ORIGINAL PAPERS AND DISCUSSIONS.

DEVITRIFICATION OF GLASS.

By N. L. BOWEN.

All ordinary glasses are undercooled liquids and as such are unstable. Were the stable condition established all such glasses would be completely crystalline at ordinary temperatures. At these temperatures, however, the rate of establishment of the stable condition, that is, the rate at which crystallization proceeds, is absolutely negligible. At higher-temperatures, the rate of crystallization (devitrification) may be great enough to become a seriously troublesome factor to the glassmaker. In the literature of glass technology there occur frequent statements that indicate much confusion of ideas concerning the nature of devitrification. Before describing the specific examples of this phenomenon that have been encountered in the course of the writer's experience in the manufacture of optical glass, it seems desirable to discuss the fundamental principles underlying crystallization or devitrification.

Definite chemical compounds almost invariably have definite melting points and the solid, crystalline substance when raised to the melting temperature usually passes promptly into the liquid condition. If the liquid is then allowed to cool and the conditions are such that equilibrium is attained, crystallization will take place at the temperature of the melting point. Melting is therefore a reversible phenomenon and the melting point of a substance is defined as the temperature at which the crystalline and liquid phases are in equilibrium. It is well known, however, that in many chemical and physical changes equilibrium is not always readily established, and in the case of cooling a molten

substance it is frequently possible to lower the temperature below the melting point without the incidence of crystallization, when the liquid is said to be undercooled.

The ease with which undercooling of the liquid can be accomplished varies enormously from one substance to another. Molten metals, for example, usually crystallize promptly when cooled to the melting point. As a rule, water behaves similarly, but with certain precautions, such as the exclusion of dust particles, bubbles, etc., water can be undercooled. Then, again, there are a great number of substances for which no particular precautions are necessary and which normally undercool. Usually, however, only a certain amount of undercooling can be accomplished and when this has been attained crystallization occurs. There are, however, certain substances that can be undercooled an indefinite amount. Such substances may be considered to pass gradually and continuously from the state of fluent liquid, through a condition of continuously increasing viscosity until finally a rigidity comparable with that of ordinary crystalline substances is attained, though the substance is still, from the point of view of the physical chemist, an undercooled liquid. The substance is then said to be in a vitreous condition or is called, simply, a glass.

Silicates are the best known representatives of this class of substances that can be readily undercooled to a vitreous condition, though there are many more or less related substances that behave similarly, such as borates, and still others wholly unrelated, such as ordinary ethyl alcohol. Indeed, the difference between various substances in this respect is only a matter of degree, and it is probable that all substances could be obtained in a vitreous state if the requisite conditions of cooling could be attained.

The conditions that favor permanent undercooling will be apparent from the following considerations. Above the melting point the tendency of a substance to crystallize is zero; at the melting point it is still zero, but as the liquid is cooled below this point the tendency increases rapidly and if there were no counter effect it would probably increase indefinitely as undercooling is increased. However, as the liquid cools there is a constant diminu-

tion in the freedom with which the atoms can arrange themselves in that configuration characterizing the crystals, because the viscosity or internal friction of the liquid continually increases. The increasing viscosity therefore works against the crystallization tendency and the result is that the actual crystallizing power usually increases rapidly as cooling proceeds below the melting point, passes through a maximum, and falls away practically to zero.

The crystallizing power may be defined as the numbers of centers of crystallization established per unit of volume in unit time. From the considerations outlined above it is apparent that its variation with temperature can be represented by curves of the form shown in Fig. 1. Curve A is that of a substance whose crystallization power increases very rapidly when the melting point is passed and attains a very great value. It represents a substance that is very difficult to cool quickly enough to prevent the formation of numerous centers of crystallization. Curve B is that of a substance in which it is difficult to avoid crystallization, but in this case it is not so much because the absolute value of the crystallizing power is so great at any given amount of undercooling, but because the crystallizing power is comparatively great through a long range of undercooling. Hence it is difficult to cool through this long range at a rate sufficiently great to prevent crystallization. Curve C is that of a substance easily undercooled without crystallizing.

Silicates do not all belong to the class of substances represented by curve C. Compounds such as MgSiO_3 , Al_2SiO_5 , and CaSiO_3 belong rather to the class of substances represented by curve B. They, therefore, can be cooled to the vitreous state only when the rate of cooling is made very great. On the other hand, a large number of silicates, particularly those of the alkalis, can be cooled quite slowly without crystallization and therefore might be represented by curve C. Nevertheless they can be crystallized with sufficiently slow cooling.

Since molten silicates have comparatively great heat capacities and are poor conductors of heat, it is not possible to cool a large mass at any very rapid rate. Silicates that crystallize readily, such as CaSiO_3 , can therefore be cooled to the glassy con-

dition only in a very small mass, usually a few grams. Such silicates cannot, therefore, be used as ordinary commercial glasses, though they may enter into the composition of such glasses because in mixtures their specific properties are modified.

Before passing to the consideration of mixtures, however, it is desirable to consider the heating of an undercooled liquid or

FIG. 1.—Types of crystallization curves.

glass, that is, the reversal of the process of cooling that has been discussed in the foregoing. When such a substance is heated the behavior is the exact reversal of that involved in undercooling. The rigid glass gradually softens, becomes a viscous liquid, and finally a fluent liquid without discontinuity of behavior at

any temperature. Properly speaking, then, a glass has no melting point.

The curves that were given to represent crystallizing power for the liquid which is being undercooled, substantially represent crystallizing power for the reheated glass also. If the substance is of the class of substances represented by curve B, then it must be heated exceedingly rapidly to a temperature above the melting point of the crystalline substance in order to prevent crystallization. Glass of the composition CaSiO_3 , for example, will crystallize in a short time if held at a temperature even several hundred degrees below the melting point of the crystalline material, and if raised to a temperature not far below the melting point, its crystallization is practically instantaneous. If the behavior of the substance is represented by curve C, on the other hand, then it may be heated slowly and maintained for comparatively long periods at temperatures not far below the melting point of the crystalline substance without crystallization occurring.

In the foregoing, consideration has been given only to the behavior of pure definite compounds. When we pass to mixtures of compounds, as represented in ordinary commercial glasses, we find that certain other factors must be considered. The principles involved in the crystallization of mixtures may be illustrated with the aid of Fig. 2, which represents the crystallization temperatures of all mixtures of CaSiO_3 and SiO_2 . From the figure it is apparent that, while the crystallization temperature of pure CaSiO_3 , under equilibrium conditions, is 1540°C , when mixed with 15 per cent SiO_2 , its crystallization temperature is lowered to 1490°C , and this is merely the temperature at which crystallization begins. Unlike the pure compound CaSiO_3 , this mixture does not crystallize entirely at a definite temperature, but as the temperature falls crystallization of CaSiO_3 continues and the remaining liquid therefore changes its composition until finally at 1435°C , when the liquid has the composition 78 per cent CaSiO_3 , the silica begins to crystallize and the whole mass solidifies at this temperature, giving a mixture of CaSiO_3 and silica. Such is the behavior when equilibrium prevails, but just as in the case of pure compounds, so in mixtures, undercooling may occur and for similar reasons. Thus the crystallizing ten-

dency of CaSiO_3 from the mixture just discussed is zero at all temperatures above 1490°C , while as cooling proceeds below this temperature the tendency increases rapidly, but the counter effect of increasing viscosity enters in so that the actual crystallizing power is never very great. Cooling to a glass is therefore quite readily accomplished with this mixture though so difficult with the pure compound CaSiO_3 . The effect of the addition of silica is to lower the temperature of crystallization of CaSiO_3 to a tem-

FIG. 2.—Temperature-composition diagram for the system calcium meta-silicate-silica (CaSiO_3 - SiO_2).

perature at which the viscosity is much greater and therefore the crystallization power much decreased. At the same time the silica in virtue of its own inherent properties makes a further addition to the viscosity of the liquid. We thus see that a substance that has a great crystallizing power when pure may nevertheless not separate readily from mixtures, and in general its tendency to separate will be in direct relation to its proportion in the liquid.

In speaking of the cooling of this mixture (85 per cent CaSiO_3 , 15 per cent SiO_2) it has been stated that below 1490°C the liquid is undercooled. Since we are dealing with a mixture containing

more than one substance we may apply the conception of solutions and the liquid may be said to be supersaturated with respect to CaSiO_3 at all temperatures below 1490°C . At 1490°C it is just saturated, and above that temperature it is unsaturated, with respect to CaSiO_3 . The statement that a certain glass is supersaturated with a certain compound is, therefore, entirely without meaning unless a temperature is specified. Ordinary glasses at room temperature are supersaturated with respect to several compounds, as we shall see in the following.

It has been shown that from the mixture whose crystallization was discussed, crystallization of CaSiO_3 began at 1490°C and was continued down to 1435°C when crystallization of silica began, assuming equilibrium. If undercooling occurs, however, the liquid becomes undercooled or supersaturated with respect to CaSiO_3 at 1490°C , and undercooled or supersaturated at 1435°C with respect to silica also. Now for each of these compounds there will be a curve of crystallization power, analogous to the curves representing that property that have already been mentioned, though differing, of course, from the curves for the pure compounds in the absolute values represented. In cooling a mixture of the composition discussed, the rate must be made such that the glass does not remain long within the temperature range where the power of crystallization of CaSiO_3 or SiO_2 , or both, is great. In practice this means that the glass must be cooled rapidly to a temperature at which the crystallization power of these substances is negligible. Similarly, in reheating the glass the temperature should not be raised above that at which their crystallizing power is negligible, or if this is done the time during which it is held above this temperature must be brief, otherwise CaSiO_3 or SiO_2 , or both, may crystallize out.

When we pass to mixtures of more than two components the same general principles hold, but in this case we have, on cooling, a certain temperature at which the liquid becomes saturated with one of the components, the so-called primary phase, a lower temperature at which it becomes saturated with the secondary phase, and so on, for all the components. If cooling is so conducted, the glass may become undercooled or supersaturated with respect to these various phases at the respective temperatures.

On reheating such a poly-component glass any or all of the components may separate if the necessary relation between crystallizing power and duration of heating is realized.

If we regard the process of manufacture of glass in the light of the foregoing discussion of the theory of devitrification, we find that there are three distinct danger periods during which devitrification is liable to occur. At the full melting or fining temperature no trouble need be anticipated, but when the glass is cooled preparatory to working, some devitrification may occur. Whether the cooling be for the purpose of gathering from pots or from the gathering end of a tank, for the purpose of casting in the case of plate glass or with the object of giving the final stirring before setting out in the case of optical glass, the same considerations apply. The temperature to which the glass is cooled and at which it is usually maintained for long periods must not be such that the glass becomes supersaturated with respect to any of its components; or, stated in another form, the composition of the glass must not be such that it becomes supersaturated with any of the components at the temperature at which it is to be maintained. When devitrification or crystallization does occur at the comparatively high temperature with which we are here concerned, it usually takes the form of the separation of large individual crystals, for the glass is fairly fluid and actual equilibrium conditions may prevail or a sufficiently close approach thereto to allow the crystals to grow slowly by diffusion without the precipitation of the myriad tiny crystals that form when the glass is colder. A particularly good case of this type of devitrification fell under the writer's experience and will be described rather fully here on account of the principles it illustrates and because it affords an example of the application of scientific methods to glass problems.

In the manufacture of the variety of optical glass known as light barium crown much trouble was experienced from the formation of crystals that ruined the greater part of the pot of glass. These crystals formed during the final stages of stirring, immediately preceding the time at which the pot was set out for rapid cooling. The most obvious remedy and the one first tried was to set the pot out at a temperature above that at which the crystals form, and permit the glass to cool more rapidly through

the dangerous temperature. This procedure was entirely successful in eliminating crystallization, but was found undesirable for another reason, *viz.*, that the final stirring of the glass should be conducted at a certain fluidity, and if the pot were set out at a higher temperature than the fluidity of the glass during the final stirring was too great. It was then necessary to attack the problem in another way, and from the principles that have been discussed in an earlier part of the paper it is obvious that if the temperature of final stirring could not be raised then the composition of the glass must be changed so that separation of the crystals would not occur at the temperature normally used. The composition could, of course, have been varied by the method of cut and try, but in this instance the method was adopted of determining the nature of the crystals and deducing therefrom what the change of composition should be. The crystals were very thin hexagonoid plates that probably could not have been identified by purely chemical means, but by determination of optical properties they were identified with the compound BaSi_2O_6 .¹ Evidently, then, the glass, at the temperature concerned, was supersaturated with BaSi_2O_6 and crystallization of that compound could be avoided by lessening the barium content of the glass. At the same time it was desirable to make as little change as possible in the optical properties of the glass so the following method was adopted of determining the minimum amount of decrease in the barium content that would produce the desired effect: The melting point of pure BaSi_2O_6 was determined and found to be 1426°C , and the temperature at which the light barium crown glass became just saturated with BaSi_2O_6 was determined and found to be 1100°C . The composition of the glass was such that it contained 57 per cent BaSi_2O_6 , that is, a change of 43 per cent ($100-57$) lowers the temperature of saturation 326°C ($1426-1100$). If, therefore, we regard the variation of the temperature of saturation as linear, each further decrease of 1 per cent should lower the temperature of saturation about 7.5°C . This assumption of a linear relation gives, however, only a minimum estimate, because all curves of this nature for silicates

¹ N. L. Bowen, "Crystals of Barium Disilicate in Optical Glass," *J. Wash. Acad. Sci.*, 8, 265 (1918).

that have been investigated are concave against the temperature axis (see Fig. 2) so that the curve would have the form shown in Fig. 3 rather than the straight line also shown in that figure. A fairly safe assumption is that the curve would have at

FIG. 3.—Diagram to illustrate the probable form of the curve of saturation temperature of a barium crown glass with respect to barium disilicate.

the point in question about twice the gradient of the straight line and therefore a change of 1 per cent BaSi_2O_6 should make a change of about 15°C in the temperature of saturation. Experience had shown that the actual separation of these crystals occurred at a temperature about 70°C above that at which it was desirable to conduct the final stirring. A change of composition

sufficient to reduce the temperature of saturation about 70°C , or a little more, should therefore be ample to permit final stirring at the desired temperature without danger of separation of BaSi_2O_6 . From the above considerations it is plain that the change of composition should be such as to reduce the BaSi_2O_6 content about 5 per cent.¹ Accordingly this change was made and the result was all that could be desired. Thereafter no rejection of light barium crown glass on account of the presence of crystals was necessary.

The case of the separation of BaSi_2O_6 is the only example, in the writer's direct experience, of the crystallization of a glass at a comparatively high temperature at which the individual crystals were enabled to grow to comparatively large dimensions. The writer has had submitted to him, however, a sample of plate glass containing crystals of wollastonite (CaSiO_3) up to 4 mm. in length that formed in the pot during the "hold-over" immediately preceding the casting of the plate. During casting, the crystals all became arranged with their longer axes parallel to the direction of rolling. The exact conditions under which these crystals formed are not available, but an analysis of the glass, kindly furnished by Mr. F. Gelstharp, shows it to contain a slightly higher amount of lime than normal plate. Whether this slight excess of lime is sufficient to render the glass supersaturated with CaSiO_3 at the normal casting temperature is a question. Whether the casting temperature was lower than normal the writer was unable to ascertain, but it seems probable that a combination of these two factors entered into the conditions controlling the separation of the crystals.

Le Chatelier describes some very large crystals of tridymite (SiO_2) that formed in a flint glass that was unintentionally held at a temperature about 800°C for a long period.² These crystals evidently grew rather freely under conditions approaching equilibrium and tridymite is the primary phase for glass of that composition. The same glass can be held for moderate periods at

¹ It should be noted that deductions as to changes of composition that will produce a specific result can be regarded as reliable only for small changes close to a known point.

² *Bull. Soc. Min. Fr.*, 39 (1916).

800° C without danger of crystallization, so the separation of crystals in the case cited illustrates the importance of the time factor.

Another danger period in the manipulation of glass is that during which it is cooled from its final temperature in the furnace or tank, when it is plastic, to lower temperatures at which it is rigid. During this period it is usually worked into form whether by blowing, drawing, casting, or otherwise, but in the case of optical glass the "metal" is usually cooled in the pot itself. Since the rate at which a large mass of glass can be cooled is limited on account of the low conductivity of glass, the cooling of glass as a large mass in the pot is likely to bring about devitrification. Under these conditions devitrification never takes the form of the separation of large individual crystals but may appear in the form of spherulites (spheroidal aggregates of crystals with a radiating fibrous structure), or in the form of very small crystals evenly disseminated. This latter form of devitrification may give an opalescent glass, a milky glass, or a dense, opaque glass, according to the size of the crystalline particles that separate. In opalescent or milky glass the crystalline particles are beyond the resolving power of the microscope but can readily be detected with the ultramicroscope. In a dense, opaque, devitrified glass the particles can be seen by the microscope and their refraction relative to that of the glass observed. In the writer's experience the crystals are apparently, in nearly all cases, one of the low-refracting forms of silica, namely tridymite or cristobalite. Certain substances, which, for want of a better term, may be called mineralizers, seem to exert an influence in promoting this form of crystallization. Among these are SO_3 and Cl .¹ Arsenic, also, when present in excess of certain amounts, acts similarly, and in one case in the writer's experience the devitrification of a medium flint ($n_D = 1.62$) was eliminated by cutting down the arsenic in the batch from about 0.9 to about 0.3 per cent. Fluorine probably acts in a similar capacity and certain glasses that are deliberately rendered opaque by the addition of fluorides no doubt owe their opacity (crystallization)

¹ Fenner and Ferguson, "The Effect of Certain Impurities in Causing Milkiness in Optical Glass," *J. Am. Ceram. Soc.*, 1, 468 (1918).

to a separation of crystals that is aided by fluorine. In some cases fluorides themselves may represent the crystalline phase. On the whole, however, little is known of the fundamental facts concerning these opaque and translucent glasses.

More definitely susceptible of solution, however, are the problems connected with the other form of crystallization that takes place during this period of cooling of the glass now being considered. The crystalline constituents of spherulites are readily determinable under the microscope, and, if the heat treatment cannot be varied in such a way as to eliminate their formation, a knowledge of the composition of the crystals enables one to make appropriate changes in the composition of the glass.

The type of barium crown glass whose devitrification at high temperatures has already been described, may further devitrify during the cooling stage with separation of spherulites of BaSi_2O_5 that grow about the larger crystals of earlier separation, or with the formation of new simple spherulites. The remedy for this is either (1) the reduction of the BaSi_2O_5 content of the glass, just as at the higher temperature (see page 269), or, (2) more rapid cooling. Moreover, even barium crown glass that is safe from devitrification at this stage, in so far as the main mass of glass is concerned, may nevertheless devitrify at the free upper surface of the glass with the formation of spherulites of BaSi_2O_5 .

From ordinary crown glasses that have an excess of lime as compared with fluxes, spherulites of wollastonite, CaSiO_3 , sometimes separate during the cooling stage.

Some types of borosilicate glasses may devitrify with separation of spherulites of tridymite, SiO_2 . A remedy for this in one instance was found to be the substitution of potash for some of the soda of the glass, a change that probably had the effect of increasing the viscosity and thus diminishing the crystallizing power at the temperature concerned.

The final period of danger of devitrification is one of considerable importance. It is that period during which the glass is reheated, whether for working it into a desired form or for annealing it if it is already in final form. The interrelation of time, temperature, composition and power of crystallization must be carefully borne in mind.

If the glass is to be worked into shape it must, of course, be

heated to a temperature such that it is subject to flow. In the case of optical glass, for example, a common procedure is to heat in molds the rough chunks from the broken-down pot, the operation being conducted at such a temperature that the glass sags down and takes the shape of the mold. There is a certain amount of choice of temperature available, for obviously the sagging will proceed at a certain rate at a certain temperature and at a greater rate at higher temperatures. In the discussion of the principles underlying crystallization it was pointed out that for any glass there is a certain temperature below which the crystallization power is negligible, and another temperature above which the crystallizing power is zero. The lower limit has no special significance in connection with the molding process, for all glasses are too rigid for molding at these temperatures. The upper limit, however, has great importance for if the molding is conducted at a temperature slightly higher than this upper limit there is absolute certainty of freedom from devitrification during the molding itself, though subsequently, of course, proper precautions must be taken to cool at an adequate rate. It is highly desirable, therefore, to know the temperature of this upper limit of devitrification for individual glasses. This temperature is, it will be recalled, that at which the primary phase begins to separate when cooling of the glass is carried on under perfect equilibrium conditions. It is identical with the temperature at which the crystallized glass becomes completely molten as the temperature is raised. This fact can be used in order to determine the temperature of this upper limit. A small piece of devitrified glass is held at a certain temperature for about an hour, is rapidly chilled and examined, this operation being repeated at successively higher temperatures until one is reached at which the last traces of crystals have disappeared. Unless it is undesirable for other reasons, such as the development of bubbles in the glass, molding should be conducted at a temperature slightly higher than that determined by the above method, absolute freedom from devitrification during the molding process itself being thereby guaranteed. Molding can be conducted at lower temperatures with some glasses whose devitrification tendency is small.

The temperatures found for various glasses examined in connection with optical glass investigation are shown in Table 1.

TABLE 1.
Data on Devitrification of Some Optical Glasses.

Glass.	Temperature of disappearance of crystals.		Composition of crystals. (Primary phase.)
Medium Flint ($n_D = 1.62$).....	910° C.	1670° F.	SiO ₂
Ordinary Crown.....	1110° C.	2030° F.	SiO ₂
Light Barium Crown.....	1100° C.	2012° F.	BaSi ₂ O ₆
Light Flint.....	1115° C.	2039° F.	SiO ₂

Glass is frequently reheated not alone for working but also for annealing. All glass must be free from excessive strain that is likely to cause breakage, and optical glass in particular must have the strain reduced below the quite moderate amount that will cause a warping of reflecting or refracting surfaces during grinding and polishing; in short, optical glass must be subjected to fine-annealing. In annealing, the glass is raised to a temperature at which the strain is relieved by relatively slow flow. Obviously there is again a certain amount of choice of temperature permissible, for the flow will take place slowly at low temperatures and more rapidly at higher temperatures. It is important, therefore, to know the crystallizing power for various temperatures of the glasses to be annealed, in order that a temperature may be chosen that will not induce devitrification. The choice is not so easily made as it was for molding purposes, for there is no definite lower limit of devitrification temperatures analogous to the upper limit that has been pointed out, and while there is for any glass a practical lower limit below which the power of crystallization or devitrification is negligible, this is, unfortunately, in the case of some glasses, a temperature at which rate of annealing is of like magnitude. At low temperatures devitrification is induced in a certain time at a certain temperature, in a shorter time at a higher temperature, and so on. It is

therefore desirable to know for any glass whether devitrification will be induced at any given temperature in a period of time which

TABLE 2.
Experiments on Devitrification of Certain Optical Glasses.¹

Time. Hours.	Temperature ° C. ° F.		Results.
Barium Flint Glass.			
15.0	660	1220	No devitrification.
27.5	700	1292	No devitrification.
29.0	750	1382	No devitrification.
68.0	800	1472	No devitrification.
Medium Flint Glass ($n_D = 1.62$) Crystals; SiO ₂ .			
1.0	650	1202	No devitrification.
12.5	650	1202	Slight surface film.
4.5	700	1292	No devitrification.
6.5	700	1292	Slight surface film.
23.5	700	1292	Marked surface film.
Borosilicate Crown Glass. Crystals; SiO ₂ .			
14.5	660	1220	No devitrification.
27.5	700	1292	Surface devitrification.
4.5	750	1382	Surface devitrification.
8.0	750	1382	Surface devitrification.
2.3	800	1472	Surface devitrification.
20.6	800	1472	Surface devitrification.
Ordinary Crown Glass. Crystals; SiO ₂ and CaSiO ₃ .			
41.0	600	1112	No devitrification.
36.0	650	1202	No devitrification.
4.0	700	1292	Slight surface film.
6.5	700	1292	Surface film.
23.5	700	1292	Thick surface layer.
33.0	700	1292	Thick surface layer.
47.0	700	1292	Thick surface layer.

is long enough to give adequate annealing at that temperature. A fore-knowledge of both rates of devitrification and of rates of

¹ Temperature measurements by J. C. Hostetter. Identification of crystalline phases by N. L. Bowen.

annealing for various glasses is therefore requisite. It is plain, too, from the foregoing discussion, that glasses will be encountered in which fine-annealing and freedom from devitrification are mutually incompatible.¹ In such a glass every effort should be made to change the composition in such a manner as to increase the annealing rate or decrease the devitrification rate, or to accomplish both these results simultaneously. In making a change of composition a knowledge of the nature of the phases that separate is again desirable, precisely as it was for devitrification at other stages in the manipulation of the glass. Devitrification during annealing may take the form of the separation of spherulites or of minute crystals more evenly distributed that give a milky or dense, opaque glass. The identification of the crystals in the spherulites is usually readily accomplished and in the opaque glass one can frequently obtain a clue as to the nature of the crystals by observation of the relative refraction of crystals and glass. In milky glass one cannot determine the crystals, but intensification of the effect can frequently be obtained by raising a piece of the glass to a somewhat higher temperature. The larger crystals thus formed may then be identifiable.

In Table 2 the results are given of a study of devitrification of various glasses at these lower temperatures. It should be remarked that frequently the devitrification may take place only at the free surface of a piece of glass, but the reason for this greater freedom of devitrification at the surface is unknown.

Summary.

Devitrification of glass is the result of the tendency of the glass to reach the stable crystalline condition, and takes place whenever the glass is held for a sufficiently long period of time within the range of temperature where its crystallizing power is great. The various forms of devitrification in glass are discussed from this point of view and suggestions are made as to the principles that must be borne in mind in deciding upon modifications of

¹ It is perhaps worthy of note that certain opaque (devitrified) glasses that are used for ornamental purposes are clear when first cooled to the desired shape and become opaque only on reheating which accomplishes the double purpose of annealing and devitrification.

procedure or changes in composition that have as their object the avoidance of devitrification. Specific examples of the devitrification of optical glasses are given, together with determinations of the temperatures of devitrification and the crystalline phases separating.

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COMMUNICATED DISCUSSIONS.

W. S. WILLIAMS: The thanks of the glass technologists are due Dr. Bowen for his able exposition of some of the fundamental principles of physical chemistry applied to glass. It is to be regretted that the compositions of the glasses which devitrified are not given. They would serve as a guide and a warning in the manufacture of these types of glasses.

In my experience in the manufacture of optical glass at the Bureau of Standards, I have never experienced devitrification of light barium crown, $n_p = 1.57$. All of the compositions used were compounded with a knowledge of ceramic chemistry and will be published in this JOURNAL. Of these, only one type tends to devitrify when the technic described in the above article is followed. This is the dense barium crown, $n_p = 1.60$. I have seen only two melts of this type devitrify during the melting stage. The composition of the first one was

	Per cent.
SiO ₂	40.7
B ₂ O ₃	6.2
ZnO.....	9.3
BaO.....	43.2
As ₂ O ₃	0.6
	<hr/>
	100.0

This batch was filled in sixteen hours at 1350° C and was closed and held at 1350° C for eight hours, during a fining period. When a proof was taken a slight scum was observed and skimmed off. Two hours later, however, a scum about 3 inches deep had formed.

This was also skimmed and about three inches of clear glass was taken out of the pot with the purpose in view of endeavoring to eliminate the nuclei, if possible. The temperature was raised 50°C to 1400°C . Three hours later, however, fully 6 inches of glass showed devitrification and the melt was abandoned. When cold the melt exhibited about 12 inches of dense, pure white opal glass on the surface and the rest of the glass was clear. Chemical analyses of the clear glass and opal glass demonstrated marked differences in their compositions. The analyses were as follows:

	Clear glass.	Opal glass.
SiO ₂	37.88	44.67
BaO.....	42.36	38.02
ZnO.....	10.52	9.25
B ₂ O ₃	9.31	8.46

A petrographic examination was baffling—due to the extremely fine state of the crystals. This was a case of devitrification occurring during melting and fining. In subsequent melts the difficulty was eliminated by the addition of Al₂O₃.

The second case of devitrification in dense barium crown, $n_D = 1.60$, occurred with a batch of the following composition:

	Per cent.
SiO ₂	37.0
B ₂ O ₃	5.0
K ₂ O.....	2.7
ZnO.....	7.8
BaO.....	47.0
As ₂ O ₃	0.5

This batch was filled in 15 hours at 1400°C and fined for two hours. During a stirring period of 12 hours the temperature was gradually reduced to 1100°C . No devitrification was observed, but when the melt was cold spherulites were seen on only one side of the pot about 8 inches down from the surface. They extended about 6 inches from the side of the pot into the glass. These spherulites were determined under the microscope to be barium disilicate. With the exception of these few nodules the glass was good.

During molding and annealing dense barium crown, $n_d = 1.60$, of all compositions, devitrifies readily and must be molded in the shortest possible time. Sticking on a punty and heating in a glory hole is the most satisfactory method of molding, as the heat is more intense and the glass more uniformly heated than by other methods.

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E. W. TILLOTSON: In this paper Mr. Bowen has made a noteworthy contribution to the subject of devitrification. As a natural consequence of his observations of the separation of crystalline material, mention is made in several places of the relation of devitrification to the production of translucent and opaque glasses. The writer would therefore like to inquire whether Dr. Bowen would exclude as possible causes of turbidity in glass the formation of "emulsions"¹ (glass in glass) or of "foams" (gas in glass).

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N. L. BOWEN: The compositions of the glasses on which we made devitrification experiments were not given in the article, because the original batches of Table 2, and of the ordinary crown and light barium crown in Table 1, had been used by the chemists of the Pittsburgh Plate Glass Company before the date when the party from the Geophysical Laboratory was invited to cooperate in optical glass manufacture at the Charleroi plant. The officials of the Company have requested that these compositions should not be published. Changes were subsequently made in the formulas of some of these glasses, particularly in the light barium crown, which, on account of devitrification, was not satisfactory until its composition had been altered as indicated on page 271.

I have seen a sample of a scum formed on barium glass similar to that described by Mr. Williams though I was not present during the making of the melt itself. Under the microscope this scum was found to consist of glass with a cloud

¹ See for example, Guertler *Z. anorg. Chem.*, **40**, 225 (1904).

of minute crystals of silica in one of its low refracting forms, tridymite or cristobalite.

Evidently Mr. Williams' scum was identical, for a simple calculation shows that if one took 9 grams of material corresponding in composition with his "Clear Glass" and added thereto 1 gram of silica, one would obtain a material of the composition of his "Opal Glass." The continued formation of this scum as observed by Mr. Williams was therefore the result of the rising of these minute crystals of silica towards the surface. Whether the formation of these crystals is a true example of devitrification is questionable; indeed, it seems rather probable that they may represent completely recrystallized silica that had never completely dissolved because the melt was too slow. The fact that undissolved silica will rise through the glass in this manner is clearly demonstrated by Fig. 1 in my paper on "Identification of Stones."¹

In reply to Dr. Tillotson, I would say that formation of emulsions and foams should not be excluded as possible causes of turbidity in glass, but in the turbid glasses that I have seen there seems little reason to believe that anything other than crystalline particles are the underlying cause. One can usually modify the treatment that renders a glass turbid in such a way (for instance, by prolonging the treatment) that the particles causing turbidity become sufficiently large for identification as crystal particles.

¹ THIS JOURNAL, 1, 598 (1918).