ON THE THEORY OF ZONE MELTING

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The problem concerning shape of the curve of distribution of solutes along the charge during zone melting for the case, when the distribution coefficient value changes in the course of zone melting, has been solved using the method of material balance, and the possibility to increase the purification effect by suitable selection of the zone length, double-pass and multi-pass zone meltings, particularly under intermittent motion, has been considered.

Zone melting is a method of purification, based on the fact that first portions of the solid phase crystallizing by cooling from a molten mixture in which the solvent highly predominates and all other components are the solutes, differ in the content of solutes from that of the liquid phase. Practical separation of first crystallizing fractions from the main body of liquid is in this method achieved by leaving the solid phase to crystallize from a molten zone which slowly passes through a longitudinal charge of the substance to be purified. By repeating the passes, accumulation of the solute at one end of the charge takes place. For the purification effect of the zone melting, most important is the distribution of solutes along the charge, which depends on the distribution coefficient value and alters with each zone pass till it attains ultimate distribution no more changing with further passes. Fundamentals of the theory of zone melting have been reported by Pfann[1,2], some extension essentially starting from the Pfann theory has been made by many authors[3-11], who at the same time mentioned some further relations. A considerable contribution to mathematical theory on the distribution of solutes along the charge in the zone melting is the paper of Matz[12]. Pfann[1,2] characterizes distribution of solutes between the solid and liquid phases which coexist in equilibrium, by the equilibrium distribution coefficient

$$k = c_S / c_L \,, \tag{1}$$

where c_S and c_L are the concentrations of solute in the solid and liquid phases, resp. The amount of solute in the molten zone either increases ($k < 1$) or decreases ($k > 1$) during the zone pass along the charge, and more rapidly, the greater is the difference from unity and the shorter is the length of the molten zone l. After the first pass ($n = 1$), the concentration of solute at point x of the charge having length L, is given according to Pfann by

$$c_{S,x,1} = c_0[1 - (1 - k)\,e^{-kx/l}] \,, \tag{2a}$$

in which c_0 is initial concentration of the solute. After n zone passes, the concentration of the solute is given by

$$c_{S,x,n} = c_{S,x,n-1}[1 - (1 - k)\,e^{-kx/l}] \tag{2b}$$

and after a sufficiently high number of passes, we obtain ultimate distribution

$$c_{S,x} = c_0 A\, e^{Bx}\,, \tag{2c}$$

where A and B are the constants which relate to the distribution coefficient k, molten zone length l, and charge length L according to relations

$$k = B\,.\,l(e^{Bl} - 1)\,, \tag{3a}$$

$$A = B\,.\,L(e^{BL} - 1)\,. \tag{3b}$$

The ultimate distribution is produced as a consequence of attaining equilibrium between the transport of solutes in the direction of the zone movement ($k < 1$) or in the opposite direction ($k > 1$), and the back diffusion of the solute within the zone length; the diffusion works against the transport of solutes ($k < 1$) or the component purified ($k > 1$) along the molten zone.

Relations (*2a,b,c*), can be considered valid for certain boundary conditions only and the expression which agrees with the distribution of solutes in a wide range of conditions[12] is rather complicated. In general, most valid are the calculations that are based on the material balance; here, minimum of simplifying assumptions have been applied.

The model of zone melting, which permits calculation of the material balance and is valid over a wide range of conditions capable of being technically carried out, is following: during the motion of a molten zone, restricted by planparallel interfaces of length l, the same amount of solid phase as is melted at the melting interface at the point between $(x + l)$ and $(x + l + dx)$, crystallizes out at the freezing interface in the course of the n-th pass to advance a small distant dx from point x to $(x + dx)$ through the charge whose cross-section is unity. Initial solute concentration, in the molten zone $c_{L,n,x}$ will be lowered by the concentration of the solute in the solid phase, crystallizing out at the freezing interface $c_{S,n,x}$ and will increase on account of the concentration, of the solute contained in the solid phase which melts at the melting interface $c_{S,n-1,x}$. This model makes it possible to calculate the material balance along the whole charge of length L, for d cells of unit cross-section of lengths dx for the case when $dx = L/d$.

The possibility of determining the distribution of solutes along the charge in zone melting with use of the material balance method has been reported by Pfann[2], mentioning that Hamming proceeded in the same way when computing the distribution curves. These curves, however, are determined under equal conditions under which even the Pfann relationship (*2a,b,c*) was derived, *i.e.* under the assumption that the distribution coefficient, remains constant during the operation and that the zone melting with single zone and at constant length of the zone is carried out. The change in the distribution coefficient value during zone refining is referred to by Kirgincev[13] or Matz[12]. Other papers[14] show that change in the zone length during single-pass and multipass zone meltings may favourably affect the purification effect and yield of refining.

We make use of somewhat modified method of material balance for our calculations, based on the given model. The method permits to determine the distribution of solutes along the charge for an arbitrary length of the molten zone, which changes after individual zone passes, for a simultaneous zone melting with an arbitrary number of molten zones, provided that the distribution coefficient definably changes with the concentration of solutes. The calculations were carried out on a digital computer NE 803 in the Computer Centre of the firm Chemoprojekt, Prague. They aimed at checking up the effect of variability of the distribution coefficient, of the change in zone length and number of zones simultaneously used for the zone melting, on the distribution of solutes along the charge, and at finding conditions under which the purification effect and yield of refining is maximum.

Program for Computing the Distribution of Solutes along the Charge

The principle of the material balance method as was used by Hamming in his calculations, has been reported[2]. Contrary to Hamming who calculated mean concentration of solutes inside each elementary volume (cell), we calculate concentration of the solute at the beginning and at the end of individual cells (*i.e.* we have $d + 1$ computational places for d cells) and assume that freezing inside the cells proceeds, so that a linear concentration gradient between the concentration, $c_{S,n,x}$, at the beginning of the cell and that at its end, $c_{S,n,x+1}$, is formed. The broken line thus produced fits the assumed continuous distribution curve well.

The concentration of solutes in the solid phase is calculated according to relations: for the first point

$$c_{S,n,0} = \frac{k}{q}\left[\tfrac{1}{2}(c_{S,n-1,0} + c_{S,n-1,q}) + \sum_{i=1}^{q} c_{S,n-1,x_i}\right] \tag{4a}$$

for points from 1 to $d - 2q$

$$c_{S,n,x} = \frac{2q - k}{2q + k}\, c_{S,n,x-1} + \frac{k}{2q + k}\left(c_{S,n-1,x-1+q} + c_{S,n-1,x+q}\right) \tag{4b}$$

for points from $d - 2q + 1$ to $d - q$

$$\begin{aligned} c_{S,n,d-2q+1} &= c_{S,n,d-2q}\,\frac{2q - k}{2q + k} + c_{S,n-1,d}\,\frac{2k}{2q + k} \\ &\vdots \\ c_{S,n,d-q} &= c_{S,n,d-q-1}\,\frac{2q - k}{2q + k} + c_{S,n-1,d}\,\frac{2k}{2q + k} \end{aligned} \tag{4c}$$

and for points from $d - q + 1$ to d

$$c_{S,n,d-q+1} = c_{S,n,d-q+2} = \ldots = c_{S,n,d} = \frac{1}{k}\, c_{S,n,d-q} \tag{4d}$$

In these calculations, length of the molten zone is chosen as to be expressed as total multiple (q) of the cells, consequently, so as to give $l = qL/d$. The accuracy of the calculation was checked by summation check criterion

$$\frac{1}{d} \sum_{i+1}^{d} c_{S,n,x_i} = 1 \,. \tag{5}$$

In order to determine the distribution coefficient value k as dependent on the concentration c, of a solute in the liquid, the value was calculated using c_L from the preceding cell. This procedure can be accepted if a small change in k is due to a change in c_L but where the k value changes with the change in c_L more considerably the summation check (5) suggested a not quite correct calculation of the material balance. The k_1 value was therefore preliminary determined from the c_L value of the preceding cell, by means of k_1 the c_S value was calculated from which c_L was derived and the distribution coefficient k_2 again determined. This iteration was carried out so long till relative difference for two successive c_S values was less than 10^{-2} or 10^{-3}. The mean number of iterations was printed for each zone pass. Thus it could be achieved that the checking according to (5) pointed to the accuracy of the balance. The program is highly variable and permits a series of alternatives: *1*. The distribution coefficient k *a*) is constant during the calculation, *b*) changes continuously with the concentration of solutes in the liquid phase, the functional dependence having shape of linear, general quadratic or cubic equations, *c*) changes continuously as in the foregoing item, but merely up to a certain upper limit which represents maximum value of the distribution coefficient, *d*) changes in jumps on attaining a certain limiting concentration of the solute in the liquid phase. *2*. Number of computational places varies from 3 to 1 000. *3*. Molten zone length may be selected over the range $1 \leq q \leq d - q - 1$, where q is the number of computational places contained in the molten zone. *4*. Molten zone length can be varied on finishing any of the zone passes. *5*. Calculation can be put to an end either on finishing certain number of passes or on attaining the chosen, sufficiently low concentration of the solute at the beginning of the charge. *6*. Print out of the results can be selected, so that a desired number of the concentration data should be printed in semi-logarithmic or decimal form, either for all zone passes or for the selected ones only. As input values for each pass an arbitrary initial distribution of solutes in the charge or that calculated in the foregoing pass is inserted, which permits to model, for example, double-pass or multipass zone melting.

Number, d, of computational places is responsible for precision of the calculation of the distribution by the material balance method: usually $d = 50$ to 100 is sufficient and the computation is fairly rapid. For a low number of computational places, a less favourable distribution is obtained (c_S is higher at the beginning of the charge and lower at the end). A comparison of calculated values for $k = 0{\cdot}3 + 0{\cdot}4c_L -$

$- 0{\cdot}05\, c_{\mathrm{L}}^2$ and $n = 10$ by means of iterations (for a relative difference of 10^{-2} and 10^{-3}) and the data on the time of computation using both methods, together with the values calculated by Hamming[2], are summarized in Table I.

Effect of Change in the Distribution Coefficient on the Shape of Distribution

Matz[12] determined dependence of k on the concentration, of the solute, the $k < 1$ value rising with the increasing concentration of the solute. The shape of the distribution is for various cases of the change in the distribution coefficient with concentration

TABLE I

Comparison of Precision and Rate of Computing

Number of computational places	Hamming			This paper						
				without iterations			with iterations			
	c_{S}, start	c_{S}, end	time, s	c_{S}, start	c_{S}, end	time s	c_{S}, start	c_{S}, end	iterat end	time s
10	—	—	—	0·068	2·42	23	0·027	2·23	10^{-3}	40
20	—	—	—	0·038	2·23	35	0·025	2·20	10^{-3}	55
	—	—	—	—	—	—	0·026	2·19	10^{-2}	45
50	0·016	2·25	42	0·029	2·21	65	0·025	2·19	10^{-3}	98
	—	—	—	—	—	—	0·025	2·19	10^{-2}	80
100	0·020	2·22	75	0·027	2·21	115	0·025	2·19	10^{-3}	145
200	0·023	2·21	137	—	—	—	—	—	—	—
500	0·024	2·20	325	—	—	—	—	—	—	—
1 000	0·025	2·19	630	—	—	—	—	—	—	—

TABLE II

Yield of Zone Refining after 10 and 20 Passes for Various or Variably Changing Values of the Distribution Coefficient, in Per Cent of the Charge

c_{S}/c_0	$k = 0{\cdot}3$		$k = 0{\cdot}5$		$k = 0{\cdot}3 + 0{\cdot}2c_{\mathrm{L}}$		$k = 0{\cdot}3 + 0{\cdot}4c_{\mathrm{L}} - 0{\cdot}05c_{\mathrm{L}}^2$		$k = 0{\cdot}3 + 0{\cdot}4c_{\mathrm{L}}^2$	
	10	20	10	20	10	20	10	20	10	20
10^{-1}	75·0	79·2	29·2	62·5	33·3	52·1	12·5	35·4	5·8	14·2
10^{-2}	45·8	66·7	—	29·2	—	41·6	—	20·8	—	3·3
10^{-3}	8·3	41·6	—	—	—	27·1	—	4·1	—	—

of the solute in the liquid phase graphically presented in Fig. 1. In Fig. 1*a*,*b* *k* is constant, in 1*c*, linear change in *k* is considered, and in Fig. 1*d*,*e*, the distribution curves for two different cases of the change of *k* with c_L are recorded, while for $c_L = 0$, *k* is always equal to 0·3, and for higher c_L values it approaches unity at varying rate. In Table II, efficiency of the zone melting is expressed in per cent of the charge which is purified to various c_S/c_0 values for $n = 10$ and 20 and for various cases of the change in *k*.

Another case of the change in the distribution coefficient during zone melting can be considered. In the course of the zone melting, conditions similar to those of the Bridgmann method of pulling a single crystal (slow shift of the sharp temperature gradient with the edge values above and below the melting point and contact of the liquid phase with the solid one) sometimes rule at the freezing interface, so that a single crystal is built up behind the freezing interface, provided that conditions even as regards the zone-refined substance had been fulfilled. Formation of a single crystal, however, can be dependent even on the attaining of certain purity. For this case, two models may be accepted, which can be realized by means of the following program:

1. With the c_L value decreasing to a limiting concentration $c_{L,\mathrm{lim}}$, the distribution coefficient k_1 changes in jump to k_2, while $k_1 > k_2$ (for $k < 1$).

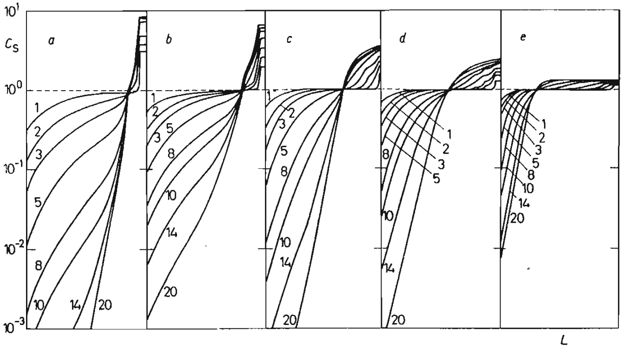

FIG. 1

Dependence of the Shape of Distribution on the Distribution Coefficient Value after One, Two, Five, Ten, and Twenty Passes

a $k = 0·3 =$ const.; *b* $k = 0·5 =$ const.; *c* $k = 0·3 + 0·2c_L$ – linear dependence of *k* on *c*; *d* $k = 0·3 + 0·4c_L - 0·05c_L^2$ – convex curved dependence of *k* on c_L; *e* $k = 0·3 + 0·4c^2$ – concave curved dependence of *k* on c_L.

2. The distribution coefficient remains constant until c_L decreases to $c_{L,\mathrm{lim}}$, afterwards, it commences to change with concentration c_L. The yield of zone refining for different k_1, k_2, and $c_{L,\mathrm{lim}}$ values after twenty zone passes is presented in Table III.

TABLE III

Yield of Zone Refining after 20 Passes for the Change of k_1 into k_2 at $c_{L,\mathrm{lim}}$

c_S/c_0	$k_1 = 0{\cdot}7$ $k_2 = 0{\cdot}3$ $c_{L,\mathrm{lim}} = 0{\cdot}1$	$k_1 = 0{\cdot}7$ $k_2 = 0{\cdot}3$ $c_{L,\mathrm{lim}} = 0{\cdot}8$	$k_1 = 0{\cdot}5$ $k_2 = 0{\cdot}3$ $c_{L,\mathrm{lim}} = 0{\cdot}8$	$k_1 = 0{\cdot}7$ $k_2 = 0{\cdot}3 + 0{\cdot}4c_L - 0{\cdot}05c_L^2$ $c_{L,\mathrm{lim}} = 1{\cdot}15$	$k_1 = 0{\cdot}7$ $k_2 = 0{\cdot}3 + 0{,}5c^2$ $c_{L,\mathrm{lim}} = 0{\cdot}285$
10^{-1}	13·8	44·3	62·3	41·5	27·2
10^{-2}	—	23·1	52·3	24·0	10·4
10^{-3}	—	6·9	38·8	4·7	—
10^{-4}	—	—	22·3	—	—

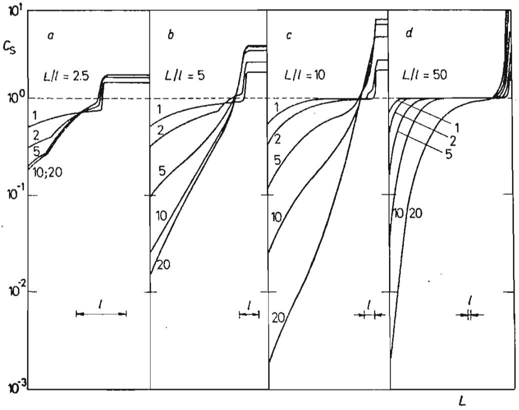

FIG. 2

Effect of Zone Length on Shape of Distribution after One, Two, Five, Ten, and Twenty Passes at the Constant Distribution Coefficient $k = 0{\cdot}5$

Ratio L/l: *a* 2·5; *b* 5·0; *c* 10; *d* 50.

It is evident that in cases, when the single crystal is formed and $k_2 \ll k_1$, distinct purification effect at the beginning of the charge may be achieved, but the yield is for a smaller number of zone passes fairly low, particularly if $c_0 \gg c_{L,\mathrm{lim}}$. In practice, longer zone melting must be carried out.

Effect of Length of the Molten Zone

The shape of the distribution for various values of the zone length expressed in term of ratio L/l, and for constant $k = 0{\cdot}5$ is graphically presented in Fig. 2. It follows from this figure as well as from Table IV that neither an extremely short, nor an extremely long zone should be used. Nevertheless, in addition to the absolute concentration value of the solute, even the change in the concentration must be taken into account when considering optimum zone length, for it is evident from the relationship for calculating the material balance (*4a* to *d*) that for different q values, the concentration effect of the solute in the solid phase in a fraction of the charge before the melting interface, *i.e.* the distribution which had been produced in the preceding zone pass, is applied in a different manner. Because of the distribution being changed during the zone melting both within single zone pass of the charge and in some part of the charge after separate zone passes, it is evident that two cases of the change in the zone length must be considered:

1. Zone length is constant within a certain pass, but it changes on finishing individual passes.

2. During each pass the zone length is changed in a definite way which is equal for all zone passes.

The effect of a change in the zone length during the pass will be noted in connection with multipass zone melting carried out by means of more than one zone under

TABLE IV

Yield of Total Charge in Per Cent for Various L/l Values, $k = 0{\cdot}5$, $n = 20$

c_S/c_0	L/l						
	2·5	5	10	20	50	[a]	[b]
$5 \cdot 10^{-1}$	32·0	60·8	72·0	80·0	43·2	80·0	80·0
10^{-1}	—	32·0	62·5	56·0	22·4	65·6	67·2
10^{-2}	—	—	29·2	18·4	4·7	25·6	30·4
10^{-3}	—	—	—	—	—	2·4	3·2

[a] For $n = 1$ to 2, $L/l = 2{\cdot}5$, for $n = 3$ to 7, $L/l = 10$, and for $n = 8$ to 20, $L/l = 20$. [b] For $n = 1$ to 3, $L/l = 5$, for $n = 4$ to 9, $L/l = 10$, for $n = 10$ to 15, $L/l = 12{\cdot}5$, and for $n = 16$ to 20, $L/l = 17$.

intermittent motion. The effect of the change in zone length for $k > 1$ was followed experimentally[9,14]. The effect achieved by using longer zone during first passes, and a shorter one only after some purification during further passes, may be rather distinct. This can be confirmed by the results given in Tables IV, V, and VI. Hence, it also follows that changing the zone length several times during the zone melting is more suitable than to exchange extremely long zone directly for a very short one.

TABLE V

Yield of Total Charge in Per Cent for the Distribution Coefficient Dependent on c_L and for Various L/l Values

c_S/c_0	$k = 0{\cdot}3 + 0{\cdot}4c_L^2$				$k = 0{\cdot}3 + 0{\cdot}4c_L - 0{\cdot}05c_L^2$						
	10	[a]	[b]	[c]	2·5	6	10	17	25	50	[d]
$5 . 10^{-1}$	24·2	22·9	24·2	22·1	20·0	40·0	48·8	36·6	25·6	43·2	48·7
10^{-1}	14·2	20·4	20·0	16·7	—	22·4	35·2	25·6	16·7	8·0	36·8
10^{-2}	3·3	14·2	15·2	10·4	—	4·8	17·6	12·7	8·7	4·8	26·3
10^{-3}	—	7·5	7·9	3·3	—	—	3·1	2·2	1·8	1·2	17·6
10^{-4}	—	—	—	—	—	—	—	—	—	—	6·4

[a] For $n = 1$ and 2, $L/l = 2{\cdot}5$, for $n = 3$ to 7, $L/l = 10$, and for $n = 8$ to 20, $L/l = 20$; [b] For $n = 1$ to 4, $L/l = 5$, for $n = 5$ to 9, $L/l = 10$, and for $n = 10$ to 20, $L/l = 20$; [c] For $n = 1$ to 7, $L/l = 2{\cdot}5$ and for $n = 8$ to 20, $L/l = 20$; [d] For $n = 1$ and 2, $L/l = 3$, for $n = 3$ to 5, $L/l = 6$, for $n = 6$ to 10, $L/l = 12$, and for $n = 11$ to 20, $L/l = 50$.

TABLE VI

Yield of the Charge in Per Cent for Change of k_1 into k_2 ($c_{L,\text{lim}} = 0{\cdot}8$) for Various L/l Values

c_S/c_L	$k_1 = 0{\cdot}5$; $k_2 = 0{\cdot}3$		$k_1 = 0{\cdot}7$; $k_2 = 0{\cdot}3$	
	10	[a]	10	[a]
$5 . 10^{-1}$	76·0	84·0	54·2	51·2
10^{-1}	62·3	73·1	44·3	44·6
10^{-2}	52·3	63·8	23·1	30·7
10^{-3}	38·8	51·9	6·9	18·3
10^{-4}	22·3	32·3	—	7·7

[a] For $n = 1$ and 2, $L/l = 2{\cdot}5$, for $n = 3$ to 7, $L/l = 10$, and for $n = 8$ to 20, $L/l = 20$.

Double Zone Melting

Ultimate distribution once produced may be exceeded merely by suppressing back diffusion of solutes within the molten zone length, either by further zone refining with use of a shorter zone or by removing the contaminated parts and further zone melting. The former case is actually implied in the procedure of zone meltin with variable zone length, and the latter case was thoroughly studied by Pfann[2] who showed that a marked effect may be expected from this procedure only if $k \ll 1$ and the sufficiently piece of the contaminated part of the charge is removed. From the practical point of view, the procedure is not advantageous because of its lengthiness and necessity to shorten the charge considerably. It was therefore checked by calculation what effect could have a removal of the whole contaminated end of the charge already after a small number of zone passes, the exchange of the feed by the part removed, and further zone melting. For the constant as well as variable distribution coefficients, effect of this procedure on the yield of zone refining is given in Table VII. The efficiency of the procedure in question might apparently be enhanced by removing larger amount of the total solute content, *e.g.* by combining two pure halves from two zone-refined charges, or three pure thirds from three charges to make one charge, and the charges would then undergo further zone melting. In addition to that actually the feed of greater purity is then zone-refined by us, even the distribution which was produced already in the preceding zone melting is favourably applied. The results of the calculation for the case that the charge was divided after ten zone passes into two or three parts and further zone melting of the pure parts combined took place using ten further passes for the constant and variable distribution coefficients, are given in Table VIII. The procedure gives a rather distinct effect, especially for the variable distribution coefficient, and may be virtually useful, particularly if we must start with the feed that has a rather high solute concentration c_0.

Acceleration of Zone Melting

Some disadvantage when practizing the zone purification is its waste of time. Time of duration of the zone melting is dependent maily on: *1.* the number of zone passes,

TABLE VII

Yield of Zone Refining Using Twenty Passes (*A*) and the Yield Using Ten Passes, Removal of Contaminated Charge Fraction and Further Use of Ten Passes (*B*), $L/l = 10$

c_S/c_0	$k = 0.5$		$k = 0.3 + 0.4c_L - 0.05c_L^2$	
	(*A*)	(*B*)	(*A*)	(*B*)
10^{-1}	62·5	64·8	35·2	40·0
10^{-2}	29·2	29·5	17·6	23·8

2. the rate of the molten zone travel, *3.* number of zones which are simultaneously used for zone refining. The number of zone passes is in practice given by the demands for final purity of the substance and must be greater, the less favourable is the value or change in the value of the distribution coefficient as dependent on the concentration of solute in the liquid phase.

The ratio of zone travel cannot be increased too much, since at high crystallization velocities the equilibrium between the solid and liquid phases is not fully established and deterioration of both the purity achieved and the yield takes place. These problems were studied earlier in detail[2,14]. Our calculations as well showed that small acceleration which allows to accomplish some zone passes more within an equal time is virtually of no effect, whereas high acceleration impairs the purification effect. The calculations were carried out under the assumption that no mixing of the liquid phase occurred, so that for the dependence of the effective distribution value k_{ef} on the rate of crystallization f, *i.e.* for the case of zone melting, on the rate of zone travel v since $f = v$, the equation

$$k_{\text{ef}} = \frac{k_0}{k_0 + (1 - k_0)\,\mathrm{e}^{-f\delta/D}} \tag{6}$$

is valid, where D is the diffusion coefficient in a liquid phase and δ is the thickness of the layer in which at the freezing interface different concentration of the solutes is equilibrated merely by the diffusion. A certain effect, even though not too a considerable one, may be seen with more rapid zone melting for several first passes with use of a longer zone, whereby a certain gain of time or, when compared with the equally lasting zone melting, a somewhat greater purification effect can be achieved. This effect, it is true, is not too pronounced, but it is apparent even when compared with the zone melting, in the first place using a long and then a short zone, carried

TABLE VIII

Yield of Zone Refining with Use of Twenty Passes as well as Ten Passes of the Charge Produced by Combining Pure Fractions of Charges Zone-Refined with Ten Passes

c_S/c_0	$k = 0.5$			$k = 0.3 + 0.4c_L - 0.05c_L^2$		
	20	[a]	[b]	20	[a]	[b]
10^{-1}	62·5	77·6	82·0	35·2	58·8	78·8
10^{-2}	29·2	33·2	40·8	17·6	34·4	50·4
10^{-3}	—	—	—	3·1	8·4	18·4

[a] After ten passes, pure halves of two charges are combined; [b] after ten passes, pure thirds of three charges are combined.

out constantly at equal rate, as can be seen from Table IX. In this Table, column (*a*) indicates less advantageous yield of zone refining for $n = 1$ to 7 at the rate 0·008 cm/s, $L/l = 2{\cdot}5$, and for $n = 8$ to 20 at triple rate, L/l being 10. In column (*b*), the most advantageous case of zone melting for $n = 1$ to 7 at the rate $v =$ $= 0{\cdot}008$ cm/s, $L/l = 2{\cdot}5$, and for $n = 8$ to 17 at triple rate with the zone having $L/l = 10$, is presented. Column (*c*) shows the yield of zone refining after 34 passes at the rate 0·024 cm/s using $L/l = 10$, column (*d*) presents yield of zone refining after 11 passes at the rate 0·008 cm/s, and finally, column (*e*) denotes the yield for $n = 1$ to 3 at the rate 0·008 cm/s using $L/l = 2{\cdot}5$, and for $n = 4$ to 11 at equal rate with the zone having $L/l = 10$. The number of passes is selected for the time of zone melting to be equal for all cases given in Table IX. It is possible to notice that the acceleration after first seven passes in case (*b*) permits to carry out 6 passes more as distinguished from cases (*d*) or (*e*). For case (*c*), neither enhanced number of zone passes equilibrates deterioration of the effective distribution coefficient by increasing the rate of zone melting. All the calculations made have been carried out for a constant value of the equilibrium distribution coefficient $k = 0{\cdot}3$; for higher k values, the effect of the speeded zone melting at the beginning of the refining, when the zone refining is carried out with a longer zone, would be less apparent, because the possibility of accomplishing some passes more will with the disadvantageous distribution coefficient affect the ultimate distribution only little.

Zone melting carried out by means of more than one zone at the same time may be regarded as the most important possibility of how to reduce time of the zone melting or to improve the refining effect during zone melting lasting equal time. In this case, two events must be distinguished:

1. The whole charge passes through a series of heaters so that each molten zone will pass through the whole charge from the beginning up to the end. Single zone

TABLE IX

Effect of Zone Melting Rate on the Yield

c_S/c_0	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)[a]
$5 \cdot 10^{-1}$	44·0	72·0	43·5	70·4	68·8
10^{-1}	—	40·0	23·4	33·6	28·0
$5 \cdot 10^{-2}$	—	20·0	—	18·4	17·6

[a] Designation is in the text.

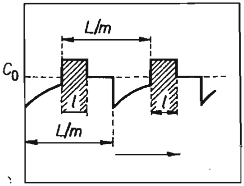

FIG. 3

Distribution in the Zone Melting under Intermittent Motion with More Heaters for the Unfinished First Pass

Number of heaters is designated m; distance of heaters L/m; l is the length of molten zone. Molten zones are section-lined.

pass for m heaters is then of the same effect on the distribution as m passes with use of a single zone.

2. The system of heaters does an intermittent motion of the same length as is the distance between the heaters, L/m, in such a way that the zone produced by means of one heater is after the end of the motion taken over by the successive heater. If the molten zone has passed distance L/m and if it is taken over by the next heater, it passes into the realm of the charge which had been already purified by passing of the zone produced by the preceding heater.

The distribution of c_S is for the unfinished first pass illustrated in Fig. 3. Multipass zone melting carried out by means of zones at the same time exhibits primarily a very marked time effect; in the procedure, where total charge passes through all m heaters, a single pass is accomplished with double of time in contrast to the zone melting with one heater, but the purification effect is the same as in the case of m passes using one zone. By refining under intermittent motion, in addition to the time effect, we obtain the more advantageous distribution than can be achieved by zone melting with one heater. For several passes under intermittent motion for the constant and variable distribution coefficients, the distribution for $m = 3$ is graphically presented in Fig. 4.

If we consider in the zone refining under intermittent motion each section between the heaters, of length L/m, to be a separate charge, provided that the end of the charge of length l represents the beginning of the charge having equal length, the distribution under intermittent motion can be calculated by the material balance method with aid of the program described, and the effects, which will be applied in this very convenient procedure, can be followed. In contrast to the zone melting with one heater, the time effect is the most distinct and is greater, the greater number of heaters is simultaneously applied to the zone refining. Likewise the effect on the efficiency of purification is great, and is greater, when the distribution coefficient during zone melting is chan-

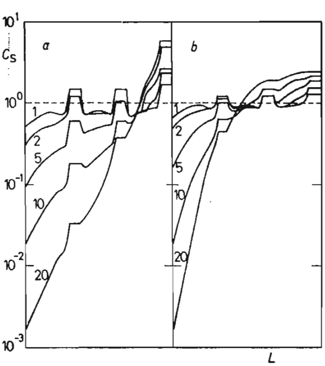

FIG. 4

Distribution in the Zone Melting with 3 Heaters under Intermittent Motion after One, Two, Five, Ten, and Twenty Passes

a $k = 0{\cdot}5 =$ const.; *b* $k = 0{\cdot}3 + 0{\cdot}4c_L - 0{\cdot}05c_L^2$.

ged. This can be seen in Table X, where the yields of zone refining with one heater ($m = 1$) with use of two and six zone passes are compared, together with yields of the zone refining with three heaters, the whole tube passing through all heaters with three and nine passes being applied. This corresponds to the time needed to carry out two and six zone passes through one heater. In Table X, likewise the yields are given, obtained in the zone melting under the intermittent motion using three heaters with so many zone passes that the time of refining should be equal as in the two preceding cases, *i.e.* after six and eighteen intermittent motions. A comparison is made for $k = 0{\cdot}5$ and for variable coefficient $k = 0{\cdot}3 + 0{\cdot}4c_L - 0{\cdot}05c_L^2$. The merits of the zone melting under intermittent motion, particularly in the case of nonconstant distribution coefficient, are apparent from Table X.

We shall now observe in a more detail zone melting under the intermittent motion. First of all, we shall consider the effect of the number of heaters and the zone length. The latter, however, especially for a great number of heaters, has some limitation: if a greater number of heaters is applied to the length L, then the ratio L/l, which must vary within technically realizable limits, will be always large enough in comparison with L/m, *e.g.* for $m = 5$ to 10 and for the technically controllable length, of the charge L, it will be within $2 < lm/L < 10$. The great density of heaters provides favourable time effect, but produces unfavourable conditions which take place during zone melting of a short charge by means of a long zone. This is apparent from Table XI, where the yield is presented of the zone refining of an equally long charge under

TABLE X

Yield of Zone Refining with One Heater ($m = 1$) and Three Heaters ($m = 3$) for the Pass of the Whole Charge through all Heaters, Intermittent Motion

c_S/c_0	$m = 1$		$m = 3$		$m = 3$ intermit.	
	1	3	3	9	6	18
			$k = 0{\cdot}5$			
$5 . 10^{-1}$	11·7	54·3	22·1	71·4	53·9	74·2
10^{-1}	—	5·7	—	28·6	6·8	48·6
10^{-2}	—	—	—	—	—	17·8
			$k = 0{\cdot}3 + 0{\cdot}4c_L - 0{\cdot}05c_L^2$			
$5 . 10^{-1}$	2·0	19·3	5·5	33·1	22·0	40·0
10^{-1}	—	—	—	11·3	0·5	22·1
10^{-2}	—	—	—	—	—	9·6

TABLE XI

Yield of Zone Refining under Intermittent Motion through Three and Five Heaters within Equal Time

c_S/c_0	$m = 3$			$m = 5$		
	$n = 3$	$n = 6$	$n = 9$	$n = 5$	$n = 10$	$n = 15$
$5 . 10^{-1}$	27·6	57·9	62·1	33·8	34·2	50·8
10^{-1}	—	5·5	27·5	0·7	7·6	8·8
$5 . 10^{-2}$	—	—	9·6	—	1·3	2·5

the intermittent motion for a number of heaters $m = 5$ and the zone length $l = L/2m$ and for three heaters ($m = 3$) and the zone length $L/4m$, for three equal times of the zone refining (3, 6 and 9 passes through three heaters and 5, 10, and 15 passes through five heaters); by using a higher number of heaters, greater purification effect of a greater part of the charge will be achieved with a lower number of zone passes, but further passes will provide rapid establishment of the equilibrium, so that the zone refining through a smaller number of heaters producing an equally long, but with respect to L/m a relatively shorter zone, is for a greater number of passes of more advantage. Consequently, it is not suitable to use for the zone melting under intermittent motion as great number of heaters as possible, as is recommended by Schildknecht for the zone melting, when the whole charge passes through all heaters[14].

Furthermore, the problem of the change in the zone length during the zone melting under intermittent motion can be solved, even when, in relation what has been just said, no such effect can be expected as in the zone melting through one heater. Two possible different cases of the change in the zone length may be here considered, because each charge is zone-refined through more heaters:

1. All the heaters provide an equally long zone and its length can change in the same way for all heaters (change in the zone length during the zone melting) only on finishing a certain intermittent motion.

2. Each heater provides a zone of different length, so that the beginning of the charge is zone-refined with a zone of another length than is the end of the charge, the length of zones being unchanged during the zone refining (different zone length along the charge).

We would be able to consider even combination of both cases, but the technical realization would be in practical use enormously complicated and the effect achieved inconsiderable. In the first case, the effect of the change in the zone length is similar to that in the zone melting through one heater, however, it is much limited by the fact that ratio L/l can only little vary within the length L/m in the zone melting under intermittent motion. Even here, however, it may be of advantage to perform some initial intermittent motions with one zone and possibly at higher rate and then to pass over to a short zone and lower rate of the zone travel.

In the second case, *i.e.* in the zone refining with the zone of varying length along the charge, two possibilities may be concerned: *a*) the beginning and the end of the charge are refined using the shortest and longest zones, respectively, *b*) the beginning and the end of the charge are refined by the longest and shortest zones, respectively. Both possibilities are compared in Table XII, using the example of the zone refining of a fairly short charge ($d = 30$) through three heaters under intermittent motion and for $k = 0{\cdot}5$.

TABLE XII

Yield of Zone Refining through Three Heaters under Intermittent Motion for Various Zone Lengths along the Charge

c_S/c_0	[a]	[b]
$5 . 10^{-1}$	51·4	55·3
10^{-1}	25·0	16·9
$5 . 10^{-2}$	18·6	6·1
10^{-2}	5·7	—

[a] $l_1 = L/4m,\ l_2 = L/3m,\ l_3 = L/2{\cdot}5m.$
[b] $l_1 = L/2{\cdot}5m,\ l_2 = L/3m,\ l_3 = L/4m.$

CONCLUSION

In this paper, the possibility of calculating the distribution of solutes along the charge in the zone melting using the material balance method has been shown, the digital computer being used for the case of the constant distribution coefficient, even when the latter changes slowly or in jumps with the concentration of the solute in liquid phase. We have found that if the coefficient can attain the unit value, unfavourable distribution is produced which is responsible for a low yield of the substance purified. We have further shown how to increase yield of the zone refining for the case, when the unfavourable distribution due to a change in the distribution coefficient during zone melting is produced.

In all cases involving unfavourable distribution, and especially where this can be caused by the change in the distribution coefficient, it is advisable to try to increase the yield by starting the zone melting with the longest molten zone possible (*e.g.* $L/l = 2$ to 5) which we make gradually shorter and in the last passes we make use of the zone melting with quite a short zone (*e.g.* $L/l = 20$ or shorter).

Where we must start from slightly pure feed, and where the assumption can be made that high concentration of solutes makes the zone melting difficult, it may be of advantage to separate pure fractions from several charges after a preliminary zone melting, to put them together and refine the charge thus produced to achieve final purity. Similarly, it is true, even the preliminary purification with use of any other purification method may be applied, but preliminary zone melting is of certain advantage in that it provides distribution of solutes, favourable for further zone refining. Other purification methods for preliminary purification prior to the zone melting (crystallization, column crystallization *etc.*), however, can be advantageous because of their capability of being accomplished within a considerable short time.

Certain acceleration of the zone refining can be achieved by carrying out first passes with a longer zone at higher rate and further passes with a short zone at slow rate. A very distinct acceleration will be achieved by refining with more heaters simultaneously; in addition, in the zone melting under intermittent motion, the favourable effect of the pass of the zone, enriched with the solute, into the region purified by the zone pass of the zone built up already by the preceding heater, will be applied, this being significant mainly where the distribution coefficient changes with concentration of the solute in liquid phase. As far as the zone length in the zone refining under intermittent motion is concerned, it holds here that, even when too a great number of heaters for the charge length has been used, even the fairly short zone is relatively long referred to the L/m section and the distribution will rapidly attain the equilibrium, limiting state, and neither a considerable purification effect, nor a satisfying yield will be achieved. When considering different zone length along the charge in the zone melting under intermittent motion, it is advisable to position a heater at the beginning of the charge, producing short zone, and a heater which melts the ingot to make a long zone at the end of the charge. A change in the length along the charge, however, is of small effect on the ultimate distribution.

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