Purification Process by Solution Zone Passages

Part 1 *Process Theory*

I. F. NICOLAU
Institute for Atomic Physics, Bucharest, Romania

The travelling heater zone-refining process and its relation to the travelling solvent and travelling heater methods of growing single crystals are described.

The variation of the zone composition during the zone passage is derived, proceeding from the solute-impurity-solvent diagrams, and the impurity distribution along the crystallisate, after a zone passage, is derived, by considering that the solute and the impurity form either a solid solution or an eutectic. The influence of the parameters which determine the distribution is discussed. The impurity distribution along the crystallisate after a number of zone passages is derived.

The application of the process is suitable in the case of a sub-unity distribution coefficient, the zone passage efficiency being higher, the smaller the distribution coefficient and the steeper the slope of the dissolution straight line. The process is particularly advantageous when the solute and the impurity form an eutectic. It is advantageous to select a high dissolution temperature, close to the solvent boiling temperature, and a crystallisation temperature as near as possible to the dissolution temperature, when the solute and the impurity form either a solid solution or an eutectic.

1. Introduction

The travelling heater method (THM) for the growth of single crystals was introduced by Wolff and Mlavsky [1]. This method differs from the travelling solvent method (TSM) [2] although it also uses a travelling solvent zone under the action of a temperature gradient. The TSM uses a thin solvent zone that travels at a slow rate under the action of a low temperature gradient, the temperature gradient being fixed along the charge and the temperatures of the leading and trailing edges increasing simultaneously with the zone passage. The THM uses a large solvent zone which travels faster under the action of a high-temperature gradient; the temperature gradient is only constant in the zone and travels along the charge with the heater, the temperatures of the leading and trailing edges remaining constant during the zone passage. This method has been successfully applied to the growth of single crystals of pure compounds and solid solutions, e.g. GaP [3],

ZnO [4], $Pb(Ti_x Zr_{1-x})O_3$ [5], $(Zn_x Hg_{1-x})Te$ and $Ga(P_x As_{1-x})$ [6], $(Pb_x Sr_{1-x})TiO_3$ [7] and CuCl [8]. In the case of solid solutions, in order to obtain single crystals of constant composition it was necessary to compensate for the segregation by using zones enriched in one of the components and supplying to the zone a solution richer in that component.

The TSM is only a renaming of the temperature gradient zone-melting process (TGZM) [9], for the growth of single crystals.

For this reason we suggest the name "travelling heater zone-refining" (THZR), because the THM of growing single crystals is considered a purification process. This latter process was originated by Pfann [10] as a zone-refining process which uses a solvent added to the zone at the beginning of the zone passage and which is eliminated from the zone at the end of zone passage. This process has two advantages over zone melting (ZM): (i) it works at lower temperatures and (ii) if the solvent is suitably chosen

it permits a better separation. However, the application of this process presents two difficulties, viz. (i) very slow travel rates are necessary to avoid solvent inclusion in the crystallisate and (ii) the elimination of the solvent at the end of zone passage.

These difficulties were overcome by using a zone heater with two temperature levels, as shown in fig. 1, so that crystallisation occurs throughout the zone passage at a temperature higher than the solvent melting temperature, and subjects the solution zone to forced convection. Since the solution zone contains a small quantity of solute, the solution zones can be decanted at the zone passage end so that the process has neither inverse impurity diffusion nor a limiting distribution. In this manner we have successfully applied the process to the purification of some inorganic salts using water as a solvent, i.e. to those salts which crystallise massively and adherently (e.g. alkali metal phosphates, coloured sulphates, alums, picromerites, alkali metal bichromates, etc.), employing solution zone travel rates of 0.25 to 1 mm min^{-1}.
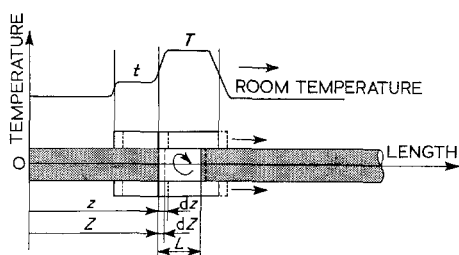

Figure 1 The principle layout of the THZR process.

The THZR process can generally be applied to the purification of any crystalline solute provided that a suitable solvent can be found in which both the solute and the impurities are soluble but which must not be soluble in the crystalline solute nor in the crystalline impurities. The solute solubility should increase with temperature and should form, on crystallisation, sufficiently adherent crystals in order to delimit the trailing edge without causing solvent inclusion. The application of the process to metal or semiconductor purification is mainly limited by the finding of a common solvent for all the mixture components, and by the possibility of subsequently eliminating solvent traces from the purified material. For many organic substances the application of this process is inconvenient because the crystallisate becomes saturated with solvent, which leads to the disappearance of the zone. The fact that, with the aid of the travelling heater zone-refining process, we can purify substances at temperatures much lower than their melting points, enables us to extend zone-refining to cases in which zone melting cannot be applied or presents difficulties, e.g. (i) for the purification of substances which decompose on melting, (ii) have too high a melting point, (iii) have, on melting, too high a vapour pressure or (iv) react with the surrounding medium and with the materials with which they come into contact at the melting point.

Reference [10] shows that by the addition of a solvent the separation of components can be favourably or unfavourably changed, the extent of which change can be estimated previously only if the ternary solubility diagram is known in detail. On this basis the author has attempted (i) to find the impurity distribution established along a semi-infinite solute-impurity solid binary mixture (AB) after successive zone passages, of a solute-impurity-solvent ternary solution (ABS) according to the THZR process, (ii) to discuss the dependence of the impurity distribution on the quantities present in its expression and (iii) to indicate the best possible values of these quantities such that the efficiency of a zone passage is a maximum. Various types of solid-solid-liquid isothermal ternary solubility diagrams exist [11] which show the compositions of phases present at equilibrium. Of the existing diagrams, those that are of interest may be divided into two distinct types [12]: type I, shown in fig. 2, corresponds to the case in which A and B form a solid solution, and type II shown in fig. 3, corresponds to the case in which A and B form an eutectic. The case in which A and B form two or more solid solutions may be reduced to type I if we restrict ourselves to the domain of a single solid solution. The case in which A and B form one or more compounds may be reduced to type II if we restrict ourselves to the domain of one component and the adjacent compound, or compounds. When the solvent forms compounds with one of the components or with their solid solutions the situation may be reduced to either case II or case I by considering the compounds with solvent as pure components.

The paper introduces several simplifying assumptions which are not entirely supported by practice. Nevertheless, our experience in the travelling heater zone-refining field shows, according to the analyses of certain systems, a
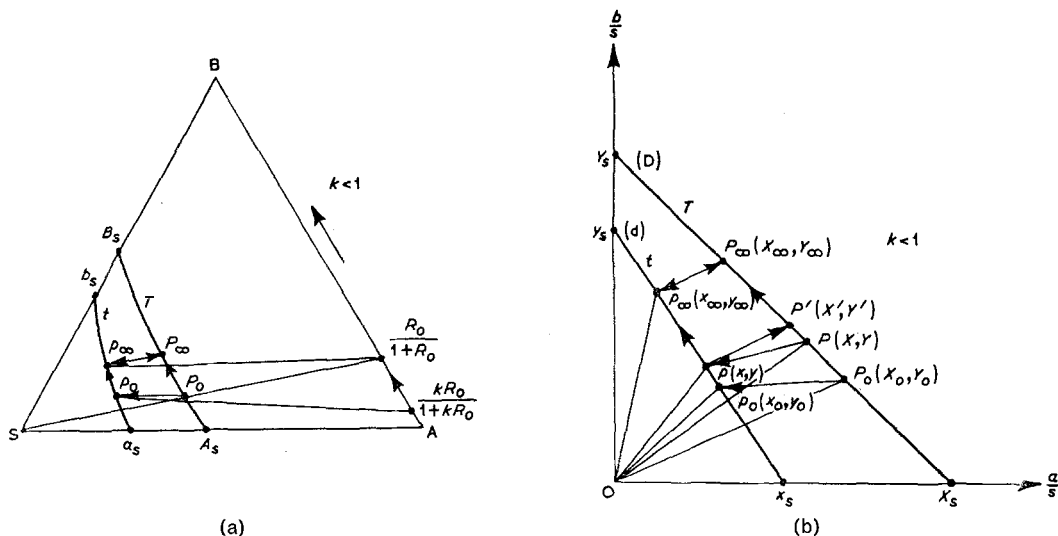
Figure 2 The ternary diagram of equilibrium solubility representing the changes of the zone and crystallisate composition during the THZR process (A and B form a solid solution). (a) Triangular diagram representation. (b) Rectangular diagram representation.

satisfactory agreement of the theory with practice.

2. Single-Pass Impurity Distribution
2.1. A and B Form a Solid Solution

Let us consider the case most frequently met in practice, viz. the functions g_A and g_B as increasing functions and t and T in the range $(mt - bt)$ such that $mt < t < T < bt$. We assume that the isotherms, which yield the saturation equilibrium composition in the liquid phase for the ternary mixture ABS, for the temperatures t and T, can be obtained by a direct comparison, an assumption close to practice for small intervals $(T-t)$. In addition, we approximate these isotherms by straight lines as shown in fig. 2. These assumptions lead to the transformation relations from t to T, which transform the straight line (d) into (D)

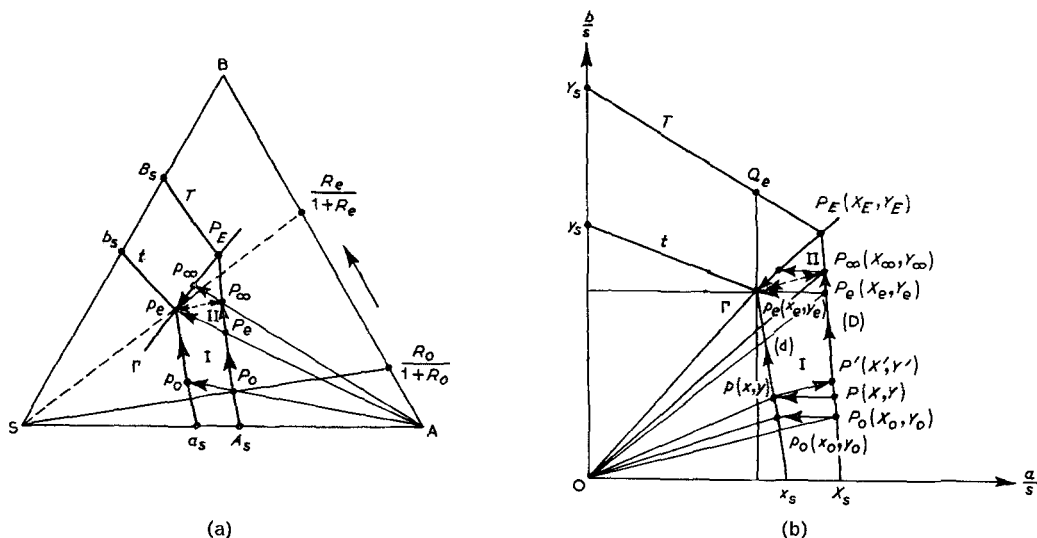$$X = \alpha x \text{ and } Y = \beta y \tag{1}$$

Figure 3 The ternary diagram of equilibrium solubility representing the changes of the zone and crystallisate composition during the THZR process (A and B form an eutectic). (a) Triangular diagram representation. (b) Rectangular diagram representation.

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where

$$\alpha = \frac{X_s}{x_s} \text{ and } \beta = \frac{Y_s}{y_s} \alpha, \beta > 1 \cdot \qquad (2)$$

In the following, as in [13], we make the following assumptions:

(i) The impurity diffusion and the solvent inclusion in the crystallisate is negligible.

(ii) In the solution zone the diffusion of the components provides a homogeneous zone composition according to the phase equilibrium.

Let us consider a situation, during the zone passage, as shown in fig. 1. We take the area of the right section through the solute equal to unity, and consider the solute composition as homogeneous. Let the heater shift an infinitesimal amount dz in the direction of zone passage. This shift causes the cooling of the infinitesimal solution volume from the temperature T to the temperature t. This solution volume contains the infinitesimal solvent quantity $ds = sdz/L$. Its composition corresponds to the point $P(X, Y)$ on the straight line (D), see fig. 2b. As a result of cooling, from this volume there crystallises $(X - x)sdz/L$ solute and $(Y - y)sdz/L$ impurity, the representative point of the saturated solution composition being shifted on the line $\overline{Pp}$ from the point $P(X, Y)$ to the point $p(x, y)$ during the crystallisation. The solvent quantity ds, being drawn into the solution zone, is reheated from the temperature t to the temperature T and contacting the impure substance dissolves from it until it reaches saturation. The representative point of the composition of the infinitesimal solution during the impure solute dissolution is shifted on the line $\overline{pP'}$ from the point $p(x, y)$ to the point $P'(X', Y')$. The line $\overline{pP'}$ has the slope R_0 since the solute dissolution takes place layer by layer irrespective of the solute or impurity. In the solution zone, which is at temperature T, the ratios X and Y must satisfy the equation of the straight line (D), fig. 2b. After the shift these ratios vary with dX and dY and the quantities a and b will vary correspondingly with sdX and sdY. Balancing the solute A in the zone after the shift we obtain the equation

$$s(X' - x) \frac{dz}{L} = s(X - x) \frac{dz}{L} + sdX \qquad (3)$$

and similarly balancing the impurity B we obtain the equation

$$s(Y' - y) \frac{dz}{L} = s(Y - y) \frac{dz}{L} + sdY \cdot \qquad (4)$$

Dividing equation 4 by equation 3 we obtain the equation

$$R_0(X - x) \frac{dz}{L} + R_0 dX =$$
$$(Y - y) \frac{dz}{L} + dY \cdot \qquad (5)$$

Replacing x and y in equation 5 by their expressions from equation 1 we obtain

$$R_0 \left(1 - \frac{1}{\alpha} \right) X \frac{dz}{L} + R_0 dX =$$
$$\left(1 - \frac{1}{\beta} \right) Y \frac{dz}{L} + dY \cdot \qquad (6)$$

However X and Y must satisfy the equation of the straight line (D)

$$\frac{X}{X_s} + \frac{Y}{Y_s} - 1 = 0 \cdot \qquad (7)$$

Eliminating X between equations 6 and 7 and grouping the terms, we obtain the differential equation

$$\frac{dz}{L'(M - R_0)} = \frac{dY}{(R_0 - kM)Y - R_0 Y_s} \qquad (8)$$

where we have denoted

$$M = - \frac{Y_s}{X_s}, \text{ with } L' = \frac{L}{1 - \frac{1}{\alpha}}$$

$$\text{and with } k = \frac{1 - \frac{1}{\beta}}{1 - \frac{1}{\alpha}} \cdot \qquad (9)$$

Equation 8 enables us to determine the manner in which the quantity of impurity varies in the solution zone as a function of the distance travelled by the heater. In order to integrate this equation we have to make an additional approximation, by considering the variation of the solution zone length, as a function of the zone position, as being negligible. Thus we assume L', in equation 8, is a constant and equals the solvent zone length l'.

Integrating equation 8 between limits

$$\int_0^z \frac{dz}{l'(M - R_0)} = \int_{Y_0}^Y \frac{dY}{(R_0 - kM)Y - R_0 Y_s}$$

we obtain

$$- \frac{R_0 - kM}{M - R_0} \frac{z}{l'} = \ln \frac{(R_0 - kM)Y - R_0 Y_s}{(R_0 - kM)Y_0 - R_0 Y_s} \quad (10)$$

or writing y explicitly as a function of z

$$Y = \frac{R_0 Y_s}{R_0 - kM} + \left[Y_0 - \frac{R_0 Y_s}{R_0 - kM} \right] e^{-hz/l'} \quad (11)$$

where we have denoted

$$h = \frac{R_0 - kM}{R_0 - M} .$$

Replacing Y_s by the relation

$$Y_s = \frac{R_0 - M}{R_0} Y_0 \quad (12)$$

resulting from the intersection of the crystallisation straight line with that characterising the initial zone composition

$$Y = R_0 X \quad (13)$$

we obtain the required function in the form

$$\frac{Y}{Y_0} = \frac{1}{h} + \left(1 - \frac{1}{h} \right) e^{-hz/l'} . \quad (14)$$

To find the expression of the ratio of quantity of impurity to the quantity of solute in the crystallisate, as a function of the heater position, we form the ratio of the quantity of impurity to the quantity of solute which crystallised by the infinitesimal heater shift

$$R = \frac{(Y - y)}{(X - x)} = k \frac{Y}{X} . \quad (15)$$

The above assumptions led to this expression for R which relates the impurity/solute ratio in the crystallisate to the impurity/solute ratio in the solution zone, by means of the distribution coefficient k. This expression differs from that for zone melting in that in zone melting the distribution coefficient between crystallisate and melt, $C_s = kC_L$, is a volumetric ratio [13] whilst in travelling heater zone-refining it is a gravimetric ratio, an expression advantageous in the treatment of the THZR process. Inserting into equation 15 the expression for X, from equation 7, and that for Y, from equation 14, we obtain, explicitly, the distribution of the impurity ratio in the crystallisate as a function of the heater co-ordinate behind the zone

$$R = kM + \frac{R_0 - kM}{1 + \left(\frac{1}{k} - 1 \right) \frac{R_0}{R_0 - M} e^{-hz/l}} . \quad (16)$$

To find the distribution of the impurity ratio along the crystallisate behind the zone passage we should express Y as a function of Z.

For this we replace dz in equation 8 by its expression as a function of dZ from the relation

$$dZ = \rho_S \frac{l}{L} \left(\frac{X - x}{\rho_A} + \frac{Y - y}{\rho_B} \right) dz$$

which becomes

$$dZ = \frac{\rho_S}{\rho_A} \frac{l}{L'} \left[\left(\frac{\rho_A}{\rho_B} k - \frac{1}{M} \right) + X_s \right] dz$$

and we integrate as above. A transcendent equation is obtained from which Y cannot be derived. However insertion of values for ρ_A, ρ_B, ρ_S, k, M, R_0 and L' and consideration of equation 15 gives the impurity ratio distribution along the crystallisate. A more precise distribution can be obtained if we replace L' in equation 8 by its development function of Y assuming the dissolution to take place without volume variation

$$L' = l' \left[1 + \rho_S \left(\frac{1}{\rho_A R_0} + \frac{1}{\rho_B} \right) Y \right] .$$

Figs. 4a and 5a show the variation of the quantity of zone impurity referred to the quantity of solvent introduced, as a function of the heater co-ordinate for $k < 1$ and for $k > 1$. It can be seen that as the zone advances, the quantity of impurity in the zone increases in the case $k < 1$, and decreases in the case of $k > 1$, and when z tends to infinity the quantity of impurity tends to the limit

$$Y = \frac{1}{h} Y_0 . \quad (17)$$

In the case in which $k = 1$ the initial quantity of impurity in the zone, Y_0, does not vary during zone passage.

Figs. 4b and 5b show the impurity/solute ratio distribution after zone passage for the case $k < 1$ and $k > 1$ corresponding to the impurity zone enrichment and impoverishment during zone passage. While z increases and tends to infinity, the impurity ratio in the crystallisate increases proportionally, from the initial value kR_0 to R_0, for $k < 1$, and decreases from the initial value kR_0 to R_0, for $k > 1$.

In fig. 2 one can examine the evolution of the ratios and gravimetric fractions that characterise the zone and the crystallisate composition during the zone passage, represented in a triangular and a rectangular diagram, for $k < 1$. At the beginning of the zone passage, the composition of the zone solution is given by the point P_0, and the composition of the corresponding layer of solution adjacent to the trailing edge after the crystallisa-
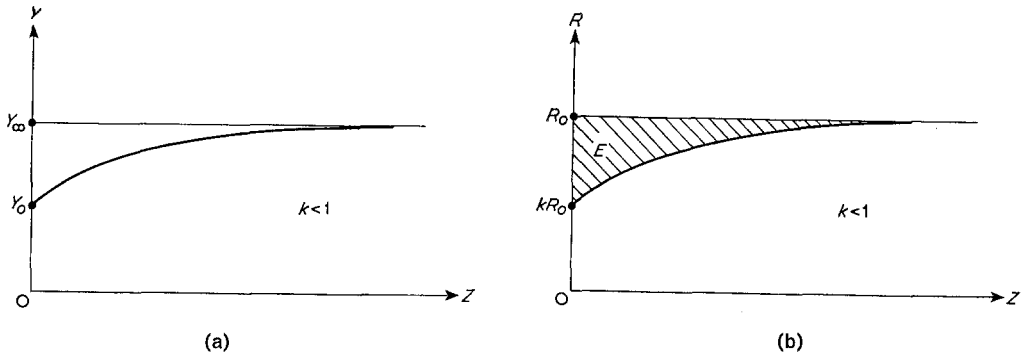
Figure 4 (a) The variation of the quantity of zone impurity as a function of the heater co-ordinate. (b) The distribution of the impurity/solute ratio in the crystallisate as a function of the heater co-ordinate behind the zone passage ($k < 1$) (A and B form a solid solution).

tion, is given by the point p_0. The crystallisation at the beginning of the zone passage is represented by the line $\overline{P_0 p_0}$. The initial impurity fraction in the crystallisate is $kR_0/1 + kR_0$. As the zone advances, the point that characterises the zone composition is shifted from P_0, on the isotherm T, to higher B fractions to the limit P_∞ when z tends to infinity. Likewise the point p_0, which characterises the layer of solution adjacent to the trailing edge, is shifted on the isotherm t and tends to $p\infty$, when z tends to infinity. The impurity fraction in the crystallisate during zone passage is shifted on the triangular edge AB to B and assumes the value $R_0/1 + R_0$, when z tends to infinity, i.e. to the initial value before the zone passage.

Fig. 6 represents the distribution of the impurity ratio in the crystallisate as a function of the heater co-ordinate, according to equation 16, for different values of k, $k < 1$ ($\alpha = 2$), $k > 1$ ($\beta = 2$) and for $R_0 = 1$, $M = -2$.

Obviously the farther the value of k from unity, the greater is the efficiency of the zone passage. Fig. 7 represents the dependence of the above unit proportionality coefficients of solubility, α and β, on the various values k, according to relation 9. It can be seen that small values of k are possible only for values of β near unity, and high values of k only for values of α near unity, respectively.

In order to estimate the zone passage efficiency, for the first zone length, as a function of k the limit of the impurity ratio derivative, as a function of the trailing edge co-ordinate is calculated when this tends to zero. We obtain

$$\left(\frac{dR}{dz'}\right)_{z'=0} = k(1-k)R_0 \qquad (18)$$

where we have denoted by $z' = z/l'$ the reduced co-ordinate.

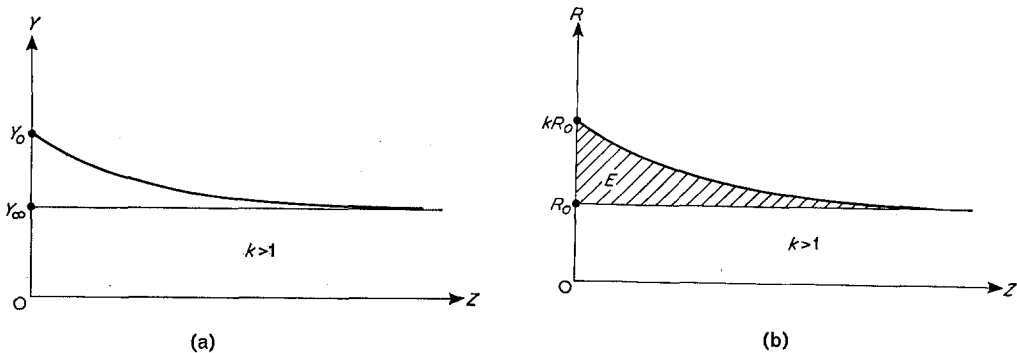The case in which $k < 1$ is favourable for the THZR process. In this case the solute is

Figure 5 (a) The variation of the quantity of zone impurity as a function of the heater co-ordinate. (b) The distribution of the impurity/solute ratio in the crystallisate as a function of the heater co-ordinate behind the zone passage ($k > 1$) (A and B form a solid solution).
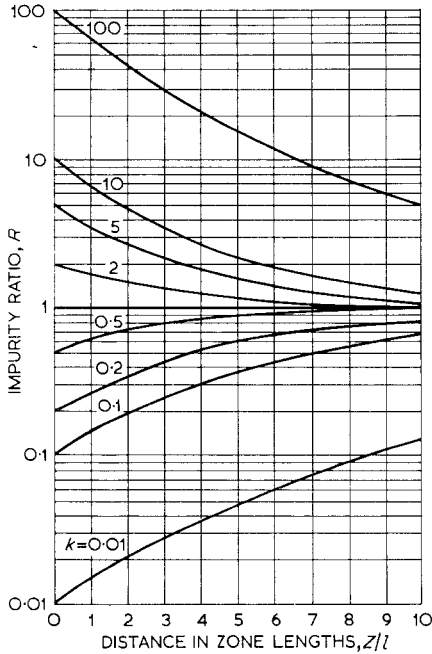
Figure 6 The distribution of the impurity ratio in the crystallisate as a function of the heater co-ordinate behind the zone passage for different values of the distribution coefficient.

$$R = kM + \frac{R_0 - kM}{1 + \dfrac{R_0(1 - k)}{k(R_0 - M)}\, e^{-hz/l}};$$

$R_0 = 1$, $M = -2$ for all curves; $\alpha = 2$ for $k < 1$, $\beta = 2$ for $k > 1$.

generally the major component. The derivative limit is close to zero for small values of R_0, and is closer, the farther k is from unity. The advanced purification that is obtained for small values of k and R_0 for the co-ordinate $z' = 0$, is maintained for a number of zone lengths.

The case in which $k > 1$ is unfavourable for the THZR process. In this case if we wish to enrich the solute with a precious impurity proceeding from a small ratio R_0, or reversing the names and proceeding from a high value of R_0 we then wish to concentrate the solute and eliminate the impurity. The latter high values of R_0 multiplied by the advantageous high values of k lead to values of the limit for the co-ordinate $z' = 0$ which are close to minus infinity. These values are inconvenient for the THZR process since the high concentration which is obtained for higher values of k affects only the crystallisate in the vicinity of the zero co-ordinate and, as we depart from $z' = 0$, the concentration decreases very rapidly.
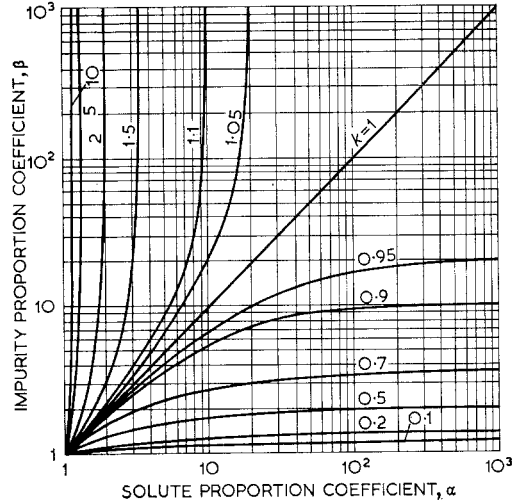

Figure 7 The dependence of the proportionality coefficients of solubility for different values of the distribution coefficient.

Fig. 8 represents the impurity ratio function of the heater co-ordinate according to equation 16 for different values of M in the interval $(-\infty, 6)$, for $R_0 = 1$ and $k = 0.1$ ($\alpha = 2$). The limiting distribution for $M = -\infty$ is the most favourable.

Fig. 9 shows the same dependence for $R_0 = 1$ when $k = 10$ ($\beta = 2$). In this case the limiting distribution for $M = 0$ proves to be the most favourable.

In figs. 8 and 9 the limiting distributions for $M = 0$ and for $M = -\infty$, are calculated, proceeding from equation 16 with the relations

$$R_{(M=0)} = \frac{R_0}{1 + \left(\dfrac{1}{k} - 1\right)e^{-z/l'}} \qquad (19)$$

and

$$R_{(M=-\infty)} = R_0[1 - (1 - k)\, e^{-kz/l'}] \quad . \quad (20)$$

It can be seen that the limiting distribution 20 is again the ZM process distribution, but instead of concentrations we have ratios. This result enables us to use all the results from the zone melting study to make estimations for travelling heater zone-refining. When $k < 1$ the most favourable results are obtained, and for $k > 1$ the most unfavourable results are obtained. As distinct from the ZM process, for which the concentration depends only on the distribution coefficient k (defined entirely by the nature of the solute-impurity system), in the THZR process the concentration distribution depends on both
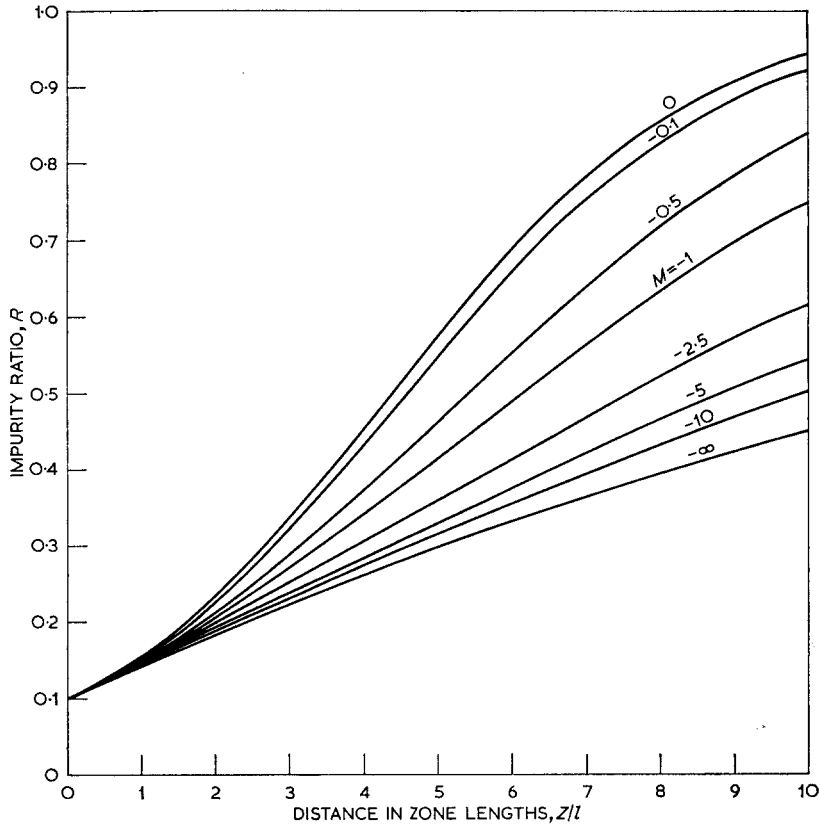
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Figure 8 The distribution of the impurity ratio in the crystallisate as a function of the heater co-ordinate behind the zone passage for different values of $M\epsilon(-\infty, 0)$.

the slope M and the distribution coefficient k while M and k both depend on (i) the nature of the solute-impurity-solvent system and on (ii) the choice of temperatures T and t.

In the following we shall attempt to determine, within the temperature range $(mt - bt)$ characteristic of the solvent, the working temperatures for crystallisation t^* and for dissolution T^* in order to obtain values of k and M which give a maximum efficiency for the zone passage. We shall consider that the zone passage efficiency is a maximum for k^* and M^* when

$$|F(k^*, M^*)| = \sup |F(k, M)| \qquad (21)$$

where

$$F(k, M) = \lim_{z' \to \infty} E = \lim_{z' \to \infty} \left(R_0 z' - \int_0^{z'} R\,dz' \right),$$
$$(22)$$

E being the shaded area in figs. 4b and 5b, contained between the impurity ratio distribution curve, the ordinate, and the initial distribution straight line. Calculating the limit we find

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$$F(k, M) = (R_0 - M) \ln \frac{h}{k} \cdot \qquad (23)$$

The function F has no maximum or minimum within the domain k and M, for the physical problem, i.e. $k\epsilon(0, +\infty)$ and $M\epsilon(-\infty, 0)$. If we neglect a relative maximum of the function F with respect to the variable M (which could occur for small M values, and which differs insignificantly from the value of the function for $M = -\infty$) i.e. if we consider that F decreases with respect to M then within a certain domain $(k_1, k_2) \subset (0, +\infty)$, $(M_1, M_2) \subset (-\infty, 0)$, where $k_1 < k_2$ and $M_1 < M_2$ for $k_2 < 1$, $\sup F = F(k_1, M_1)$ and for $k_1 > 1$, $\inf F = F(k_2, M_2)$. Expressing M and k as a function of T and t, by means of the functions g_A and g_B and their definition relations, we obtain

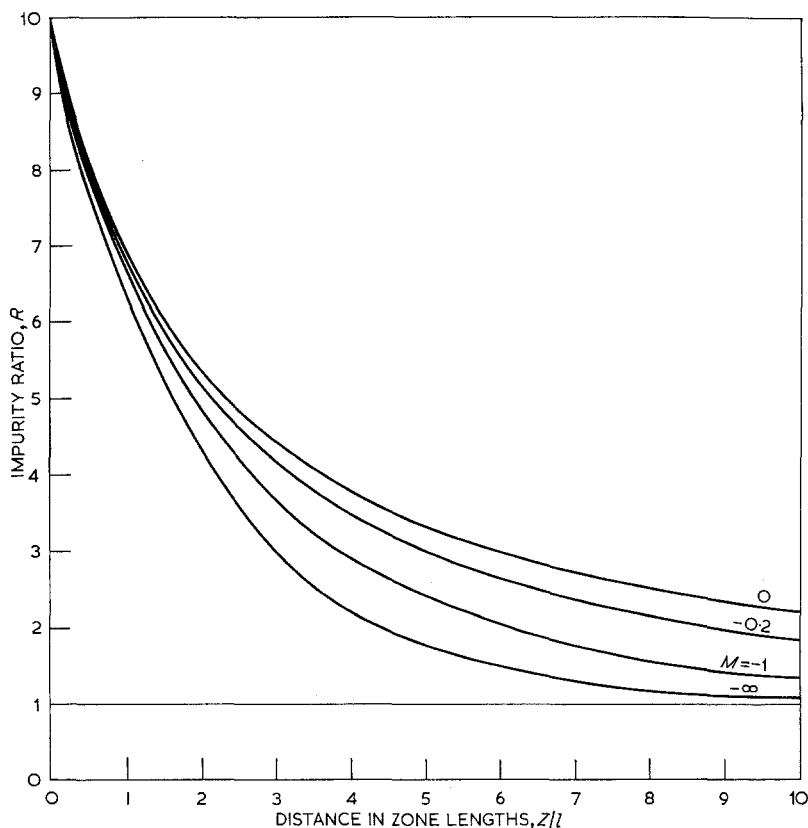$$M(T) = -\frac{g_B(T)}{g_A(T)} \qquad (24)$$

and

Figure 9 The distribution of the impurity ratio in the crystallisate as a function of the heater co-ordinate behind the zone passage for different values of $M\epsilon(-\infty, 0)$.

$$k(T, t) = \frac{g_B(T) - g_B(t)}{g_A(T) - g_A(t)} \cdot \frac{g_A(T)}{g_B(t)} \qquad (25)$$

where $t\epsilon[mt, bt - (T - t)]$ and $T\epsilon[mt + (T - t), bt]$. On examining the behaviour of the functions $M(T)$ and $k(T, t)$ within the possible temperature domain for t and T we shall determine the corresponding variation domain for M and k, $(\inf M, \sup M)$ and $(\inf k, \sup k)$. In the case in which $\sup k < 1$, $k^* = \inf k$ and $M^* = \inf M$ satisfy the condition 21 and we determine T^* so that $M(T^*) = \inf M$, then we determine t^* so that $k(T^*, t^*) = \inf k$. In the case in which $k > 1$, $k^* = \sup k$ and $M^* = \sup M$ satisfy the condition 21 and we determine T^* so that $M(T^*) = \sup M$, then we determine t^* so that $k(T^*, t^*) = \sup k$. In the case in which $\inf k < 1 < \sup k$ then $|F(\inf k, \inf M)|$ and $|F(\sup k, \sup M)|$ must be calculated and we select those extreme values for k and for M that give the greatest value of $|F|$.

On the other hand, from the viewpoint of process productivity, it is desirable to work with as large a crystallisation rate as possible. The selection of a high crystallisation rate, i.e. a high supersaturation, and hence a large temperature difference $T - t$ (besides the fact that increases in the solvent quantity are inevitably included in the crystallisate, thus favouring zone loss and preventing the dissolution and crystallisation taking place at equilibrium), is inconvenient in that it determines high proportionality co-efficients of solubility, α and β, much higher than unity. As can be seen in fig. 7 in such cases k is close to unity and the process efficiency decreases substantially. From fig. 7 it can be seen that for k to be far from unity it is necessary that one of the two coefficients α and β be small, which require a small temperature difference $T - t$. In addition, the calculation of the optimum conditions often leads to the result $t^* = T^*$, so that the selection of the crystallisation temperature is based on technological considerations.

2.2. A and B Form an Eutectic

As in section 2.1 we consider the functions g_A

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and g_B as increasing functions, and t and T within the range $(mt - bt)$, so that $mt < t < T < bt$. Of course we assume that the isotherms giving the saturation equilibrium compositions in the liquid phase for the ternary ABS mixture, for the temperatures t and T, can be obtained by a direct comparison. In addition, we approximate these isotherms by straight lines, as is shown in fig. 3b. We also make the assumptions (i) and (ii). We distinguish, according to fig. 3, between two domains denoted by I and II. Domain I corresponds to the quadrilateral $x_s X_s P_e p_e$ and domain II corresponds to the triangle $p_e P_e P_E$. The THZR process occurs differently in the two domains.

We select the point P_0, which characterises the solution zone composition at the beginning of the zone passage, on the straight line (D), according to fig. 3, below the point P_e belonging to the domain I, i.e. in that part which separates the homogeneous liquid phase from the heterogeneous phase consisting of solution and crystallisated solute A.

The transformation relations from t to T which transform the straight line (d) into the straight line (D) are

$$X = X_s + \frac{Y}{M}, \; Y = y \cdot \tag{26}$$

Giving an infinitesimal shift to the heater dz in the direction of zone passage, according to fig. 1, and retaining the notation used in section 2.1 we obtain the balance equations 3, 4 and 5, which are also valid in this case. Replacing y in equation 5 by Y, according to equation 26, we obtain

$$R_0(X - x)\frac{dz}{L} + R_0 dX = dY \; . \tag{27}$$

x and y must satisfy the equation of the straight line (d)

$$y = m(x - x_s), \quad m = \frac{y_e}{x_e - x_s} \tag{28}$$

and X and Y must satisfy the equation of the straight line (D)

$$Y = M(X - X_s), \quad M = \frac{Y_e}{X_e - X_s} \cdot \tag{29}$$

Eliminating in equation 27 X and x, with the help of equations 28 and 29, we obtain the equation

$$\frac{1}{G}\frac{dz}{L} = \frac{dY}{HY + (X_s - x_s)} \tag{30}$$

where we have denoted

$$G = \frac{1}{R_0} - \frac{1}{M} \text{ and with } H = \frac{1}{M} - \frac{1}{m} \; .$$

Making, as in section 2.1, the approximation that the solution zone length does not vary as a function of position and considering it equal to the solvent zone length, we can integrate equation 30 between limits

$$\int_0^z \frac{1}{G}\frac{dz}{l} = \int_{Y_0}^{Y} \frac{dY}{HY + (X_s - x_s)} \; .$$

Giving

$$\frac{H}{G}\frac{z}{l} = \ln \frac{HY + (X_s - x_s)}{HY_0 + (X_s - x_s)}, \tag{31}$$

or writing Y as an explicit function of z

$$Y = -\frac{X_s - x_s}{H} + \left(Y_0 + \frac{X_s - x_s}{H}\right) e^{Hz/Gl} \cdot \tag{32}$$

From fig. 3 we can examine as in section 2.1 the evolution of the gravimetric ratios which characterise the zone and crystallisate compositions during zone passage. At the beginning of the zone passage the solution zone composition is given by the point P_0, and the composition corresponding to the trailing edge after crystallisation by the point p_0. The crystallisation at the beginning of the zone is represented by the line $\overline{P_0 p_0}$. The initial impurity fraction in the crystallisate is zero. The point characterising the zone composition is shifted, by the zone passage, from P_0, on the isotherm T, and reaches the point P_e when the co-ordinate $z = z_e$. Similarly the point p_0, characterising the composition of the solution layer adjacent to the trailing edge, is shifted on the isotherm t and reaches p_e when the co-ordinate $z = z_e$. Along the length z_e the impurity fraction in the crystallisate remains equal to zero, if crystallisation takes place in domain I.

The co-ordinate z_e can be determined with the aid of equation 31 by setting $Y = Y_e$ and replacing Y_0 by the value corresponding to the intersection of the straight line (D) with the straight line which determines the initial composition $Y = R_0 X$, namely $Y_0 = X_s/G$

$$\frac{z_e}{l} = \frac{G}{H} \ln \frac{Y_e + \dfrac{X_s - x_s}{H}}{\dfrac{X_s}{G} + \dfrac{X_s - x_s}{H}} \cdot \tag{33}$$

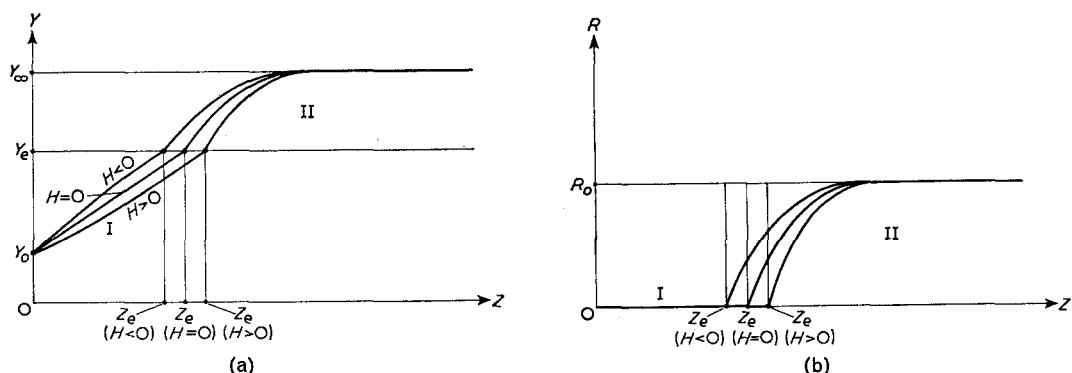For $H = 0$, i.e. for $M = m$ the relation 32 becomes a linear function

Figure 10 (a) The variation of the quantity of zone impurity as a function of the heater co-ordinate. (b) The distribution of the impurity/solute ratio in the crystallisate as a function of the heater co-ordinate behind the zone passage (A and B form an eutectic).

$$Y = Y_0 + \frac{X_s - x_s}{G} \frac{z}{\ell}$$

and the relation 33

$$\frac{z_e}{\ell} = \frac{GY_e - X_s}{X_s - x_s} = G \frac{Y_e - Y_0}{X_s - x_s} .$$

The co-ordinate Z_e can be expressed more simply by introducing into equation 30 the expression of dz as a function of dZ from the relation

$$dZ = \rho s \frac{\ell}{L} \frac{X - x}{\rho_A} dz$$

which becomes

$$dZ = \rho s \frac{\ell}{L} \frac{HY + (X_s - x_s)}{\rho_A} dz$$

and integrating as above, we obtain the expression

$$\frac{Z_e}{\ell} = \frac{\rho s}{\rho_A} (GY_e - X_s) .$$

Fig. 10 represents the variation of the quantity of impurity in the solution zone, and the impurity ratio in the crystallisate, as a function of the heater co-ordinate. According to equation 33 large values of z_e are obtained for high values of the difference $Y_e - Y_0$. If the initial impurity content is $R_0 > R_e = Y_e/X_e$ the $Y_0 > Y_e$ and z_e tends towards zero. To obtain high Y_e values which lead to large values of z_e, we shall choose (i) the dissolution temperature T near the solvent boiling temperature and (ii) the temperature difference, between the dissolution temperature and the crystallisation temperature, to be as small as possible.

Continuing the zone passage, the heater co-ordinate exceeds z_e, and the point representing the solution zone is shifted away from P_e, in the sense shown in fig. 3 on the straight line (D), thus leaving domain I, entering domain II.

When the heater co-ordinate tends to infinity the solution zone composition tends to a limit, represented by the point P∞. Within domain II, as distinct from domain I, the line totally characterising crystallisation ends at the invariant point p_e (represented by dots in fig. 3b). More exactly, only the solute A crystallises initially from the infinitesimal volume of solution in the vicinity of the trailing edge, which was cooled from temperature T to t. The temperature of the infinitesimal volume of solution reaches θ, $t < \theta < T$, and the point representing the composition of the solution during cooling is shifted, when z tends to infinity, from $P∞$ to $p∞$. Cooling from θ to t, mixtures of A and B of variable composition crystallise from the infinitesimal volume of solution. The point representing the solution composition on the curve, Γ, which gives the invariant compositions in the crystallisate, shifts on cooling from $p∞$ to p_e. The impurity fraction in the last crystallisate from the infinitesimal volume, $R_e/1 + R_e$, is obtained, according to fig. 3a at the intersection of the edge BA with the straight line $\overline{Sp_e}$.

The partial balance equations for the solute and impurity 3 and 4 are written in this case

$$s(X' - x_e) \frac{dz}{L} = s(X - x_e) \frac{dz}{L} + s dX \quad (34)$$

$$s(Y' - y_e) \frac{dz}{L} = s(Y - y_e) \frac{dz}{L} + s dY . \quad (35)$$

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Dividing equation 35 by equation 34 we obtain the equation

$$R_0(X - x_e)\frac{\mathrm{d}z}{L} + R_0\mathrm{d}X =$$

$$(Y - y_e)\frac{\mathrm{d}z}{L} + \mathrm{d}Y . \tag{36}$$

Replacing X in equation 36 as a function of Y, according to the equation of the straight line (D), equation 29, we obtain

$$\frac{\mathrm{d}Y}{G(Y - Y_e) - (X_e - x_e)} = -\frac{1}{G}\frac{\mathrm{d}z}{L} \tag{37}$$

where we have retained the significance of the notation used in equation 30 for the domain I. Equation 37 also enables us to determine, in this case, the manner in which the quantity of impurity from the solution zone varies as a function of the distance travelled by the heater. Integrating between limits, and retaining the approximation that L remains constant during the zone passage end equal to l, we obtain

$$\int_{Y_e}^{Y} \frac{\mathrm{d}Y}{G(Y - Y_e) - (X_e - x_e)} = -\frac{1}{G}\int_{z_e}^{z} \frac{\mathrm{d}z}{l}$$

$$\ln\left(1 - \frac{G(Y - Y_e)}{X_e - x_e}\right) = \frac{z_e - z}{l}$$

or writing Y as an explicit function of z

$$Y = Y_e + \frac{X_e - x_e}{G}\left(1 - \mathrm{e}^{\frac{z_e - z}{l}}\right) . \tag{38}$$

When z tends to infinity, Y tends to the limiting value

$$Y_\infty = Y_e + \frac{X_e - x_e}{G} < Y_E . \tag{39}$$

Fig. 10a represents the variation of the zone impurity contents as the heater advances for domain II, according to equation 38.

When the heater exceeds the co-ordinate z_e, the impurity ratio in the crystallisate ceases to be zero, because, according to the crystallisation scheme of the domain II, B, in addition to A, also crystallises. Thus,

$$R = \frac{(Y - y_e)\frac{s}{l}\mathrm{d}z}{(X - x_e)\frac{s}{l}\mathrm{d}z} = \frac{Y - Y_e}{X - x_e} =$$

$$\frac{Y - Y_e}{\dfrac{Y - Y_e}{M} + X_e - x_e} . \tag{40}$$

Inserting into relation 40 the expression for Y from relation 38 then

$$R = \frac{1}{\dfrac{1}{M} + \dfrac{G}{\dfrac{z_e - z}{1 - \mathrm{e}^{\frac{z_e - z}{l}}}}} . \tag{41}$$

Expression 41 shows that for values of z tending to infinity, the impurity ratio in the crystallisate tends to R_0.

To find impurity ratio distribution as a function of the trailing edge co-ordinate we must replace $\mathrm{d}z$ in equation 37 by its expression as a function of $\mathrm{d}Z$ from the relation

$$\mathrm{d}Z = \rho_S \frac{l}{L}\left(\frac{X - x_e}{\rho_A} + \frac{Y - y_e}{\rho_B}\right)\mathrm{d}z$$

which becomes
$$\mathrm{d}Z =$$

$$\frac{\rho_S}{\rho_A}\frac{l}{L}\left[\left(\frac{1}{M} + \frac{\rho_A}{\rho_B}\right)(Y - Y_e) + (X_e - x_e)\right]\mathrm{d}z$$

which we integrate as above. We obtain in this case as in section 2.1, a transcendent equation from which Y cannot be derived. However, insertion of values for ρ_A, ρ_B, ρ_S, M, R_0, L and (x_e, y_e) and consideration of equation 40 allow us to determine the impurity ratio distribution along the crystallisate.

The variation of the impurity ratio, as a function of the heater co-ordinate, has been derived in this section, proceeding from an initial impurity ratio in the solute of $R_0 < R_e < R_E = Y_E/X_E$. After a zone passage, beginning with the starting zone passage extremity, we can distinguish, in the crystallisate, a section I in which the impurity ratio is zero and a section II, in which the impurity ratio is less than that in the initial solute for a finite part of it. If however $R_e \leqslant R_0 < R_E$, then after the zone passage the impurity distribution corresponds only to that of section II. If in the solute $R_0 > R_E$ then all deductions remain as above, if we consider the solute as the impurity and conversely. If accidentally $R_0 = R_E$ then the impurity ratio in the substance remains unchanged after the zone passage. This case of inefficiency of the process may be avoided, however, by selecting a higher dissolution temperature T' such that $R_0' = R_E < R_E'$ (where we have denoted R' as the impurity ratio corresponding to the dissolution temperature T').

3. Multipass Impurity Distribution
3.1. A and B Form a Solid Solution

The THZR process efficiency improves, as does the ZM process, when the zone passage is repeated a number of times. In the following we shall try to find the distribution of the impurity ratio in the crystallisate after n zone passages as a function of the heater co-ordinate z by considering, for each zone passage, the crystallisate extremity at which the zone passage begins. We shall retain the significance of the notation used in section 2, but introduce the subscript n, which indicates the zone passage rank. We shall keep all the assumptions and approximations made for a single zone passage in section 2.1. In addition we shall assume that, for $z = 0$, the impurity ratio in the n-th zone is equal to the impurity ratio in the crystallisate at the co-ordinate $z = 0$ from zone passage n-1

$$\left(\frac{Y_n}{X_n}\right)_{z=0} = R_{n-1}(0) \cdot \tag{42}$$

That is, we do not introduce pure solvent zones at the zone passage starting extremity, but instead, solution zones containing both solute and impurity, so that the impurity ratio in the solution is equal to the impurity ratio in the crystallisate with which it comes into contact. The zone does not dissolve the crystallisate. Because, in practice, we work with pure solvent zones for reasons in addition to those mentioned in the introduction, the impurity ratio values in the crystallisate, given by the distributions derived in the following, must be consequently considered as ideal values.

To find the impurity ratio distribution along the crystallisate behind the rank n zone passage $R_n(z)$, we shall proceed from relation 15, which for the n-th zone passage is,

$$R_n(z) = k \frac{Y_n}{X_n} \cdot \tag{43}$$

The material partial balance equations 3 and 4 for the n-th zone passage are

$$s(X'_n - x_n)\frac{dz}{L} = s(X_n - x_n)\frac{dz}{L} + s\,dX_n \tag{44}$$

$$s(Y'_n - y_n)\frac{dz}{L} = s(Y_n - y_n)\frac{dz}{L} + s\,dY_n \ . \tag{45}$$

Dividing equation 45 by equation 44 and replacing x_n and y_n by their values as a function of X_n and Y_n, from transformation relation 1, we obtain

$$R_{n-1}(z) = \frac{\left(1 - \frac{1}{\beta}\right)Y_n\,dz + L\,dY_n}{\left(1 - \frac{1}{\alpha}\right)X_n\,dz + L\,dX_n} \tag{46}$$

The impurity and solute quantities, related to the solvent quantity in the solution zone for the n-th zone passage, must satisfy the equation of the straight line (D), equation 7, i.e.

$$X_n = \frac{Y_n}{M} + X_s \cdot \tag{47}$$

Eliminating X_n and Y_n between relations 43, 46 and 47 and replacing in the relation thus obtained, the differential dY_n by a function of differential dR_n, resulting from the differentiation of equation 42, and taking into account the condition $dY_n = M\,dX_n$ we obtain the differential equation

$$(R_{n-1} - M)\frac{dR_n}{dz'} + R_n{}^2 - (R_{n-1} + kM)R_n +$$
$$kMR_{n-1} = 0 \tag{48}$$

with the initial condition

$$R_n(0) = k^n R_0$$

which resulted from relation 42. The differential equation 48 is a recurrent differential equation of the Riccati type which governs the impurity ratio distribution in the crystallisate after the n-th zone passage. Making the substitution

$$R(z') = kM + \frac{1}{r_n(z')} \tag{49}$$

we obtain the differential equation

$$\frac{dr_n}{dz'} + h_n r_n - \frac{1}{R_{n-1} - M} = 0 \tag{50}$$

where we have denoted

$$h_n = \frac{R_{n-1} - kM}{R_{n-1} - M}$$

with the initial condition

$$r_n(0) = \frac{1}{k(k^{n-1}R_0 - M)} \cdot \tag{51}$$

The differential equation 50 is a linear differential equation, which, when integrated with the initial condition 51, leads to the solution

$$R_n(z') = kM + \frac{\int_0^{z'} h_n\,dz'}{C_n + \int_0^{z'} \frac{\int_0^{z'} h_n\,dz'}{R_{n-1} - M}\,dz'} \tag{52}$$
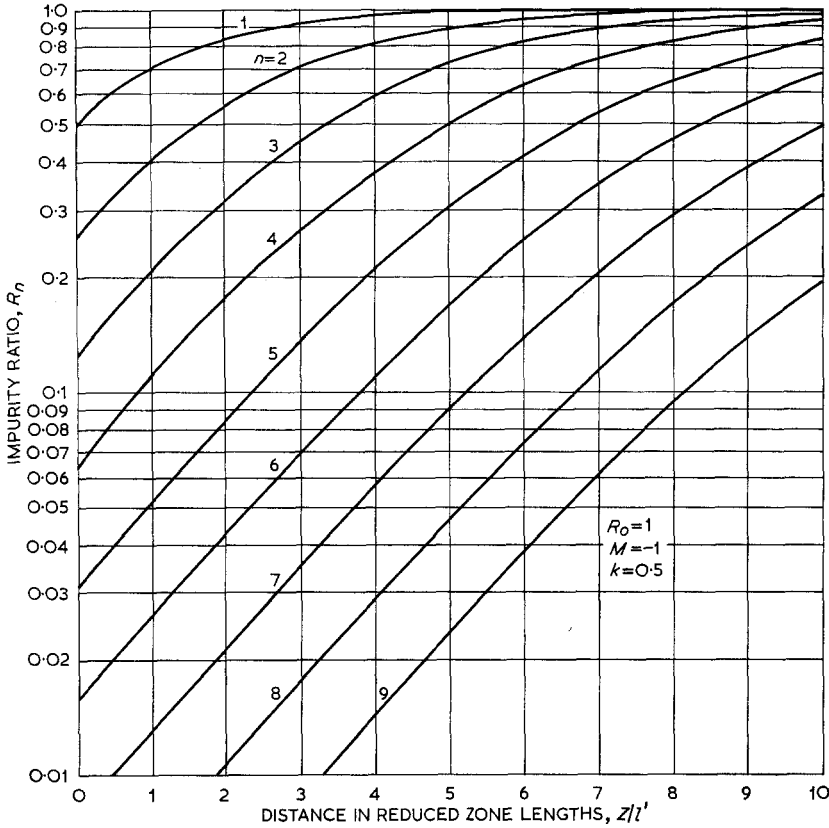
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Figure 11 The distribution of the impurity ratio along the crystallisate behind the first nine zone passages (A and B form a solid solution).
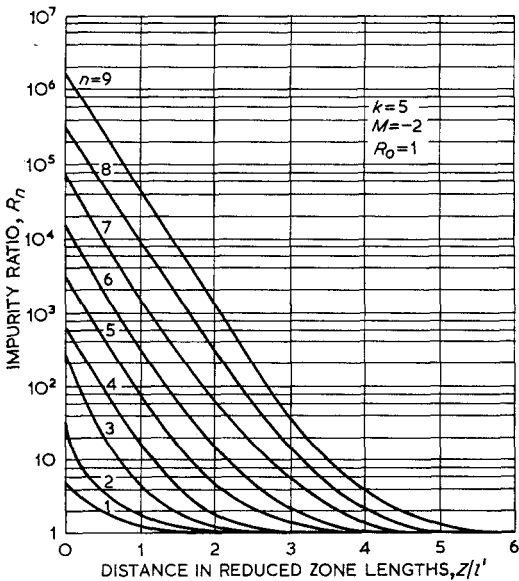

Figure 12 The distribution of the impurity ratio along the crystallisate behind the first nine zone passages (A and B form a solid solution).

where the integration constant, C_n, must be determined for the initial condition for each n. We have obtained a recurrence integral equation which gives R_n, when R_{n-1} is known. When $n = 1$, then R_{n-1} is equal to R_0 and R_1, known from section 2.1, is obtained. For $n > 1$, equation 52 becomes more and more complicated with increasing values of n, and the analytical solution becomes impossible. An exact solution, as a series with exponential terms similar to that found by Lord [14] for the concentration distribution in the Z M process, cannot be found in this case.

Fig. 11 represents the solutions R_{1-9} obtained from equation 52, as a function of the number of reduced zone lengths, by means of a computer for $k = 0.5$ and $M = -1$ starting from $R_0 = 1$, while fig. 12 represents the same solutions but for $k = 5$, $M = -2$, also starting from $R_0 = 1$. The exact solution 52 is only convenient for small values of n. If however we wish to find the impurity ratio distribution in the crystallisate for higher values of n, then solution 52 is no

longer practical. For finding suitable approximate solutions for higher numbers of n we shall proceed as Reiss [15]. We shall consider the subscript n as a continuous variable and the sequence of functions, $R_n(z')$, as a two-variable function $R(z', n)$. Replacing $R_{n-1}(z')$ in equation 48 by the first two terms of its development into a Taylor series about (z', n)

$$R_{n-1}(z') = R(z', n-1) =$$
$$R(z', n) - \frac{\partial R(z', n)}{\partial n} \quad (53)$$

we obtain the first-order partial differential equation

$$\frac{\partial R}{\partial n} \frac{\partial R}{\partial z'} - (R - M)\frac{\partial R}{\partial z'} - (R - kM)\frac{\partial R}{\partial n} = 0 \quad (54)$$

the solutions of which have to fulfil the initial condition

$$R(z', 0) = R_0 \quad (55)$$

and the boundary conditions

$$R(0, n) = k^n R_0 \text{ and } R(\infty, n) = R_0 . \quad (56)$$

The distribution given by the complete integral of the differential equation 54 departs, however, too much from the exact distribution calculated from equation 52, being incompatible with the boundary conditions and with the initial condition of the problem. However, we can use the approximate solution,

$$R = R_0[1 - (1 - k^n)\, e^{-kz'}] \quad (57)$$

which is an exponential function with a linear exponent with respect to the variables z' and n, as the complete integral of the differential equation 54, but which satisfies the boundary conditions and the initial condition of the problem.

From the application point of view, due to the boundary condition

$$\frac{d\, Rn(0)}{dz'} = k^n(1 - k)R_0 \quad (58)$$

which is obtained from equation 48 and from the first boundary condition 56, it is apparent that the case $k > 1$ is unfavourable for the THZR process as well as for the ZM process. Unlike the ZM process, the THZR process does not form a limiting distribution with an increase in the number of zone passages.

3.2. A and B Form an Eutectic

We shall try now to find the impurity ratio distribution along the crystallisate after n zone passages, considering the impurity ratio in the initial solute as being $R_0 > R_e$.

Equation 34 and 35 from section 2.2, for domain II, written for the n-th zone passage are

$$s(X'_n - x_e)\frac{dz}{L} = s(X_n - x_e)\frac{dz}{L} + sdX_n \quad (59)$$

$$s(Y'_n - y_n)\frac{dz}{L} = s(Y_n - y_e)\frac{dz}{L} + sdY_n . \quad (60)$$

Dividing equation 60 by equation 59 we obtain

$$R_{n-1}(z) = \frac{(Y_n - y_e)\, dz + L\, dY_n}{(X_n - x_e)\, dz + L\, dX_n} . \quad (61)$$

Relation 40 is

$$R_n(z) = \frac{Y_n - y_e}{X_n - x_e} \quad (62)$$

and equation 29, of the straight line (D), is written more suitably in the form

$$Y_n - Y_e = M(X_n - X_e) . \quad (63)$$

Eliminating X_n and Y_n between equations 61, 62 and 63, we obtain the differential recurrent equation

$$(R_{n-1} - M)\frac{dR_n}{dz'} + R_n^2 - (R_{n-1} + M)R_n +$$
$$MR_{n-1} = 0 \quad (64)$$

where the reduced co-ordinate $z' = z/l$.

This first order differential equation of Riccati type is identical to equation 48 from section 3.1 for $k = 1$. But the initial condition for equation 64

$$R_n(0) = \frac{M(R_{n-1}(0) - R_e)}{\frac{x_e}{X_e} R_{n-1}(0) - R_e + M\left(1 - \frac{x_e}{X_e}\right)} \quad (65)$$

is obtained in a recurrent form from condition 42. The general solution of the problem is obtained from the solution of equation 52 in which we set $k = 1$

$$R_n(z) = M + \frac{e^{z'}}{C_n + \int_0^{z'} \frac{e^{z'}}{R_{n-1} - M}\, dz'} \quad (66)$$

where C_n must be determined, taking into account the initial condition 65, for each n. In this way we can obtain the solutions up to $n = q$ for which $R_q(0) < R_e < R_{q-1}(0)$. The impurity ratio distributions along the crystallisate, beginning with R_{q+1}, may be obtained in another way, namely

$$R_n(z') = 0 \text{ for } z' < z'_{n,e}, n \geqslant q + 1 \qquad (67)$$

and

$$R_n(z') =$$

$$M + \cfrac{e^{z'-z'_{n,e}}}{C_n + \displaystyle\int_0^{z'} \cfrac{e^{z'-z'_{n,e}}}{R_{n-1} - M} dz'},$$

$$z' > z'_{n,e}, n \geqslant q + 1 \qquad (68)$$

with the initial condition $R(z'_{n,e}) = 0$, which determines the constant C_n for each n. In order to find the sequence $z'_{n,e}$ let us consider the differential equation 30 applied to the zone passage of rank n

$$\frac{1}{G_n} dz' = \frac{dY_n}{HY_n + (X_s - x_s)} \qquad (69)$$

where

$$G_n = \left(\frac{1}{R_{n-1}} - \frac{1}{M}\right).$$

Integrating between limits we obtain

$$\int_0^{z'_{n,e}} \frac{1}{G_n} dz' = \int_{Y_{n-1}(0)}^{Y_e} \frac{dY_n}{HY_n + (X_s - x_s)}$$

i.e.

$$\int_0^{z'_{n,e}} \frac{1}{G_n} dz' = \frac{1}{H} \ln \frac{HY_e + X_s - x_s}{HY_{n-1}(0) + X_s - x_s}.$$
$$(70)$$

For $n \geqslant q + 2$, the right hand side of equation 70 remains constant because $Y_{n-1}(0) = 0$; the function $1/G_n$ is obtained from $1/G_{n-1}$ by the translation $z' = z' + z'_{n-1,e}$ which leads to a constant value for the difference

$$\Delta z'_{n,e} = z'_{n,e} - z'_{n-1,e}. \qquad (71)$$

In addition $R_{n-1}(z') \cong R_0$ for $n \geqslant q + 2$ so that $R_{n+1}(z')$ is also obtained from R_n by the same translation. Consequently, beginning with the rank $q + 3$ of zone passage it is advantageous to begin the zone passage from the co-ordinates $z'_{q+3,e}, z'_{q+4,e}, \ldots$ and to collect successively the crystallisate present up to these co-ordinates as a pure finite solute.

Fig. 13 represents the variation of the impurity ratio along the crystallisate behind four zone passages for the case for $p_e(4,5)$, $P_E(5,6)$, $x_s(8)$, $X_s(11)$ and $R_0 = 1$. The curves from fig. 13 are obtained graphically.

4. Conclusions
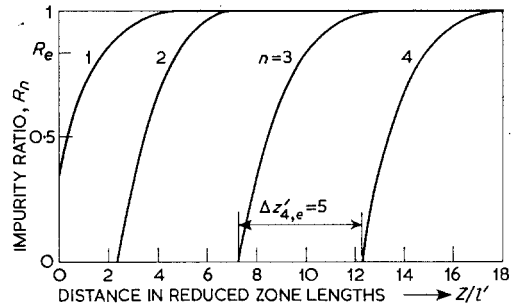From the foregoing theoretical analysis of the THZR process we may draw the following conclusions:

Figure 13 The distribution of the impurity ratio along the crystallisate behind the first four repeated zone passages (A and B form an eutectic).

(i) The process is particularly advantageous for solutes which form eutectics with the impurities, a frequent case in the field of inorganic salts.
(ii) The process is suitable for the purification of solutes that form solid solutions with the impurities since they permit $k < 1$ to be as far as possible from unity.

When the substance and the impurity form either an eutectic or a solid solution it is convenient to select a high dissolution temperature near the solvent boiling temperature and a crystallisation temperature as near as possible to the dissolution temperature.

Notation
A – the solute
B – the impurity
S – the solvent
ρ_A, ρ_B, ρ_S – the solute, impurity and solvent densities
t – the crystallisation temperature
T – the dissolution temperature
z – the co-ordinate of the heater
Z – the co-ordinate of the trailing edge
z' – the reduced co-ordinate of the heater
l' or subscript $_l$ – the solvent zone length
l' or subscript $_{l'}$ – the solvent reduced zone length
L – the solution zone length
L' – the solution reduced zone length
a – the quantity of solute dissolved in the solvent zone
b – the quantity of impurity dissolved in the solvent zone
s – the quantity of zone solvent
a_s – the quantity of solute dissolved, at saturation, in the solvent zone, at the crystallisation temperature, and in the absence of impurity
A_s – *idem*, but at the dissolution temperature
b_s – the impurity quantity dissolved, at satura-

tion, in the solvent zone, at the crystallisation temperature and in the absence of solute

B_s – *idem*, but at the dissolution temperature

x – the gravimetric ratio between the quantity of solute dissolved in the solvent zone (at saturation, and at the crystallisation temperature) and the solvent zone quantity

X – *idem*, but at the dissolution temperature

x_s, X_s – the same significance as x and X but in the absence of impurity

y – the gravimetric ratio between the quantity of impurity dissolved in the solvent zone (at saturation, and at the crystallisation temperature) and the zone solvent quantity

Y – *idem*, but at the dissolution temperature

Y_0 – *idem*, for $z = 0$

y_s, Y_s – the same significance as y and Y but in the absence of solute

g_A – the experimental function that gives the solubility of the solute in the solvent as a gravimetric ratio, in the absence of impurity, as a function of temperature

g_B – the experimental function that gives the solubility of the impurity in the solvent as a gravimetric ratio, in the absence of solute, and as a function of temperature

mt – the solvent melting temperature

bt – the solvent boiling temperature

α, β – proportionality coefficients of solubility for the solute and impurity, respectively

(D) – the dissolution straight line

(d) – the crystallisation straight line

M – the slope of the dissolution line

m – the slope of the crystallisation line

k – the impurity distribution coefficient between the crystallisate and the solution zone

h – the exponential function constant

R – the gravimetric ratio impurity/solute in the crystallisate

R_0, R_e, R_E – *idem*, but in the zone solution corresponding to the points P_0, P_e and P_E

Γ – the curve described by the return point of the saturation solubility isotherms as a function of the temperature for the case when A and B form an eutectic

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