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Optimization of Zone Refining with Decomposition

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Abstract

When decomposition occurs during zone melting, a maximum purification is obtained for an optimal number of zone passes and zone travel rate. The optimal zone travel rate increases with increasing stirring, decreasing distribution coefficient, and increasing length of rod. The optimal number of zone passes is frequently small, but increases with decreasing reaction kinetics and decreasing distribution coefficient. If the decomposition reaction is moderately fast, it does not pay to make more than a few zone passes over a rod a few zone lengths long.

INTRODUCTION

In a previous paper we showed that carbon tetrabromide undergoes thermal decomposition to form at least one of the impurities being removed by zone refining (*1*). Because of this, we expected that the optimal operating conditions would be different than in the absence of decomposition (*2, 3*). Here we report on a theoretical analysis of zone refining with thermal decomposition.

EQUATIONS

Imagine that a molten zone lies between x and $x + l$ distance from the front of the ingot. If the zone is now moved by distance dx, a material balance may be written for an impurity:

$$\begin{pmatrix}\text{Added by}\\ \text{melting solid}\\ \text{of}\\ \text{composition}\\ (W_{N-1})_{x+l}\end{pmatrix} + \begin{pmatrix}\text{Added by}\\ \text{decomposition}\\ \text{of melt}\end{pmatrix} - \begin{pmatrix}\text{Subtracted}\\ \text{by freezing}\\ \text{solid of}\\ \text{composition}\\ (W_N)_x\end{pmatrix} = \begin{pmatrix}\text{Increase}\\ \text{in amount}\\ \text{in zone}\end{pmatrix}$$

$$(W_{N-1})_{x+l}\,\rho_s\,dx \quad + \quad \frac{Kl\,dx}{V} \quad - \quad (W_N)_x\rho_s\,dx \quad = \quad \rho_l\,l\,dW_l \quad (1)$$

where the subscript N denotes the zone pass number, ρ_s and ρ_l are densities of solid and liquid, respectively, V is the zone travel velocity, and K is the reaction rate constant. It is implicitly assumed that the impurity content is small and that the impurity itself does not influence the rate of decomposition of the melt. The melt is also assumed to be at constant temperature, which is reasonable because of the extensive free convection that occurs in zone melting.

For further steps in our analysis it is assumed that

$$W_N = k_{\text{eff}} W_l \qquad (2)$$

where

$$k_{\text{eff}} = \frac{k}{k + (1 - k)e^{-\nu}} \qquad (3)$$

is the effective distribution coefficient for incomplete mass transfer as given by the Burton, Prim, Slichter equation for a stagnant film of thickness δ (*2*), k is the interfacial ($\approx$ equilibrium) distribution coefficient, $\nu = (\delta V/D)(\rho_s/\rho_l)$ is a dimensionless freezing rate, and D is the diffusion coefficient for impurity in the melt.

For the first zone pass, the feed ingot composition is assumed to be uniform at W_0. This allows Eqs. (1) and (2) to be integrated to find

$$(\phi_1)_z = 1 + (\eta/\nu) - [1 + (\eta/\nu) - k_{\text{eff}}] \exp(-k_{\text{eff}} z) \qquad (4)$$

where $\phi_N = W_N/W_O$ is the dimensionless impurity concentration in the solid, $\eta = Kl\delta/W_O D\rho_l$ is a dimensionless reaction rate, and $z = (x/l)(\rho_s/\rho_l)$ is a dimensionless distance down the rod.

The concentration profiles for subsequent zone passes must be determined numerically. We divide the rod into segments Δz long, with $1/\Delta z = m$ being the number of increments in the zone itself. Expressing Eqs. (1) and (2) in dimensionless finite difference form, we obtain

$$\frac{(\phi_{N-1})_{i+m-1} + (\phi_{N-1})_{i+m}}{2}\,\Delta z + \frac{\eta}{\nu}\,\Delta z - \frac{(\phi_N)_{i-1} + (\phi_N)_i}{2}\,\Delta z = \frac{(\phi_N)_i - (\phi_N)_{i-1}}{k_{\text{eff}}} \qquad (5)$$

which can easily be solved for $(\phi_N)_i$. This gives ϕ at any point i from the concentration profile ϕ_{N-1} for the previous zone pass and $(\phi_N)_{i-1}$, the concentration at the previous point. To start pass N it is therefore necessary to know the initial impurity concentration in the solid $(\phi_N)_1$ which freezes from a zone formed by melting back the previous $N-1$ solid to distance

$$(\phi_N)_1 = k_{\text{eff}} \int_0^1 (\varphi_{N-1})_z \, dz$$

$$\approx k_{\text{eff}} \frac{\Delta z}{3} \left[(\varphi_{N-1})_1 + (\phi_{N-1})_{m+1} + 4 \sum_{i=1}^{\frac{m}{2}} (\Phi_{N-1})_{2i} + 2 \sum_{i=1}^{\frac{m}{2}-1} (\Phi_{N-1})_{2i+1} \right] \tag{6}$$

by Simpson's rule with m even, with $z = (i-1)\Delta z$.

For a rod of finite length $z_{\max}$, the melt undergoes progressive freezing as the zone runs off the end of the rod, i.e., for $(z_{\max} - 1) \leq z \leq z_{\max}$. The differential equation for this differs from Eq. (1) and is found via a material balance when amount dz of melt is converted to solid, i.e.,

$$\begin{pmatrix} \text{Impurity added} \\ \text{to melt by} \\ \text{decomposition} \end{pmatrix} - \begin{pmatrix} \text{Impurity} \\ \text{taken into} \\ \text{solid} \end{pmatrix} = \begin{pmatrix} \text{Change in amount} \\ \text{of impurity} \\ \text{in melt} \end{pmatrix} \tag{7}$$

$$\frac{\eta}{\nu} dz - (\phi_N)_z dz = - \frac{(\phi_N)_z}{k_{\text{eff}}} dz + (z_{\max} - z) \frac{d(\phi_N)_z}{k_{\text{eff}}}$$

where Eq. (2) has been used. This may be rearranged and integrated from $z_{\max} - 1$ to z to obtain

$$(\phi_N)_z = - \frac{k_{\text{eff}}\eta}{(1 - k_{\text{eff}})\nu} + \left((\phi_N)_{z_{\max}-1} + \frac{k_{\text{eff}}\eta}{(1 - k_{\text{eff}})\nu} \right) (z_{\max} - z)^{(k_{\text{eff}}-1)} \tag{8}$$

However, for $k_{\text{eff}} < 1$, this leads to $(\phi_N)_{z_{\max}} = \infty$. To avoid this in the numerical solution we use an overall material balance,

$$\int_0^{z_{\max}} \phi_N \, dz = z_{\max} + N \frac{\eta}{\nu} (z_{\max} - ½) \tag{9}$$

where the first term on the right-hand side is the original amount of impurity and the second term is the amount of impurity added by decomposition. The integral may be expressed by Simpson's rule, and solved for the concentration at the end of the ingot:

$$(\phi_N)_{i_{\max}} = 3\{i_{\max} - 1 + N\frac{\eta}{\nu}(i_{\max} - 1 - M/2)\} - (\phi_N)_1 - 4\sum_{i=1}^{(i_{\max}-1)/2}(\phi_N)_{2i} - 2\sum_{i=1}^{(i_{\max}-3)/2}(\phi_N)_{2i+1} \quad (10)$$

where $i_{\max} = z_{\max}/\Delta z + 1$.

In order to judge the effectiveness of the separation we define the purification P as the reduction in the amount of impurity in the front end of the ingot (for $k < 1$) up to the point $z_p = (i_p - 1)\Delta z$ where the concentration hasn't changed, i.e., at $W_N = W_0$ or $\phi_N = 1$. Thus in dimensionless form

$$P_N = \int_0^{z_p}\frac{W_0 - W_N}{W_0}\,dz = \int_0^{z_p}(1 - \phi_N)\,dz$$
$$\approx i_p - 1 - \frac{\Delta z}{2}\left[(\phi_N)_1 + 1 + 2\sum_{i=1}^{i_p-1}(\phi_N)_i\right] \quad (11)$$

The rate of purification is also of interest and is proportional to $P\nu$. For the first zone pass of an infinitely long rod we find P_1 by substituting Eq. (4) into Eq. (11):

$$P_1 = \frac{(1 - k_{\text{eff}})}{k_{\text{eff}}} - \frac{\eta}{\nu k_{\text{eff}}}\ln\left[1 + \frac{(1 - k_{\text{eff}})\nu}{\eta}\right] \quad (12)$$

RESULTS

The conditions for the maximum purification P_1 resulting from a single zone pass of a long rod were found numerically using Eq. (3) and (12). As shown in Fig. 1, the optimal velocity parameter $\nu_{\max}$ decreases as the distribution coefficient k increases and as the reaction parameter η decreases. Without reaction ($\eta = 0$), the maximum purification is obtained for $\nu \rightarrow 0$, i.e., an infinitely slow freezing rate. For $k \rightarrow 0$ and $\eta \rightarrow \infty$, $\nu_{\max} \rightarrow 1$. For multipasses one might expect the single pass purification rate $P\nu$ to be a better predictor of optimal conditions. This is shown in Fig. 2. For $\eta = 0$ the

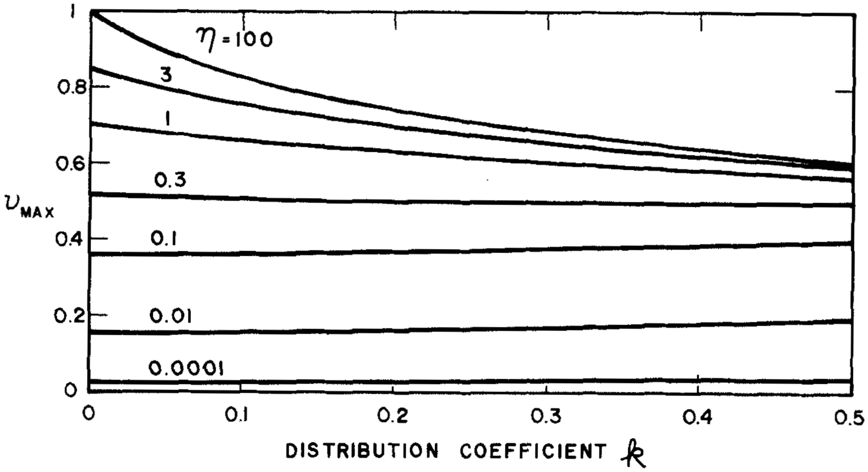

FIG. 1. Velocity parameter ν yielding maximum purification P after a single zone pass of an infinitely long rod.

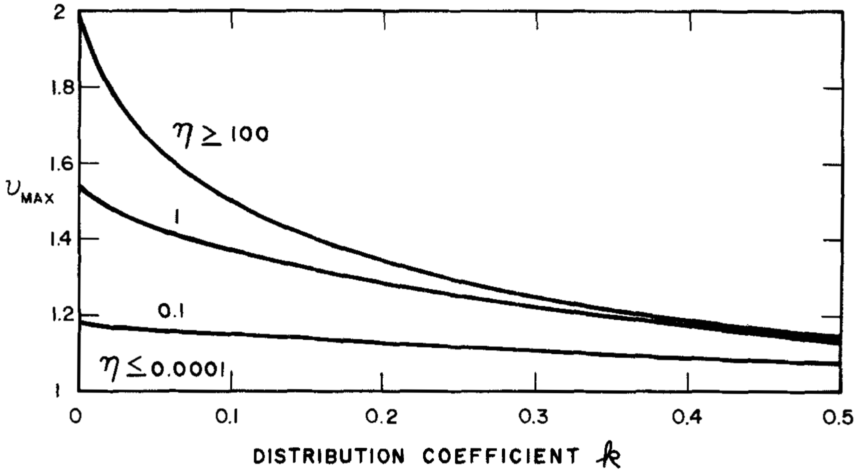

FIG. 2. Velocity parameter ν yielding maximum purification rate $P\nu$ after a single zone pass of an infinitely long rod.

optimum is $\nu = 1$, as has been found previously (*2, 3*). For $k \to 0$ and $\eta \to \infty$, $\nu_{\max} \to 2$.

For the finite difference solution of the multipass distribution, it is necessary to find the optimal value of Δz. It was found that only small differences occurred in ϕ after many passes if Δz was increased from 0.05 to 0.1. To make certain numerical errors did not accumulate, $\Delta z = 0.025$ was employed for all of the computations reported here. This is an increment of 1/40 of a zone length. For $z_{\max} = 15$ about 3 min per zone pass was required on the Texas Instruments 99/4 computer.

A typical multipass result is shown in Fig. 3. Unlike the situation without decomposition ($\eta = 0$), the concentration never reaches an ultimate distribution. Impurity is continually generated and accumulates at the end of the ingot. Backmixing eventually causes this additional impurity to move toward the front of the ingot (compare Pass 24 with Pass 4).

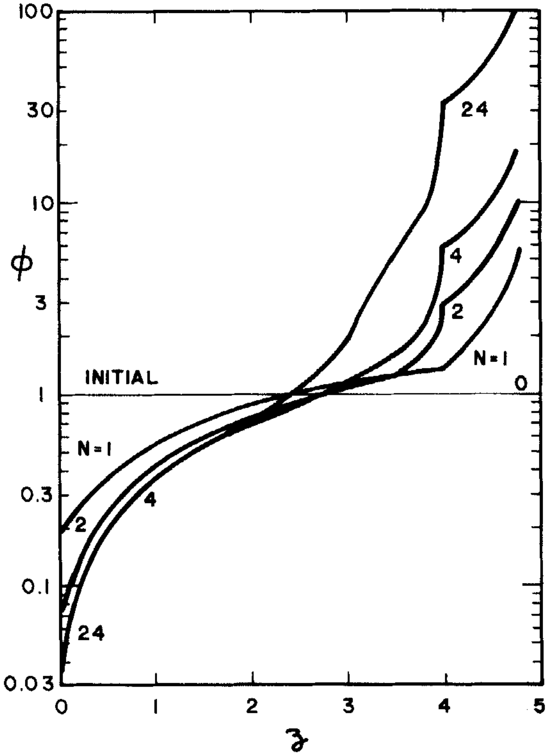

FIG. 3. Multiple zone pass impurity concentration profiles for $k = 0.1$, $\eta = 1$, $z_{\max} = 5$, and $\nu = 0.661$ (optimum for single pass).

Typical multipass purification behavior is shown in Fig. 4. For this example, note that the purification reaches a maximum at the second to third pass (depending on ν). Similarly P is a maximum for $\nu \approx 0.8$, as shown in Fig. 5. Thus there is a combination of velocity parameter ν and zone pass number N giving the maximum purification P possible. Figure 6 shows how the optimal ν and N depend on the reaction parameter η. Figure 7 shows the dependence on the distribution coefficient k and Fig. 8 on rod length $z_{\max}$. From Figs. 8 and 9 it can be seen that the purification is sensitive to rod length for small reaction parameter η, but not for large η. The number N of zone passes required to achieve the maximum P increases rapidly with rod length $z_{\max}$ for small η, but is almost independent of $z_{\max}$ for large η.

DISCUSSION

The optimal velocity parameter $\nu_{\max}$ was seldom far from 0.8, which in turn does not differ significantly for the optimal purification rate condition of $\nu \approx 1$ without decomposition. In practice neither the reaction kinetics

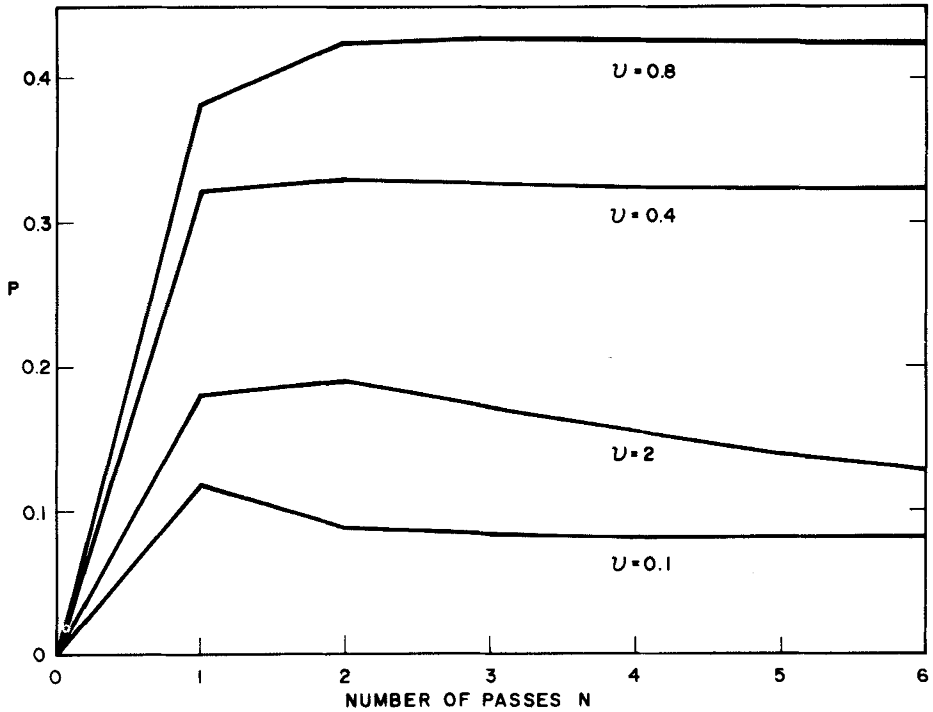

FIG. 4. Purification for $k = 0.1$, $\eta = 3$, and $z_{\max} = 15$.

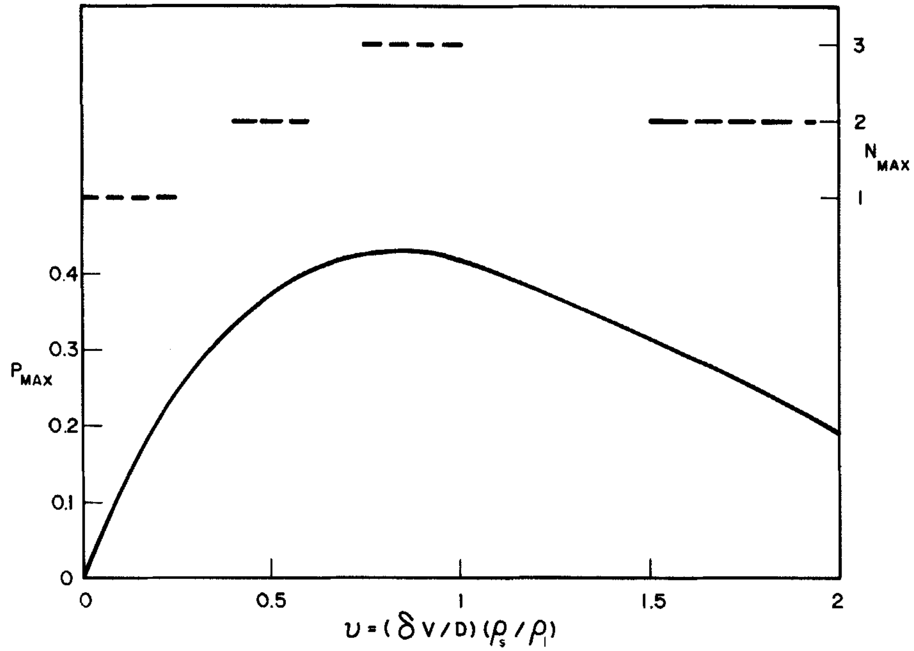

FIG. 5. Maximum purification P_{max} and number of zone passes required to achieve it vs velocity parameter ν for $k = 0.1$, $\eta = 3$, and $z_{max} = 15$.

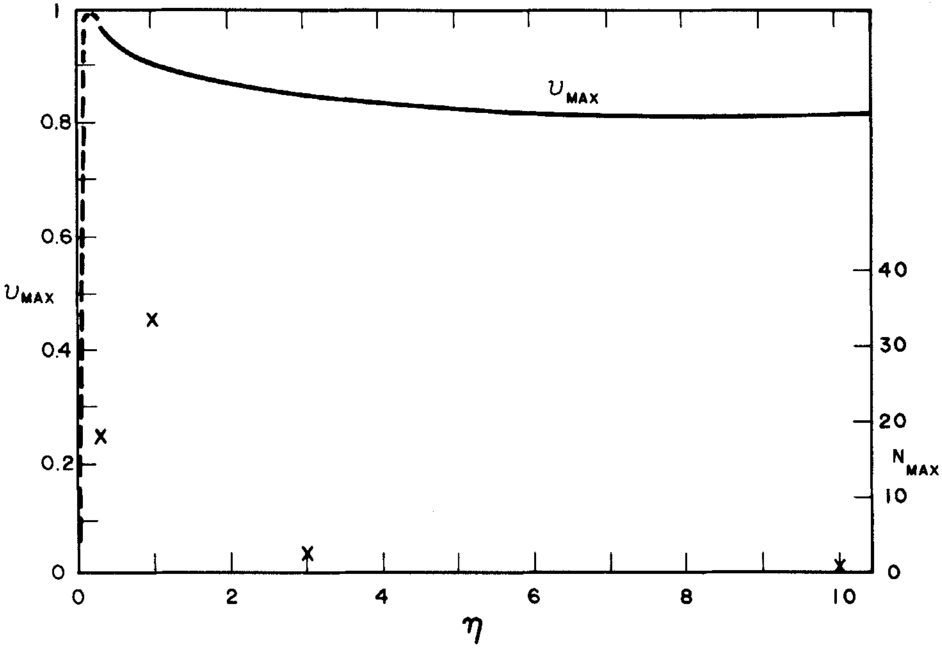

FIG. 6. Influence of η on velocity parameter ν and number N of zone passes yielding maximum purification for $k = 0.1$ and $z_{max} = 15$. (×) N_{max}, (——) ν_{max}.

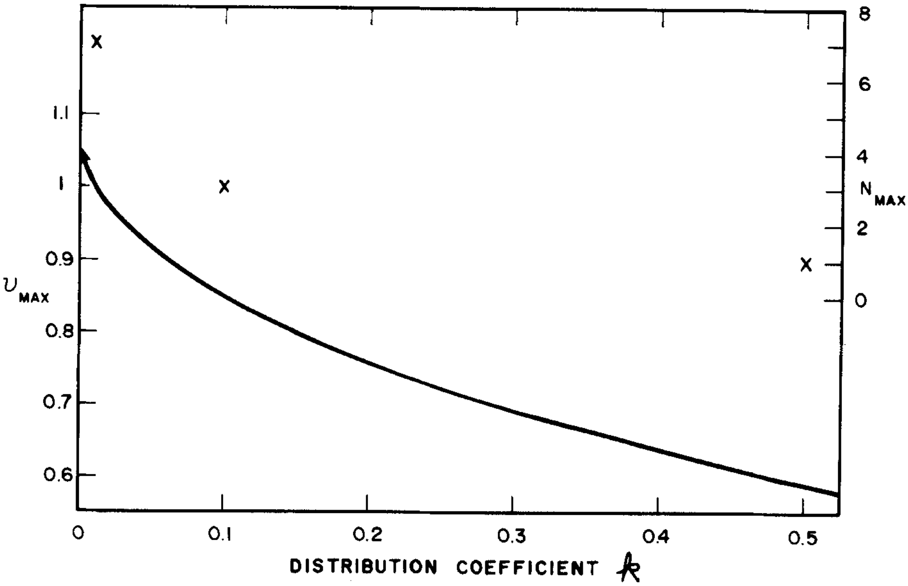

FIG. 7. Influence of k on velocity parameter ν and number N of zone passes yielding maximum purification for $\eta = 3$ and $z_{\max} = 15$. (×) $N_{\max}$, (——) $\nu_{\max}$.

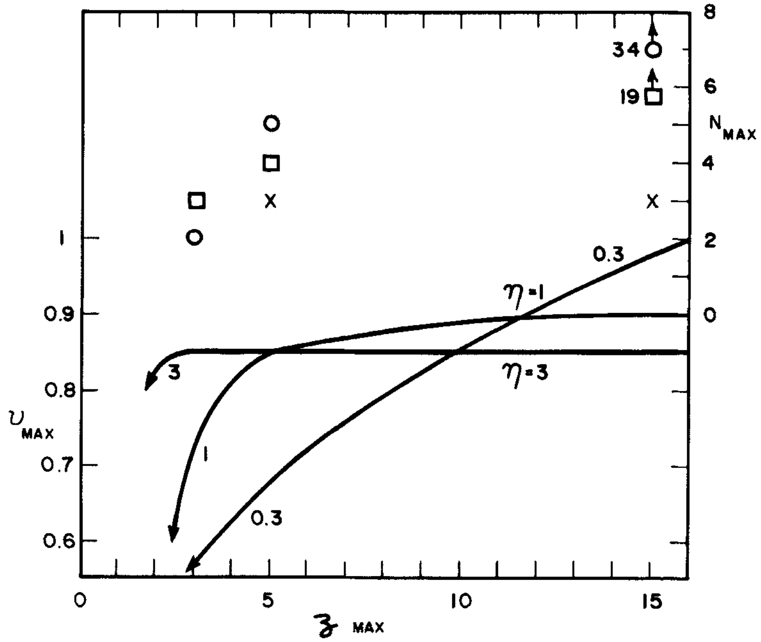

FIG. 8. Influence of rod length $z_{\max}$ on ν and N yielding maximum P for $k = 0.1$. (□) $N_{\max}$ for $\eta = 0.3$, (○) $N_{\max}$ for $\eta = 1$, (×) $N_{\max}$ for $\eta = 3$.

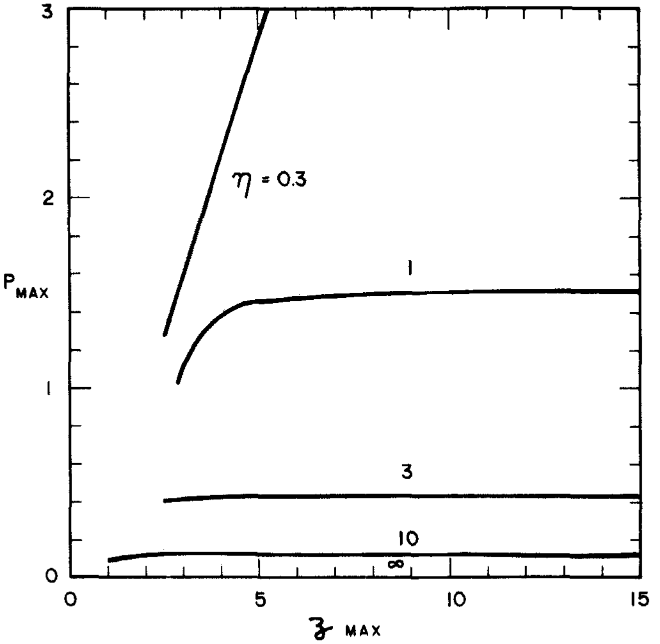

FIG. 9. Influence of z_{max} and η on maximum P for $k = 0.1$.

coefficient K, nor the stagnant film thickness δ (*2–4*), nor the diffusion coefficient D are well known. Therefore it is recommended that the experimentalist try several zone travel velocities V over short rods for only a few zone passes. This should enable the optimal V to be determined fairly readily.

SYMBOLS

D	diffusion coefficient of impurity in melt (m^2/s)
i	mesh point
i_{max}	maximum mesh point ($= z_{max}/\Delta z + 1$)
i_p	mesh point nearest which $\phi_N = 1$
K	decomposition rate constant for melt ($kg/m^3 \cdot s$)
k	equilibrium distribution coefficient
k_{eff}	effective distribution coefficient ($= W_N/W_l$)
l	length of zone (m)
L	length of rod (m)
m	number of mesh points across molten zone ($= 1/\Delta z$)
N	number of zone passes
N_{max}	number of zone passes yielding maximum purification

$P_{\max}$	maximum purification vs N for fixed ν.
P_N	total purification achieved after N zone passes, as defined in Eq. (11)
δ	fictitious stagnant film thickness (m)
η	reaction parameter ($= Kl\delta/W_0D\rho_l$)
ν	velocity parameter [$= (\delta V/D)(\rho_s/\rho_l)$]
$\nu_{\max}$	value of ν at which maximum purification achieved
ρ_l	density of liquid (kg/m^3)
ρ_s	density of solid (kg/m^3)
$(\phi_N)_z$	dimensionless concentration in solid [$= (W_N)_x/W_0$]
V	velocity of zone travel (m/s)
W_l	mass fraction of impurity in liquid zone
$(W_N)_x$	mass fraction of impurity in solid after Nth pass at distance x from front of ingot
W_0	mass fraction of impurity in initial ingot
x	distance down rod from front end (m)
z	dimensionless distance down rod [$= (x/l)(\rho_s/\rho_l) = (i - 1)\Delta a$]
Δz	increment of z in finite difference techniques
$z_{\max}$	dimensionless length of rod [$= (L/l)(\rho_s/\rho_l)$]

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