Recent Developments In Separation Science

Volume I

Norman N. Li, Sc.D.

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Editor:
Norman N. Li, Sc.D.
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PREFACE

This book, in two volumes, is meant to be a reference book on the postgraduate and professional level. It discusses recent developments in the science and technology of separation and purification. Although there are several books of selected topics on separation methods, this is the first comprehensive reference book which covers a wide range of topics that are of notable importance and timely due to new developments and a high level of current interest.

Volume I of the book discusses such topics as absorption, chromatography, crystallization, microcapsules, adsubble methods, chemical complexing, parametric pumping, molecular sieve adsorption, enzyme-membrane systems, immobilized solvent membranes, and liquid surfactant membranes; whereas Volume II focuses on the topics of extraction, filtration, heatless adsorption, hydrometallurgical extraction, interfacial phenomena, separation of gases by regenerative sorption, various polymeric membrane systems, such as electrodialysis, ultrafiltration, reverse osmosis, gas and liquid separations by selective permeation through polymeric membranes, and the origin of separation systems. The last topic, as a special feature of interest, provides an analysis of the genesis and development of new separation techniques.

The unusually broad nature of separation science and technology demanded the expertise that could only be provided through multiple authorship; and some of the authors are actually the original inventors of the separation techniques discussed in their respective chapters. Although the subject matter treated in each chapter is, in general, the author's research work and his critical review of the current state of the art, the authors had complete freedom in choosing the particular important areas to be emphasized. As a result, some chapters treat the related chemistry or mathematics in more detail than others, and some deal more with the engineering and economics aspect of a separation process. Each chapter, therefore, possesses its own special feature and appealing points. However, because of the limited space in the book, even the most important topics in the authors' views could not be treated in great detail, and many less important topics had to be merely mentioned or commented on briefly. As a remedy, all of the authors have provided an excellent list of references at the end of each chapter for the benefit of the interested readers, and detailed author and subject indexes have been provided at the end of each volume.

I would like to express my sincere appreciation to the authors and the Staff of The Chemical Rubber Co. for their efforts in making these volumes possible. Finally, I would like to thank my wife, Dr. Jane Li, for her assistance in reviewing some of the mathematical treatments in both volumes and in preparing the author and subject indexes.

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Norman N. Li, Sc.D. is a senior member of the research staff in the Corporate Research Laboratories of Esso Research and Engineering Company. He has numerous scientific publications and patents on topics of crystallization, extraction, blood oxygenation, enzyme membranes, water treatment, liquid membranes, and polymeric membranes. Of the many patents he holds, seven alone deal with the basic invention and various applications of liquid surfactant membranes. He was a consultant on gas permeation through polymers for the Apollo project. He has given lectures at many universities and research laboratories and has served as chairman of Gordon Research Conference on Separation and Purification and several symposia on separations for the American Institute of Chemical Engineers.

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DEVELOPMENTS IN MELT CRYSTALLIZATION
G. R. Atwood

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INTRODUCTION

Without question, the utility and scope of crystallization, particularly melt crystallization, are growing rapidly, possibly exponentially. A unit process once carried out more as an art than a science, crystallization has yielded to systematic study of ever increasing sophistication and proficiency. The quantitative aspects of the parameters involved are being understood and incorporated into the improved design of separation and purification systems.

This chapter will not constitute a review of the field. First of all, a competent review would go well beyond the limitations of space available here. Furthermore, there are many excellent reviews published periodically in a number of domestic and foreign journals. *Industrial and Engineering Chemistry* in particular publishes an excellent annual review, usually divided into two or more successive parts. For a broad discussion of the field prior to 1967 we can recommend *Fractional Solidification,* edited by Zief and Wilcox.[1]

It will be our intent here to consider the past and current trends in the field using, by way of example, only a fraction of the pertinent literature. We will further restrict our discussion to the crystallization of organic chemicals, and principally with respect to their separation and purification. The melt crystallization of metals constitutes a separate field of study in itself, as does also the consideration of inorganics. The basic principles of all these fields in terms of thermodynamics and phase equilibria are the same, but the phenomenology differs, due primarily to the different types of binding forces involved. The electrostatic forces in inorganics are the strongest, and these are for the most part extremely high melting — even refractory. Crystallization from solution is generally involved in the purification of most of these. The electronic binding forces of metals are next in strength, and perhaps the most difficult to interpret and understand. Weakest are the organics, which are held together in ordered patterns simply through van der Waals attractions. These last are consequently lower melting and (if thermally stable) much more amenable to practical melt purification techniques. In addition, the specific sizes and shapes of organic molecules make the occurrence of solid solutions quite infrequent, so that purification by crystallization is often in theory a simple single stage operation.

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Such supposedly simple procedures, however, have in the past been thwarted in practice by secondary phenomena, e.g., liquid inclusion or poor crystallization kinetics. Such phenomena have been extensively studied in recent years, and, whereas all is not yet known, the improved fundamental understanding and increasing number of recent laboratory and industrial developments instill confidence for the future growth and economic significance of melt crystallization processes.

LABORATORY DEVELOPMENTS

Melt crystallization appears to have gone through a number of successive periods or stages of development as a laboratory technique. The art of crystallization for the purification or separation of chemical constituents has been practiced throughout recorded history, but most generally in the form of solvent processes. Probably the earliest applications of melt crystallization involved the freezing of water from aqueous solutions, perhaps the sweat-melting of sea ice by whalers for drinking water as described by Wilcox,[2] or possibly the conversion of cider to "apple-jack" by partial freezing. In any case, early applications constituted more of an art (frequently secret) than a science.

With the growth of organic chemistry and with an understanding of phase equilibria, the potential for purification by melt crystallization increased many fold. Organics were frequently identified by their melting points, and their melting ranges were used as indications of purity. However, most crystallization techniques involved a solvent of some sort, principally because the mechanical methodology of melt crystallization had not been developed. It was quite often possible to form a slurry of crystals in their own melt, but the clean physical separation and washing of these was extremely difficult; for a high yield, i.e., a thick slurry, it was impossible. Even with a thin slurry it was found next to impossible to control the temperature precisely enough to avoid freezing the liquor and sintering together the crystals during the separation step. The obvious approach was to add a diluent, which, though present in only a small proportion, would increase the quantity of and the freezing range of the mother liquor. Although this solvent serves to aid the separation of the desired substance from other

impurities, it makes ultrahigh purification impossible.

Probably the closest approximation to melt crystallization as a purification tool was the technique of "sweating" or fractional melting. Used industrially as early as 1919[2] to fractionate petroleum waxes, it could be used in the laboratory to further purify semipure organic chemicals. The object of this technique is, of course, to heat the entire solid slowly enough so that melting will occur throughout the solid at the least pure regions, e.g., intercrystalline boundaries, rather than directionally from the source of heat. Furthermore, the melt so formed must not encounter colder crystal and refreeze as it drains from the system. Where the crystals are small, the process is not very economical, for the intercrystalline passageways act as a sponge, and a considerable fraction of the crystal must be melted before an appreciable quantity of liquor, along with the impurities, can be drained away. Squeezing or centrifuging out the liquor is an aid to this sort of operation. The low recovery (of purified compound) and frequently low purification per treatment were often augmented by the use of multistep procedures in which both the drained melt and the subsequently melted residue were both recrystallized and retreated, portions of melt and purified solid being appropriately combined at each series of steps according to the classical fractional crystallization scheme.

The first major advance in what might be considered ultrapurification techniques was that of directional or progressive freezing. It was recognized that, whereas it was very difficult to cleanly separate suspended crystals from their liquor, it might be feasible in many cases for carefully grown solid crystals to drive back the liquor themselves as they grow, with the liquor presumably carrying with it the impurities. A number of papers were published on such techniques, and perhaps that of Schwab and Wichers[3] is typical of the best such work on organic compounds. These authors described the purification of benzoic acid by the slow freezing in a flask from the outside inward. When about 2/3 frozen, the remaining melt was rejected, and the solid was then melted back slightly from the inside to "sweat" away the impurities still adhering to the surface, this additional melt also being rejected. This procedure reduced the impurity content from 0.09% to as low as 0.014%. Similar

procedures were found to be effective with other compounds, and in general the success of the technique was found to be dependent upon the purity of the starting material and the slowness of crystal growth (both factors appearing to reduce the impurity entrapped within or between the crystals) as well as the specific chemical system being so purified (some compounds forming such small microcrystals that more liquor is entrapped than rejected). Progressive freezing within a tube, which could be slowly lowered from a Bridgemen type furnace, was also carried out, but obviously this procedure was slower in terms of volume of product for a given linear rate of crystal growth than were procedures using flasks or other forms. The crystallization rate, however, was more easily controlled by the tube technique, and thus frequently gave superior product. Where it was desired to concentrate trace impurities (rather than purify the bulk material) the tube method could lead to ultimately higher concentrations.

The next major development in melt crystallization was the invention of zone melting by W. G. Pfann[4] of the Bell Telephone Laboratories in 1952. The technique was developed for the purification of germanium, but the concept was rapidly picked up by those concerned with organics (e.g., Herington[5]). It had, of course, been generally recognized that one could carry out a series of progressive or directional freezing steps, rejecting impure melt between each step. The difficulty in this procedure is that the successive rejects must be purer at each step and the overall proportion of total reject becomes very high as the number of steps is increased. In addition, the procedure is very time consuming. Pfann's idea was not to melt and progressively freeze the entire sample, but rather to pass a molten "zone" through an ingot of the sample from one end to the other. Thus, the impurities, which were more soluble in the melt, would be transferred to one end, just as in progressive freezing. Now the single narrow zone would not likely carry the impurities as thoroughly or as efficiently as a progressive freezing, but the zone melting could be repeated. Without rejecting the impure end, it would then be possible to pass a second, a third, and additional successive zones, obtaining increased purification with each pass and building up a maximum impurity level at the far end. Thus, the technique was capable of giving not only higher purification than ever before, but doing so with high yield.

This in itself would have been a major advance, but the *coup de maitre* was the fact that the successive zone passes could be carried out orders of magnitude faster than successive crystallizations for the same linear crystallization rate. For the zones did not have to be passed one at a time. They could be passed simultaneously, separated from each other by only enough solid ingot to maintain zone individuality. This was of great significance in the field of metallurgy where solid solution is quite common and the separation per pass fairly low. For organics, where solid solution is less often encountered, it is still of importance, for liquor entrapment in most organic systems is high enough to require many successive passes for purification.

Zone melting was found to be ideally suited for microseparations as was demonstrated by Schildknecht[6] and his associates, who studied the constituents of natural insect body fluids. Techniques were developed for samples less than 500 μg.[7] Scale-up, however, into large batches, e.g., ingots greater than 1 in. diameter, has not been feasible for organic substances principally because of their low thermal conductivity in the solid state. It can be demonstrated, however, that conventional zone melting in ingot form is one representative type of a schematic mode of separation which we have chosen to call the "progressive" mode.[8] Other forms of this progressive mode operation (which we will discuss later) are amenable in principle to scale-up.

The most recent major development in melt crystallization is that of column crystallization, a technique developed by Schildknecht and Vetter[9] in 1961 for the ultrapurification of large volumes of benzene. The concept of refluxing purified product melt countercurrent to crystals within a column had not been previously ignored, but the realization that there could be no diffusion within the crystal to permit solid-liquid interchange dissuaded most from actually trying it. As is now recognized, high purification with respect to eutectic impurities requires extremely effective washing of the crystal surface, a process which the countercurrent column does well. And, in spite of no solid state diffusion, solid solution systems can be purified by the continued melting and recrystallization which occurs as the crystals proceed into ever purer liquor within the column. Column crystallization accordingly represents the major melt crystallization technique under study in the

laboratory today, with particular emphasis being placed on the establishment of design parameters for scale-up.

Fundamental Developments

We will not take the space to review the fundamentals of solid-liquid equilibria here. A number of good texts and review articles are available. For a reasonably concise discussion with emphasis on binary and ternary solid-liquid equilibria, the chapter on Phase Equilibria in the *Encyclopedia of Industrial Chemical Analysis*[10] is suggested.

Basically, however, simple binary chemical systems are either of two types, eutectogenic or solid solution. In the latter case the crystal, growing in equilibria with a liquid solution of the two components, is itself a solution of the same two components (designated in most European literature as "mixed crystals"). These are in a different ratio than in the liquid, the crystal solution containing usually (if there be no discontinuities in the system) a higher proportion of the higher melting component or, as in most discontinuous systems, perhaps a higher proportion of the major component. If we consider the major component as the solvent and the minor component as the solute, then the ratio of the solute in the liquid, x_L, to that in the crystal, x_C, can be expressed by a distribution coefficient, k_E. This coefficient is obviously not a constant over the entire range of the phase diagram, though it does usually approach constancy as the solute concentration approaches zero, and can be considered a constant for the further purification of an already reasonably pure solvent.

A eutectogenic system is one in which the crystalline phase in equilibrium with a liquid solution is a single pure component. In essence, this means that the distribution coefficient for the other component(s) or solute(s) is zero, i.e., $k_E = 0$, and is the limiting case of no solubility in the solid state. In theory, k_E can never be absolutely zero, but for organic molecules of different sizes and shapes, it can be so low as to be indistinguishable from zero.

For a eutectogenic system, purification by crystallization should be absolute in a single step. Practically, such is not the case. Whereas the true crystal grown may itself be pure, the solid in toto consists of crystal along with certain quantities of

included and adhering mother liquor, which liquor, frozen subsequent to the major crystal growth, contains quantities of the solute component. If the concentration of solute in the liquid is x_L, and the fraction of liquid entrapped is F_L, then the concentration of solute in the solid will be

$$x_S = x_L F_L + x_C(1-F_L) \qquad (1)$$

This leads to an apparent distribution coefficient, $k_A = x_S/x_L$ or

$$k_A = F_L + k_E(1-F_L) \qquad (2)$$

and for a eutectogenic system,

$$k_A = F_L. \qquad (3)$$

Obviously, whereas k_E is a function of liquid composition alone, k_A will also be a function of the crystallization rate and other factors influencing the size and habit of the crystal.

It has been pointed out by a number of investigators (e.g., Burton, Prim, and Slichter[11]) that during the growth of solid from solution, the rejected solute must build up at the surface of the growing crystal, forming a so-called boundary layer. This is perhaps a misnomer, since there is no finite layer, but rather a concentration gradient, highest at the crystal surface, and decreasing to that of the bulk liquid (Figure 1). At any finite rate of growth some gradient must exist, for diffusion, the only mechanism for its reduction, is proportional to the slope of the gradient, and becomes nil when the gradient is small. The consequence of this solute build-up is that (1) the crystal is growing from a liquid richer in solute than the bulk, and for a given value of k_E (not zero) the solute incorporated in the crystal will be higher than normally anticipated and (2) that liquid entrapped in the solid will have a higher solute concentration than the bulk, increasing the value of k_A (whether $k_E = 0$ or not). Under these circumstances, $k_A > F_L$ if k_A is estimated in relation to the bulk liquid solute concentration. The further influence of the higher solute on the actual fraction of liquor entrapped (i.e., the crystal quality) may not be insignificant, so it is generally desirable to reduce the boundary layer as far as possible, hence crystallize as slowly as practicable. The phenomena related to the boundary layer act in particular to confuse crystallizations carried out for the purpose of evaluating the phase equilibria
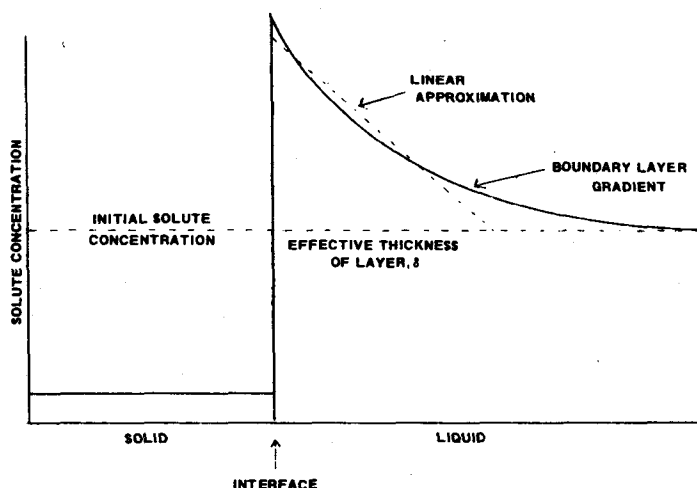
FIGURE 1. Diagrammatic representation of the solute concentration gradient of the boundary layer at the solid-liquid interface of a growing crystal.

or k_E. It becomes essential to carry out such studies at several crystallization rates and extrapolate to zero.

A particularly adverse effect of the boundary layer appears during progressive or zone crystallization. The concentration gradient automatically leads to a freezing temperature gradient in which the liquor closest to the crystal surface has a lower freezing temperature than that a short distance away. Unless the actual thermal gradient is steeper than this freezing temperature gradient, further crystallization occurs not by growth on the existing surface, but rather by dendritic extension or fresh nucleation out beyond the normal surface. This phenomenon, designated as "constitutional supercooling," practically guarantees the entrapment of a large fraction of mother liquor. Hence, one endeavors to crystallize as slowly as practicable to minimize the concentration gradient in the boundary layer, while simultaneously providing a reasonably high thermal gradient across the interface. Such a procedure is quite wasteful of heat, but this is seldom of consequence for laboratory purifications, though it would be prohibitive industrially.

The above phenomena have been mathematically modeled and analyzed by a number of workers. We will not attempt to reproduce and evaluate these models here. By way of example, however, Burton, Prim, and Slichter[11] derived the expression

$$k = \frac{k_E}{k_E + (1 - k_E) e^{-\Delta}} \qquad (4)$$

for the apparent increase in k due to the boundary layer alone, exclusive of entrapment. Their derivation is for the growth of a rotating crystal, and $\Delta = f\delta/D$, where δ is a practical thickness for the boundary layer (beyond which the concentration is essentially that of the bulk liquid; see Figure 1). D is the diffusion coefficient for the solute, and f, the linear crystal growth rate. If f = 0, then $k = k_E$.

The above, of course, presumes that the actual growth at the interface itself occurs under equilibrium conditions with the equilibrium value of k, the observed deviation being principally the result of the concentration build-up in the boundary layer. Many investigators have questioned this, i.e., have suggested that at finite growth rates the solid being grown is not that which would be in equilibrium with the liquid (at the interface) at zero growth rate. The concept is basically that actual growth occurs due to a driving force (i.e., supercooling), and the relative rates of crystallization of solvent and solute change thereby. Jindal and Tiller,[12] for example, view the process as a combination of transformation and redistribution reactions, the resultant of which at finite growth rate leads to a nonequilibrium partitioning of the solute, the coefficient of which is dependent upon the interface temperature and the

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growth rate, V. They show that as $V \to 0$, $k \to 1$, a conclusion which also results from boundary layer theory alone. It is extremely difficult to determine experimentally whether observed variations in k are simply boundary layer dependent or are partially the result of distribution effects at the interface itself. Secondary phenomena, e.g., liquid entrapment, lead to experimental variations above and beyond the precision required to differentiate among the various combinations of causative factors.

Studies similar to those above were made by Kirwan and Pigford,[13] later extended by Cheng and Pigford,[14] and augmented by microinterferometric observations of crystal growth. They derived an expression for the free energy of fusion, ΔG_f, of a solid solution of composition x_i into a liquid of composition y_i as a function of the equilibrium values, x_{ie} and y_{ie}, for the temperature in question. For a binary system,

$$\frac{\Delta G_f}{RT} = x_A \ln (x_{Ae} y_A / y_{Ae} x_A) + x_B \ln (x_{Be} y_B / y_{Be} x_B)$$
$$+ x_A \ln \left(\gamma_A^L \gamma_{Ae}^S / \gamma_{Ae}^L \gamma_A^S \right) + x_B \ln \left(\gamma_B^L \gamma_{Be}^S / \gamma_{Be}^L \gamma_B^S \right) ,$$

$$(5)$$

where the superscripts L and S on the activity coefficients, γ_i, refer to liquid and solid states, respectively. If it is assumed that the activity coefficients in either the solid or the liquid do not change appreciably with concentration, the expression reduces to:

$$\frac{\Delta G_f}{RT} = (1-x_B) \ln(1-x_{Be})(1-y_B)/(1-y_{Be})(1-x_B)$$
$$+ x_B \ln(x_{Be} y_B / y_{Be} x_B) . \qquad (6)$$

Figure 2 shows plots of $\Delta G_f/RT$ as a function of the concentration of B in the solid, x_B, for two liquid concentrations, y_B. When $\Delta G_f/RT$ is positive, the solid solution may be considered stable in the presence of the liquid specified.
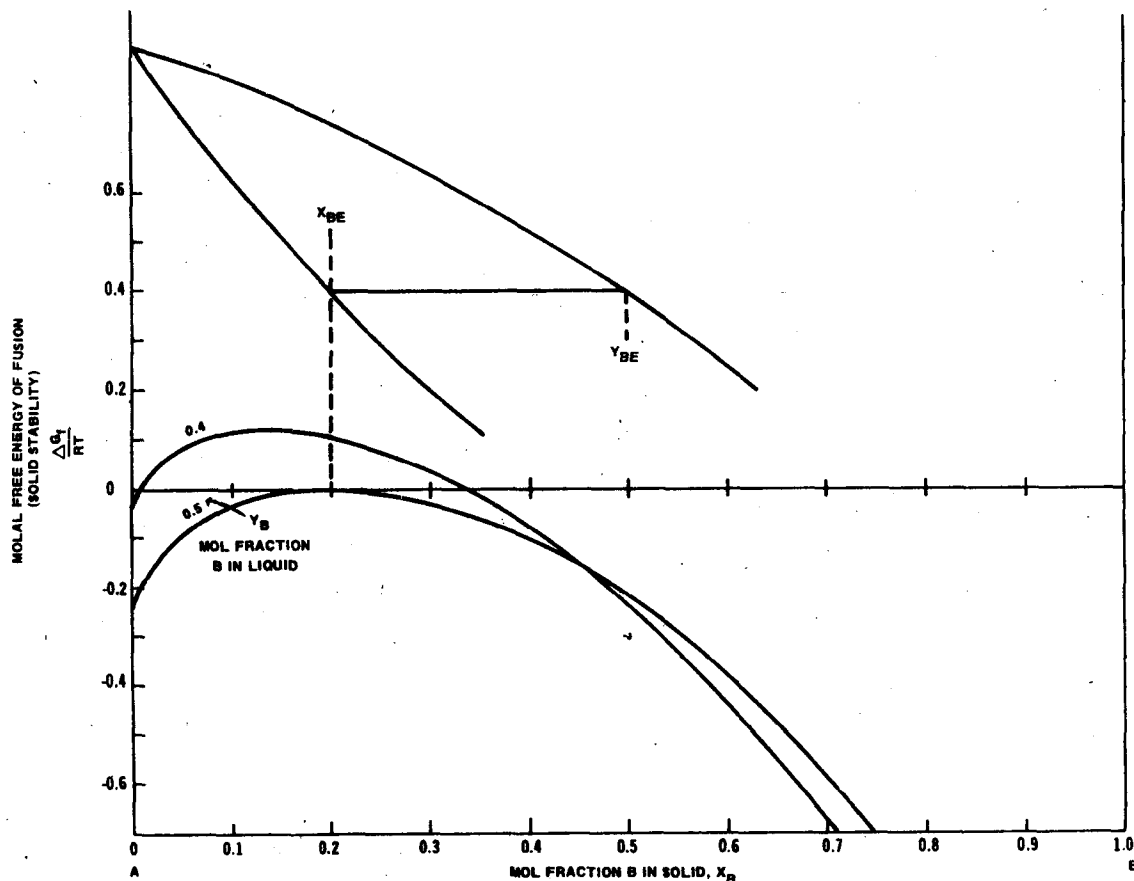

FIGURE 2. Solid solution stability vs. solid composition in two different liquid compositions, one of which ($y_B = 0.5$) is at its equilibrium freezing temperature, and the other of which ($y_B = 0.4$) is supercooled. (From equation of Kirwin and Pigford.[13])

When $y_B = y_{Be} = 0.5$, the only stable solid is x_{Be}, but when $y_B < y_{Be}$ (e.g., 0.4) the liquid is supercooled, and a range of solids is stable. The question of which solid solution will crystallize on an existing solid-liquid interface is not easily answered. One is tempted to conclude that the most stable, highest ΔG_f, would crystallize preferentially. However, there are valid mass transfer arguments for the crystallization of compositions closer to that of the liquid phase. Interferometric studies of Cheng and Pigford[14] were found to be consistent with the latter assumption. However, in view of the experimental difficulties, and the extreme precision required to elucidate the phenomena, the results would really not be inconsistent with the former as well. The problem is that if a lower concentration solid is initially formed, the boundary layer gradient becomes larger and the higher concentration ultimately crystallizes out for boundary layer reasons. It is this writer's opinion that there is no need to speculate on other than equilibrium growth at the interface itself, because at any finite growth rate the build-up of a micro boundary layer rapidly shifts the interface to a near equilibrium, rather than a supercooled state.

An indication of how complex the situation might be is shown in the paper by de Leeuw den Bouter, Heertjes, and Jongenelen,[15] who not only demonstrate that the build-up of the solute boundary layer reduces the rate of crystal growth for unidirectional crystallization (as do many other authors), but point out in addition how the difference in diffusion rates between the solvent and built-up solute must be considered in evaluating the heat conduction and bulk liquid flow in the boundary layer itself.

From a more macroscopic and practical standpoint, however, Wilcox[16] has shown that crystal growth is seldom the steady, uniform process which so many have attempted to model. "A host of phenomena occur which make the interface of irregular shape, cause the freezing rate to fluctuate, greatly influence mixing of the melt, and cause melt inclusions to move into or out of the solid."[17] Among these phenomena are the tendencies toward faceting (in which growth rates and even solute distribution differ as a function of direction), adsorption of impurities on the solid surface, constitutional supercooling, freezing rate fluctuations or oscillations, cracking of the solid (and subsequent sucking in of liquid) due to thermal strains, and even the movement of liquid inclusions within the solid due to thermal gradients. In particular, it must be recognized that any phenomenon (such as constitutional supercooling) which results in entrapment or disruption of a good deal of the boundary layer will lead to an oscillitory situation, for if the boundary layer is destroyed, particularly favorable crystallization conditions are set up until the layer can be rebuilt. In some situations, it is reasonable to expect microconvection to act periodically to supplement the normal diffusion phenomena occurring within the layer.

In any case, it is generally conceded that for separation and purification purposes, it is advantageous to crystallize as slowly as feasible, and from as pure a melt as might be available. Pfann[18] illustrates the breakdown of crystal quality with growth velocity or impurity level as a series of transitions from (1) a smooth flat interface, to (2) a cellular-type surface, to (3) a dendritic structure, and finally to (4) multicrystalline solidification with a complete loss of any coherent surface (Figure 3). Condition 2 is well described in detail by Chadwick.[19]

Thus, we see that the process of crystallization, though better understood now than ever before, is subject to many uncertainties of both a theoretical and practical nature. Much remains to be learned, and Mullin[20] has aptly called it "a study in molecular engineering."

Progressive Freezing and Zone Melting

We cannot review all the techniques of progressive freezing and zone melting here; they have been adequately discussed elsewhere.[1,5,6,18] We might, however, consider some of the problems particularly relevant to organics, and some of the recent developments.

First of all, organics must be treated within a tube of some sort, and this leads to a variety of problems. Lacking the physical strength of metals or adequate surface tension in the liquid state, ingots of organic crystals cannot be subjected to the floating zone techniques so widely used in metallurgy. Then too, their volatilities, usually so much higher than metals or inorganics, require some sort of containment to avoid evaporative loss of the sample. Organics have been zone refined in boats, but sublimation from the impure end makes ultrapurification impossible. The common and most obvious solution is to use a glass tube, which

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