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Zone Refining of Systems with Varible Distribution Coefficient under the Condition of No Liquid Mixing

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Summary

Mass transfer equations for the zone refining of systems with variable distribution coefficient have been solved using a Laplace transformation under the condition of no liquid mixing. It is suggested that this solution will describe more appropriately the solute distribution after a single zone pass through an organic solid than the conventional theory which assumes a constant distribution coefficient and complete liquid mixing.

INTRODUCTION

In a recent paper (*1*) it was pointed out that the general theories developed for the purification of solids by fractional solidification processes are not applicable to organic solids because of some special problems associated with them. Due to low thermal conductivity of organic compounds, the ingot sample has to be thin. This causes the convection in the melt to be far from complete, and the situation can be more appropriately described by assuming no liquid mixing at all. Again, the organic substances are often not found in a very pure state, which may result in a considerable curvature in the relevant portion of the phase diagram, and hence it may no longer be correct to assume a constant distribution coefficient. Therefore it becomes obvious that the general theories (*2*) of fractional solidification processes which assume a constant distribution coefficient and complete liquid mixing require reconsideration.

There have been several attempts to solve the problem of zone refining with reconsideration of either of the two assumptions mentioned above, but no solution is available which reconsiders both assumptions simultaneously. Wilcox (*3*) and Wilcox and Wilke (*4*) have solved the case of constant distribution coefficient with no liquid mixing whereas Herington (*5*), Matz (*6*), Kirgintsev et al. (*7*), Nelson et al. (*8*), and Gouw et al. (*9*) have considered the case of variable distribution coefficient with complete liquid mixing. Mathur and Singh (*1*) have recently solved the problem for progressive freezing of a system with variable distribution coefficient under the condition of no liquid mixing. Here we report the solution of the zone refining problem under the same two assumptions.

FORMULATION OF THE PROBLEM

When the solid and liquid phases are in equilibrium with one another, the solute concentration w_s in the solid phase and w, that in the liquid phase, are assumed to be correlated by a second degree relation of the form (*1, 9*)

$$w_s = k_1 w + k_2 w^2 \tag{1}$$

where k_1 and k_2 are constants, the former of which will have a value very near to the conventional distribution coefficient and $k_2 < k_1$. The differential equation and the boundary conditions (*1, 10*) governing diffusive mass transfer (mass transfer will proceed entirely by molecular diffusion under the assumption of no liquid mixing) in the zone refining

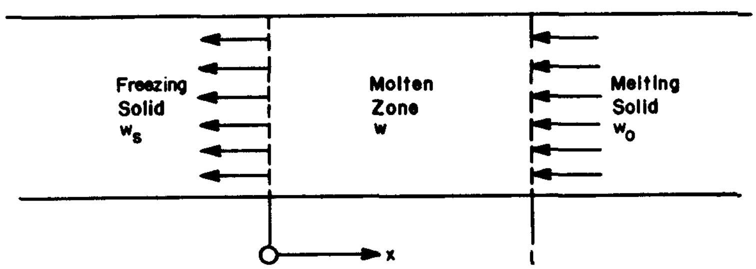

FIG. 1. Coordinate system to describe mass transfer in zone melting.

of a semi-infinite ingot can be written as

$$\frac{\partial^2\phi}{\partial\eta^2} + \frac{\partial\phi}{\partial\eta} = \frac{\partial\phi}{\partial\tau} \tag{2}$$

$$d\phi/d\eta = (k_1 - 1)\phi + k_2 w_0 \phi^2 \qquad \text{at} \quad \eta = 0 \tag{3}$$

$$d\phi/d\eta = 1 - \phi \qquad \text{at} \quad \eta = l \tag{4}$$

$$\phi = 1 \qquad \text{at} \quad \tau = 0 \tag{5}$$

where

$$\eta = \frac{x}{D}\left(V\frac{\rho_s}{\rho_l}\right), \qquad \tau = \frac{t}{D}\left(V\frac{\rho_s}{\rho_l}\right)^2, \qquad \phi = w/w_0$$

The origin $x = 0$ of the coordinate system is chosen at the stationary freezing interface across which the molten zone is assumed to traverse (Fig. 1). w_0 is the uniform initial concentration, V the freezing rate, D the diffusion coefficient in the melt, l the zone length, ρ_s and ρ_l the densities in solid and in liquid, respectively. η and τ are the dimensionless distance and time parameters.

SOLUTION OF THE PROBLEM

The nonlinear boundary condition (3) necessitates the use of Laplace transforms. First, the system of Eqs. (2)–(5) is solved with the boundary condition (3) replaced by

$$d\phi/d\eta = f(\tau) \qquad \text{at} \quad \eta = 0 \tag{6}$$

Taking Laplace transformation of Eqs. (2), (6), and (4)

$$\frac{d^2\bar{\Phi}}{d\eta^2} + \frac{d\bar{\Phi}}{d\eta} = p\bar{\Phi} - 1 \tag{7}$$

$$d\bar{\Phi}/d\eta = \bar{f}(p) \qquad \text{at} \quad \eta = 0 \tag{8}$$

$$\frac{d\bar{\Phi}}{d\eta} = \frac{1}{p} - \bar{\Phi} \qquad \text{at} \quad \eta = l \tag{9}$$

where

$$\bar{\Phi}(\eta,p) = \int_0^\infty e^{-p\tau}\phi(\eta,\tau)\, d\tau$$

is the Laplace transform of ϕ.

The solution of Eqs. (7)–(9) is given by

$$\bar{\phi} = \frac{1}{p} + e^{-\eta/2} \times \frac{(q \sinh ql + \frac{1}{2} \cosh ql) \sinh q\eta - (q \cosh ql + \frac{1}{2} \sinh ql) \cosh q\eta}{[q^2 + \frac{1}{4}] \sinh ql + q \cosh ql} \bar{f}(p) \tag{10}$$

where

$$q = \frac{(1 + 4p)^{1/2}}{2}$$

Applying Duhamel's theorem (*11*) to Eq. (10), one obtains (see Appendix)

$$\phi(\eta,\tau) = 1 - e^{-\eta/2} \sum_{n=1}^{\infty} \frac{\cos \alpha_n\eta + (2\alpha_n)^{-1} \sin \alpha_n\eta}{(2\alpha_n^2)^{-1}[(\alpha_n^2 + \frac{1}{4})l + 1]} \times \int_0^\tau f(t) \exp - [(\alpha_n^2 + \tfrac{1}{4})(\tau - t)]\, dt \tag{11}$$

where $\pm\alpha_n$, $n = 1, 2, \ldots$ are the roots (all real and simple) of equation

$$[\alpha - (4\alpha)^{-1}] \tan \alpha l = 1 \tag{12}$$

Now, the solution of the system with the actual boundary condition (3) may be written by analogy to Eq. (11) as

$$\phi(\eta,\tau) = 1 - e^{-\eta/2} \sum_{n=1}^{\infty} \frac{\cos \alpha_n\eta + (2\alpha_n)^{-1} \sin \alpha_n\eta}{(2\alpha_n^2)^{-1}[(\alpha_n^2 + \frac{1}{4})l + 1]} \times \int_0^\tau [(k_1 - 1)\phi(0,t) + k_2 w_0 \phi^2(0,t)] \exp - [(\alpha_n^2 + \tfrac{1}{4})(\tau - t)]\, dt \tag{13}$$

For purification purposes, one is mainly interested in impurity distribution at the freezing interface $\eta = 0$, where the solution (13) simplifies to

$$\phi(0,\tau) = 1 - \sum_{n=1}^{\infty} \frac{2\alpha_n^2}{(\alpha_n^2 + \frac{1}{4})l + 1} \times \int_0^{\tau} [(k_1 - 1)\phi(0,t) + k_2 w_0 \phi^2(0,t)] \exp - [(\alpha_n^2 + \tfrac{1}{4})(\tau - t)]\, dt \tag{14}$$

from which the solute concentration in solid can be obtained by the use of Eq. (1).

However, any extensive practical application of Eq. (14) can not be made at present as very little reliable data on phase diagrams and diffusion coefficients for organic systems are available.

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APPENDIX

In applying Duhamel's theorem to Eq. (10) one requires to find the inverse Laplace transform of

$$\frac{(q \sinh ql + \frac{1}{2}\cosh ql)\sinh q\eta - (q\cosh ql + \frac{1}{2}\sinh ql)\cosh q\eta}{(q^2 + \frac{1}{4})\sinh ql + q\cosh ql}$$

which can be written as

$$L^{-1} = \frac{1}{2\pi i}\int_{\gamma - i\infty}^{\gamma + i\infty} e^{\lambda\tau} \times \frac{(\mu \sinh \mu l + \frac{1}{2}\cosh \mu l)\sinh \mu\eta - (\mu\cosh \mu l + \frac{1}{2}\sinh \mu l)\cosh \mu\eta}{(\mu^2 + \frac{1}{4})\sinh \mu l + \mu\cosh \mu l}\, d\lambda \tag{A-1}$$

where

$$\mu = (1 + 4\lambda)^{1/2}/2$$

The poles of the integrand are the values

$$\lambda = -\alpha_n^2 - \tfrac{1}{4}, \qquad \mu = i\alpha_n, \qquad n = 1, 2, \ldots \tag{A-2}$$

where $\pm\alpha_n$, $n = 1, 2, \ldots$ are the roots (all real and simple) of

$$(-\alpha^2 + \tfrac{1}{4}) \sinh i\alpha l + i\alpha \cosh i\alpha l = 0$$

or

$$[\alpha - (4\alpha)^{-1}] \tan \alpha l = 1 \tag{A-3}$$

Residues at these poles are given by

$$\frac{d}{d\lambda} [(\mu^2 + \tfrac{1}{4}) \sinh \mu l + \mu \cosh \mu l]_{\lambda=-\alpha_n^2-1/4}$$

$$= \frac{i}{2\alpha_n} [(\alpha_n^2 - \tfrac{1}{4})l - 1] \cos \alpha_n l + i \frac{l+2}{2} \sin \alpha_n l \tag{A-4}$$

Using this result in Eq. (1), finally

$$L^{-1} = - \sum_{n=1}^{\infty} \frac{\cos \alpha_n \eta + (2\alpha_n)^{-1} \sin \alpha_n \eta}{(2\alpha_n^2)^{-1}[(\alpha_n^2 + \frac{1}{4})l + 1]} \exp - [(\alpha_n^2 + \tfrac{1}{4})\tau] \tag{A-5}$$

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