Traditionally, most applications are found in the food industry for the concentration of fruit juice, wine, beer and coffee extract. In this field, the advantages of freeze concentration over competing technologies (membranes and evaporation) are the superb preservation of aromas and colour while decay reactions are slowed down by the low operating temperature.

Recently, world-scale installations have come on-stream where wastewater from chemical plants is concentrated. The produced melt water can be reused as process water while the residual concentrate is incinerated. Here the advantages of freeze concentration are the low energy costs and the capability to concentrate beyond the eutectic point, where salts start to precipitate.

Drawbacks of freeze crystallization are the relatively high investment cost and the above-average maintenance intensity (there are many pieces of rotating equipment).

**Conclusion and Future Outlook**

Melt crystallization is the third most applied physical separation technology after distillation and extraction. Conventional processes are based on layer or suspension growth by indirect cooling.

- **Layer growth** may be considered as proven and mature technology, whereby the absence of slurry handling is a major advantage. Fully automated semi-continuous units can be delivered as turnkey projects. The need for repeated recrystallization steps to achieve a high product purity, however, increases both investment and operating cost. The desire to develop economically attractive continuously operated equipment seems to be in conflict with the basic characteristic of layer growth on a cooled surface.

- **Suspension growth** is also proven but not yet mature technology. The superior selectivity and high specific productivity of crystal growth in a suspension create a huge potential, which can be further exploited by simplification of equipment design and minimization of slurry handling.

**Evaporative melt crystallization** is a relatively young technology which combines the merits of suspension growth with a minimum of slurry handling. For certain applications, such as caprolactam, this technique is expected to take off in coming years.

**Pressure crystallization** is an alternative technology, which is well suited to purify components with a very low melting point at ambient temperature but elevated pressure. Outside this niche use, pressure crystallization probably cannot compete with indirect/direct cooling crystallization due to high equipment cost.

See Colour Plate 36.

**Further Reading**


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**Polymorphism**

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**Introduction**

When the molecules of a chemical substance are able to crystallize in more than one three-dimensional structure arrangement, the substance is said to display polymorphism. This phenomenon was discovered in the early nineteenth century but only since the middle of the twentieth century have its wider implications been appreciated by scientists investigating the crystallization, properties and interconversion of solid phases. These implications stem from the fact that different polymorphs of a given substance may
display very significant differences in physical properties such as melting point, colour, hardness, density, electrical conductivity, heat of fusion, solubility and dissolution rate, as well as differences in chemical reactivities. Polymorphism is a common phenomenon which has vital ramifications in the crystallization and processing of pharmaceuticals, in food chemistry, explosives manufacture and in crystal engineering. The profusion of polymorphic forms that might be encountered for a single compound (e.g. up to ten in some instances) has often been viewed as an unwelcome source of confusion, threatening to undermine reproducible isolation of a specific crystalline form. However, those engaged in the study of polymorphism see the benefits this diversity of forms may offer. At the same time, it is recognized that in order to control the polymorphic outcome of the crystallization process, systematic research aimed at a full understanding of the interplay of thermodynamic, kinetic and structural factors involved is paramount. This is a daunting task, however, since the phenomenon of polymorphism is acknowledged to be a complex one with many questions as yet unanswered. Further progress depends critically on a multidisciplinary approach.

**Terminology/Nomenclature**

Figure 1(A)–(C) are schematic illustrations of different polymorphs of a compound. In (A) and (B), the molecular conformation is retained but the crystal structures are different. The occurrence of a form such as (C), in which the molecule crystallizes with a significantly different conformation gives rise to the term ‘conformational polymorphism’. In addition to the possibility of forming different (but chemically identical) polymorphs, the molecules of a given substance may upon crystallization from solution incorporate solvent molecules (stoichiometrically or non-stoichiometrically) in the resulting crystal structure. These solvated crystalline forms (examples shown schematically in Figure 1(D) and (E)) are often referred to as ‘pseudopolymorphs’ and are no less important in practice than polymorphs of the parent substance. Thus, for a single organic compound, it is frequently possible to crystallize from solution a series of polymorphs as well as a series of pseudopolymorphs (in the latter case species containing different solvent molecules, either individually or as mixtures). Furthermore, it is possible for a compound to yield pseudopolymorphs which are chemically identical, but structurally distinct (e.g. a monoclinic dihydrate and an orthorhombic dihydrate). Such species may be considered as polymorphic pseudopolymorphs. Since physical properties are ultimately dependent on crystal structure, each of these species will therefore have unique properties. It is also noteworthy that the desolvation (e.g. by controlled heating) of pseudopolymorphs such as those in Figures 1(D) and (E) would yield polymorphs of the parent compound. Hence, this represents another route to isolation of polymorphs in addition to crystallization from solution, melt or vapour.

In the above descriptions of polymorphism and pseudopolymorphism, the simplest connotations of these terms have been used and a digression into semantics has deliberately been avoided. However, it is important to note that difficulties with terminology do arise due to inconsistent use and the multiplicity and overlap of synonymous terms (e.g. ‘crystal form’

![Figure 1](https://example.com/image.png)  
**Figure 1** Schematic diagram illustrating polymorphism (A)–(C) and pseudopolymorphism (D), (E); Filled circles represent included solvent molecules.
and ‘crystal modification’ as synonyms for polymorph; ‘solvate’, ‘inclusion compound’, ‘clathrate’ for pseudopolymorph). Pharmaceutical chemists tend to use ‘polymorph’ to describe a one-component system and ‘pseudopolymorph’ for a multi-component system. Finally, it should be noted that amorphous (non-crystalline or ‘glassy’) states of matter are also relevant in the context of polymorphism, since such phases may arise during transformation of one polymorph into another or during trituration of a crystalline polymorph. Amorphous phases are thermodynamically unstable and will tend to undergo spontaneous crystallization to yield a stable polymorph.

**Polymorphic Crystallization and Polymorphic Transformations**

**Thermodynamic Aspects of Polymorphism**

Thermodynamic treatment of a system displaying polymorphism is based on considerations of the Gibbs free energy, $G_i$, of each polymorph as well as the variation of $G_i$ with the thermodynamic variables temperature ($T$) and pressure ($p$). Furthermore, since each polymorph is distinct, each has a characteristic value for its entropy, $S_i$ ($\geq 0$), under any given conditions of $T$ and $p$. Considering constant pressure, the thermodynamic relationship \( \left( \frac{\partial G_i}{\partial T} \right)_p = -S_i \), therefore indicates that the slope of the $G$–$T$ curve for each polymorph of a compound at any given value of $T$ is (a) negative and (b) different. The stable phase at any given temperature is that polymorph with the lowest value of $G_i$ and since the $G$–$T$ curves for the various polymorphs will generally intersect one another at various temperatures owing to their different slopes, it follows that at a given $T$, one polymorph will be stable and all others metastable with respect to it. When two $G$–$T$ curves intersect, the polymorphs they represent are in thermodynamic equilibrium at their transition temperature ($T_i$) and these phases then have identical values for their Gibbs free energy. Each polymorph thus has a temperature range within which it is stable. (From a thermodynamic viewpoint, the co-existence of several polymorphs of a given substance at e.g. 1 atm, 25°C is a paradox; the reason that this situation arises frequently in practice is that the activation energies for solid–solid transformations to the stable phase are generally very high and such transitions are therefore under kinetic control).

The general principles outlined above can be applied to a dimorphic system, for which the thermodynamic behaviours are classified as being either enantiotropic or monotropic, each of which has practical implications as far as interconversion of the two polymorphs is concerned. **Figure 2** illustrates these cases. Here A, B, and L denote the lower and higher melting polymorphs and their common liquid phase respectively. Intersections of the Gibbs free energy curves of A and B with that of L coincide with the respective melting points $T_{mA}$ and $T_{mB}$. In the case of enantiotropy, the curves for A and B intersect at the transition temperature $T$, which lies below either of the melting points; furthermore, on either side of $T$, the stability order of A and B is reversed. Each polymorph therefore has a temperature range in which it is stable and the transition between the two is reversible. In practice, processing conditions which involve temperatures near $T$, could therefore induce a polymorphic transformation from one stable form to the other (which may or may not be desirable). In the monotropic system, the higher melting polymorph (B) is always the more stable one and the other (A) is metastable with respect to it. If a metastable polymorph is prepared, it may spontaneously convert to the more stable polymorph under conditions conducive to phase transformation.

Using experimental data from differential scanning calorimetry (DSC) together with the thermodynamic relationship $G = H - TS$, the simple curves of **Figure 2** can be resolved into their constituent curves depicting the variation of the individual terms $H$ and $TS$ with temperature. An example of such a diagram is shown in **Figure 3**. Such a composite ‘energy/temperature’ diagram for a dimorphic system, which includes the curves for both polymorphs, was recommended by Burger and Ramberger in 1979 as a valuable aid in the interpretation of thermal data and for determining polymorphic stability relationships. A set of rules supported by arguments based on statistical mechanics was subsequently formalized from consideration of such diagrams. These rules were intended to be applied in practical situations to determine whether a polymorphic system is enantiotropic or monotropic. For example, according to the ‘Heat-of-Transition’ Rule, observation of an endothermic effect in a dimorphic system implies the existence of a transition point below it, which in turn requires the dimorphs to have an enantiotropic relationship. In practical cases, where the heat of transition is not measurable due to the slow rate of transformation, the melting points and heats of fusion of the low- and high-temperature polymorphs are determined separately by DSC. The difference between the heats of fusion may then be used instead as an estimate of the heat of transition, leading to a special case of the above rule called the ‘Heat-of-Fusion’ Rule. A ‘Density Rule’ relating polymorphic density to thermodynamic stability, and the ‘Infrared Rule’ which allows entropy rankings from observations of specific
infrared frequencies for hydrogen bonded molecular crystals, were also formalized. In more detailed studies of polymorphism, these rules are often applied in an attempt to deduce relative thermodynamic stabilities in a dimorphic pair (especially to determine which is the more stable species at room temperature). Exceptions to the rules are known (conformational polymorphism being acknowledged as a complication) and this may account for the fact that they are not applied universally when the necessary thermal data are available. In 1995, Yu addressed the issue of inferring thermodynamic stability relationships for polymorphs from thermal data using a purely thermodynamic approach. This led to formulae for calculating the Gibbs free energy difference between the polymorphs, $\Delta G$, as well as its temperature derivative. The relative stability of polymorphs can thus be estimated by extrapolation of the value of $\Delta G$ to any desired temperature. This work also provided a critical comparison of the derived 'thermodynamic' rules.
with those of Burger and Ramberger showing that, with little exception, they are effectively equivalent, despite the different routes for their derivation. It is likely that this recent endorsement of the Burger and Ramberger rules will lead to more frequent attempts to classify polymorphic systems in terms of enantiotropy or monotropy. A further important outcome of the more recent treatment is that the transition temperature, $T_t$, is easily estimated by extrapolating the value of the temperature-dependent quantity $\Delta G(T)$ to zero. Knowledge of the value of $T_t$ for a pair of polymorphic forms is of practical importance in the case of enantiotropy and of theoretical interest in the case of monotropy, since for the latter, it is a virtual temperature.

Solubility data provide an alternative means of determining polymorphic transition temperatures. Over a small temperature range, a plot of $\ln$(solubility) against $1/T$ (a van’t Hoff plot) for a polymorph is linear, with a slope related to the enthalpy of dissolution. If the solubility data for two polymorphs of the compound in a common solvent are treated in this way, the point of intersection of the plots will yield the polymorphic transition temperature $T_t$. An example is illustrated in Figure 4. Furthermore, the heat of transition ($\Delta H_t$) may be calculated as the difference between the enthalpies of dissolution, since dissolution of either of two polymorphs A and B (distinguishable only in the solid phase) leads to the same species in solution. The above description neglects a common practical problem, namely the possibility...
of solvent-mediated polymorphic phase transformation during solubility measurement. This type of transformation is but one of several which polymorphs may undergo.

**Kinetics of Nucleation and Polymorphism/ Pseudopolymorphism**

A prerequisite for crystallization of a specific polymorphic phase is the formation of viable nuclei of that phase, nuclei being defined as the smallest molecular aggregates with a configuration resembling that of the final crystal. The probability of nucleation occurring increases with increasing supersaturation of the solution; in such a solution, where incipient nuclei of all possible polymorphs may exist, kinetic factors determine which of these will become viable, i.e. lead to crystallization of a specific polymorph. The critical parameter associated with the formation of a nucleus is the Gibbs free energy of activation, $\Delta G^*$. Nucleation, which proceeds with a rate dependent on $\Delta G^*$, may occur heterogeneously or homogeneously depending on whether random impurities or substrates promoting nucleation are present or not. In the former case, the mechanism of nucleation is associated with a reduction in $\Delta G^*$, relative to the uncatalysed process.

A detailed treatment of homogeneous nucleation shows that the value of $\Delta G^*$ is determined by several factors including a geometrical factor specific to the shape of the nucleating cluster, the molecular volume, the interfacial energy (between the nucleating cluster and the crystallization medium), and the chemical potential difference between the crystal and the medium. The crucial point that emerges as regards crystallization of different polymorphs of a given compound is the Gibbs free energy of activation, $\Delta G^*$. Nucleation, which proceeds with a rate dependent on $\Delta G^*$, may occur heterogeneously or homogeneously depending on whether random impurities or substrates promoting nucleation are present or not. In the former case, the mechanism of nucleation is associated with a reduction in $\Delta G^*$, relative to the uncatalysed process.

**Types of Polymorphic Transformation**

Phase transformations are driven by the tendency for minimization of the Gibbs free energy of the system. In the absence of a liquid phase, the transformation of one polymorph to another of lower Gibbs free energy is possible in principle, but such a process is generally very slow due to the high activation energy associated with nucleation and growth of a new polymorph within the solid matrix of the old one.

The presence of a liquid phase can significantly reduce the activation energy for transformation. Melt-mediated and solution-mediated phase transformations are thus common. In the former, following the melting of a metastable polymorph, the stable polymorph crystallizes (Figure 2, monotropic case, applies here). Solution-mediated polymorphic transformations have received much attention because of their practical importance. Here, a stable solid phase crystallizes from a solution which originally contained a metastable phase, mass transfer being effected through the solution medium. The rate of such a transformation depends on several factors, the most important of which are the difference in solubility of the two polymorphs, the nature of the solvent, temperature and the rate of agitation of the solution. Kinetically, this process has been satisfactorily modelled in terms of dissolution of the more soluble metastable phase (characterized by $k_D$, the rate constant for dissolution), and crystallization and growth of the stable, less soluble polymorph (rate constant $k_C$). Experimentally, $k_D$ and $k_C$ are determined from the time-dependence of the supersaturation with respect to the stable phase. Hence, the kinetics of transformation can be either growth-limited or...
dissolution-limited depending on whether the ratio $k_D/k_G$ is large or small. In Figure 5, theoretical supersaturation profiles for these extreme cases are compared with the case where the rate constants are equal.

**Structural Aspects**

The various polymorphs of an organic compound (e.g., those shown schematically in Figure 1(A)–(C)), are characterized by different sets of intermolecular interactions (e.g., van der Waals forces, hydrogen bonding, $X-H\cdots\pi$ interactions, where $X=C$, $N$, $O$ typically). For molecules containing hydrogen bond donor and acceptor groups, the incidence of polymorphism generally increases owing to the variety of ways in which such molecules can self-assemble to form supramolecular arrays. Figure 6 shows portions of the crystal structures of two polymorphs of the drug paracetamol. Despite similar molecular conformations, the intermolecular relationships differ very significantly as a result of the different hydrogen bonding arrangements adopted. Ultimately, it is these features which determine all the observed differences in the physical properties of these polymorphic forms.

Prediction of the crystal structure (or rather, of the family of possible polymorphic structures) of an organic compound from a knowledge of the molecular structure alone is considered a highly desirable goal, but the current state of knowledge of the nature of intermolecular interactions generally prevents its achievement. As to prediction of the outcome of polymorphic crystallization, it would be necessary to invoke additional considerations of thermodynamic, kinetic and solvent effects. These problems are currently being addressed by computational methods with moderate success.

**Practical Detection and Analysis of Polymorphs and Pseudopolymorphs**

For industrial crystallization, analytical techniques are required for identification of individual polymorphs, quantification of polymorphic mixtures and detection and analysis of pseudopolymorphs. As shown in Table 1 (which is not exhaustive), many techniques may be used to distinguish polymorphs and to analyse pseudopolymorphs. The primary method is X-ray diffraction, since each crystal structure yields a unique X-ray pattern. As an example, Figure 7 shows the distinctive powder X-ray diffraction (PXRD) patterns obtained for the monoclinic and orthorhombic polymorphs of a drug substance.
Detection of more than one polymorph in an industrial crystallization batch may be achieved using this technique since the PXRD patterns are additive. Levels of an adulterating polymorph down to a few percent are detectable. (Near-IR spectroscopy can be equally sensitive in this regard).

When suitable single crystals of the individual polymorphs of a compound can be isolated, complete structural elucidation of each species by X-ray methods is usually possible and highly desirable (cf. Figure 6). The information derived contains all intramolecular parameters (bond lengths, bond angles, conformational parameters) as well as those associated with the crystal packing (intermolecular van der Waals contacts and hydrogen bonding) characteristic of each polymorph. These structural parameters can be used to interpret data obtained from other methods. A typical example would be the observation of unequal C=O bond lengths in the molecules of a dimorphic pair, which would account for differences observed in the C=O IR data. For pseudopolymorphs, the observed topology of solvent inclusion (e.g., location within channels, isolated cavities, or layers) and the nature of ‘host–guest’ hydrogen bonding may be used to explain differences in crystal solvent volatility observed by thermal methods such as DSC. Thus, a knowledge of the crystal structure of each polymorph and pseudopolymorph of a given compound represents a robust foundation for interpretation of many other physicochemical data.

Another major advantage of complete structural elucidation of a polymorph or pseudopolymorph is that the refined parameters may be used to compute an idealized powder XRD pattern for that phase. Such a pattern is invaluable as a primary reference for future identification of that species and for monitoring the purity of the material experimentally during industrial processing.

**Implications of Polymorphism and Control of Polymorphic Crystallization**

Since the Gibbs free energy differences between polymorphs of the same substance are small (typically 2–3 kJ mol⁻¹), even minor changes in crystallization conditions (intentional or otherwise) can lead to the
precipitation of an undesired polymorph or to mixtures of polymorphs. Hence practical difficulties associated with polymorphism manifest themselves prominently in areas where the same compounds undergo repeated crystallization. One notable example is the pharmaceutical industry, where polymorphism and pseudopolymorphism of active agents used in solid dosage forms may have a very significant effect on the efficacy and quality of the formulation. In particular, since different polymorphs of a drug may have different solubilities and different dissolution rates, use of the inappropriate polymorph in a formulation will compromise the bioavailability of the drug. Other problems which could arise include: (a) use of a thermodynamically unstable polymorph which subsequently undergoes spontaneous transformation into a more stable polymorph, with consequent reduction in bioavailability; (b) solvent-mediated conversion of a drug in a suspension resulting in the slow precipitation of an insoluble drug pseudopolymorph (e.g. a hydrate), again leading to reduction in the concentration of therapeutically active material; (c) transformation of the original polymorph to an undesired one induced by processing conditions, e.g. heating, compression, grinding; (d) precipitation of the drug hydrate instead of the desired anhydrous species due to traces of water in the organic crystallizing solvent. Since reproducible behaviour of the dosage form is of paramount importance, pharmaceutical scientists recognize the necessity for a thorough investigation of the polymorphic and pseudopolymorphic behaviour of a drug during its development in order to avert problems of the type described above. Analogous problems, seriously compromising product performance, occur in other industries. Very detailed documentation of crystallization procedures listing all possible parameters is therefore essential in attempting to ensure reproducible outcomes.

Polymorphism can affect other important technological properties such as tablet compaction. In the case of paracetamol (Figure 6), the crystal structure of the monoclinic polymorph has a complex three-dimensional hydrogen bonding network which is not conducive to plastic deformation during pressurization. The crystals consequently resist direct compression during tabletting. The facile direct compressibility of the orthorhombic polymorph is attributed to the presence of slip planes in the crystal structure which separate the planes of hydrogen bonded molecules (Figure 6), rendering this the industrially desired form of the drug.

In the development of solid-state devices, target species displaying second-harmonic generation are crystallographically non-centrosymmetric polymorphs; their selective crystallization, in preference to inactive centrosymmetric polymorphs of the same compound, is therefore a goal of crystal engineering. Amino acid crystallization is another area affected by polymorphism. For example, precipitation of the α-rather than the β-polymorph of L-glutamic acid is preferred in industry since the former yields a higher solid–liquid separation efficiency.

The above examples highlight the necessity for controlling crystallization mechanisms to ensure precipitation of the desired polymorph. In addition to the computational studies referred to earlier, there are several experimental approaches to this problem (other than solvent-selective pseudopolymorphic crystallization), all of which depend on detailed structural knowledge of the stable and metastable polymorphs of the material in question as a basis for understanding the relationship between molecular interactions in the crystallization medium and the supramolecular structures of the polymorphs that might ensue.

Selective crystallization of metastable polymorphs has been achieved by adding inhibitors which retard the growth of the stable polymorph. Inhibitor design is based on identification of the fastest growing crystal faces of the stable polymorph and tailor-making a substrate which will be incorporated along the direction of fastest growth, thereby blocking crystal development. Polymeric inhibitors have been used to control polymorphism in induced enantiomeric resolution of racemates. Essential to these approaches is detailed knowledge of the relationship between crystal morphology and internal structure and this information can usually be obtained only by X-ray diffraction methods.

Another approach to controlling crystallization is based on the knowledge that the molecular topology of a substrate can affect polymorph selectivity and that such heterogeneous nucleation is energetically more favourable than homogeneous nucleation. The mechanism of ledge-directed epitaxy (LDE), illustrated in Figure 8, utilizes these principles. Here, a selected substrate, with surface ledges characterized by θ_{sub}, directs the preferred crystallization of that polymorph exclusively whose prenucleation aggregate has a matching dihedral angle θ_{agg} between close-packed crystal planes. A metastable polymorph with θ_{agg} matching θ_{sub} can thus be induced to crystallize in preference to a stable polymorph for which this geometrical condition is not met.

**Future Developments**

The renewed vigour with which polymorphism as a phenomenon is currently being investigated is motivated by the demand for reliable methods of reproducible crystallization of specific polymorphs of
industrially important compounds. In the case of pharmaceuticals, further motivation comes from drug-regulatory bodies (e.g., the FDA) which require details of crystallization procedures for specific drug polymorphs and pseudopolymorphs. It is vital that theoretical development of the subject of polymorphism continues to keep pace with these demands. Computational and experimental techniques, which have during the last decade led to substantial advances in the understanding of the primary event in the crystallization process, namely nucleation, are expected to improve in terms of the complexity of the models employed and in the systems investigated. The strategy of ‘rational crystal seeding’ epitomized by the LDE technique is likely to be applied more widely to the control of polymorphic crystallization. A consequent growth is expected in the number of reports documenting successful isolation of specific polymorphs utilizing approaches based on deliberate intervention at the nucleation stage. Detailed structural elucidation of metastable polymorphs and microcrystalline polymorphs will be facilitated by the combined use of methods such as computational crystal structure prediction, solid state NMR, high-resolution X-ray and neutron powder diffraction, and single crystal X-ray methods employing synchrotron radiation sources. Accompanying the demand for isolation of particular polymorphs, methods for more rapid analysis and quantification will be needed to satisfy both production and legal requirements. An increase in the number and types of on-line systems for continuous monitoring of polymorphic purity in the industrial environment is also envisaged.

**See also:** I/Crystallization.

### Further Reading


Zone Refining

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Introduction

Zone refining is a powerful tool for applying coupled melting and freezing operations for manipulating impurities in crystals, as well as for separating liquid or solid mixtures. It was first used to purify germanium in 1952. Zone refining combines the well-known fact that a freezing crystal differs in composition from its corresponding liquid phase, so that passing a short heater along a solid ingot leads to a purification of the ingot. For improving the separation efficiency and reducing time, a series of narrow heaters moving slowly over a solid ingot can be used in multi-pass zone refining.

Several mathematical models have been presented for modelling multi-pass zone refining processes when zone length affects the separation efficiency. Furthermore, variable cross-sectional area ingots with specified volumes have been introduced to improve the separation efficiency. Analogue simulators were used to simulate zone refining by means of a single mathematical equation that expresses solute concentration as a function of distance for any initial distribution of solute and any number of passes through an ingot of a specified length. These simulators include liquid mechanical and electrical analogue simulators. Thousands of significant papers devoted entirely or largely to some aspect of application of zone refining have appeared in the last two decades. For instance, silicon-on-insulator (SOI) films, and semiconducting and superconducting materials were prepared by zone refining operations.

Separation Theory in Multi-pass Operation

Eqn (1) can be derived by taking the mass balance within the moving zone ABCD or A'B'C'D' as shown in Figure 1. It is based on the following assumptions: (a) constant distribution coefficient; (b) uniform composition and no diffusion in the molten zone; (c) no change in density during melting and freezing; (d) a constant cross-sectional area for the ingot.

\[
\frac{dC_n(Z)}{dZ} + \left( \frac{dY_n(Z)}{dZ} + k \right) C_n(Z) = 0, \quad 0 \leq Z \leq 1 - Y_n(Z) \quad [1]
\]

and the boundary conditions of eqns (1) and (2) become:

at \( Z = 0 \), \( C_n = \frac{k}{Y_0} \int_0^{Y_0} C_n(Z) dZ \quad [3] \)

at \( Z = 1 - Y_n(Z) \),

\[
C_n = \frac{k}{Y_0} \left[ 1 - \int_0^{1 - Y_n(Z)} C_n(Z) dZ \right] \quad [4]
\]

in which:

\[
C_n(Z) = C_n(x)/C_0 \quad [5]
\]

\[
Y_n(Z) = l_n(x)/L \quad [6]
\]

\[
Z = x/L \quad [7]
\]