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# PURITY OF CRYSTALS GROWN FROM BINARY ORGANIC MELTS

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## ABSTRACT

Binary liquid mixtures of stilbene and bibenzyl form mixed crystals which, according to the phase diagram, should be considerably richer in stilbene than the liquid in which they grow. By watching the growth under a microscope using interference fringes to follow concentration changes, the solid phase composition can be determined as a function of growth rate and interface subcooling. The deviations from equilibrium are considerable. They are found to depend on the growth mechanism in accord with a theory following Eyring and Frank.

## INTRODUCTION

The demand for ultrapure crystals in the solid state industry has stimulated extensive study of the processes by which crystals grow from the melt. The zone refining process, for example, has been very successful for producing pure metals but evidently has not yet been applied on a large scale in the organic chemical industry. The obvious need for improved continuous processes for the purification of high-melting organic compounds suggests that better understanding of the interface kinetic process itself--a key piece of information for rational design--is required.

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The process of crystal growth includes the diffusive transport of molecules from the bulk liquid to the interface, orientation of the molecules for attachment to the solid surface, and conduction of the latent heat of fusion from the interface. The resistance to diffusion and to heat conduction can be minimized easily by mechanical stirring but if the major resistance is in the interface itself stirring is of no help.

In zone refining studies the assumption of interfacial equilibrium has been used frequently as a boundary condition to solve the liquid phase mass transfer equation in order to obtain the distribution of the minor component. The slowness of the process may make this assumption acceptable in many cases. However, when the impurity content is large or when the process is to operate rapidly and especially when the phase diagram exhibits solid solution behavior the equilibrium assumption can hardly be justified. Under these conditions the separation effect owing to crystallization may be severly reduced owing to interface kinetics.

Most of the previous work on crystal growth rate phenomena has been confined to pure substances, the key relationship being that between the growth rate and the thermal undercooling of the melt (Van Hook, 1963, and Chalmers, 1964). Cahn, Hillig, and Sears (1964) reviewed such information with particular emphasis on the distinction between theories involving attachment of molecules to the whole of a microscopically flat crystal surface and those involving attachment to a few surface sites connected with dislocations. The use of assumption that the whole surface is effective has been criticized by Jackson et. al. (1967), who concluded that such theories can only be applied to second-order phase transitions.

Among the theories which involve surface defects there are several possibilities but a suggestion made originally by Frank (1948) has appeared to be the most promising for many substances. According to Frank, the surface imperfection to which liquid molecules are able to attach themselves is a self perpetuating spiral defect consisting of a ledge step of molecular dimensions. Molecules can attach themselves in the corner of the step; as a result, the spiral winds around its center and eventually covers the whole crystal surface. Chernov (1961) has asserted that this screw dislocation mechanism, if it is not the only type of growth process, must be regarded as quite typical and universal.

## THEORY OF THE GROWTH RATE OF A CRYSTAL FROM A SUBCOOLED BINARY MELTS

Following the usual assumption of Eyring (1941), the expression for the flux of component B toward the surface of a crystal to which both A and B molecules attach themselves is

$$N_B = f\,(\lambda_L k_B^F \rho_L y_B - \lambda_S k_B^R \rho_S x_B)\,, \qquad (1)$$

where the k's represent forward and reverse first-order rate coefficients, respectively, and where $\rho_L y_B$ and $\rho_S x_B$ are the molar concentrations of B in the interfacial liquid and solid, respectively. The fraction of the interface surface which is available for the attachment of molecules coming from the liquid is f, which may be a small number if the interface structure contains very few vacancies. The $\lambda$'s represent the increments of distance accompanying the removal of one molecular spacing in the liquid or the addition of one layer of solid, respectively. If we assume that the lattice dimensions are inversely proportional to the molar densities we

may write Eq. (1) alternatively as

$$N_B = f\,\lambda_S \rho_S k_B^F \left(y_B - \frac{k_B^R}{k_B^F} x_B\right) . \qquad (2)$$

Since at equilibrium between the phases the flux must be zero we identify the ratio of the rate coefficients with the equilibrium phase compositions by

$$k_B^F/k_B^R = x_{Be}/y_{Be} , \qquad (3)$$

which, in a binary system at constant pressure, is a function of the interface temperature only.

Completion of the theory requires that expressions be developed for one of the rate coefficients, following Eyring, and for the surface fraction, based on some assumption about the geometry of lattice imperfections at the interface. Before going into these steps, however, we first call attention to some aspects of the theory which appear to have escaped attention in the past.

If we define $u_A$ as the average of the velocities of the A molecules as they move toward the surface we obtain

$$u_A = N_A/\rho_L y_A = f\,\lambda_L k_A^F \left(1 - \frac{y_{Ae} x_A}{x_{Ae} y_A}\right) . \qquad (4)$$

Similarly,

$$u_B = N_B/\rho_L y_B = f\,\lambda_L k_B^F \left(1 - \frac{y_{Be} x_B}{x_{Be} y_B}\right) , \qquad (5)$$

and in a binary system the two velocities are obviously related to each other. In fact, since each of the coefficients in front of the parenthesis is positive and since the parenthetical expressions in Eq. (4) and (5) must be of opposite sign, $u_A$ and $u_B$ can not both be positive. If B-molecules move toward the surface then A-molecules must move away from it, according to the equations.

This anomolous situation is easily resolved if one notes that each of the equations so far developed is true in a coordinate system which moves toward the interface at a velocity given by

$$u^* = y_A u_A + y_B u_B = f \lambda_L (k_A^F \Delta_A + k_B^F \Delta_B) . \qquad (6)$$

In Eq. (6) the symbols $\Delta_A$ and $\Delta_B$ have been introduced as abbreviations for the driving forces,

$$\Delta_A = y_A - (y_{Ae}/x_{Ae})x_A \qquad (7a)$$

$$\Delta_B = y_B - (y_{Be}/x_{Be})x_B . \qquad (7b)$$

Obviously $u^*$ can be positive, zero, or negative, depending on the ratio of the two forward rate constants.

Experimentally, it is difficult if not impossible to adjust the fluid velocity at the interface to the value $u^*$. In our experiments and in most others we have held the liquid-solid interface stationary and have measured the velocity, V, of the whole mass of liquid and solid needed to accomplish this. Thus, V is the velocity of propagation of the interface and the growth velocity of the crystal. The velocity of the liquid as it

approaches the stationary solid surface is not zero. A mass balance shows that the liquid moves at the velocity $V(\frac{\rho_S}{\rho_L})$ toward the interface, a value which can easily differ from $u^*$. Therefore, in order to obtain equations for the flux of each component in the laboratory coordinate system we must modify Eq. (1) by adding terms representing the convective transport of the components.

$$N_A = f\,\lambda_S \rho_S k_A^F \Delta_A + [V(\rho_S/\rho_L) - u^*]\rho_L y_A \,, \tag{8}$$

and a similar equation for $N_B$. By substituting $u^*$ from Eq. (6) we obtain

$$N_A = f\,\lambda_S \rho_S\,(k_A^F \Delta_A\, y_B - k_B^F \Delta_B\, y_A) + V\,\rho_S y_A \,, \tag{9}$$

and

$$N_B = f\,\lambda_S \rho_S\,(k_B^F \Delta_B\, y_A - k_A^F \Delta_A\, y_B) + V\,\rho_S y_B \,. \tag{10}$$

It is not difficult now to obtain an equation for the composition of the solid which forms, for diffusion rates in the solid phase are so slow that the ratio of the mole fractions of the components is equal to the ratio of the molar fluxes onto the interface, i.e. $x_B = N_B/V\,\rho_S$, and Eq. (9) and (10) give

$$x_B = y_B + \frac{f\lambda_S}{V}\,(k_B^F \Delta_B\, y_A - k_A^F \Delta_A\, y_B) \,, \tag{11}$$

and a similar equation for $x_A$. It is clear now that the difference in composition between solid and interfacial liquid depends on the growth rate

parameter, $g_B = f\lambda_S k_B^F/V$, and on the ratio of the two first-order coefficients. When the values of $k^F$ are very large the parenthetical expression in Eq. (11) must be zero, which will require that both the $\Delta$'s must be zero. Thus, phase equilibrium will be achieved. On the other hand, when the growth rate parameter is small the second term on the right will be negligible, despite a finite value for each of the $\Delta$'s. Then $x_B = y_B$ and no enrichment of the crystal occurs as it grows, the composition of the solid being the same as that of the contiguous liquid.

An alternative method for expressing the result given in Eq. (11) has come into popular use in metallurgy and in zone refining technology. It is to define an "effective distribution coefficient" for each component as the ratio of the actual solid mole fraction to the mole fraction in the interface liquid: $K_B^* = x_B/y_B$ and $K_A^* = x_A/y_A$. These values may differ from the values based on the equilibrium phase diagram, $K_A = x_{Ae}/y_{Ae}$ and $K_B = x_{Be}/y_{Be}$, owing to the rate effects we have been discussing. From Eq. (11) we obtain

$$K_B^* = \frac{1 + (f\lambda_S k_B^F/V)\ \{[1 - (k_A^F/k_B^F)]\ y_A + (k_A^F/k_B^F)(1/K_A)\}}{1 + (f\lambda_S k_B^F/V)\ \{(y_A/K_B) + (k_A^F/k_B^F)(y_B/K_A)\}} \quad . \qquad (12)$$

The equation for $K_A^*$ is similar and can be obtained by exchanging subscripts in Eq. (12). According to Eq. (12), $K_B^*$ approaches unity as the growth velocity increases or the forward rate constant decreases. As Eq. (12) indicates, the effective distribution coefficient, $K^*$, is not a constant, as has often been assumed; it depends on the temperature, the interfacial liquid composition and on the growth velocity. Its numerical value always lies between unity and the equilibrium value, K.

The result given by Eq. (11) can also be expressed in terms of the effective separation factor, defined by $\beta = (x_B/x_A)(y_A/y_B)$. This factor can be expected to be more nearly independent of composition than either $K_A^*$ or $K_B^*$, at least for thermodynamically ideal systems. It is given by

$$\beta = \left(\frac{x_B}{x_A}\right)\left(\frac{y_A}{y_B}\right) = \frac{1 + (f\lambda_S k_B^F/V)\{[1 - (k_A^F/k_B^F)]\cdot y_A + (k_A^F/k_B^F)(1/K_A)\}}{1 + (f\lambda_S k_B^F/V)\{[(k_A^F/k_B^F) - 1]\cdot y_B + (1/K_B)\}} . \quad (13)$$

In the limit of very large $V$, $\beta$ approaches unity; there is no separation effect when the solid forms instantly in the liquid. At very small values of $V$, $\beta$ approaches the value $K_B/K_A$.

ESTIMATION OF THE SURFACE STEP DENSITY, f

The surface step density, f, represents the fraction of the surface of the crystal which is available for attachment of individual molecules arriving from the liquid. For a surface that is sufficiently rough on a molecular scale, f is unity. According to Jackson (1967), many metals and some organic compounds which have very low values of the entropy of fusion are able to accept new atoms or molecules over their whole surfaces. For most substances, however, and particularly for more complex organic molecules only a very few positions on the crystal surface are available. The acceptable sites are in the corners of dislocation imperfections on the surface.

When a dislocation line intersects the crystal interface the dislocation winds itself into a screw as growth proceeds and provides a self perpetuating spiral step into the corner of which new molecules can become

attached. According to Frank (1948) the spiral structure is approximately the shape of an Archimedean spiral having a constant spacing between adjacent branches that depends on the radius of curvature at the center of the spiral, $r_c$. Thus, the surface fraction for such a structure is equal to the ratio of the width of one molecule to the distance between branches of the spiral, or

$$f = \lambda/4\pi r_c \ . \tag{14}$$

Furthermore, if we assume that the size of the spiral at its center, where it has the smallest radius of curvature and the greatest ratio of surface to volume of any point along the spiral, is equal to the size of a two-dimensional nucleus which is just critically stable thermodynamically, we can equate $r_c$ to $\sigma/\rho_S \Delta G$ where $\Delta G$ represents the difference of the Gibbs free energy of a mole of solid and a mole of liquid of the same composition and $\sigma$ is the excess Gibbs free energy per unit of surface in the interface. Then the equation for $f$ becomes

$$f = \lambda \rho_S \Delta G/4\pi\sigma \ . \tag{15}$$

Using Turnbull's (1958) empirical expression for the surface energy,

$$\sigma = 0.3 \frac{\Delta H_f}{N^{1/3} V_S^{2/3}} \ , \tag{16}$$

where $\Delta H_f$ is the enthalpy of fusion and $N$ is the Avagadro number, we get

$$f = \frac{1}{1.2\pi} \left(\frac{\Delta G}{\Delta H_f}\right) = \frac{1}{1.2\pi} \left(\frac{\Delta G}{T_m \Delta S_f}\right) . \qquad (17)$$

Our expression for $f$ must now be completed by an evaluation of the Gibbs free energy change, $\Delta G$.

CHANGE IN GIBBS FREE ENERGY DURING SPONTANEOUS CRYSTAL GROWTH

If we have a pure melt from which the crystal is growing the free energy difference is very nearly equal to $\Delta S_f \Delta T$, where $\Delta T$ represents the difference between the equilibrium melting point and the interfacial temperature, i.e. the amount of subcooling. When the crystal is formed in a solution, however, the free energy change depends both on the composition of the liquid and on the interfacial temperature.

Consider first the formation of a pure crystal of compound B in a liquid mixture having interfacial mole fraction $y_A$ of the "impurity" component, A. Then the chemical potential difference of B across the interface is given by Kirwan and Pigford (1969).

$$\Delta G = \mu_B^L - \mu_B^S = \left[\Delta S_f - \Delta C_{PB}\left(1 - \frac{T}{T_{Bm}}\right) - R \ln(\gamma_B y_B)\right]\Delta T , \qquad (18)$$

where $\gamma_B$ represents the activity coefficient of B in the interface liquid. The second term in the brackets is often negligible. Under these conditions the surface fraction $f$ is somewhat reduced as compared with the value expected for crystallization from the pure liquid.

Moreover, for a system which forms a solid solution crystal, the thermodynamic driving force for growth can not be expressed simply in terms

of the interface subcooling, $\Delta T$. As can be anticipated from Eq. (18), $\Delta G$ now depends both on interfacial temperature and on the interface composition driving forces.

The free energy change owing to phase transformation of one mole of liquid into one mole of solid solution, both liquid and solid having the solid's composition, is

$$\Delta G = (\mu_A^L - \mu_A^S)x_A + (\mu_B^L - \mu_B^S)x_B \ , \tag{19}$$

and the chemical potentials can be expressed in terms of their equal values on the liquidus and solidus curves of the phase diagram by the equations

$$\mu_B^L(y_B,T) = \mu_B^L\,(y_{Be},T) + RT \ln\,(\gamma_B y_B/\gamma_{Be}y_{Be})$$

$$\mu_B^S(x_B,T) = \mu_B^S\,(x_{Be},T) + RT \ln\,(\Gamma_B x_B/\Gamma_{Be}x_{Be}) \ ,$$

and two similar equations for component A. The $\gamma$'s represent activity coefficients in the liquid solution; $\Gamma$'s, in the solid solution. Substituting these expressions into Eq. (19) we get

$$\Delta G/RT = x_A \ln(x_{Ae}y_A/y_{Ae}x_A) + x_B \ln(x_{Be}y_B/y_{Be}x_B) + x_A \ln(\gamma_A\Gamma_{Ae}/\gamma_{Ae}\Gamma_A)$$

$$+ x_B \ln(\gamma_B\Gamma_{Be}/\gamma_{Be}\Gamma_B) \ . \tag{20}$$

The first two terms represent the free energy changes if the liquid and solid solutions were ideal mixtures; the last two terms take care of

deviations from ideality. The activity coefficients can sometimes be obtained from the phase diagram without resorting to any assumptions about solution behavior. Note that temperature appears in this expression for $\Delta G$ through its effect upon the equilibrium mole fractions, $y_{Be}$, $x_{Be}$, etc. Note also that $\Delta G = 0$ when both the temperature and the compositions fall on the solidus and liquidus lines of the phase diagram. Presumably $\Delta G$ must be positive for the spontaneous growth process to occur. To bring these ideas out more clearly we refer to the hypothetical phase diagram in Fig. 1, which shows a possible location for the real and the equilibrium liquid and solid compositions at the observed interface temperature. Note that the liquid is cooled below its equilibrium freezing temperature on the liquidus curve and therefore has a greater free energy than at equilibrium; the solid, on the other hand, is at a temperature above its equilibrium melting point and is therefore superheated. It, too, has a greater free energy than it would have at equilibrium. The value of $\Delta G$ for the process of solidification is positive when the liquid is subcooled far enough and the solid is not superheated too far.

Some concern may be felt over the fact that the solid phase is indicated to be superheated, in view of the fact that all attempts to superheat solids above their melting points have proved fruitless. Note in connection with the present situation, however, that the solid is not only superheated but is also growing as a result of the continuous bombardment by molecules which come from the over-energetic liquid.

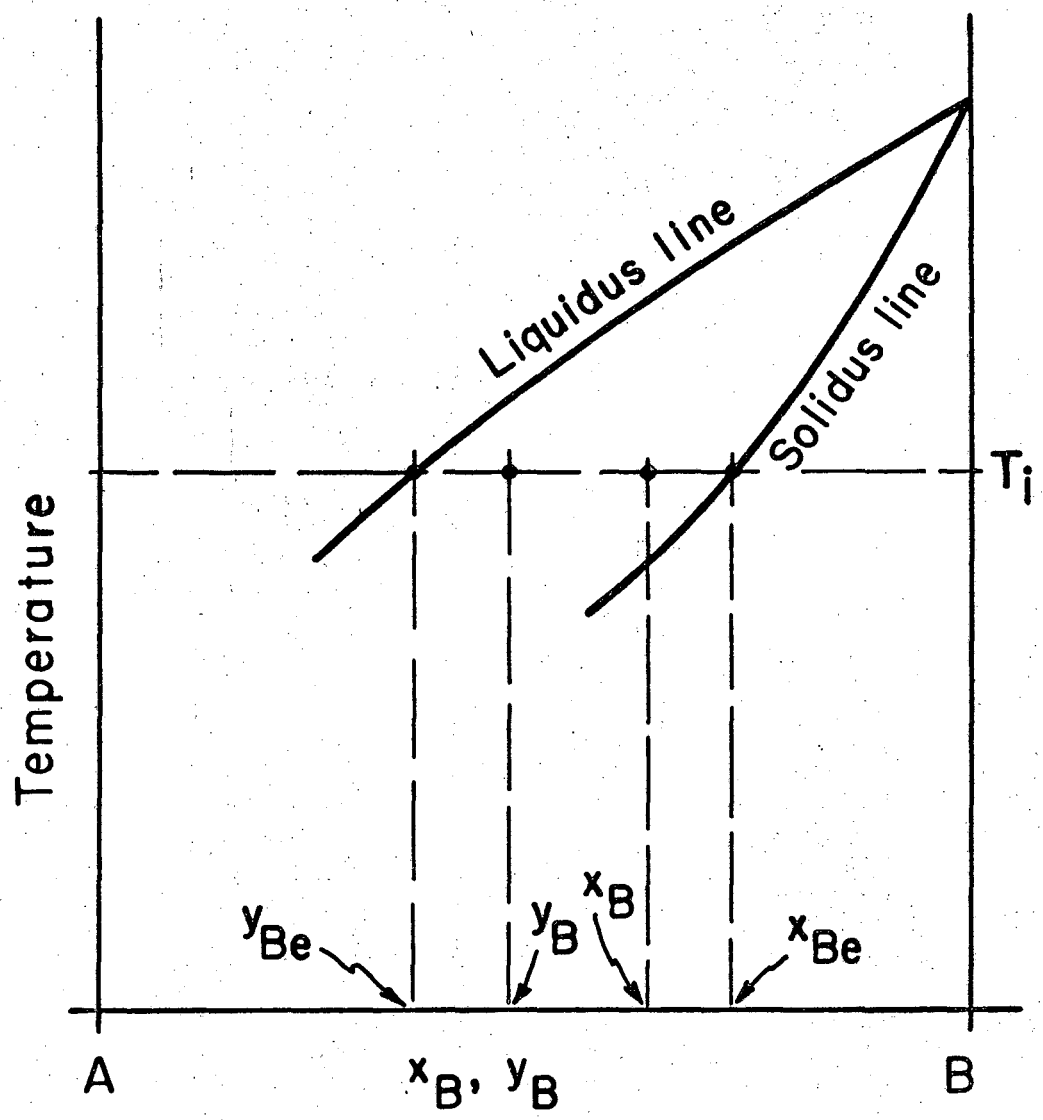


Fig. 1. Hypothetical phase diagram, bibenzyl and trans-stilbene system.

THE COMPUTATION OF THE CRYSTAL GROWTH VELOCITY, V

For a pure substance the crystal growth velocity is fixed when the temperature of the surrounding liquid is given; for growth from a binary solution fixing the interface temperature and the interface liquid composition are sufficient to determine V. How is such a relationship expressed by the equations given here?

From Eq. (12) one can compute the composition of the solid which forms in a liquid of fixed composition provided the ratio of the two forward rate constants (a function of temperature alone) is known and provided also that the group of variables, $f\lambda_S k_B^F/V$, is known. Thus for fixed T and $y_B$, $x_B$ will be uniquely a function of $f\lambda_S k_B^F/V$. A typical relationship of this sort, computed for the binary system stilbene-bibenzyl, is shown in Fig. 2. As expected, the greater the value of the group the closer $x_B$ approaches its equilibrium value at the assumed temperature.

Having found the solid composition it is now possible to compute $\Delta G$ and f, through Eq. (17). Furthermore, $k_B^F$ is fixed by the temperature and is known. Thus, for each assumed value of the group, $f\lambda_S k_B^F/V$, all the quantities but V are determined, from which V follows by a simple computation. Fig. 2 also shows the relationship between $\Delta G$ and the dimensionless group for the illustrative example. By assuming $f\lambda_S k_B^F/V$ constant and varying $y_B$ for fixed T it shows the values of $V/\lambda_S k_B^F$, which is proportional to f, is related to the undercooling, $\Delta T = T_e - T$, almost linearly as for pure compounds.

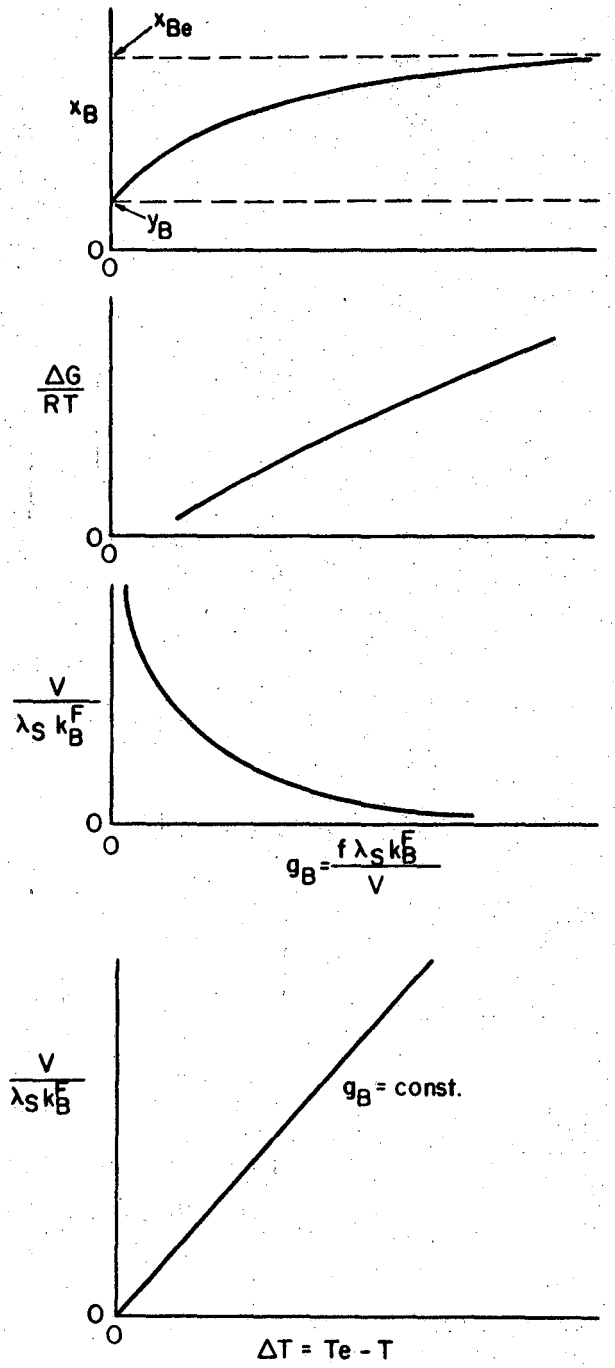


Fig. 2. Relationship for the determination of mixed crystal growth velocity.

DETERMINATION OF THE RATE COEFFICIENTS, $k_A^F$ and $k_B^F$

Following the method of Eyring (1941), the expression for the first-order rate coefficient is

$$k_B^F = \chi\ (kT/h)\ \exp(-\Delta G_C^{\ddagger}/RT) = \chi\ (kT/h)\ \exp(\Delta S_C^{\ddagger}/R)\ \exp(-\Delta H_C^{\ddagger}/RT)\ , \qquad (21)$$

and a similar expression for $k_A^F$. In Eq. (21) $\chi$ represents the fraction of the activated molecules which pass over the activation barrier in the direction. $\Delta G_C^{\ddagger}$ is the excess of the standard free energy of the molecule which is activated for crystallization over the value in the liquid, and $\Delta S_C^{\ddagger}$ and $\Delta H_C^{\ddagger}$ are the related entropy and enthalpy differences, respectively. Use of such an expression required a knowledge of the numerical values of these thermodynamic properties of the activated state for each substance in the mixture.

There is some reason to believe that, even though numerical values of the activation properties may not be available from direct measurement of crystal growth rates, values can be estimated by using the corresponding values derived from viscosity. Viscosities of liquids are far easier to measure experimentally than are growth velocities and the molecular mechanisms involved may be similar.

On the other hand, as pointed out by Kirwan and Pigford (1969), there are some differences in the molecular processes involved in crystal growth and in viscous flow. For instance, the molecule which approaches the crystal and becomes attached has to have the orientation that is required in the crystal lattice. The molecule which is ready to undergo viscous flow displacement may need to be oriented too, but the requirement

is not likely to be as stringent. Thus, it may be possible to estimate $\Delta S_C^{\ddagger}$ from $\Delta S_V^{\ddagger}$ by subtracting the entropy of fusion, $\Delta S_f$ from the latter, plus a small correction of R entropy units to account for the observation that perfectly spherical molecules undergo an entropy increase of R units upon melting. Moreover, there is reason to believe that the enthalpy of activation for crystallization may be smaller than that for viscosity (Kirwan and Pigford, 1969). To detach itself from its neighbor molecules in the liquid is all that is needed for crystal growth, but flow of a molecule also requires that a vacancy or hole be formed in the liquid at an adjacent site. Thus it may be that

$$\Delta H_C^{\ddagger} = c\Delta H_V^{\ddagger} , \tag{22}$$

where c is a constant probably smaller than unity. The best course of action, however, is not to try to compute $\Delta H_C^{\ddagger}$ unless no experimental crystallization data are available; a better plan is to make at least one measurement of the growth velocity and to determine the enthalpy of activation from that value, using it in Eq. (21) for estimates at other temperatures. Determination of both $\Delta S_C^{\ddagger}$ and $\Delta H_C^{\ddagger}$ from experimental data is not likely to be possible because it is unusual to be able to cover a wide enough range of temperatures in experimental work to give a reliable value of the slope of the curve of log (V) versus 1/T.

## EXPERIMENTAL RESULTS

Data were obtained for the binary system bibenzyl-stilbene, for which there is a wide range of solid compositions over which homogeneous

solid solutions are formed. The phase diagram for the system is shown in Fig. 3, based on the data of Kolosov (1958). The diagram shows that over most of the range of $x$ the crystal structure resembles that of pure stilbene. At low mole fractions of stilbene there is a peritectic reaction but the compositions that were used in the experiments were all to the right of this range.

Crystallization rates and interfacial compositions and temperatures were observed with a temperature-gradient microscope stage, as described elsewhere (Cheng, 1969). The interface mole fraction of stilbene, $y_B$, was computed from the known composition of the liquid mixture introduced into the optical wedge of the apparatus and from the observed shift of the diffraction fringes owing to the concentration variation which accompanies the diffusion boundary layer in the liquid. The equation relating these quantities is

$$y_B = y_B(\infty) - \Delta N(\lambda_0/2t)(\partial n/\partial y)_T^{-1} , \qquad (23)$$

with $\Delta N$ = the number of fringe displacements at the interface, $\lambda_0$ = the wavelength of the laser light used, $t$ = the wedge thickness at the observation point, and $(\partial n/\partial y)_T$ = the derivative of refractive index of the solution with respect to composition.

Compositions of the solid phase were determined in two ways. First, the same diffraction pattern was used in combination with a diffusion flux balance at the interface,

$$x_B = y_B + (\rho_L D/\rho_S V)(dy_B/dz)_{z=0} , \qquad (24)$$

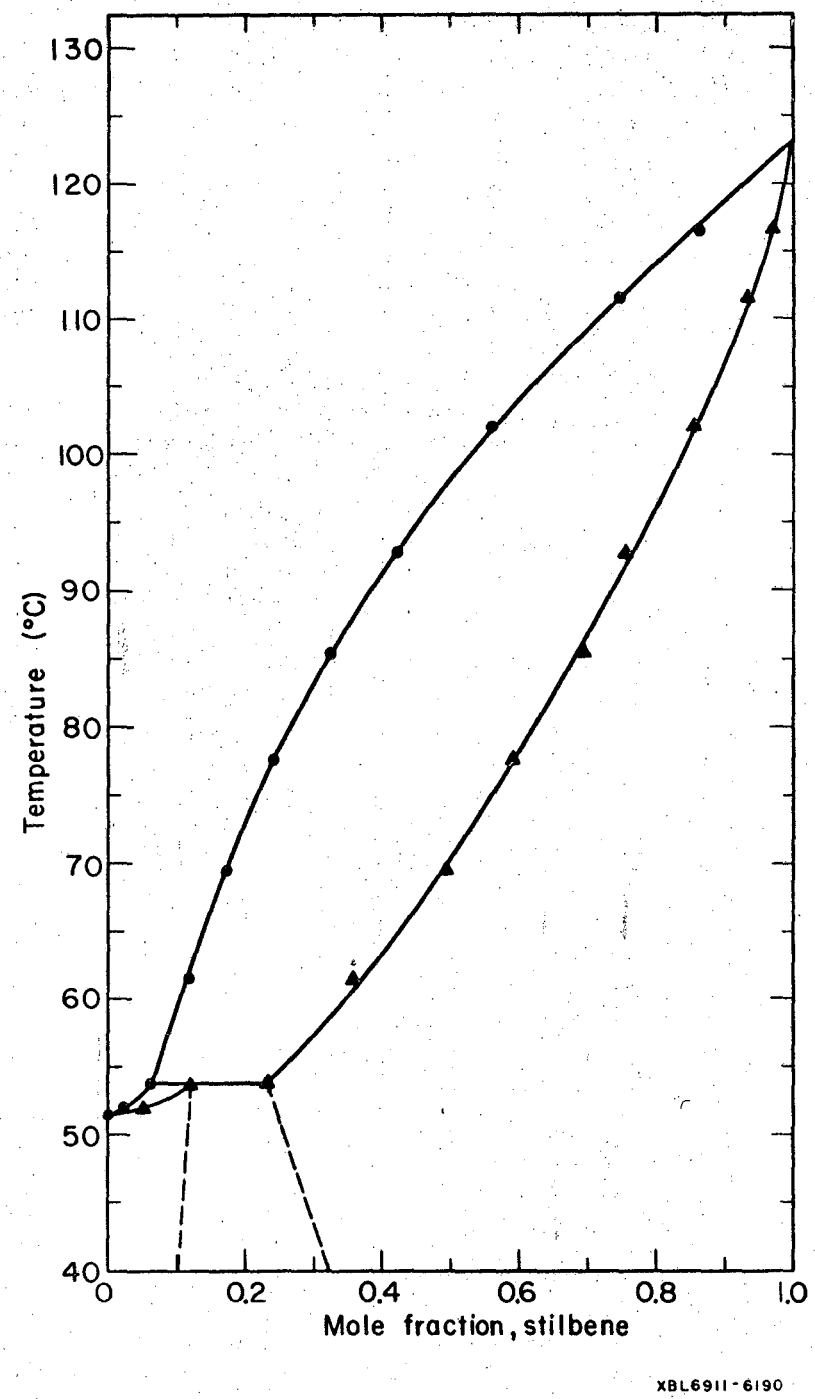


Fig. 3. Phase diagram, bibenzyl and trans-stilbene system.

in which $D$ is the binary diffusion coefficient in the liquid and $dy_B/dz$ is the normal gradient of mole fraction at the interface. The latter quantity could be computed from careful measurements of the slopes of several diffraction lines using the equation

$$dy_B/dz = \frac{\lambda_0 S}{2\ s\ t\ \cos\ \alpha(\sin\ \beta + S\ \cos\ \beta)(\partial n/\partial y)_T} \quad , \tag{25}$$

where $S$ represents the measured slope of the diffraction fringes and $s$ is their spacing. The angles $\alpha$ and $\beta$ represent inclinations of the crystal face and of the distant straight diffraction lines, respectively. A detailed derivation of these equations is given elsewhere (Cheng, 1969).

In order to obtain an independent check of the computed solid compositions, a few measurements were obtained by taking small samples of the solid phase obtained from the diffraction wedge and subjecting these to ultra violet absorption analysis in ethanol. Such measurements were tedious and somewhat inaccurate but they agreed fairly well with the computed compositions using Eqs. (23) and (24), as will be seen shortly.

The pure materials were carefully purified by zone refining and sublimation. Measured melting points of the purified samples were 123.0° C for trans-stilbene (vs. 123.3° C reported (Kolosov, 1958)) and 52.03° C for bibenzyl (vs. 51.1° C reported (Kolosov, 1958)). Other properties of the pure components are shown in Table I.

The liquid diffusion coefficient was not measured directly. A value observed by Kirwan (1967) was combined with an estimate based on the empirical correlation of Wilke and Chang (1955); the value used was

$7.6 \times 10^{-6}$ sq. cm/sec at 63.3° C. It is believed to have a probable uncertainty of about ±20%. The intermolecular spacing for the solid, $\lambda_S$, was computed by taking the cube root of the column of the solid phase per molecule. Liquid viscosity data were determined by Kirwan (1967).

Table I. Physical Properties of Pure Materials[a]

| Substance | M.W. | $T_m$ | $\Delta H_f$ | $\Delta S_f$ | $\sigma \times 10^7$ | $\eta$ | $\Delta H_V^{\ddagger}$ | $\Delta S_V^{\ddagger}$ |
|---|---|---|---|---|---|---|---|---|
| | | °K | cal/g mole | | (cal/cm$^2$) | c.p. | cal/g mole | |
| Bibenzyl | 182.27 | 325.18 | 5580 | 17.18 | 4.76 | 2.0 | 3243 | -3.709 |
| t-stilbene | 180.25 | 396.15 | 7080 | 17.87 | 8.70 | 1.0 | 3625 | -3.083 |

[a]Dimensions see notation

DATA FOR PURE STILBENE

Figure 4 shows the experimentally observed growth velocities for pure trans-stilbene. The data are plotted in the form V vs. the square of the undercooling, $\Delta T$. It can be shown that for the screw dislocation surface mechanism and for values of $\Delta S_f \Delta T / RT_m$ that are sufficiently small.

Equating the average velocity of movement toward the surface of the B molecules to the fluid velocity toward the same surface, $V(\rho_S/\rho_L)$, we get

$$V = f \lambda_S k_B^F \Delta_B = f \lambda_S k_B^F [1 - \exp(- \frac{\Delta S_f \Delta T}{RT})]$$

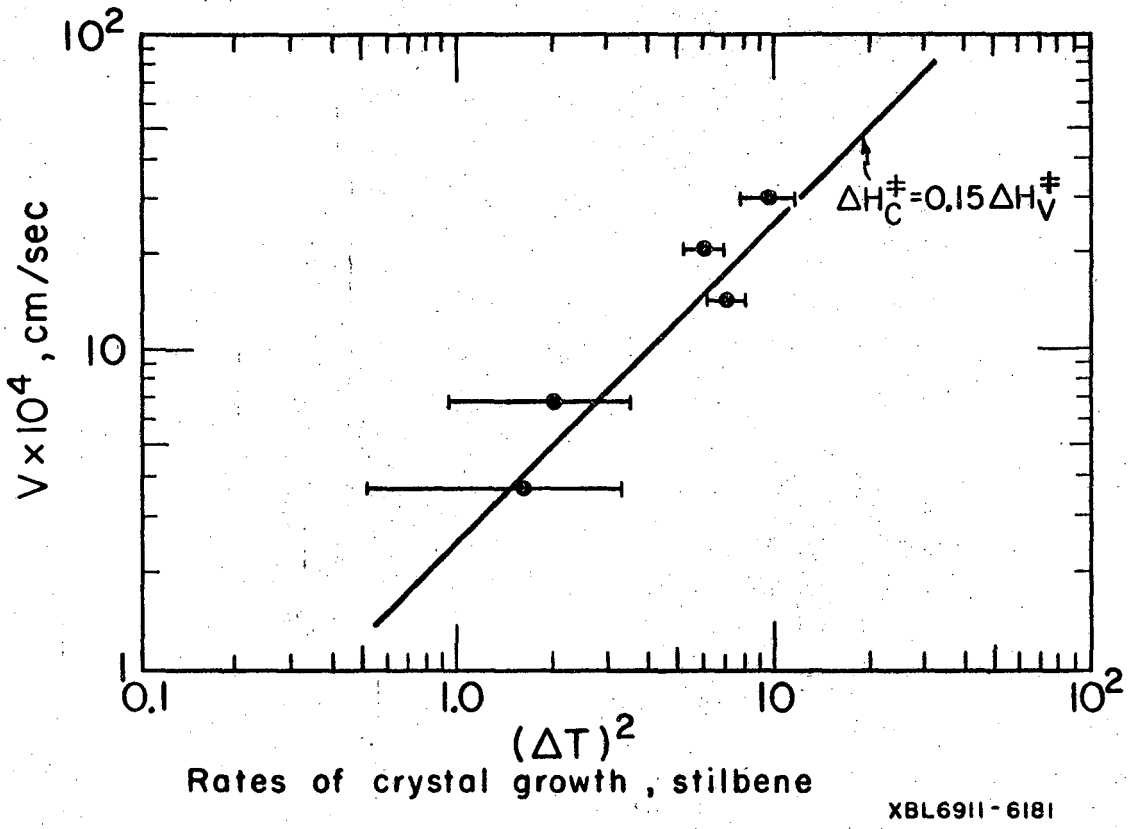
$10^2$
10
1
$V \times 10^4$, cm/sec
$\Delta H_C^{\ddagger} = 0.15 \Delta H_V^{\ddagger}$
0.1
1.0
10
$10^2$
$(\Delta T)^2$
Rates of crystal growth, stilbene
XBL6911-6181

Fig. 4

or

$$V \sim (1/1.2\pi)(\lambda_S k_B^F)(\Delta S_f \Delta T/\Delta H_f)(\Delta S_f \Delta T/RT_m)$$

$$= (1/1.2\pi)(\lambda_S k_B^F)(\Delta S_f/R)(\Delta T/T_m)^2 , \qquad (26)$$

in which the exponential term has been expanded in a series. The data on the figure are not sufficiently accurate, owing to uncertainties in the interface temperature, to test the hypothesis that $V$ is proportional to the square of $\Delta T$. However, if we evaluate the entropy of activation in $k_B^F$ from the equation,

$$\Delta S_C^{\ddagger} = \Delta S_V^{\ddagger} - (\Delta S_f - R) , \qquad (27)$$

and approximate the enthalpy of activation by choosing $c = 0.15$ in Eq. (22) we obtain a line from Eq. (26) which passes through the data points. In view of the reasonable values of the activation quantities and the at least approximate agreement of the exponent on $\Delta T$ with the expected value, it seems likely that the pure stilbene crystals grew by the screw dislocation mechanism.

Evaluation of the surface fraction leads to $f \sim 6 \times 10^{-4}$ for stilbene at one degree of subcooling.

DATA FOR STILBENE-BIBENZYL SOLUTIONS

The experimental data for interface liquid and solid compositions and interfacial liquid temperatures are listed in Table II for three series of runs, each series corresponding to a constant value of the liquid mole

fraction of stilbene at a great distance from the crystal, $y_{BO}$. The observed liquid and solid compositions are plotted in Fig. 5. There one sees that, owing to the finite growth velocity, the interfacial liquid mole fraction of stilbene fell slightly below $y_{BO}$ at finite values of V. The greatest deviation from equilibrium occurred in the solid composition, as shown by the upper lines in the figure. At very small values of V the values of $x_B$ tended toward the equilibrium value but at most of the values of V used $x_B$ fell considerably below its equilibrium value. At large values of V the crystal's composition differed only very slightly from that of the liquid from which it grew. The figure shows that the principal cause of the failure to reach equilibrium was not the diffusional resistance of the liquid but the slowness of phase growth.

Although the measurements were carried out with great care it is of course possible that the solid compositions which were obtained by calculation from the diffusion flux balance, Eq. (24), were in error. This could have occurred if any of the measurements were not precise, if the estimated diffusion coefficient was wrong, or if the growing crystals did not fill the optical wedge completely. By computation of the possible errors of measurement it was concluded that the true value of $y_B$ might have been off by about 0.0042 mole fraction and that the derivative, $dy_B/dz$ might be in error by about 0.0052 mole fraction units. The probable error of D was estimated to be about 20 percent. The other quantities in the equation were precise. Thus, the total probable error in $x_B$ should have been about 0.01 mole fraction units, which is smaller than the vertical difference between the pairs of curves on Fig. 5.

Table II. Crystallization of Mixed Crystals from Binary Melts of Stilbene and Bibenzyl System

| Run No. | V, (cm/sec)×10$^3$ | $y_B(0)$, mole fraction | $x_B(0)$, mole fraction | T(0), °C | $T_e$[a], °C | $y_{Be}$, mole fraction | $x_{Be}$, mole fraction | $x_{B,cal}$[b], mole fraction |
|---|---|---|---|---|---|---|---|---|
| $y_{BO} = y_B(\infty) = 0.15$ mole fraction, stilbene | | | | | | | | |
| III- 72 | 0.68 | 0.1356 | 0.1498 | 63.53 | 64.22 | 0.131 | 0.397 | 0.150 |
| III- 73 | 1.00 | 0.1319 | 0.1411 | 64.17 | 63.70 | 0.135 | 0.407 | c |
| III- 75 | 1.92 | 0.1388 | 0.1437 | 62.11 | 64.67 | 0.120 | 0.374 | 0.157 |
| III- 76 | 0.51 | 0.1263 | 0.1671 | 63.61 | 62.93 | 0.131 | 0.398 | c |
| III- 77 | 0.50 | 0.1407 | 0.1585 | 63.08 | 64.97 | 0.127 | 0.390 | 0.189 |
| III- 99 | 0.74 | 0.1273 | 0.1513 | 63.37 | 63.07 | 0.129 | 0.394 | c |
| III-101 | 0.34 | 0.1295 | 0.1707 | 62.86 | 63.38 | 0.126 | 0.386 | 0.150 |
| III-102 | 0.40 | 0.1370 | 0.1662 | 62.68 | 64.41 | 0.125 | 0.383 | 0.190 |
| III-103 | 0.15 | 0.1365 | 0.2055 | 62.48 | 64.35 | 0.123 | 0.380 | 0.249 |
| III-104 | 0.13 | 0.1397 | 0.2224 | 63.17 | 64.78 | 0.128 | 0.391 | 0.252 |
| III-105 | 0.39 | 0.1415 | 0.1702 | 62.73 | 65.04 | 0.125 | 0.384 | 0.210 |
| III-106 | 0.21 | 0.1452 | 0.1784 | 61.82 | 65.53 | 0.118 | 0.370 | 0.281 |
| III-107 | 0.31 | 0.1436 | 0.1736 | 63.28 | 65.32 | 0.129 | 0.393 | 0.220 |
| III-140 | 0.42 | 0.1436 | 0.1651 | 63.65 | 65.32 | 0.131 | 0.399 | 0.196 |
| III-141 | 0.35 | 0.1358 | 0.1624 | 62.49 | 64.19 | 0.123 | 0.380 | 0.189 |
| III-143 | 0.23 | 0.1401 | 0.1760 | 63.76 | 64.84 | 0.132 | 0.400 | 0.198 |
| III-144 | 0.15 | 0.1410 | 0.2019 | 63.06 | 64.98 | 0.127 | 0.389 | 0.258 |
| III-145 | 0.09 | 0.1461 | 0.1923 | 63.49 | 65.66 | 0.130 | 0.396 | 0.307 |
| III-146 | 0.03 | 0.1445 | 0.3168 | 62.13 | 65.44 | 0.121 | 0.375 | 0.381 |

(continued)

Table II. continued

| Run No. | V, (cm/sec)×10³ | $y_B(0)$, mole fraction | $x_B(0)$, mole fraction | T(0), °C | $T_e$[a], °C | $y_{Be}$, mole fraction | $x_{Be}$, mole fraction | $x_{B,cal}$[b], mole fraction |
|---|---|---|---|---|---|---|---|---|
| $y_{B0} = y_B(\infty) = 0.15$ mole fraction, stilbene | | | | | | | | |
| III-147 | 0.20 | 0.1371 | 0.1973 | 62.66 | 64.43 | 0.124 | 0.383 | 0.225 |
| III-148 | 0.73 | 0.1466 | 0.1519 | 60.10 | 65.73 | 0.106 | 0.342 | 0.228 |
| III-149 | 0.25 | 0.1398 | 0.1864 | 62.22 | 64.80 | 0.121 | 0.376 | 0.240 |
| IV - 1 | 0.21 | 0.1428 | 0.1907 | 63.13 | 65.21 | 0.128 | 0.391 | 0.243 |
| IV - 2 | 0.15 | 0.1425 | 0.2123 | 63.94 | 65.16 | 0.134 | 0.403 | 0.232 |
| IV - 3 | 0.10 | 0.1431 | 0.2483 | 62.93 | 65.25 | 0.126 | 0.387 | 0.301 |
| IV - 4 | 0.07 | 0.1424 | 0.2801 | 63.12 | 65.15 | 0.128 | 0.390 | 0.313 |
| IV - 5 | 0.79 | 0.1429 | 0.1508 | 64.86 | 65.23 | 0.140 | 0.417 | 0.150 |
| IV - 6 | 0.65 | 0.1404 | 0.1542 | 62.90 | 64.89 | 0.126 | 0.387 | 0.180 |
| IV - 7 | 0.35 | 0.1381 | 0.1616 | 62.37 | 64.57 | 0.122 | 0.379 | 0.208 |
| IV - 8 | 0.15 | 0.1417 | 0.2014 | 62.74 | 65.08 | 0.125 | 0.384 | 0.271 |
| IV - 9 | 0.24 | 0.1459 | 0.1647 | 63.64 | 65.63 | 0.131 | 0.399 | 0.237 |
| IV - 10 | 0.12 | 0.1416 | 0.2256 | 63.42 | 65.08 | 0.130 | 0.395 | 0.261 |
| $y_{B0} = y_B(\infty) = 0.25$ mole fraction, stilbene | | | | | | | | |
| III- 78 | 0.48 | 0.2314 | 0.2623 | 74.04 | 76.33 | 0.212 | 0.548 | 0.333 |
| III- 79 | 0.87 | 0.2307 | 0.2494 | 75.86 | 76.25 | 0.227 | 0.571 | 0.244 |
| III- 80 | 1.33 | 0.2271 | 0.2364 | 74.77 | 76.84 | 0.218 | 0.557 | 0.269 |
| III- 81 | 1.62 | 0.2353 | 0.2411 | 74.36 | 76.77 | 0.215 | 0.552 | 0.276 |

(continued)

Table II. continued

| Run No. | V, (cm/sec)×10³ | $y_B(0)$, mole fraction | $x_B(0)$, mole fraction | T(0), °C | $T_e$[a], °C | $y_{Be}$, mole fraction | $x_{Be}$, mole fraction | $x_{B,cal}$[b], mole fraction |
|---|---|---|---|---|---|---|---|---|
| $y_{B0} = y_B(\infty) = 0.25$ mole fraction, stilbene | | | | | | | | |
| III- 84 | 0.16 | 0.2327 | 0.3257 | 75.56 | 76.48 | 0.225 | 0.568 | 0.350 |
| III- 85 | 0.52 | 0.2404 | 0.2574 | 75.03 | 77.42 | 0.220 | 0.561 | 0.344 |
| III- 86 | 1.24 | 0.2357 | 0.2486 | 75.13 | 76.81 | 0.221 | 0.562 | 0.274 |
| III- 89 | 0.89 | 0.2276 | 0.2452 | 74.83 | 75.89 | 0.219 | 0.558 | 0.260 |
| III- 91 | 2.00 | 0.2392 | 0.2450 | 74.26 | 77.22 | 0.214 | 0.550 | 0.280 |
| III- 92 | 0.71 | 0.2247 | 0.2474 | 74.80 | 75.56 | 0.218 | 0.558 | 0.254 |
| III- 93 | 0.96 | 0.2297 | 0.2439 | 74.34 | 76.13 | 0.214 | 0.552 | 0.278 |
| III- 94 | 0.57 | 0.2330 | 0.2505 | 74.26 | 76.51 | 0.214 | 0.550 | 0.323 |
| III- 96 | 0.10 | 0.2345 | 0.3953 | 76.42 | 76.68 | 0.232 | 0.579 | 0.301 |
| III- 97 | 0.06 | 0.2377 | 0.5202 | 76.42 | 77.04 | 0.232 | 0.579 | 0.411 |
| III- 98 | 0.13 | 0.2368 | 0.3842 | 74.90 | 76.94 | 0.219 | 0.559 | 0.442 |
| $y_{B0} = y_B(\infty) = 0.45$ mole fraction, stilbene | | | | | | | | |
| III-108 | 0.83 | 0.4350 | 0.4546 | 92.74 | 93.88 | 0.419 | 0.762 | 0.506 |
| III-109 | 0.58 | 0.4356 | 0.4685 | 93.88 | 93.93 | 0.435 | 0.774 | 0.441 |
| III-110 | 0.39 | 0.4412 | 0.4790 | 92.59 | 94.33 | 0.417 | 0.761 | 0.597 |
| III-113 | 0.16 | 0.4436 | 0.5000 | 91.37 | 94.50 | 0.401 | 0.749 | 0.707 |
| III-115 | 0.76 | 0.4308 | 0.4646 | 91.17 | 93.58 | 0.399 | 0.746 | 0.556 |
| III-116 | 0.34 | 0.4398 | 0.4934 | 92.75 | 94.23 | 0.420 | 0.763 | 0.594 |

(continued)

Table II. continued

| Run No. | V, (cm/sec)×10³ | $y_B(0)$, mole fraction | $x_B(0)$, mole fraction | T(0), °C | $T_e$[a], °C | $y_{Be}$, mole fraction | $x_{Be}$, mole fraction | $x_{B,cal}$[b], mole fraction |
|---|---|---|---|---|---|---|---|---|
| $y_{BO} = y_B(\infty) = 0.45$ mole fraction, stilbene | | | | | | | | |
| III-117 | 0.29 | 0.4427 | 0.4946 | 93.00 | 94.44 | 0.423 | 0.765 | 0.609 |
| III-118 | 0.15 | 0.440 | 0.5795 | 93.38 | 94.53 | 0.428 | 0.769 | 0.645 |
| III-119 | 0.14 | 0.4309 | 0.5815 | 90.32 | 93.59 | 0.388 | 0.738 | 0.704 |
| III-132 | 0.86 | 0.4318 | 0.4678 | 87.55[d] | 93.65 | 0.353 | 0.708[d] | 0.616[d] |
| III-133 | 0.47 | 0.4276 | 0.4784 | 95.63 | 93.34 | 0.460 | 0.791 | c |
| III-134 | 0.72 | 0.4412 | 0.4648 | 93.23 | 94.33 | 0.426 | 0.767 | 0.519 |
| III-135 | 2.08 | 0.4412 | 0.4470 | 92.96 | 94.33 | 0.422 | 0.765 | 0.480 |
| III-136 | 2.99 | 0.4428 | 0.4471 | 91.19 | 94.45 | 0.399 | 0.747 | 0.500 |
| III-137 | 1.49 | 0.4388 | 0.4485 | 92.39 | 94.16 | 0.415 | 0.759 | 0.502 |
| III-138 | 2.06 | 0.4361 | 0.4443 | 91.90 | 93.97 | 0.408 | 0.754 | 0.490 |
| III-139 | 0.45 | 0.4318 | 0.4704 | 95.62 | 93.65 | 0.459 | 0.791 | c |

[a] Equilibrium temperature based on interfacial composition, $y_B(0)$.

[b] With $k_B^F$ calculated from Eq. (21) using $\chi = 0.01$, and $\Delta T = T_e - T(0)$ for computing step density f.

[c] Because of negative $\Delta T$, this value is not computed.

[d] Measured interfacial temperature T(0) was in error.

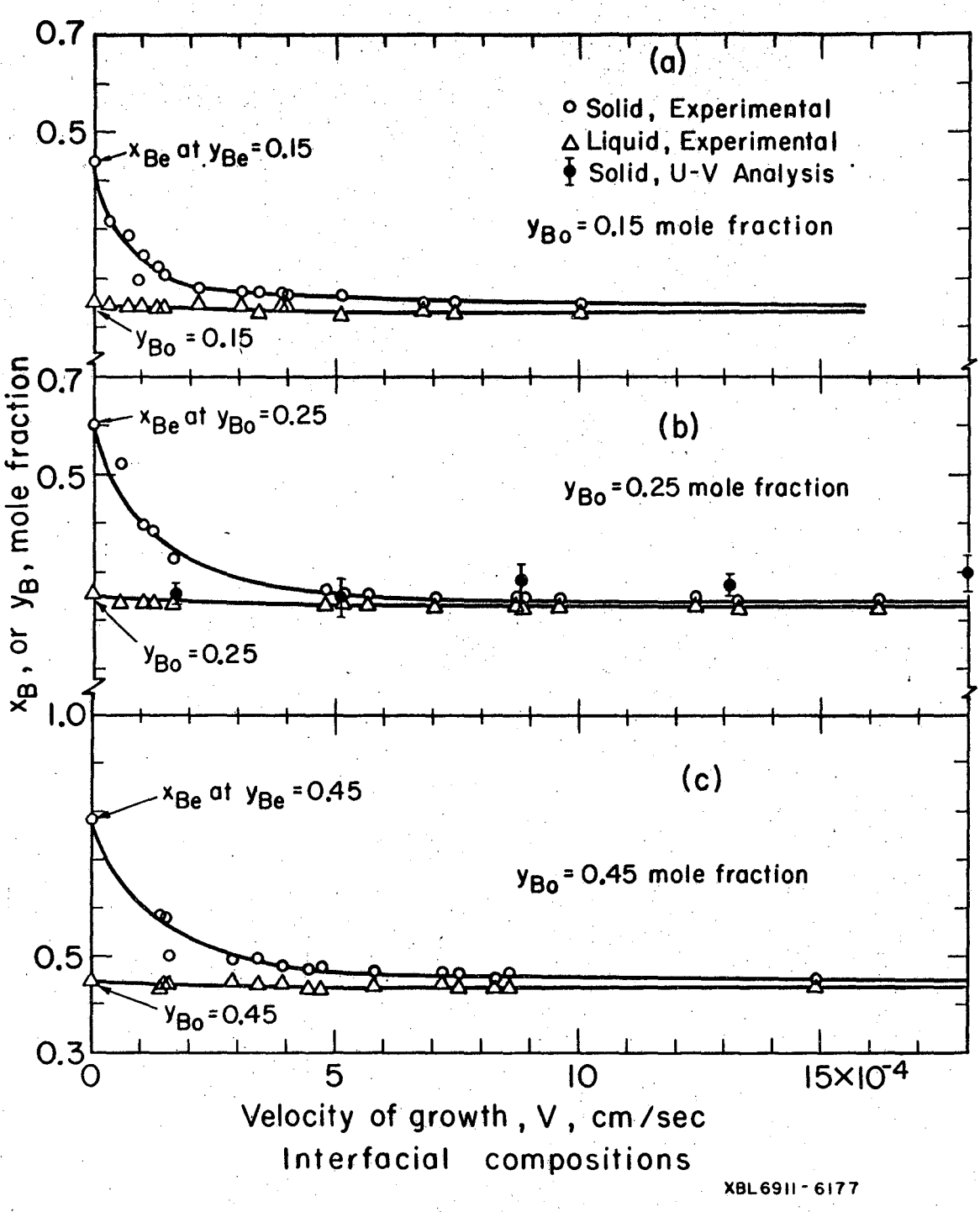


Fig. 5. Interfacial compositions, bibenzyl and trans-stilbene system.

An even stronger indication that the measured values of $x_B$ are reliable was obtained when some of the crystallization runs were repeated and small samples of the solid were taken from the optical wedge and analyzed by ultra violet absorption. The following table summarized the values obtained and supports the use of Eq. (24) The results of such analyses are also shown in Fig. 5.

Table III. Comparison of Solid Compositions Computed from Flux Balance with Values from Ultra Violet Absorption

| Growth Velocity $V \times 10^3$, cm/sec | Mole Fraction Stilbene, $x_B$ | |
|---|---|---|
| | From Eq. (24) | From Ultra Violet Analysis |
| 1.85 | 0.240 ± 0.010 | 0.300 ± 0.031 |
| 1.31 | 0.243 ± 0.010 | 0.274 ± 0.019 |
| 0.88 | 0.251 ± 0.010 | 0.284 ± 0.033 |
| 0.51 | 0.260 ± 0.015 | 0.248 ± 0.039 |
| 0.17 | 0.340 ± 0.015 | 0.252 ± 0.017 |

One other piece of evidence is available to support the reported values of $x_B$. It consists of the measurements, also using Eq. (24), of the composition of the solid phase which grows at a finite rate in the system of salol-thymol. These compounds are completely insoluble in each other as solids, the phase diagram indicating that to the right of the eutectic point, $x_{Be} = 1$ and $x_{Ae} = 0$. Application of Eq. (11) shows that the rate theory is satisfied under these conditions only by the value $x_A = 0$ at finite V. Compute values of $x_A$ based on the diffraction fringes, were not precisely zero but were close. The average value for several experiments

was about 0.1. Recognize, however, that the theory which we have used may be defective in such a situation for it assumes that the surface fraction for attachment of A molecules and that for B molecules is exactly the same. In fact, it may be possible that $f_A$ is zero on a pure-B surface.

INTERPRETATION OF THE RESULTS

The Separation Factor, β: Figure 6 shows values of the separation factor based on Eq. (13) using the thermodynamic properties of the stilbene-bibenzyl system and assuming c = 0.15 in Eq. (22). The dimensionless quantity $g_B = f\lambda_S k_B^F/V$ is sufficient to determine β as a function of the interface composition and temperature. As $g_B$ increases the equilibrium separation factor is approached. Figure 7 compares the separation factors computed from the observed compositions with values found from Fig. 6. Some of the data points are based on c = 1.0; others, on c = 0.15. The difference is small because only the ratio of the two forward coefficients, $k_A^F/k_B^F$, is affected in the rate theory. The agreement is satisfactory.

Determination of the Surface Step Density and the Rate Coefficient: Using the observed solid and interfacial liquid compositions and temperature and the crystal growth velocity it is possible to compute values of the product $fk_B^F$ from Eq. (11). The determination of the separate values of f and $k_B^F$ is not possible; one has to be found from the theory in order to determine the other from the data.

There are two ways in which the surface fraction, f, can be determined from the experimentally observed interface temperature, and the interface liquid and solid compositions. First, the values of V, T, $y_B$, and

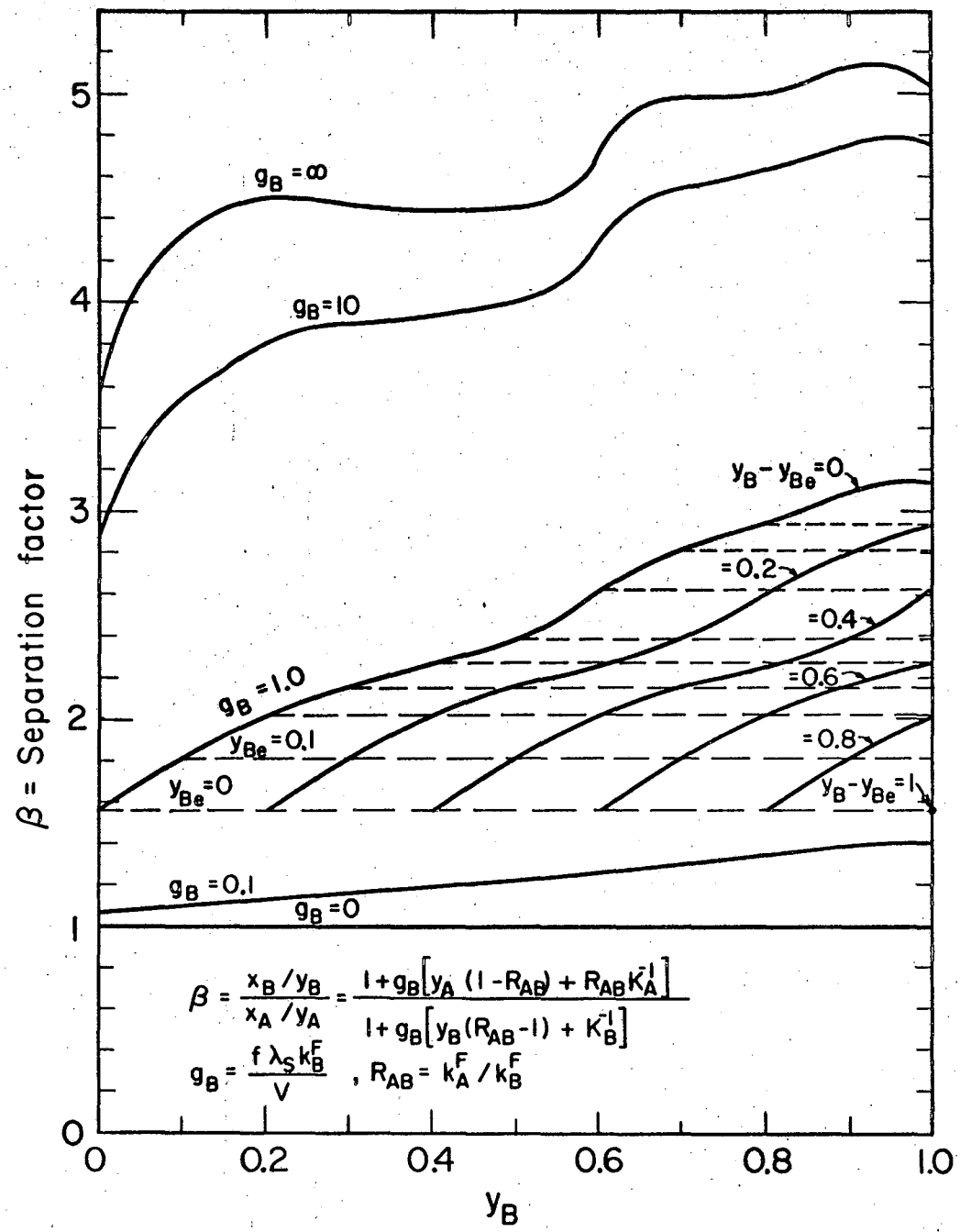


Fig. 6. Separation factor, bibenzyl and trans-stilbene system.

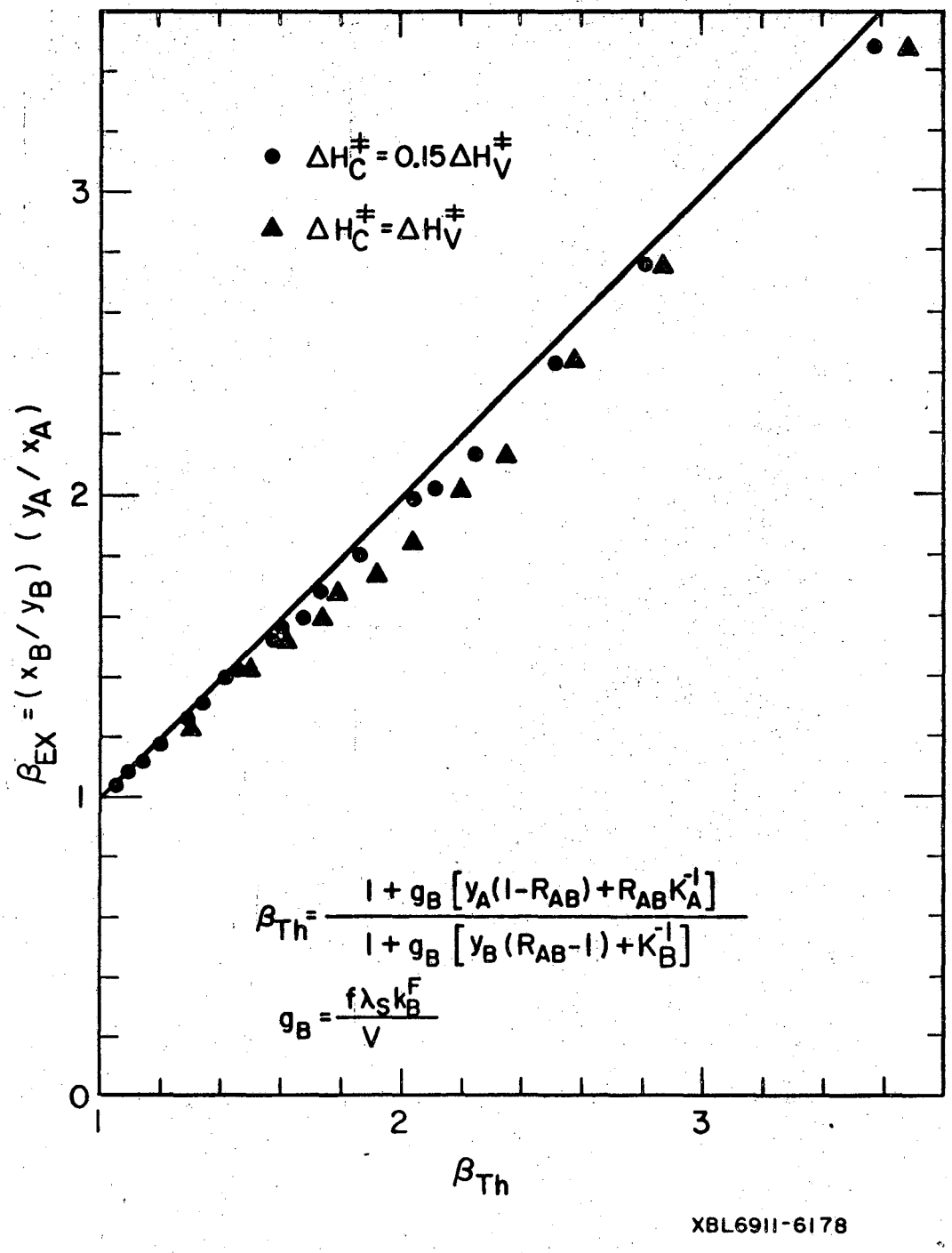


Fig. 7. Comparison of separation factors, bibenzyl and trans-stilbene system.

$x_B$ can be substituted in Eq. (11) to obtain values of the group $f\lambda_S k_B^F$. Then with estimates of $\lambda_S$ and of $k_B^F$ and $k_A^F$ (the latter from the Eyring theory, Eq. (21), and $\Delta S_C^{\ddagger}$ and $\Delta H_C^{\ddagger}$ from Eq. (27) and (22) with $c = 0.15$) $f$ follows directly, provided $\chi$ is known. Assuming $\chi = 1$ yields $f \approx 10^{-5}$, which is about two orders of magnitude greater than the value obtained from the data for pure stilbene. Thus, in order to reconcile the data for the pure crystal with those for the solution one may assume $\chi \approx 10^{-2}$.

Alternatively, $f$ can be computed from Eq. (17) using values of $\Delta G$ found from the compositions and temperatures using Eq. (20) and, in the absence of any data, assuming ideal solution behavior in both the solid and the liquid phases. According to such calculations, $\Delta G$ was negative for all but two of the experimental runs--a situation which is manifestly impossible since it implies that the spontaneous process of phase growth occurs with an increase in the Gibbs free energy of the material forming the crystal surface.

It seems very possible that in a system which exhibits peritectic phase behavior over some part of the composition range there will be deviations from ideal solution behavior throughout the phase diagram and that the values of chemical potential estimated by assuming that $\gamma$ and $\Gamma$ are both unity will be erroneous. No data are available to test this belief but, in order to determine how sensitive the computations might be to small deviations in ideality the regular-solution equation for activity coefficients was introduced:

$$\ln \gamma_B = (\omega^L/RT)\, y_A^2 \quad \text{(liquid phase)}$$

$$\ln \Gamma_B = (\omega^S/RT)\, x_A^2 \quad \text{(solid phase)}$$

The result of adding the non-ideal terms to Eq. (20) is to increase the value of $\Delta G/RT$ by the quantity

$$(\omega^S/RT)(x_{Be} - x_B)^2 - 2(\omega^L/RT)(y_B - y_{Be})\left(x_B - \frac{y_B + y_{Be}}{2}\right) .$$

The first term, reflecting the influence of non-ideal behavior in the solid phase, has a positive coefficient; the coefficient of the second term is negative. In a typical experiment, Run No. III-93 of Table II, the expression above is $-0.0007(\omega^L/RT) + 0.095(\omega^S/RT)$ and the uncorrected ideal value of $\Delta G/RT$ based on the observed liquid and solid compositions and the temperature was -0.359. The coefficient of $(\omega^L/RT)$ is small because the interface liquid composition was rather close to the equilibrium value; the coefficient of $(\omega^S/T)$ is larger because $x_B$ was considerably less than $x_{Be}$. Since $\omega^L$ is likely to be smaller than $\omega^S$ it seems likely that the term representing the lack of ideality in the liquid can be neglected completely and that we can conclude that $(\omega^S/RT)$ must have been at least $0.359/0.095 = 3.78$ or $\omega^S = 2.5$ kcal/mole in order to force the change in Gibbs free energy negative for the transition from liquid to solid.

In the absence of reliable thermodynamic information for the solid solution we can only conclude that the experimentally observed compositions probably do not violate the Second Law. When the information is available it will be possible to recalculate the values of $\Delta G$ and to estimate the

surface fraction $f$ from the assumption of growth by a screw dislocation mechanism. In the mean time we have no reason to doubt the validity of Eq. (11) for the solid composition or of Eq. (17) for the surface fraction.

Table II shows values of the solid composition, $x_B$, computed from the theory using $\chi = 0.01$ and taking the activation quantities from viscosity with modifications according to Eq. (21) and (22) with $c = 0.15$. The values are by no means in perfect agreement with those observed but the departure from equilibrium is of the right magnitude and the variation with the growth velocity is about right. When no experimental information whatever is available this procedure is suggested.

## CONCLUSIONS

Use of the temperature-gradient microscope stage with provisions for determination of interface conditions by optical interference is a promising method for investigating the interfacial kinetic phenomena. For the binary system used here and probably for most other high-melting organic compounds which form solid solutions the interfacial rate of phase growth is the controlling factor in the determination of the solid composition; the diffusion process in the interfacial liquid is of minor importance.

A theory based on Eyring's theory for the first-order process of solid deposition and on a screw-dislocation mechanism for surface attachment accounts approximately for the observed phenomena, including the large departure of the solid composition from its equilibrium value according to the phase diagram. In the absence of any experimental rate data, estimates of the interfacial rate coefficients can be based on activation enthalpy and viscosity from viscosity data suitably adjusted to account for differences in the molecular phenomena accompanying crystal growth and viscous flow.

ACKNOWLEDGMENTS

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NOTATION

$C_p$ = molar heat capacity, cal/g mole °C

D = diffusion coefficient, or interface transport coefficient, sq cm/sec

f = surface step density, dimensionless

$g_B$ = dimensionless growth rate parameter, $\lambda_S f k_B^F / V$

G = molar free energy, cal/g mole

h = Planck's constant

H = molar enthalpy, cal/g mole

k = interfacial rate constant, $sec^{-1}$, or Boltzmann's constant, erg/°K

K = equilibrium or effective distribution coefficient, a function of composition

M = molecular weight

n = refractive index of liquid

N = crystallization flux, g mole/sq cm sec, or Avogadro's number, or integer in Eq. (38)

$r_c$ = critical radius of two -dimensional nucleus, cm

R = gas constant, cal/g mole °K, or ratio of interfacial rate constants for species A and B

s = interference fringe spacing, mm

S = molar entropy, cal/g mole °K

t = thickness of optical wedge at observation point, mm.

T = temperature, °C or °K.

u = average molecular velocity, cm/sec.

v = specific volume, cc/g.

V = freezing velocity, cm/sec, or molar volume, cc/g mole.

x = mole fraction in solid phase

y = mole fraction in liquid phase

GREEK LETTERS

$\alpha$ = angle, degree

$\beta$ = separation factor, or angle, degree

$\Gamma$ = solid phase activity coefficient

$\gamma$ = liquid phase activity coefficient

$\eta$ = viscosity, poise

$\lambda$ = interatomic spacing, cm.

$\lambda_0$ = wavelength, 6328 Å, for He-Ne gas laser

$\mu$ = chemical potential, cal/g mole

$\rho$ = molar density, g mole/cc

$\sigma$ = interfacial surface free energy, cal/sq cm

$\chi$ = transmission coefficient

$\omega$ = excess free energy, cal/g mole

SUPERSCRIPTS

F = forward process

L = liquid state property

0 = standard state property

R = reverse process

S = solid state property

‡ = activated state property

* = equilibrium condition

SUBSCRIPTS

A = component A, minor component, bibenzyl

B = component B, major component, stilbene

C = crystallization activated state property

e = equilibrium condition

ex = experimental condition

f = fusion process

i = interfacial condition

L = liquid state property

m = melting process

0 = initial condition

S = solid state property

T = constant temperature condition

V = viscous flow activated state property

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