

Zone Melting  
of  
Organic Compounds

E. F. G. Herington

**Zone Melting of  
Organic Compounds**

**E. F. G. Herington**

D.Sc. A.R.C.S.

**Blackwell  
Scientific Publications  
Oxford**

## Preface

Zone melting is the name of a family of techniques that have in common the passage of a narrow molten zone through a long solid rod. Refining is probably the most important object of zone-melting experiments but variants of the zone-melting process can be used to concentrate impurities, study phase diagrams or produce specimens with a uniform distribution of impurity.

Zone refining is a powerful method for the preparation of extremely pure samples of certain materials. The supply of specimens of elements and compounds of the utmost purity is currently of great interest for the following reasons:

(i) It is now widely recognized that knowledge of the properties of highly purified materials leads directly to improvements in technology.

(ii) Pure standards are required for instrument calibration in the determination of the purity of chemical intermediates by ultra-violet, infra-red and mass spectrometry. These chemical intermediates of carefully controlled purity are used in large quantities for the manufacture of such substances as plastics, fibres and insecticides.

Zone refining is playing an increasingly important part in the preparation of pure substances for these purposes, and is now also being applied to the preparation of standards such as benzoic acid for volumetric analysis.

Zone melting provides a versatile separation technique and has been employed, for example, to concentrate heat-labile biological materials and to fractionate polymers. Whereas the chemist of today reports that a new compound was 'recrystallized to a constant melting point' the chemist of tomorrow will, no doubt, state that his compound has been 'zone refined to a constant melting point'.

There are several excellent texts on the zone melting of elements and inorganic compounds. Organic compounds, however, require a rather different treatment. The present book, which collects together extant information on the zone melting of organic materials, also discusses the certification of the purity of samples and the manipulation of specimens. This volume should, therefore, be of interest to many chemists.

I wish to thank Mr D. P. Biddiscombe for reading the manuscript and for making numerous suggestions to improve the clarity of presentation.

E.F.G.H.

# Contents

Preface	vii
1 A Short History of Zone Melting and Zone Refining	1
2 Theory	3
3 Important Factors	25
4 Experimental Techniques	35
5 Pure Materials	56
6 Some Applications of Zone Melting	77
7 Study of Phase Relationships by Directional-Freezing and Zone-Melting Experiments	100
8 Zone Levelling	126
9 Related Separation Techniques	128
<b>Appendixes</b>	
1 Melting Points and Latent Heats of Fusion of Some Common Organic Compounds	147
2 Volume Changes accompanying the Melting of Some Common Organic Compounds	151
References	153
Index	157

## Chapter 1    **A Short History of Zone Melting and Zone Refining**

Zone refining, which is a particular application of zone melting, was developed by Pfann (1952) for the purification of materials employed as semiconductors in transistor diodes and other electronic devices. In the manufacture of these components extraordinarily pure specimens of certain elements, such as germanium or silicon are required. In Pfann's initial experiments a molten zone was caused to travel along a rod of germanium by passing the rod through a short furnace. It was found that the impurities were carried forward, and by repeating the process a number of times a high degree of purification was achieved. In some experiments the amount of impurity was reduced to one part in a thousand million. Since 1952 many papers have appeared describing applications of this technique to the purification of metals and inorganic and organic compounds. Zone melting has also been used to concentrate impurities prior to their analysis and modifications of the method have been employed to obtain rods of uniform composition.

Zone refining resembles distillation and gas chromatography in that it depends upon the distribution of material between two phases. However, whereas the distribution in zone refining is between liquid and solid, in distillation and gas chromatography the distribution is between liquid and vapour.

The fundamental phenomena on which zone refining is based have long been understood, but it needed Pfann's genius to devise this elegantly simple yet powerful technique of purification. At the present time, when so much money is spent on research and so little is understood of the conditions favouring the awakening of dormant originality, it is worth while studying, wherever possible, the circumstances leading up to scientific discoveries. Pfann had, of course, long known of the segregation of impurities

that takes place during the freezing of a metal ingot, and the idea of using short molten zones had occurred to him some years before but had remained at the back of his mind. Then the need for very pure germanium arose. In his own description of the circumstances attending his discovery, Pfann (1956) states that he conceived the idea 'while napping at my desk after lunch'. One is reminded of the origin of the molecular structure theory. Kekulé was dozing in a 'bus when he saw the atoms gambolling before his eyes and observed how two smaller atoms united to form a pair and how some formed chains. The cry of the conductor awoke him and he spent part of the night putting on to paper the forms he had seen in his dreams (Holmyard, 1929). The histories of these two discoveries thus possibly exemplify the combination of diligence and relaxation which gives birth to new ideas.

Since Pfann's first application of the principle to inorganic materials the process has been extended by applying it, with necessary modifications, to the treatment of organic compounds.

Zone melting has found wide application and the considerable scientific literature on the treatment of organic compounds forms the subject of this book.

## Chapter 2    **Theory**

Before the technique of zone refining can be usefully applied to any purification problem, the foundations of the processes must be understood. The theory of zone refining is the same whether applied to metals or to organic compounds but it plays a different rôle in the two fields. In the zone refining of metals it is often feasible to study separately the movement of every impurity present by chemical analysis or by a radioactive labelling technique. When organic compounds are studied, however, the possible number of impurities is so large that only rarely are attempts made to identify all of them. Thus while the theory can be applied to calculate the expected distribution of an impurity at any stage in the zone refining of a metal, theoretical considerations can usually do no more than indicate a rational technique for the zone refining of an organic compound.

When a homogeneous liquid mixture is cooled, the composition of the solid that crystallizes out is usually different from that of the liquid: the purification of a substance by zone refining depends on this difference.

Consider the simple zone-refining experiment shown diagrammatically in Fig. 2.1. Suppose that initially the tube is filled by a uniform binary mixture consisting of a small quantity of impurity in the main component. Such a solid mixture might have been prepared by rapidly freezing a homogeneous solution. Suppose further that the impurity is less soluble in the solid main component than in the liquid main component. Then, because of this solubility difference, as the molten zone moves from left to right the material which resolidifies behind the heater contains less impurity than the liquid mixture from which it crystallized. Provided the molten zone is well mixed, the impurity thus tends to accumulate in the liquid and is carried towards the right-hand end of the rod. The process can be repeated, and successive movements of impurity thus obtained, by returning



the heater rapidly to its starting position after each complete traverse of the rod. Fortunately diffusion in the solid is so slow as to be negligible, so that practically no remixing of the impurity with the purified portion takes place between successive zone passes. Zone refining owes much of its attraction as a purification process to the accumulative effect of multiple zone passes. Even though, as will be seen later, it may be necessary to pass the zone many times, this does not raise insuperable difficulties because zone movement can be controlled automatically.

When a liquid contained in a tube is allowed to freeze from one end, impurity is segregated because of the difference in composition between the liquid and the solid. Such directional freezing, like zone melting, owes its efficacy as a purification process to the negligible movement of the impurity within the solid. In

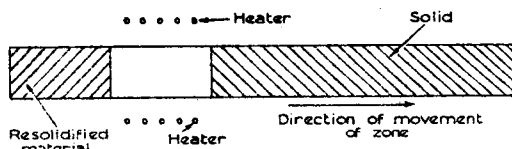


FIG. 2.1 Arrangement of components in a zone-melting experiment.

a zone-melting experiment directional freezing normally takes place in the last zone. Before considering the more complicated conditions that arise in the main part of the charge, it will be convenient to treat this directional freezing process mathematically. This necessitates the study of certain types of phase diagram.

### Phase Diagrams

The development of phase diagrams is linked with the names of Willard Gibbs, Roozeboom, Van't Hoff and others. In the following discussion the main component will be represented as component *A* and the impurity as component *B*. Fig. 2.2 shows a very common form of phase diagram where the components *A* and *B*, when mixed in a certain proportion, form a eutectic *U*. In this Cartesian diagram the vertical axis represents temperature and the horizontal axis represents composition with pure *A* on the left and pure *B* on the right. The lines *AU*, *UB*, *DF* and *UE* divide the figure into areas representing liquid systems, liquid plus pure solid systems and pure solid plus eutectic

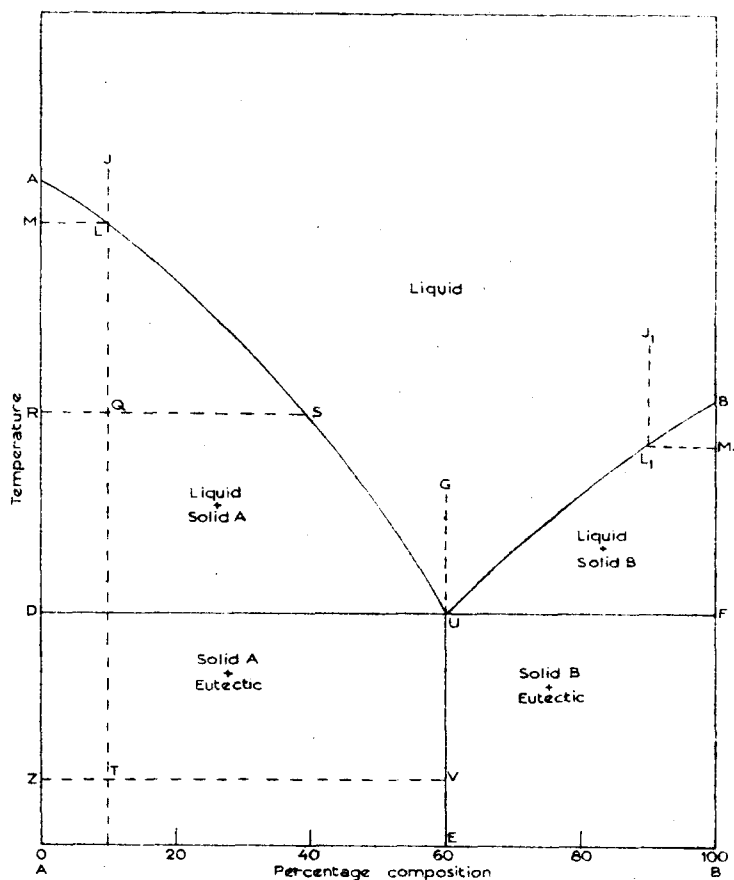


FIG. 2.2 Phase diagram for a system with a simple eutectic.

systems as shown. Consider the course of events if a liquid of composition and temperature represented by point *J* is slowly cooled. The composition remains unchanged as the temperature falls until the point *L* on the diagram is reached, when pure solid *A* begins to separate and the liquid, of course, becomes richer in component *B*. As cooling continues more solid *A* separates while the remaining liquid follows the composition and temperature curve *LU*. When the composition of the liquid reaches point *U* the liquid proceeds to solidify without change of composition or temperature. The temperature starts to fall again only when all the liquid has frozen. The point *Q* (Fig. 2.2) represents the state of the system at an intermediate stage in the process just considered, when the temperature is *R*. Note that *Q* is in the area marked Liquid + Solid *A*. The mixture at this stage

consists of solid  $A$ , in fractional amount  $QS/RS$ , in equilibrium with liquid of composition  $S$ , in fractional amount  $RQ/RS$ . Similarly point  $T$  represents the mixture at the temperature  $Z$ . At this stage the system contains solid  $A$  and eutectic, in fractional amounts  $TV/ZV$  and  $ZT/ZV$  respectively. The overall composition of the mixture is, of course, the same for all points on the vertical line  $JLQT$ .

Similar considerations apply to the cooling of a liquid whose initial composition and temperature are represented by point  $J_1$ . Pure solid  $B$  separates on slow cooling and the composition and temperature of the remaining liquid changes as denoted by the line  $L_1U$ . When the conditions represented by point  $U$  are reached, the liquid freezes without further change of composition or temperature to form the solid eutectic. In the special initial condition where the liquid composition  $G$  is that of the eutectic, cooling produces no separation of components: solid of the same composition as the liquid is formed without further change of temperature when the point  $U$ , which is called the eutectic point, is reached. Note that the addition of a small amount of  $B$  to pure  $A$  depresses the freezing point: the initial freezing point of such a mixture lies on the curve  $AU$  (Fig. 2.2).

Another type of phase diagram important in the theory of zone refining is shown in Fig. 2.3.

In this figure, which represents a system exhibiting solid solutions, there are two curved lines,  $ALB$ , known as the liquidus, and  $ANB$ , known as the solidus, and three areas, representing liquid, liquid plus solid, and solid. Suppose heat is slowly abstracted from a liquid of composition and temperature represented by point  $J$ . The temperature falls until point  $L$  is reached and then solid of composition  $N$  separates. This solid contains less of component  $B$  than the liquid, represented by point  $L$ , from which it has come. The line  $NL$  is called a tie line and connects the points denoting the composition of the liquid and the solid which are in equilibrium at the temperature  $M$ .

Consider now the rate of attainment of equilibrium between the bulk solid and a liquid. This is dependent on the rate of diffusion in the solid and the liquid. If we assume that the liquid is well mixed throughout, two extremes of behaviour may be envisaged; the first is where there is very rapid diffusion in the solid and the second where diffusion in the solid is so slow that it can be neglected. Suppose first that diffusion in both solid and liquid is so rapid that equilibrium between these two phases is maintained throughout the cooling process under consideration (i.e.

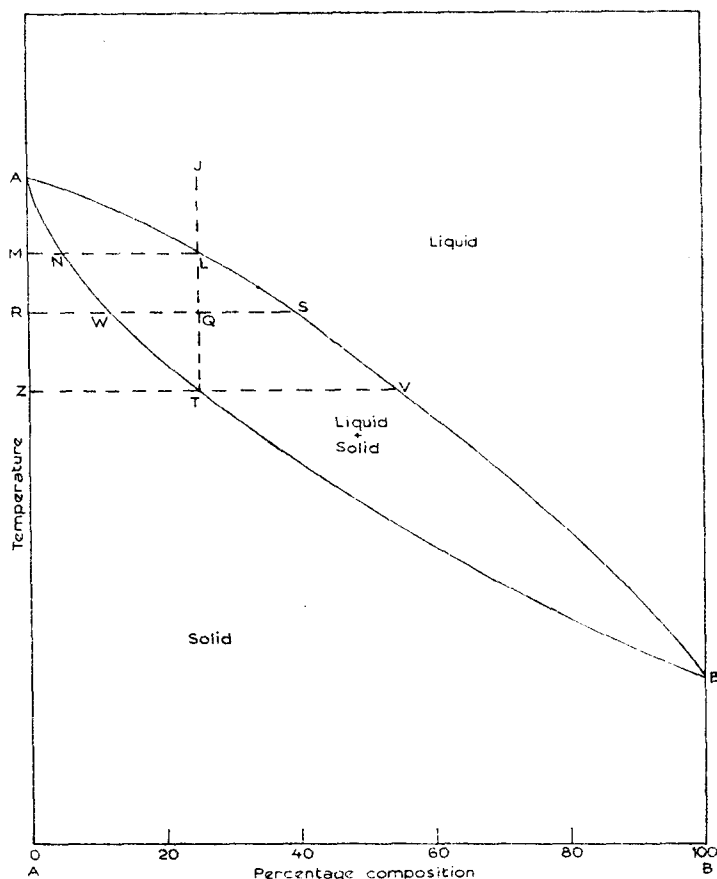


FIG. 2.3 Phase diagram for a system exhibiting solid solutions. Component *A* melts at a higher temperature than component *B*.

Fig. 2.3 starting at *J*). Then further cooling below the temperature *M* causes the liquid composition to move along the curve *LS* while the solid composition moves along *NW*. It is important to realize that because rapid diffusion has been postulated, the solid has the uniform composition denoted by point *W* when the liquid composition reaches point *S*. The whole charge finally freezes when point *T* is reached and the uniform composition of the solid is then that of the original liquid. Now if these were indeed the conditions prevailing during a directional-freezing or zone-refining experiment no purification would be possible because the initial and final compositions of the solid would be uniform. Fortunately practically no diffusion, in fact, takes place

in the solid during directional-freezing or zone-melting experiments, and thus segregation is possible. Therefore let us now suppose there is no diffusion in the solid. When liquid *J* (Fig. 2.3) is cooled, the first solid deposited has composition *N*, but as

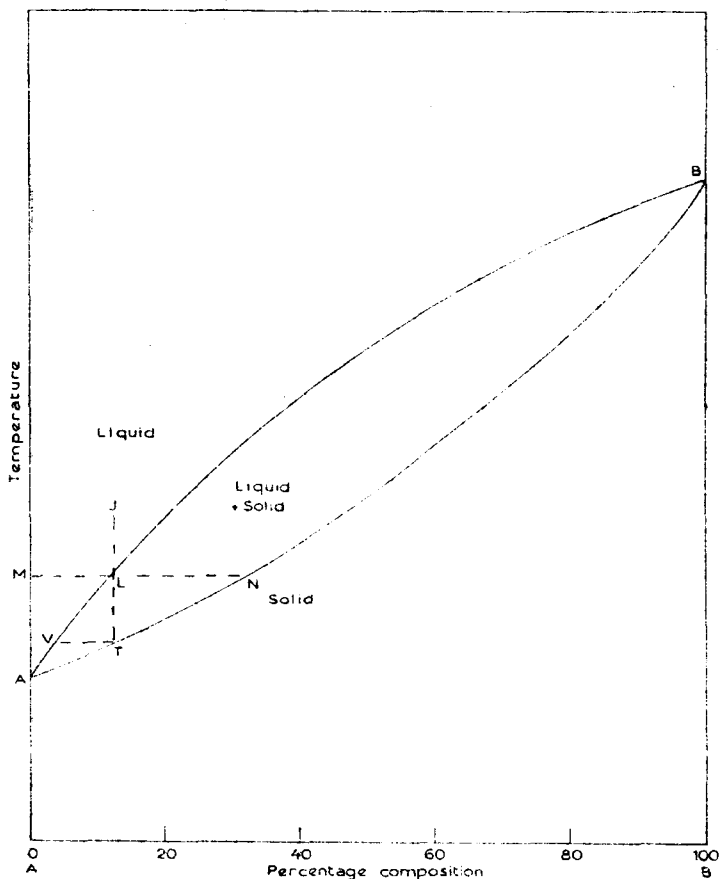


FIG. 2.4 Phase diagram for a system exhibiting solid solutions. Component *B* melts at a higher temperature than component *A*.

cooling continues the solid first formed becomes encrusted with solid of different composition. Thus when the liquid composition reaches *S* the solid being deposited at that instant has composition *W*. The composition of solid being deposited at the instant when a certain fraction of the charge has frozen under these conditions can be calculated provided certain simplifying assumptions are made. The mathematical treatment of this process is,

in fact, the theory of directional freezing and will be considered later.

Another diagram of significance in the theory of zone refining is Fig. 2.4. This represents a system in which the addition of impurity to the main component (A) raises the melting point. If

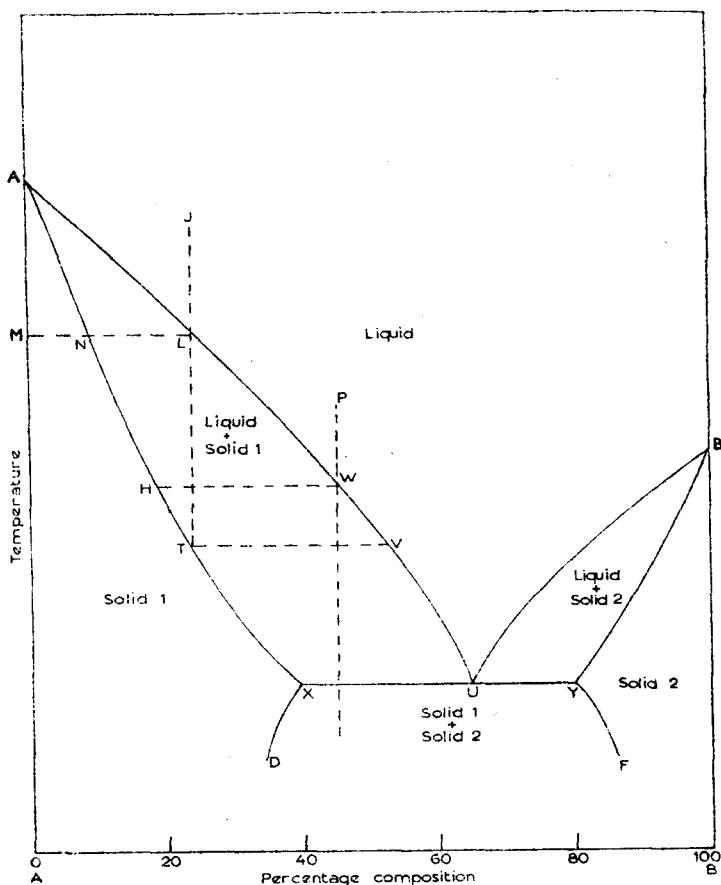


FIG. 2.5 Phase diagram for a system with an eutectic and solid solutions.

a liquid solution represented by J (Fig. 2.4) is cooled, the composition of the solid deposited initially is N. The solid contains more of the component B than the original melt. The liquid composition follows curve LA and the solid composition follows curve NA when the system is cooled further.

Fig. 2.5 shows a type of solidus-liquidus curve that is of some importance in zone refining. The components in the system here

represented are only partially miscible in the solid state; they form two series of solid solutions and the system exhibits a eutectic, *U*. Solid solutions in the first series, collectively designated as 'Solid 1', have compositions represented by points on the curves *AX* and *XD*. Similarly, solid solutions in the second series, collectively designated as 'Solid 2', have compositions represented by points on the curves *BY* and *YF*. The diagram has some features resembling parts of Fig. 2.2, Fig. 2.3 and Fig. 2.4. Some workers (e.g. P. M. Arnold, see Findlay & McKay, 1959) have expressed the opinion that many systems that are usually represented by diagrams like Fig. 2.2 have, in fact, diagrams of the type shown in Fig. 2.5 with the points *X* and *Y* near to the pure component axis. If liquid of composition *J* (Fig. 2.5) is cooled, the solid which first crystallizes out has composition *N*. Further cooling causes the liquid composition to move along the curve *LU* and the solid composition to move along *NX*. When the liquid composition and temperature correspond to point *U*, solid is deposited consisting of a mixture of solid solutions of composition *X* and *Y*. The temperature does not then change further until all the liquid has solidified. There are many other types of phase diagram, some of which will be found in Chapter 7, but Fig. 2.2 to Fig. 2.5 exhibit most of the features that are significant in the study of zone-refining theory.

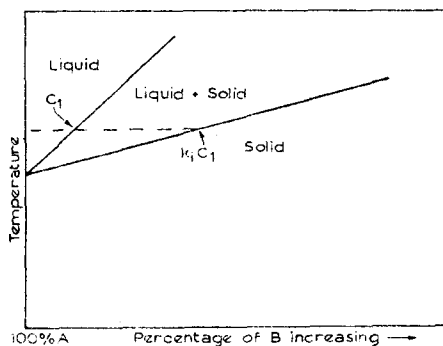
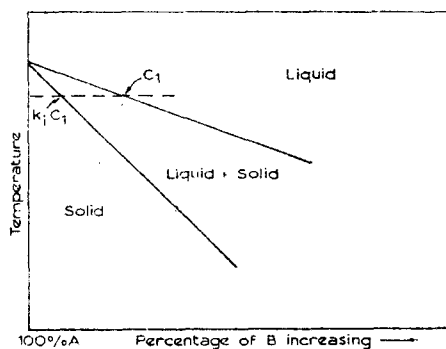
### The Distribution Coefficient

In developing the theory of directional freezing and zone refining it is convenient to employ an ideal distribution coefficient,  $k_i$ , defined as the ratio of the concentration of impurity in the solid to the concentration of impurity in the liquid in equilibrium with that solid. In Fig. 2.3, Fig. 2.4 and Fig. 2.5, the quantity  $k_i$  for liquid of composition *J* equals *MN/ML*. In Fig. 2.3,  $k_i$  is less than unity, while in Fig. 2.4  $k_i$  is greater than unity. In Fig. 2.2 points *M* and *N* can be considered to coincide and  $k_i$  is zero.

Zone refining is normally applied to materials already of high purity and therefore the most important points in Fig. 2.2 to Fig. 2.5 are those near the left-hand axes. Fig. 2.6 and Fig. 2.7 show a simplification of these parts of Fig. 2.3 and Fig. 2.4 which is applicable when the impurity concentration is low.

The solidus and liquidus lines have been assumed to be straight in this small composition range so that  $k_i$  is now a constant for the system independent of concentration. If  $C_l$  is the impurity concentration in the liquid then  $k_i C_l$  is the impurity concentration in the solid in equilibrium with it. Clearly,  $k_i$  can always be

calculated from the solidus and liquidus curves, but a quantity of more importance in zone melting is  $k$ , the effective distribution coefficient, which is the ratio of the impurity concentration in the solid being deposited to the impurity concentration in the liquid from which the solid is separating during a real experiment. In general,  $k$  is nearer to unity than  $k_1$  when the rate of freezing is not infinitely slow. In the simple mathematical



FIGS. 2.6 and 2.7 Diagrams illustrating the meaning of the ideal distribution coefficient,  $k_1$ .

treatment it is usual to regard  $k$  as a constant for all mixtures of given components; Chapter 7 discusses the theory when  $k$  is not constant but varies with the composition of the mixture.

### Phase Diagrams and Zone Refining

Consider the zone refining of a solid mixture containing a small amount of component  $B$  in component  $A$  when the phase diagram is similar to Fig. 2.2. Theoretically, one passage of the zone should suffice to produce completely pure  $A$  throughout the bar



except for a portion near the end which should contain eutectic. However, in practice, because of trapping of liquid and imperfect crystal growth, such a system will generally behave as if the phase relationships were such as are depicted in Fig. 2.5. During the zone refining of a uniform mixture of this type, or of the type represented by Fig. 2.3, having the compositions  $J$  (Fig. 2.3 and Fig. 2.5), the solid deposited behind the zone contains less  $B$  than the liquid from which it crystallizes. Thus the impurity,  $B$ , is carried forward with the molten zone and the material which resolidifies behind the zone contains less impurity than initially. Impurity rapidly continues to accumulate in the liquid as the zone passes along the tube until the liquid composition approaches  $V$  (Fig. 2.3 or Fig. 2.5). The composition of the solid immediately behind the zone is then closely similar to that of the original charge. In the last zone length the freezing is usually directional and all the impurity accumulated in the molten zone is deposited in this zone length. Repeated zone passes cause more of component  $B$  to be carried along the sample.

In a system of the type represented by Fig. 2.5, if the composition of the initial uniform charge lies between  $X$  and  $U$  (e.g. at  $P$ ), then the first solid to be deposited contains a smaller amount of component  $B$  than the charge. The liquid will therefore accumulate component  $B$  until composition  $U$  (Fig. 2.5) is attained, when the eutectic will start to be deposited (see Chapter 7 for a more detailed discussion).

If a uniform mixture of composition  $J$ , with a phase diagram resembling Fig. 2.4, is zone refined the solid first deposited will contain a higher concentration of component  $B$  than the liquid and the liquid thus becomes depleted in this component. This process continues until the liquid composition closely approaches  $V$ . The composition of the solid deposited is then closely similar to the initial composition. The solid deposited in the last zone contains less  $B$  than the original charge. Repeated zone passes cause component  $B$  to be concentrated near the end where the zone started its traverse.

These considerations lead to the formulation of the important rule:

*If an impurity depresses the freezing point of the main component it travels in the same direction as the zone, but if it raises the freezing point it travels in the opposite direction to the zone.*

There is an important difference in behaviour associated with the direction of the movement of impurity. Whereas any