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Various Modes of Recrystallization of Ice

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Abstract

The term recrystallization has been applied to structural changes occurring in aqueous solutions solidified at low temperatures, in which the crystallizable water has either crystallized, or has remained amorphous, or is partly crystalline and partly amorphous. —These changes, most of which are illustrated in photomicrographs, are classified into four main types: (1) the abrupt turning opaque of the preparations (irruptive recrystallization); (2) the slow coarsening or their structure (slow-pace recrystallization); (3) the growth of some crystalline particles near the melting point (premelting recrystallization); (4) a transition from one crystalline structure to another (reorientative recrystallization). The first type comprises four subtypes classified on the basis of the conditions under which the opacity is produced and the kind of crystallization units affected. —The temperature at which irruptive recrystallization occurs depends primarily on the molecular weight of the solute and varies only slightly with its concentration. Slow-pace recrystallization occurs in the range between the temperature of irruptive recrystallization and the melting point. —The mechanism involved in the changes reported appears to consist in a transition either from the amorphous to the crystalline phase (a true devitrification), or from a partly crystalline to a more completely crystalline composition (a crystallization), or from one crystalline formation to another (a true recrystallization). The latter may take place in two ways: crystalline particles of a given size may grow larger, at the expense of small ones by migration of molecules from the small to the large ones (migratory recrystallization); or a reorientation may be involved, as in the transition from cubic to hexagonal ice (reorientative recrystallization).

I. Introduction

On several occasions, when I brought up for discussion with physicists the subject "recrystallization", I was asked what I meant. When I presented the facts, I generally found an interested audience to which many of the phenomena described appeared as new, as they could not be identified with those generally discussed in treatises of physics. A consultation of encyclopedic dictionaries indicated a rare use of the term recrystallization by physicists, except in some unrelated sense, such as, to designate a crystallization repeated for the purpose of purifying a product. The metallurgists, however, have been using the term to designate a process which is closely related to some forms of the phenomena that I am to discuss here. The subject of this lecture being, thus, one which has not been recognized as a distinct item in the field of physics, my first task is to relate the *facts* on which the notion of recrystallization is based. My lecture will then consist (1) in a presentation of the *factual data*, and (2) in a *discussion* of these data, in which an attempt will be made at obtaining an insight in the basic concepts involved.

Since the nature of the phenomena described is still to be established, I use the term "recrystallization" on a tentative basis, without commitment on its final retention,

although, in using it, I anticipate the conclusion of this paper, that the use of the term, in its broad sense, is justified.

Unless indicated otherwise, the findings to be surveyed are the result of investigations on aqueous solutions carried out by my collaborators and myself during the last 30 years.

Most of the observations reported were made on thin layers of solutions mounted between two cover glasses, and refrigerated by immersion in a precooled bath. Photographs or motion pictures were then made through our cryomicroscope assembly (developed by Luyet and Rapatz, 1957, and by Rapatz and Luyet, 1957).

II. The Fundamental Facts

Before presenting the facts about the structural changes grouped under the name "recrystallization", I will describe the main types of crystallization units which are to undergo the changes in question. The presentation of the facts will itself consist of two parts: a descriptive exposé of the changes encountered, and an account of the temperatures at which they occur.

PRINCIPAL TYPES OF CRYSTALLIZATION UNITS

The conditions under which a specimen is frozen, in particular the freezing rate, determine the crystalline pattern obtained. For the purpose of the present survey three characteristic patterns should be mentioned; they are shown, respectively, in 1, 2 and 3 of Fig. 1. When the rate of crystallization is low, one has well-formed hexagonal structures (Fig. 1-1), in which six axial columns of ice originate from a center of crystallization, at 60° angles from each other, and grow branches at 60° angles from them; then secondary branches arise at 60° angles from the primary, and so on. (One should note that, since we are dealing with solutions, the structure is not a solid crystal, but a dendrite bathed in a concentrated solution.) When crystallization is faster, the dendrite acquires an irregular structure. As shown in 2 of Fig. 1, the number of axial columns arising from the center is variable and so are the angles between them, and the regularity of the branching is not maintained. When the freezing rate is increased further, the number of axial columns arising from the center of crystallization is enormous and no branching can be distinguished (Fig. 1-3). The structure obtained is typically what the crystallographers call a "spherulite". I shall designate the three patterns described as: "regular dendrites", "irregular dendrites" and "spherulites".

At still higher freezing rates, the radii of the spherulites become so thin that they are no longer visible and the structure is transparent in ordinary light. In polarized light, between crossed polarizer and analyzer, it shows the Maltese cross, as illustrated in 4 of Fig. 1. Since the spherulites vanish out of view at high freezing rates, I named them "evanescent spherulites".

A study at higher magnifications of the structure of the spherulites showed the branching. Thus, the three crystallization units described have essentially the same structure; what differs is the regularity in the arrangement of the parts, the size of the parts and the frequency of the dichotomies.

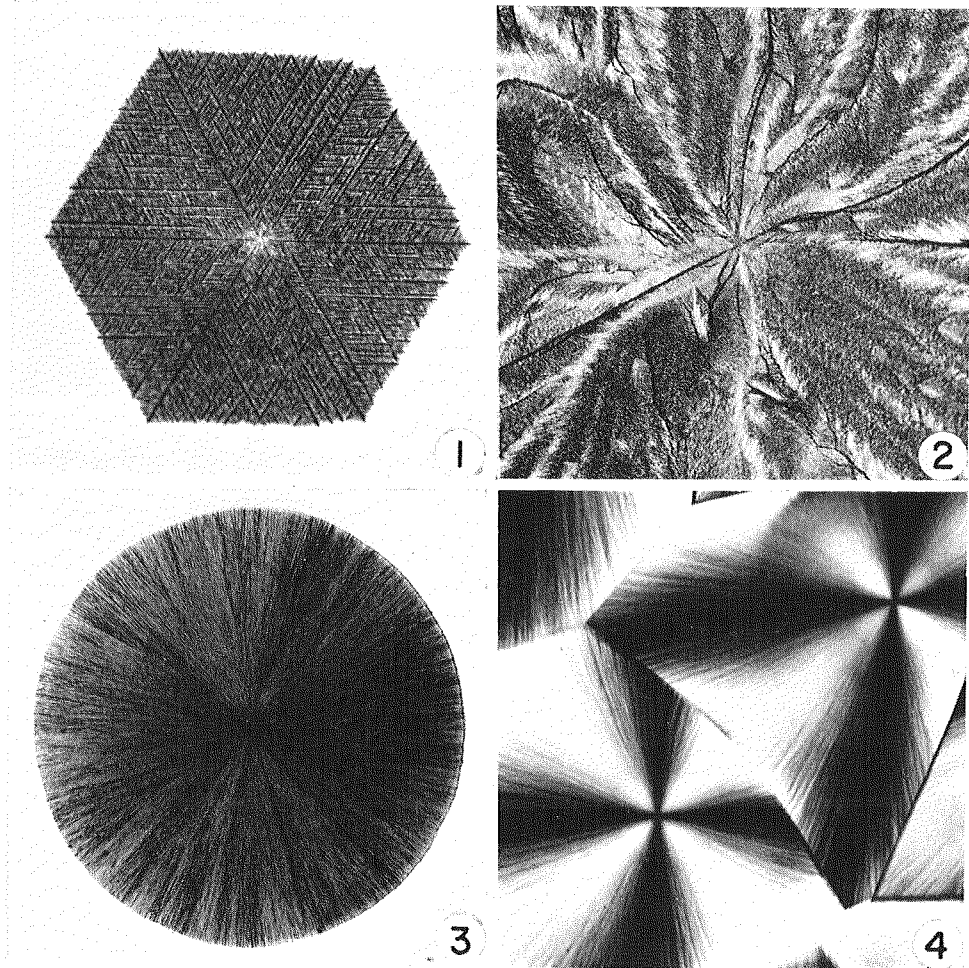


Fig. 1. The principal types of crystallization units obtained when glycerol solutions of various concentrations are frozen at various rates. $\times 95$. 1: Hexagonal form, 6M solution, -35°C ; 2: "Irregular dendrite", 1M solution, -60°C ; 3: Coarse spherulite, 6M solution, -60°C ; 4: "Evanescent" spherulite, 3M solution, -80°C (1 and 3 from Luyet and Rapatz, 1958; with permission of Biodynamica)

I. PRINCIPAL CHANGES OBSERVED IN FROZEN PREPARATIONS UNDER VARIOUS CONDITIONS

The changes to be examined will be classified into seven series. In the fourth series I gathered a variety of changes of which some are readily recognized as belonging to Series 1, 2 and 3, while others are not sufficiently known to be assigned to a particular category.

1. *The turning opaque, upon rewarming, of rapidly grown spherulitic structures*

As illustrated in 1 and 2 of Fig. 2, an evanescent spherulite (transparent area in 1) turns rather abruptly opaque (Fig. 2-2) when its temperature is raised to a certain value (-10°C in the case of gelatin solutions).

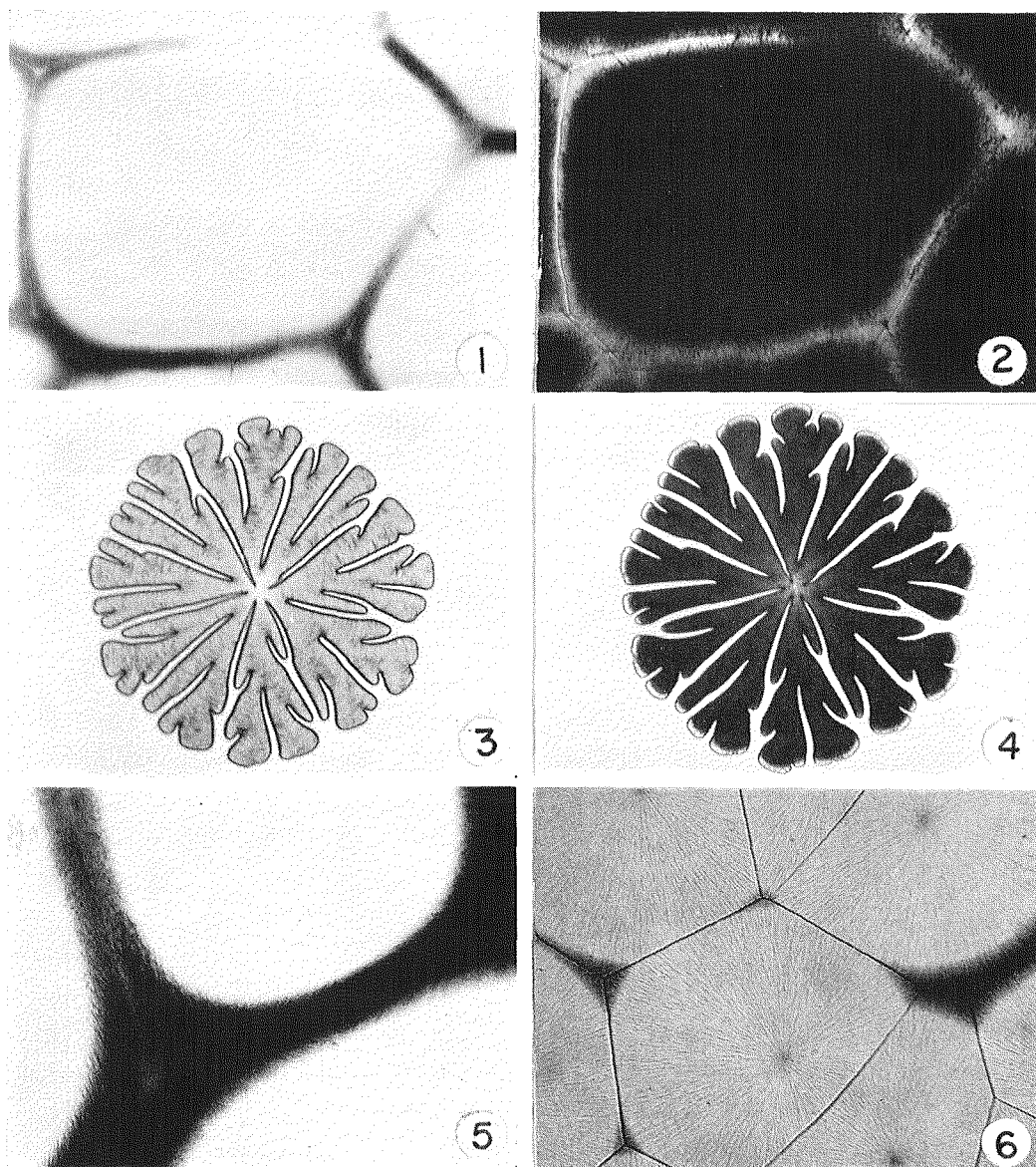


Fig. 2. The three main cases of formation of opacity clouds during the freezing or the rewarming of solutions. $\times 95$ 1: An evanescent spherulite (white area) formed in the freezing at -35°C of a 35% solution of albumin; 2: The same area as in 1 after the preparation had been rewarmed to -5°C ; 3: An irregular dendrite (rosette) formed in the relatively slow freezing, at -30°C , of a 50% gelatin gel; 4: The same rosette as in 3 after the preparation had been rewarmed to -10°C ; 5: Large opaque borders of evanescent spherulites developed during the freezing, at -30°C , of a 30% gelatin gel; 6: Development of dark areas at the meeting points of three spherulites during the freezing at -40°C of a 50% sucrose solution (3 and 4 from Rapatz and Luyet, 1959; 6 from Luyet and Rapatz, 1958; with permission of Biodynamica)

2. *The turning opaque, upon rewarming, of some slowly grown irregular dendrites*

The change just described in spherulitic structures takes place, under similar conditions, in irregular dendrites (such as the rosette represented in 3 and 4 of Fig. 2), when the temperature is raised to the same point as for the spherulites.

3. *The turning opaque, during cooling, of the borders of spherulitic structures*

The borderlines between two evanescent spherulites, and the areas where three or more adjacent units come in proximity or in contact, may turn opaque in the course of the cooling process, as shown in 1, 5 and 6 of Fig. 2.

4. *Miscellaneous cases in which specimens turn opaque under various conditions*

The behavior of solutions of various solutes, at various concentrations, subjected to rapid or slow freezing and rewarming, is very complex. In an attempt at a systematic study of that behavior, I tabulated (Fig. 3) the patterns obtained with gelatin gels of concentrations varying from 35 to 65%. The concentrations studied are given in Column 1, and the treatments applied are indicated at the top of the subsequent columns. These treatments consisted in: (a) freezing at a moderate rate in a bath at -30°C so that the crystallization units obtained be of the type irregular dendrites (Column 2); (b) freezing quite rapidly, in a bath at -100°C , so that the units obtained be evanescent spherulites (Column 3), although they are identifiable as such only at the lower concentrations; (c) rewarming to -30°C (Column 4); and rewarming to -10°C (Columns 5 and 6).

The facts reported in Fig. 3 can be classified as follows:

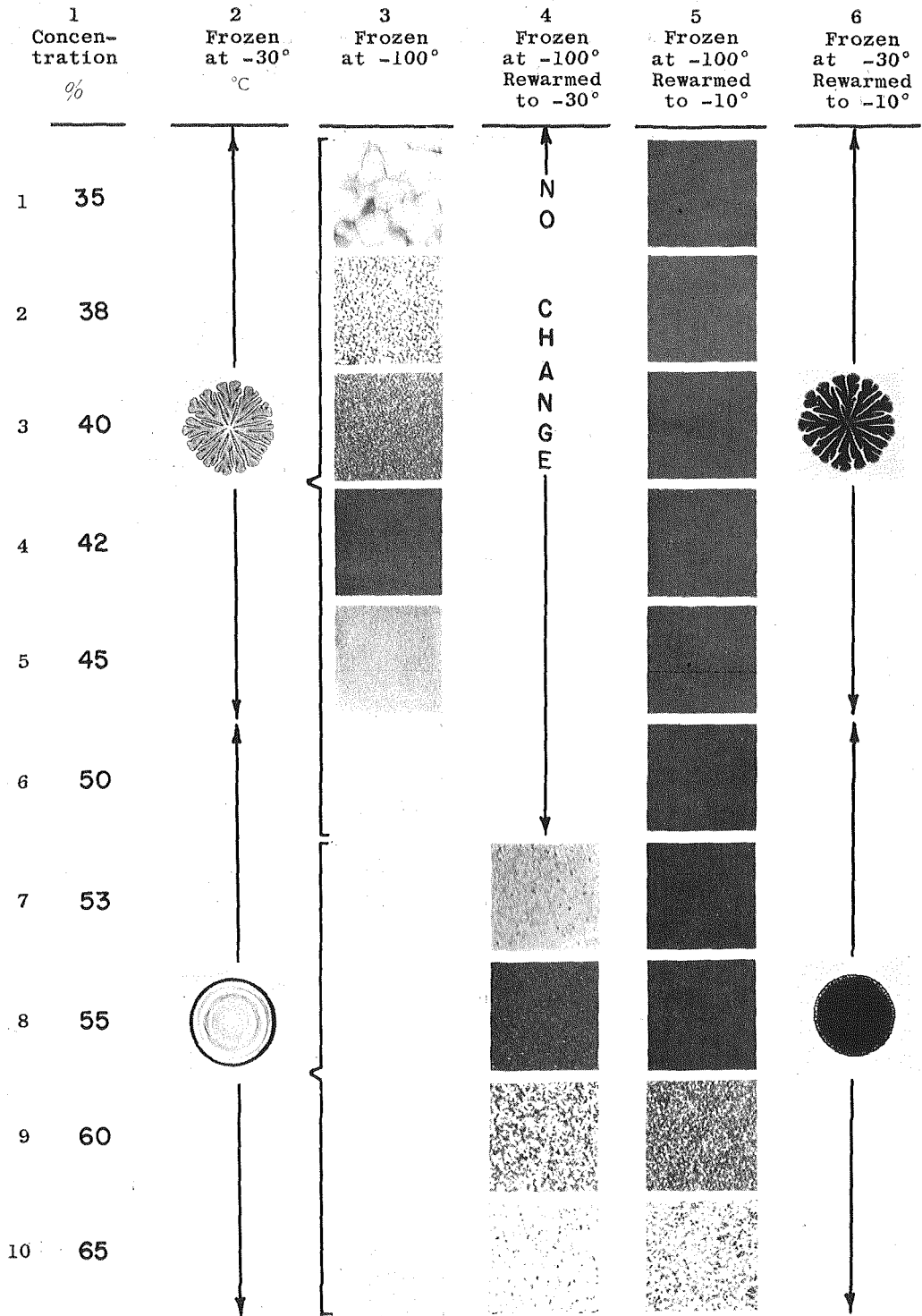
(A) *Cases in which the preparation turns opaque (six cases).* (1) when rapidly cooled solutions of concentrations varying from 35 to 40% are rewarmed to -10°C (Column 5, horizontal Rows 1 to 3); (2) when rapidly cooled solutions of 45 to 50% concentrations are rewarmed to -10°C (Column 5, Rows 5 and 6); (3) when slowly cooled solutions of 35 to 65% concentrations are rewarmed to -10°C (Column 6); (4) when a 42% solution is rapidly cooled by immersion in a bath at -100°C (Column 3, Row 4); (5) when a rapidly cooled 55% solution is rewarmed to -30°C (Column 4, Row 8); and (6) when a rapidly cooled 53% solution is rewarmed, first, to -30°C , and then, to -10°C (Column 5, Row 7). Another case, not represented in Fig. 3, should be mentioned, namely, when a 30% solution is rather slowly frozen at -25°C (see Fig. 6-3).

(B) *Cases in which the preparation turns partly opaque (four cases).* (1) when solutions of concentrations varying from 35 to 40% are rapidly cooled to -100°C (Column 3, Rows 1 to 3); (2) when a 45% solution is cooled rapidly to -100°C (Column 3, Row 5); (3) when a 53% solution, cooled rapidly to -100°C , is rewarmed to -30°C (Column 4, Row 7); (4) when 60 to 65% solutions, cooled rapidly, are rewarmed to -30°C and to -10°C (Columns 4 and 5, Rows 9 and 10).

(C) *Cases in which the preparation remains transparent (two cases).* (1) when a 50% solution is rapidly cooled to -100°C (Column 3, Row 6); (2) when 53 to 65% solutions are cooled rapidly to -100°C (Column 3, Rows 7 to 10). Another case, not mentioned in Fig. 3, should be added, namely, when solutions of concentrations higher than 65% receive any of the treatments used in this series of experiments.

5. *Slow coarsening of the structure at gradually rising temperatures*

Material frozen into irregular dendrites, which either has a finely granular structure,



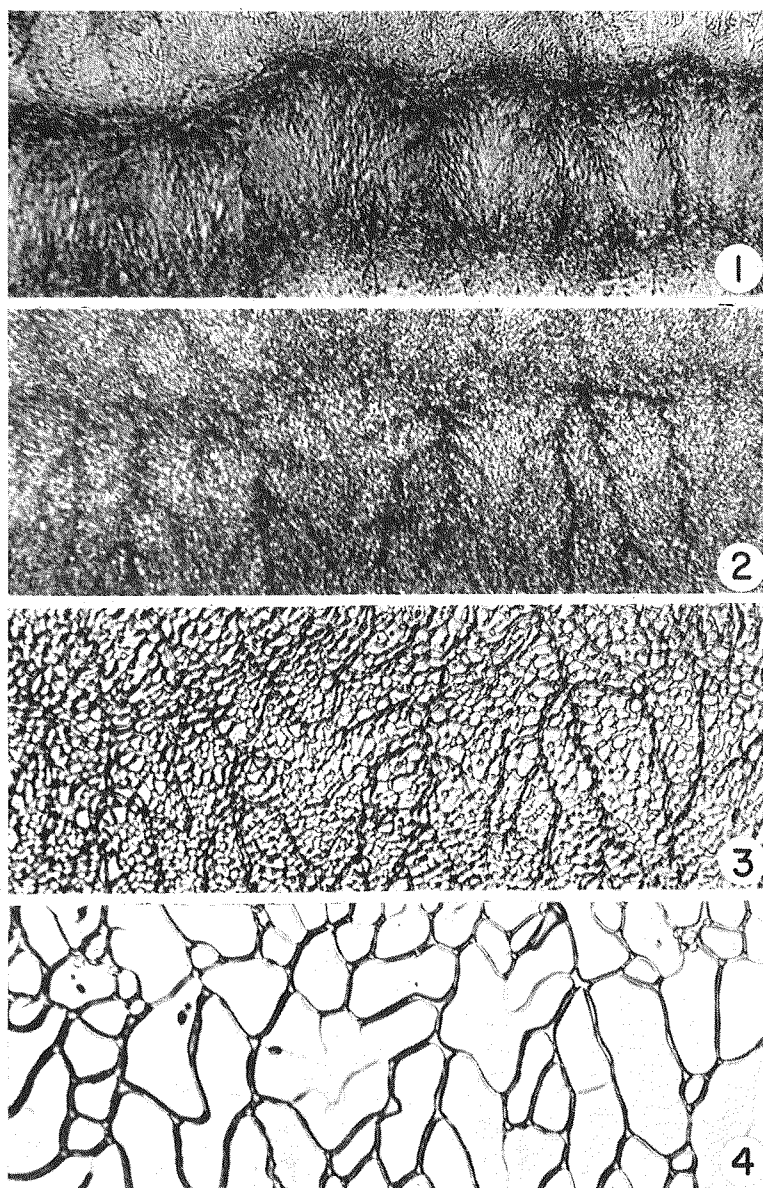


Fig. 4. Coarsening of the structure in a solution of 10% albumin rewarmed to various temperatures after having been frozen at -40°C . $\times 95$. 1: Specimen frozen at -40°C and warmed to -7°C ; 2: Same field as in 1 after the temperature was raised to -3°C ; 3: Same field after the temperature was raised to -2°C ; 4: Same field after the temperature was raised to -1°C (from Luyet, 1966; with permission of Biodynamica)

Fig. 3. Photomicrographs of the patterns of ice formation observed in gelatin gels of various concentrations (as indicated in Column 1), (A) after rapid freezing at -100°C (Column 3), and rewarming to -30°C (Column 4) or to -10°C (Column 5); or (B) after slower freezing at -30°C (Column 2) and rewarming to -10°C (Column 6). Magn.: $\times 37$, except for the balls in columns 2 and 5 which are magnified $\times 75$ (from Luyet, 1966; original data from Persidsky and Luyet, 1959; with permission of Biodynamica)

or in which no granularity can be detected, acquires slowly a coarser structure when the temperature is raised above a certain value. This is illustrated in Fig. 4, which represents a solution of 10% albumin frozen at -40°C and warmed to -7°C (Fig. 4-1), and further warmed, at a rate of the order of a degree per minute, to -3°C (Fig. 4-2), to -2°C (Fig. 4-3), and to -1°C (Fig. 4-4). In this latter photograph, the frozen specimen consists of large plates of ice (the white areas).

6. *Crystal growth taking place near the melting point*

When the ice from a frozen solution is melting, and the preparation is maintained at or near the melting point, one observes a growth of some of the larger particles at the expense of the small ones, which disappear. This is illustrated in Fig. 5, in which 1 and 2 show the transformation, in 10 minutes, of a preparation crowded with small ice

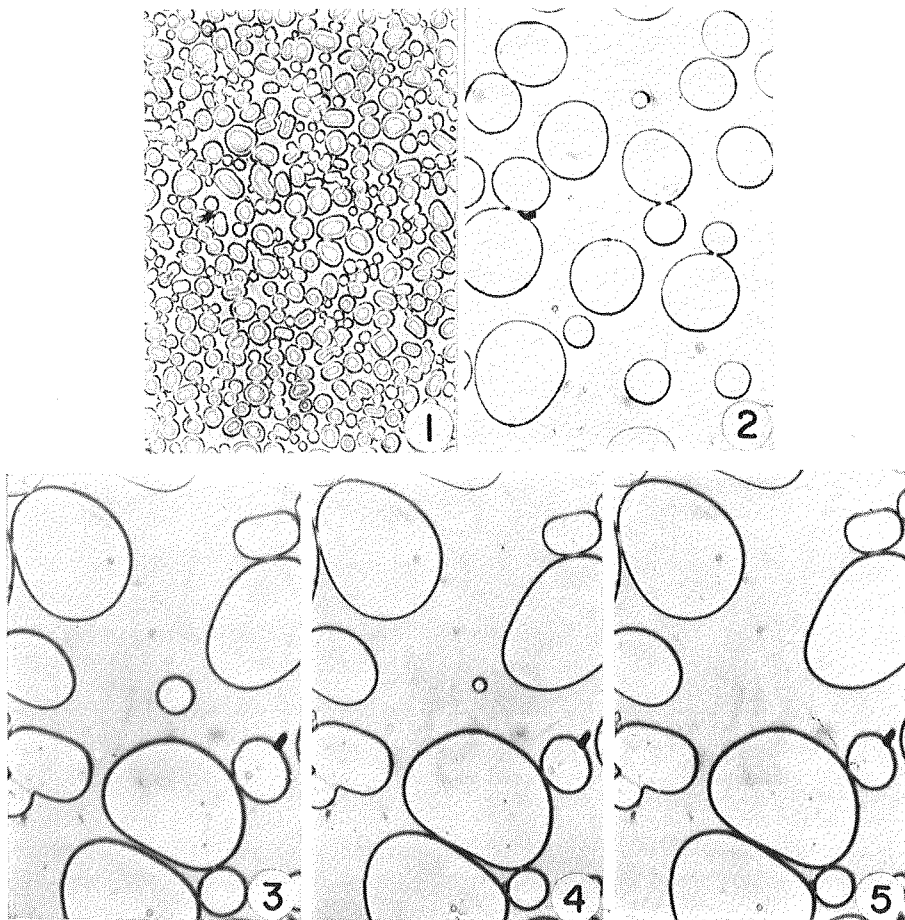


Fig. 5. Growth of large ice particles at the expense of small ones, in a solution of 10% albumin maintained close to its melting point. $\times 440$. 1 and 2: Two frames from a time-lapse motion picture, separated from each other by a time interval of 10 minutes. 3, 4 and 5: Three frames of a time-lapse motion picture, the first of which preceded the second by 20 seconds, and the third by 25 seconds (from a paper in press by Luyet, Gehenio and Sager; with permission of Biodynamica)

particles of various shapes, into one with a few large spheroidal particles, and 3, 4 and 5 show the gradual decrease in size and disappearance of small particles (such as the one in the center of 3 and 4).

A motion picture film (projected at the Conference) showed that the disappearance of a small particle near a large one coincides with a growth and bulging out of the large particle toward the small one, indicating that the two phenomena, melting of one particle and growth of the other, are correlated.

The growth of large particles and the melting of small ones, and the opposite process, the melting of large particles and the growth of small ones, were also shown in motion pictures to alternate when the temperature was alternately raised and lowered by means of a microheater in the preparation.

Another motion picture film, taken by Drs. MacKenzie and Rapatz of our Laboratory, showed a passage from polyhedral ice crystals to particles of spheroidal shape, and *vice-versa*, when the temperature was, respectively, raised and lowered. The changes were alternated several times in succession.

7. *Changes interpreted as indicative of a reorientation of the crystalline structure*

Several investigators have reported that pure water crystallizes into cubic ice at very low temperatures and that, upon warming, a reorientation of the structure takes place, resulting in the formation of hexagonal ice. Dowell, Moline and Rinfret (1962) reported the same change in the case of gelatin gels. (Since the conclusion that cubic ice is changed into hexagonal ice involves an interpretation of the factual data, I wish to point out that only the changes reported that is, the X-ray or electron diffraction data could be classified under the title "Fundamental Facts", not their interpretation.)

II. TEMPERATURES OF OCCURRENCE OF THE CHANGES DESCRIBED

1. *Solutions frozen into evanescent spherulites.* The temperatures at which solutions frozen into evanescent spherulites (Fig. 2-1) turn opaque (Fig. 2-2) on being rewarmed are only slightly affected by the solute concentration and are greatly dependent on the nature of the solute; they are apparently related to its molecular weight. Thus a 1 M sucrose solution turns opaque at -31.4°C , and a 2 M at -31.8°C , whereas the temperature of the change for glucose (2 M) is -40.6°C , and that for raffinose (1 M) is -27.2°C

Table 1. Temperatures at which thin layers of aqueous solutions of concentrations between 25 and 50%, rapidly cooled, become intensely opaque in one minute upon being rewarmed

Solute	Temp. $^{\circ}\text{C}$	Solute	Temp. $^{\circ}\text{C}$	Solute	Temp. $^{\circ}\text{C}$
Hemoglobin	-3.5	Gelatin*	-11.5	Dextrose	-38
Soluble Starch	-5.0	Polivinylypyrrolidone	-14.5	Glycerol	-58
Albumin	-5.3	Raffinose	-25.4	Ethylene Glycol	-63
Dextrin	-9.9	Sucrose	-30.5	Acetamide	-65
				Formaldehyde	-72

* A thin layer of gelatin solution turns intensely opaque in one minute at -11.5°C , and in a few seconds at -10°C . This last figure will be the one generally used in the present paper

(for details, see Luyet, 1939).

I summarize in Table 1 the essentials of the information now available on the temperatures at which thin layers of solutions, of concentrations between 25 and 50%, of solutes of a wide range of molecular weights, turn opaque in one minute. For convenience, I will tentatively designate the figures tabulated as "recrystallization temperatures".

2. *Solutions frozen into irregular dendrites.* These crystallization units (for instance, the rosette shown in Fig. 2-3) turn opaque (Fig. 2-4) at the same temperature as the evanescent spherulites.

3. *Solutions turning opaque during cooling.* The dark borders of the spherulites are wider when the temperature of the freezing bath is closer to the "recrystallization temperature". They may become so wide that they occupy the entire spherulitic areas, that is, the entire preparation becomes opaque. This gradual increase in opaque areas is illustrated in Fig. 6 in three cases in which the freezing bath temperature was -40 , -30 and -25°C (1, 2 and 3, respectively).

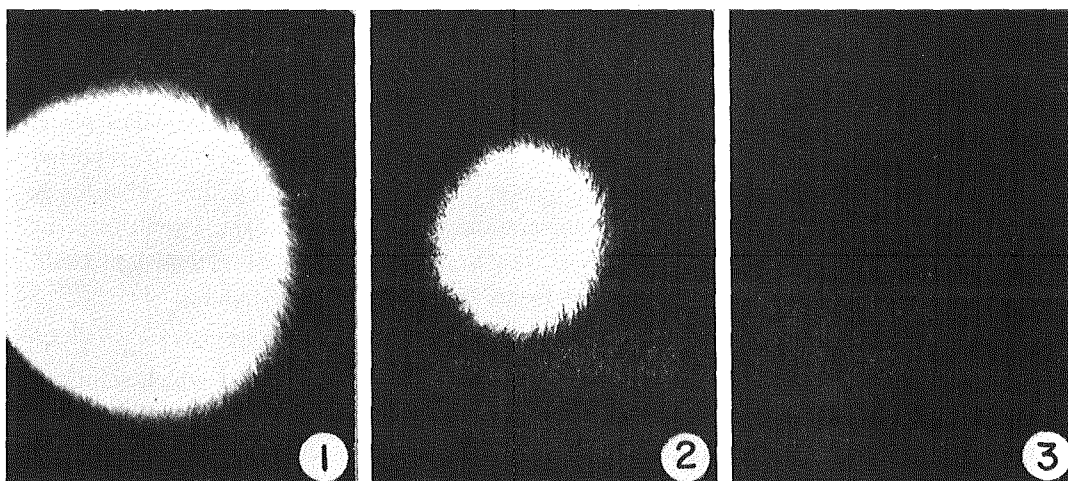


Fig. 6. Decrease in transparent areas (white areas in photographs) in preparation 100 micra thick of a 30% gelatin gel, when the freezing temperature approached the "recrystallization temperature". —Freezing bath temperatures: 1, -40°C ; 2, -30°C ; 3, -25°C . $\times 85$ (from Luyet and Rapatz, 1958; with permission of Biodynamica)

4. *Solutions subjected to various treatments.* The temperatures at which the specimens subjected to the various treatments reported in Fig. 3 turn opaque, are indicated on the top of the columns. One should note that gelatin gels of different concentrations, cooled rapidly, become opaque when rewarmed to two different temperatures, -10 and -30°C . (The temperatures at which the changes took place in one minute were actually -11.5 and -37°C ; to produce the changes in a shorter time, we set the baths at, respectively, -10 and -30°C ; see Gehenio and Luyet, 1959.)

5. *Preparations acquiring slowly a coarser structure.* The transformation described in Fig. 4 begins to take place when the slowly rising temperatures reach the values given in Table 1 (that is, the values at which transparent spherulites turn opaque); then it continues at an accelerated pace in the range between those values and the melting

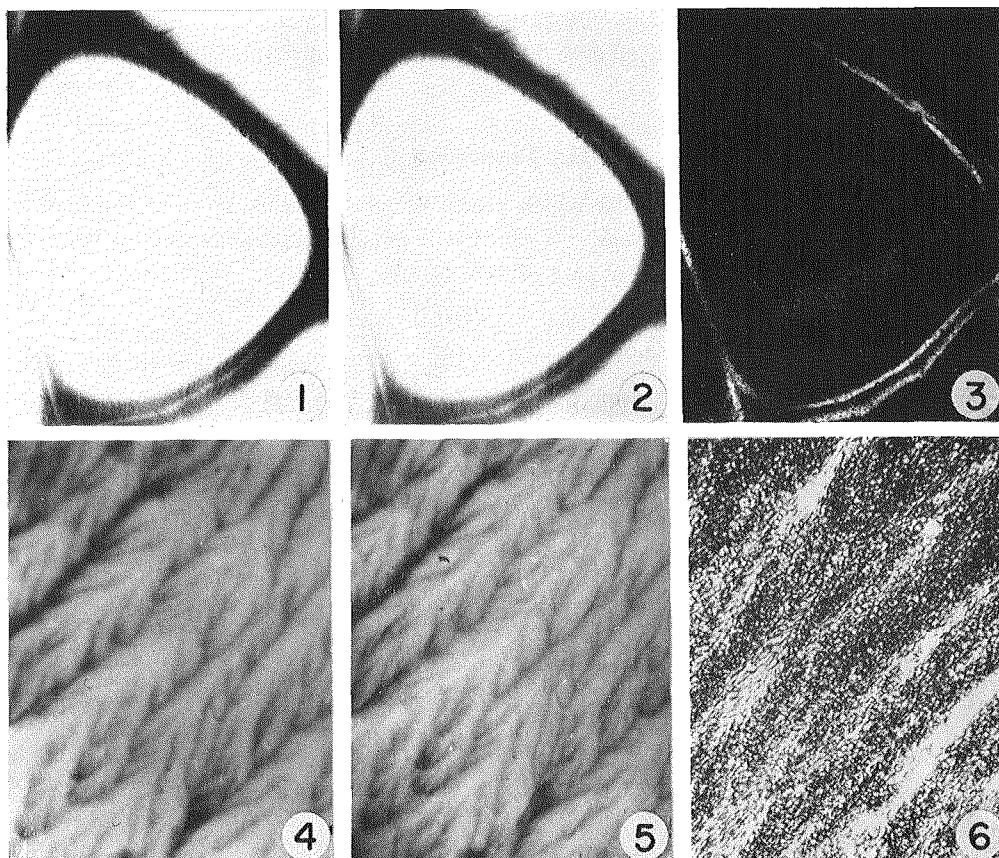


Fig. 7. Changes produced in frozen gelatin gels by short exposures at or above the "recrystallization temperatures", and absence of change after long exposures to temperatures a few degrees below. $\times 60$. 1: Preparation consisting of a 30% gelatin gel, frozen at -40°C into transparent spherulites (white areas with dark borders). 2: Same field as in 1, unchanged after a 5-hour exposure to -15°C . 3: Same field, after the spherulites have turned opaque, following a one-minute exposure to -10°C . 4: Preparation consisting of 10% gelatin, frozen at -20°C into irregular dendrites. 5: Same field as in 4, unchanged after a 5-hour exposure to -15°C . 6: Same field, after the preparation has turned granular, following a 1-to-2-minute exposure to -5°C

point. Figure 7 illustrates the facts (1) that, a few degrees below the temperature of the onset of opacity, transparent spherulites remain transparent for hours, while, above that temperature, they turn opaque in times of the order of seconds (1, 2 and 3 of Fig. 7), and (2) that crystallization units of the type irregular dendrites maintain their fine-grain structure for hours a few degrees below the same temperatures, and acquire a coarser grain in a relatively short time above those temperatures (4, 5 and 6 of Fig. 7).

6. *Crystal growth near the melting point.* The phenomena described in Fig. 5 take place one tenth, or a few tenths of a degree below the melting point.

7. *Transition from cubic to hexagonal ice.* The temperature at which the transition is reported to have occurred in pure water varies from -80 to -100°C (Blackman and Liggarten, 1957; these authors survey the earlier literature on the subject). According

to Dowell and Rinfret (1960), the rate of the transformation is related exponentially to the temperature; what is done in one and a half hour at -80°C would take about 17 hours at -100°C .

III. Discussion

I shall examine first a process which seems to take place in most of the changes reported, "migratory recrystallization". Then, I will consider separately each of the seven series of changes listed in the first part of this lecture.

I. MIGRATORY RECRYSTALLIZATION

The first and outstanding change reported, the turning opaque of transparent spherulites (Series 1 in the list), has been shown to result from a transformation of invisible ice particles or spears (too small to be seen) into particles of the order of a few micra,

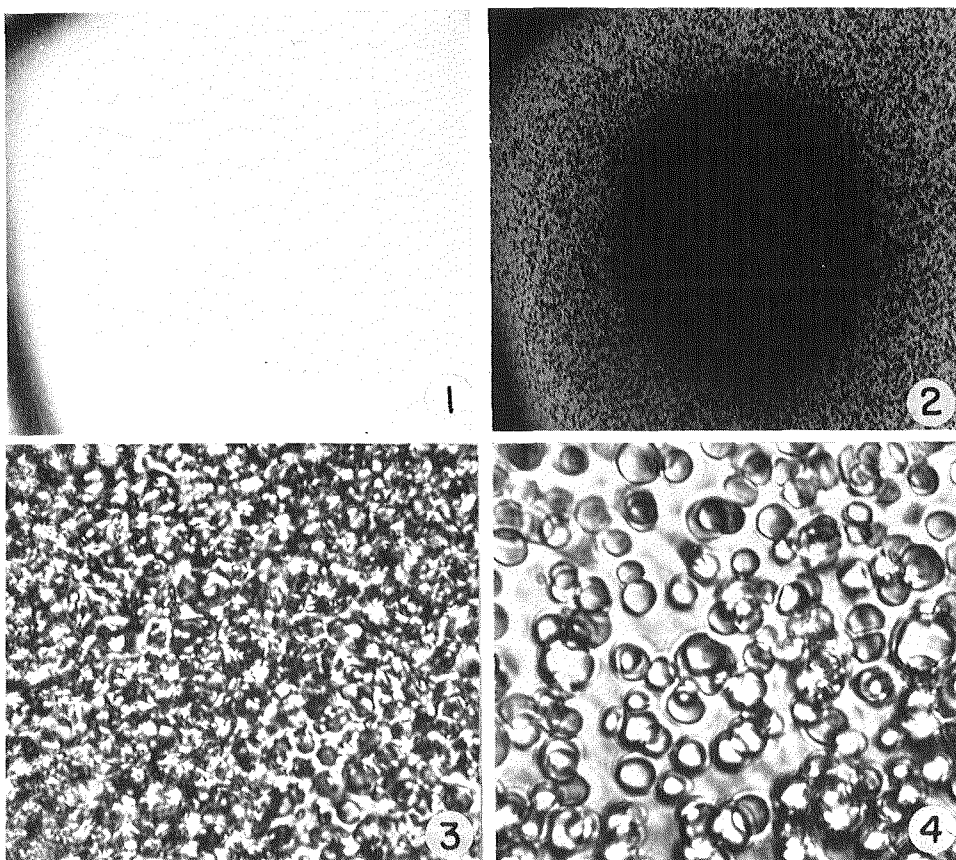


Fig. 8. Structure of the opacity cloud and changes that it undergoes at rising temperatures. 1: Portion of an evanescent spherulite (the white area) formed in the freezing, at -35°C , of a 30% gelatin gel; parts of the opaque borders are shown at left. 2: Area represented in 1, after the temperature had been raised to -11°C . 3: Magnified view of the opacity cloud formed in the central region of 2. 4: Same area as in 3, after the temperature had been raised to -3°C . Magn.: 1 and 2, $\times 100$; 3 and 4, $\times 990$ (from the files of Luyet and Rapatz)

which make up the opacity clouds. This is illustrated in Fig. 8, where Phot. 1 shows an evanescent spherulite in the transparent state (white area), Fig. 8-2 the same field after the formation of the opacity cloud (the dense central area), and Fig. 8-3 a portion of the cloud at a higher magnification. Thus, the phenomenon as a whole consists in a passage from a large agglomeration of small particles into a smaller agglomeration of larger particles. The turning opaque of slowly grown units, such as that shown in 3 and 4 of Fig. 2 (Series 2), and the darkening of the borders of the spherulites during cooling (Series 3) shown in 1, 5 and 6 of Fig. 2 involve probably a change of the same nature and of the same order of magnitude. The coarsening of the grain and the subsequent formation of plates of ice represented in Fig. 4, and the increase in size and decrease in number of particles when the temperature is raised in the specimen shown in 3 and 4 of Fig. 8 (Series 5) are themselves direct illustrations of the passage from a large number of small particles to a smaller number of large blocks; and even more so is the change occurring at the melting point, illustrated in 1 and 2 of Fig. 5 (Series 6). Although the transformation seems to be of the same general nature in these five series of events, the particles are of quite different orders of magnitude, as shown in the photographs cited.

What all these cases apparently have in common is the instability of particles of a given size at a given temperature. The smaller particles having a higher energy content become unstable at rising temperatures. The process which has important applications in metallurgy, is designated by the professionals in that field as "recrystallization" and is described graphically as follows: "a few of the crystals slowly grow larger at the expense of many smaller crystals" (Holden, 1963). Specifically, in the case of ice, the higher vapor pressure at the surface of smaller particles causes the migration of the molecules from them to the larger ones. Dorsey (1948, p. 412), speaking of ice, called this phenomenon, "migratory recrystallization". Although it may not give the final and complete answers to our questions, migratory recrystallization seems to play a major role in the changes reported.

II. ANALYSIS OF THE VARIOUS CHANGES REPORTED

1. *The turning opaque, upon rewarming, of rapidly grown spherulitic structures*

In the case of evanescent spherulites rewarmed after rapid freezing, other phenomena than migratory recrystallization probably take place. A study of the changes in volume undergone by solutions of polyvinyl pyrrolidone of various concentrations, in the course of rapid cooling followed by rewarming, indicated that an appreciable quantity of water was prevented from crystallizing during cooling, and crystallized during rewarming. The findings are plotted in Fig. 9. The percent by weight of the solution which was changed into ice during cooling, I_C , is the amount below the curve connecting the triangular marks; the percent which was left in the amorphous state after rapid freezing and which crystallized upon rewarming, I_R , is the amount between that curve and the one connecting the circular marks. The data reported in Fig. 9 indicate (1) that a part of the water does not crystallize during the rapid freezing, and (2) that it does crystallize during the rewarming, when the temperature reaches the "recrystallization" point.

The opacity cloud resulting from the growth of ice particles to visible size may,

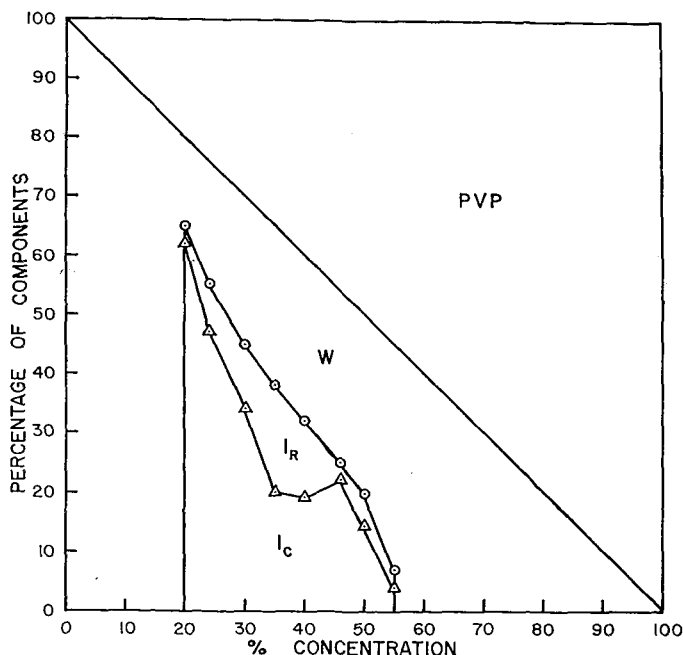


Fig. 9. Diagram showing the percent by weight (1) of the ice formed during rapid cooling, I_C , (2) of the ice formed during rewarming I_R , (3) of nonfrozen water W , and (4) of solute (PVP), in solutions of the initial concentrations given in abscissa (from a paper in press by Luyet, Vehse and Gehenio; with permission of Biodynamica)

thus, be formed in three ways: (1) preexisting crystals may grow larger at the expense of the material left amorphous in the previous rapid freezing; the process would then be a resumption of an interrupted crystallization; (2) new crystals may originate in the amorphous material and grow at its expenses; the process would then be a true devitrification; (3) the larger of the previously formed crystals may grow further at the expense of the small ones; which is the process described as migratory recrystallization.

Using the term recrystallization in its broad sense, which includes the resumption of an interrupted crystallization, I designated as "*irruptive recrystallization*" the abrupt change in opacity of the sort described here, occurring upon rewarming, in solutions which had undergone a previous crystallization.

2. *The turning opaque, upon rewarming, of slowly grown irregular dendrites*

The changes of the type represented in 3 and 4 of Fig. 2, which are very similar to those represented in 1 and 2 of Fig. 2, are probably explainable on the same basis, although we have no evidence that some material remains amorphous after the relatively slow crystallization of the water into irregular dendrites (rosettes in this case).

Like in the preceding series (under No. 1) the change would be an "*irruptive recrystallization*".

3. *The turning opaque, during cooling, of the borders of spherulitic structures*

Apparently, the heat of crystallization released while the spherulite is formed (that is, during rapid cooling) is enough, mostly along the borderlines of two or three adjacent

units where growing spears of ice converge, to raise the temperature locally to the point at which the opacity clouds develop (the temperatures given in Table 1).

To test this interpretation, we froze layers of 30% gelatin gels at temperatures 30, 20 and 15 degrees below that at which the opacity cloud would appear upon rewarming, and we observed that the dark bands between adjacent spherulites were broader at higher temperatures, until, at the highest temperature mentioned (15 degrees below that of recrystallization, at -25°C) the entire preparation turned opaque. This gradation is shown in the three photographs of Fig. 6 (Luyet and Rapatz, 1958).

Whereas the turning opaque of preparations described in Series 1 and 2 was "induced" by rewarming, that described here, which takes place during cooling, appears to be a self-induced phenomenon and is called "*spontaneous irruptive recrystallization*".

4. *Miscellaneous cases in which specimens turn opaque under various conditions*

Let us now examine the 14 cases of changes undergone by specimens treated in various ways, as stated in the description of the changes of Series 4. The 14 cases (12 of which are represented in Fig. 3) were classified into three categories, depending on whether the preparations (a) turned entirely opaque, (b) turned partly opaque, or (c) remained transparent.

(a) *Preparations turning entirely opaque (7 cases).* *Cases 1 and 2:* Solutions of 35 to 40%, and of 45 to 50% concentrations, exposed to -100°C , turning opaque when rewarmed to -10°C (Columns 3 and 5, Rows 1 to 3 and 5 to 6 of Fig. 3). These cases are interpreted as being typical representatives of *irruptive recrystallization, induced* by the rewarming to -10°C , of spherulites grown at -100°C . The spherulites, well identifiable in polarized light, at lower concentrations, become so numerous and so small from 38 to 45% that they can no longer be recognized as such by that criterion. But their behavior is practically the same as that of spherulites.

Case 3: Rosettes or balls, slowly grown at -30°C , turning opaque when rewarmed to -10°C (Columns 2 and 6). The process is classified as *irruptive recrystallization of slowly grown units* (rosettes or balls).

Cases 4 and 7.—Case 4: A 42% solution turning opaque during cooling to -100°C (Column 3, Row 4). The change is interpreted as being a *spontaneous irruptive recrystallization*. The dark borders of the numerous spherulites apparently cover the entire preparation and make it solidly black.—*Case 7:* a 30% solution, turning opaque during cooling to -40 , -30 or -25°C (illustrated in Fig. 6). The change is classified in the same category as that of Case 4, though only a few large spherulites were involved in the spontaneous recrystallization.

Case 5: A 55% gel, exposed first to -100°C , becoming opaque when rewarmed to -30°C (Fig. 3, Column 4, Row 8). This case probably belongs to a quite different category. The fact that the preparation turns opaque at -30°C , while those of 35 to 50% concentration did not change at that temperature, suggests a different type of crystallization units. The fact, furthermore, that, at high concentrations and low temperatures, the rate of crystal growth becomes very low suggests that the crystallization units, which may be balls, have to be warmed to -30°C to grow sufficiently to become visible in an appreciable time. If so, the process leading to the formation of opaque preparations

would be a mere *acceleration of the growth process*. Whereas, at concentrations, from 35 to 50%, the spherulites could grow fully at -100°C until their growth was stopped by neighbour spherulites, thus leaving no unoccupied territory, the balls formed at -100°C in 55% gels grew only to a certain diameter, leaving unoccupied territory between them. In the former case, resumption of growth (at -10°C) would be at the expense of inter-radial material within the spherulites, in the latter (at -30°C), at the expense of the material in the unoccupied territory, between the balls.

Case 6: A 53% preparation, exposed to -100°C , then to -30°C , then to -10°C , becoming completely opaque at this latter temperature (Column 5, Row 7). The crystallization units, assumed to be of the type balls, would grow to a limited extent at -30°C , rendering the preparation quite opaque (Column 4, Row 7), and these would undergo an *irruptive recrystallization* (of slowly grown units, the balls), rendering the field entirely opaque (Column 5, Row 7).

(b) *Preparations turning partly opaque (4 cases)*. *Cases 1 and 2*: Solutions of 35 to 40% and of 45% concentrations, turning partly opaque when cooled to -100°C (Column 3, Rows 1, 2, 3 and 5 of Fig. 3). The partial opacity seems attributable to the darkening of the borders of the spherulites (*spontaneous irruptive recrystallization*). The gradual increase in opacity from 35 to 42% would be due to a gradual increase in the number of spherulites; at 45% their number would still be higher than at 42%, but, on account of the corresponding decrease in size, many of them would be too small to be seen.

Cases 3 and 4: Solutions of 53% and of 60 to 65% concentrations, exposed to -100°C , turning partly opaque when rewarmed to -30°C (Column 4, Rows 7, 9 and 10), and turning more opaque when rewarmed to -10°C (Column 5, Rows 9 and 10). The partial opacity acquired at -30°C is probably due to a *resumption of growth* by crystallization units of the type balls which were formed at -100°C but could not grow at that temperature and remained invisible. The degree of opacity is apparently related to the number of units which could reach visible size. Upon a further rewarming to -10°C , the crystallization units darken (*irruptive recrystallization of slowly grown units*) but the background, never nucleated, remains transparent.

(c) *Preparations remaining transparent (3 cases)*. *Case 1*: A 50% solution cooled rapidly to -100°C and rewarmed to -30°C (Columns 3 and 4, Row 6). The preparations exposed to -100°C would be filled with fully grown spherulites, too small to be seen; at -30°C nothing would happen since the water *between* the spherulites is already frozen; at -10°C the preparations would turn black as a result of recrystallization and/or of the crystallization of the water left unfrozen *within* the spherulites.

Case 2: Solutions of 53 to 65% concentration cooled to -100°C (Column 3, Rows 7 to 10). The preparations would contain quite large numbers of crystallization units of the type balls which grow too slowly at -100°C to become visible, but are able to grow to a certain degree when the temperature is raised to -30°C (in the 55% gel, they would be just of the number and size to fill the preparation and render it entirely opaque). The spaces between the balls, which were never nucleated, would remain transparent even at -10°C .

Case 3: Solutions of concentrations higher than 65% (not represented in Fig. 3).

The material would remain entirely transparent, as no structural change would take place in it, no matter what treatment it received.

The processes encountered in the many cases of Series 4 which have been reviewed are: *irruptive recrystallization, induced or spontaneous, of rapidly or of slowly grown units* and *resumption of an interrupted crystallization* of either the type spherulites or the type balls of crystallization units.

5. *Slow coarsening of the structure at gradually rising temperatures*

The changes reported in Fig. 4-2, 3 and 4, and in Fig. 7-6 would be accountable primarily by the process described as migratory recrystallization. The change would begin, upon rewarming, at the temperature that I designated as "recrystallization temperature", (of which I listed a few in Table 1), it would proceed at an accelerated pace at higher temperatures and become precipitous near the melting point. To distinguish this process, which is relatively slow over the major part of its range, from the irruptive process discussed above, I called it "*slow-pace recrystallization*".

6. *Crystal growth taking place near the melting point*

The growth of large crystals at the expense of small ones, near the melting point, illustrated in Fig. 5, is a clear case of *migratory recrystallization*. To distinguish it from other recrystallization phenomena which may be fundamentally of the same nature, but occur at different temperatures, I designated it as "*premelting recrystallization*".

The passage from spheroidal to polyhedral, or from polyhedral to spheroidal forms at different temperatures, so well illustrated in the motion picture film by MacKenzie and Rapatz (1966) is probably attributable, to a considerable extent, to the differences in heat transfer due to the different geometrical configuration of corners and rounded surfaces, as analyzed by Vogel (1921).

I wish to note that migratory recrystallization may tell only a part of the story. The multiple processes that I assemble under the name of premelting recrystallization have apparently several characters in common with those reported by others, under various denominations, such as, regelation, coalescence, sintering, ripening, formation of colloidal ice, formation of quasifluid interfacial film on ice crystals (*cf.*, in particular, Barnes, 1928, p. 7; Jellinek, 1959, 1961; Kingery, 1960; Nielsen, 1964).

7. *Changes interpreted as indicative of a reorientation of the crystalline structure*

The transition from cubic to hexagonal ice at rising temperatures, reported by several investigators in the case of pure water, has been claimed to take place also in solutions, in particular, in a 50% solution of gelatin (Dowell, Moline and Rinfret, 1962). Luyet, Tanner and Rapatz (1962) who also investigated, by X-ray diffraction, the same solution, proposed a different interpretation of the data. But, since this problem is to be examined in the other paper (Luyet, 1967), I will not discuss it any further here. At present, we consider "*reorientative recrystallization*" in solutions as a possibility.

IV. Supplementary Notes

Recent investigations revealed some new aspects of the recrystallization phenomenon or suggested new approaches to its study. I shall mention here briefly three such investigations.

(1) The method of differential thermal analysis permitted us to distinguish two steps in the process, in the case of a 45% solution of glycerol: (a) a resumption of an interrupted crystallization at about -112°C and (b) a recrystallization proper around -60°C (Luyet, Rasmussen and Kroener, 1966).

(2) Determinations of the dielectric constant of a solution of 38.4% PVP, at various temperatures, suggested that the recrystallization temperature may correspond to an incipient melting (Amrhein and Luyet, 1966).

(3) Studies with the freeze-drying microscope (developed by Dr. MacKenzie, 1964) of the changes occurring during the sublimation of the ice in frozen solutions, indicated a "collapse" of the structure when the temperature of the specimen reached the recrystallization point (MacKenzie and Luyet, 1965).

The first two of these investigations were presented in some details in the other paper (Luyet, 1967 a) in this volume; the third has been briefly outlined in a paper in the other volume of the Proceedings of Sapporo Conference (Luyet, 1967 b); the reader will find more information about it in a survey paper by Dr. MacKenzie (1965).

V. General Conclusion

Altogether, in this survey, we encountered two main processes: (1) a passage from crystalline particles of one size into those of another, and (2) a resumption, during rewarming, of a crystallization interrupted during cooling. There is also the possibility of a direct passage from the amorphous to the crystalline state in the absence of pre-existing crystallites, a true devitrification, although we have no evidence that such a passage does actually occur in solutions. In fact, the only solutions in which we could prevent the formation of crystalline ice were those of very high concentrations (generally above 60%) and, in those, no change took place upon rewarming.

The first of the two processes mentioned is a recrystallization in the proper sense of the word; the second could be called a recrystallization in the sense that it is a resumption of crystallization.

Accepting that broad definition, I will summarize the analysis of the changes observed or reported by distinguishing four types of recrystallization: irruptive, slow-pace, pre-melting and reorientative, and by subdividing four kinds of the type irruptive: induced or spontaneous, affecting rapidly frozen or slowly frozen ice formations, as shown in Table 2.

Table 2. Types of recrystallization

(A) Irruptive
(a) Induced or spontaneous
(b) After rapid or after slow freezing
(B) Slow-pace
(C) Premelting
(D) Reorientative

A process which may play a predominant role in each of the first three types (A, B and C) is "migratory recrystallization", which may be defined summarily as the growth of large crystalline particles at the expense of smaller ones.

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