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Attacks from Different Fronts on Some Complex Cases of Instability in Aqueous Solutions Solidified at Low Temperatures

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Abstract

The structural changes which take place when aqueous solutions solidified at low temperatures become unstable upon being rewarmed have been studied by three methods. (1) *Differential thermal analysis* of changes occurring in the rewarming of a rapidly cooled 45% solution of glycerol indicated a heat-releasing crystallization at -112°C , and a transition without liberation of heat (a recrystallization) when the preparation turned opaque, at about -60°C . (2) Determinations of the *dielectric constant* of a 38.4% solution of polyvinyl pyrrolidone, at various temperatures from $+20$ to -150°C , suggested that the "recrystallization temperature" might coincide with an incipient melting. (3) *X-ray diffraction* diagrams obtained during the rewarming of a 50% gelatin gel showed a successive gradual rise of peaks which seems better explained by a gradual growth of hexagonal crystals in preferred axial directions, far below the recrystallization temperature, rather than by a transition from cubic to hexagonal ice, as has been proposed.

I. Introduction

The structural instability of aqueous solutions of various sorts, cooled at various rates and solidified at various low temperatures, has been investigated in this laboratory by methods permitting the measurement of changes in thermal, optical and electrical properties, by dilatometry, by X-ray analysis, and by direct observation, photography and cinematography of the phenomena. I shall select for presentation at this session of the Conference on Physics of Snow and Ice three series of observations which throw new light, and...raise new questions, on some of the complex cases of instability and molecular mobility encountered when a solution solidified by cold is exposed to various temperatures from -150 to 0°C . The solidified solutions to be examined are assumed to contain a crystalline and an amorphous component.

Let us first glance at the known cases of instability and molecular mobility in the range of temperatures mentioned. The most outstanding case is, of course, *melting*. Next in importance is perhaps *recrystallization*, though the phenomenon, as such, is hardly known outside of the field of metallurgy. Then, in the case of material solidified in the amorphous state, one has *devitrification*, and the *glass transition*. There is also the possibility that a *crystallization* initiated during cooling, but interrupted, be *resumed* during rewarming. In the present study, I shall examine a few complex cases in which two or more processes occurring simultaneously or consecutively might be involved, or in which there is an overlapping of the temperature ranges, or in which the evidence for the occurrence of a change is too weak to be detected by most of the current

methods and calls for the use of a particular one.

The three series of experiments selected are: (1) the recording, by *differential thermal analysis* (DTA), of the changes occurring during the rewarming of a solidified 45% solution of glycerol, (2) the measurement of the *dielectric constant* of solutions of polyvinylpyrrolidone (PVP) of concentrations such that either all of their water, or a part of it solidifies in the amorphous state, (3) the establishment of the *X-ray diffraction* diagrams during rewarming of a 50% gelatin gel previously solidified at -150°C . These will be examined separately after a short introductory survey of two phenomena which need some clarification: (1) recrystallization, and (2) devitrification.

1. *Recrystallization.* I refer the reader to my lecture "Various Modes of Recrystallization of Ice" (in the Proceedings of this Conference) for a detailed description and for illustrations of the complex series of phenomena involved in recrystallization. The essential features of the process of recrystallization which are of significance for the present survey are the following: (a) in rapidly cooled solutions of concentrations varying from about 25 to 50%, water crystallizes into spherulites; (b) preparations of these solidified solutions are transparent in ordinary light, and (c) turn rather abruptly opaque when the rising temperature reaches a certain value; (d) that temperature (referred to hereafter as "recrystallization temperature") is only slightly affected by the concentration of the solute, but (e) is greatly affected by the nature of the solute (it drops with decreasing molecular weight of the latter).

2. *Devitrification.* Devitrification was originally conceived as a transition from the vitreous to the crystalline state during the rewarming of a rapidly cooled liquid. But there were often indications that the so-called vitreous material contained crystallites; this observation gave rise to the "crystallite theory" of the vitreous state (*cf.* Randall, 1934). If crystallites are present, devitrification becomes essentially the resumption, upon rewarming, of a crystallization interrupted during cooling. To what extent one has a passage from the amorphous to the crystalline state, or from crystalline particles of one size (or type) to those of another, or a resumption of an interrupted crystallization, will depend on the conditions of a particular experiment. To illustrate the situation, I will mention the case of a 35% solution of PVP shown in Fig. 9 of my paper on Modes of Recrystallization, in which some 18 g of water out of 100 g of solution remained unfrozen after rapid cooling, and froze upon rewarming to the recrystallization temperature.

II. Experimental Data and Their Significance

1. *Differential thermal analysis of some changes encountered in glycerol solutions**

Using a miniature DTA apparatus in which the specimen consisted of about 30 μl of a 45% solution of glycerol, enclosed in a copper-foil cylinder 10 mm long and 2 mm in diameter, we recorded the thermal changes encountered during the rewarming of material which had been cooled rapidly by immersion in liquid nitrogen. A thermocouple indicated the actual temperature of the specimen, and another thermocouple gave the DTA record.

The DTA curve and the directly recorded curve DR are reproduced in Fig. 1. The

* *cf.* LUYET *et al.*, 1966.

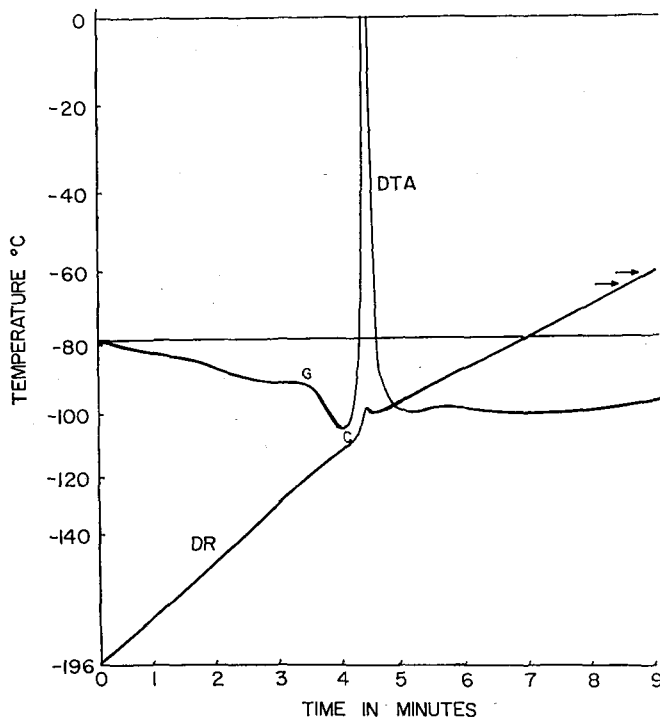


Fig. 1. Differential thermal analysis curve (DTA), and directly recorded temperature curve (DR), obtained during the rewarming of rapidly cooled samples of a 45% glycerol solution. The temperature scale applies only to the directly recorded curve. G denotes the time of the onset of the glass transition, C the time the heat-releasing crystallization begins, and the two arrows mark the temperature range of recrystallization (from Luyet, Rasmussen and Kroener, 1966; with the permission of Biodynamica)

latter curve shows only one change, namely when the rising temperature approaches -115°C ; the DTA curve shows two changes, one marked G, at -123°C , the other marked C, at -112°C . The first is evidently the glass transition, which is characterized by a large increase in specific heat; the second must be the crystallization of the part of water left amorphous in the previous rapid cooling, a process which would result in the release of latent heat.

But, the most significant point in these findings is that the DTA curve does not show any change when the temperature approaches -60°C , that is, when it enters the range at which solutions of glycerol of the concentration used are known to turn opaque (range shown by the arrows in Fig. 1). It seems quite evident that the turning opaque of the preparation does not involve a heat production or absorption; in all probability, it is a true recrystallization. Thus, the DTA method led to the separation of two processes occurring some 60 degrees apart, which were not distinguished previously.

2. Study, by determination of the dielectric constant, of some changes encountered in PVP solutions*

Determinations of the dielectric constant, between $+20$ and -150°C , (1) of solutions

* cf. Amrhein and Luyet, 1966.

which vitrify completely upon being cooling (60% PVP), or (2) of solutions which vitrify partially (38.4%), and (3) of pure water, which crystallizes entirely, permitted a comparative study of the changes in stability in these three types of material.

The dielectric constants thus measured are plotted, in terms of temperature, in the curves (B), (C) and (A), respectively, of Fig. 2, and the portions of the curves (B) and (C) obtained between -150 and -70°C are plotted on a larger ordinate scale in the inset of the figure. The curve of the dielectric constant of water (A) consists of three segments: one for liquid water, one for ice, and a third which represents an abrupt jump between the other two, at the freezing or melting point. The curve for the 60% solution (B) consists of two segments: one, rectilinear, for the vitreous material, below the glass transition (V, V' in the inset), and the other, S-shaped, which is characteristic of a

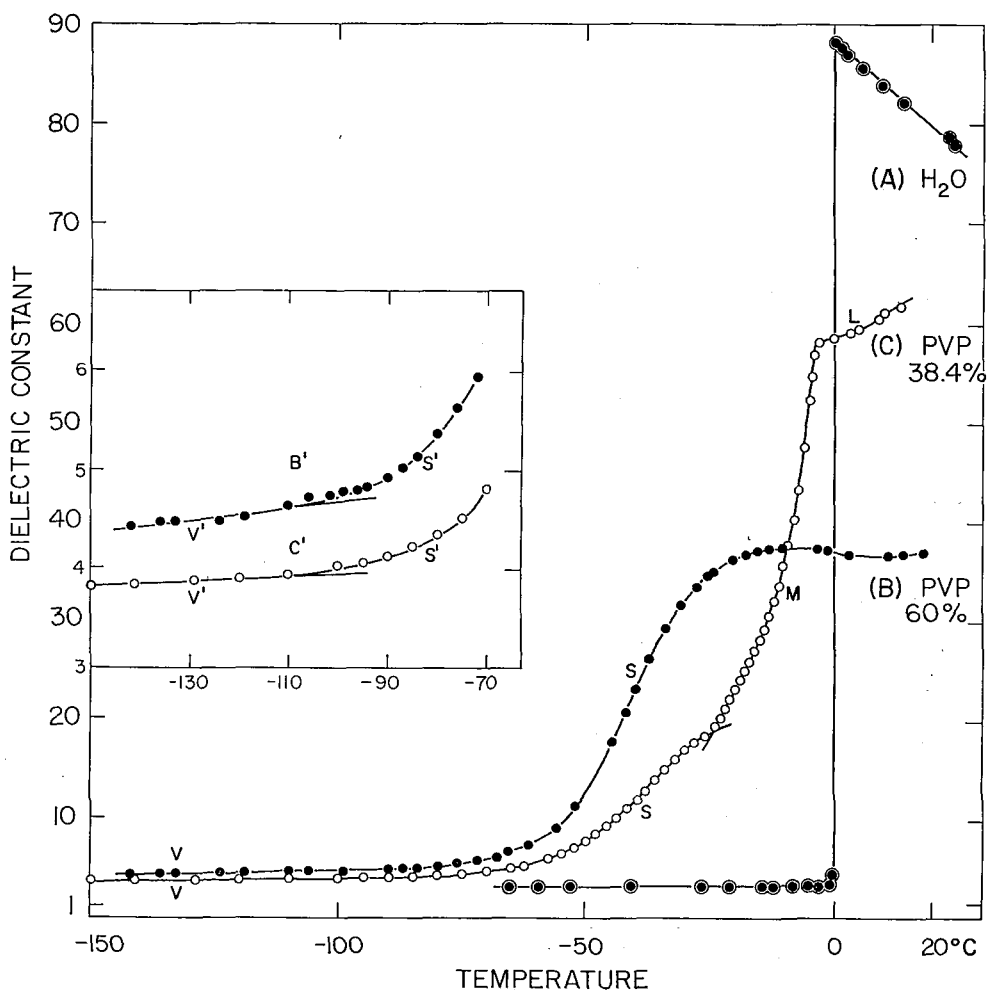


Fig. 2. Dielectric constant of water (Curve A), of a 60% solution of PVP (Curve B), and of a 38.4% solution of PVP (Curve C), when the temperature varies from $+20$ to -150°C . (See text for an analysis of the curves, and for the reasons for their division into segments V, S, M, L.) (From Amrhein and Luyet, 1966; with the permission of Biodynamica)

supercooled liquid, above the glass transition (S, or S'). The curve for the 38.4% solution (C) consists of four segments: one, rectilinear, for the vitreous material (V, or V'), another, S-shaped, for the supercooled material (S, or S'), a third, arc-shaped, corresponding to the gradual melting or freezing (M), and the fourth for the liquid phase (L).

Out of the rich crop of information that these curves contain on the changes in stability and molecular mobility in solutions of PVP solidified at low temperatures, I will point out one item which is of particular interest in this study: melting begins at -22°C (where Segments S and M or Curve (C) intersect), a temperature close to that at which one begins to detect traces of opacity with photocells, in solutions of PVP. This coincidence suggests that the changes described as recrystallization are triggered by the loosening up of the structure when melting begins. The suggestion is most interesting, though I would not want to elaborate further on it without more factual information.

The lowest melting temperature of a solution has been designated as the eutectic temperature. But, while the phenomena of eutectic freezing and eutectic melting are clearly defined in the case of true solutions of crystalloids (in the old sense of the term), what happens in the case of solutions of a substance which does not crystallize is much more complex and less known. This, however, is no argument against the possibility that the temperature at which recrystallization starts, in the course of a gradual rewarming, be that at which the first traces of liquid appear at melting.

3. *Study, by X-ray diffraction, of some changes encountered in gelatin gels**

The use of a photocell, as was just mentioned, permits the detection of the onset of opacity, upon the rewarming of spherulites, at a lower temperature than direct observation. The use of the X-ray diffraction method indicates some changes at temperatures even considerably lower. This is illustrated in the X-ray diffraction diagrams represented in Fig. 3, which were obtained by Luyet, Tanner, Sager and Rapatz (1962) with thin layers of a 50% gelatin gel, cooled rapidly enough to permit the formation of transparent spherulites, and rewarmed slowly.

As shown in the first diagram, at -125°C , none of the 7 peaks indicated under "Pk. No." has arisen yet. At -60°C , an elevation, in the form of an inverted V, appears at the 2-theta angle of Peak 2; at -30°C , such elevations appear at the angles of Peaks 5 and 7; at -20°C , Peaks 1 and 3 are also arising; at -15°C , Peaks 1, 2, 3, 5 and 7 are quite well developed and Peak 4 is at an incipient stage; finally, at -10°C , all the 7 peaks are fully developed.

The fact that the 3 peaks which are the first to arise in the X-ray diagram of gelatin gels rapidly frozen and slowly rewarmed are common to cubic and to hexagonal ice crystals led Dowell, Moline and Rinfret (1962) to the conclusion that the ice formed in such gels at low temperatures is cubic ice and that it becomes transformed into hexagonal ice at higher temperatures. Changes of this sort were known to crystallographers: Fenner (1914) had studied such a conversion in SiO_2 ; Blackman and Lisgarten (1958), Dowell and Rinfret (1960), and Shimaoka (1960), among others, reported the transformation from cubic to hexagonal ice in the case of pure water.

On the other hand, Luyet, Tanner and Rapatz (1962) pointed out the following

* *cf.* Luyet *et al.*, 1962.

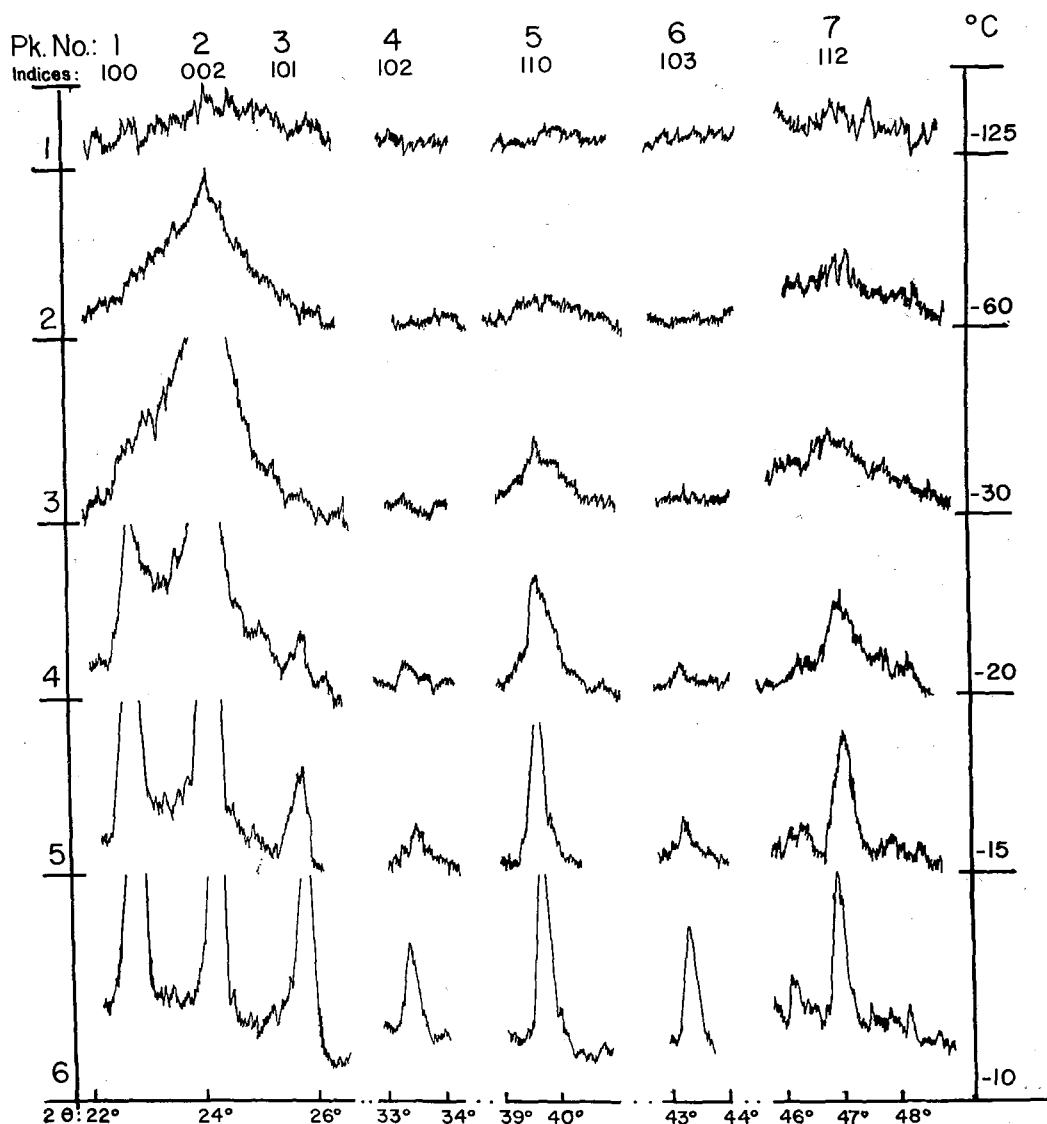


Fig. 3. X-ray diffraction diagrams of ice in gelatin gels of 50% concentration, frozen in thin layers by immersion in a bath at -150°C , and rewarmed successively to the temperatures indicated on the right side of each diagram. The order numbers of the angles, or peaks, are given in the top line, the indices on the second line, the order numbers of the tracings in the column at left, the rearming temperatures in the column at right, and the scale of two-theta angles underneath the tracings (reproduced from paper in press by Luyet, Tanner, Sager and Rapatz; with permission of Biodynamica)

features in their X-ray diagrams: (1) The three peaks common to the cubic and hexagonal systems do not arise alone, as a separate group, they are mixed with peaks which do not belong to the cubic system, such as Peaks 1 and 3; (2) There is no sharp transition from one group of peaks to another at a given temperature, the peaks arise gradually over a broad range of temperatures.

According to these investigators, the X-ray diagrams reported would be more adequately explained on the assumption that, at rising temperatures, the ice crystals grow preferably in some particular directions. Thus, if needles of ice develop first in the direction of the c -axis (the optical axis), they will produce Peak No. 2 by reflection on Planes 002 (the basal planes), as represented under A in Fig. 4; needles developing in the direction of the a -axis will produce Peak No. 5, by reflection on Planes 110 (B in Fig. 4); and needles developing in the direction of the d -axis (at a 30° angle from a) would produce Peak No. 1 by reflection on Planes 100. Preferential growth along the c - and a -axis would result in the formation of a slab, like that shown under D in Fig. 4.

A growth in preferred orientation (instead of a transition from cubic to hexagonal symmetry) does not exclude a recrystallization; the growth at -10°C of crystals large

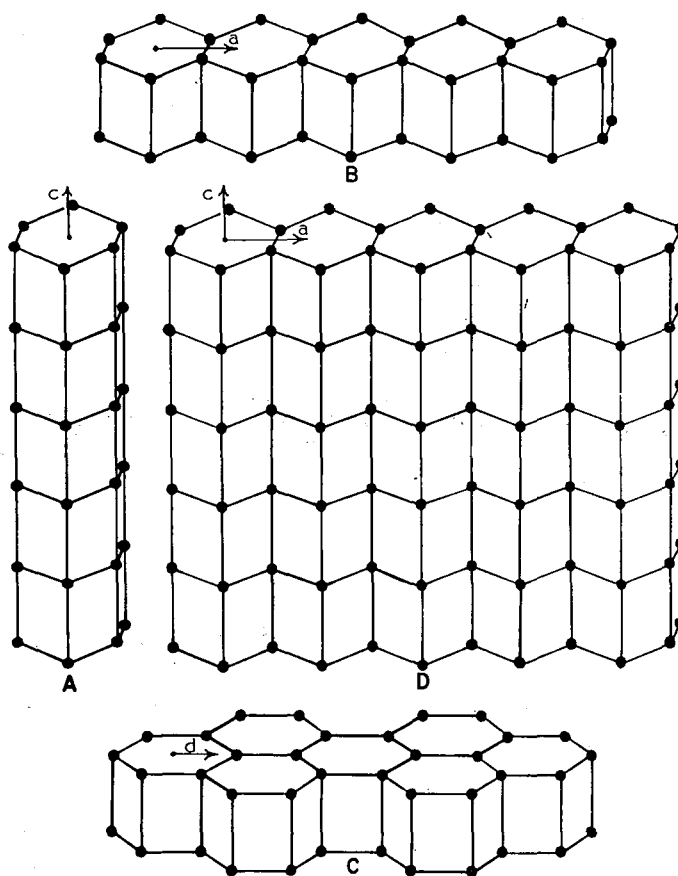


Fig. 4. Diagrams illustrating the structure of the needles and of the slab which one would obtain if hexagonal ice crystals would grow preferentially in some directions. The molecules of water are represented by dots; the molecules which form hexagonal rings are connected by lines, and so are the rings when piled up vertically. Diagram A: Needle formed when preferential growth is along the c -axis; Diagram B, when growth is along the a -axis; Diagram C, when growth is along a direction d at 30° from a . Diagram D: Slab formed when preferential growth is along the c - and the a -axes (from Luyet, Tanner and Rapatz, 1962; with permission of Biodynamica)

enough to reflect all the peaks may take place at the expense of small ones (thin needles or thin slabs) previously grown in preferred orientations.

It is of interest to note that longer exposures to a given temperature did not permit the development of those peaks which appeared only at higher temperatures. This observation is to be correlated with that reported in my other paper at this Conference, and illustrated in Fig. 7 of that paper, to the effect that a long exposure to a temperature a few degrees below that of recrystallization does not appreciably change the picture which, in that case, was detected by less sensitive methods of observation.

III. General Outlook on the Data Reported

The three series of determinations reported contribute to the clarification of a few questions in a long-range research program which consists in establishing, for solidified solutions of various concentrations of several substances, "phase diagrams" giving the temperatures at which the system becomes sufficiently unstable to permit (a) the glass transition (not discussed in this paper), (b) devitrification, (c) the resumption of an interrupted crystallization, (d) recrystallization, and (e) melting.

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