CRYSTALLIZATION

THEORY AND PRACTICE

by Andrew VanHook

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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on Chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

ACKNOWLEDGMENTS

The following figures and quotations have been taken from current literature and other sources. The author wishes to thank the separate authors, publishers and sources for permission to reproduce them.

Acta Crystallographica, published by the International Union of Crystallography: Quotation p. 277.

Analytical Chemistry, published by the American Chemical Society; Figures 4-4 and 6-12.

Canadian Journal of Chemistry, published by the National Research Council; Figures 3-20 and 4-20.

Chemical Reviews, published by Williams and Wilkins Co.: Figures 6-41 and 6-42.

Industrial and Engineering Chemistry, published by the American Chemical Society: Quotation p. 20, Figures 2-13, 4-11, 6-11, 6-19, 6-20, 6-21, 6-22, and Tables 6-3 and 6-5.

Journal of Agricultural and Food Chemistry, published by the American Chemical Society: Figures 6-43 and 6-44.

Journal of the American Chemical Society, published by the American Chemical Society: Figures 6-33 and 6-34.

Journal of Chemical Physics, published by the American Institute of Physics: Figures 3-18, 3-19, 3-21 and 4-6.

Journal of the Franklin Institute, published by the Franklin Institute: Figures 6-30 and 6-31.

Journal of Physical Chemistry, published by the American Chemical Society: Figure 4-17.

National Bureau of Standards Journal of Research, published by the U. S. National Bureau of Standards: Figure 4-5 and Table 4-6.

Nature, published by Macmillan and Co., Ltd: Figure 6-2.

Philosophical Magazine, published by Taylor and Francis, Ltd.: Figure 3-15.

Proceedings of the Royal Society, published by the Royal Society: Figure 1-17.

Quarterly Reviews (London), published by the Chemical Society: Quotation p. 103.

Review of Scientific Instruments, published by the American Institute of Physics: Figure 5-7.

Transactions of the American Geophysical Union, published by the American Geophysical Union: Figure 1-4.

Transactions of the Faraday Society, published by the Faraday Society: Figures 3-24, 3-25, 5-12, 6-17, and Quotation p. 274.

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Bell Telephone Laboratories: Figures 5-8, 6-35 and 6-40.

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Dekeyser, W., and Amelinckx, S., "Les Dislocations et les Croissance des Cristaux," 1955, published by Masson & Cie., Paris: Figure 3-16.

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Dorr Co.: Figures 5-17 and 5-18.

General Electric Research Laboratory: Figures 6-37, 6-38, 6-39 and 6-45.

Harshaw Chemical Co.: Figures 6-23, 6-24, 6-25, 6-32 and 6-36.

Honolulu Iron Works Co.: Figure 5-18.

International Salt Co.: Figure 6-15.

Linde Air Products Co.: Figures 6-27, 6-28 and 6-29.

Matz, G., "Die Kristallisation in der Verfahrensrechnik," 1954, published by Springer-Verlag: Table 4-8.

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Struthers-Wells Co.: Figures 5-24, 5-25, 5-26 and 5-27.

Weissberger, A., "Technique of Organic Chemistry," 1952, published by Interscience Publishers, Inc.: Figures 5-1, 5-4 and 5-5.

PREFACE

The beauty of crystals has always fascinated man. While their perfection and form are completely described and catalogued by means of the established laws of classical and X-ray crystallography, the same cannot be said about their generation and growth. Although considerable experimental observation and empirical explanation accumulated during the last part of the nineteenth century and beginning of the twentieth, activity in this field then waned. It was soon revived, however, by interest in the production of large monocrystals. This was especially evident at the "Discussions on Crystal Growth" held by the Faraday Society in 1949 at Bristol. The current state of both theoretical and practical interests is indicated by the symposia, books, and reviews given in the Appendix.

It was originally intended to review the entire subject of crystal growth in considerable detail in the present work. However, the appearance of Buckley's book, as well as that of Matz, rendered this unnecessary, so that the original plan was drastically revised to emphasize recent theories (Chapter 3) and to describe principal crystallization processes (Chapter 5) and industries (Chapter 6). It is believed that the data presented in Chapter 4 represent the variety and form that are available in the scientific literature and it is hoped that the references cited in this chapter, as well as in the others, will serve as a good lead for anyone desiring further information and details. It will be obvious that Chapter 1 was written by a chemist for chemists. Chapter 2 indicates only those basic ideas considered to be important for an effective appreciation of the subsequent chapters.

Many friends have helped me directly or indirectly in the writing of this book. Dr. Stookey has contributed the section on nucleation in glass. Dr. H. Klug and my son W. Alexander have read the manuscript in its entirety, while Messrs. Dunning, Honigmann, Powers, Turnbull, J. VanHook, and Walker have read and corrected separate parts. The Sugar Research Foundation Inc. has supported many of the author's investigations on sugar crystallization which were the original stimulant for considering a more general work.

My daughters, Suzanne and Jane, and others have helped with the onerous job of typing from a longhand manuscript. Many figures and some quotations were copied from current literature and are so indicated. However, I wish to make here a general acknowledgment and to express my gratitude to the many friends who have helped me in so many ways in the preparation of this monograph.

Leicester, Mass.
August, 1961

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Chapter 1

HISTORICAL REVIEW

INTRODUCTION

It is only natural to speculate on the birth and growth of crystals while yet admiring the perfection of the final form as found in nature or fashioned otherwise. While this latter aspect of crystals has evolved into the science of crystallography since the early work of Steno (1669), Rome de l'Isle (1772), and Haüy (1801), the development of the kinetic features has by no means been as steady and exact. As P. R. Rowland[52] expressed it in a remark at the Faraday Society Discussion on crystal growth in 1949, "The subject is still in the alchemical stage." Other workers[37, 136] have expressed a similar opinion (but perhaps not as strongly) in pointing out the need for a complete dynamic theory of crystal growth.

In any event, there is a vast accumulation of observations and empirical explanations regarding the generation and growth of crystals under many circumstances. Much of it is unsuited for theoretical use except in qualitative ways and it seem necessary to the author that much more discriminating information will be required for fuller tests of existing theories and those to come.

The alchemists and early chemists and crystallographers recognized many of the well-known features of the crystallization process.[218] Geber (720–813) mentions the purification of many salts by recrystallization, and Caesalpinus (1600) observed that sugar, saltpeter, alum, and the vitriols separated from solution in typical, easily recognized forms. Biringuccio (1540) gave detailed instructions for the leaching of saltpeter and its purification by recrystallization. He also indicated that the purity of the product depends to a great extent upon the purity of the mother liquor from which it is obtained. Somewhat later, Glauber (1604–1670) made frequent reference to the use of crystallization in the separation and purification of "Glauber's salt" (Sal Mirabile).[152] This salt was later observed to supersaturate very readily and much of the early work on this phenomenon was conducted with it.

Robert Boyle recognized, in 1691, that crystal habit may be modified by the rate of deposition from solution, and at about the same time it was discerned that crystals were frequently more regular and characteristic when their growth was slower, the solvent more fluid, and the substance more soluble. The first recorded recognition of the not uncommon possibility of supercooling water was also noted at this time by Fahrenheit.[70, 252] He was able to chill water 6 to 8°F below the normal freezing point, and noted the release of heat when ice formation ensued. This was confirmed by Joseph Black, in 1761, who reaffirmed the earlier implied requirement of a supercooled or supersaturated condition for the initiation of growth of a solid substance.

It was not long afterward that the first systematic description of the crystallization process appeared. This was the very extensive work of Lowitz,[157, 270] in which he investigated and described most of the now well-known features of supersaturated solutions. Although Lowitz dealt primarily with salt solutions, he recognized the similarity between supersaturation of a solute and supercooling of a liquid. He emphasized the common occurrence of these conditions—situations that are even currently overlooked in spite of frequent notice[52, 53, 166] to the contrary. Lowitz pointed out that the ability to form supersaturated solutions varied considerably with different salts and also depended upon the history and treatment in any particular case. For instance, previous heating of the solution ("curing"), or removal of the first crystals formed, often increased the subsequent degree of supercooling or supersaturation that could be attained. From his experiments on the addition of fragments of different crystals to particular salt solutions, he recognized a specificity of nucleating agents over and above the powerful initiating influence of dust particles. He found that only $NaNO_3$ or $Na_2SO_4 \cdot 10H_2O$ deposited, respectively, from a mixed supersaturated solution upon seeding with the separate salts. The identity of crystallizing salt and nucleating agent was not required in all cases.

This observation, added to those of Rome de l'Isle (1772), Le Blanc (1784), Vauquelin (1797) and others, prepared the way for the generalizations of Mitscherlich[34, 173] in 1819 regarding isomorphism and epitaxy. Lowitz also regarded glasses, strong syrups, and the vitreous products of fused salts as matter in the supercooled or supersaturated condition. This same worker[267] has also been credited with the discovery of the use of carbon for the purification of sugar, saltpeter and other solutions, thereby improving their crystallizing behavior.

Gay-Lussac[90] confirmed and extended many of Lowitz's observations in his studies of the separation of a wide variety of salts (Na_2SO_4, Na_3PO_4, Na_2CO_3, alums, $NaNO_3$, $Ba(OH)_2$, $H_2C_2O_4$, K_2SO_4, NH_4Cl, etc.) and gases from water solutions. He also extended the supercooling of water in bulk to −10 to −12°C. At the same time Schweigger[249] made the significant observations that previous filtration of supersaturated solutions increased the resistance to subsequent crystallization, that a magnetic field had no effect on the extent of supercooling, and, perhaps most significant of all, that a seed or nucleus must be of a certain size in order to initiate crystallization. This first concept of a critical-size nucleus was studied in much detail later on by Wilhelm Ostwald,[188] and it occupies a prominent role in most of the theories of crystal growth.

One of the first of many early papers on the Na_2SO_4–H_2O system was reported by Zis in 1815. He[281] recognized that sodium sulfate aqueous solutions could be supersaturated simultaneously with respect to both the anhydrous and the hydrate salts. This pioneer work was followed by the very intensive investigations of Löwel,[156] and still later by the papers of Goskgnski (1851), Selmi (1851), Dess, and other workers[188] on the same system as well as those of $MgSO_4$, Na_2CO_3 and the alums. The excellence of Löwel's data is indicated in Figure 1-1 where some of his values[75] are compared with more recent ones.[115] The metastable relationships of the two hydrates are evident and Löwel pointed this out by the fact that a solution saturated at 18°C showed a crystal of the heptahydrate rather than the stable decahydrate when cooled to 8 or 9°C. Ostwald credits these observations as basic to the formulation of his Law of Stages. Löwel also appreciated the powerful catalytic effect of the dust of the atmosphere in inducing

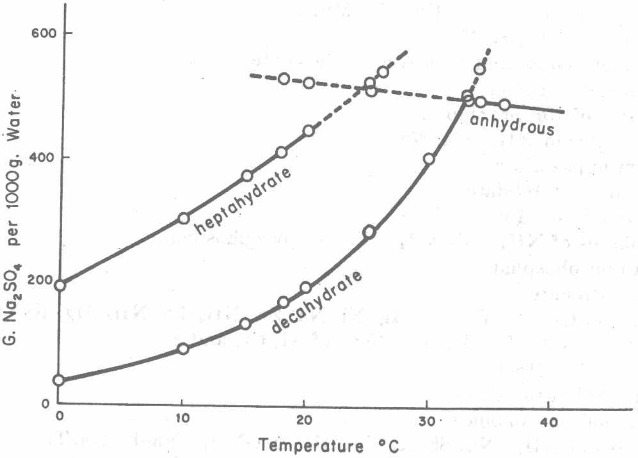

Figure 1-1. Na_2SO_4-H_2O system; illustrating the excellence of Löwel's data.
o and dotted lines—Löwel's values[75]
Full lines—later values[115]

crystallization in many supersaturated solutions, as had Lowitz[157] and also Lieben.[154] These observations were soon confirmed and extended by Violette.[263]

There now ensued a period of very active investigation, stimulated largely by the work of Gernez[91] in Paris. Gernez' early work continued the pattern of qualitative studies of previous investigators, while his later work introduced quantitative measurements into this field. For the first part he repeated much of the previous work on the causes of crystallization of sodium sulfate. Then, from observations on the behavior of over 100 different salts which form supersaturated solutions readily, he compiled a list of 27 groups within which reciprocal crystallization occurs. This original list is given in Table 1-1.

This list of Gernez' stimulated a flood of papers during the last third of the 19th century. Many of these were concerned with the question of what

TABLE 1-1. GERNEZ' LIST OF RECIPROCALLY CRYSTALLIZING SALTS.[91]

1. Acetates of NH_4, Ba, Ca, Co, Mg, Mn, Pb, Na, Sr, Zn, K
2. Nitrates of NH_4, Ag, Ca, Co, Cu, Mn, Sr, U, Zn
3. Nitrites of Pb, K
4. Arsenates of K, Na
5. Benzoates of K, NH_4
6. Borates of NH_4, Na
7. Sodium carbonate
8. Chlorates of Ag, Ba, Na, Sr
9. Chlorides of Sb, Ba, Ca, Cu, Mg, Mn, Fe
10. Nitrates of NH_4, K, Na
11. Sodium chromate and potassium dichromate
12. Formates of Na, Sr
13. Hydrates of Ba, Sr, chloral
14. Thiosulfates of NH_4, Ca, Na
15. Sodium hyposulfate
16. Ammonium molybdate
17. Ammonium oxalate
18. Phosphates of NH_4, Na-NH_4, Na; Na pyrophosphate
19. Potassium phosphate
20. Sodium selenate
21. Sulfates of Co, Cu, Fe, Be, Mg, Ni, Na, Zn; NH_4–Fe, NH_4–Mg, K–Ni, Zn–Mn; $KHSO_4$, NH_4, Th, K, Na, alums of Al, Cr, and Fe
22. Na_2SO_3, NH_4HSO_3
23. K and Na hydrosulfides
24. Sodium sulfoantimonate
25. Tartrates of NH_4, Na, Sb–K, Sb–NH_4, Na–NH_4, Na–K, Na–Tl
26. Citric acid and racemic tartaric acid
27. Mannite, lactose and sucrose*

* The present author has been unable to confirm this particular reciprocity.

salts would start and grow in which solutions, etc. The work of de Boisbaudran,[24] among others, indicated that certain demands of isomorphism of the Mitscherlich type were required for reciprocal nucleation and growth in solution, although many exceptions were noted. Especially disturbing was the fact that sodium formate and sodium valerate, which are almost isomorphous with sodium acetate, do not nucleate and grow in these solutions, or vice versa.

Many polemics started over such confusing observations and while no definite conclusions were reached (nor do we yet know the complete answer to all these questions[193]), it is obvious from many of these early papers that a liberal interpretation of what constitutes isomorphism is necessary (epitaxy, *vide infra*), and that surface energy considerations are most significant in determining the generation and growth of nuclei in supersaturated solutions.

The second phase of Gernez' work dealt with the linear rates of growth of sulfur (which had been observed to supercool readily by Michael Faraday in 1826[71]) and phosphorus from their melts. According to Tammann,[240b] the leading exponent of such measurements, Gernez was the first to make measurements of this kind. Gernez' data for the linear crystallization velocity of yellow phosphorus (m.p. 44. 2°C) are given in Figure 1-2. These results do not indicate the usual tendency of the crystallization velocity to reach a maximum and then decrease; but then neither do more recent and accurate measurements on this same substance.[196] These investigations of Gernez clearly indicated for the first time the significance of a crystallizing potential and some of the kinetic factors involved in the crystallizing

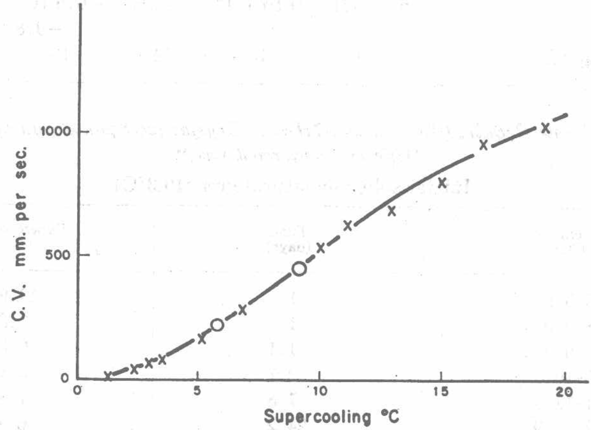

Figure 1-2. Crystallization velocity of phosphorus.[91]

process. Intensive speculations on these aspects of the crystallization of undercooled melts and supersaturated solutions were stimulated further by the work and theories of de Coppet,[48] who contributed and argued in the literature for 35 years.

de Coppet's basic observations were that there appears to be a limit to which supersaturated solutions and supercooled melts remain stable and that the adjustment of such labile systems depends upon the size of the sample being observed. His data suggest that the limits of supersaturation under ordinary conditions of observation do not depend greatly on the initial concentrations (at least for highly soluble substances) but do vary with the time (Table 1-2).

The observations represented in Table 1-2 were made in large tubes. In small tubes the duration of supersaturation is increased considerably in almost inverse proportion to the mass of the solution or melt. Othmer,[189] later, did not find this to be so. de Coppet extended his observations over exceptionally long periods. For instance, his sodium bromide solution took 2½ years to crystallize when in large vials, yet smaller amounts required over 4 years to exhibit crystallization when supercooled to the same extent of 15 degrees or more. Salol was maintained in a highly supercooled condi-

TABLE 1-2

(A) *Supersaturations Sustained by Sodium Sulfate Solutions.*[48]

Na_2SO_4/100 water	—	35	30	25	20
Saturated with respect to the heptahydrate at, °C	19.3	13.3	10	5	0
Crystallization observed at, °C	5 to 5.4°	0 to 1.4°	−4.35	−6.5 to −9.8	−10.4 to −11.5
Supercooling, °C	14	13	14	13	11

(B) *Time Required for $Na_2SO_4 \cdot 7H_2O$ to Crystallize Spontaneously at Different Supercoolings.*[48]

(Initial solution saturated at 19.3°C)

Temp. (°C)	Time (days)	Supercooling (°C)
5–5.9	1	13.8
8–8.9	1	10.8
9–9.9	1.1	9.8
10–10.9	2.1	8.8
11–11.9	7.8	7.8
12–12.9	24.2	6.8

tion for 6 years; and many of the supersaturated solutions prepared in de Coppet's first investigation (1872) were still intact at the time (1907) of his last review and report.*

To de Coppet, the results of his experiments at once suggested a rather simple explanation of the formation of crystal embryos via ordinary collisions. He had no reason to alter this opinion in his last work, even in the face of considerable criticism, principally from the pen of Wilhelm Ostwald. The principles of de Coppet's interpretation were adopted by Tammann,[240] Othmer,[184] Jones and Partington,[130] Kornfeld,[142] Gopal,[96] and others. These principles gradually assumed the form of what is usually referred to as the "Homogeneous Theory of Nucleation."[63] In effect, the theory suggests that crystal embryos are the result of multiple collisions which result in stable nuclei which then continue to grow. The theory considers these centers of growth entirely a matter of chance and thus demands that any supercooled melt or supersaturated solution, no matter how small the degree of supercooling, will adjust to its proper equilibrium condition provided sufficient time elapses for the formation of the first nucleus. It is on this score that many later experimentalists and current theories take exception.

To illustrate the random nature of the nucleation process we may cite a typical example from Tammann (Ref. 240b, p. 240). In 50 crystallizations of piperonal he observed a dispersion of 19.44 about the mean time value. The dispersion about 50 throws of 6 dice was 19.40. This expedient of comparing observation with actual trials of chance operations was introduced by Othmer and Kornfeld after recognizing that agreement with straightforward probability theory was frequently incomplete.[21, 102] Later investigations found the distribution frequency curves to be normal when a sufficient number of observations were made. Figure 1-3 illustrates this. This figure is from the work of Dorsch and Hacker[62] and is a typical example of over 5,000 observations of the spontaneous freezing temperature of supercooled water droplets of various sizes. The form of these curves certainly suggests the fortuitous nature of spontaneous freezing. This, however, does not necessarily signify a homogeneous collisional process, but may equally well indicate fortuitous inoculation with motes which serve

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* There seems to be no particular difficulty in preserving supercooled melts and supersaturated solutions for appreciable periods of time.[171] One finds frequent reference to such cases in the literature. The author has several sealed ampules of sodium acetate solutions which were prepared to be saturated at 35°C over 13 years ago and have since been kept at room temperatures without crystallizing. He also has several pure sucrose syrups which have been maintained without crystallizing at a supercooling of 20 to 25°C for over three years. It seems that highly impure solutions are even more reluctant to crystallize.