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Institute of Physical Chemistry, USSR Academy of Sciences,
Institute of Radio Technology and Electronics, USSR Academy of Sciences, Moscow

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Countercurrent Fractional Crystallisation

Yu.A.Chikin and V.I.Lukhovitskii

Countercurrent fractional crystallisation (CFC) has been attracting increasing attention in recent years. The role of CFC among other methods of separation and purification based on crystallisation is described. Various specific arrangements for applying CFC are given. Different theories of CFC are examined, and the limitations of the process are discussed. 73 references.

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I. INTRODUCTION

Effective methods of separation and purification of materials involve repeated application of the elementary processes which constitute the basis of separation. These processes are: evaporation–condensation (in the case of distillation); sorption-desorption (in chromatographic separation); evaporation–crystallisation (in fractional sublimation); fusion–crystallisation (in countercurrent fractional crystallisation), etc. Thermodynamic partition coefficients, calculated from the chemical potentials of the various phases[1], can be defined for each elementary process.

As a rule, partition coefficients for the fusion–crystallisation process are high enough to ensure efficient separation and purification of materials. These high partition coefficients are due to the fact that in most systems of practical importance the impurities form eutectics with the main component. The thermodynamic partition coefficient of a mixture of a eutectic and a pure component tends to infinity. In some systems, however, mixed crystals, peritectics, or intermediate compounds are formed. Even more complicated systems exist, particularly in multicomponent mixtures. These mixtures are characterised by a finite partition coefficient, which makes their separation more difficult. Systems of this type can be used to evaluate the effectiveness of apparatus and to determine the parameters of the separation process. Most convenient for this purpose are the two-component systems which give rise to solid solutions (just as systems giving ideal solutions are used to study fractional distillation).

The present review will examine the theory and practice of only one of the methods of separation and purification based on crystallisation: countercurrent fractional crystallisation.

The theoretical aspects of the crystallisation process have already been adequately discussed in review articles[2,3].

Modern crystallisation methods of separation and purification can be classified into a number of groups, each of which has its own advantages and disadvantages.

The most widely known of these is the zone melting method[4], which gives products of the highest purity and is generally applied in the production of ultrapure metals, semiconductors, etc. However, in spite of later refinements to increase the number of zones per pass, to provide continuous operation, and to raise the efficiency[5], the purification process remains very slow, requiring many days or at least many hours, and its production capacity is therefore low. Furthermore, the separation of large amounts (tens per cent) of impurities is problematic. The same strictures apply to the directional crystallisation method.

The fractional crystallisation method, widely used in the past, is now hardly ever used as it is extremely laborious, and has been replaced by more satisfactory methods. Somewhat improved variants of the fractional crystallisation method are the continuous methods of fractional melting[6] and partial freezing[7], which can be used in laboratory practice but are hardly likely to find industrial applications because of the low efficiency of separation which they afford.

The method called chromatographic crystallisation by Findlay and McKay[8], proposed by Bowman[9] in 1947, consists in the following procedure: a temperature gradient is applied to a column filled with a filtration medium, and the mixture to be separated is applied at the top in the solid form. The mixture is brought into the liquid form by dissolution in a solvent which does not freeze at the separation temperature (or, alternatively, by fusion). The liquid is allowed to flow downwards, simultaneously moving the temperature gradient in the

direction of the flow. The solid phase, consisting of the recrystallised mixture, is retained by the filtration medium. This process is equivalent to a countercurrent of the phases in the temperature gradient. The method gives good results only if a solvent is used. When working with a melt, as described in the original patent[9], we can expect a large amount of melt to be retained in the packing, and this can make the operation of the equipment difficult. Successful separation of paraffins has been achieved by using large volumes of solvent, but in this case the output of the apparatus falls off considerably. The method was later proposed for use in polymer fractionation[10], and is now mainly used for that purpose.

Countercurrent fractional crystallisation (CFC) has become very widely used in recent years, and has reached the stage of industrial application in many countries. The present review is devoted to this method.

II. BASIC PRINCIPLES OF CFC

Any method of separation, to be fully efficient, must meet the following requirements:

1. A multiplicity of elementary separation steps, which in principle should lead to a large number of theoretical plates.
2. Countercurrent motion of the phases, ensuring a large number of elementary steps and a distribution of the component concentrations along the length of the separating equipment.
3. Flow reversal (reflux), which leads to products of maximum purity.

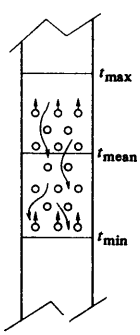


Figure 1. Schematic representation of countercurrent fractional crystallisation.

These factors also characterise the separation of materials by continuous (countercurrent) fractional crystallisation, using separating equipment working on the following principle (Fig. 1). A temperature gradient such that the maximum temperature t_{max} and the minimum temperature t_{min} are respectively higher and lower than the melting point of the mixture and of all its components and eutectics is imposed on the column. The solid phase is continuously moving with respect to the temperature field towards higher temperatures, and melts, and the liquid countercurrent flows between the crystals in the direction of lower temperatures, and freezes. Elementary fusion–crystallisation (or dissolution–crystallisation steps take place over the entire length of the separation layer, leading to a redistribution of the components between the phases. As a result, the less fusible (or less soluble) components migrate towards the hot end of the separation layer, and the more fusible components migrate towards the cold end.

It can be seen from this schematic description of the process that a fairly close analogy exists between CFC from the melt and fractional distillation: this analogy has been pointed out by a number of workers[11,12]. However, there are also a number of essential differences between the two processes. Firstly, because of diffusional limitations in the solid phase[13], the redistribution of components between the phases is achieved mainly by complete fusion of the crystals and formation of crystals of different composition. Secondly, the density difference between crystals and liquid is not usually very large, and countercurrent of the phases is usually achieved by moving one phase relative to the other by some mechanical device. Thirdly, a much greater amount of liquid is entrained in the solid phase by surface tension in its most general sense (occlusion, adsorption, capillarity). As a result, the real partition coefficient is significantly lower than the thermodynamic partition coefficient.

Due allowance for these differences must be made when the formulae and ideas used in fractional distillation are applied to the operation of crystallisation apparatus.

The profound influence of pressure on crystallisation and melting processes must also be stressed[14–16]. Excess pressure can modify the phase diagram of the system and thus affect the separation process: in this context, the application of fluctuating pressure offers the promise of new and improved types of apparatus[17–19] for the separation of materials by CFC (by varying the rates of fusion and crystallisation during each cycle of pressure change).

III. TYPES OF APPARATUS FOR THE SEPARATION AND PURIFICATION OF MATERIALS BY CFC

The equipment described in the literature can be divided into a number of groups, differing in respect of the method used to impart relative motion to the liquid and the solid phase, the extent to which the separator is filled, the method of extracting and supplying heat, and so on.

1. One variant of CFC from solution was described above under the heating "chromatographic crystallisation"[9]. In another similar variant the column is filled with solvent instead of a filtration medium[20]. The cooler is at the top of the column, the heater at the bottom, and the temperature gradient is produced by the moving streams of the phases. Countercurrent motion of crystals and solution is produced by the density difference of the phases, and is assisted by stirring the solution.

2. The use of drums for the separation and purification of materials is described in the patent literature[21,22]. The apparatus consists of a number of stages. Solid phase freezes from the melt on to the surface of the drum, which is cooled from below, and is transferred to the high-temperature region by the rotation of the drum. The drum and its associated equipment for the countercurrent transfer of crystals and melt from stage to stage can be either horizontal or sloping. A heater and a cooler are provided at each stage. The only difference in principle between this process and fractional crystallisation is the absence of filtration. The separation is not induced by a temperature gradient, but by the different rates of melting and crystallisation of the various components. The separation

efficiency is not high, because each stage contributes much less than one theoretical plate to the separation.

3. Graham's rotary crystalliser[23] is an example of the application of pressure to crystallisation processes. The partially crystallised material is passed through rollers, the lower roller being cooled and the upper being heated. The rollers squeeze the mother liquor from the crystals; also, due to the combined effect of the temperature difference on the rollers and of the pressure on the crystals, part of the crystals melts, providing additional scrubbing of the crystals. The purification efficiency is low. Even in the purification of mixtures which form a eutectic the enrichment of the desired component is only from 76 to 90%.

4. Various forms of scraping crystalliser for the separation of materials have been described[24,25]. The crystals, formed on the cold walls of the cooled end of the column, are transferred by scrapers to the hot end. However, these crystallisers have a low separation efficiency and are used only as an auxiliary means of supplying the crystalline paste to the main separating column[8].

5. The apparatus described by Carney[26] is an example of another type of crystalliser for the purification of materials. The layout is shown diagrammatically in Fig. 2: it consists of a column with a cooler *1* at the bottom and a heater *2* at the top. Countercurrent of the crystals and the melt is induced as follows: the crystals are caught in perforated compartments attached to an endless conveyor belt *3*, and move upwards, and the liquid flows under the influence of gravity. Feed material is supplied in the middle of the column (*4*), and the pure product and the near-eutectic mixture are taken off at the top (*5*) and the bottom (*6*) of the column respectively.

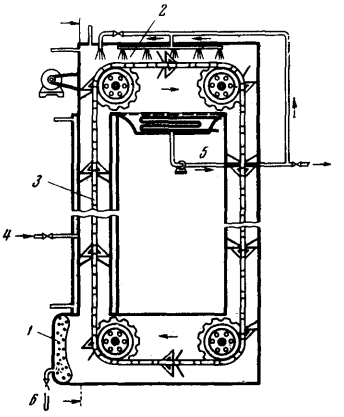


Figure 2. Carney's apparatus.

Using a reflux ratio of 9, dimethylbutane of 99% purity has been produced with a throughput of 3.1 kg h^{-1}.

6. The following types of crystalliser for the purification of materials are disclosed in a number of patents by Weedman and Findlay[27-29]. The crystalline paste is loaded into the column, which can be vertical or horizontal, or alternatively is produced directly in the column. The crystals are moved by a perforated or porous piston towards the heater: they melt, and the resulting liquid flows in the opposite direction towards the piston and filters through it. After one pass of the piston the crystalline residue is taken off as pure product. Although products (such as benzene) of up to 98–99% purity have been obtained in this apparatus, the efficiency of the apparatus must be judged unsatisfactory, since the impurities gave eutectics with the main component.

None of these types of separating equipment has found industrial application, and they are rarely used even in laboratory practice. This is due first and foremost, we believe, to their low efficiency (of the order of 1–2 theoretical plates); furthermore, they are quite complicated when fully engineered and their throughput is low.

7. The use of centrifugation for CFC was proposed by Findlay[30], but the process was first described in full detail by Fleischer[31] in 1962. Essentially, countercurrent of crystals and melt (which must have different densities) is induced in a centrifuge exposed to a temperature gradient such that the minimum temperature (sufficient to cause crystallisation) is near the axis and the maximum temperature (sufficient to cause melting) is near the periphery of the centrifuge. The crystals which have grown to a critical size (determined by the speed of rotation of the centrifuge and by the density difference between crystals and liquid) are impelled in the direction of higher temperatures by the centrifugal field, and the liquid undergoes the opposite flow towards lower temperatures. Supply of feed material and take-off of the separated components are provided on a continuous basis.

The theory of the CFC method in a centrifugal field was developed by Anikin[32] in 1963, but the first purifications[33] (by a batchwise variant) were reported in 1966. Sixteen-fold enrichment of triphenylchlorosilane was achieved in 30 min, but the separation could not be improved by longer operation. Unfortunately, the type of impurity removed is not stated, nor whether the impurity gave rise to mixed crystal or eutectic formation, and therefore the efficiency of the separation cannot be estimated.

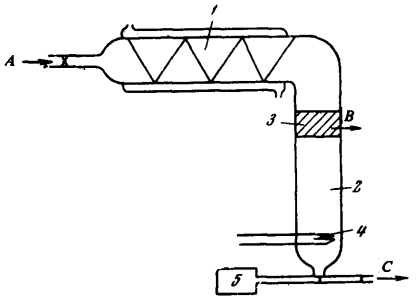


Figure 3. Diagram of the apparatus used by the Phillips company: *A*) input of feed material; *B*) take-off of mother liquor; *C*) take-off of pure product.

8. The variant proposed by Arnold[34,35] and realised by Thomas[36] has proved to be the best for use in industry. The principle of this process has been discussed by McKay and coworkers[8,37,38]. The apparatus (Fig. 3) consists of a preliminary scraping crystalliser *1*, where the crystalline paste is formed, the enrichment section *2* (corresponding to the purification column) with a porous partition *3*, heater *4*, and the pulsatory pump *5*. In a previous form of the apparatus a piston located above the porous partition

was used instead of the pulsatory unit. The piston (or pulsatory unit) operates at 90–350 cycles per minute, and alters the pressure by approximately 1–100 atm during each cycle.

The crystalline paste from the preliminary crystalliser is fed to the enrichment section of the column, the crystal content of the paste being more strictly controlled the higher the required purity of the product. During the period of pulsation corresponding to rarefaction, the paste is drawn downwards and some air is sucked through the porous filter, creating voids in the crystalline paste. During the compression period of the pulsation unit the melt is forced upwards through the crystals, and some of the mother liquor is run off through the porous filter. In the region of the heater the crystals melt: part of the melt is taken off as pure product, and part is displaced upwards by the feed crystals as a reflux. Under these conditions, both scrubbing and recrystallisation of the settling crystals occur in the region between the heater and the porous filter. In this way, a countercurrent of crystals and melt is generated in the column. The temperature gradient in the separating part of the column is generated by the flow of heat carried by the reflux from the heater to the cooler.

A later variant[39] of the same apparatus has the heater in the upper and the cooler in the lower part of the column, so that the directions of motion of the liquid and the solid phase are reversed.

The separation efficiency of the piston version of the apparatus is 3.3 theoretical plates for a column approximately 25 cm in diameter and 2.5 m long operated at a reflux ratio of 95. The capacity of these installations for the separation of eutectic-forming impurities is extremely high. An industrial column operated by the Phillips Company, with pulsation unit, has an output of 60 000 metric tons of *p*-xylene per annum.

9. There is a very large group of assemblies[40–43] in which the countercurrent flow of crystals and melt (or solution) is obtained by moving the crystals from the cooler to the heater by means of a worm-screw or spiral. The melt formed in the vicinity of the heater is displaced by the flow of crystals or flows under the influence of gravity towards the cooler. The most efficient assemblies of this kind are the laboratory crystallisation columns for batchwise or continuous operation developed by Schildknecht and coworkers[44–47].

An apparatus of this type is shown diagrammatically in Fig. 4. It consists of a glass column R_1 with a graded heater winding W and a spiral S, which rotates between the inner (R_2) and the outer tube, impelling the crystals downwards in the temperature gradient (i.e. towards the hotter part of the column). Liquid is displaced upwards by the crystals. Assemblies of this type have been tested for the purification of many organic compounds such as phenanthrene, benzene, cyclohexane, biphenyl, fluorene, azobenzene, β-naphthol, etc. Columns of this type have been used also for the separation of inorganic salts[48]. The results indicate a high operating efficiency, but the data quoted in different papers are somewhat contradictory. Schildknecht et al.[49] published a graph of the melting point of fractions at different heights in the crystallisation column for the purification of phenanthrene. Most of the material (the purer fractions) had a melting point of about 110°C, but after three zone-melting passes the melting point of the purer fractions was raised to 210°C. †

† Although the increase in melting point achieved seems surprising, these data are in fact more or less consistent with the claims advanced in the original paper (Ed. of Translation).

Schildknecht and Vetter[50] have compared the results of the purification of hexadecanol by zone melting and column crystallisation methods. The highest melting point after zone melting (20 passes, velocity of the zone 1 mm h^{-1}) was ~ 50°, and after 2.5 h column crystallisation the melting point was ~ 53°. In both cases, the main bulk of the material had a melting point of ~ 49.5°. Thus, in the purification of phenanthrene the purest product was obtained by zone melting, whereas column crystallisation gave the purest hexadecanol.

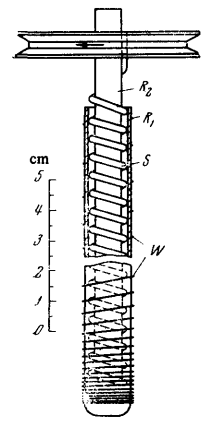


Figure 4. Schildknecht's apparatus.

There are some discrepancies between the published estimates of the efficiency of this method. Thus, Ammon[48] quotes an efficiency of up to 5 theoretical plates for a column length of 25 cm. Schildknecht[51], referring to Rössler's thesis[52], obtained an efficiency of 8–10 theoretical plates in a 20 cm column, corresponding to a value of 2–2.5 cm for the height equivalent to the theoretical plate (HETP). Powers[53] measured the efficiency in terms of the number of unit transfers (NUT) and height for unit transfer (HUT). Using the same data from Rössler, the HUT was 3.3 cm for the azobenzene–stilbene system, which forms mixed crystals, and 12.3 cm for systems giving rise to eutectics. Since the details of Rössler's work are not available in the literature, it is not profitable to discuss the origin of these discrepancies.

To achieve comparable purification (i.e. similar concentration distributions along the column), zone melting requires ~ 10 days as compared with ~ 2.5 h for column crystallisation. The output of crystallisation columns 1–2 cm in diameter and 15–20 cm long is 8–10 g h^{-1}, which makes them fully acceptable for laboratory purposes in spite of some constructional difficulties.

10. The following variant of CFC was proposed[54] in 1964. Column *1* (Fig. 5), with a layer of crystals frozen on its walls to a thickness of not more than 1–2 mm, is moved with respect to the heat exchanger *4*, designed to give a temperature gradient sufficient to keep the upper part of the column above (and the lower part of the column below) the melting points of all the components and eutectics of the mixture to be separated. The liquid flows by countercurrent between the crystals towards the lower-temperature regions under the influence of gravity. Fusion

and recrystallisation processes take place over the entire length of the layer to be separated, and as a result a gradient of component concentrations arises along the column. This process differs from those already described in the following respects: separation takes place in a thin (0.1–0.2 mm) layer which is moving with respect to the heat-conducting column wall, and the heat exchanger imposes a forced temperature gradient (independent of the mixture to be separated). These two special features offer the following advantages: (1) much faster supply of heat to the crystals and removal of heat from the liquid, accompanied by a higher rate of mass exchange, since heat exchange between the phases can occur by heat transfer through the wall as well as by direct contact between the phases; (2) formation of the main bulk of the crystals directly on a heat-conducting surface, which minimises the entrainment or partially melted crystals by more fusible material; (3) the fusion and crystallisation processes and the temperature gradient are practically independent of the mixture to be separated, leading to minimal retention of material by the separation apparatus: in the batchwise variant of the method separation of a mixture into its primary components can be achieved without appreciable formation of intermediate fractions; (4) stable operation of the apparatus, since the liquid moving towards temperatures below the melting point and the crystals moving towards temperatures above the melting point are subjected to ever-increasing temperature differences which tend to arrest their motion; (5) temperature uniformity over the cross-section of the layer to be separated.

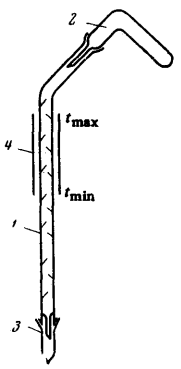


Figure 5. Thin-layer CFC apparatus.

Because of these advantages, the separation apparatus has a very high efficiency. The number of theoretical plates and the number of unit transfers, measured with a standard benzene–thiophen mixture giving mixed crystals[55], are practically equal, and can be as high as 25–30 in the most favourable cases. The HUT and HETP are 2–2.5 cm. The maximum purity of the product (in the absence of eutectic-forming impurities) was 99.9995%. The output of the batchwise laboratory variant of the apparatus is about 10 g h^{-1}. With the continuous variant the output should be at least 1–2 kg h^{-1} from a meter of column perimeter.

The way in which the temperature gradient is moved with respect to the layer to be separated has been shown to be immaterial. It is possible to move the column, the heat exchanger, or even the temperature gradient directly (for example, by passing through the heat exchanger a liquid whose temperature is increased according to a predetermined programme).

Thin-layer operation of CFC is discussed in a number of American papers published in 1965. However, the construction of the apparatus[56,57] is described sketchily, and nothing is said about process parameters or about the operating efficiency of the equipment. The only statement is that the purity of the product can be as high as 99.999–99.9999%.

The high efficiency (8–10 theoretical plates) achieved in devices of the Schildknecht type is probably due to the fact that they operate under conditions approximating to those obtaining in thin-layer separation.

IV. THEORIES OF CFC

A single theory encompassing all methods of CFC is not available at present. Hence, different variants of the theory must be considered, each of which is applicable only to a particular method of separation. The only feature which is common to all these variants is that the CFC process is treated by analogy with fractional distillation, with large or small departures. As in fractional distillation, the efficiency of the separation apparatus is discussed in terms of HETP and N (the height and number of theoretical plates) or of HUT and NUT, of the throughput, and of mass and heat balance.

However, whereas in fractional distillation the partition coefficients are always finite, the thermodynamic partition coefficient for crystallisation with eutectic formation is infinite, and in principle complete separation into one component and the eutectic should be possible with an efficiency of a single theoretical plate. In this case two approaches can be used to calculate the efficiency of separation. In the first the degree of enrichment (and therefore the extent of the approximation to a theoretical plate) is calculated. The second approach requires allowance for the real composition of the phases: the composition of the liquid phase is assumed to remain unchanged, but the composition of the crystalline phase is calculated with allowance (by various means) for the liquid which wets the crystals. Both approaches are found in the literature, and we shall mention them again in the discussion of the various theories. The principles of the calculations for some of the methods described in Sections III.1–III.10 will now be briefly reviewed.

Section III.1 describes a column in which the motion of the crystalline phase in the solvent is caused by density differences. Ciolan[58] has calculated the dependence of the yield on the enthalpies and specific heats of the components starting from the mass and heat balance equations for the enrichment and the exhaustion sections of the column.

Section III.7 describes the operating principle of crystallisation columns in a centrifugal field. The theory developed by Anikin[32] for this system assumes the fullest analogy between CFC and fractional distillation, with the hypothesis that diffusion is fast enough in a solid in a "state of pre-fusion" to produce concentration uniformity in the crystalline phase. The expressions for the time needed to reach steady state and for the ratio of the ultimate concentrations are the same as those obtained by

Cohen[59] for fractional distillation. The fluxes are calculated by combining the centrifugal field and the rate of growth of the crystals.

Devyatykh[60] holds similar views on the overriding role of diffusion in the solid phase during the separation process. By considering the material balance in the column and assuming a steady state he arrives at the following expression for the efficiency under total reflux:

$$\mathrm{HETP} = \omega^2/3D_1\kappa,$$

where L is the flux of solid phase, 2ω is the mean thickness of the platelets of crystalline phase, D_1 is the diffusion coefficient of the minority component in the solid phase, and κ is the fraction of the volume of the column occupied by the solid phase.

It should be noted that most workers consider diffusion in crystals in a state of pre-fusion to be abnormally high but nevertheless 1–2 orders of magnitude lower than in the liquid[13,61]. Using a stage-by-stage treatment of the crystallisation process, Anikin[62] obtained an expression for the number of theoretical plates also analogous to the equations used in distillation and zone melting.

In Section III.8 we have mentioned the efficient separation achieved by the piston column used by the Phillips Company on a pilot-plant scale. The efficiency was determined for the separation of a mixture of cyclohexane and methylcyclopentane, whose phase diagram is quite complicated but can be interpreted as mixed crystal formation in the concentration region between 50 and 100% of cyclohexane. The HETP is 75 cm. Subsequent refinements, including replacement of the piston by a pulsation unit, more precise control of the operating conditions[63,64], on-line computer control[65,66], etc. must obviously have increased the separation efficiency somewhat, but the Phillips columns are still used exclusively for the separation of eutectic-forming impurities. We note that in this case a single theoretical plate is sufficient in principle. Hence, the main interest is not in calculations of efficiency but in the column fluxes and throughputs.

The influence of a number of variables on the purity of the product and on the yield of the column has been discussed[37,38]. Factors such as the crystal content of the paste, the viscosity of the mother liquor, the size of the crystals, the pulsation frequency, etc. have been shown to play an important part. However, the basic factors which determine the operation of the column are: the reverse flow of liquid (reflux), the heat balance, and the degree of recrystallisation in the purification zone. In the words of the authors, recrystallisation is "the key to purification in the column". The degree of recrystallisation can be calculated by carrying out a mass and heat balance for the purification section, making the following assumptions for any cross-section of the column: the occluded liquid is in equilibrium with the crystals; the free liquid rising in the column is at the freezing point and its composition is given by the phase diagram for the system; the ratio of the amounts of solid phase and of occluded liquid is constant; the flow of heat through the column wall is zero.

With these assumptions, the mass and heat balance equations take the form

$$S = W + L - O;$$

$$\Delta H = H_L L - H_O O - H_S S + K(t_L - t_S);$$

$$O = \frac{(1-X_L)[H_S W + \Delta H - K(t_L - t_S) + W(1-X_W)(H_L - H_S)]}{(1-X_O)(H_L - H_S) - (1-X_L)(H_O - H_S)},$$

$$L = \frac{O(1-X_O) - W(1-X_W)}{1-X_L},$$

where S is the flux of solid phase, W is the flux of product, L is the flux of rising liquid, O is the flux of occluded liquid, H is the enthalpy, ΔH is the nett flow of heat in the column, t are temperatures, K is a parameter (including the thermal conductivity of the solid phase, the cross-sectional area of the column, the constant temperature difference between the rising liquid and the falling crystals, and the rate of change of temperature per unit height of the layer), and X is the concentration of the desired component. If the concentration of the crystalline paste entering the column is also known, the degree of recrystallisation can be calculated as the ratio of the amount of newly formed crystals to the amount of crystals entering the column.

McKay and Goard[67] give the following formula for the degree of recrystallisation in the piston column:

$$R = \frac{(T_p - T_c)C_p}{H_f},$$

where R is the degree of recrystallisation, T_p and T_c are the melting points of the pure crystals and of the crystals entering the purification zone, C_p is the mean specific heat of the crystals in the temperature range between T_p and T_c, and H_f is the heat of fusion of the purest component.

In the purification of *p*-xylene the optimum degree of recrystallisation was ~ 0.2–0.3, and the throughput of the column was as high as 3.23 $m^3\ h^{-1}$ for a cross-sectional area of 1 m^2. It should be noted that the reflux ratio of the liquid must be raised very considerably (to 95 : 1) when the impurities form mixed crystals with the main component: under these conditions the throughput of the column decreases sharply.

A crystallisation column in which the crystalline phase moves with the help of a rotating spiral is described in Section III.9. The CFC variants proposed by Schildknecht and coworkers have been discussed theoretically by Powers[53]. When the system contains mixed crystals, the author makes the following assumptions: phase equilibria are not reached; diffusion in the solid phase is negligibly small; the flux of crystals is constant along the length of the column. Under these conditions the rate of transfer of component A from one phase to the other is defined by the expression

$$\zeta_A = y_A L - x_A C - \rho D A \Phi \frac{dy_A}{dZ}.$$

For equilibrium within an element dZ at a height Z in the column the expression for the rate of transfer takes the form

$$\frac{d(x_A C)}{dZ} = K_t a A (y_A^* - y_A),$$

where x_A is the concentration of component A in the solid phase, y_A is the concentration of A in the liquid, L and C are the fluxes of liquid and of crystals, ρ is the density of the liquid phase, D is the diffusion coefficient in the liquid, A is the total area of the column cross-section, Φ is the volume fraction of the liquid phase, a is the contact area of the phases per unit volume of the column, and K_t is the mass transfer coefficient.

At steady state we can write

$$L = C; \qquad \frac{dX_A}{dZ} = \frac{dy_A}{dZ}.$$

In this case we obtain the following expression for the nett rate of transfer under total reflux:

$$\tau_A = C(y_A^* - x_A) - \left[\frac{C^2}{K_t a A} + \rho D A \Phi\right]\frac{dx_A}{dZ}.$$

Noting that at equilibrium $\tau_A = 0$, and assuming that all factors in square brackets are independent of Z, we can write the equation in an integral form:

$$\frac{Z}{\left[\frac{C}{K_t a A} + \frac{\rho D A \Phi}{C}\right]} = \int_{x_A(0)}^{x_A(Z)} \frac{dx_A}{y_A^* - x_A} .$$

The denominator of the left-hand side of this equation contains all the parameters of the column referred to unit length: it may be termed the height for a unit transfer (HUT). The value of the integral depends only on the final compositions and on the equilibrium equation $y_A^* = f(x_A)$. It is a direct measure of the difficulty of separation, and is usually expressed as the number of unit transfers (NUT).

Given the indeterminate but fixed lower limit of the integration, it is possible to evaluate the integral as a function of x_A for any system from the phase diagram. We note that for $x_A = 0$ or $x_A = 1$ the integral tends to infinity. Hence, Powers considers complete separation theoretically impossible. Once the distribution of the concentration x_A along the column is known, the integral can be evaluated as a function of the length Z.

The slope of this linear equation, given by

$$m = \frac{1}{\left[\frac{C}{K_t a A} + \frac{\rho D A \Phi}{C}\right]} = \frac{1}{\text{HUT}} ,$$

defines the HUT. The NUT can be calculated from the formula NUT = Z/HUT. Experimental results actually give straight plots, showing that all factors in square brackets are indeed independent of Z.

In his discussion of eutectic systems Powers makes the following assumptions: the system component A–component B is treated as a binary component A–eutectic system in which the eutectic plays the part of a new component B_1; the liquid containing the impurity is in contact with pure crystals of composition A everywhere along the layer to be purified except at the upper end, where the composition of the crystals changes discontinuously to the eutectic composition.

Let the crystals be the pure component A ($x_E = 0$), and let the liquid in contact with them have the composition y'_E and velocity L', in contrast to the composition y_E and velocity L of the main bulk of the liquid. But for these special features, the subsequent discussion is in no way different from the case of mixed crystals. The rate of mass transfer between the adherent liquid and the rising liquid is proportional to the concentration difference:

$$W_E = K_t a (y'_E - y_E) .$$

Introducing the balance equations, we arrive at the following expression for the transfer in the total reflux region:

$$\tau_E = C y'_E - \left[\frac{L'(L'+C)}{K_t a A} + \rho D A \Phi\right] \frac{dy'_E}{dZ} .$$

At steady state $\tau_E = 0$, and the integral form is

$$\frac{y'_E}{y'_E(L)} = \exp\left[\frac{C(Z-L)}{\frac{L'(L'+C)}{C K_t a A} + \frac{\rho D A \Phi}{C}}\right] ,$$

where $y'_E(L)$ is the concentration of the adherent liquid at the top of the column, L is the total length of the column, and y'_E is the concentration of the adherent liquid at the point Z. When using this expression, we must remember that the model changes as soon as the liquid reaches the eutectic composition. Under these conditions the crystals, the adherent liquid, and the rising liquid all have the eutectic composition.

To test the application of this equation to experimental data, a linear variation of composition with temperature was assumed. In this case we have

$$\frac{y'_E}{y'_E(L)} = \frac{T_B - T(Z)}{T_B - T(L)} ,$$

where T_B is the melting point of the pure component, $T(Z)$ is the temperature at point Z, and $T(L)$ is the temperature at the upper end of the column. As stated above, when Rössler's experimental results are examined in the light of this theory, large differences are found between the heights for unit transfer in the case of systems forming mixed crystals or eutectics (3.3 and 12.3 cm respectively).

The separation process described in Section III.10 for binary mixtures forming mixed crystals has been discussed[68] by making the following assumptions: steady state is not achieved; fusion of the crystals is not accompanied by change in composition, because diffusion in the solid phase can be ignored; a change in composition occurs when the liquid crystallises, the composition of the resulting crystals being determined by the liquidus curve.

Hence, using the expressions for material balance and for the rate of transfer of a component from one phase to the other, the following expression was obtained for a given instant:

$$\int_0^Z \pi D \frac{\delta_l \bar{l}}{S} dZ = \int_{y_0}^{y} \frac{dy}{x^* - y}$$

where Z is the length of the layer, δl is the effective thickness of the liquid, $\bar{l}$ is the rate of melting (mole cm^{-3} h^{-1}), S is the flux of solid phase, y and x are the concentrations of one of the components in the crystals and in the liquid, x^* is the concentration of the same component in crystals in equilibrium with x. As was shown from experimental data, replacing y by $\bar{x}$ (where $\bar{x}$ is the mean of the concentrations x and y) and x^* by $\bar{x}^*$ does not introduce significant errors. The integral thus obtained,

$$\int_{\bar{x}_0}^{\bar{x}} \frac{d\bar{x}}{\bar{x}^* - \bar{x}}$$

can be taken as the NUT to a first approximation. The values of HUT and NUT calculated by this method are close to the HETP and N values respectively, calculated from the final concentrations by the Fenske–Underwood formula[69].

Equations have been obtained[68] relating the efficiency of operation of the separating equipment to the following process parameters: h (the length of advance of the column with respect to the temperature gradient), between 12 and 120 cm; v (the rate of advance), between 6 and 480 cm h^{-1}; m (the loading), between 0.5 and 5.3 ml per cm of column periphery. The equations are of the form

$$\text{HUT} = 12 h^{-0.44} v^{0.2} m^{0.5} ,$$

$$\text{NUT} = 1.5 + 3.9 h^{0.44} v^{-0.2} m^{-0.2} - 0.2 h^{-0.56} v^{0.8} m^{-0.5} .$$

The variation of the separation efficiency with composition of the initial mixture and with temperature gradient has also been determined. All these expressions were obtained from experiments with a standard benzene–thiophen mixture, which gives mixed crystals.

The expression obtained above,

$$\text{NUT} = \int_{y_0}^{y} \frac{dy}{x^* - y} \approx \int_{\bar{x}_0}^{\bar{x}} \frac{d\bar{x}}{\bar{x}^* - \bar{x}}$$

is not accurate enough, because it was derived without

allowance for the wetting (in its most general sense, including occlusion, adsorption, and capillarity) of the crystals by liquids of different composition. Chikin and coworkers[70] have obtained an equation which allows for wetting. If the wetting is not a sensitive function of the height (i.e. composition) of the layer to be separated, the equation has the form

$$\mathrm{NUT}_E = \frac{1}{1-C}\int_{\bar{x}_0}^{\bar{x}} \frac{d\bar{x}}{\bar{x}^* - \bar{x}} ,$$

where C is the wetting coefficient, expressed as the ratio of the mole fraction of the wetting liquid to the sum of the mole fractions of the wetting liquid and of the crystals. At low values of C, corrections for the wettability have a minor effect on the calculated separation efficiencies in systems which form mixed crystals.

In the theoretical discussion of systems giving rise to eutectics the following assumptions have been made: the system consists of two components (the eutectic and one of the pure components); the composition of the liquid along the height of the column (i.e. along the temperature gradient) is determined by the liquidus curve, whereas the composition of the solid is determined by the wettability (in its widest sense) of the crystals of the pure component by a liquid whose composition is determined by the equilibrium curve. For this system, the last formula takes the form

$$\mathrm{NUT}_E = \frac{Z}{\mathrm{HUT}_E} = \frac{1}{1-C}\int_{x_0}^{x} \frac{d\bar{x}}{-\bar{x}} = \frac{1}{1-C}\ln\bar{x}\Big|_{\bar{x}}^{\bar{x}_0} ,$$

where Z is the total length of the layer to be separated. Efficiencies calculated by this formula agree almost exactly (except for the region of concentrations close to the eutectic) with the results obtained under the same conditions for the separation of materials forming mixed crystals.

V. FIELD OF APPLICATION OF THE CFC METHOD

Countercurrent fractional crystallisation is most successfully used with materials whose composition changes at their boiling point (by decomposition, polymerisation, etc.). Compounds such as methylvinylpyrrolidone and styrene[71] have been successfully purified; juices, tea, and beer[72] have been concentrated, etc. In some cases the method is economical also for the purification of materials such as *p*-xylene, naphthalene[72], etc. In all these applications the impurities formed eutectics with the main component, and therefore only moderate efficiency (but a high throughput) was required of the separation equipment. Apparatus of this type includes the Phillips columns and also the continuous variant of the centrifugal column.

For laboratory use, and for the preparation of specially costly materials in a high state of purity (drugs, some monomers, etc.), columns of the Schildknecht type or the thin-layer variant of CFC are the most suitable. These types of equipment when operated at a moderate output (tens of grammes per hour) offer extremely high separation efficiencies. The thin-layer variant is simpler to construct and offers somewhat greater efficiency.

In addition to the preparation of super-pure materials, these variants of the separation equipment can be used for the concentration of impurities, for the direct determination of eutectic compositions, etc. Apparatus for the analysis of mixtures can be designed on the basis of these assemblies.

The limitations of the CFC method must be mentioned. Separation is impossible when the composition of materials changes at the melting point or when they are very viscous at the melting point. In these cases a third substance can be added to lower the melting point or the viscosity, but this expedient lowers the output and complicates the separation.

However, in spite of these limitations, the CFC method deserves, on the whole, extensive application both in industry and in the laboratory.

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Branch of the Karpov
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