

INSTRUMENTS AND TECHNIQUES

Zone Melting

This technique offers unique advantages in purification and in control of composition in various substances.

W. G. Pfann

Introduced about a decade ago (1), the techniques of zone melting have provided the semiconductor industry with germanium and silicon of extreme purity and precisely controlled composition. They have also provided research metallurgists with a variety of metals at new levels of purity. And the application of these techniques to a wide range of organic and inorganic chemicals has steadily increased in scope. In this article the techniques of zone melting are reviewed, and some potential applications in new fields of endeavor are discussed.

Zone melting is the general term for a varied group of methods for controlling the purity and composition of crystalline substances. In all of these methods a small melted region, or zone, slowly travels through a solid charge. As the zone travels it takes in, at its leading, or melting, solid-liquid interface, impure material, which mixes with the contents of the zone by natural or forced convection and by diffusion. At the trailing, or freezing, interface, solid differing in composition from the liquid freezes out. The magnitude of the difference depends on the solute (impurity) involved. Because of the difference in composition at the freezing interface, the zone is able to move solutes along the solid charge. Depend-

ing on the size and number of zones and on the initial make-up of the charge, various useful distributions can be achieved.

Zone Refining

The most important zone-melting technique is zone refining, by which impurities are moved to one or the other end of a charge by a series of molten zones all passed in the same direction. Impurities that lower the freezing point of the parent substance, or solvent, travel *with* the zones and accumulate at the end of the charge; impurities that raise the melting point travel *opposite* to the zones and accumulate at the beginning of the charge.

The distribution coefficient k determines the ease with which a given solute is moved by the zones; k is defined as the ratio of the solute concentration in the freezing solid to that in the bulk liquid. The solute-moving power of the zone increases as the absolute value of the quantity $(1 - k)$ increases. For binary systems of the simple eutectic type, with limited solid solubility, k may be very small— $\sim 10^{-3}$ to $\sim 10^{-1}$. For systems of the complete-solid-solution type, k generally lies between ~ 0.2 and ~ 3.0 . If k is close to unity—and this is common for systems in which the two components

are very similar—zone refining becomes relatively ineffective (just as would any other physical separation method based on a solubility difference between two phases). Typically, from about five to as many as 100 zone passes are used, depending on the magnitude of $(1 - k)$ and the purity desired.

Figure 1 shows schematically how successive zones pick up impurities in traversing an ingot. The impurity contents of successive zones, indicated by dots (2), decrease because each successive zone travels through purer and purer solid. The concentration in the solid behind a given zone is shown as lower than that in the zone—the case when k is less than unity.

Although the equilibrium value of the distribution coefficient k is determined by phase equilibrium and can be obtained from a phase diagram, the actual value depends on the degree of mixing in the molten zone and the rate of travel of the zone. This has an important bearing on just how zone melting is carried out. Consider a solute for which $k < 1$. The concentration freezing out is less than the concentration in the zone. Therefore, solute must be rejected by the advancing solid-liquid interface. Ideally this rejected solute would be mixed instantly with the bulk liquid, but actually there always exists a thin layer in the liquid adjacent to the interface, through which solute can pass only by diffusion. A concentration gradient of solute builds up in this diffusion layer, and the concentration of solute next to the interface is higher than that in the bulk liquid. Since the freezing solid “sees” only the liquid adjacent to it, the actual value of k is closer to unity than the equilibrium value. In fact, if the travel rate is high enough, the effective k will be unity and the solute-moving power of the zone will be nullified. It is therefore necessary, in zone refining, either to stir the liquid or to design the apparatus to enhance natural convection, or to advance the zone at an appropriately low

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rate. Typical rates range from ~ 0.5 centimeter to ~ 15 centimeters per hour.

As the zones continue to transfer solute toward the end of the charge, a concentration gradient builds up along the charge and successive zones transfer less solute. Eventually an ultimate, or limiting, distribution is reached, which cannot be altered by more zone passes.

Mathematics of Zone Refining

To use the zone-refining technique intelligently one needs to know the solute distribution along the ingot after any given number of zone passes. Oddly, it is easy to calculate the distribution after one pass and after an infinite number of passes (the ultimate distribution), but it turns out to be very difficult to calculate the distribution after an arbitrary number of passes. The problem has been solved mathematically, but the solution involves laborious iterative computations. For-

tunately, the behavior of a traveling molten zone can very easily be simulated by a computer, and a sizable collection of computed, multipass zone-refining curves have been published (3).

The way in which a single zone pass alters an originally uniform distribution of solute is shown in Fig. 2 (4). The mean concentration in the charge is C_0 . To start the process, one zone length of solid is melted at the beginning of the charge. The concentration in the liquid is, naturally, C_0 . As the zone begins its advance, the first concentration to freeze, at $x = 0$, is kC_0 . As the zone continues its advance, solute accumulates in the liquid and the concentration in the freezing solid rises. The concentration in the liquid continues to rise and approaches asymptotically the value C_0/k . Once this value is attained, the concentrations entering and leaving the zone are equal, and a level region, of concentration C_0 , is produced. When the front of the zone reaches the end of the charge, a discontinuity occurs and the concentration begins to rise

sharply, because the volume of the zone decreases. This last process is called normal freezing.

The single-pass operation illustrated in Fig. 2 is neither fish nor fowl. True, there is a region of purification at the beginning of the charge, but a greater purification could have been obtained by performing a normal freezing operation on the charge as a whole. There is a level region in the middle, which is also desirable for certain purposes, but, as we shall see later, there are ways to increase the length of this region. The distribution of solute after this single zone-melting pass is expressed mathematically in the following equation (valid for all but the last zone length), which was derived by W. T. Read (3):

$$\frac{C}{C_0} = 1 - (1 - k)e^{-kx/l}$$

Here x denotes distance from the beginning of the charge, and l denotes zone length.

It is when repeated passes are made

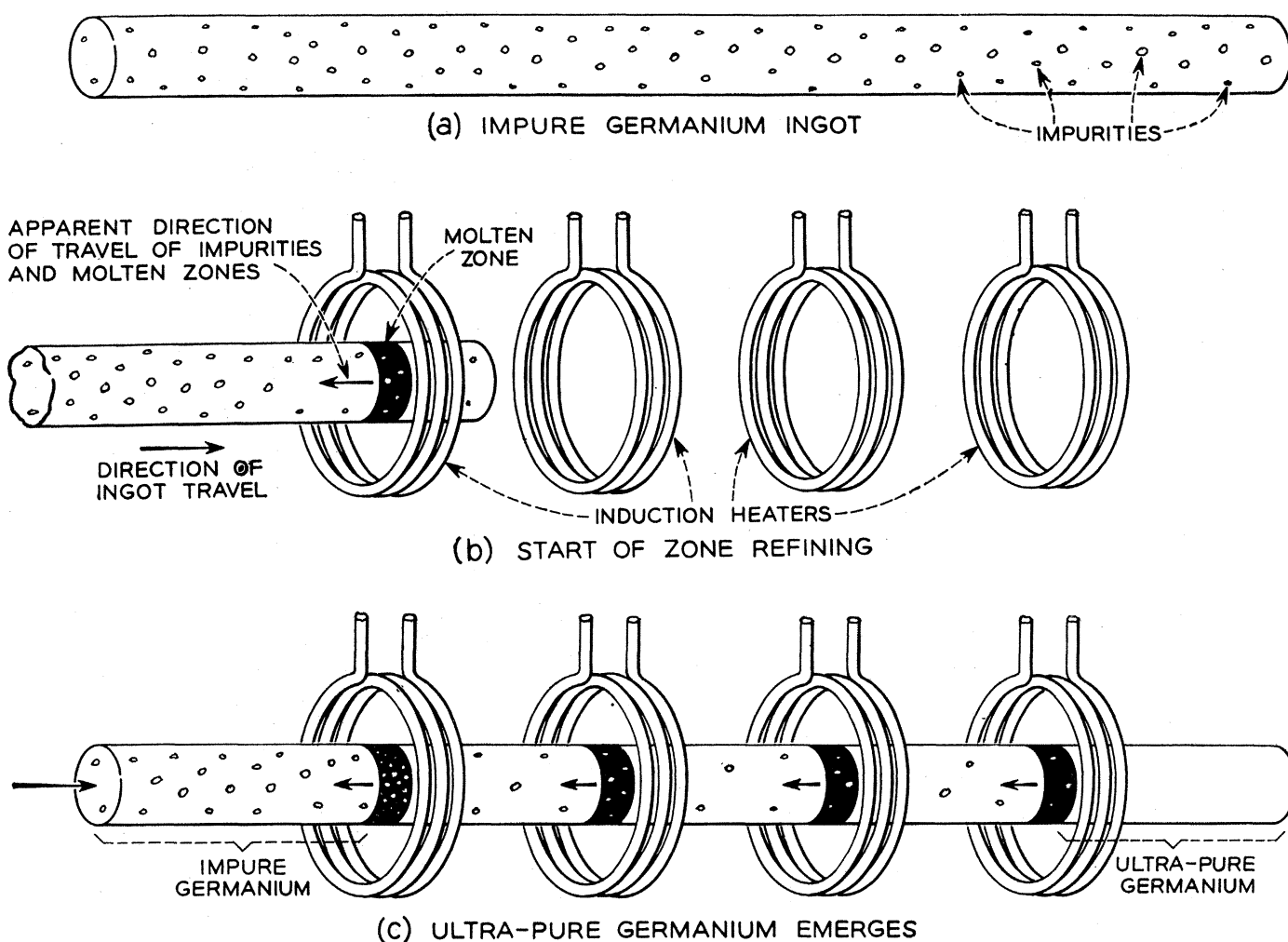


Fig. 1. Schematic diagram of a germanium zone refiner, illustrating the redistribution of an impurity that lowers the melting point. [Bell Labs. Record (June 1955)]

that the true advantages of zone refining become evident. For, by using apparatus such as that indicated in Fig. 1, the beginning and middle of the charge can be made purer and purer by simply passing more heaters along the charge. There is no need for separating pure and impure fractions and recombining them in accord with a complex program, as is done in conventional repeated fractionation. In fact, the charge does not have to be handled at all.

The effectiveness of multipass zone refining is illustrated by the calculated curves of Fig. 3. These are for a charge 10 zones long and for a k of 0.5—a more or less average value, neither particularly favorable nor particularly unfavorable. An idea of what can be achieved for other values of k is given in the ultimate distribution curves for various k 's (Fig. 4). The equation for the ultimate distribution is given to a good approximation by a simple exponential, valid for all but the last zone length:

$$C = Ae^{Bx}$$

The curves are therefore straight lines when plotted semilogarithmically, as in Fig. 4. Here A and B are constants, given by $A = C_0BL/(e^{BL} - 1)$ and $k = BL/(e^{BL} - 1)$, where L denotes charge length. The slope of each straight line in Fig. 4, proportional to the constant B , becomes greater as k becomes smaller. For k 's of ~ 0.1 or 0.2 , the theoretical solute concentrations at the beginning of the charge are almost unbelievably small, so small that other factors, such as contamination by the container or the atmosphere, usually prevent attainment of the theoretical concentrations.

The curves of Fig. 4 are for a ratio (L/l) of 10. If the zone length is halved, the ultimate purification is greatly enhanced, as shown by the dashed curve for $k = 0.5$, for which (L/l) is 20.

Examples of Zone Refining

I shall give some examples of various classes of substances that have been raised to new levels of purity by zone refining and also describe various commonly used types of equipment.

Germanium. It is appropriate to begin with germanium, because the story of zone refining began with germanium, which was urgently needed in ultrapure condition for the transistor industry. Even today it remains, with the possible

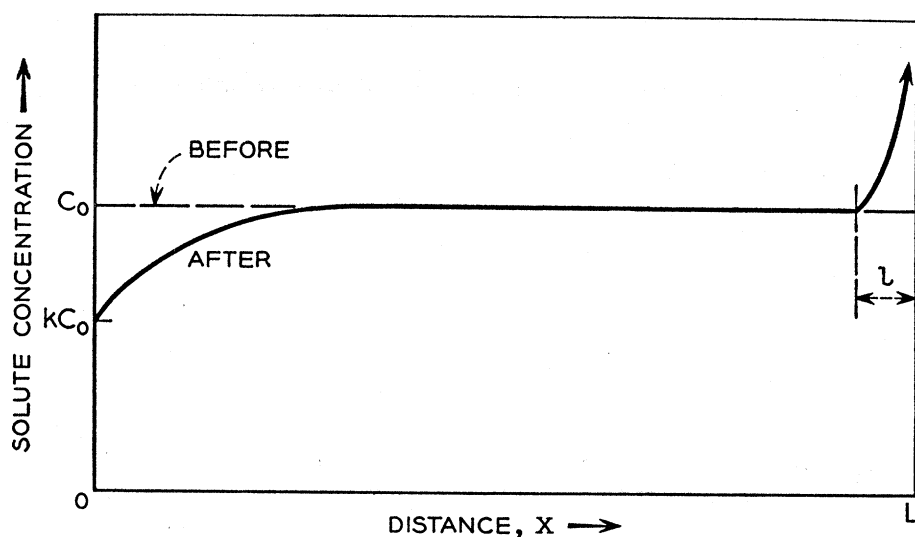


Fig. 2. Approximate concentration of solute after passage of 1 molten zone through a charge of uniform mean concentration C_0 . [Trans. Am. Inst. Mining Met. Petrol. Engrs. 202, 747 (1952)]

exception of silicon, the purest commercial substance available to man. Once the method had been conceived, the odds that it would succeed for germanium were favored by three circumstances: availability of a very pure starting material; availability of a suitable container, high-purity graphite; and favorable distribution coefficients for the critical impurities.

A typical zone refiner for germanium is shown in Fig. 5. Around a fused silica tube are wound, in series, six four-turn induction coils of water-cooled copper tubing powered by a 450-kilocycle generator. The impure ingot is cast in a graphite boat and pulled through the coils by a fused silica rod in an atmosphere of purified nitrogen. This six-pass treatment reduces the concentrations of elements of groups III and V, as well as many others, to less than 1 part per 10 billion parts of germanium in about 80 percent of the ingot. A zone-refined ingot, etched to show the elongated crystal structure that is characteristic of many zone-refined metals and semiconductors, is shown in Fig. 6, together with a single crystal, referred to later.

Silicon. In a few years silicon became the favorite of the transistor industry, and zone refining was applied. However, silicon was a tougher nut to crack than germanium because it reacted with all known container materials. Fortunately, the floating-zone technique appeared on the scene (5, 6). In this technique, shown schematically in Fig. 7, silicon serves as its own container. A vertical rod is held by rigid clamps at the ends, and a molten zone is pro-

duced by a narrow induction-heating coil. Surface tension holds the zone in place as it is moved along the rod. An actual silicon floating zone is shown in Fig. 8. Although there is no theoretical limit to the diameter of rod that can be treated, there is a maximum height of zone that surface tension can support (7). The greater the surface tension and the lower the density of a substance, the greater the maximum height. Zones longer than the theoretical maximum have been supported through clever design of the induction coils to achieve a certain amount of levitation by electromagnetic forces.

Boron, one of the common impurities in highly pure silicon, has an unfavorable distribution coefficient. Even though boron could be removed by very many zone passes, ways have recently been found to eliminate it in chemical processing prior to zone refining. Another approach has been to remove it by introducing a bit of water vapor into the hydrogen atmosphere of the floating zone apparatus (6). The water vapor combines with the boron to form a volatile oxide, which leaves the molten zone while other impurities are being segregated by the zone.

The first floating-zone ingots were rather irregular and wormy in appearance, but soon extremely sophisticated control techniques were developed by the semiconductor industry. Now it is common to pass some tens of zones through a rod completely automatically and to end up with something resembling a machined cylinder. Single crystal rods about an inch in diameter are available commercially.

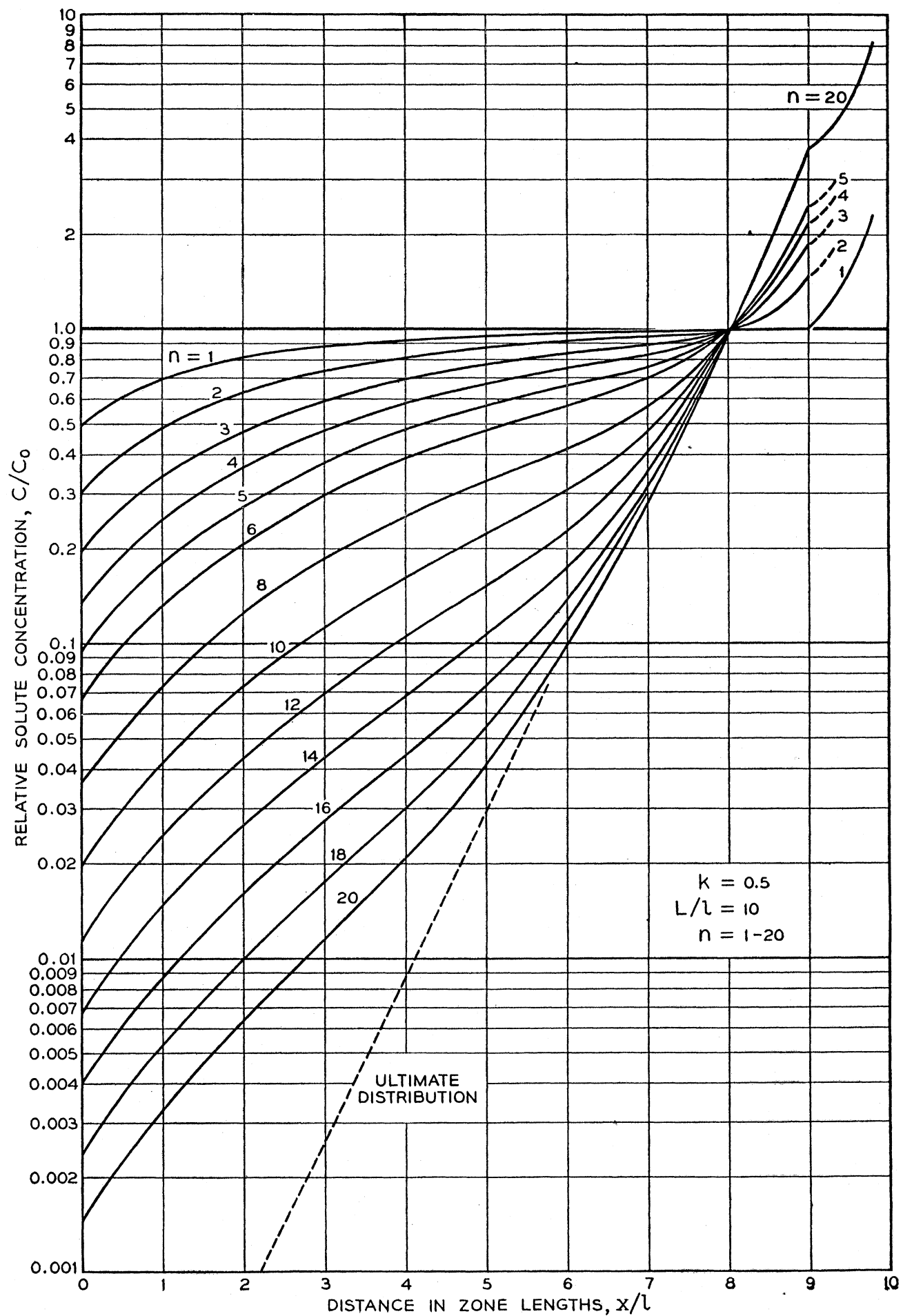


Fig. 3. (left). Relative solute concentration C/C_0 (logarithmic scale) plotted against distance in zone lengths, x/l , from the beginning of a charge, for various numbers of passes n . L denotes charge length. [W. G. Pfann, *Zone Melting* (3)]

Other semiconductors. While silicon and germanium are by far the most widely used of the newer semiconductors, and the techniques described here are used with minor variations the world over, zone refining is being applied to a host of other semiconductors, mainly compounds, on a research and development basis. Among the more important of these are indium antimonide, gallium arsenide, gallium phosphide, and cadmium telluride—the so-called “3-5’s” and “2-6’s,” referring to the group numbers of these elements in the periodic table. Indium antimonide and cadmium telluride can be refined in boats, but gallium arsenide and gallium phosphide have required floating zones. A serious problem arises in refining some of these compounds—the excessive volatility of one of the constituents. This has given rise to operation at some tens of atmospheres of pressure of the volatile element. Dealing with such compounds has also focused much attention on a previously little-known fact—that the highest melting composition is sometimes a bit off the 1 : 1 stoichiometric ratio.

Metals of high melting point. In recent years intensive effort has been expended on the purification of metals of high melting point—tungsten, molybdenum, niobium, iron, tantalum, beryllium, and some of the precious metals. A variant of the floating-zone technique, called electron-beam zone melting and illustrated in Fig. 9, has been most effective for preparing certain of these metals in research quantities (8). Operation is in a vacuum; the rod of metal to be purified serves as anode to a cathode usually of tungsten. Focusing plates are used to concentrate the electron beam to a narrow ring on the anode, an ideal arrangement in view of the fact that the floating zone must not exceed a certain critical height. The method is subject to troubles from outgassing and cannot be used if the vapor pressure is at all high, but it has provided some of our purest samples of refractory metals. Often purification occurs as much by evaporation as by segregation.

Other means have been devised for getting around the container problem

for metals of high melting point. An electric arc between a tungsten electrode and a charge resting on a water-cooled copper boat has been used in purifying thorium and uranium alloys (9). Induction melting has also been used for purifying metals in water-cooled metal boats (10).

Metals of low melting point. Quite a few of the metals of low melting point are available commercially, in small quantities, at new levels of purity as a result of zone refining—for example, tin, lead, bismuth, antimony, and aluminum. Resistance heaters, such as the zone refiner (Fig. 10), as well as induction heating, are commonly used.

Significant scientific findings have

been made with these ultrapure metals. We do not know exactly where these will lead, but some of the results are striking. For example, in the past it has been taken for granted that any metal can be hardened by mechanical working. However, zone-refined aluminum better than 99.9999-percent pure cannot be work-hardened at room temperature. The distorted grains immediately recrystallize and grow (11, p. 79). The fundamentals of grain growth in slightly strained zone-refined lead have recently been under intensive study. It was found that certain recrystallized grains grew into strained grains with startling speed but that the speed could be reduced by a factor of

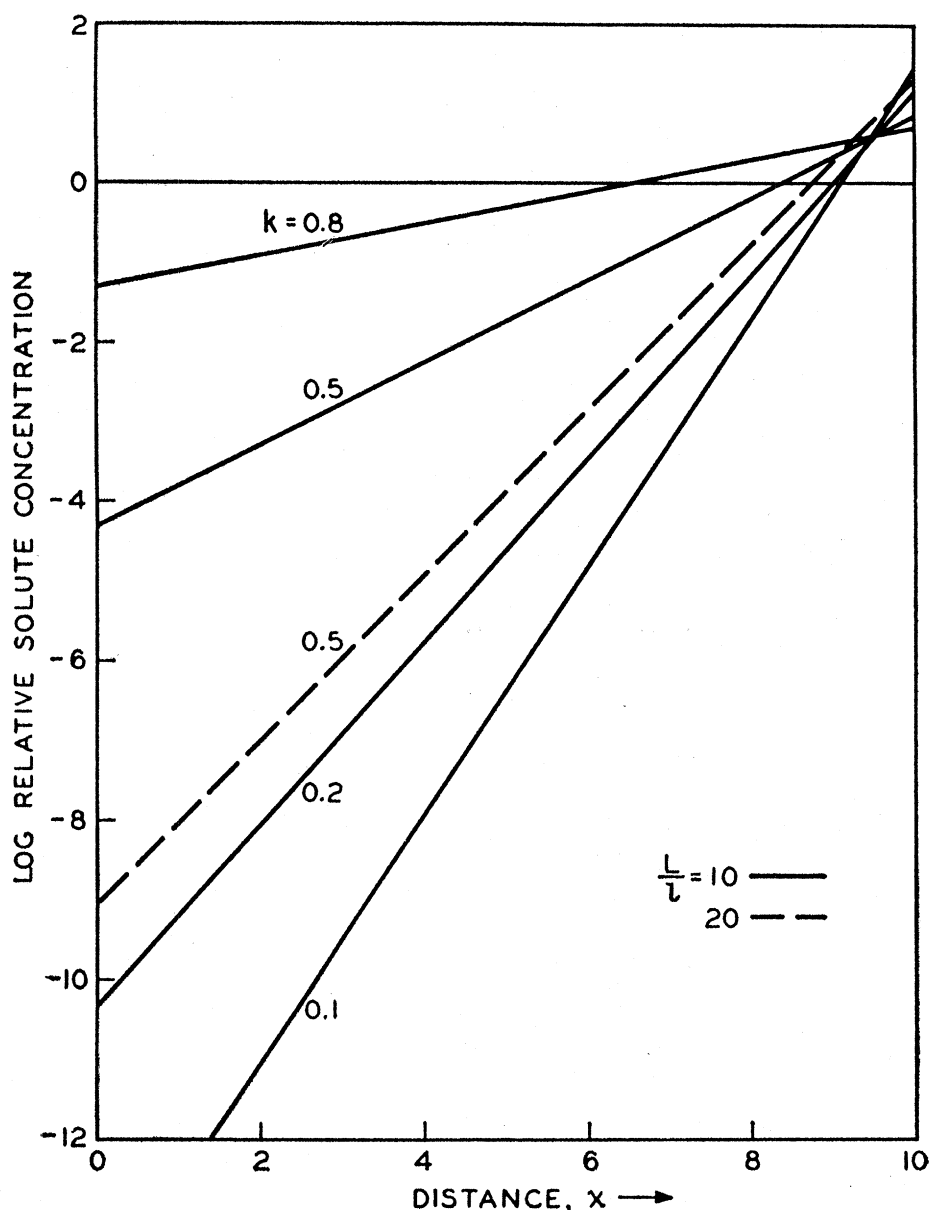


Fig. 4. Ultimate distribution attainable through zone refining for a charge 10 zones long for various values of the distribution coefficient k . Dashed line indicates distribution for a charge 20 zones long.

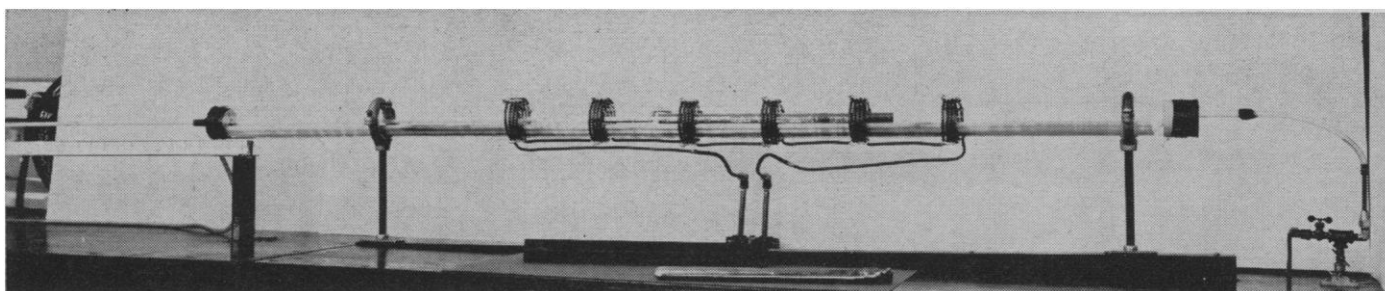


Fig. 5. Induction-heated zone-refining apparatus used for purifying germanium. [W. G. Pfann, *Zone Melting* (3)]

10^8 by the addition of a few thousandths of a percent of a critical solute element (12). The preferred growth direction (with respect to the crystal lattice) in grains of lead castings changes drastically when the purity of the lead exceeds a certain value (13). Mechanical and magnetic properties of many metals and alloys depend on casting textures and recrystallization textures. With the help of these ultrapure metals more

is being learned about the fundamental mechanisms.

Zone-refined iron exhibits ductility at 4.2°K, whereas less pure iron becomes brittle at a far higher temperature (14). As iron is made purer, its solubility for oxygen decreases, and this solubility becomes nil in zone-refined material (11, p. 259). An oxide-iron interface in corroding iron is irregular in ordinarily pure material and smooth in

zone-refined material (11, p. 259). The reasons for such differences are not entirely clear at present, but, as Morris Cohen has put it, "we are getting to the point [in purification] where the true properties of the metals are at last beginning to show through."

Inorganic compounds. A variety of alkali halides and related compounds have been purified by zone refining. Interest in these materials has been both fundamental (as in the study of vacancy formation, color centers, and transport properties) and practical (as in the development of scintillation detectors, photographic chemicals, and masers). The properties of interest are structure-sensitive and impurity-sensitive, hence single crystals of the highest purity have been needed.

As a class, these materials have posed some purification problems. Many of them have such a high melting point that the choice of a container is a serious, although not an insurmountable, problem. Some partly decompose on melting, so halogen atmospheres have been necessary. Their surface tension, although high as compared with that of most chemicals, has not been high enough to permit use of the floating-zone technique. Having high electrical resistance, they are not readily melted by induction, and being transparent, they are not readily melted by focused radiation. Nevertheless, some excellent, painstaking work has been done. The content of divalent cations in potassium chloride and potassium bromide has been reduced to less than 1 part in 100 million (15), and silver chloride has been purified to the point where startling changes in its sensitivity to light have been discovered (16).

Organic compounds. In my opinion, zone refining will prove to be more useful in the field of organic compounds than in any other area, if only because organic compounds are so numerous. Furthermore, many of them have low



Fig. 6. At left, polycrystalline zone-refined germanium ingot; at right, zone-leveled single crystal germanium ingot. [Bell Labs. Record (June 1955)]

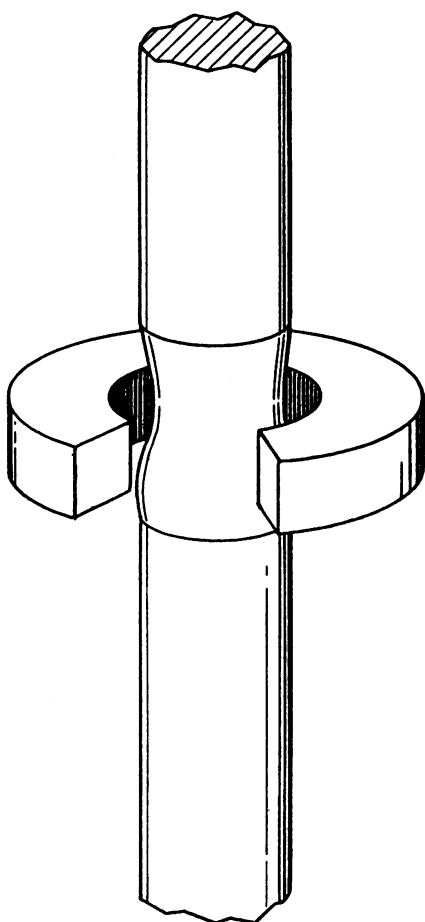
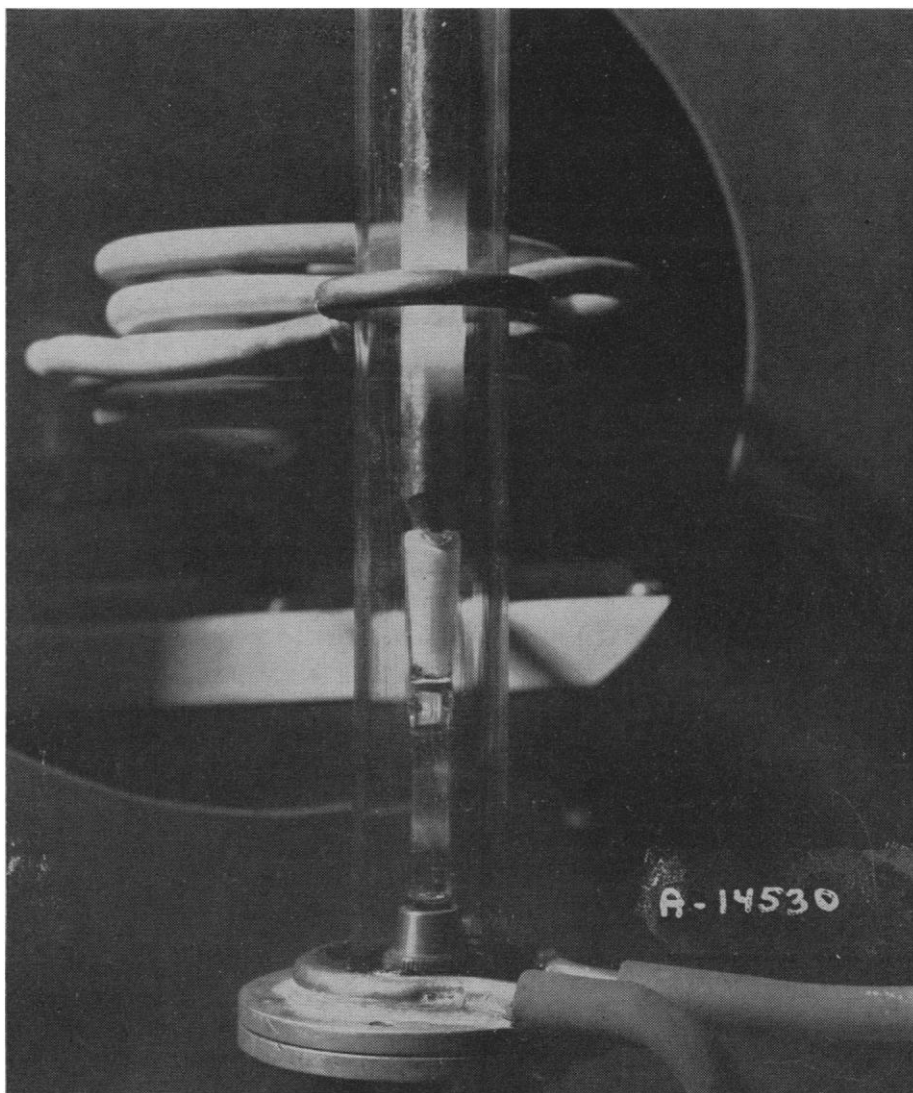


Fig. 7 (above). Schematic representation of the floating-zone technique. [W. G. Pfann, *Zone Melting* (3)]

Fig. 8 (right). Floating zone in silicon.



melting points and are relatively easy on containers. Many compounds which decompose on vaporization can be melted without being harmed. While conventional resistance-heated zone refiners can be used, the low thermal conductivity of the organic compounds calls for somewhat different apparatus. Ideally there should be heat sinks between successive heaters, and the cross section of the charge should have a large surface-to-area ratio.

Impressive early work was done, with more or less conventional equipment, on nitrogen compounds derived from oil shale, by workers of the U.S. Bureau of Mines (17). It is of interest that some of the chemicals they purified could not be treated by other conventional techniques, such as distillation.

Zone refining of a large group of organic chemicals was reported by workers at I.C.I. Ltd. in England. One amusing result was that skatole lost its

bad odor on zone refining, showing that its hitherto notorious reputation was due to an impurity (18).

Much work has been done at the University of Erlangen on the purification of natural substances from insects and plants. Ingenious microrefiners, capable of handling milligram quantities, have been designed (19).

Many organic substances are liquid at room temperature. These can be zone refined by refrigerating the charge sufficiently to freeze most of it, so that heaters can move molten zones through it (20). The term *zone freezing* has sometimes been used to describe such operations. In my opinion this term is undesirable because, whether by intent or accident, it tends to make people think that there is a difference in principle between the zone refining of a solid and the zone refining of a substance that happens to be liquid at room temperature.

The organic chemicals for which zone refining is most likely to succeed are those which crystallize readily and which have low viscosity in the liquid state. High viscosity makes for low diffusivity in the liquid and therefore for an effective distribution coefficient that readily rises to unity. Polymers, in themselves, show little promise. However, there is evidence that by special techniques it may be possible to fractionate polymers according to molecular weight (21). The technique is to dissolve a small amount of polymer in a solid solvent such as naphthalene and then to pass zones through the charge. The polymer fractions move at different speeds, according to molecular weight, although it is not clear that a simple solid-liquid phase equilibrium is the only mechanism involved. Only scanty results have been published to date. Mathematics for this operation have been developed recently (22).

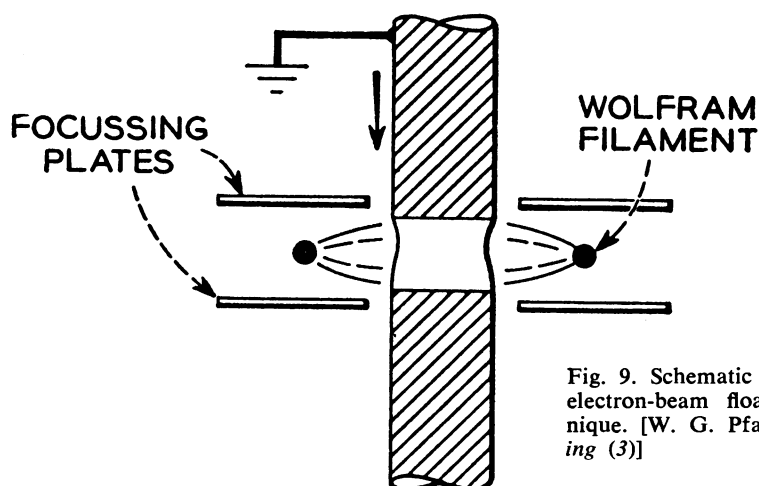


Fig. 9. Schematic diagram of the electron-beam floating-zone technique. [W. G. Pfann, *Zone Melting* (3)]

Zone Leveling and

Temperature-Gradient Zone Melting

An important problem of long standing is that of the controlled addition of a desired solute to a single crystal. It is virtually impossible to obtain, by conventional means, a uniform concentration of a soluble impurity from one

end to the other of a crystal grown from the melt or from solution because of the normal freezing action described earlier. A group of zone-melting techniques known as zone leveling have been devised to solve this problem.

In one such technique (3, p. 154) an impurity with a very small value of the distribution coefficient k is dissolved

in the first zone length of a charge of pure solid solvent. For example, the solvent might be zone-refined germanium and the impurity might be antimony (one of the useful, conductivity-producing impurities), for which k is less than 0.01. As the zone travels along the charge its content of antimony decays exponentially, but, because k is so small, the rate of decay is negligibly low. Thus, a single crystal 10 or 20 zones long can be grown in which the antimony content does not vary by more than a few percentage points except in the last zone length, which undergoes normal freezing. A typical crystal is shown in Fig. 6. The method is widely used by the semiconductor industry.

The unwieldy name of temperature-gradient zone melting has been given to one of the most intriguing, albeit least used, zone-melting techniques. Heretofore I have discussed molten zones which usually contained small amounts of solute and which were caused to move by external heaters. In temperature-gradient zone melting the

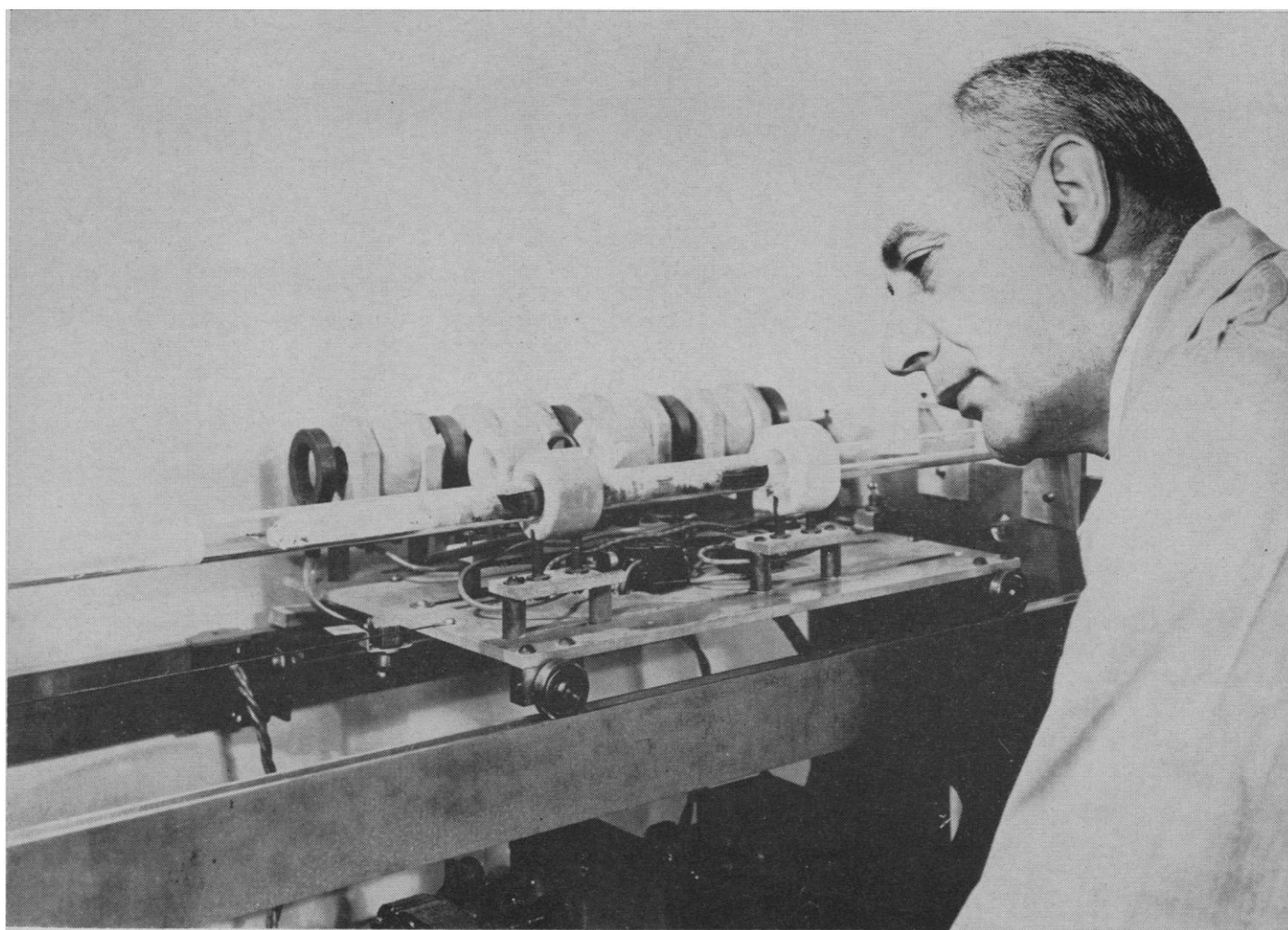


Fig. 10. A resistance-heated zone refiner for chemicals and metals of low melting point.

zones are usually very rich in solute and they are caused to move by a temperature gradient along the charge.

To illustrate, let us consider the gold-germanium system, which is a simple eutectic system exhibiting very small solid solubility. If a tiny piece of solid gold is placed on a slab of germanium and heated above the eutectic temperature (the lowest temperature at which a liquid phase can exist) a molten alloy droplet forms. It continues to grow in size, by dissolving more and more germanium, until it becomes saturated with germanium. If, now, there is a temperature gradient along the surface of the slab, the tiny molten droplet will migrate along the surface, seeking the hottest point on the slab. It does so because the hot edge of the droplet can dissolve more germanium than the cooler edge. A concentration gradient of germanium is thus produced in the droplet, and this causes germanium to diffuse to the cooler edge of the droplet. The liquid at the cooler edge, now supersaturated, freezes out the excess germanium (with a small amount of gold in solid solution). The net effect is to move the droplet as a whole toward the region of higher temperature. If the temperature gradient had existed in the thickness direction of the slab, then the droplet would have migrated through the slab.

This little-known phenomenon, described here in microscopic terms and originally applied in making complex p-n junction shapes for special transistors, is undoubtedly very common in the world of technology and in nature. Quite a few years ago it was observed that droplets of brine migrate toward the outer, warmer surfaces of blocks of sea ice. It is possible that one might efficiently purify salt water by freezing thin layers of salt ice on internally cooled metal plates of large area, allowing the droplets of brine to migrate outward by temperature-gradient zone melting to the surface of the ice, where they could be removed by draining, washing, or whirling. When one considers the complex of substances that

comprise the earth's crust and realizes that a radial temperature gradient exists in this crust, it is conceivable that temperature-gradient zone melting, perhaps carried on over very long periods, played a part in producing present geologic formations.

Other Aspects

There are several reasons why zone refining might appeal particularly to analytical chemists (23). It has been used extensively to provide high-purity standards, as well as melting-point standards of metals such as tin and lead. It has been used to concentrate trace impurities to levels within reach of the analysts' methods. This technique can be made quantitative by preparing standard samples, adding known concentrations of radioactive tracers, and then concentrating the tracers through a standardized zone-refining and cropping procedure.

Along with other purification methods, it has posed a problem for analysts by confronting them with ever purer substances to analyze. Increasingly, they have resorted to methods of physical measurement, such as special electrical measurement techniques, rather than to the refinement of existing analytical techniques.

Zone refining has been used in the determination of phase diagrams (23). It provides an ideal method of determining eutectic compositions, and it has been used to resolve disagreements over the existence or location of eutectic or peritectic points; space does not permit description of the methods here.

Summary

So far, most work in the field of zone melting has been done on a small scale, use of heavier than 100-pound ingots of certain metals notwithstanding. However, there is no basic reason why tons rather than pounds cannot be treated. Continuous refiners have been designed

and operated, and a suitable design theory exists (3).

The zone-melting techniques stem from the combination of an old and well-known principle—that a freezing crystal differs in composition from the liquid—with the new and simple idea of melting part of a solid rather than all of it. Zone refining is by no means the answer to all problems of purification. It is, after all, a physical separation method and can be no more effective than the distribution coefficient allows it to be. Nevertheless, it has been of value in commerce and research and probably will continue to be, as more substances are tried, as more efficient equipment is developed, and as new variations and principles are introduced.

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