and Results

1. Influence of heating rate of surface

Two pieces of plate glass (approximately 2x2x.6 cm.) were

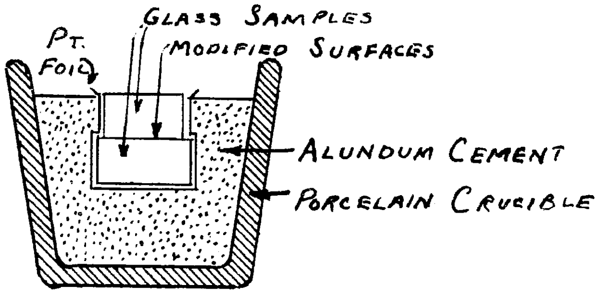


Fig. 31. Assembly Used in Studying Influence of Heating Rate of Surface on Surface Devitrification.

placed in contact, wrapped in platinum foil, and imbedded in Alundum cement as is shown in Fig. 31. The samples were placed in an electric furnace, and heated to approximately 800°C for twelve hours to enable devitrification to take place. The resulting specimens were broken and sectioned.

Devitrification proceeded on the top surface, on the sides, and at the interface between the specimens. The zone of devitrification at the interface was approximately twice that of the top surface and the sides.

2. Effect of surface treatments

Small pieces of glass similar to the above were cut from a sheet of plate glass. Pairs of these specimens were given different surface treatments on one face of each as follows: ground; polished with rouge; polished with tin oxide; polished with pumice; polished with chromic oxide; polished with alumina; and polished with rouge and boiled in water. The modified surfaces of the pairs of samples were placed in contact; the samples were wrapped with platinum foil and imbedded in cement as before; and the crucibles were placed in an electric furnace where they were heated at 800°C for twelve hours.

The Alundum was removed from around the samples, the platinum foil was removed, the samples were broken, and the thickness of the devitrified zone measured.

All samples devitrified at the interface; the boiled samples had a slightly thicker zone than did similar samples which had just been ground; polishing the samples increased the thickness of the devitrified zone to a certain extent as compared with samples that had their surfaces ground; the use of different polishing agents produced little effect.

3. Influence of bubbles

Three samples of glass containing bubbles were obtained. One was taken from a piece of commercial plate glass; the second, from an experimental glass; the third was a sample of plate glass which was heated in an oxy-gas flame until it bubbled extensively. These samples were placed on platinum foil and heated at 750°C overnight. They were sectioned and the manner of crystal growth noted.

No crystals were found around the bubbles in the above samples although considerable crystal growth took place along the surfaces.

4. Influence of soda vapors

Two samples of plate glass, one with a freshly fractured surface, were placed in a crucible and devitrified at 800°C overnight in the presence of soda vapors (sodium carbonate near the samples). The samples were broken and the thickness of the devitrification zone measured.

Surface devitrification occurred in both samples to approximately the same degree.

5. Influence of cracks

A sample of plate glass was broken; the pieces were fitted together, wrapped in platinum foil, and imbedded in Alundum cement. A similar sample was cracked by a thermal shock treatment but the sample did not fall apart. The samples were wrapped and imbedded similarly to the above and heated at 800°C overnight.

Devitrification occurred at the interface between the two samples which were broken completely and reassembled. The sample which was not completely broken apart sealed together with little or no devitrification along the cracks.

6. Influence of temperature of devitrification

There are some indications that the temperature of devitrification may influence surface crystallization. In Part III, many samples of various glasses were devitrified at various temperatures, and it was noted that there was a greater tendency towards internal crystallization as the temperature was increased.

7. Removal of "surface layer"

Samples of plate glass were placed in contact, wrapped in platinum foil, and surrounded by Alundum cement as in Fig. 31. These were heated at 1100°C for 30, 60, and 120 minutes after which they were placed in a furnace at 800°C for twelve hours. The samples were then broken apart and the extent of devitrification at the interface determined visually.

The interface between the samples heated for 30 minutes at 1100°C was markedly devitrified; the samples that had been heated for 60 minutes had a slight zone of crystals at the interface; while the crystalline boundary was practically absent with samples that had been heated in contact for 120 minutes.

8. Residual "surface layer" in manufactured articles

Three pieces of glass were cut from commercial articles for studying possible inhomogeneities within the glass. The first was a section of a goblet which had obviously been formed by two steps with the bottom section joined to the top during the manufacturing process; the second was a small piece of capillary tubing; the third was a section of one inch glass tubing with a one-quarter inch hole which was probably hand-formed using at least two gathers of glass. These pieces were imbedded in flint and devitrified at 750°C for approximatly six hours. The pieces were then removed from the flint, sectioned, and polished.

The specimens are shown in Fig. 32. The goblet showed a zone of crystals at the interface where the two sections had been joined; the capillary tube had a very thick ring of crystals concentric with the outside devitrification layer (probably formed

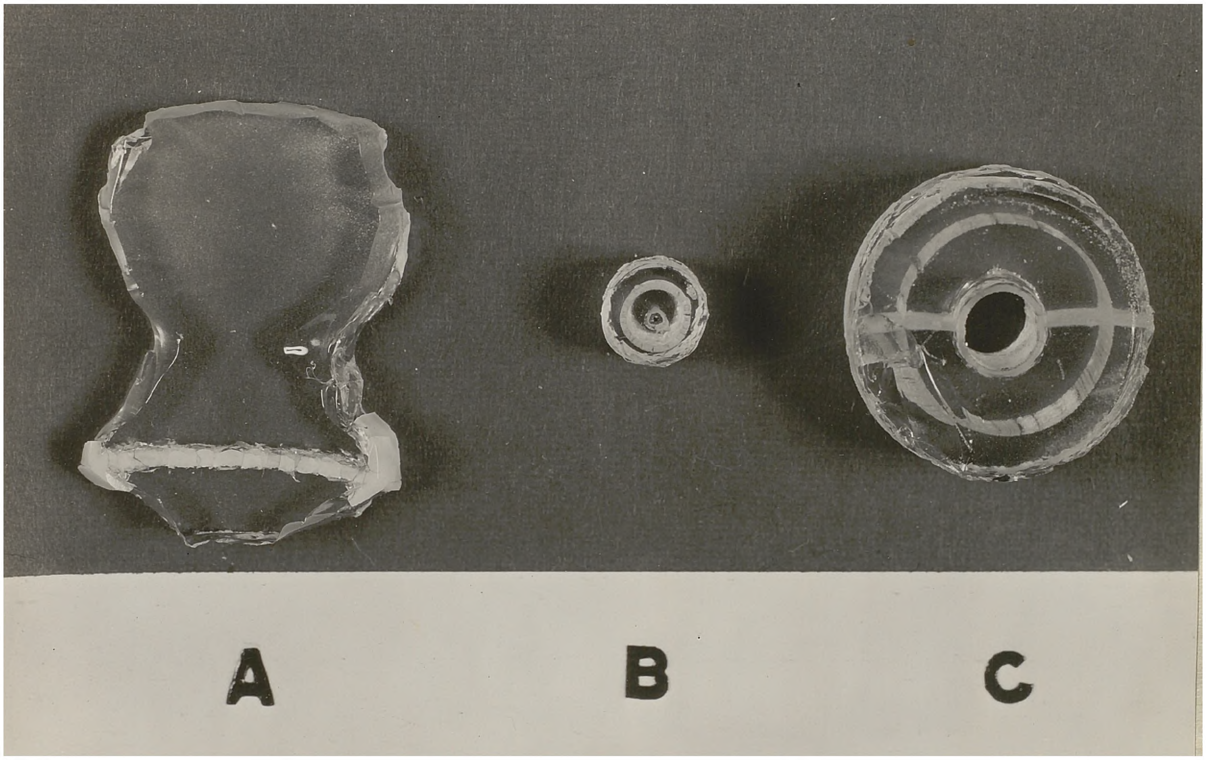


Fig. 32. Internal Devitrified Zones in Manufactured Articles

by two gathers); while the large tube showed a faint ring of devitrification down the center of the specimen as well as a plane of devitrification parallel to the axis of the tube. As other samples of this tubing did not show this plane of crystals after devitrification, it was assumed that this particular sample cracked during heating.

9. Effect of dust

To ascertain the effect of dust in the air on surface devitrification, the following experiments were made. A "Vycor" tube, sintered glass crucible, glass funnel, platinum foil, and sample of plate glass were cleaned with water, chromic acid, ethyl alcohol, and ether and were assembled as shown in Fig. 33.

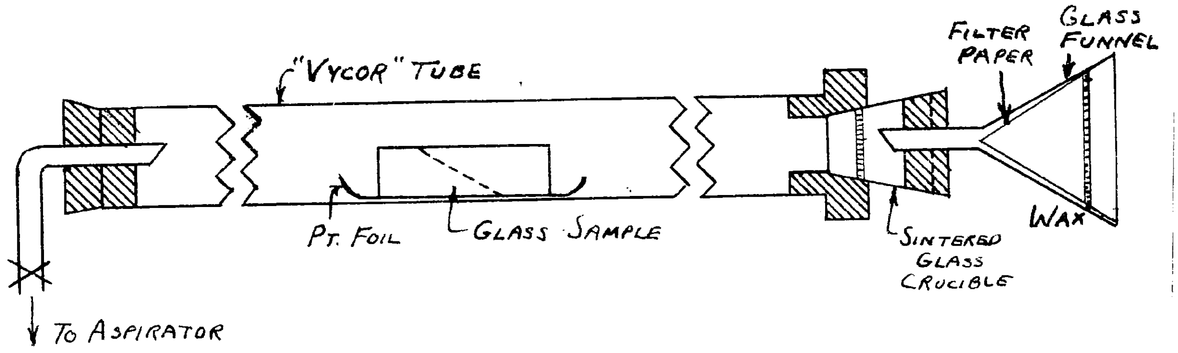


Fig. 33. Assembly Used in Measuring Effect of Dust

Air was drawn through the apparatus with the aspirator for three hours; the sample of glass was broken, while in the tube, by thermal shock; the broken surfaces were separated somewhat by shaking the assembly, and the tube was inserted in an electric furnace. The sample was heated at approximately 800°C for ten hours.

A similar experiment was conducted with two samples in the tube. Hydrochloric acid vapors were allowed to permeate over one sample after it was broken. The hydrochloric acid was then flushed with air and the other was broken. These were given the same heat treatment as before.

A third experiment was conducted as a check. Conditions were identical with the first test except that the filter was omitted.

When the air passing over the sample was filtered and every precaution was taken to reduce the amount of dust present, the freshly exposed surface of the sample showed very little devitrification as compared with the rest of the sample. This is shown in Fig. 34. The fresh surface, on the right side of the sample, had a few crystals arranged in spherulites but is almost clear while the original surface, the left side, shows a very thick white zone of crystals.

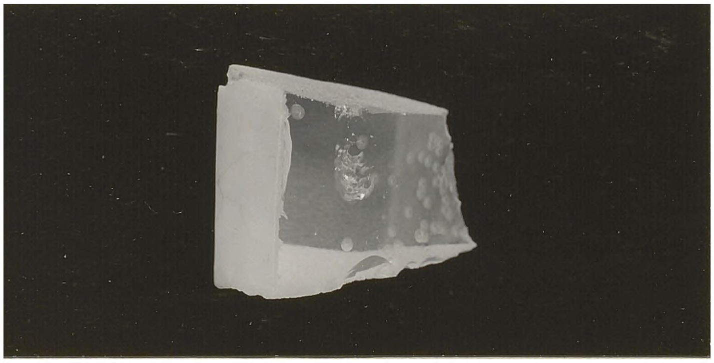


Fig. 34. Sample of glass which was devitrified in an atmosphere with reduced dust content.

The sample which was devitrified in an atmosphere which contained dust, when no filter was used, showed extensive devitrification even on the freshly exposed surfaces.

The sample which was exposed to acid vapors, but not to dust to any extent, devitrified appreciably more on the fresh surface than did a similar sample which had not been exposed to the acid vapors.

C. Analysis of Data Concerning Surface Devitrification

It was shown in the preceding section that polishing or boiling a piece of glass increases the surface devitrification; that devitrification will occur around cracks if they are opened to the air but not around cracks which have been unexposed to the air; that there is a greater tendency for internal devitrification at higher temperatures; that the "surface skin" can be removed by heating two glasses in contact for a prolonged period at elevated temperatures; that two pieces of glass which have been joined while working exhibit a slight discontinuity at their interface where devitrification will occur; and that dust and acid vapors in the air promote surface devitrification.

The experiments on the effect of heating rate on surface devitrification and on the loss of alkali from the surface were negative, but insufficient data were obtained to allow conclusions.

The theory that dust and other material in the air are largely responsible for the promotion of surface devitrification will explain several of the above experiments. The breaking of a piece of glass with a replacement of the parts exposes the fractured surfaces to dust and the surface devitrifies; while if the surfaces are not pulled apart and exposed to air, the surface does not devitrify. It would be expected that any dust layer would be removed by prolonged heating of two pieces of glass in contact at elevated temperatures and reduce the interfacial devitrification, as was confirmed. It would also be expected that surface devitrification, if caused by dust, would be reduced somewhat as the temperature of crystal growth is increased due to the solution of the dust. The collection of dust during the marvering operation in the manufacture of glass articles or on the surface of two pieces of glass prior to their being joined should also produce a discontinuity, if two gathers are taken, where devitrification would proceed.

Many of the above experiments could be explained by considering the loss of alkali from the surface or by the adsorption of water vapor on the surface. However, in the experiments where the amount of dust in the air was reduced with filters, loss of alkali and adsorption of water vapor could take place with both the samples which were exposed to dust and those which were not. However, it was found that the one devitrified extensively on the fresh surface while the other did not.

The word "dust" is used in a vague sense intentionally in the above discussion. It refers to the material floating in the air which is extremely difficult to remove from any surface. The action of dust in promoting surface devitrification is probably due to the establishment of nuclei, either through the formation of microscopic areas of more fluid glasses or as a corner-stone at which the building of the crystal begins.

It is not claimed that dust is the only factor which is capable of promoting surface devitrification, but its importance is emphasized.

V. OTHER EXPERIMENTS RELATING TO CRYSTAL GROWTH

During the course of this investigation, several exploratory experiments concerning crystal growth were made which were not completed since they were beyond the scope of this investigation. Some interesting information was obtained and the data are included.

A. A Note on Diffusion of Silicates

1. Purpose

It was the purpose of this phase of the investigation to explore possible methods of measuring diffusion rates of glasses of similar composition. Pask[55] measured the diffusion rate of metallic ions in glasses, and Bowen[56] studied the diffusion of diopside into a plagioclase at high temperatures, but information is lacking concerning the inter-diffusion of similar glasses.

2. Procedure

Two glasses were selected from the potash-lime-silica system which would not devitrify at 930°C, but would form, when inter-diffused, such a composition that crystals of $4K_2O \cdot CaO \cdot 10SiO_2$[32b, 32c] would be precipitated, the melting point of this compound being 946°C. The glasses had the following compositions:

Composition:	A (%)	B (%)
Potassium Oxide . . .	39.7	34.8
Calcium Oxide	8.0	4.0
Silicon Dioxide . . .	52.3	61.2

Batches were prepared from C.P. chemicals and the glasses were melted at about 1400°C in platinum. Slugs of each glass were formed in platinum-rhodium combustion boats. These slugs were removed from the boats, cut in halves, and the ends were ground so that when the half-slugs of A and B were placed in the same combustion boat, their ends were in close contact. The boat was placed in an electric furnace at 930°C and held there for 32 hours.

3. Results

Microscopic examination of the interface between the two glasses revealed that crystals were formed, which were presumed to be $4K_2O \cdot CaO \cdot 10SiO_2$. The crystals varied in length at different parts of the interface as is indicated in Fig. 35.

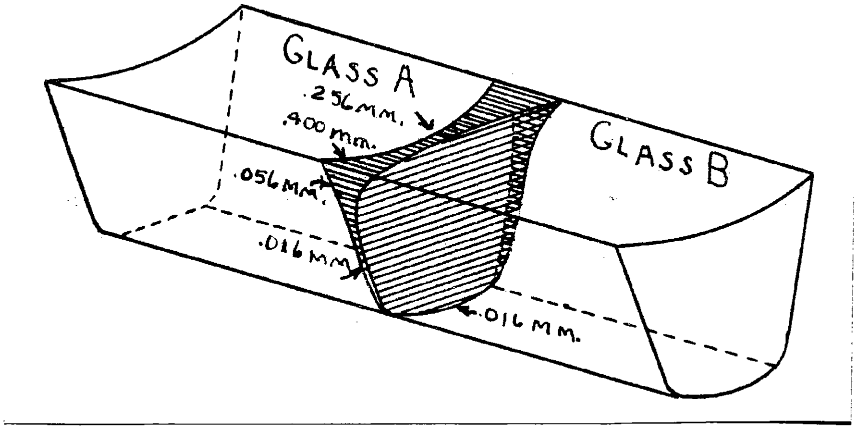


Fig. 35. Variation in Crystal Length at the Interface of the Diffused Glasses

4. Discussion of Results

The relatively small thickness of the crystalline zone was somewhat surprising. This may have been due to either the slow rate of duffusion at 930°C, or due to the action of the crystalline phase as a hindrance to further diffusion. The thicker portions of the crystalline layer at the surface and sides of the sample were probably due to improper fitting of the two slugs of glass with a certain amount of flow taking place.

The method is capable of further extension. Diffusion processes may be carried out at higher temperatures with a subsequent devitrification below the liquidus of the primary phase and above the liquidus of the diffusing glasses.

B. Influence of Minor Additions on Rate of Crystal Growth

1. Introduction

Little is known of the effect of minor constituents commonly present in commercial glasses on the rate of crystal growth in these glasses. It was the purpose of this phase of the investigation to make a preliminary survey of the effect of adding water, fluoride, arsenic oxide, sulphate, and sodium chloride to the batch.

2. Procedure

A soda-lime-silica glass composition was selected which precipitates devitrite as the primary phase (Glass A-0, Table I). The regular carbonate batch was made as well as batches containing 5% water, 0.4% sulphate, 0.5% fluoride, 0.1% arsenic oxide, and

0.05% of the soda added as sodium chloride. The six glasses were melted and broken into fragments for devitrification tests.

Fragments were placed on platinum foil and heated to 880°C for 1.7 hours. The samples were sectioned and the thickness of the devitrified zone measured.

3. Results

The devitrified zone of the glass containing water in the batch was 13% greater than that of the base glass; fluoride, 14% greater; sulfate, 5% greater; sodium chloride, 10% smaller; and arsenic trioxide, 8% smaller.

4. Discussion of Results

The changes in the amount of crystallization may have been due to changes in the affinity for the ions, molecules, or groups in the growing crystals; they may have been due to viscosity changes, or other factors. If it is assumed that the changes are due to viscosity and that the rate of crystal growth is a function of viscosity, the viscosities of the glasses can be approximated at this temperature.

The results of such assumptions show that water decreased the logarithm of the viscosity by 2%; fluorides decreased it by 2.5%; sulfate decreased it by .4%; while sodium chloride and arsenic trioxide increased it by 1.7%.

Some of the above data are confirmed by experiments. The General Research Laboratory of the Owens-Illinois Glass Company report that fluoride will decrease the viscosity.[57] An interpolation of their data indicate that 0.5% fluoride would decrease the logarithm of the viscosity about 1.8%. A. E. J. Vickers' data[58] on the effect of atmosphere on the viscosity of a simple soda-silica glass indicate that water vapor over the surface would decrease the logarithm of the viscosity at 1000°C by 4.1% and sulphur dioxide over the glass would decrease the logarithm of the viscosity at 1000°C by 6.2%.

The decrease in rate of crystal growth with the addition of arsenic may be due to a change in the viscosity of the glass, if arsenic acts similarly to alumina; it may be due to preferential adsorption on the crystal; or other factors.

The decrease in the rate of crystal growth with the addition of chloride may be due to an increase in viscosity, although no data are available on the subject; the change may have been brought about by a loss of alkali due to volatilization of sodium chloride with a subsequent decrease in rate of growth, or through other factors.

C. Effect of Oscillating Temperature on Crystal Development

1. Purpose

It was reasoned that if the temperature of a glass was oscillated between the temperature of maximum growth velocity and the temperature of maximum rate of nucleation, that a maximum number of large crystals would be formed; and if an oscillation of the temperature were made between the maximum rate of growth temperature and some point slightly above the liquidus, that a few large crystals would be formed.

It was the purpose of this phase of the investigation to find the effect of oscillating the temperature of crystallization on the particle size distribution of the crystalline phase.

2. Procedure

A platinum-wound resistance furnace was used in these experiments. A constant voltage transformer in the line kept the temperature fluctuations due to line-voltage variations at a minimum. The temperature of the furnace was oscillated along an approximate sine curve by oscillating the voltage input of a variable transformer in the circuit.

Various samples of glass, principally a commercial plate glass, were placed in a combustion boat which was placed in the furnace. A probing thermocouple was used to measure the gradient of the furnace. Temperature oscillations were made varying the period of oscillation, the amplitude of the oscillation, and the entire temperature ranges. Samples with crystals were given this thermal treatment as well as clear glasses.

3. Results

The results were inconclusive in regard to any changes in the particle size distribution due to difficulties in the measurement. It was found that the temperature at which the last crystals appeared was approximately at the liquidus temperature of the glass

4. Discussion of results

Experiments on surface devitrification made subsequent to the above indicated that dust in the air is largely responsible for nucleation of glasses. Since this factor must necessarily enter in affecting the particle size distribution, and since such a factor must necessarily be quite variable, measurements of the particle size distribution lose some of their significance in such experiments.

Experiments on the rate of solution of crystals, as reported in Part III, indicated a very rapid solution rate above the liquidus. It was hoped in these experiments, which were made prior to the others, that solution would be slow enough so that only the small particles would dissolve as the temperature was above the liquidus, but this was not the case.

VI. SUMMARY

In this investigation, it was shown that changes in composition of a glass change the rate of crystal growth, the temperature of the maximum rate of crystal growth, and the nature of the crystalline phases precipitating. These changes were explained by considering the viscosity and liquidus temperature changes of the glasses, a low viscosity and a high liquidus temperature in a given series of glasses being associated with a high rate of crystal growth.

It was also shown that:

1. The linear growth of crystals in glasses proceeds at a practically constant rate until the crystallization zones of the glass meet.
2. The rate of growth vs. temperature curve is continuous through the luquidus temperature with the rate of solution vs. temperature curve, if solution is considered to be negative growth.
3. The rate of solution of crystals by the glass from which they were derived increases rapidly with an increase in temperature above the liquidus.
4. Alumina additions up to approximately seven percent decreased the maximum rate of crystal growth in a soda-lime-silica glass, while larger additions increased the rate.
5. The replacement of lime with magnesia up to approximately seven percent in a soda-lime-silica glass decreased the maximum rate of crystal growth; further replacement increased the rate of growth.
6. A sodium magnesium silicate, $Na_2O \cdot 2MgO \cdot 6SiO_2$, can occur as a devitrification product in high magnesia glasses.
7. No simple relation is evident for the effect of viscosity on the rate of crystal growth in glasses with a variable alumina or magnesia content.

8. Dust and other material in the air play a major role in the promotion of surface devitrification.
9. Liquidus temperatures can be determined rapidly by measuring the rate of crystal growth and rate of crystal solution in a decreasing temperature interval.
10. Minor constituents in the glass may influence the rate of crystal growth considerably.
11. A method is presented by which the inter-diffusion of similar-type glasses may be followed.

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