Pure Diffusional Mass Transfer in Zone Melting

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In the derivation of theoretical expressions for separation in zone melting it is usually assumed that the bulk of the molten zone is well mixed (5). Under some conditions, and especially in capillary tubes below about 3-mm I.D., this is not true (*10*). In the limit mass transfer may even proceed entirely by molecular diffusion. This limit is the situation examined in detail here.

DERIVATION OF THE DIFFERENTIAL EQUATION AND BOUNDARY CONDITIONS

The most convenient coordinate system for analysis of this problem is one in which the position of the zone is fixed and material flows through it. This is illustrated in Figure 1.

The interface at which crystallization is taking place is chosen as the origin. The interfaces are assumed planar and the cross section uniform, so that the problem becomes a one-dimensional one. Furthermore the density and diffusivity are assumed to be independent of concentration and temperature, although the density may be different in the solid and liquid. The diffusivity in the solid is assumed to be negligible. With these assumptions the fluxes in and out of a cross-sectional element of the zone are shown in Figure 2. A material balance over this element of the zone yields

$$DA\rho_l\left[\left(\frac{\partial w}{\partial x}\right)_{x+\Delta x}-\left(\frac{\partial w}{\partial x}\right)_x\right]+G(w_{x+\Delta x}-w_x)=A\rho_l\left(\frac{\partial w}{\partial t}\right)\Delta x \qquad (1)$$

Dividing Equation (1) by Δx and taking the limit as Δx goes to zero, one obtains

$$DA\rho_l\left(\frac{\partial^2 w}{\partial x^2}\right)+G\left(\frac{\partial w}{\partial x}\right)=A\rho_l\left(\frac{\partial w}{\partial t}\right) \qquad (2)$$

Making the following substitutions

$$\eta=\frac{xG}{DA\rho_l}$$

$$\phi=\frac{w}{w_o}\ (w_o=\text{initial concentration, uniform})$$

$$\tau=\frac{t}{D}\left(\frac{G}{A\rho_l}\right)^2$$

one obtains

$$\frac{\partial^2\phi}{\partial\eta^2}+\frac{\partial\phi}{\partial\eta}=\frac{\partial\phi}{\partial\tau} \qquad (3)$$

which is the desired differential equation governing diffusive mass transfer in zone melting.

Boundary Conditions

Figure 3 shows the fluxes at the freezing and melting interfaces of the zone. Making material balances at these interfaces one obtains

$$\text{at } x=0,\ -D\rho_l\,A\frac{dw}{dx}=G(w-w_s) \qquad (4)$$

$$\text{at } x=L,\ -D\rho_l\,A\frac{dw}{dx}=G(w-w_o) \qquad (5)$$

where w_s is the weight fraction of component in the recrystallized material at the freezing interface.

Note that no assumption as to the relationship between w_s and w at $x=0$ has been made yet. Also note that w does not necessarily equal w_o at $x=L$, the melting interface.

When one makes the substitutions for η, ϕ, and τ, and lets

$$p=\frac{LG}{DA\rho_l},\quad \phi_s=\frac{w_s}{w_o}$$

the boundary conditions become

$$\text{at } \eta=0,\ \frac{d\phi}{d\eta}=\phi_s-\phi \qquad (6)$$

$$\text{at } \eta=p,\ \frac{d\phi}{d\eta}=1-\phi \qquad (7)$$

In addition there is the condition that the initial concentration in the zone is the same as the overall initial solid concentration, or

$$\text{at } t=0,\ \phi=1 \qquad (8)$$

Equations (6), (7), and (8) are therefore the general boundary conditions for diffusion in zone melting.

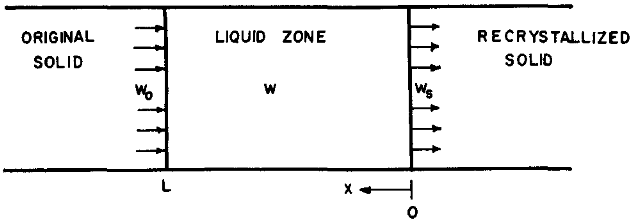

Fig. 1. Concentrations (in weight fractions) and coordinate system for zone-melting mass transfer theory.

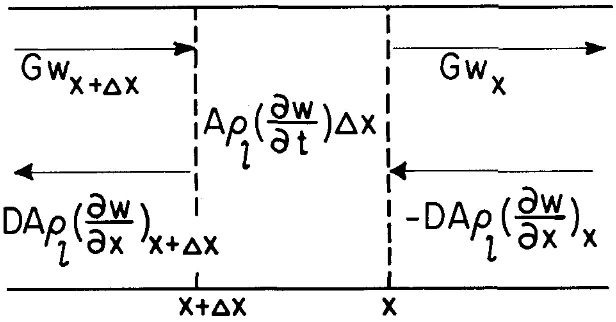

Fig. 2. Differential element of zone showing material fluxes in pure diffusional mass transfer.

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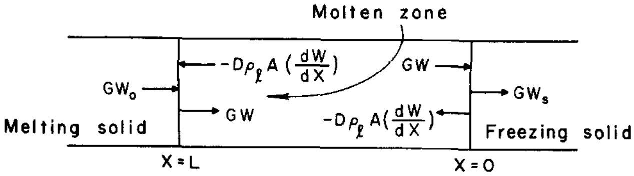

Fig. 3. Melting and freezing interfaces showing material fluxes in pure diffusional mass transfer.

Constant Distribution Coefficient

It is the usual assumption in zone melting theory that the solid concentration is always proportional to the liquid concentration when solid and liquid are in equilibrium. It is further assumed that equilibrium is attained at the freezing interface. Hence at $x = 0$, $w_s = kw$, where k is the constant distribution coefficient. With this Equation (6) becomes,

$$\text{at } \eta = 0, \frac{d\phi}{d\eta} = \phi\,(k-1) \tag{9}$$

Equations (3), (7), (8), and (9) constitute the mathematical statement of the problem for constant distribution coefficient.

Eutectic Forming Systems

As basis for establishing the proper boundary conditions for the zone melting of a binary mixture which forms a simple eutectic it is necessary to consider what a eutectic is and how it crystallizes physically. Figure 4 is a schematic phase diagram for this type of system. The eutectic point w_e is usually taken to be the point at which the solid and liquid in equilibrium have the same composition.

Compounds which form a eutectic do so because their basic crystal structure is sufficiently different that molecules of one cannot fit into a crystal of the other. In other words a eutectic mixture of the two is not really a homogeneous mixture but instead consists of microscopic crystals of the separate components (*2*, *8*).

Therefore when a liquid mixture of eutectic composition w_e begins to crystallize, a microscopic crystal of one component must form first. This event however depletes the adjacent melt of that component. The melt, being richer in the other component, then yields a microscopic crystal of it. This in turn makes the adjacent melt richer in the first component, and so the process repeats. It is thus seen that on the microscopic scale this type of crystallization is not a continuous and smooth process but actually a cyclic one. Note that the concentration fluctuations in the melt are unobservably minute and extend only an extremely short distance into the melt which surrounds the growing solid.

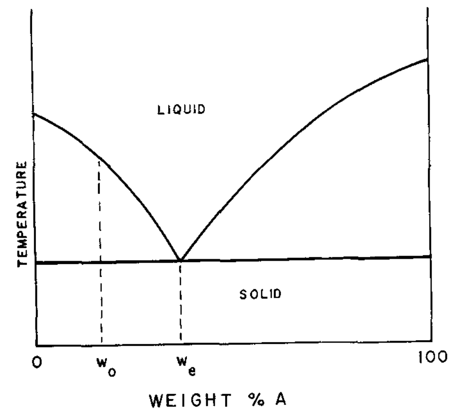

Fig. 4. Schematic solid-liquid phase diagram for systems forming simple eutectics, showing original weight fraction, w_o, and eutectic weight fraction, w_e.

Consider now the behavior of the system when a eutectic forming mixture is subjected to zone melting. With reference again to the schematic phase diagram, assume that the initial composition is w_o. If equilibrium is attained at the freezing interface, the first solid to come out will be pure $B(0\% A)$. This will cause the liquid to become richer in A. Thus while pure B comes out, the liquid composition moves towards the eutectic composition w_e. When the liquid composition at the freezing interface reaches w_e, it might be expected that the solid would deposit at composition w_e, and that this would be the steady state condition. This however would require that material of composition w_o was being supplied to the zone and material of composition w_e was being removed. This would be impossible as a steady state condition. What must happen is that when the liquid composition at the interface first exceeds w_e, a small amount of pure A comes out.* When this happens however the liquid composition moves slightly below w_e, and so pure B comes out. Again here is the cyclic crystallization process. The difference is that here is a convective flux of material to the interface and a diffusive flux away. The balance between these two regulates the relative amounts of A and B that come out. In the steady state the average concentration coming out must be w_o.

The foregoing discussion requires revision of the meaning customarily attached to the eutectic point of the phase diagram. Since liquid at the eutectic composition can yield solid of virtually any average composition, the eutectic point w_e on the diagram must not indicate a point at which a solid and liquid in equilibrium have the same composition. Instead it is a point above which one component comes out and below which the other component comes out, the relative amount of each being determined by the mass transfer conditions.

It is now possible to state the boundary conditions for the zone melting of a system of this type. The average conditions at $\eta = 0$ are obviously (with $\epsilon = w_e/w_o$):

$$\text{for } \phi < \epsilon, \frac{d\phi}{d\eta} = -\phi;\ \phi_s = 0 \tag{10}$$

$$\text{for } \phi = \epsilon, \frac{d\phi}{d\eta} = \phi_s - \epsilon \tag{11}$$

This means that until ϕ at $\eta = 0$ reaches ϵ, ϕ_s is zero and ϕ is calculated from the expression for the differential. When ϕ reaches ϵ it remains at that value, on the average, and the average ϕ_s is given by the differential expression above. The other boundary conditions are the same as for constant distribution coefficients, namely Equations (7) and (8).

SOLUTIONS

Steady State

At steady state Equation (3) becomes

$$\frac{d^2\phi}{d\eta^2} + \frac{d\phi}{d\eta} = 0 \tag{12}$$

The general solution to this is

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* This argument assumes that A and B experience no difficulty in nucleating on the solid previously laid down. This is not always true, particularly in the early stages where only the pure opposite component has solidified. In such a case the fluctuations in concentration may become appreciable.

$$\phi = a + b \exp{(-\eta)} \tag{13}$$

where a and b are constants to be determined. For constant distribution coefficient the boundary conditions, Equations (9) and (7), yield

$$\text{at } \eta = 0; -b = (a + b)(k - 1)$$

$$\text{at } \eta = p; -b\, e^{-p} = 1 - a - b\, e^{-p}$$

from which $a = 1$, $b = (1 - k)/k$. Therefore the steady state solution is

$$\phi = 1 + \frac{1 - k}{k} \exp{(-\eta)} \tag{14}$$

For eutectic forming systems the steady state solution is found from Equations (11), (7), and (13) in a like manner to be

$$\phi = 1 + (\epsilon - 1) \exp{(-\eta)} \tag{15}$$

Several conclusions of particular importance may be reached from these solutions.

1. Equation (14) is the same for variable distribution coefficient, provided that the k for $w_s = w_o$ is used.
2. The concentration profile in the zone does not depend on the size of the zone at steady state.
3. The concentration w at the melting interface does not equal w_o, although it approaches w_o as the size of the zone increases.

Computer Solutions for Unsteady State

The unsteady state problem may be solved analytically only for constant distribution coefficient (see following section). In order to solve the problem for a eutectic forming system a finite difference technique was employed with an IBM-650 digital computer. The corresponding problem for constant distribution coefficient was also solved numerically by Landau for the case of progressive freezing (infinite zone size) (*1*).

The finite difference equation corresponding to the differential Equation (3) is

$$\phi_{\eta,\tau}{}^{+}\,{}_{\Delta} = \frac{\Delta\tau}{(\Delta\eta)^2}\left[\phi_{\eta+\Delta\eta,\tau}\,(1 + \Delta\eta) + \phi_{\eta,\tau}\left(-2 - \Delta\eta + \frac{(\Delta\eta)^2}{\Delta\tau}\right) + \phi_{\eta-\Delta\eta,\tau}\right] \tag{16}$$

where $\phi_{\eta,\tau} = \phi$ at any particular η and τ, $\Delta\tau$ = size of interval of τ, and $\Delta\eta$ = size of interval of η.
For simplicity set

$$-2 - \Delta\eta + \frac{(\Delta\eta)^2}{\Delta\tau} = 0$$

Then Equation (16) becomes

$$\phi_{\eta,\tau+\Delta\tau}\frac{1}{2 + \Delta\eta}\left[\phi_{\eta+\Delta\eta,\tau}\,(1 + \Delta\eta) + \phi_{\eta-\Delta\eta,\tau}\right] \tag{17}$$

The boundary conditions result in a similar manner. For constant distribution coefficient they are

$$\text{at } \eta = 0,\ \phi_{o,\tau} = \frac{\phi_{\Delta\eta,\tau}}{1 + (k - 1)\,\Delta\eta} \tag{18}$$

$$\text{at } \eta = p,\ \phi_{p,\tau} = \frac{\phi_{p-\Delta\eta,\tau} + \Delta\eta}{1 + \Delta\eta} \tag{19}$$

In carrying out a solution ϕ was intially set equal to 1.0 over the entire interval of the zone. The $\phi_{\eta,\tau}$ were all calculated by Equation (17) except for the end points which were found by Equations (18) and (19). This process was repeated over and over until a sufficient amount of τ had been covered. ϕ_s was calculated from the fact that $\phi_s = k\phi_{o,\tau}$ at any particular τ.

To develop the computer program test calculations were made for constant distribution coefficient and compared with the analytical solution. Calculations were made for k from 0.1 to 5 and for p from 0.1 to 10. It was found necessary, in general, to make $\Delta\eta$ approximately 0.05, since solutions for larger values were unsatisfactory.

A correct solution to any mass transfer problem must satisfy an overall material balance. For the case of zone melting this means that the total amount of a component added to the zone must equal the total amount of that component removed from it. At the steady state this is expressed by the condition that

$$\int_0^p (1 - \phi)\, d\eta = \int_0^\infty (\phi_s - 1)\, d\tau \tag{20}$$

It was found that the computer results of the previous paragraph did not satisfy this condition. Because of a suspicion that the cause of the deviation may have been the assumption of a linear concentration profile at the freezing interface [which was the basis for Equation (18)] a cubic profile was tried. This did yield results which satisfied Equation (20) and compared very well with the analytical results in the following section.

In a like manner numerical solutions were made for eutectic forming systems. A typical result is shown in Figure 5. The curved portion of the plot was found to be exponential. These solutions were found to satisfy the overall material balance. From this fact, and several other observations from the computer results, the results can be summarized in a more convenient approximate form.

It has been found that after $\phi = \epsilon$ is obtained at the freezing interface the following is approximately true:

$$(\phi - 1) = (\epsilon - 1) \exp{(-r\eta)} \tag{21}$$

where $r = r(\tau)$. Noting from the boundary conditions at $\eta = 0$ that

$$\frac{d\phi}{d\eta} = \phi_s - \epsilon \tag{22}$$

one obtains

$$\phi_s = r(\epsilon - 1) + \epsilon \tag{23}$$

However at the time parameter τ_o, when at $\eta = 0$, $\phi = \epsilon$ for the first time, $\phi_s = 0$, and so

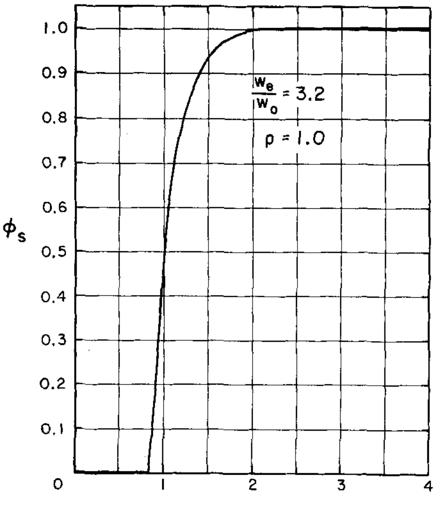

Fig. 5. Sample finite-difference solution for pure diffusional mass transfer in zone melting of eutectic formers. ϕ_s vs. τ for $\epsilon = 3.2$ and $p = 1.0$.

$$r(\tau_o) = \frac{\epsilon}{\epsilon - 1} \tag{24}$$

But it is known that $\phi_s = 0$ for $\tau \leqq \tau_o$, that from the computer solution

$$(1 - \phi_s) = \exp\left[-(\tau - \tau_o)q\right] \tag{25}$$

and that at steady state $(\phi - 1) = (\epsilon - 1) \exp(-\eta)$. With these facts an overall material balance for $\tau \geqq \tau_o$ yields

$$\int_{\tau_o}^{\infty} e^{-q(\tau-\tau_o)}\, d\tau = \int_0^p (\epsilon - 1) \{\exp(-\eta) - \exp[-r(\tau_o)\eta]\} d\eta \tag{26}$$

From Equations (24) and (26) one finds

$$\frac{1}{q} = (\epsilon - 1)\left\{(1 - e^{-p}) - \left(\frac{\epsilon - 1}{\epsilon}\right)\left[1 - \exp\left(-\frac{\epsilon}{\epsilon - 1}p\right)\right]\right\} \tag{27}$$

Likewise a material balance for $0 \leqq \tau \leqq \tau_o$ yields

$$\tau_o = \int_0^p (\epsilon - 1) \exp[-r(\tau_o)\eta] d\eta = \frac{(\epsilon - 1)^2}{\epsilon}\left\{1 - \exp\left(-\frac{\epsilon}{\epsilon - 1}p\right)\right\} \tag{28}$$

With these expressions approximate concentration profiles can be drawn for a single zone melting pass of an initially uniform eutectic forming mixture.*

Analytical Solution for Constant Distribution Coefficient

In order to solve the complete unsteady state problem exactly the solution is split into parts, a steady state solution which has already been given as Equation (14) and an unsteady state solution. The boundary condition at $\eta = p$ for the unsteady state solution is altered to become

$$\text{at } \eta = p, \frac{d\phi}{d\eta} = -\phi \tag{29}$$

The sum of the steady state and unsteady state solutions are seen to satisfy the original boundary condition (7).

The following transformation is now applied so that the unsteady state problem forms a Sturm-Liouville system after separation of variables is performed. Let

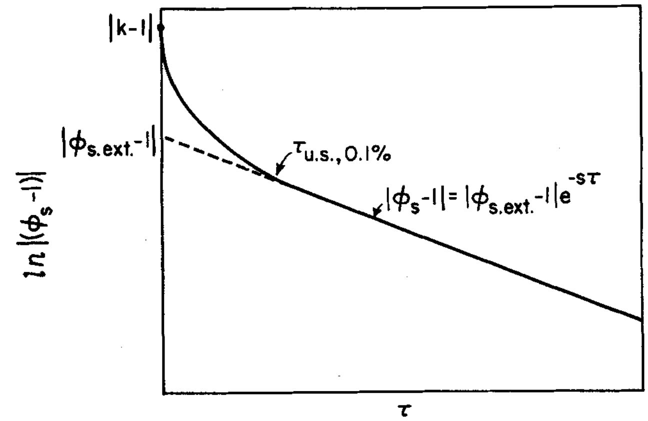

Fig. 6. Schematic sketch of a concentration profile for a single zone pass of a material with constant distribution coefficient, with pure diffusional mass transfer, showing the parameters characterizing the curve: ln | (ϕ_s — 1) | vs τ.

$$\phi = \psi \exp(-\eta/2) \tag{30}$$

Then Equations (3), (29), (9) become

$$\frac{\partial^2\psi}{\partial\eta^2} - \frac{1}{4}\psi = \frac{\partial\psi}{\partial\tau} \tag{31}$$

$$\text{at } \eta = 0, \frac{d\psi}{d\eta} = \psi\,(k - 1/2) \tag{32}$$

$$\text{at } \eta = p, \frac{d\psi}{d\eta} = -\psi/2 \tag{33}$$

By this method the sum of the steady state and unsteady state solutions is found to be (*10*)

$$\phi = 1 + \frac{1-k}{k}e^{-\eta} + e^{-\eta/2}\sum_{j=1}^{\infty} C_j\left(\cos m_j\frac{\eta}{p} + b_j \sin m_j \frac{\eta}{p}\right) \exp\left[-\left(\frac{1}{4} + \frac{m_j^2}{p^2}\right)\tau\right] \tag{34}$$

where

$$C_j = \frac{16\, p\, m_j\, (k - 1)}{(p^2 + 4m_j^2)\,[2m_j(1 + b_j^2) + (1 - b_j^2)\sin^2 m_j + 4b_j \sin^2 m_j]}$$

$$\tan m_j = \frac{4m_j\, pk}{4m_j^2 - p^2\,(2k - 1)}$$

$$b_j = p(k - 1/2)/m_j$$

For the concentration profile of the recrystallized solid note that $\phi_s = k\,\phi\,(0, \tau)$, to obtain

$$(\phi_s - 1) = k \sum_{j=1}^{\infty} C_j \exp\left[-\left(\frac{1}{4} + \frac{m_j^2}{p^2}\right)\tau\right] \tag{35}$$

As the size of the zone gets larger, that is p increases, the number of terms needed for the exact solution increases rapidly. It would be convenient therefore to have a solution for an infinite sized zone, that is for progressive freezing into an infinite body of liquid. Fortunately this problem has already been solved by Pohl (*6*), Hulme (*3*), Smith et al. (*7*), and by Memelink (*4*). Pohl's solution however holds only for small k, which is given quite well anyway by the approximate solution of Tiller et al. (*9*). The solutions of Hulme, Smith, and Memelink are basically the same; that is

$$\phi_s = 1/2\left\{1 + \text{erf}\left(\frac{\sqrt{\tau}}{2}\right) + (2k - 1)\exp[-k(1 - k)\tau]\,\text{erfc}\left(\frac{2k - 1}{2}\sqrt{\tau}\right)\right\} \tag{36}$$

Smith (*7*) also gives solutions for a sudden change in the rate of solidification in infinite progressive freezing and for the terminal transient in finite progressive freezing.

In a sample calculation it was found that for $p = 8$ Equation (35) for zone melting is approximately the same as Equation (36) for normal freezing. This was suspected from the computer calculations for zone melting, which showed that the concentration change in the zone did not reach the melting interface for $p > 8$ and gave very little change for $p = 5$.

Calculations Based on Analytical Results

It is apparent that the calculation of concentration profiles in zone melting can be a tedious process. Consequently certain characteristics of these profiles have been

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* Note that since $z = tV$, and $V = G/A\rho_s$, $\frac{\tau}{p} = \frac{z}{L}\left(\frac{\rho_s}{\rho_l}\right)$.

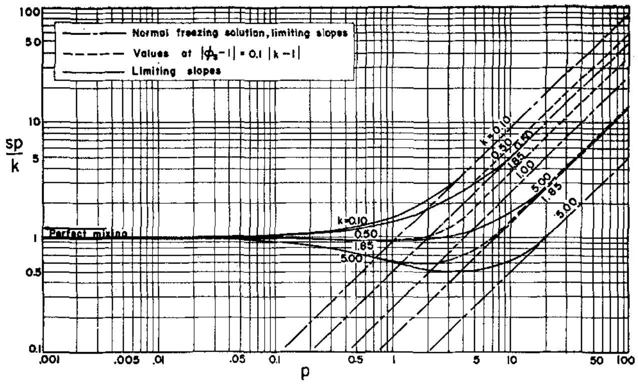

Fig. 7. Plot of ln (sp/k) vs. ln p.

calculated and plotted to make them conveniently available. A schematic profile of $\ln|(\phi_s - 1)|$ vs. τ is shown in Figure 6. All curves begin at $\tau = 0$ with $(\phi_s - 1) = (k - 1)$ and infinite slope (except for $p = 0$, perfect mixing). After sufficient time all but the first term in the infinite series of the analytical solution, Equation (35), become negligible. At this time the equation of the profile simplifies to

$$(\phi_s - 1) = (\phi_{s,\,\text{ext}} - 1)\cdot \exp(-s\tau) \qquad (37)$$

where $|(\phi_{s,\,\text{ext}} - 1)|$ is the intercept at $\tau = 0$ of the straight-line portion of a semilogarithmic plot of $|(\phi_s - 1)|$ vs. τ. By comparison with the analytical solution

$$(\phi_{s,\,\text{exp}} - 1) = kC_1 \qquad (38)$$

and $s = (1/4 + m_1^2/p^2)$. As $p \to \infty$ however, $s \to 0$, and the usefulness of this approach vanishes. Instead the value of s, the slope of the semilog plot, at some low value of $|(\phi_s - 1)|$ would be of the most use. This was chosen to be $(\phi_s - 1) = 0.1\ (k - 1)$.

Another valuable parameter is the value of τ at which the concentration profile first deviates significantly from an exponential form. For convenience this was chosen as the value of τ at which the second term of the infinite series in Equation (35) is equal to 0.1% of the first term. τ at this point is designated as $\tau_{us,\,0.1\%}$. It is given by

$$\tau_{us,\,0.1\%} = \left[\frac{p^2 \ln\,(C_2/0.001\,C_1)}{m_2^2 - m_1^2}\right] \qquad (39)$$

Values of these various parameters were calculated for $k = 0.1$, 0.5, 1.00, 1.85, and 5.00. They are plotted in various fashions vs. p in Figures 7, 8, and 9. It is readily seen that the analytical solution reduces to perfect mixing for $p < 0.01$ and effectively to infinite progressive freezing for $p > 6$.

These plots enable one to make a quick sketch of the expected concentration profile for a single zone melting pass.

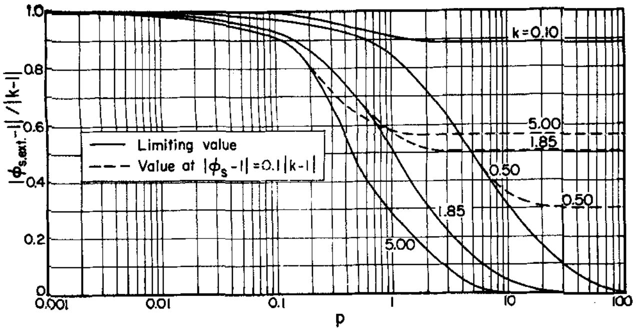

Fig. 8. Plot of $(\phi_{s,\,ext} - 1)/(k - 1)$ vs ln p.

In making these calculations it was noted that the first eigen value m_1 becomes imaginary under certain conditions, namely for $k < 0.5$ when $p > (4k)/(1 - 2k)$.

Example Calculations

Problem. It is desired to produce a 2-cm. zone of composition 3% w β-naphthol in naphthalene. The starting mixture is 5% w β-naphthol. Assume that the cross section is sufficiently small that convection is negligible. What zone travel rate is necessary to achieve this separation? What will be the resulting concentration profile in the zoned solid?

Data: $w_0 = 0.05$

$$\frac{1}{L}\int_0^L w\,dx = 0.03 \qquad (40)$$

$$L = 2 \text{ cm.}$$

From reference (*10*) the physical properties are

$$k = 1.85$$
$$D = 2.9 \times 10^{-5} \text{ sq.cm./sec.}$$
$$\rho_s = 1.15 \text{ g./cc.}$$
$$\rho_l = 0.97 \text{ g./cc.}$$

Solution:

Substituting Equation (14) and (41) into Equation (40) one obtains

$$\frac{0.03}{w_0} = 1 - \frac{k-1}{k}\ \frac{1-e^{-p}}{p}$$

or

$$p = \frac{1-e^{-p}}{0.87}$$

By trial and error

$$p = \frac{LV}{D}\ \frac{\rho_s}{\rho_l} = 0.29$$

or $V = 1.28 \times 10^{-2}$ cm./hr. This is the minimum velocity that is necessary to achieve this separation. If convective mixing occurred in the zone, much higher velocities could be used.

Now estimate the concentration profile. From Figure 7 with $p = 0.29$

$$\frac{sp}{k} = 0.95, \quad \text{or} \quad s = \frac{(0.95)(1.85)}{(0.29)} = 6.06$$

From Figure 8

$$\frac{(\phi_{s,\,\text{ext}} - 1)}{k - 1} = 0.8;\ (\phi_{s,\,\text{ext}} - 1) = (0.8)(0.85) = 0.68$$

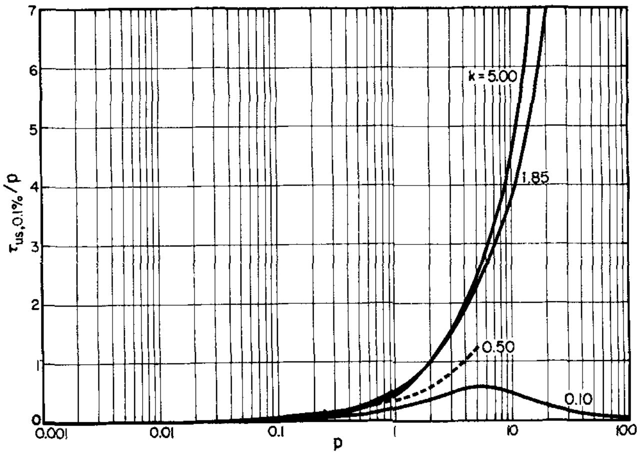

Fig. 9. Plot of $\tau_{us,\,0.1\%}/p$ vs ln p.

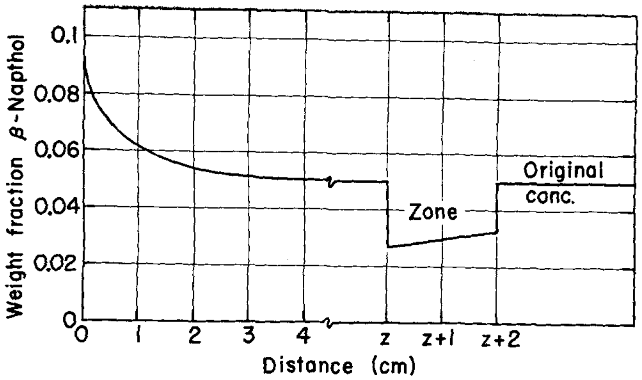

Fig. 10. Concentration profile calculated for example problem, using Figures 6, 7, 8, 9, and Equation (41).

From Figure 9

$$\frac{\tau_{us.\,0.1\%}}{p} \approx 0.1; \quad \tau_{us.\,0.1\%} = (0.1)(0.29) = 0.029$$

With these three numbers a plot of the type of Figure 6 was prepared. The data is transposed to a linear plot of w_s vs. z by noting that

$$w_s = w_o\,[1 + (\phi_s - 1)]$$

and that

$$z = \frac{L}{p}\,\frac{\rho_l}{\rho_s}\,\tau = \frac{2}{0.29}\,\frac{0.97}{1.15}\,\tau = 5.82\ \tau \text{ cm.}$$

It was noted that the curve is exponential past 0.17 cm. because of the low $\tau_{us.\,0.1\%}$. The result is shown in Figure 10. The concentration profile for the zone is also shown as calculated from [Equation (14)],

$$w = w_o\left[1 + \frac{1-k}{k}\exp\left(\frac{xV}{D}\,\frac{\rho_s}{\rho_l}\right)\right]$$
$$= 0.05\,[1 - 0.46\ e^{-0.145x}] \tag{41}$$

EXPERIMENTS

Zone melting studies were made with two organic systems, naphthalene-β-naphthal and naphthalene-benzoic acid. These systems are simple eutectic forming and completely isomorphous respectively. Solid mixtures from these systems were enclosed in 5- to 20-mm. glass tubes and pulled through a stationary heater which generated the liquid zone. The separation that was attained was considerably better than predicted from the results of this paper. The results were analyzed and correlated on the basis of a boundary-layer treatment with mixing by free convection in the zone (*10, 11*). It is apparent that the zone melting tubes would have to be reduced considerably below 5 mm. (about 3-mm. I.D.) to eliminate convective mixing and so duplicate the theoretical results derived here.

CONCLUSIONS

Rapid methods have been given for the approximate calculation of concentration profiles resulting from a single zone pass for eutectic forming systems and for constant distribution coefficients, with no convective mixing in the zone. A method of numerical solution is given whereby the profile resulting from arbitrary phase behavior, nonuniform initial profile, and multipasses can be calculated.

ACKNOWLEDGMENT

Andreas Acrivos suggested the transformation which made possible the analytical solution. W. R. Wilcox is grateful to the National Science Foundation and to the General Electric Foundation for their financial assistance.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

NOTATION

a = arbitrary constant
A = cross-sectional area of solid and of zone, sq.cm.
b = arbitrary constant
b_j = jth constant in Equation (33)
C_j = jth constant in Equation (33)
D = molecular diffusivity, sq.cm./sec.
d = differential operator
G = mass rate of flow of material through zone, g./sec.
k = equilibrium distribution coefficient, w_s/w at freezing interface
L = length of zone, cm.
m_j = jth eigen value in Equation (32)
p = $(LG)/(DA\rho_l) = (LV\rho_s)/(D\rho_l)$
q = negative slope of $\ln(1-\phi_s)$ vs. $(\tau - \tau_0)$ plot
r = negative slope of $\ln(\phi - 1)$ vs. η plot
s = negative slope of $\ln|\phi_s - 1|$ vs. τ plot
t = time, sec
x = distance from freezing interface into zone, cm.
V = $G/(A\rho_s)$, velocity of zone travel, cm./sec.
w = weight fraction of component in zone at x
w_e = eutectic composition, weight fraction
w_o = initial concentration throughout, weight fraction
w_s = weight fraction in solid at z
w_z = average weight fraction in zone
z = distance from the first material to freeze out of the zone, tV, cm.

Greek Letters

ϵ = w_e/w_o
η = $(xG)/(DA\rho_l) = xV\rho_s/D\rho_l$
ρ_l, ρ_s = density of liquid and solid, respectively, g./cc.
τ = $\dfrac{t}{D}\left(\dfrac{G}{A\rho_l}\right)^2 = p\,\dfrac{z}{L}\left(\dfrac{\rho_s}{\rho_l}\right)$
τ_0 = τ at which ϕ first equals ϵ at freezing interface
$\tau_{us,\,0.1\%}$ = value of τ at which $C_2 = 0.001\ C_1$
ϕ = w/w_o
ϕ_s = w_s/w_o
$(\phi_{s,\,ext} - 1)$ = intercept at $\tau = 0$ of straight-line portion of semi logarithmic plot of $(\phi_s - 1)$ vs. τ

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Manuscript received November 7, 1962; revision received August 12, 1963; paper accepted August 16, 1963.