**Separation & Purification Reviews**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597294

# Studies in Melt Crystallization

G. Richard Atwood[a]
[a] Union Carbide Corporation, Tarrytown, New York

**To cite this Article** Atwood, G. Richard(1973) 'Studies in Melt Crystallization', Separation & Purification Reviews, 1: 1, 297 — 369

**To link to this Article: DOI:** 10.1080/03602547308068943

**URL:** http://dx.doi.org/10.1080/03602547308068943

# STUDIES IN MELT CRYSTALLIZATION

G. Richard Atwood
Union Carbide Corporation
Tarrytown, New York

A great number of separation techniques and associated devices based upon melt crystallization have evolved over the past decades. Among them have been several variants of normal freezing, zone refining, and column crystallization as examples. It is not the purpose of this chapter to describe any new techniques or even critically review the old. Rather, we are combining here a series of partially related solid-liquid studies, which may help to broaden our understanding of the phenomenon of crystallization itself, which in turn is essential to the development and evaluation of such techniques and processes.

Not all the studies, or rather series of studies, described here are directly related to separation methods. Nor, indeed, are they all our own. Many are related to analytical techniques; some to the heterogenous behavior of functional systems. Some are principally considerations based upon the work of others. All, however, contribute in a partial way to one's concept of solid-liquid phenomena, and indirectly to melt crystallization as a separation tool.

Although "melt crystallization" encompasses a wide range of chemical species and environmental conditions, the work described here is primarily on organic systems. Whereas the fundamentals of phase equilibria are independent of specie type, the practical aspects are not. The simple concept of a crystal differs among metals, ionic salts, and organic compounds, due particularly to the differing types and relative strengths of the binding forces involved. Organic crystals are ordered agglomerations of neutral organic molecules, and the binding forces, principally Van der Waals, are the weakest of the lot. Accordingly, most simple organics melt at reasonably low temperatures, and many, where the symmetry is poor and crystal packing difficult, melt far below ambient. The conclusions which one draws with respect to crystallization or related phenomena, when based upon the simple molecule concept, cannot necessarily be extrapolated to "ionic" or metallic systems.

The prevalence of solid solution in particular is much lower for organics than with the other types of crystals. However, the phenomenon, though rare, is nonetheless significant for many commercially important systems. The problem of accurately measuring solid solution equilibria, along with that of understanding and predicting solid-liquid behavior under non-equilibrium conditions, has been an area of considerable interest. Accordingly, much of the following work is related to the recognition and behavior of solid solution.

## A. FUNDAMENTALS

Let us first examine the concept of solid-liquid equilibrium as it pertains to the growth and melting of organic crystals. The crystal itself consists of a three dimensional arrangement of molecules, packed in an ordered fashion such as to maximize the cohesive forces between molecules, and thus minimize the total enthalpy of the system. From a simple standpoint we can imagine two types of molecules, those in the interior of the crystal, and those on the surface. The interior molecules are subjected to cohesive forces on all sides, in addition to which they are trapped within limited volumes of defined shape. Accordingly, one would expect such molecules to require considerable thermal energy to disrupt the pattern and to "melt" internally. Indeed, though crystals do expand as they are heated, their volume at the melting point is generally 10-15 percent less than that of the liquid, indicating little or no tendency toward internal instability or disintegration.

Surface molecules, however, are bound only partially by the "maximum" cohesive forces, and do have a greater freedom of motion. As a crystal is heated, therefore, it is these molecules which can achieve release from the structure and which will do so at the lowest temperatures. Thus, a crystal, though stable internally, can "melt" from its surface. At equilibrium (i. e., the melting temperature) the number of surface molecules with sufficient energy to leave the crystal is about equal to the number of liquid molecules with sufficiently low energy and appropriate orientation to join the structure. Thus the crystal as a whole neither melts nor grows. At higher temperatures more molecules will leave the surface (exposing additional surface) and the crystal melts or dissolves into the liquid. (The classical question as to whether the sugar melts or dissolves into a cup of coffee is merely an exercise in sematics, the mechanism being the same.) At lower temperatures the crystal grows.

Actually, the mechanism is much more complex, for we have various types of surface molecules with various cohesive energies. Actual melting occurs where the molecule is bound the least (as at a corner) and growth occurs where the most forces can act at once (at an "inside" corner). These can be considered "active" sites, and are typified by some dislocation lines, etc. For our purposes, it will be simple enough to visualize the phenomena as solid surface—liquid equilibrium.

## Simple Eutectic Behavior

Let us now review the phase equilibria of a simple eutectic system such as that shown in Figure 1. A simple eutectic system is characterized

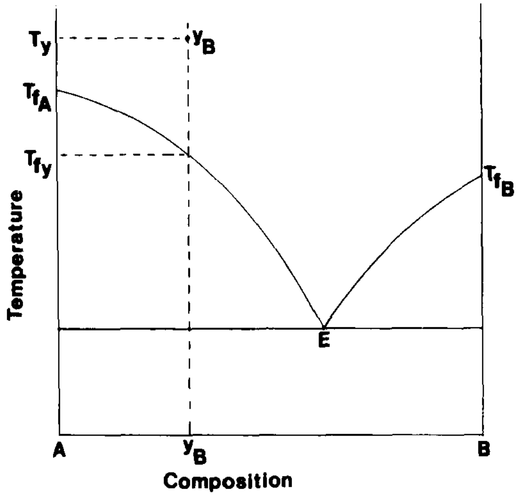

Figure 1. Phase Diagram for Simple Eutectic System.

by the fact that the crystalline phases are pure single components. Curves $T_{fA}E$ and $T_{fB}E$ define the equilibrium freezing temperatures for the binary liquid compositions indicated, or conversely, the melting temperatures of A or B crystal into liquid phases of these compositions. It can be readily recognized that the freezing/melting temperature of a pure substance would be reduced when a second component is present in the liquid phase. For this dilution of the crystallizable component reduces the number of molecules which can settle on the crystal surface (thermodynamically, the activity in the liquid is reduced), while not affecting in the least the number of existing surface molecules with sufficient energy to leave. Only at lower temperatures can equilibrium be reestablished.

It must be pointed out that the shape of curve $T_{fA}E$ is in no way affected by the melting point, $T_{fB}$ of compound B, nor is the curvature of $T_{fB}E$ affected by the melting point, $T_{fA}$, of A. These curves are affected somewhat by the thermodynamic ideality of the liquid solution, but the stabilities of crystals A and B can never affect each other. Only at the eutectic point E where curves $T_{fA}E$ and $T_{fB}E$ coincidentally intersect can solids A and B even exist together in equilibrium with the liquid (of composition E). Below this temperature all liquid crystallizes. The solid eutectic mixture which is formed is not a solid solution (often designated "mixed crystals" in Europe), but a simple physical mixture of pure A and pure B crystals in the eutectic ratio. This ratio has no thermodynamic significance of itself, but is only the coincidental intersection of the two independent solid-liquid equilibrium curves.

If, now, a liquid composition, $y_B$, initially at a temperature above $T_y$, is cooled, say by the continuous removal of heat at a constant rate, and if thermodynamic equilibrium is maintained, pure A will start to crystallize at temperature $T_{fy}$. The heat of fusion released as A crystallizes acts to resist the cooling, and the temperature falls less rapidly. The continued crystallization of A, however, changes the composition of the liquid, lowering its freezing point, and both the liquid composition and the temperature gradually fall along curve $T_{fA}E$. Once point E is reached, both pure A and pure B crystallize out simultaneously, and the temperature remains $T_E$ until the entire system is solid. Typical examples of such cooling curves are given in Figure 2.

If any sample so frozen is now heated (again by the constant, continuous addition of heat), and equilibrium is still maintained, the temperature will hold constant at $T_E$ as both A and B melt in eutectic proportions until either A or B is completely melted, after which the temperature will rise again, retracing the original freezing pattern. Physically this process is not really feasible to its limits. The dotted lines (Figure 2) show the practical extent to which one might freeze a system and maintain sufficient agitation to achieve (and measure) a reasonably homogenous equilibrium temperature. As the solids content increases, the system

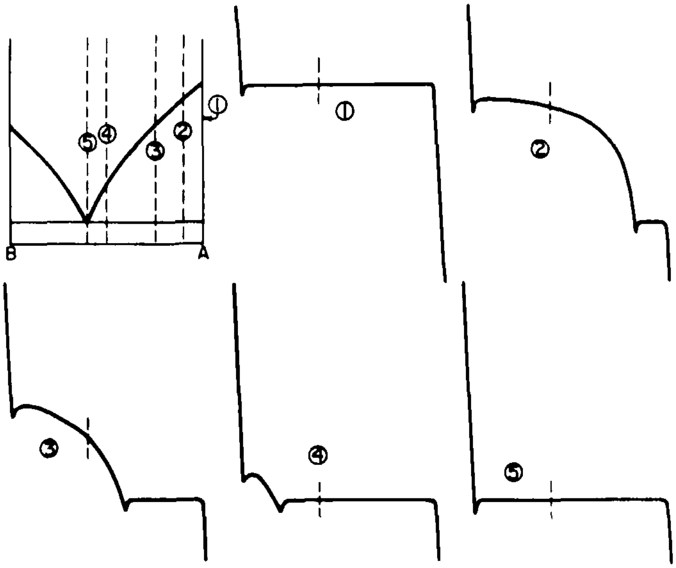

Figure 2. Theoretical Cooling Curves for Compositions in a Simple Eutectic System.

becomes unstirrable and poor internal heat transfer prohibits any consistent or homogenous cooling or heating.

We have discussed thus far only equilibrium phenomena. Suppose that we cool the sample faster than it can theorectically respond by crystallization. There are several possible sources of kinetic lag, the major one being the paucity of crystal surface (or surface dislocations) for growth. Our concept of equilibrium presumes an ample availability of such surface, but it is not possible to spontaneously generate an abundance of surface by nucleation at the equilibrium freezing (or crystal growth) temperature. The thermodynamic stability of a "nucleus" is far less than that of an established crystal of finite dimensions, and accordingly, the formation of such a nucleus must occur under supercooled conditions. Consequently, when a liquid sample such as $y_B$ is cooled through its freezing temperature, it first supercools, during which time nuclei are formed (see Figure 2). When enough such nuclei are generated that their growth can release substantial heat of fusion, the temperature can rise again, but never all the way to the equilibrium freezing temperature, since the surface so generated will never be quite sufficient to permit true equilibrium.

A second kinetic barrier is molecular diffusion within the liquid. As we have pointed out, the growth of crystal from a binary liquor results in a composition depleted in the crystallizing component and hence a reduced equilibrium freezing temperature. If molecular diffusion were sufficiently rapid to maintain a homogeneous liquid composition, this would be no problem. Depletion, however, occurs next to the crystal surface, leading to a so-called "boundary layer", the freezing temperature of which is lower than that of the bulk liquid (or higher if the crystal is being melted). The rate of corrective diffusion is proportional to the magnitude of the gradient, and hence is never enough to eliminate it entirely. Thus we must always crystallize or melt with what amounts to a thermal (or concentration) driving force, and the bulk system will be supercooled during crystallization and superheated during melting even though equilibrium has been nearly achieved at the crystal surface.

The net result, thermodynamically, of non-equilibrium crystallization is identical to that of equilibrium crystallization, in the sense that two pure crystalline phases are ultimately formed, A and B. Physically, there will be a difference in that the rapidly frozen crystals will be smaller, more intimately mixed, and will have entrapped considerable proportions of each other. This is because under supercooled conditions a greater quantity of nucleation can take place, leading to more, and more widely distributed, surface. In addition, the sharp concentration gradients established induce the crystals to grow preferentially in directions defined by the higher freezing temperature liquid (i. e., higher concentrations of A or B, whichever is crystallizing), giving what is known as a dendritic (multineedled) structure. The meeting and fusion of adjacent crystallites or crystal branches invariably leads to the entrapment of liquid, and the subsequent formation (when cooled below the eutectic) of regions of crystal B within crystal A (or vice versa) along with entrapped voids (the liquid being less dense prior to ultimate solidification).

Thus we obtain a poor quality "solid" from the standpoint of any purification process, in spite of the fact that we have still formed crystals of only pure A and pure B. Let us now arbritrarily define the term "solid" to mean the composite of crystal and its entrapped liquor (whether such liquor is ultimately frozen or not). The term "crystal" will be reserved for the actual growing phase, and it may be pure or it may not, depending upon whether the system in question exhibits solid solution.

## Solid Solution Behavior

Let us now consider the phenomenon of solid solution. Normally, the variable size and shape of organic molecules prohibits the inclusion of one kind in the close packed lattice of another. If the intruder is too large, it cannot fit; if too small, it adds little to the lattice stability, does not induce overgrowth, and soon leaves the surface to be replaced by a proper molecule. There are, however, molecules sufficiently alike in size and shape such that they can grow in a single lattice in variable ratios. Because, however, the two (or more) molecules do not contribute exactly the same to the crystal stability, their composition ratio in the growing crystal will not be the same as in the melt from which they grow.

Figure 3 shows a system exhibiting a continuous series of solid solutions. Unlike the simple eutectic system, the crystal phase growing in equilibrium with the liquid of a given composition, e. g., $y_B$, is not a

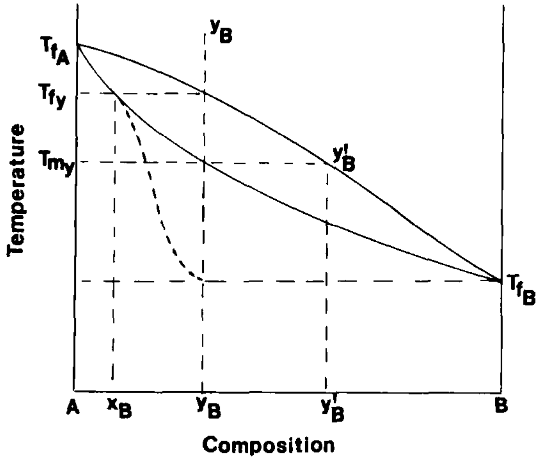

Figure 3. Phase Diagram for Solid Solution System.

pure component, but is a solution of components having a thermodynamically defined composition, e. g., $x_B$, in which the activity of any one component is identical in both the crystal and liquid phases. The difference in composition between $x_B$ and $y_B$ results from a difference in activity coefficients in these phases, the crystalline phase in general being much less ideal than the liquid phase. Just as the upper $T_{fA}T_{fB}$ curve defines the liquid phase and is called the liquidous line, so does the lower $T_{fA}T_{fB}$ curve define the crystal phase and is called the "solidous" line.

If one cools a solution $y_B$ below temperature $T_{fy}$, so as to reversibly freeze the sample at equilibrium, crystals of composition $x_B$ can be formed. The growth of a significant proportion of crystal richer in A than the liquor will result in a liquor enriched in B. The composition and temperature will, therefore, follow the liquidous line toward $T_{fB}$. If the crystals were able to undergo the internal diffusion of fluid phases, the crystal composition would change (via interchange with the liquid), along with that of the liquid, following the solidous line. At temperature $T_{my}$

the entire sample would be frozen to crystal of composition $y_B$, the last traces of liquid being of composition $y'_B$. However, organic crystals cannot undergo any appreciable internal diffusion, and the composition of any layer of crystal, once grown and overlayed with a new surface, cannot change. Accordingly, as the sample is frozen and the concentration of the liquid proceeds down the liquidous line, only that composition of the crystal surface follows along the solidous line. The overall composition of the crystal follows the dashed curve, and its final surface, as well as the last trace of liquid to freeze, is nearly pure B.

If such a reversibly frozen sample is slowly reheated, so that the crystal is allowed to remelt reversibly, the compositions and equilibrium temperatures can retrace their original paths.

What about the behavior, now, of such a system under nonequilibrium conditions, i.e., conditions under which crystal is grown or melted irreversibly with a driving force, or perhaps in which crystal of a given composition is introduced into a liquor with which it cannot possibly be in equilibrium.

The writer's understanding of such behavior was helped immensely by the use of an equation given by Cheng and Pigford[1]. The free energy of fusion, $\Delta G_f$, of a solid solution can be expressed in terms of the crystal composition, x, and the chemical potentials, $\mu$, of the components in the solid and liquid phase.

$$\Delta G_f = x_A(\mu_A^L - \mu_A^S) + x_B(\mu_B^L - \mu_B^S) \tag{1}$$

The chemical potentials can in turn be expressed as functions of their values under equilibrium conditions,

$$\mu_A^S = \mu_{Ae}^S + RT\ln(a_A^S/a_{Ae}^S) \tag{2}$$

and the activities in terms of the activity coefficients.

$$a_A^S = x_A\gamma_A^S \tag{3}$$

Substituting into (1), and realizing that $\Delta G_{fe}$, the free energy at equilibrium, is zero, i.e.,

$$\Delta G_{fe} = x_A(\mu_{Ae}^L - \mu_{Ae}^S) + x_B(\mu_{Be}^L - \mu_{Be}^S) = 0 \tag{4}$$

we have:

$$\begin{aligned}\frac{G_f}{RT} &= x_A\ln(x_{Ae}y_A/y_{Ae}x_A) + x_B\ln(x_{Be}y_B/y_{Be}x_B)\\ &\quad + x_A\ln(\gamma_A^L\gamma_{Ae}^S/\gamma_{Ae}^L\gamma_A^S) + x_B\ln(\gamma_B^L\gamma_{Be}^S/\gamma_{Be}^L\gamma_B^S)\end{aligned} \tag{5}$$

If we assume that the activity coefficient does not change appreciably with composition in either the solid or the liquid, and if we also replace $x_A$ by $(1-x_B)$, we get

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

Let us now consider Figure 4, which is a series of plots of $\Delta G_f/RT$ versus the concentration of B in the solid, $x_B$, for various values of $y_B$, the concentration of B in the liquid. These were computed for an arbitrarily chosen temperature at which the equilibrium values of solid and liquid composition, $x_{Be}$ and $y_{Be}$ respectively, are 0.2 and 0.5. A negative value of $\Delta G_f/RT$ tells us that the solid will melt spontaneously, and hence these may be considered plots of crystal stability.

Consider first the curve for $y_B = y_{Be} = 0.5$. This curve shows, as we would expect, that at a temperature, $T_{fy}$, at which $x_{Be}$ and $y_{Be}$ are the equilibrium values, no crystal except $x_{Be}$ is stable in a liquor of composition $y_{Be}$. $\Delta G_f$ is negative, and any crystal with $x_B$ greater or less than 0.2 would spontaneously melt.

Consider next the stability curve for $y_B = 0.4$, a liquor which is obviously superçooled, being at a temperature below the liquidous curve. Now a range of crystal compositions, $0.01 < x_B < 0.33$, is stable. No

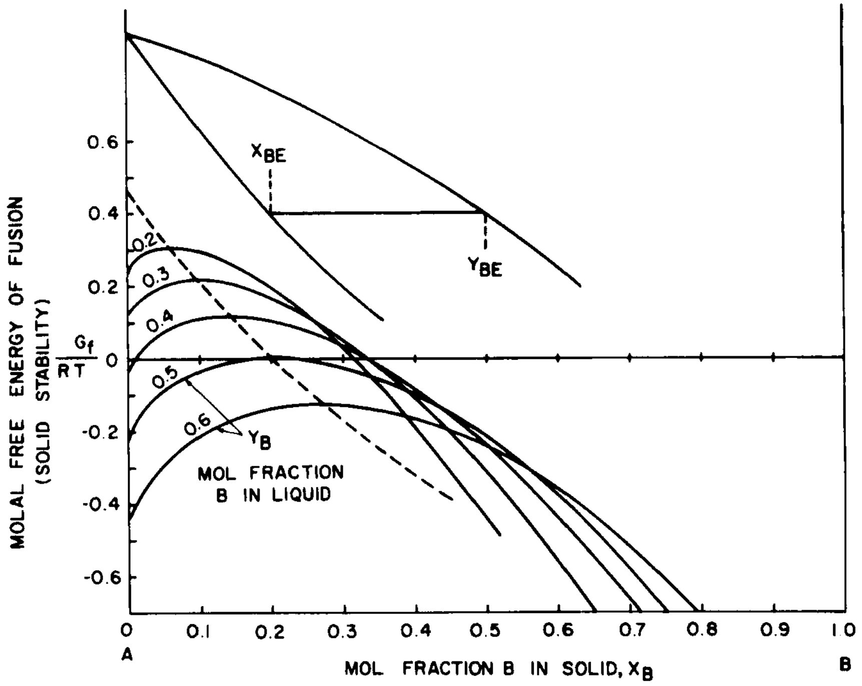

Figure 4. Solid Solution Stability as a Function of Solid and Liquid Compositions.

crystal within this range will melt; indeed their surfaces will support further growth from the supercooled liquid. What composition will overlay these surfaces? In theory any composition within the range could crystallize. However, the most probable composition will be that with the maximum value of $\Delta G_f$, and this, about 0.15, will initially overlay whatever stable surface is provided. Because the crystallization is spontaneous, two phenomena, the release of heat and the enrichment of the boundary layer in Component B tend to move the system to an equilibrium situation on the micro scale. The temperature rises slightly and the liquid concentration of B at the surface increases to nearly $y_{Be}$. Under these circumstances, we crystallize out a composition somewhat higher than the 0.15 but still slightly lower than $x_{Be}$ or 0.2. As the temperature of the system rises (or if it should be deliberately raised) such that the initial crystal underlaying the new surface is in theory no longer stable (to the liquid $y_B = 0.4$), it cannot now melt. It has been removed from contact with the liquid by the new crystal and it is perfectly stable to all environments until the outer surfaces, which cover it much like the layers of an onion, are first melted off.

Figure 4 shows the family of stability curves from $y_B = 0.2$ to $y_B = 0.6$. Naturally, the further the compositions are from their equilibrium values, the less accurate will be the quantitative aspects of the plots, since the activity coefficients of both solid and liquid will indeed change with composition. However, the essential nature of their shapes will be qualitatively valid.

We might now ask what happens to a homogeneous solid solution crystal as it is raised through its initial melting temperature. Such a homogeneous solid solution might be difficult to obtain, but a small quantity could be slowly grown in a large volume of liquor and the crystals separated and effectively cleaned. Let us assume our solid solution is 0.2, i.e., $x_{Be}$, and that we have no liquid initially present. At temperature $T_{fy}$, the solid should melt to give liquor of composition $y_{Be} = 0.5$. However, if we melt an appreciable quantity of liquor, its composition would have to be 0.2, and we see from the curve for $y_B = 0.2$ that a crystal of $x_B = 0.2$ is perfectly stable to that liquor and cannot melt at $T_{fy}$. What must happen as the temperature rises is that an incremental quantity of liquid of $y_B = 0.5$ must form from the simultaneous melting and recrystallization of a lesser quantity of slightly lower ($x_B =< 0.2$) crystal. The new crystal would to some extent tend to overlay the old, but not everywhere, and eventually the old might be entirely eroded away and replaced, though we would expect this procedure to be kinetically slow. As we further raise the temperature, this process can go on repetitively until we reach our final melting point, $T_{fx}$, and the last crystal to melt is of composition $x'_B = 0.06$. Refreezing, of course, cannot give homogeneous $x_B = 0.2$ again. Instead we would build up variable composition crystals of $x_B = 0.06$ internally to $x_B = 1$ on the surface.

Often one attempts to form a homogeneous solid solution by quick freezing or "quenching" the liquid. The basis for this is that by initially freezing out seeds or nuclei of composition $x_B$ (Figure 3) from a liquid of $y_B$, one might rapidly build up a liquid boundary layer of composition $y'_B$, from which crystal $y_B$ can be grown. The "thickness" of such boundary layer will be directly proportional to the rate of diffusion and inversely proportional to the rate of crystal growth, and its composition at the crystal surface can never exceed $y'_B$ as long as the bulk liquid is $y_B$ and crystal growth is reasonably continous (not erratic). When the system is almost completely frozen, however, there will be no bulk liquid of composition $y_B$ left, and final crystallization of the boundary layer liquid gives crystal of composition varying from $y'_B$ to pure B. We, therefore, have a small quantity of initial crystal of composition $x_B$ to $y_B$, a large fraction of crystal with composition $y_B$, and another small final quantity with composition from $y_B$ to B. If we wish reasonably homogeneous solid solution, it is desirable to reduce both the initial and final crystal, and this is equivalent to reducing the volume of the necessary boundary layer. For liquids with reasonable rates of diffusion, therefore, it would appear essential to crystallize as rapidly as possible. However, this implies a good deal of supercooling, and though the boundary layer might be thin, its volume, which is also related to the surface area, might be increased due to excessive nucleation, and dendritic branching. Whether there might be an optimum rate is a topic worthy of further study.

Figure 5 illustrates schematically a system which can be considered a hybrid of solid solution and eutectic type behavior. In this case we have limited solubility in the solid state, i. e., thianaphthene is soluble in the naphthalene lattice up to that concentration indicated by point D. For liquid compositions beyond the eutectic, E, the thianaphthene lattice with small concentrations of naphthalene is the more stable. From a liquid of the eutectic composition, we can crystallize out physical mixtures of solid solutions D and F (more F than D, since the eutectic is closer to F). The dashed line BGA on the figure shows the average crystal composition as a liquid of initial composition A is slowly frozen. Not until the eutectic is reached, and solid solution F is precipitated out can the overall mass balance of the crystals reach composition A.

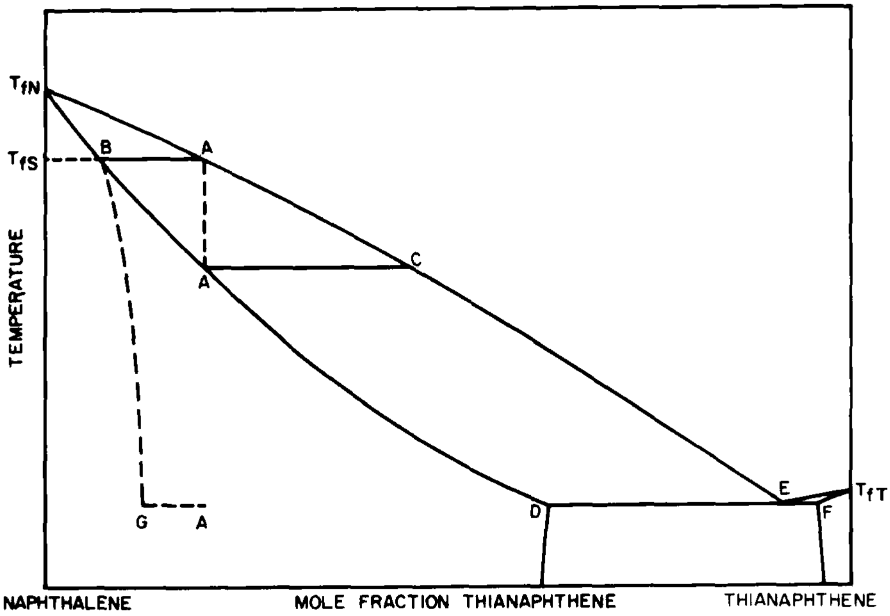

Figure 5. Phase Diagram for the Naphthalene - Thianaphthene System.

## Recognizing Solid Solution

The existance of solid solution is frequently difficult to recognize. It is not usually possible to identify solid solution through the examination of freezing curves per se. Figure 6 shows typical freezing curves (computed) for naphthalene containing about 5 wt. % thianaphthene or the equivalent amount of a simple eutectic forming solute to lower the initial freezing temperature to about 78°C. The temperature is plotted against fraction frozen instead of time, so that these curves represent what might be obtained calorimetrically as well as cryoscopically. For simplification, the distribution coefficient, k, for the thianaphthene in naphthalene (%t in solid/%t in liquid) was assumed to be a constant value of 0. 35. That, of course, for the solid-insoluble impurity would be 0. 0. The only apparent

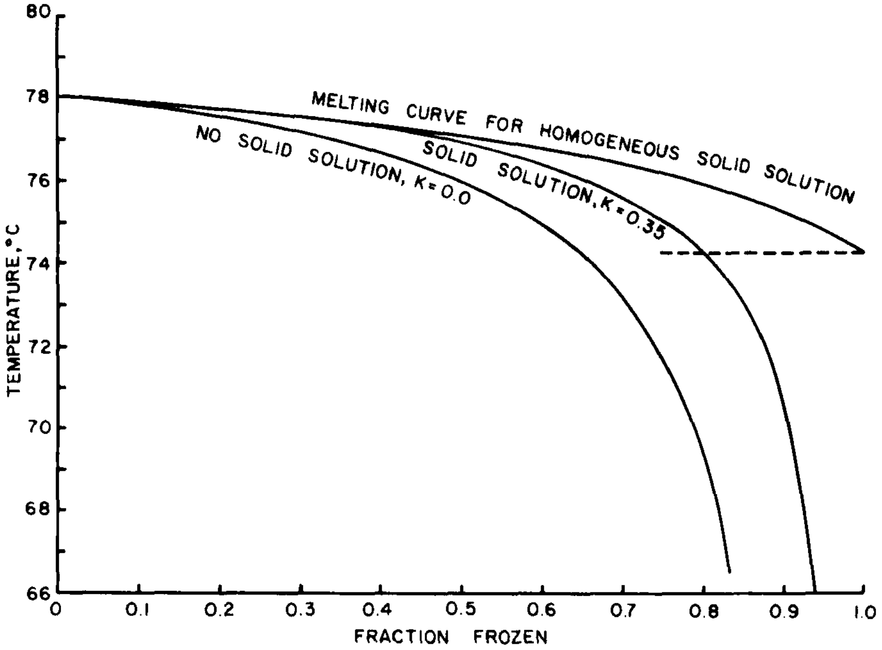

Figure 6. Theoretical Freezing Curves for Naphthalene with 5% Solute.

difference is the less rapid fall of the curve for the solid soluble impurity. Since this solute is incorporated partially into the crystal, the concentration build-up in the liquid is slower and the consequent temperature fall less rapid.

The upper curve in Figure 6 represents the curve one would obtain by the melting of a homogeneous solid solution if one could be obtained. (The equivalent of time would, of course, be read from right to left.) If a cold homogeneous sample were heated through its melting point, there would be a sharp break at a temperature such as that indicated by the dotted line, and the temperature would then rise more slowly until the sample was melted. Recognition of the initial melting temperature is the basis for the calorimetric method (which we will discuss later) of evaluating solid solution. (However, it would be obviously impossible to obtain a completely homogeneous solid solution for this evaluation by freezing a liquid of the same composition.) Note that the other curves on this figure would not show such a sharp break. Melting would start at the eutectic (with perhaps a brief plateau) and the temperature would then rise fairly rapidly, curving gradually into the low slope representative of significant melting.

Inasmuch as the difference between solid solution and simple eutectic behavior does not appear obvious from freezing or melting curves, attempts have been made to clarify the situation by plotting the temperature against the reciprocal of the fraction of the sample in the liquid form, Figure 7. Here we find that the plot for a simple eutectic system (no solid solubility) is essentially linear (at least at the higher temperatures), and extrapolates to the freezing temperature of the pure solvent. That for a solid solution system is curved and would not so extrapolate (if extended linearly). Consequently, many use these criteria for judging the existance of solid solution. This is a valid technique only if one can precisely eval-

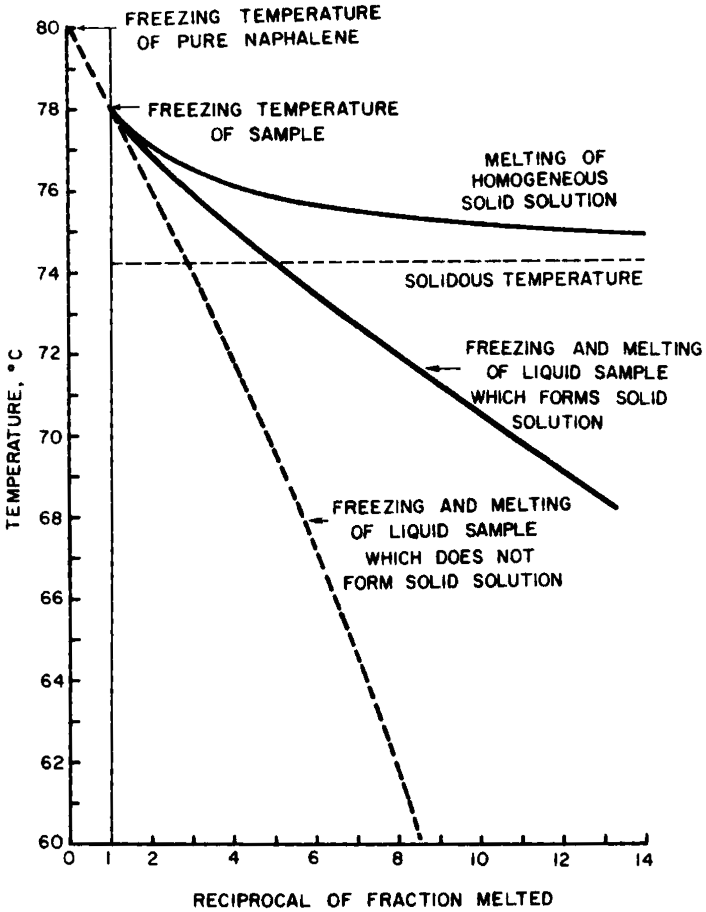

Figure 7. Plots of Temperature vs. Reciprocal Fraction Liquid for Theoretical Freezing Curves.

uate the fraction frozen, and if the liquid solutions are nearly ideal, for considerable curvature can result from solution nonidealities.

The most reliable way to recognize solid solution is to compare the experimental cryoscopic constant molal freezing point depression) for the solute in question with that for other solutes in the same solvent. The cryoscopic constant is essentially the slope of the freezing temperature -- composition curve (specifically at infinite dilution), and is usually expressed in mol % solute/degree. Several examples are shown in Figure 8. Inasmuch as the majority of solutes will be solid-insoluble (at least for organics), the plot for most solutes can be easily established. Deviations result from either solid solubility (upper curve) or solute dissociation (lower curve, not common for organics). Extreme liquid non-idealities, as for example, solvent-solute association, can produce marked curvature, though in this case the initial slope of the line, i.e., the cryoscopic constant at infinite dilution, is unaffected. Extreme positive deviation from Raoult's Law would produce a similar curvature upward from that plot for most solutes, but still the initial slope would be the same. No phenomenon other than solid solution has been found to raise the initial value of the cryoscopic constant.

Figure 9 illustrates how a comparison of the experimental phase diagram with the "ideal" diagram (or those for other solutes) can disclose solid solution. The system benzene-cyclohexane is a unique one with solid solution on only one side. Cyclohexane will not fit in the lattice of slightly smaller and planer benzene molecules, but benzene is soluble in solid cyclohexane. The figure represents a comparison of the experimental data (curve D) with the ideal (curve A, calculated from heats of fusion, etc.) and curves (B and C) computed with the aid of experimental vapor pressure data (which permitted the calculation of liquid nonidealities) extrapolated down from 40°C. We need not discuss that work[2] here, but it is significant to note that the experimental curve agrees with calculated curves on the benzene side of the diagram, whereas it does not agree on the cyclohexane side. Disagreement at finite concentrations is not so significant, but these curves disagree in their initial slopes at infinite dilution. Hence, there must be solid solubility. Unfortunately, the

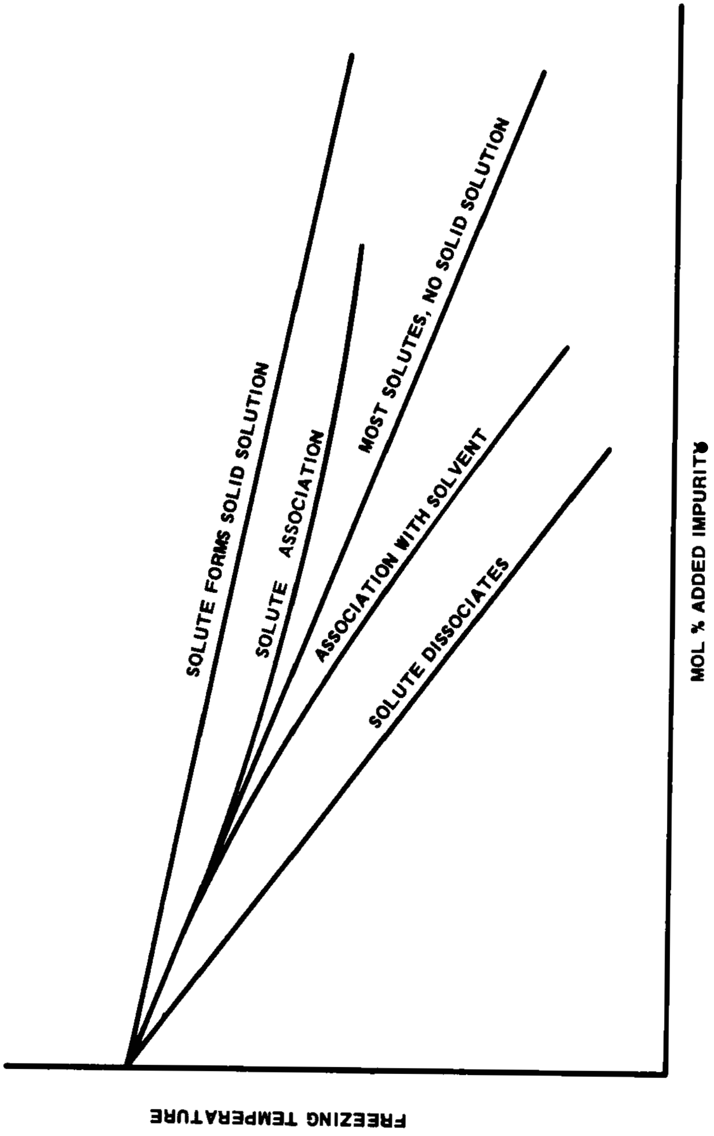

Figure 8. Cryoscopic Indications of Various Molecular Phenomena.

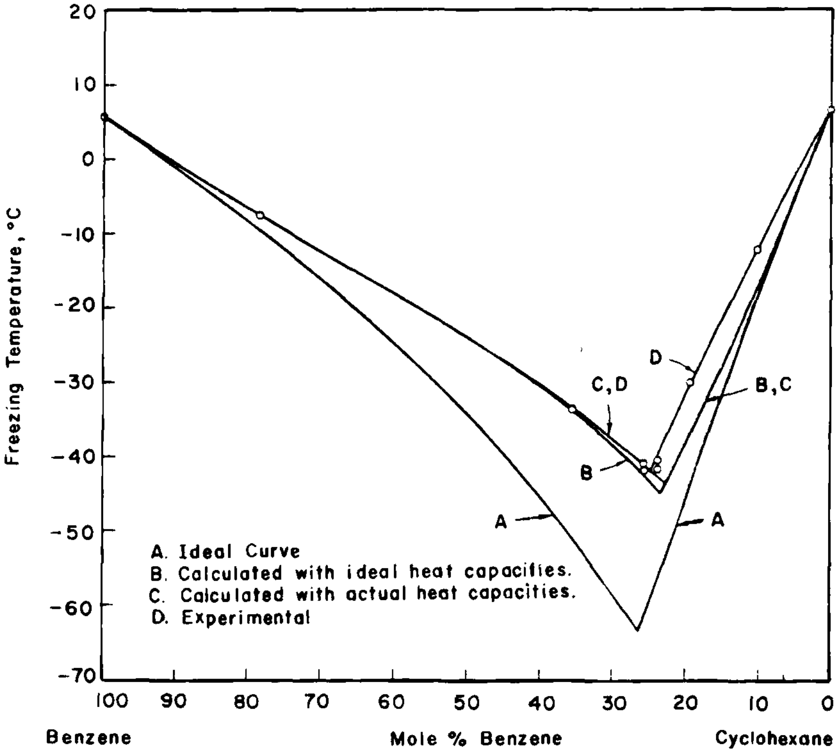

Figure 9. Calculated vs. Experimental Phase Diagram for Benzene - Cyclohexane.

magnitude of the deviation does not enable us to evaluate the degree of solid solubility, i. e., the position of the solidous line. This is dependent upon the solid phase activity coefficients, and must be determined independently. Methods for this will be discussed later in this chapter.

## Universal Solid Solubility?

We have discussed thus far two distinct types of systems, those which involve solid solubility, and those which do not. The philosophical question regularly arises as to whether the latter type, the simple eutectic system can exist at all. Should not all substances exhibit at least some solubility, however small, in any crystal lattice? There are many who believe that they should, and a number of writers habitually show, or apologizé for not showing, some limited range of solid solution in every phase diagram. This is particularly common in metallurgy, where extensive solid solution is to be expected; not so common, however, in the organic field, where recognizable solid solution is the exception rather than the rule.

The argument for universal solid solution is based upon the fact that any component in a system at equilibrium must have the same chemical potential in all available phases. If it is totally absent from one or more phases, then it must be concluded that its activity coefficient in that phase is infinite. There are other, parallel thermodynamic arguments. However, many authorities in the field interpret the pure crystal as a separate case where the continuous laws of thermodynamics do not extend. Ricci[3], for example, says "Theoretically it is not necessary that the phase be variable," and describes how the concept of the phase rule is modified thereby. Zernike[4], in his book, appears to accept the infinite activity coefficient and does not find any conflict with thermodynamics. A more recent text by Arnold Reisman[5] says, ". . . the setting up of a boundary of complete solid phase immiscibility represents an idealized version of nature that, to a lesser or greater degree, . . . , cannot be realized in practice."

Can an absolutely pure single component crystal be theoretically in equilibrium with a binary liquid or not? We are not asking whether we can actually grow such a perfect crystal, but only whether the pure crystal might not be more stable thermodynamically than the impure one. The answer to this question can be related to a yet more fundamental one. Is a perfect crystal ever more stable thermodynamically than an imperfect one, i.e., one containing "Schottky" defects or holes, Figure 10? Is the perfect crystal on the left always more stable than the one with the holes, regardless of how few holes there are?

It can be seen that the creation of a hole results in a loss of the binding forces for that site, and accordingly, the energy required to create the holes is proportional to the number of holes (if non-adjacent). The entropy of mixing, however, is not proportional, and although it decreases as the number of holes decreases, it actually increases on a per-hole basis. It can be shown by statistical mechanics that a crystal with some small, but finite, proportion of holes is more stable thermodynamically than the perfect crystal[6]. This proportion for the xenon crystal, for example, is $8 \times 10^{-6}$, or eight vacant sites per million. This would put the holes about 50 sites apart if evenly spaced. We can question the validity of the quantitative aspects of such calculations, particularly when

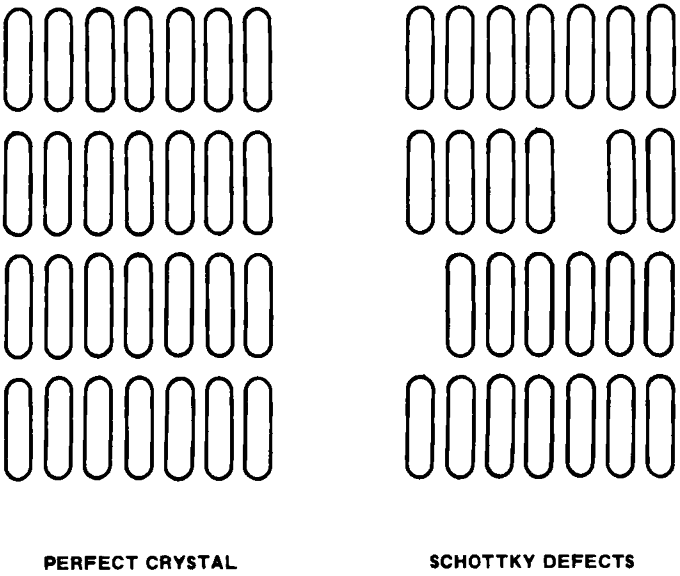

Figure 10. Illustration of Schottky Defects.

we consider that our concept of stability must really be relative to the crystal surface, not the entire bulk. However, the qualitative implication is clear; a finite number of holes is more stable than none at all.

Now, if holes alone are stable, then holes further stabilized by the presence of solute molecules will be even more prevalent, for the binding forces contributed by the solute alleviate to a great degree the energy required to create the holes, while not affecting the entropy of mixing. We can say unequivocally that if the solute molecule is physically smaller than the solvent molecule, there will be some degree of solid solution, the actual solid solubility depending upon how closely the solute binding forces simulate those of the solvent. (Indeed, if they are greater, the distribution coefficient is likely to be greater than unity, i. e., the solute may show greater solubility in the solid than in the liquid.) Suppose, however, the solute is larger, and cannot fit a single lattice site. In this case it must occupy two (or more), and for solid solution to be at all significant, it must make up for the binding forces of two (or more) solvent molecules. Yet, in any case, there must still be some solid solubility. For if we find a finite probability for individual holes, there must also be a finite, though much smaller, probability of adjacent hole pairs, pairs which will be stabilized to some degree by the binding forces of those solutes.

The above arguments, of course, do not consider other types of lattice defects or dislocations which can be enhanced by the presence of solutes or themselves stimulate solute inclusion. These circumstances would tend to strengthen the argument for universal solid solution.

## B. CRYOSCOPY

The determination of the liquidous curves of solid-liquid phase diagrams is usually best carried out cryoscopically, i.e., by means of time-temperature freezing or melting diagrams. Typical equipment for this type of measurement would be as in Figure 11. Lagged heating or

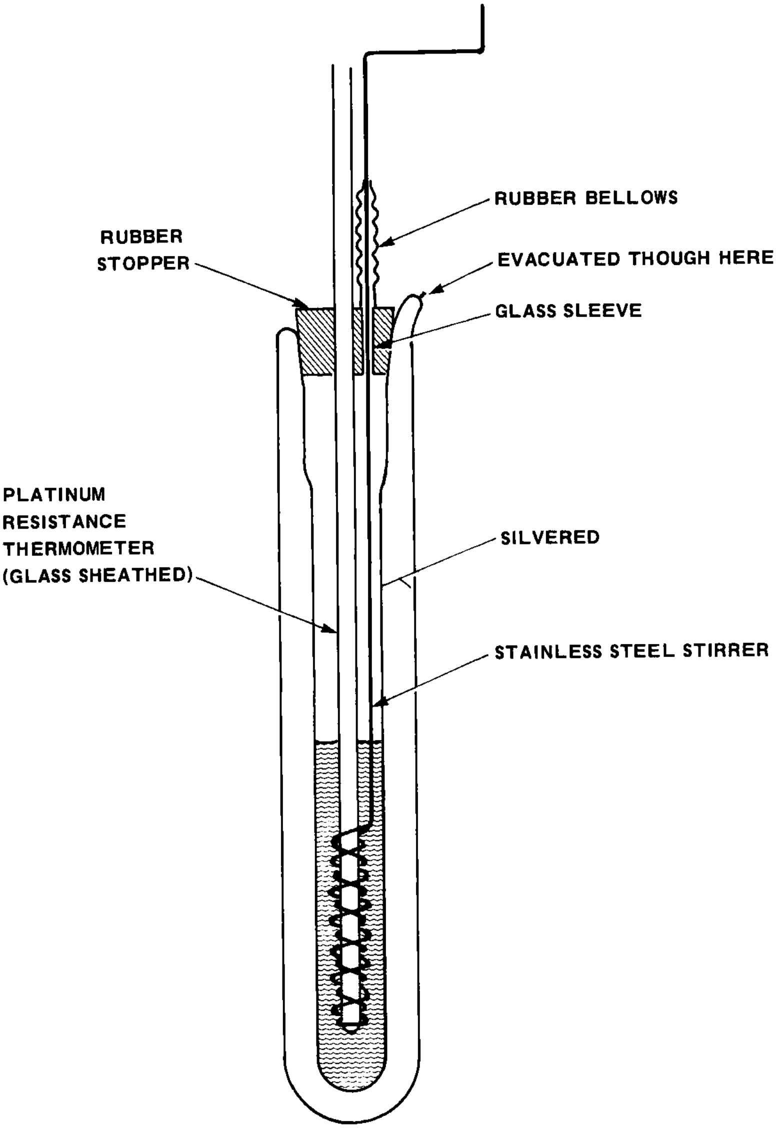

Figure 11. Cryoscopic Apparatus.

cooling is carried out through the evacuated double walls of the cryometer and the sample inside is constantly stirred while its temperature is measured via a thermocouple, resistance thermometer, or other means. Extremely precise methods for such measurements were developed by Rossini et al[9] who discussed the specialized equipment and precautions for accurate work. It is not, however, always easy to determine freezing temperatures precisely, even if all due precautions are taken, because the nature of the system may be such that equilibrium is hard to achieve and all measurements are made under conditions of extreme driving forces or thermal heterogeneity.

Figure 12a illustrates ideal freezing and melting curves, on which extrapolations, indicated by the dotted lines, permit one to establish the equilibrium freezing temperature. In theory, that temperature found by freezing should be identical to that found by melting. Practically, the necessity for a driving force usually leads to a slightly higher melting temperature. Figure 12b is an extreme example of the curves resulting from poor kinetic behavior. The initial supercooling is extreme, and, as a result of slow crystal growth, the temperature never does recover from its supercooled condition. The melting curve shows an irregular pattern due to a different phenomenon. Some substances crystallize readily in large chunks or as a single sheath on the cryometer wall. Upon melting, such large crystal cannot be sufficiently mixed into the liquid to provide thermal homogeniety throughout the sample. Accordingly, the measurements are completely irreproducible and useless. Fortunately, substances which have poor crystallization kinetics, and which supercool excessively, usually form many nuclei or seed crystals, thus providing a smooth slurry from which one can get a decent melting curve. Hence, either one curve or the other (freezing or melting) will usually be appropriate for cryoscopic studies.

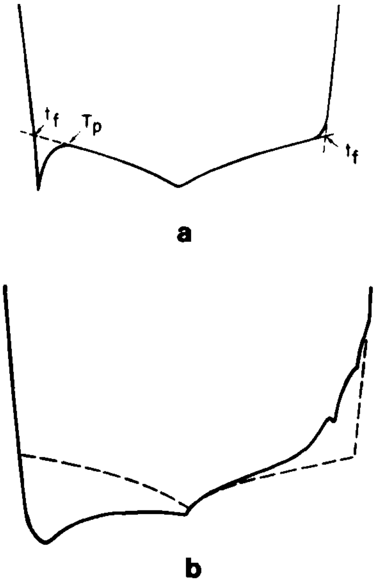

Figure 12. Theoretical (a) and Realistic (b) Freezing and Melting Curves.

In the past cryoscopic studies were important not only for establishing phase equilibria, but also for the evaluation of the molar purities of chemical compounds. Gas chromatography has to a great extent eliminated cryoscopic analysis as a routine assay technique. However, some chemicals, e. g., benzene, are still sold on the basis of freezing point specifications, and cryoscopic analysis is still useful as an occasional means of supplementing chromatographic analysis.

The development of an analytical technique for a given compound involves first the evaluation of the freezing temperature of the pure compound, $T_{fo}$, and its cryoscopic constant, k. Elaborate techniques[8] have been developed for the former based upon the shape of the freezing curve, or, more precisely, the differential shape of different parts of the curve. These techniques presume a true hyperbolic shape to the curve, and are very sensitive to slight errors in temperature measurement or to the effects of liquid nonidealities on curve shape. More practical, though less mathematically elegant, is the empirical technique of plotting the initial slopes for curves of several purities against the freezing temperature, and extrapolating to zero. It is normally argued that this requires more measurements than does the single curve technique, but one needs several such determinations anyway to establish the cryoscopic constant.

Figure 13 illustrates how one evaluates the initial slope of the freezing curve. What is actually used is the slope ratio as illustrated, since the slope itself is dependent upon the rate of cooling (or heating if a melting curve is used). Plots of slope ratio vs. freezing temperature are shown in Figure 14 a, b, and c. Whereas 14a shows a typical such plot, it must be recognized that not all compounds behave well enough to give the desired reliability, e.g., 14b. The slope ratio is an excellent parameter to use in identifying which of two or more possible crystalline modifications one might obtain in a given experiment, 14c.

Figure 15 illustrates the evaluation of the cryoscopic constant. To a sample with a freezing temperature of $T_f$, one can add successive quantities of a typical solute and obtain a plot of freezing temperature vs. concentration. The slope of this line, k', is not itself the cryoscopic constant because the initial sample is not 100 percent pure. If it is assumed that the initial impurity is approximately the same molecular weight as the compound in question, a correction can be made as indicated, where $T_{fo}$ is the freezing temperature of the pure material estimated from a plot such as those in Figure 14. Whether one is developing an analytical technique or establishing a phase diagram, it is well to make measurements as in Figure 15 with two or more different types of solutes. Any solute which gives abnormally high results for k is bound to be solid soluble.

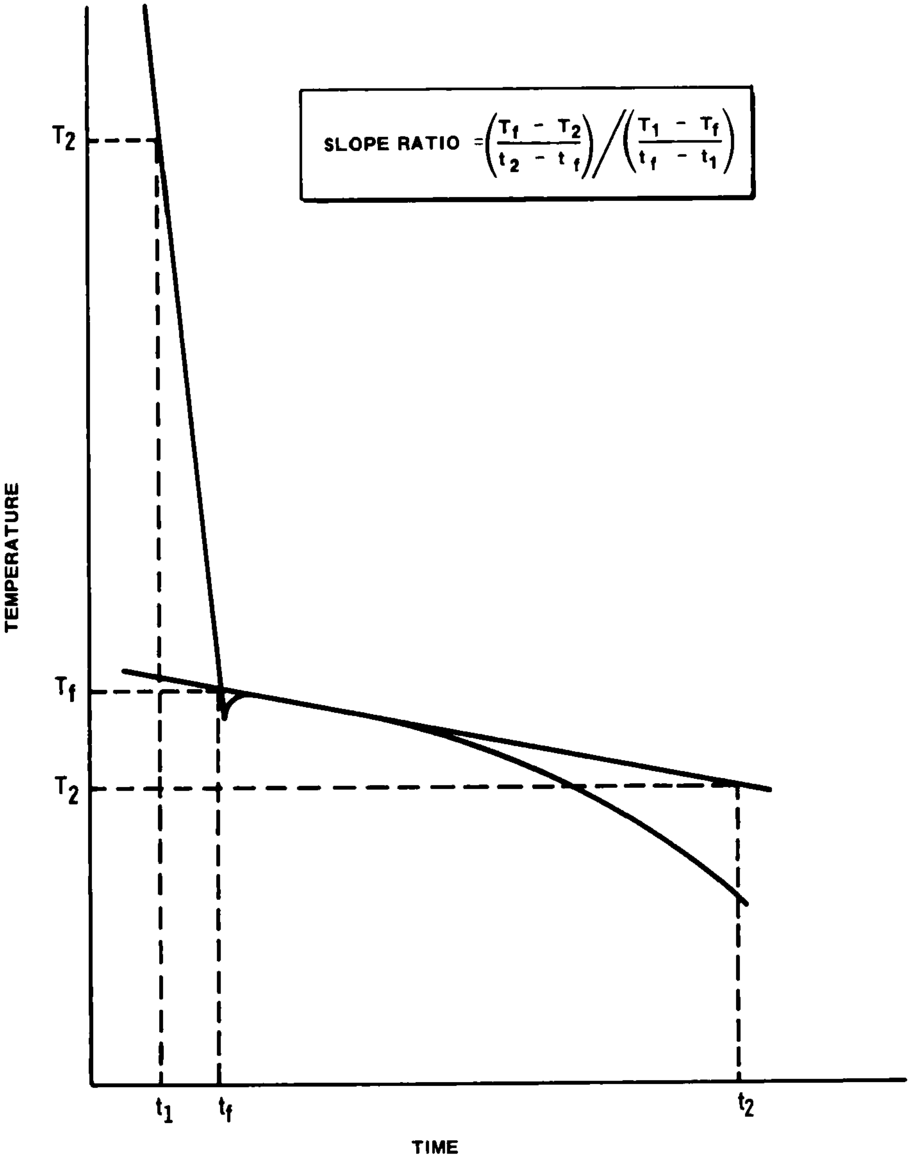

Figure 13. Evaluation of the "Slope Ratio" from a Cryoscopic Freezing Curve.

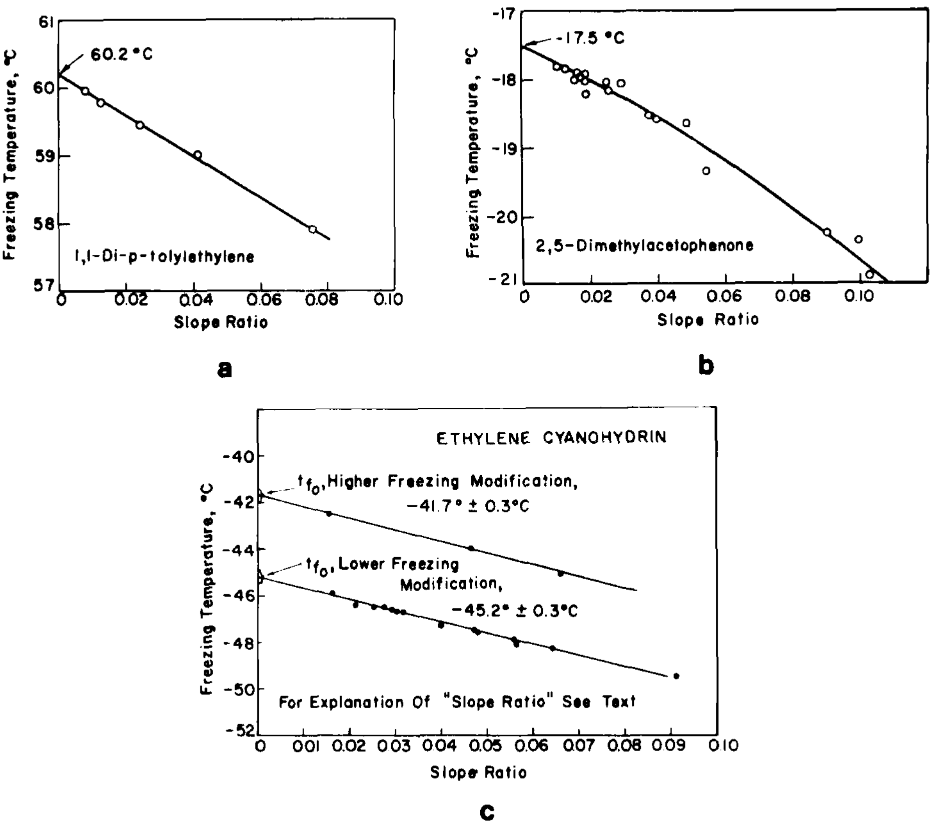

Figure 14. Typical Freezing Temperature -- Slope Ratio Plots; a) Ditolylethylene; b) Dimethylacetophenone; c) Ethylene Cyanohydrin.

## Cryoscopic Anomalies

We have discussed some of the common problems related to the kinetics of crystallization or diffusion. Occasionally situations arise requiring special explanations, and these can often be observed as variations in the shapes of cryoscopic curves with freezing or melting rates. Figures 16a and b are two such examples.

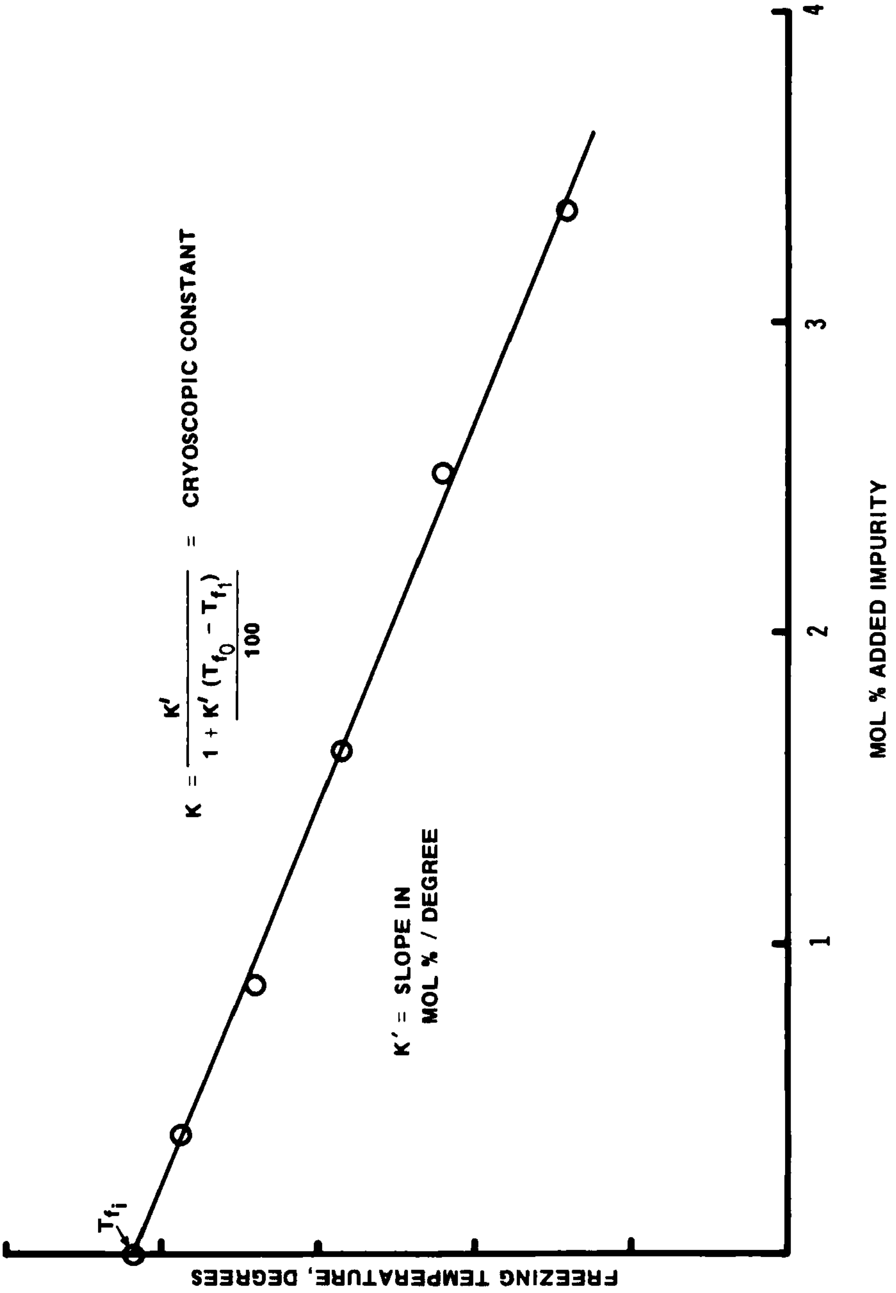

Figure 15. Evaluation of the Cryoscopic Constant.

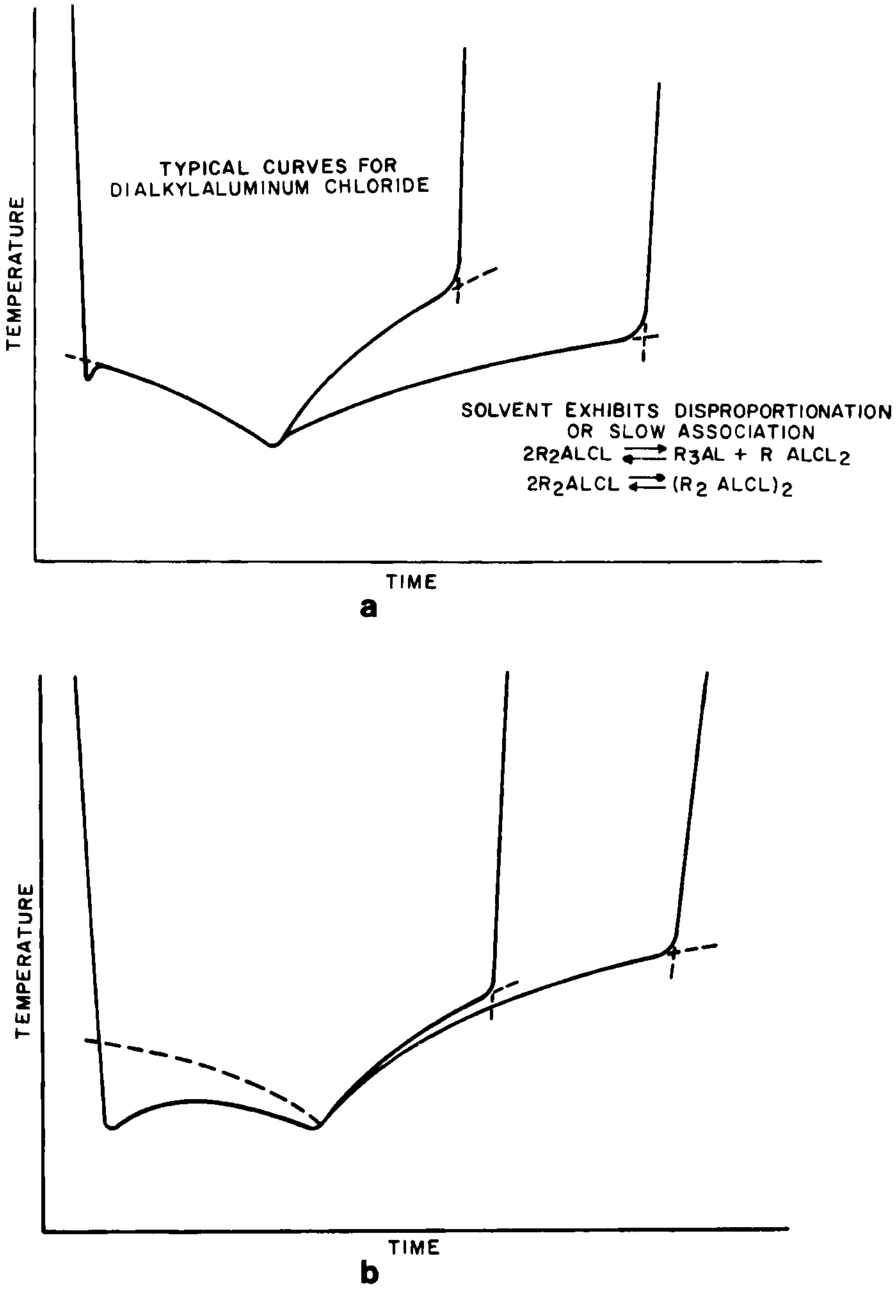

Figure 16. Kinetic Effects on Cryoscopic Freezing and Melting Curves; a) A Dialkylaluminum Chloride; b) β-Ethylnaphthalene.

Figure 16a shows freezing and melting curves for a dialkylaluminum chloride. Unless the sample is melted quite slowly the melting temperature is excessively high relative to the freezing temperature. When it is melted slowly the values are more consistent. This phenomenon cannot be explained by solid solubility, diffusional kinetics, or even melting kinetics (i. e., paucity of crystal surface). Rather, it must be the result of a relatively slow equilibrium reaction occurring in the liquid state. If the molecule exhibits either disproportionation or association, and the crystal is formed of only one of the possible species, then the other species will behave as impurities. Even an ultrapure sample will show a freezing curve slope ratio typical of an impure sample. As part of the sample is frozen, however, and the "impurities" concentrated, the equilibrium is shifted so that those concentrations are brought back toward their initial levels. As the sample melts, the equilibrium is shifted once more, but there now being fewer molecules of "impurity", the sample melts higher than it initially froze, the difference being less the more slowly it is melted. Note that the rapidity of freezing cannot affect the value of the measured freezing temperature, although it will have some affect on the slope ratio. Cryoscopic studies are insufficient to tell us which of the two (or more) possible reactions is occurring, but in this particular instance, other evidence suggested the dimerization.

Figure 16b cannot be explained so simply. Here the kinetics of crystallization are so poor as to make the freezing curve useless, but the melting temperature and apparent purity increase the more slowly the sample is melted. Indeed, plotting the melting temperature and slope ratio vs. the length of time the sample is frozen yields curves as in Figure 17. This implies a sort of ripening or other phenomenon occurring in the crystal state. These results were obtained for B-ethylnaphthalene, and it is known that at least one of its possible impurities, B-vinylnaphtha-

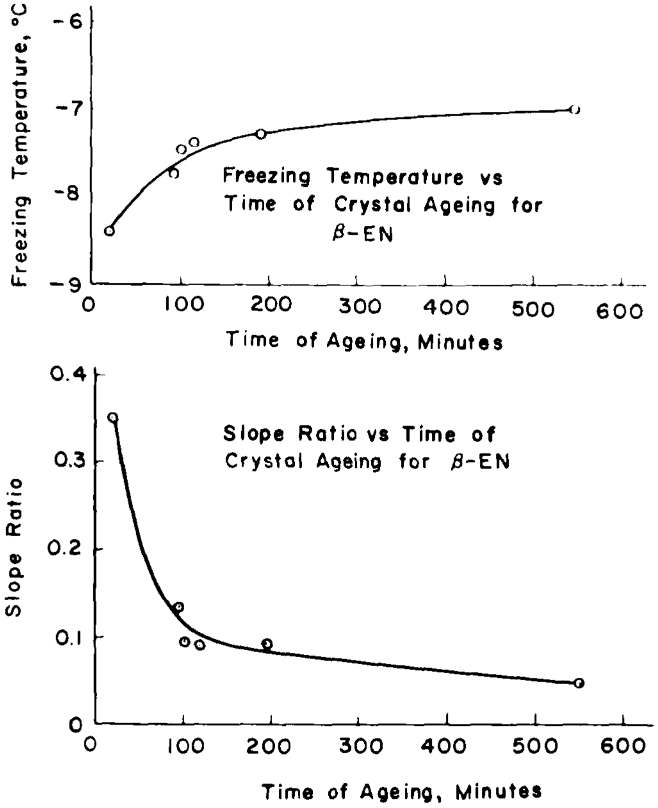

Figure 17. The Effect of Ageing on Crystals of β-Ethylnaphthalene.

lene, is solid soluble in B-EtN. It is reasonable to expect that if liquid diffusion is kinetically hindered, the solid solution grown from the system will contain more solute than it would under true equilibrium conditions. Upon standing, however, the process of melting and refreezing can occur to produce a more stable, and hence higher melting, solid phase.

One final example of kinetically affected cryoscopic phenomena is the propane hydrate system. The phase equilibria are illustrated by the pressure-temperature diagram of Figure 18a. A composition axis is not

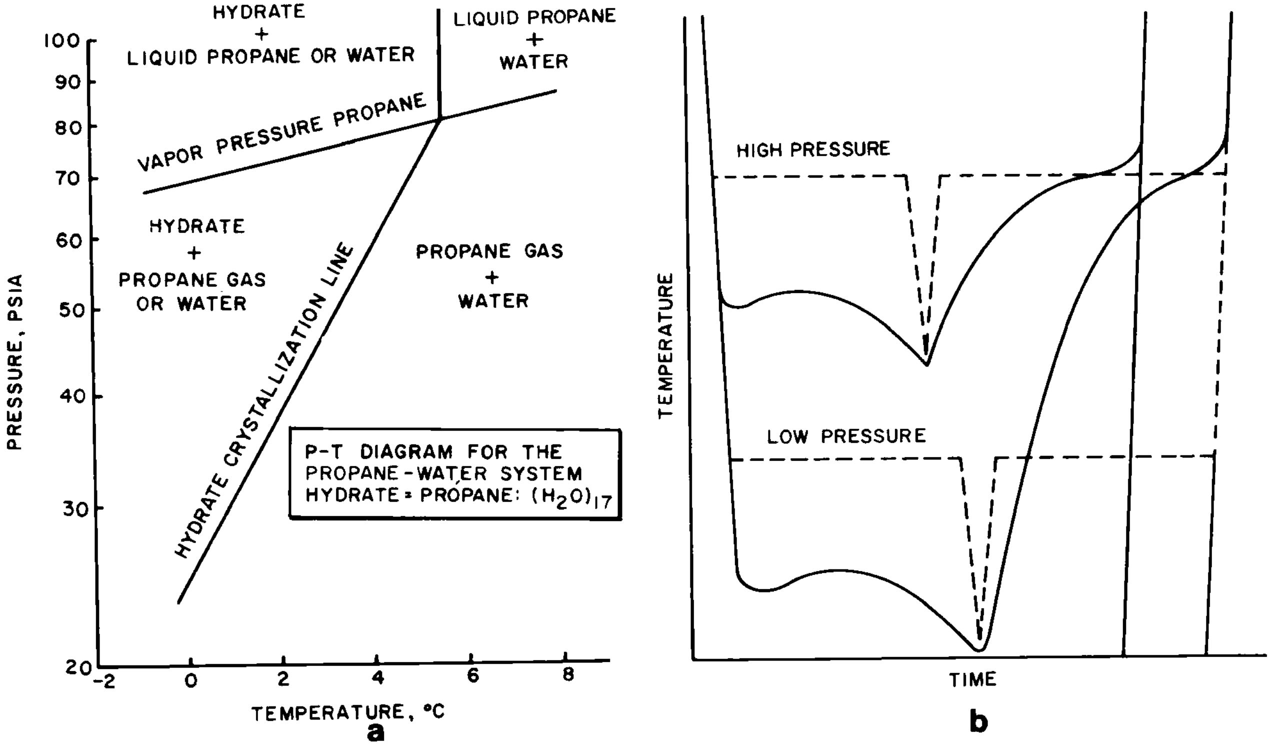

Figure 18. The Pressure - Temperature Phase Diagram (a) and Anomolous Cryoscopic Curves (b) for the Propane Hydrate System.

needed here, because the mutual solubilities of water and propane are so low that the presence of any finite quantity of one can be considered sufficient to saturate the other. Above the propane vapor pressure line, any propane in the system is a liquid; below it is a gas. To the right of the hydrate crystallization line propane and water both exist mutually saturated with each other. To the left of this line propane hydrate crystal is stable, and, given sufficient time, will grow until either all the water or all the propane is used up. On the line itself, of course, all three phases are in equilibrium. The intersection of the hydrate crystallization line with the propane vapor pressure line is a quadruple point at which all four phases, propane liquid and gas, propane hydrate, and water, can exist in thermodynamic equilibrium. The quadruple temperature is 5.5°C.

Figure 18b shows freezing and melting curves for the system, the dashed lines being the theoretical curves one would get if there were no kinetic barriers and equilibrium could be obtained. At high pressure, above the propane vapor pressure line, the upper set of curves are obtained. Crystallization occurs with much supercooling, and the kinetic barrier in this case is the low solubility of propane in water (or vice versa), far below the 1/17 mole ratio. Crystallization actually appeared to take place at the liquid-liquid interface, though the crystals were subsequently dispersed in the aqueous phase. The melting curve, other than exhibiting the slightly higher temperature suggestive of low heat transfer relative to the melting rate, is reasonably normal, and the melting temperature is slightly above 5.5°C.

At low pressure, in the presence of propane gas, the freezing curve is similar to that at high pressure, exhibiting the same kinetic lag. It is, of course, lower as predicted by the phase diagram. The melting curve, however, exhibits an unusual kinetic phenomenon. The crystals refuse to melt close to the theoretical equilibrium temperature, and significant melting does not occur until near the quadruple temperature of 5.5°C. No physical means, including pressure reduction, would induce the crystals to melt any lower. The explanation lies in the extremely low solubility of propane in water. That propane released by the melting of hydrate supersaturates the aqueous phase and the propane activity or chemical potential rapidly increases. Its theoretical vapor pressure would be above the ambient, and it should flash out of solution. But vaporization from a liquid phase can only occur at a vapor-liquid surface or bubble nucleus. However, the stability of a bubble nucleus decreases with size, and the quantity of propane per unit volume of water is insufficient to promote the formation of stable nuclei, in spite of the high chemical potential. There is, therefore, no mechanism to reduce the chemical potential and thus promote melting. When the quadruple temperature is reached, the chemical potential of the propane molecules is so high that agglomeration can occur to give a pseudo-liquid phase which, in turn, provides sufficient propane for stable bubble nuclei. Only then can the propane flash off to reduce its chemical potential and permit further melting.

Thus, we see that crystallization and even melting are kinetically regulated phenomena, and process designs or concepts made in the light of phase equilibria alone are likely to be inadequate.

## C. MELT CRYSTALLIZATION SCHEMATICS

The greatest interest in melt crystallization today is for separation and/or purification in either the laboratory or the plant. Although solvent crystallization has had a long history of industrial applications, melt crystallization has lagged somewhat behind, being at present more useful in the laboratory than the plant. This is presumably related to the problems of handling systems which can, when out of thermal control, freeze up completely, or, when melted carelessly, expand with destructive force. The low thermal conductivity of solid organics has not been conducive, either, to the use of such systems. Nevertheless, the recognition that in most cases there is possible a theoretical distribution coefficient of nearly zero has prompted a great deal of work in the field, most of which has been useful in the laboratory, but which has defied scale-up. It would appear, in fact, that the successful plant operations which can be classified as melt crystallization were developed independently of laboratory processes, and this primarily because of the completely different thermal conductivity requirements of small and large scale processes.

## Zone Refining

It goes without question that the most remarkable development in laboratory crystallization in the past twenty years was the invention of zone melting by W. G. Pfann.[9] This technique, though developed specifically for metals, rapidly found its way into organic systems. We do not intend to discuss the details of the many zone refining methods here; they are very effectively described by Pfann, Schildknecht,[10] and others. A brief description will suffice.

The solid sample, if organic, is contained in a tube, usually glass, Figure 19. (Metals can be refined in boats or even as self-sustaining ingots, but we will concern ourselves only with organics.) One end of the sample is heated, creating a molten "zone." The heater is then slowly passed along the length of the tube, with the result that a new portion of sample melts while solid crystallizes behind the heater. In this manner the molten zone is passed the full length of sample. Since the solid crystallizing is theoretically poorer than the liquid from which it is growing (as in most simple eutectic and solid solution systems) the impurities are carried with the molten zone and collect at the final end to freeze. The beauty of the system is that successive zones can be passed

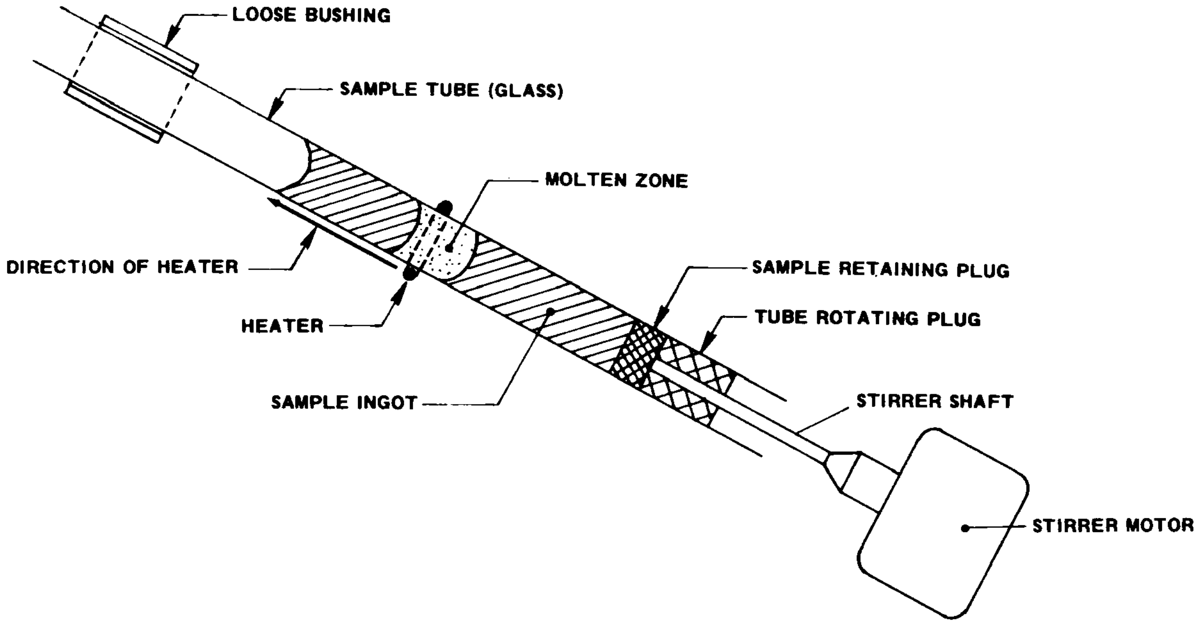

Figure 19. Oblique Zone Refining (from Atwood,[24] reproduced by permission of The Chemical Rubber Company)

through the ingot either consecutively or simultaneously so that extremely high degrees of purification or solute concentration might ultimately be achieved. There are limits, of course. The ultimate purification is related inversely to the zone length, but the purification rate is related directly to the same zone length. Similarly, while fast rates of zone travel might be expected to do the job quicker, the slower zone travel rates give better quality crystal with consequently better purification per zone pass (particularly for simple eutectic systems).

Zone refining may be carried out vertically or horizontally, although in our own laboratory we prefer an oblique arrangement as in Figure 19. Rotation of the tube (either continuous or intermittant) promotes mixing within the molten zone, reducing the concentration boundary layer and improving the separation. Note that the glass tube is free to slide on the sample retaining plug. This allows safe expansion as the zone is first melted into the bottom of the sample ingot.

Although laboratory zone refining has been extremely valuable for the preparation of high purity standards or the concentration of solutes, it represents a typical example of the difficulty of scaling up laboratory melt crystallization techniques to plant processes. Figure 20 is a plot of potential production rate vs. ingot diameter for various zone travel rates. Present laboratory techniques are limited to ingots less than one inch in diameter and travel rates below one inch per hour, if decent quality (i.e., purified) crystal is to be grown. (Much faster rates have recently been made possible by the inertial agitation techniques of Bolen, Van Essen, and Smit.[11] The tube is rotated alternately clockwise and counterclockwise every second with angular accellerations of 1000 revolutions/second$^2$, but the energy requirements restrict the technique to very small tubes.)

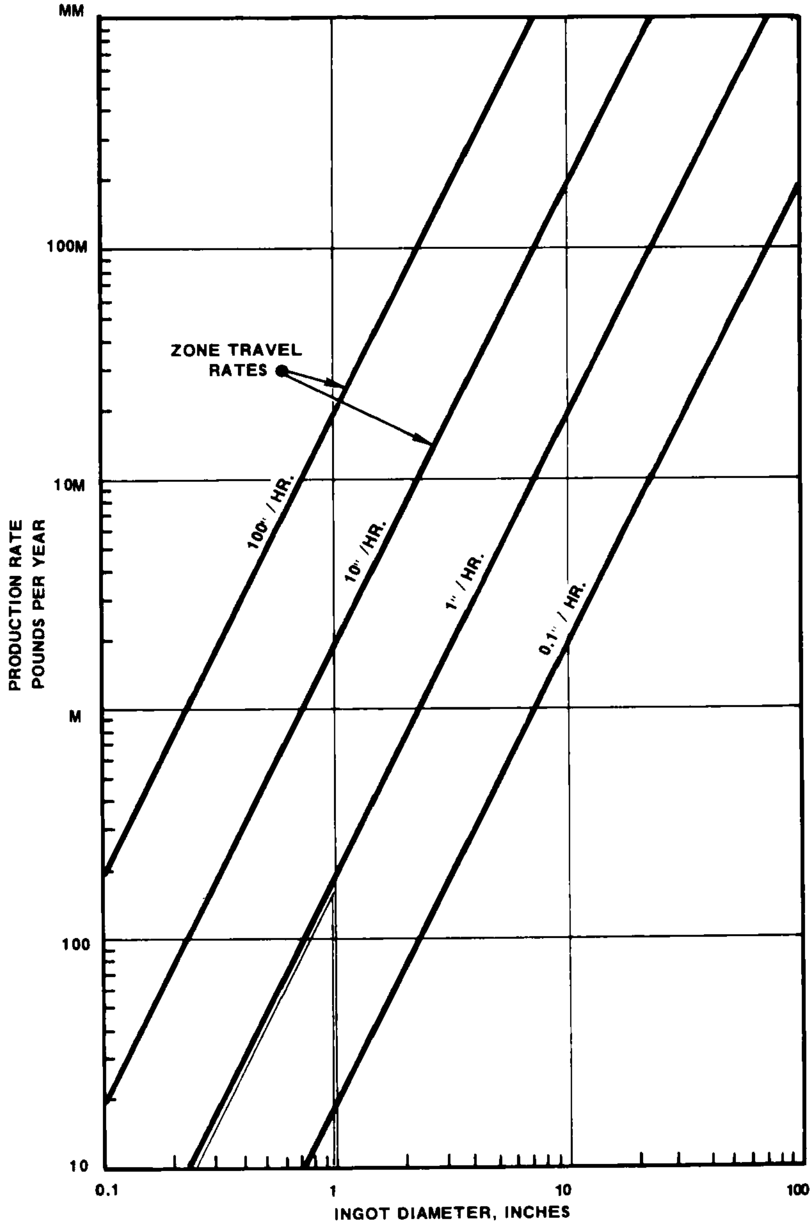

Figure 20. Potential Production Rates for Industrial Zone Refining as a function of Tube Size and Zone Travel Rate (from Atwood, [24] reproduced by permission of The Chemical Rubber Company)

The practical limits to ingot size and zone travel rate are not dictated exclusively by product quality, but also by the physical impossibility of moving reasonably short, but wide diameter zones at practical rates. As the heater moves forward and the crystal grows, the heat of fusion must be removed radially through the solid phase. Because of the low thermal conductivity of the solid, there is created a well in the center of the ingot, the depth of which is proportional to the zone travel rate and to the square of the tube diameter. Figure 21 illustrates how the relative shape of the crystal face changes with tube diameter for a constant zone travel rate. The very deep wells created in the larger tubes not only necessitate a greater interzone spacing, but lead to the danger of periodic "pinching off" and entrapment of liquid. One can reduce the zone travel velocity to compensate for larger diameters and maintain a given zone shape. In this case, however, the production rate is proportional only to the diameter and not its square. Inasmuch as the capacity of the apparatus of holdup is proportional to the zone volume or diameter cubed, the ratio of production rate to holdup becomes inversely proportional to the square of the diameter, an impossible prospect for scale-up.

Obviously other ingot shapes have been suggested, i.e., flat plates, concentric tubes, etc. Thus far none have proven sufficiently successful for scale-up.

## Progressive Mode

We should recognize that, whereas the specific technique of zone melting resists successful scale-up, the inherent schematics of the method might be applicable to industrially practical forms of melt crystallization, possibly to unit operations which might be otherwise multi-staged. An analysis of continuous zone refining schematics led to the concept of the "progressive" mode[12] of multi-stage operations. This is illustrated in

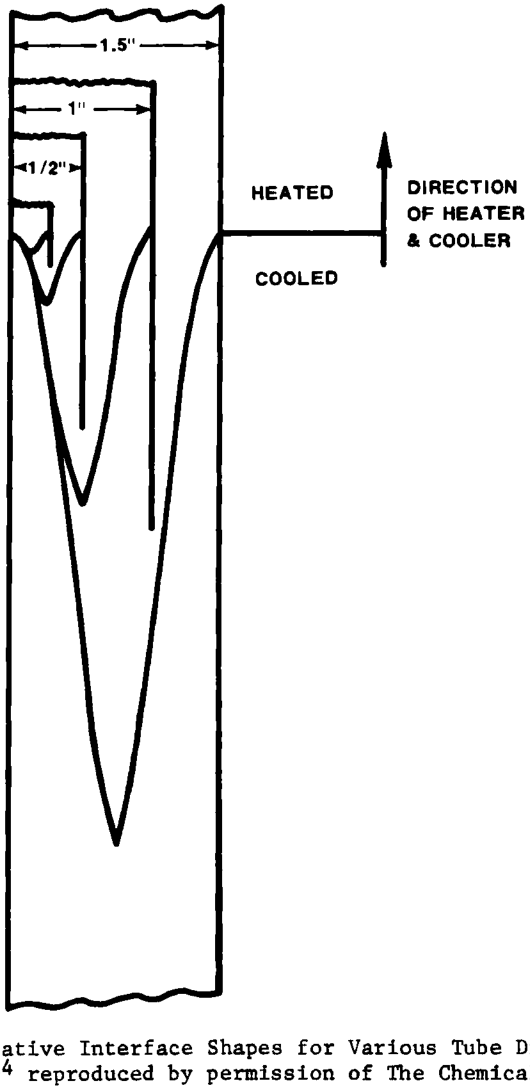

Figure 21. Relative Interface Shapes for Various Tube Diameters (from Atwood,[24] reproduced by permission of The Chemical Rubber Company).

Figure 22b, using as an example the unit operation of drum crystallization. Figure 22a shows the traditional mode of multi-staging with reflux. In this case the drums, rotating counterclockwise, carry purified crystal to the left, where it is melted into the next reservoir. Reflux is passed back to the right, while purified, $P_1$, and waste, $P_2$, products are continuously taken off as shown. In the progressive mode there is no reflux, so that the charge as a whole moves to the left. Purified product, $P_1$, is removed continuously from the left hand drum until such time as it no longer meets quality specifications. At that time a new reservoir and drum are added to the left hand end to provide an additional stage of purification. Waste product, $P_2$, is not collected continuously; rather, the right hand drum is operated until the last reservoir is nearly empty and of the waste quality desired for $P_2$. Then the reservoir is emptied and the drum removed, the very next reservoir to the left now becoming the new waste product reser-

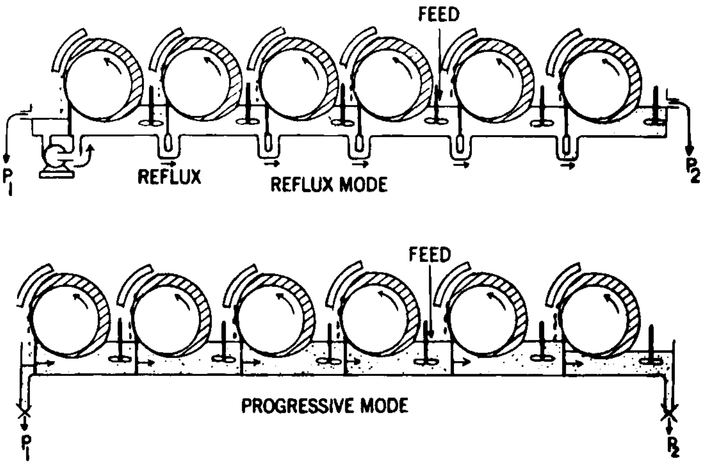

Figure 22. Reflux and Progressive Modes of Multiple Rotary Drum Crystallization (from Atwood,[12] reproduced by permission of the Am. Inst. Chem. Eng.)

voir. The feed point is, of course, moved periodically one stage to the left.

A comparative analysis of the two modes, using the same solute-solvent distribution coefficient, k, showed that the progressive mode was twice as efficient, in terms of total required crystal growth per unit of feed or specification product, as was the reflux mode. This is equivalent to saying that we need twice as many stages in the reflux mode at equal drum rates.

The term "progressive" mode was adopted because the entire operation essentially progresses along an infinite series of stages, drums being periodically removed from the right and added to the left. One does not intend, of course, to physically move drums and reservoirs. The same effect can be accomplished by appropriate piping and valve control. However, the sequential order is more obvious if the drums are arranged in a circle, Figure 23. Here there is a periodic clockwise progression of feed and take-off points while the drums themselves remain fixed.

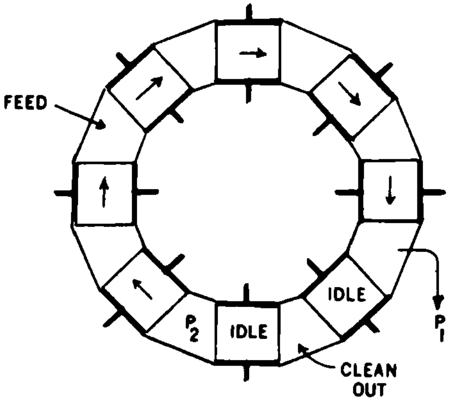

Figure 23. Circular Form of the Progressive Mode of Rotary Drum Crystallization (from Atwood,[12] reproduced by permission of the Am. Inst. Chem. Eng.)

It must be borne in mind that the comparative superiority of the progressive mode over the reflux mode is based on the assumption of equal distribution behavior (i. e., same value of k) and crystal quality. For the most part this would appear to be a valid assumption. However, it will be noted that in the progressive mode new crystals are started periodically on that drum added to the pure product end of the train. In the reflux mode the same crystals are perpetuated indefinitely. To the extent that the quality of the crystal being grown is dependent upon that of the prior layer on which it is being deposited, this may make a difference, reducing or even reversing the relative efficiencies of the two schemes. This might depend to a large extent on the particular crystallization technique chosen (drum crystallization being only a typical example). One specific laboratory device, for instance, that of C. P. Saylor,[13] has been designed especially to promote crystal "ripening" with time. Rotation of the growing (and melting) crystal leads to a situation where initial imperfections cannot be propagated indefinitely, but are automatically removed from the melting side. In such an instance it would be expected that the technique would be far superior in the reflux mode than the progressive mode, for in the latter the crystals must be destroyed and replaced by new ones before they have a chance to ripen.

Studies have also been made of other schematic modes of multistage operation. It was found that most of these were essentially hybrids of progressive and reflux schematics and that their efficiencies lay midway between these two. They will not be enumerated here.

## Column Crystallization

The concept of purification by the countercurrent contact of crystals and liquor has existed for some time. However, it had been generally recognized that this would not be as effective for solid-liquid processes as for liquid-liquid and vapor-liquid schemes because of the extremely limited diffusion in the crystal state. Molecular interchanges between the phases cannot freely occur, except possibly with respect to the crystal surface. Impure crystal, grown from an impure solution, would be trapped beneath layers of pure crystal, and although it would be thermodynamically unstable in the presence of highly pure liquor, molecular interchange would be prohibitively slow.

Nevertheless, in 1961, Schildknecht and Vetter[14] described a melt crystallization column in which extremely pure benzene was produced. The concept of possible solid-liquid interchange, perhaps by simultaneous melting and refreezing, caught on and numerous investigators entered the field. A variety of column types were tried in which the crystals were transported countercurrent to the liquid, either upward or downward, by means of rotating spirals or screws, or, downward only, by means of gravity. These devices, when operated continuously at finite reflux, were either center fed, or end fed, and the analogy with distillation was ever retained by freezing at one end and melting at the other.

A number of mathematical modeling studies have been made on these devices, and it has generally been concluded that they are remarkably effective for crystal washing, but that little real solid-liquid interchange occurs. For simple eutectic systems, the actual crystal grown at the cold end is effectively pure, though if of poor quality (e.g., dendritic), that solid will contain trapped liquor. The column crystallizer serves to remove adhering liquor, but cannot remove that truly trapped. The recent experimental and mathematical studies of Moyers[15] on dense packed, gravity driven, beds showed this to be essentially the case. The product quality is that of the crystals as originally grown at the cold end, but very effectively washed. It would seem then that more attention must be given to the crystal growth step itself (and the environment in which the growth takes place) to obtain the best product.

Studies by Gates and Powers[16] on solid solution systems were disappointing in terms of effective separation, though these investigators were able to quite adequately describe mathematically the behavior of the system. They demonstrated that models incorporating solid state diffusion were completely untenable with reality, and that for those models involving melting and refreezing with subsequent diffusion from the boundary layer, the mass transfer coefficients corresponding to the experimental results were surprisingly low. Gates and Powers attribute this to the possible non-uniformity of solute with only the most impure or "active" centers of impurity taking part in the interchange. It is quite feasible that only "active" sites in the surface do take part, though these need not necessarily be determined by the degree of impurity, but perhaps by the type of site. This we will discuss further on the last pages of this chapter.

Numerous attempts have been made to scale up the Schildknecht type of column crystallizer for industrial use. Considerable technical success has been realized for some of those systems in which the crystal washing appears to be a critical part, and in which only a few theoretical stages of rectification were required. Betts, Freeman, and McNeil,[17] for example, have published studies for a variety of systems on 1" and 2" conlumns, and report 4-8 theoretical stages with the smaller of these (HETP of 2-5"). More recent studies by Betts[18] on a 4" column indicated 3 stages over a 45" length. Further scale-up, 8" and possibly larger, has been carried out successfully (e. g., Newton Chambers Engineering Ltd.[18]), though it has not really been established how economical this type of column will eventually be.

A practical and economical industrial scale column crystallizer has been developed, however, and this is the UCAL (Union Carbide Australia, Ltd.) process of J. A. Brode.[19] This process, developed for the purification of p-dichlorobenzene, cannot only produce a high purity product, but does so with a remarkably efficient thermal utilization.

The basic schematics are given in Figure 24. Unlike other colum column crystallizers, in which all solid is grown at one end, crystals are grown over the entire length of the UCAL column, heat being removed through the outside. The crystals are tumbled and transported toward the larger end by the slowly rotating vanes. In the attached purifying section the crystal product is melted, and some of the melt is refluxed back countercurrent to the solid. Because the crystallization occurs over the entire length of the column, the total mass flow is greater at the high purity than the low purity end; hence the tapered shape, which reflects

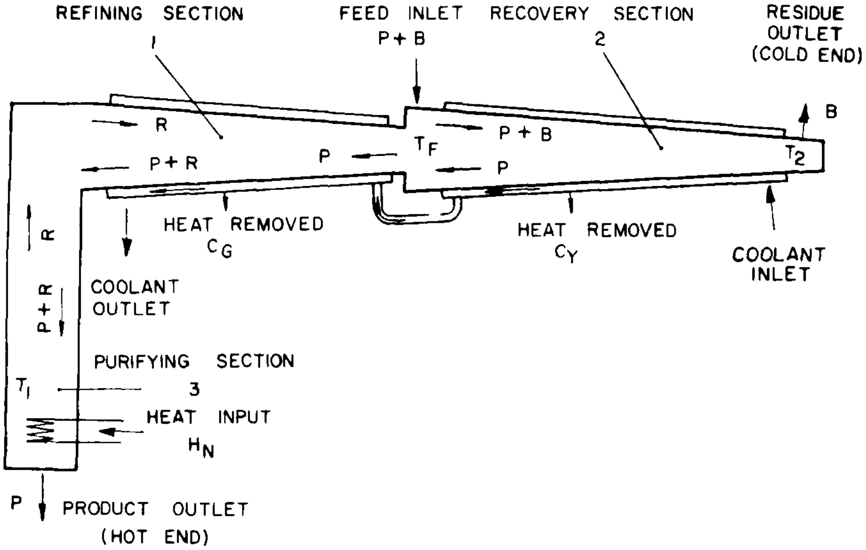

Figure 24. The Brode Purifier (UCAL Process), Schematic Form. (Reproduced from Mech. & Chem. Eng. Trans. of the Institute of Engineers, Australia[19].)

that difference in flow rates. The conservation of heat (or rather "cold" in this case) is obtained by passing the low purity product (or a fluid thermally exchanged with it) through the cooling jacket to promote the crystallization. Only a minimum of extra refrigeration is thus required.

As might be expected, the slow tumbling of the crystals in the UCAL column would promote considerable back-mixing of the liquor. Accordingly, the actual plant design, Figure 25, consists of four units (plus purifier) of varying diameter, which together constitute a very long column. Residence time in this column may be up to 16 hours, so that a high ratio at holdup/throughput is required. However, this is no disadvantage as long as the relative heat losses are small and the equipment is simple.

Specification PDCB of 99.5 purity is routinely obtained at 88 percent recovery from 75 percent/25 percent para/ortho feed at a reflux ratio of 0.25/1. At a reflux ratio of 0.5/1, however, product quality was increased to 99.99 percent purity, and at a 2/1 reflux ratio product purity after only 2.5 hours was found to be greater than 99.997 percent. At least 12 hours would be required to achieve steady state, so the ultimate possible purity obtainable has not really been established.

The UCAL melt crystallization process has certain fundamental reasons for its success relative to other column crystallizers. Perhaps most important is that the usual distillation analogy is abandoned and crystallization is carried out over the entire length instead of at one end. In this sense it might be considered analogous to the unlagged laboratory Vigeroux column in which there is no deliberate reflux from the top, though there is partial condensation (and reflux therefrom) within the column. The advantages of this are (1) crystal is always grown from as pure a liquor as possible, thus maximizing crystal quality, and (2) crystal is grown slowly (over several hours), again maximizing quality. Next in

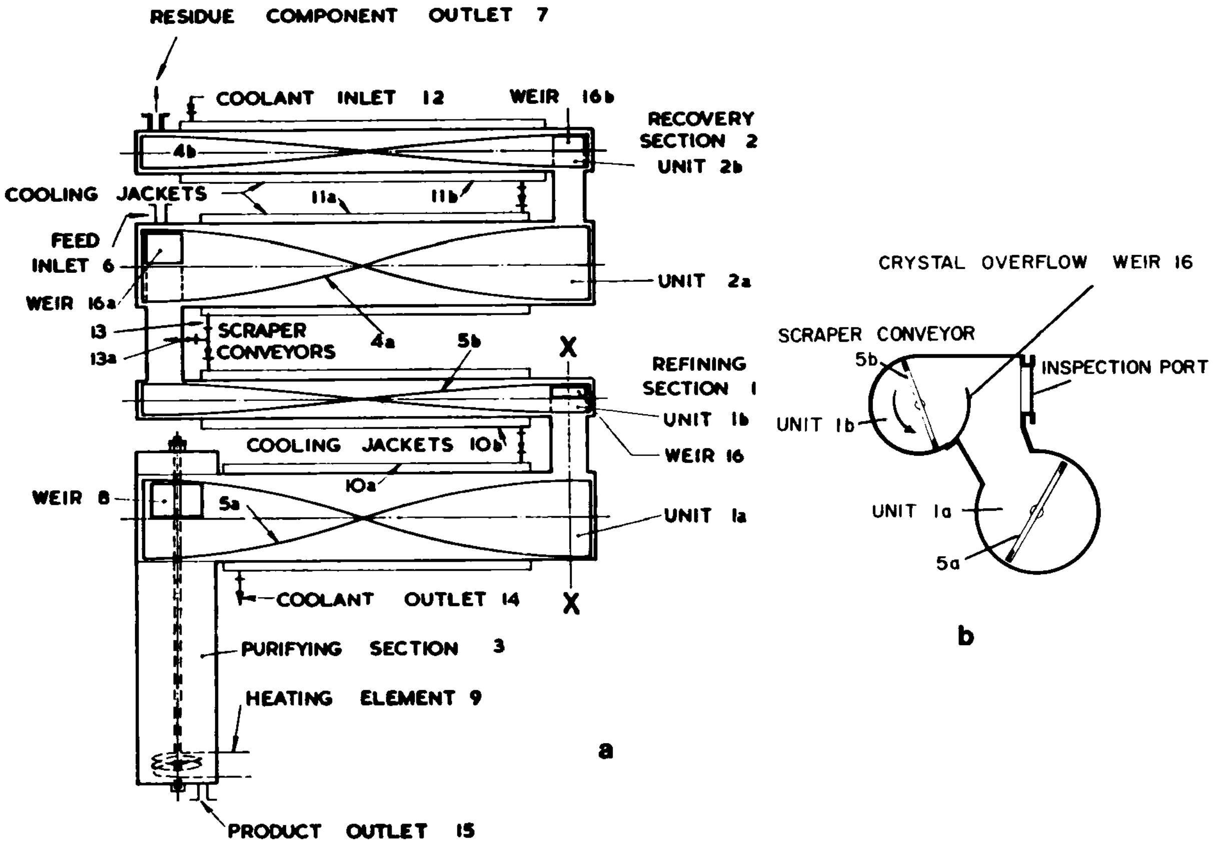

Figure 25. Practical Form of the Brode Purifier; a) Overall View; b) Cross - Section at X--X, Showing Crystal Overflow Wier. (Reproduced from Mech. & Chem. Eng. Trans. of the Institute of Engineers, Australia[19].)

importance is the time permitted for countercurrent solid-liquid contact, for effective washing, i. e., removal of the boundary layer, is ultimately dependent upon diffusion, regardless of the degree of solid-liquid shear achieved by agitational techniques. The slow tumbling of the UCAL crystallizer is sufficient to keep the boundary layer in contact with ever purer liquid reflux, and the long residence time permits diffusion to do an efficient washing job.

Remarkably enough, the first prototype plant, a 1500 tons/annum p-dichlorobenzene unit, was designed full size by its inventor, and did not result from the scale-up of laboratory or pilot equipment. This fact is especially significant when one recognizes that the problems of heat transfer and thermal control are of a different magnitude and type than for small scale operations. Whereas it would not be impossible to design a laboratory prototype of the UCAL process, it might be extremely difficult to control, heat transfer to and from the surroundings being most significant relative to internal heat flows and causing uneven rates of crystal growth and possible plugging. Accordingly, had development proceeded in the usual way, complications in the laboratory step might have prevailed and precluded further scale-up. A recognition of the fundamental differences between laboratory and industrial process characteristics is essential when one wishes to pursue developments in either area.

In this specific instance, scale-down was subsequently made to a pilot unit, and several systems have been studied therein. Extremely pure products have been obtained for simple eutectic systems, and substantial success has been obtained even for solid-solutions. For example, studies with benzene at a 0.75/1 reflux ratio showed a thiophene reduction from 0.05 percent in the feed to 0.01 percent in the product. Similarly, thianaphthene in naphthalene was reduced from 1.1 percent to 0.12 percent.

## D. STUDIES OF SOLID SOLUTION

The evaluation of the stage equivalencies of column crystallizers requires, of course, an accurate knowledge of the true solid-liquid equilibria of the system. The difficulties of making such measurements would lead one to suspect that perhaps most of the available data would be in error. There is little difficulty in establishing the liquidous line (by thermal analysis), but contrary to classical beliefs, one cannot expect a thermal break at the solidus line. Such a break would require solid state diffusion during the freezing process or else continual melting and refreezing, melting in an environment of decreasing temperature being thermodynamically impossible if there is any driving force at all for crystallization. One must rely on calorimetric studies of the melting of homogeneous solid solutions (which, as we have pointed out, would be very difficult to obtain) or the compositional analysis of crystal carefully grown from the liquor. The former would be expected to give low results (the initial melting point of the lowest melting of the non-homogeneous crystal), and the latter would give high results due to entrapped or adhering liquor. Certain experiments, in fact, indicated that the entrapped liquor would be greater for the crystallization of solid solution then for a pure (eutectic forming) component.

Zone refining studies showed that it was quite easy to remove visibile solutes (such as dyes) from reasonably pure naphthalene. Indeed, it was also found quite easy to remove such dyes from a eutectic mixture of naphthalene and p-nitroaniline. Eutectic mixtures are necessarily microcrystalline in that both constituents must crystallize simultaneously in separate crystallites which exclude each other. Interstitial liquor entrapment would be expected to be high, but nevertheless the removal of a red dye from this system was found to require only a few zone passes. The separation of the same red dye from a solid solution of naphthalene with about 5 percent thianaphthene was in contrast found very difficult, requiring many more passes and slower crystallization rates. This indicates that solid solutions — at least this one — may be much more microcrystalline than even eutectic mixtures, and the question naturally rises as to whether the inclusion of the solute in the solid solvent surface severely reduces the crystal stability or at least the growth rate. Indeed, the actual solute in the surface layer may be greater than the equilibrium value, thus retarding further growth, and the quantity of liquor entrapped between crystals (and then subsequently frozen) must represent a large proportion of the total solid.

Consequently it was concluded that solid-solution grown for analytical study was very likely to show erroneously high solid solubility. As a result, successful separation of such systems would suggest the availability of many more stages than a process or its equipment might actually provide. It was felt essential to develop more reliable techniques for the evaluation of the degree of solid solution.

In order to reliably use an analytical approach, it becomes essential to know the degree of liquid entrapment in the growing solid. This can be estimated by the use of a tracer solute, one which is known not to form solid solution with the solvent. If we assume the solid to be made of crystal and entrapped liquor (which freezes subsequent to entrapment), the concentration of solute in the overall solid, $x_s$, is a function of that in the crystal, $x_c$, and that in the liquor, $x_L$.

$$x_s = x_L F_L + x_c(1-F_L), \qquad (7)$$

where $F_L$ is the fraction of entrapped liquor. The true distribution coefficient, $k_e$, and the apparent coefficient, $k_a$, are $x_c/x_L$ and $x_s/x_b$ respectively, so that

$$k_a = F_L + k_e(1-F_L) \tag{8}$$

and

$$F_L = (k_a-k_e)/(1-k_e) \tag{9}$$

For a tracer solute, i.e., one not soluble in the crystal, $k_e = 0$, and $F_L = k_a = x_s/x_L$. The tracer thus gives us an estimate of $F_L$, and for other solutes,

$$k_e = (k_a-F_L)/(1-F_L) \tag{10}$$

Experimental studies of the naphthalene-thianaphthene system were carried out with the apparatus shown schematically in Figure 26. The sample tube, which consisted of a 10 ml buret squared off at the zero line, was mounted in a modified Fisher zone refining apparatus. The motor shown (a standard laboratory stirrer motor) served to permit intermittent rotation of the tube (e.g., 4 sec. on and 2 sec. off alternately) and thus provide some initial shear at the solid-liquid interface. The usual zone heaters were replaced by the concentric tube arrangement as shown so as to permit progressive freezing instead of zone refining. Because the intermittent rotation did not of itself provide any longitudinal bulk mixing, a glass rod was introduced into the tube as shown, just the tip of which when inserted into the sample, induced considerable turbulance and vertical currents to maintain liquid homogeneity. (Experiments were tried with the stirrer inserted to within a few millimeters of the interface, using the optional stirer support so that it rose with the heater. However, this resulted in a deeply dished interface which froze sporadically, sometimes trapping considerable liquid.)

In practice, the tube was filled with a liquid naphthalene-thianaphthene sample at the desired concentration which also contained as tracer compounds small amounts of dodecane and diisobutylketone, along with a

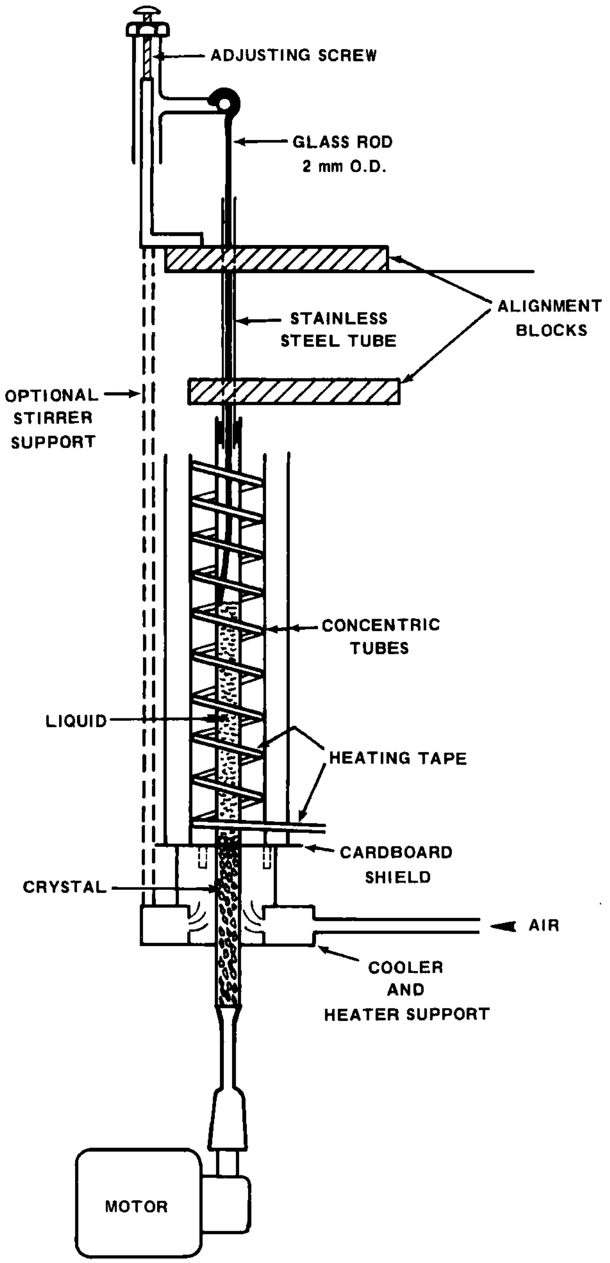

Figure 26. Progressive Freezing Apparatus for Measuring Solid Solution (not to scale).

trace of red dye for visual observations of gross entrapment. The sample was then frozen from the bottom up at a constant rate (typically 0.28"/hr.) while the tube was intermittently rotated. When approximately two-thirds had been frozen, the remaining liquor was drawn off for analysis. The tube was then sawed into segments and the solid analyzed for its constituents by gas chromatography.

Figure 27 shows the results for a typical run, the concentration (log scale) of the constituents for the various solid segments plotted against the fraction of the frozen ingot. The thianaphthene and tracer levels in the liquid were obtained by back calculation from the top oil composition and a mass balance with that appearing in the solid (correcting for the mass lost in the saw cuts). From the concentrations in the liquid and solid at the midpoints of the segments, apparent values of the distribution coefficients were calculated. These were corrected for liquor entrapment as shown in Table I. Note that the actual entrapment was quite small, normally less than 1 percent. Entrapment was higher at the beginning than later on, possibly due to rapid crystallization of supercooled liquid when the first solid seed was formed. Entrapment also appears to increase with solute (thianaphthene) concentration in the system as might be expected. The results are plotted in Figure 28, which shows an apparent increase in $k_e$ with increasing thianaphthene concentration. This, however, was found to be questionable in the light of additional runs.

Prior to discussing our own results, let us first examine the available literature data, Figure 29. That of Mastrangelo and Dornte[20] was obtained calorimetrically, hence required homogenous solid solution for evaluation of the solidous line. This was obtained by "quenching" the liquid in the calorimeter, a process which actually took several minutes[21] and which would have been expected to yield a non-homogenous solid which would subsequently show an excessively low initial melting point. The data

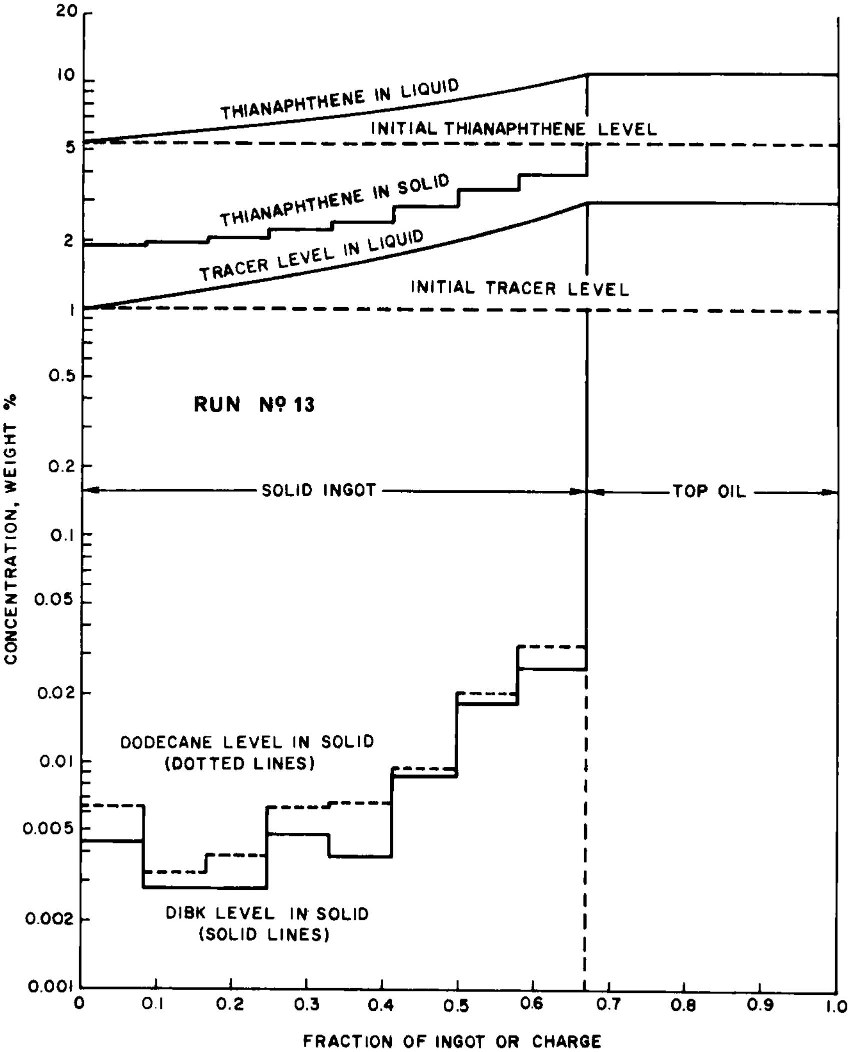

Figure 27. Typical Analytical Results for Completed Run.

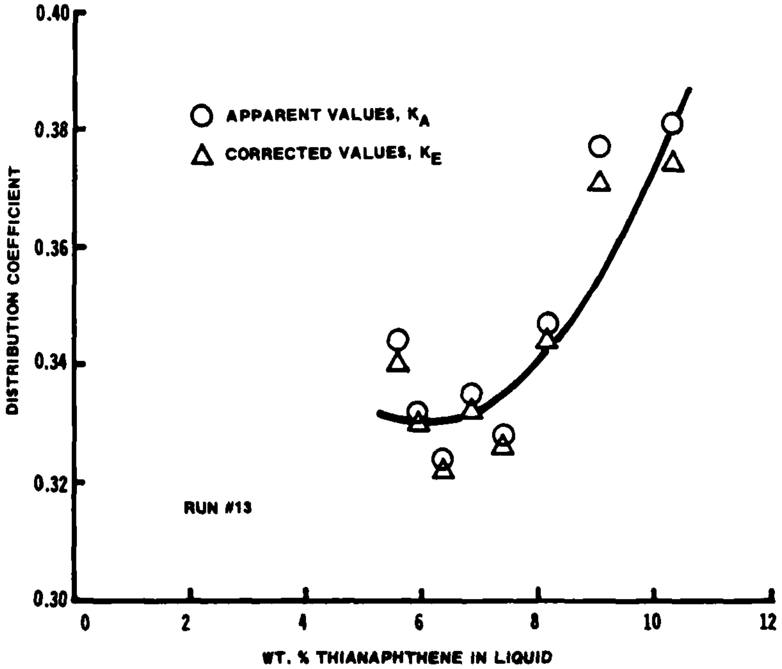

Figure 28. Typical Distribution Coefficient Results For a Completed Run

of Kravechenko and Pastukhova[22] were obtained by thermal analysis. There is no indication in their paper or its references as to how the solidous line was recognized.

The dotted line, Figure 29, is our own data, which covers only a small range of composition, principally because only that range is really significant for the desulfurization of naphthalene. Figure 30 is a blow-up of that range showing our individual data points along with the solidous line of Mastragelo and Dornte (obtained by data points lying outside of the plot blow-up). Our own results are higher than those of Mastragelo and

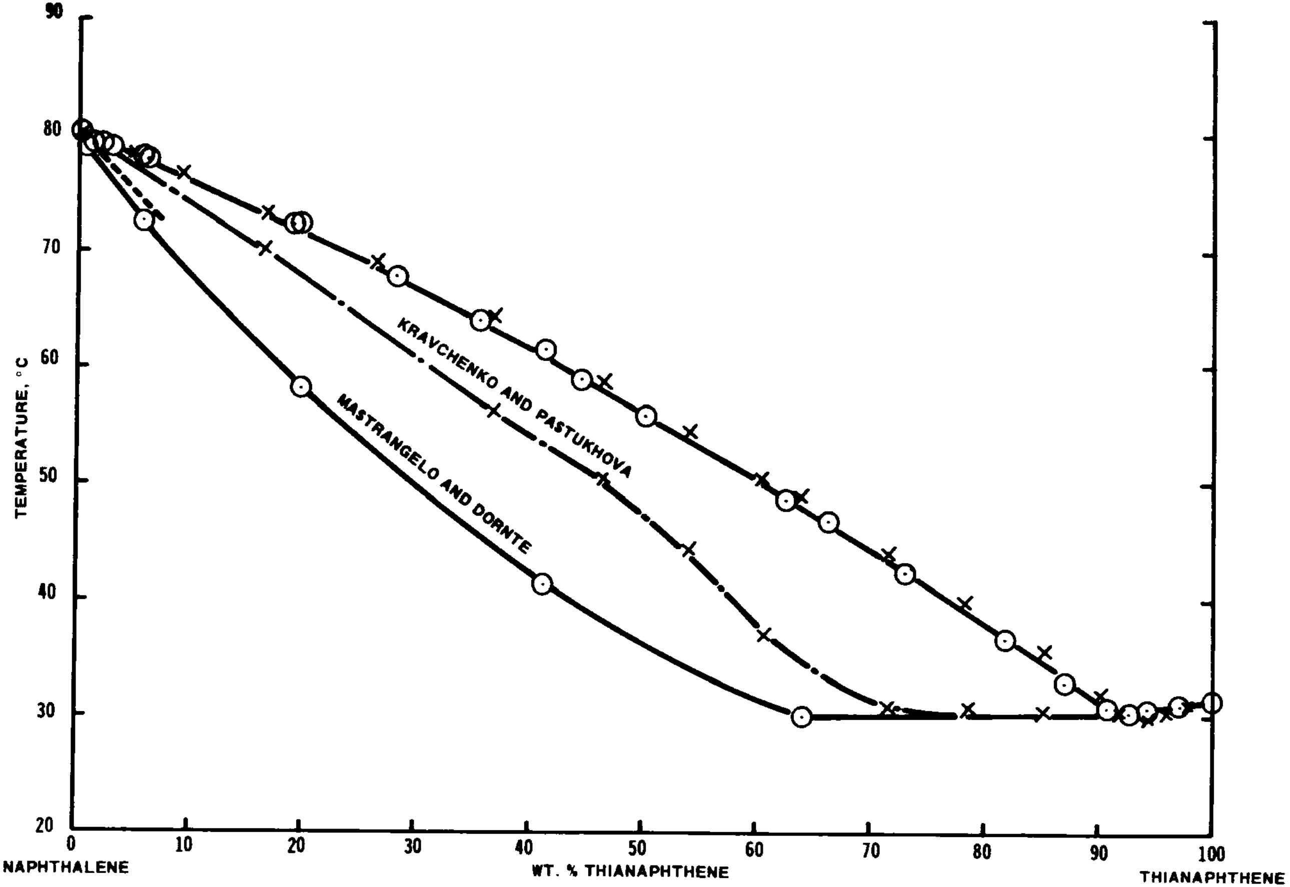

Figure 29. Literature Data for the System: Naphthalene - Thianaphthene.

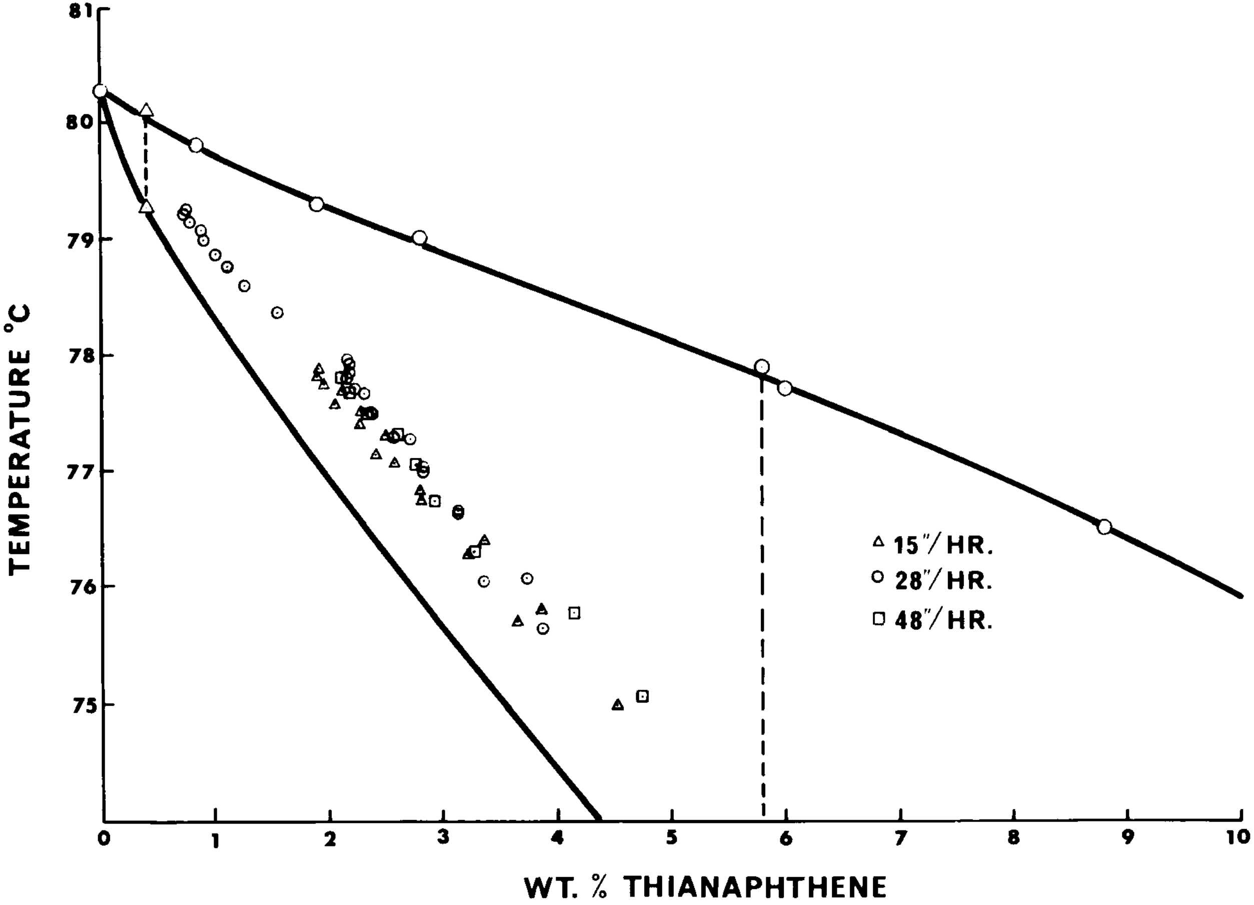

Figure 30. Blow-up of Figure 29, Showing Data Points.

Dornte though not as precise as desired. The difference in the curves is obviously much greater than the dispersion in our data, however, and can be considered significant. Our runs were made at three different crystal growth rates, on the realization that our agitational technique would not eliminate boundary layer effects entirely, but that an extrapolation of the data to zero growth rate would do so. Such an extrapolation could not be made. Figure 31 shows regression curves for the various rates and no consistent trend appears, certainly not one which would extrapolate all the way to the Mastragelo and Dornte data.

The question of which data are correct becomes significant if one wishes to establish the stage efficiency of a crystallizer such as the

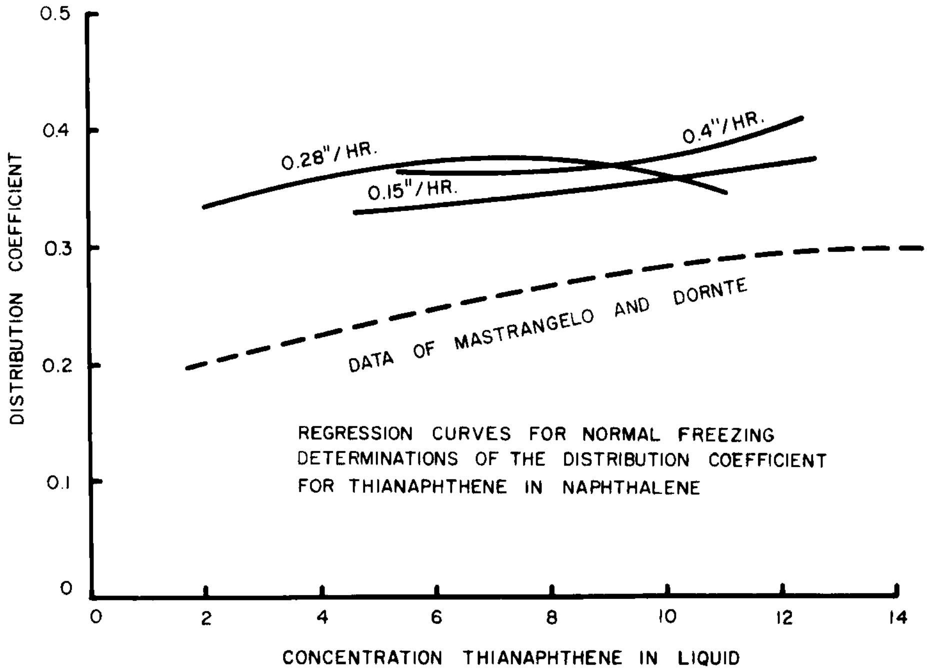

Figure 31. Regression Curves for the Distribution Data Points of Figure 30.

Schildknecht or UCAL variety. For example, the UCAL pilot unit was able to upgrade naphthlene from 1.1 to 0.12 wt % thianaphthene at a 0.5/1 reflux ratio. This corresponds to 1.3 stages in the purification section if the literature data are correct, but to three stages if our own data are correct. This is a factor of six in the rectification, since one stage is expected in the initial crystal growth. Accordingly, improved techniques are desirable to eliminate the sources of data variation. One such source, may be uneven or sporadic crystallizations. Figure 32 shows data obtained at 0.15"/hour overall growth rate. The height of the crystal face varied as shown against a scale attached to the heater (and viewed via a cathetometer). These data were obtained on an early run without the outer of the concentric tubes on the heater, and the correlation with room temperature is not insignificant. Improved screening of the system reduced the observable variations to zero, but this does not eliminate the possiblity of microvariations in growth rate (in the presence of a boundary layer) affecting the overall results.

A probably superior technique has been used by A. R. McGhie and G. J. Sloan[23]. In their method, samples enclosed in a sealed tube are slowly (0.9mm/hr) lowered through a Bridgeman furnace such that they are progressively frozen. Simultaneously, tubes with reference samples are also lowered through the furnace, and the entire group of tubes is rotated such that they all experience the same environment. The positions of the interfaces in the reference samples define the thermal gradient in the system, so that the temperatures of the interfaces in the sample tubes can be determined. The sample crystals are ultimately analyzed for solute along their lengths, and solidus concentration can be plotted vs. temperature directly. This makes the solidous data independent of any knowledge of the liquid composition and hence it is not affected by the magnitude of the boundary layer. Actually, the very slow growth rate of

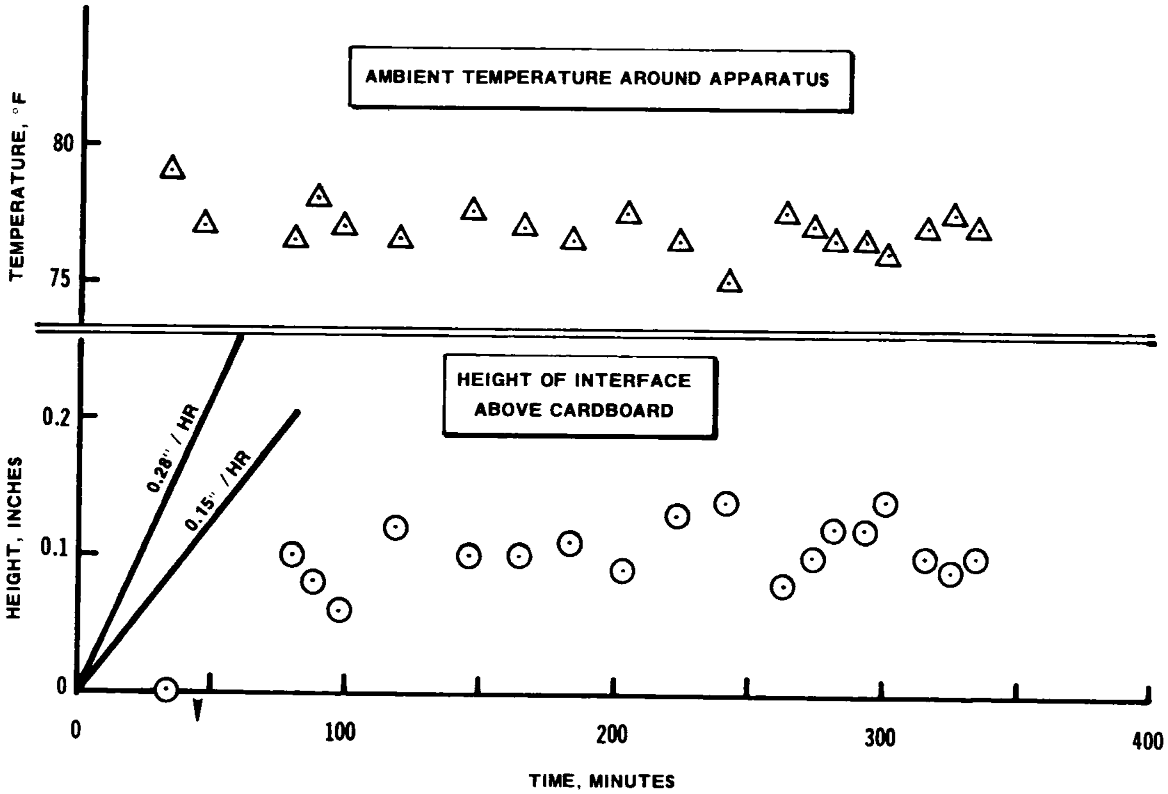

Figure 32. Growth Rate Fluctuations and Their Relationship to Ambient Temperature Variations.

0.9 mm/hr. minimizes the boundary gradient in spite of no agitation. The possibility of liquid entrapment still exists however, and combining the McGhie-Sloan technique with the use of a tracer compound may prove even more reliable.

It will be noted, Table I, that the actual liquid inclusion in our own studies was less than 1%. It had earlier been postulated on the basis of zone refining studies that solid solution crystals appeared to incorporate more liquor than crystals grown from simple eutectic systems. To test this postulate, comparable runs were made with and without thianaphthene present. It will be noted, Figure 33, that no significant difference was observed. A second set of runs was then made at a high crystallization rate and without the initial agitation provided by the oscillatory motion. Without this shear at the crystal face, the inclusion was gross, up to 50%, Figure 34. Under these conditions, the inclusion for the solid solution system was indeed higher, and it was concluded that under conditions which promote gross inclusion, that inclusion might be greater for solid solutions. Of course, this has not been generalized by tests with other solid solution systems.

A final experiment with the apparatus of Figure 26 consisted of freezing a ingot of solid solution from about 2/3 of the sample charge, pouring off the liquor, and slowly melting back. This forces the solid to melt into a liquid with which it cannot possibly be in equilibrium. Consider Figure 35. Let the final crystal surface to freeze be at composition C and the liquid which was poured away be of composition D. Now as we melt back, the surface wants to melt at temperature $T_{bC}$ into liquid D, but as soon as any actually melts, the liquid is not D, but C, which has a freezing temperature of $T_{fC}$, and from which composition E should crystallize. The prior explanation of the melting of a solid solution by the formation of a small quantity of net liquid while the whole sample melts

| SEGMENT # | CONCENTRATION OF THIANAPHTHENE, WT. % | | APPARENT COEFFICIENT $K_A$ | FRACTION OF LIQUID ENTRAPPED, | CORRECTION TO K FOR ENTRAPMENT | CORRECTED COEFFICIENT $K_E$ |
|---|---|---|---|---|---|---|
| | SOLID | LIQUID | | | | |
| 1 | 1.93 | 5.61 | 0.344 | 0.0052 | 0.0034 | 0.341 |
| 2 | 1.98 | 5.86 | 0.332 | 0.0026 | 0.0017 | 0.330 |
| 3 | 2.06 | 6.36 | 0.324 | 0.0026 | 0.0018 | 0.322 |
| 4 | 2.29 | 6.83 | 0.335 | 0.0040 | 0.0027 | 0.332 |
| 5 | 2.43 | 7.41 | 0.328 | 0.0033 | 0.0022 | 0.326 |
| 6 | 2.82 | 8.12 | 0.347 | 0.0050 | 0.0033 | 0.344 |
| 7 | 3.41 | 9.04 | 0.377 | 0.0091 | 0.0057 | 0.371 |
| 8 | 3.94 | 10.34 | 0.381 | 0.0114 | 0.0071 | 0.374 |

Table 1. Results for Run #13.

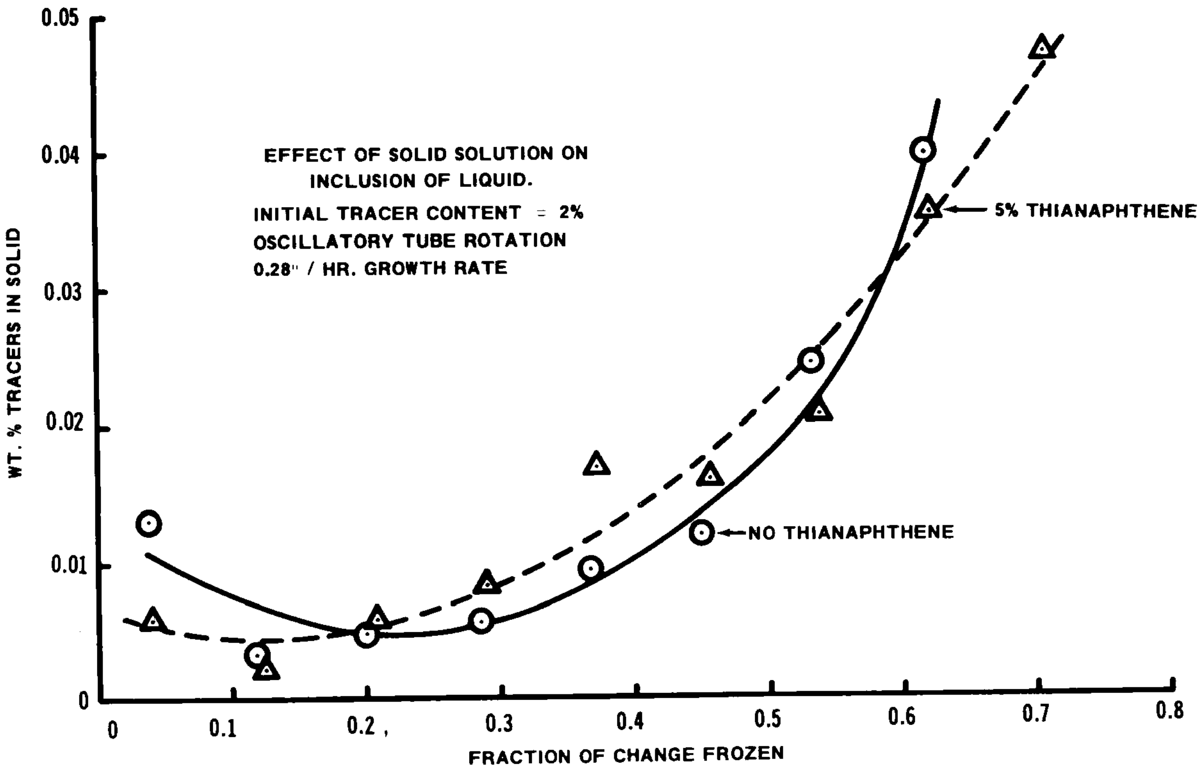

Figure 33. Effect of Solid Solution on Liquid Occlusion at Low Growth Rates and With Good Agitation.

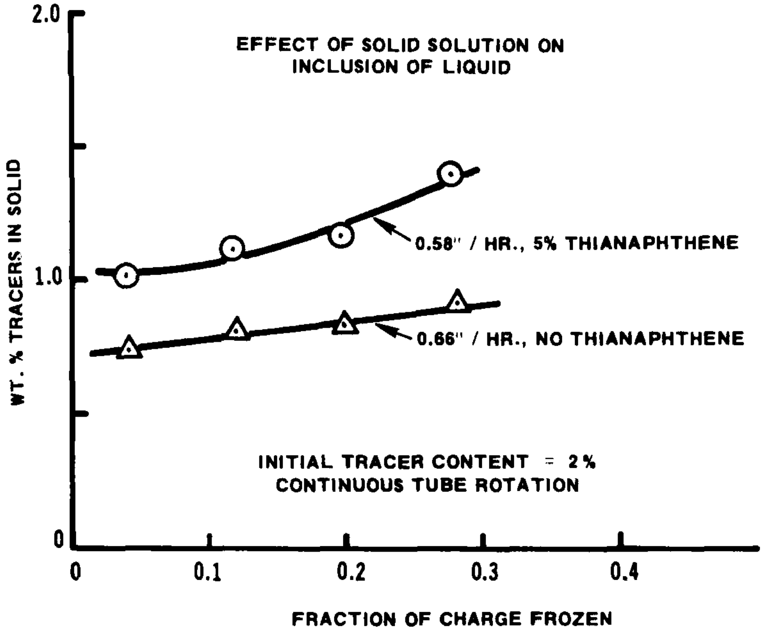

Figure 34. Effect of Solid Solution on Liquid Occlusion at High Growth Rates and with Poor Agitation.

and refreezes in a leaner (higher melting) composition cannot hold here, since the sample as a whole is trapped, only the surface being available for such interchange. Should a second composition (e.g., E) refreeze at the interface as the ingot melted to give liquid of C, then the interface would appear cloudy. In these experiments it remained clear. Accordingly, it was concluded that the liquid formed (composition C) was stable and that the interface must have been at the higher temperature, $T_{fC}$. How can this be?

One principle worthy of note is that wherever any phase is forced to convert into another in an nonequilibrium manner, there is built up a boundary layer of different composition in the phase being so converted.

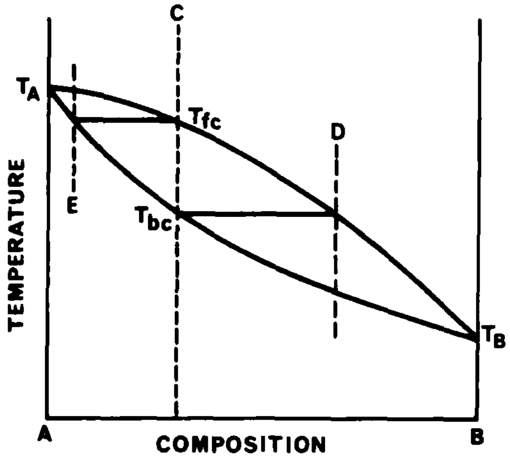

Figure 35. Diagram to Illustrate Boiling and Freezing Relationships.

If, for example, we quick-freeze a liquid of composition C, solid E starts to crystallize at temperature $T_{fC}$, but soon a boundary layer of D builds up, and we crystallize out C at temperature $T_{bC}$. The sharpness of the boundary layer is usually inversely proportional to the rate of diffusion in the phase. Can we possibly build up such a boundary layer in the solid when we melt? The answer would appear to be yes, and since the rate of diffusion in the solid is nil, the boundary layer would all be at the surface.

As we know, solid is formed by a mechanism such as screw dislocation or other means by which sites are formed which can readily accept new molecules. Such a new molecule will not "sit" on a perfect surface, the attractive forces on one side alone being insufficient to hold it. Nor is it likely to find its way into a hole in which the sites on all sides but one are occupied. Rather it can find its way into, and be held to, a site already surrounded by two to four occupied sites, an "inside corner" so to speak. A two dimensional analogy is shown in Figure 36. Wherever a molecule occupies such an "active" site for growth, another such site is

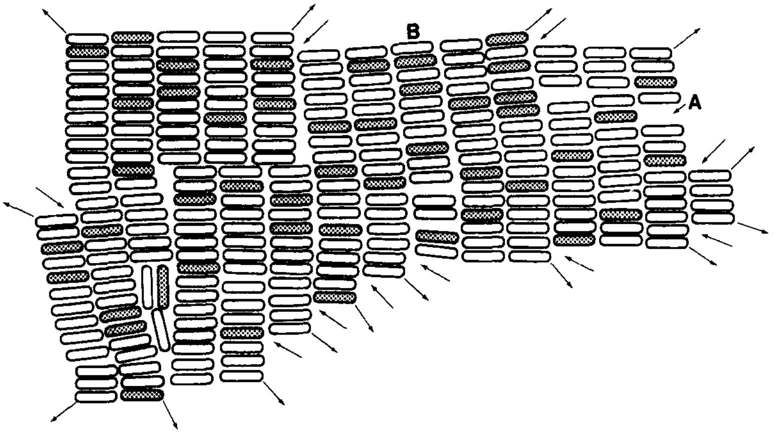

Figure 36. "Imperfect" Solid Solution Crystal, Illustrating Growth (inside corner) and Melt (outside corner) Sites. (Arrows pointing in or out show ability of crystal to accept or give up molecules respectively. Hole A will not likely be filled because of exact orientation required. Molecules such as B are too stable to leave, but their surfaces alone do not provide enough attractive forces to hold new molecules.)

created, and growth continues indefinitely. Melting must occur similarly. Those molecules within the flat surface cannot be the first to leave as they are bound on too many sides to be unstable. Rather, those molecules which form "outside corners" are most easily lost, and when one leaves, a new "outside corner" or "active" site is created. Such sites would be expected to contain solvent and solute molecules in proportion to the overall composition of the solid (composition C). However, when melting, the solute molecules may be less tightly bound and may tend to erode a little faster. If the liquid contains a sufficiently higher ratio of solute molecules to set them down at the same rate (e.g., composition D), then we are at equilibrium. If, however, the liquid does not contain a higher ratio of solute molecules (e.g., is composition C), then the ratio of solute to solvent at active sites is decreased (i.e., is of composition E). Thus the meltable surface, the active sites, are of composition E, while both the bulk solid and bulk liquid are of composition C. A temperature of $T_{fC}$ is required to erode molecules from these sites faster than they will be filled from liquid C. Under these conditions, in which the crystal melts to give liquid C, the active sites remain at composition E, for while the relative probabilities of uncovering solute and solvent molecules, i.e., changing them into active sites, is represented by composition C, the solvent molecules are then released slower from these sites.

Thus, in considering melt crystallization, we must think really not only in terms of solid-liquid equilibria, but rather in terms of active site-liquid equilibria.

## ACKNOWLEDGMENT

Whereas the writer is grateful to a large number of persons for their varied contributions to the several experimental studies discussed here, special acknowledgement is due to Mr. R. W. Greiner, who carried out the recent progressive freezing solid solution studies along with the associated analytical work. Thanks are due, too, to Mr. D. A. Dunnery, who spent considerable time consulting with Mr. Greiner and the writer on that particular project.

Acknowledgement in a broader sense should be made to Dr. J. R. Anderson (now of the Permutit Company) who was this writer's supervisor at the time some of the earlier studies were made, and who originally guided the writer's interests into the fascinating realm of phase equilibria and specifically crystallization from the melt.

## BIBLIOGRAPHY

1. C. T. Cheng and R. L. Pigford, AIChE 63rd Annual Meeting, Chicago, Dec. 3, 1970.
2. G. R. Atwood, "Heat Capacities For the System Benzene-Cyclohexane", Doctoral Dissertation, Univ. of Pittsburgh, Feb. 1958, p. 53.
3. J. E. Ricci, The Phase Rule and Heterogeneous Equilibrium, Van Nostrand, New York, 1951, p. 19.
4. J. Zernike, Chemical Phase Theory, A. E. Kluwer, Antwerp, 1955, p. 9.
5. A. Reisman, Phase Equilibria, Academic Press, New York, 1970, p. 284.
6. C. Kittel, Introduction To Solid State Physics, Wiley, New York, 1953, pp. 308-9, 321-2.
7. E. A. Moelwyn-Hughes, States Of Matter, Oliver & Boyd, London, 1951, pp. 24-5.
8. B. J. Mair, A. R. Glasgow, Jr., and F. D. Rossini, J. Res. Nat. Bur. Std., 26, 591-620 (1941).
9. W. G. Pfann, Zone Melting, 2nd Ed., Wiley, New York, 1966.
10. E. F. G. Herington, Zone Melting Of Organic Compounds, Wiley New York, 1963.
11. N. J. G. Bollen, M. J. Van Essen, and W. M. Smit, Anal. Chim. Acta., 38, 279-84 (1967).
12. G. R. Atwood, Chem. Eng. Prog. Sym. Ser., 65, 95, 112-21 (1969).
13. C. P. Saylor, "The Freezing Staircase Method", Chap. 11, Purification Of Inorganic and Organic Materials, M. Zief, ed., Dekker, New York, 1969, pp. 125-38.
14. H. Schildknecht and H. Vetter, Angew. Chem., 73, 612 (1961).

15. C. J. Moyers, "Macroscopic Characteristics Of a Continuous Center-Feed Column Crystallizer", Doctoral Dissertation, Univ. of Delaware, June, 1971.

16. W. C. Gates, Jr. and J. E. Powers, AIChE J., 16, 648-58 (1970).

17. W. D. Betts, J. W. Freeman, and D. McNeil, J. Appl. Chem., 17, 180-7, (June, 1968).

18. W. D. Betts, private communication.

19. J. A. Brode, Mech. & Chem. Eng. Trans., Inst. Of Eng., Aust., May, 1971, 37-44.

20. S. V. R. Mastrangelo and R. W. Dornte, Anal. Chem., 29, 794-7 (1957).

21. S. V. R. Mastrangelo, Anal. Chem., 29, 841-5 (1957).

22. V. M. Kravchenko and I. S. Pastukhova, Doklady Akad. Nauk. U.S.S.R., 119, 285 (1958).

23. G. J. Sloan, private communication, to be published in the Journal Of Crystal Growth.

24. G. R. Atwood, "Developments In Melt Crystallization," Recent Developments In Separation Science, N. Norman Li, Ed., The Chemical Rubber Company, Cleveland, 1972.