Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Wilcox, W. R.(1966) 'Comparison of Yield for Zone Melting and Progressive Freezing', Separation Science and Technology, 1: 2, 147 — 157

To link to this Article: DOI: 10.1080/01496396608049442

URL: http://dx.doi.org/10.1080/01496396608049442

SEPARATION SCIENCE, 1(2 & 3), 147–157 (1966)

Comparison of Yield for Zone Melting and Progressive Freezing

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Summary

The conditions under which the yield of purified product is identical for progressive freezing and zone melting have been determined. When the distribution coefficient is less than 1, the yield of progressive freezing is increased by lowering the amount of material rejected after each operation. When the distribution coefficient is greater than 1, however, the usual zone-melting conditions result in a greater yield than is possible with progressive freezing.

Zone melting and progressive freezing are both useful for multistage purification of solids and liquids (*1*,*2*). In progressive freezing the entire sample is melted and slowly frozen from one end. For subsequent purification steps the impure portion of the solid must be repeatedly removed and the remainder remelted and refrozen. In zone melting only a thin zone in a solid bar is melted. This molten zone is moved through the solid repeatedly to provide a multistage purification.

Among the advantages claimed for zone melting over progressive freezing techniques are (*1*–*3*):

1. Multistage operation is much easier with zone melting.
2. The risk of contamination during handling is much less with zone melting, because no removal and cropping is necessary following each purification step, as must be done with multistage progressive freezing.
3. The sample is liquid for much less time in zone melting, resulting in less opportunity for attack of the crucible, thermal decomposition, and evaporation.

4. The yield of purified material is greater for multistage zone melting than for multistage progressive freezing with cropping.

The purpose of this paper is to examine the conditions under which point 4 is valid.

THEORETICAL ANALYSIS

The exact impurity redistribution brought about by zone melting and progressive freezing depends on the nature of the phase diagram for the impurity and the host material. However, most practical situations correspond approximately to a constant distribution coefficient. (The distribution coefficient k is defined as the ratio of the impurity concentration of a solid to that of the melt from which it is freezing.) With the usual simplifying assumptions (*1*,*2*), the solute distribution following progressive freezing of a melt is given by

$$\frac{w}{w_0} = k(1-g)^{k-1} \tag{1}$$

where w_0 is the initial concentration of impurity (in weight fraction) and w is the impurity concentration in the solid freezing out when weight fraction g of the melt has already frozen. Similarly, the ultimate concentration profile following a great many zone melting passes is given approximately by

$$\frac{w}{w_0} = A \exp\left(\beta \frac{z}{L}\right) \tag{2}$$

where β is given by

$$k = \frac{\beta(l/L)}{\exp[\beta(l/L)] - 1} \tag{3}$$

$$A = \frac{\beta}{\exp(\beta) - 1} \tag{4}$$

and l is the length of each zone and L the length of the ingot. In this result we have ignored the effect of the progressive freezing of the last zone, which alters the concentration profile primarily at the tail end of the ingot.

Equation (1) predicts that for $k < 1$ the impurity concentration increases without bound at the end of the ingot ($g \rightarrow 1$). Theoretical consideration of normal freezing of the terminal zone leads to a similar prediction for zone melting. This, however, is impossible. The impurity concentration cannot increase beyond a singular point on the phase diagram, such as a eutectic point or pure impurity. Hence some portion of the tail end of the treated ingot must be at the concentration corresponding to this singular point. This fact is important in considering the relative yield between zone melting and progressive freezing. The impurity concentration at the singular point is the maximum that can be removed by cropping the ingot. If only material of this concentration is removed following each progressive freezing step, then multistage progressive freezing clearly provides a larger yield of pure material than does multistage zone refining. If more material than this is discarded the yield declines, although fewer purification steps are required to attain a desired average purity level. For given conditions there is, then, a discard fraction at which the yield is identical for zone melting and progressive freezing. Therefore, the conditions under which the yield is identical for the two processes are determined here both for $k < 1$ and for $k > 1$. Decreasing the discard fraction increases the yield for progressive freezing, whereas decreasing l/L increases the zone-melting yield. In these analyses Eqs. (1) to (4) are assumed valid, which introduces only small errors.

ANALYSIS FOR $k < 1$

The yield Y is defined here as the weight fraction of the processed material that has some desired average product concentration w_p. Integration of Eq. (1) shows that the product concentration following multistage progressive freezing may be given by

$$\frac{w_p}{w_0} = \left[\frac{1 - (1 - g_s)^k}{g_s}\right]^n \tag{5}$$

where g_s is the fraction of the ingot that is saved following each freezing operation and n is the number of freezing operations. The yield of product is

$$Y = (g_s)^n \tag{6}$$

Simultaneous solution of Eqs. (5) and (6) yields the relationships between the various operating parameters, as shown in Figs. 1 and 2 and in (*4*). Figures 1 and 2 show that the number of freezing operations necessary to achieve a given purification increases rapidly

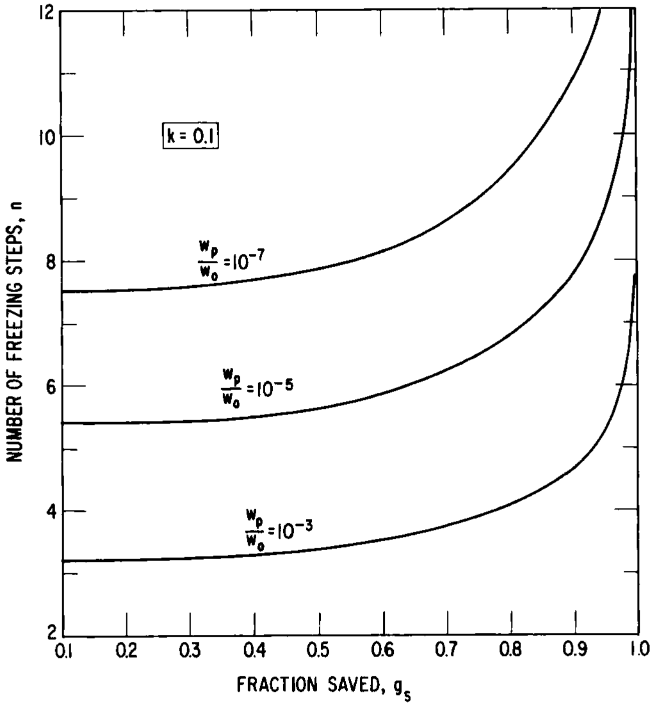

FIG. 1. Number of freezing steps n necessary to produce various reductions w_p/w_0 in impurity content as a function of the fraction saved g_s in each progressive freezing operation, for $k = 0.1$. From Eqs. (5) and (6).

as the fraction saved approaches unity and as the distribution coefficient increases.

For multipass zone melting we integrate Eq. 2 to obtain

$$\frac{w_p}{w_0} = \frac{1}{z_p} \int_0^{z_p} A \exp\left(\frac{\beta}{L} z\right) dz$$

$$= \frac{AL}{\beta z_p} \left[\exp\left(\beta \frac{z_p}{L}\right) - 1\right] \tag{7}$$

where z_p is the length of product of average composition w_p. Noting that $Y = z_p/L$ and rearranging, Eq. (7) yields

$$\frac{\beta Y}{\exp(\beta Y) - 1} = \frac{A}{w_p/w_0} \tag{8}$$

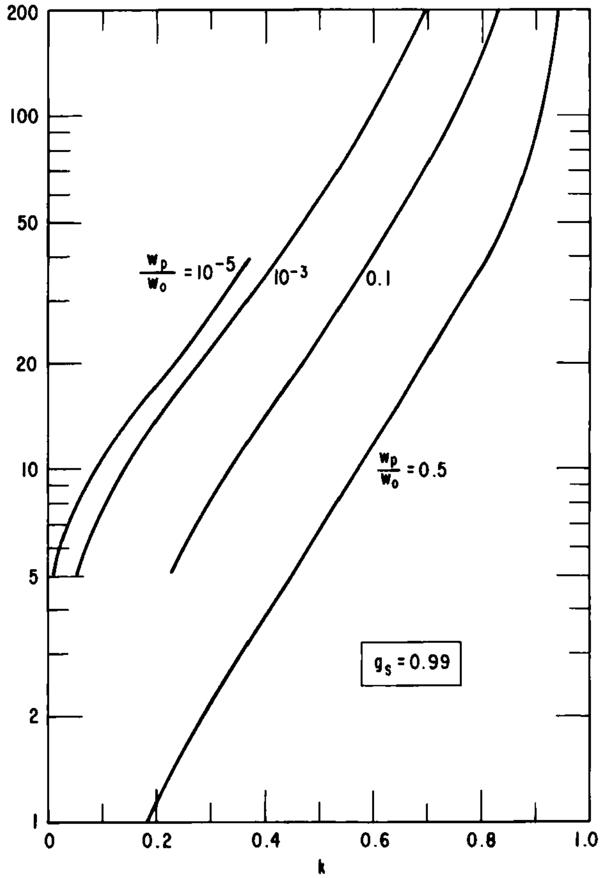

FIG. 2. Number of freezing steps n necessary to produce various reductions w_p/w_0 in impurity content as a function of the distribution coefficient k, *for* $g_s = 0.99$. From Eqs. (5) and (6).

which is of the same form as Eqs. (3) and (4). The relationships between the progressive freezing and zone-melting parameters necessary to give equal yields for the two processes are found from Eqs. (3), (4), (5), (6), and (8). Figure 3 shows the number of progressive freezing steps n as a function of k and w_p/w_0 for $l/L = 0.1$. The fraction saved, g_s, is also shown as a function of k and is found to be relatively insensitive to w_p/w_0 or k. Note that g_s lies very near unity for many conditions. This would be difficult to achieve in practice. The yield (for both processes) is given in Fig. 4 as a func-

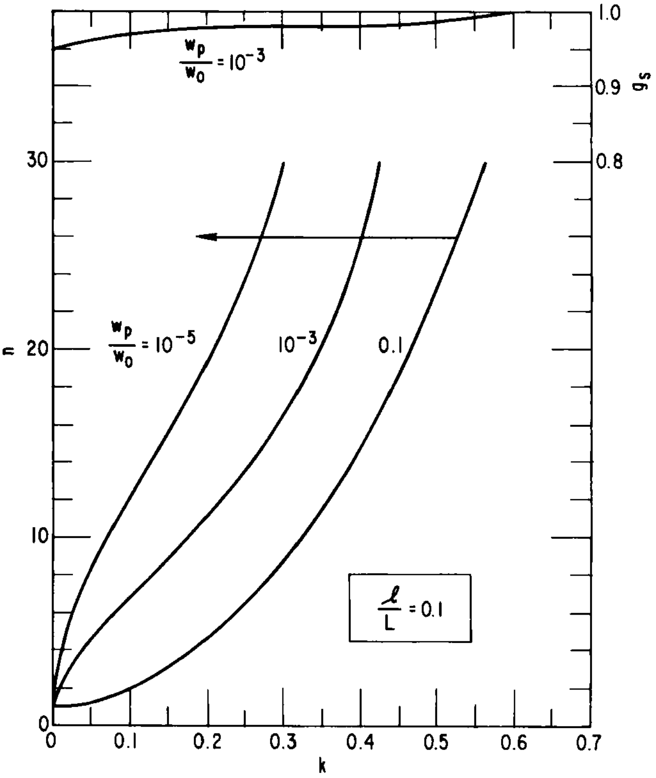

FIG. 3. Conditions for equal yield in zone melting and progressive freezing for $l/L = 0.1$. From Eqs. (3), (4), (5), (6), and (8).

tion of (w_p/w_0) and of k for $l/L = 0.1$. The influence of zone length on n and g_s is shown in Fig. 5 for $(w_p/w_0) = 10^{-3}$ and $k = 0.1$. For comparison, the approximate number of zone passes n_{zm} necessary to achieve the ultimate distribution is also shown. This was determined from

$$n_{zm} = 2\left(\frac{L}{l}\right) + 1 \tag{9}$$

which is approximately valid except when k is near unity (5). Thus it is seen that, for the same yield, progressive freezing will achieve a given separation with fewer operations than zone melting. This does not necessarily favor progressive freezing, however, as sev-

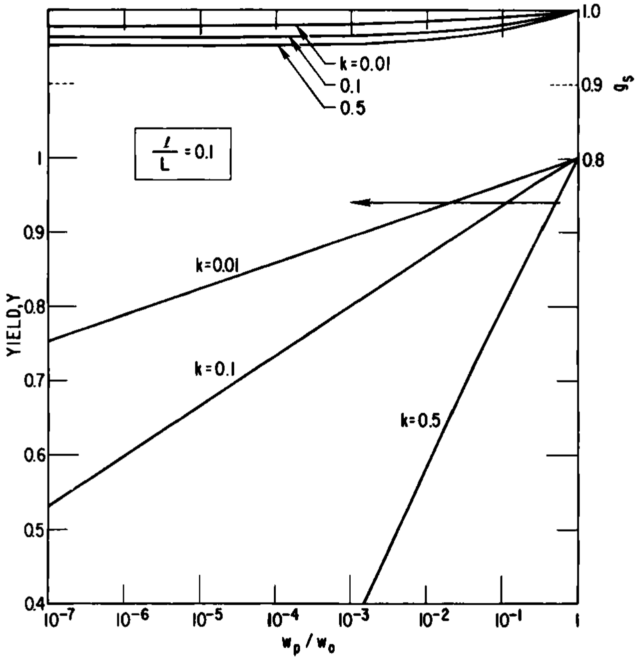

FIG. 4. Yield of zone melting and progressive freezing as a function of reduction in impurity content for several values of k with $l/L = 0.1$.

eral molten zones may traverse an ingot simultaneously—and continuously.

ANALYSIS FOR $k > 1$

Although most impurities are segregated to the tail end of the ingot ($k < 1$), there are a few instances in which the reverse is true—$k > 1$. The purified product in the latter case lies at the tail end of the ingot rather than at the front. In progressive freezing the liquid concentration after fraction g has solidified is w_s/k. After n stages, then, the liquid product has concentration

$$\frac{w_p}{w_0} = [(1 - g_d)^{k-1}]^n \tag{10}$$

where g_d is the fraction discarded at each stage. The yield is

$$Y = (1 - g_d)^n \tag{11}$$

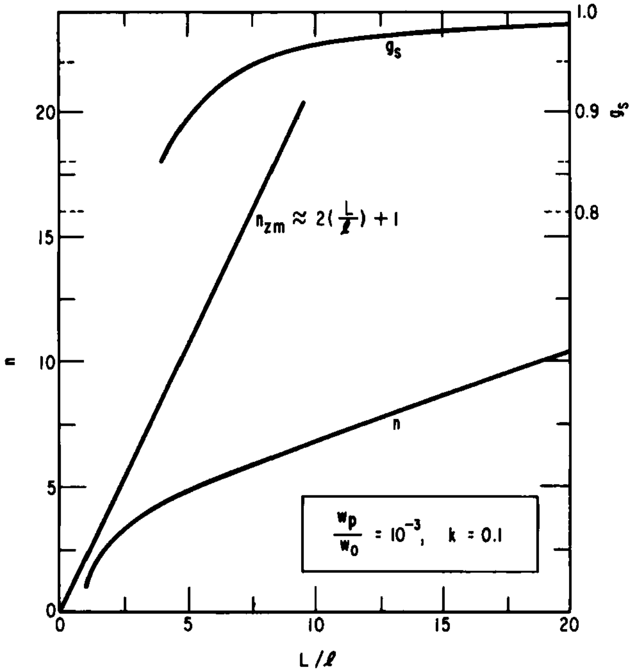

FIG. 5. Number of stages n as a function of L/l for equal yields, with $w_p/w_0 = 10^{-3}$, $k = 0.1$.

Substituting Eq. (11) in (10) we obtain

$$\frac{w_p}{w_0} = Y^{k-1} \tag{12}$$

which shows that the product concentration depends only on the yield and not on n or g_d. Hence the sensible operating procedure is to employ only one freezing operation with $(1 - g_d) = Y = (w_p/w_0)^{1/(k-1)}$.

The product concentration in zone melting (ultimate distribution) is

$$\frac{w_p}{w_0} = \frac{1}{L - z_d} \int_{z_d}^{L} A \exp\left(\frac{\beta}{L} z\right) dz$$
$$= \frac{A \exp(\beta)}{\beta Y} [1 - \exp(-\beta Y)] \tag{13}$$

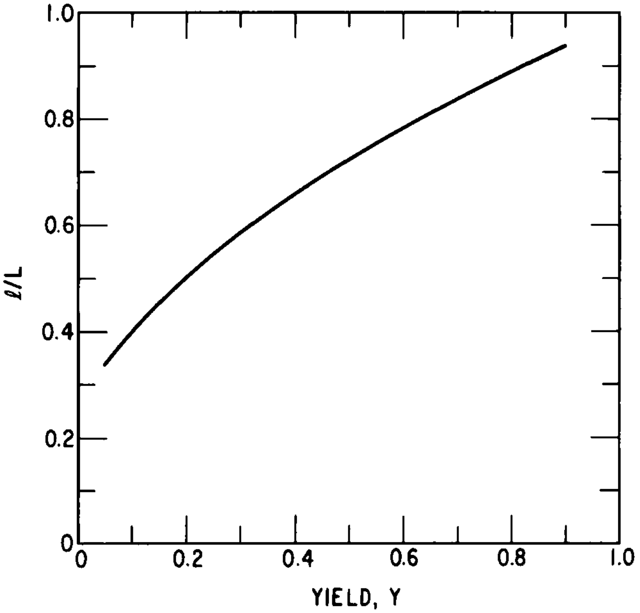

FIG. 6. Zone length as a function of yield for $k > 1$ with identical zone melting and progressive freezing yields. From Eqs. (3), (4), (12), and (13).

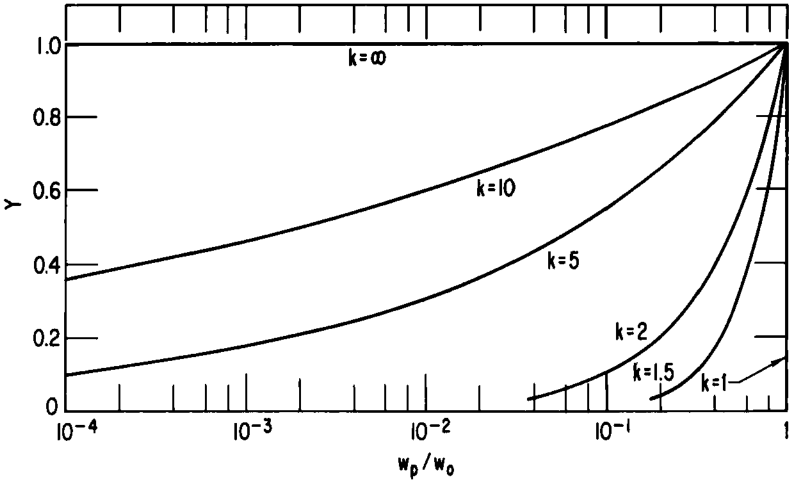

FIG. 7. Yield as a function of impurity reduction for several values of k, for $k > 1$.

where $z_d = L(1 - Y)$ is the length of the discarded portion of the ingot. Using these equations, relationships between the various parameters for equal yields were calculated. It was found that, surprisingly, the zone length for equality depended almost entirely on the yield (Fig. 6) and was relatively unaffected by variations in k and (w_p/w_0). The dependence of yield on (w_p/w_0) for several values of k is shown in Fig. 7.

These results differ in one important respect from those for $k < 1$. For $k < 1$ an increase in the fraction saved (g_s) beyond the value given in Figs. 3, 4, and 5 causes the yield for progressive freezing to exceed that for zone melting. This is possible because the increase in the average impurity concentration caused by rejecting less of the impure tail end may be compensated for by increasing the number of freezing operations. When $k > 1$, however, the product concentration depends only on the final yield (Y), not on the number of freezing operations [as shown by Eq. (12)]. Therefore, Y is fixed when (w_p/w_0) is fixed. The yield in zone melting, however, is increased merely by shortening the zone length. Figure 6 shows, in fact, that unreasonably large zone lengths are necessary to "lower" the zone-melting yield to that for progressive freezing. Typical experimental values for (l/L) range from 0.05 to 0.2, which would produce a much larger yield for zone melting than for progressive freezing.

CONCLUSIONS

We have determined the combination of parameters under which the yield of purified product is identical for multistage zone melting and progressive freezing, with the final average impurity content being specified. When the distribution coefficient is less than 1, the yield of progressive freezing may be increased by lowering the amount of impure material removed following each freezing operation. However, this increases the number of freezing operations necessary to achieve the desired purity. When the distribution coefficient is greater than 1, the yield for progressive freezing is uniquely specified by the desired final purity and cannot be improved by increasing the number of freezing steps. The yield in zone melting may be increased by decreasing the zone size, which increases the number of zone passes required to reach the ultimate distribution. However, when $k > 1$, the usual convenient range of zone sizes results automatically in a yield greater than with progressive freezing.

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Received by editor February 24, 1966
Submitted for publication March 4, 1966