

This simple technique, in which a solid is refined by passing a liquid zone through it, has been of profound value in those technologies that call for materials of extremely high purity

by William G. Pfann

About a third of the elements and hundreds of organic and inorganic compounds have been produced in their purest form by a simple technique called zone refining. If two of these elements, germanium and silicon, had not been available in the desired purity, the whole development of solid-state electronics would have been crippled. Other elements, when highly purified, have revealed their true properties for the first time, leading to new fields of research. All of this has happened since the basic paper on zone refining was published in 1952.

What is zone refining? It is one of a general family of techniques known as zone melting, by which materials can be purified or given desired compositions or variations of composition. In zone melting a short liquid (or molten) zone travels through a relatively long charge (or ingot) of solid, carrying with it a portion of the soluble impurities in the charge. The final distribution of impurities, or components, depends on the size, number and direction of travel of the zones, on the distribution of impurity in the original charge and on an intrinsic property of the impurity known as the distribution coefficient.

In zone refining, which is probably the most important zone melting technique, a number of molten zones are passed through the charge in one direction. Each moving zone carries a fraction of the impurities to the end or, in some cases, to the beginning of the charge, thereby purifying the remainder and concentrating impurities at one or both ends. In the 15 years since my original paper on the subject I have been asked over and over: "How could such a simple idea have been missed all these decades? How did you think of it?"

I really cannot answer either question. Several years after my paper had appeared I learned that Peter Kapitza, the Russian physicist, had actually performed a one-pass zone melting operation and had described it in a paper published in 1928. He was concerned with crystal growth, however, and apparently did not recognize the potential of a molten zone as a distributor of solutes, and it would seem that neither did any of the hundreds of physicists who must have read his paper.

My own conception of the process dates back to 1939, when the late Earle E. Schumacher, head of the metallurgy laboratory of the Bell Telephone Labora-

tories, told me I could spend half my time on fundamental research of my own choosing. I chose to study "slip bands" produced by deforming single crystals of lead containing a fraction of a percent of antimony. I recognized that if I used a standard freezing technique to grow the crystals, the antimony would tend to segregate, thus producing a crystal with a nonuniform distribution of the solute. To remedy this I thought to grow the crystal by passing a short melted zone along the ingot in the hope of leveling out the distribution of antimony. This procedure, now called zone leveling, did not strike me as particularly remarkable and nothing came of it at the time. I assumed that such a simple idea must be common knowledge. Also, about that time Bell Laboratories became heavily engaged in technical problems of World War II. It was not until years later, when the need arose for germanium of uniform purity for transistors, that I again thought of zone leveling. Suddenly the lightning of zone refining struck: a molten zone moving through an ingot could do more than level out impurities—it could remove them.

With the help of colleagues at Bell Laboratories zone refining was quickly developed into a successful manufacturing procedure. The purity achieved was spectacular. The harmful impurities—those affecting transistor properties—were reduced to less than one atom of impurity in 10 billion atoms of germanium. This ratio is equivalent to a grain of salt in a freight-car load of sugar. Since then zone refining has been applied successfully to many other semiconductors and metals, as well as to organic and inorganic compounds.

In order to understand zone refining, and zone melting in general, one must understand what is meant by the distri-

ROTATION-CONVECTION ZONE REFINER, shown in operation on the opposite page, illustrates how a traveling molten zone can remove impurities from a material. The material in this case is naphthalene, to which a red dye has been added. The first step of the sequence (top) shows the dye uniformly distributed among molten zones and crystallized zones that alternate inside a one-inch glass cylinder, which rotates a few times a minute. The molten zones are created by single-turn Nichrome heaters. The adjacent zones are solidified by a flow of cooling water between loose-fitting brass rings and the surface of the glass cylinder. The rotation of the cylinder produces liquid-solid interfaces that are practically flat and promotes diffusion in the liquid region. The cylinder travels to the left at the rate of about two centimeters an hour, thus sweeping the molten zones to the right. In addition the cylinder has a ratchet motion resembling that of a typewriter carriage: after traveling slowly to the left one heater spacing it jumps quickly to the right the same distance. Thus the purified zones are carried to the right in the manner illustrated. The rotation-convection zone refiner was built by the author and his colleagues at Bell Telephone Laboratories.

buison coefficient. A solution of salt in water provides a familiar example. When the temperature of such a solution is lowered to the freezing point, the first ice crystals to form do not contain the same concentration of salt as the original solution does. In fact, the ice crystals contain a significantly lower concentration because the salt redistributes itself between the solid phase and the liquid phase while the crystal is being formed. The distribution coefficient is defined as the concentration of the solute in the solid divided by its concentration in the liquid; thus the coefficient is less than one. Indeed, for ordinary table salt in freezing water, the distribution coefficient is close to zero, meaning that salt is almost totally excluded from ice crystals as they form. As a consequence the concentration of solute in the remaining

solution tends to rise steadily until all the liquid is frozen. When the solute is not table salt but a more typical substance, the crystals become progressively richer in the solute as they freeze from a more and more concentrated solution. Concomitantly the freezing point of the solution drops steadily as the solute concentration of the remaining solution rises.

All of this can be summed up in a phase diagram that shows how the composition of the liquid phase (bounded by the "liquidus" curve) is related under equilibrium conditions to the composition of the solid (bounded by the "solidus" curve) for all concentrations of the solute in the solvent, together with the freezing point for each concentration [see illustration below].

There is an equilibrium, or ideal, dis-

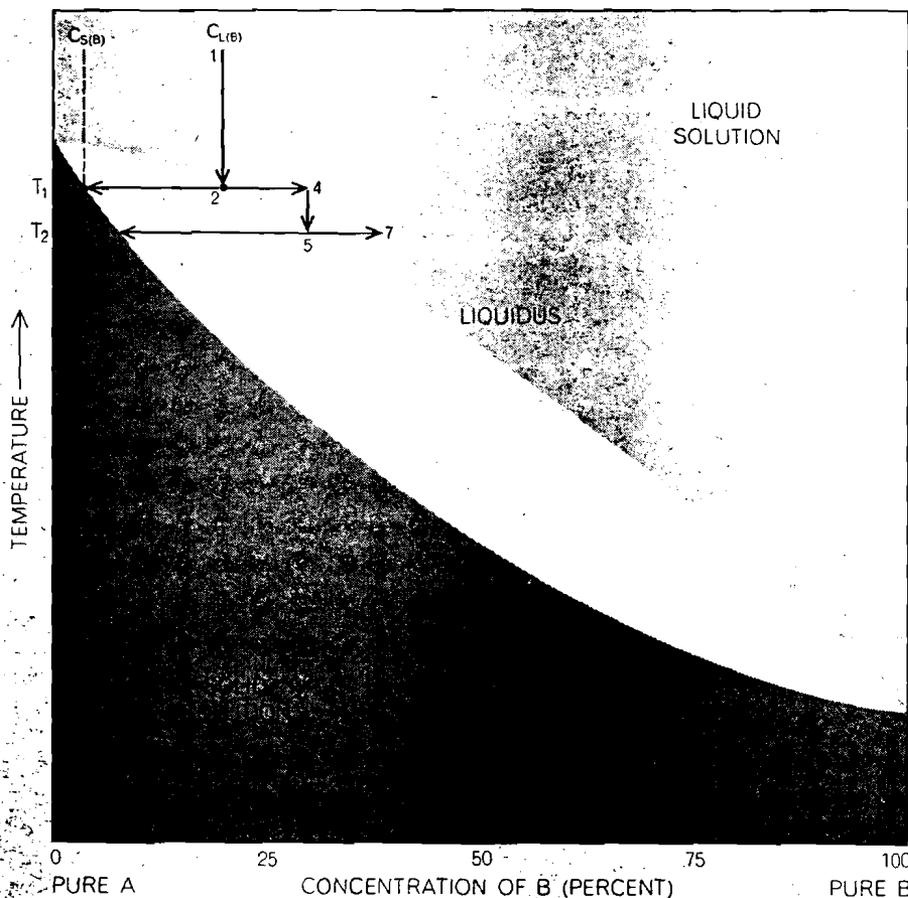
tribution coefficient, designated  $k_0$ , and an effective value, designated  $k$ . The whole success of zone refining depends on the fact that under ordinary freezing conditions equilibrium is far from being achieved. If freezing of, say, a solution or an alloy took place so slowly that the entire solid at all times had the composition of the solidus curve in the phase diagram, the last crystals to form would have the same composition as the entire solid. This implies, in turn, that the final frozen solid would have precisely the same solute concentration as the original solution. Paradoxically equilibrium freezing consists in two simultaneous and opposed processes: the rejection of the solute by the advancing solid-liquid interface and the diffusion of the solute back into the solid that has frozen.

In practice equilibrium freezing is almost impossible to achieve if one is dealing with substantial volumes of material. Diffusion rates in solids are almost always too low to permit back diffusion of the solute. For practical purposes, therefore, the solute-rejection process is the only one that counts. In consequence a severe segregation of the solute is achieved; the last solid to freeze will normally contain a much higher concentration of the solute than existed in the original solution.

In normal freezing, back diffusion is effectively prevented if the solid-liquid interface advances at a rate of from one to 20 centimeters per hour. This speed is also usually slow enough so that the concentration of solute in the liquid is equalized by diffusion or convection. Under these conditions the solute distribution along an ingot will follow that predicted by a normal freezing curve for some constant value of  $k$ , say .5 [see illustrations on opposite page]. At low solute concentrations the assumption of constant  $k$  is reasonable.

Mixing processes in the liquid can include forced convection in addition to natural convection and diffusion. If the mixing is rapid enough, the effective distribution coefficient,  $k$ , will approach the equilibrium, or ideal, value,  $k_0$ . But if the mixing is sluggish, solute will accumulate in the liquid at the advancing solid-liquid interface, with the result that  $k$  will be larger than  $k_0$  and will lie between  $k_0$  and unity. An effective distribution of unity implies, of course, no segregation, because the concentration of solute in the newly formed solid will exactly equal that in the bulk of the liquid.

Let us now consider what happens if a single molten zone is passed through a solid cylinder, or ingot, that has a uni-



**PHASE DIAGRAM** for a binary system of two components, *A* and *B*, clarifies the relations on which zone refining is based. The diagram shows that adding solute *B* to solvent *A* lowers the freezing point of an *A*-rich solution. Conversely, adding *A* to *B* raises the freezing point of a *B*-rich solution. Zone refining works because the composition of the solid that freezes out at any given temperature differs from the composition of the solution. Thus if a solution of composition 1 is lowered to its freezing point, 2, the solid that forms, 3, contains much less *B* than the original liquid. The exclusion of some *B* from the solid raises the concentration of *B* in the remaining liquid, 4, which now has a lower freezing point, 5. Again the solid that forms, 6, excludes *B* and raises the concentration of *B* in the liquid, 7, and so on. The critical relation is the equilibrium distribution coefficient,  $k_0$ , defined as the ratio of "solidus" concentration to "liquidus" concentration at a given temperature. Here that ratio is  $C_{S(B)}/C_{L(B)}$ . The effective distribution coefficient,  $k$ , is usually higher than  $k_0$ .

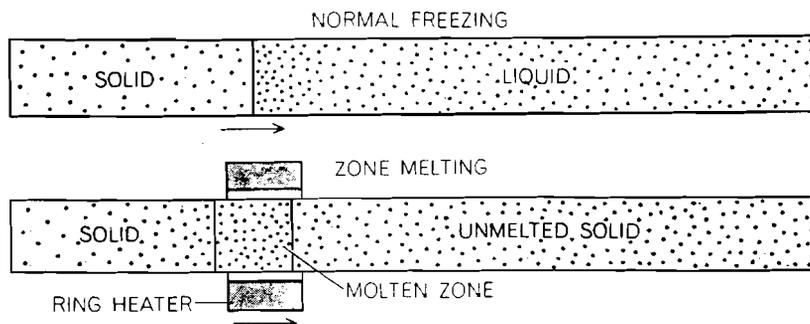
form concentration of solute  $B$  in solvent  $A$  [see illustrations at right]. Let the initial concentration of  $B$  in  $A$  be represented by  $C_0$ . It is not necessary that the ingot be an ordinary rapidly frozen casting; it can be a mixture of sintered powders or even two long rods side by side whose cross section at any point corresponds to concentration  $C_0$ .

A molten zone, say a tenth of the length of the ingot, is formed by a heating coil placed at one end of the charge. The heating coil is then moved slowly along the charge. As it advances, the first solid to freeze behind it has a concentration of solute  $B$  equal to  $C_0$  times the distribution coefficient  $k$ , or  $kC_0$ . Since  $k$  is less than one, the newly formed solid contains less of solute  $B$  than the original charge does. This means that some of  $B$  must be rejected into the molten zone, raising its concentration of  $B$ . Simultaneously solid of concentration  $C_0$  is being melted into the zone at its leading interface. These concurrent processes increase the solute concentration in the molten zone and also in the solid that is freezing at the trailing interface.

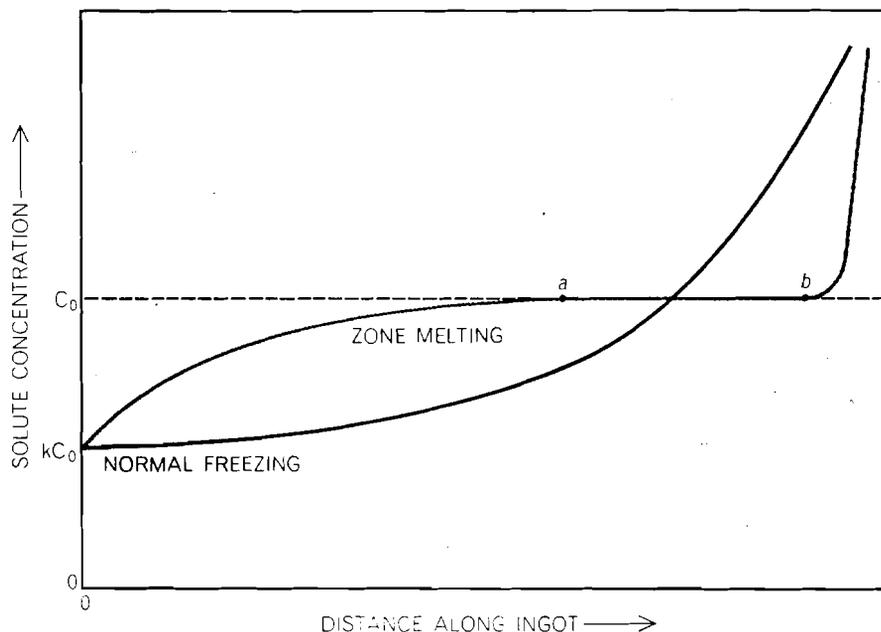
This rise continues until the solute concentration in the molten zone reaches the value  $C_0/k$ . At that point the concentrations of solid entering and leaving the zone are equal. The concentrations in the liquid and in the freezing-out solid now remain constant for several zone lengths, producing a region of zone leveling—the phenomenon that I erroneously thought was common knowledge in 1939. Zone leveling continues until the front of the molten zone reaches the end of the ingot. From there on the volume of liquid decreases as in normal freezing and the solute concentration follows a normal freezing curve in the last zone length of the ingot.

Thus the net effect of passing a molten zone through an ingot just once is to produce an ingot with three regions: a region of purification in which the solute concentration rises rather steeply from  $kC_0$  to  $C_0$ , a "zone-leveled" region of concentration  $C_0$  and a short terminal region in which the concentration greatly exceeds  $C_0$ . Single-pass zone melting, therefore, is neither fish nor fowl. As a purification step it is actually less effective than one normal freezing step and as a leveling step it leaves much to be desired.

The "secret" of zone refining, which now seems altogether obvious, is to pass a molten zone through an ingot repeatedly. The idea of using repeated crystallizations to purify substances is actually very old. The impure substance was dis-



**ORDINARY FREEZING AND ZONE MELTING** both alter the distribution of a solute in a solvent. Oddly enough, one-pass zone melting (*bottom*) is actually less effective as a refining method than normal freezing (*top*). This can be inferred from the illustration below.



**IMPURITY DISTRIBUTION** produced by normal freezing and that produced by one-pass zone melting are quite different. The curves are plotted for sample charges of the same initial concentration of solute ( $C_0$ ) and the same distribution coefficient (.5). The amount of solute, or impurity, in the newly formed solid rises much more steeply in zone melting than in normal freezing. The virtues of zone melting emerge, however, when a molten zone is passed through an ingot many times (see illustrations on next page). Moreover, the flat region between  $a$  and  $b$  in the zone melting curve can be exploited to produce an ingot whose content of a desired impurity is extremely uniform. This process is termed zone leveling.

solved in a solvent (itself a source of contamination); the solution was cooled to freeze out a fraction of crystals (by normal freezing), then the partly purified crystal fraction was separated from the "mother liquor" and redissolved. The operation was repeated many times on both the crystals and the liquors, with recombination of various fractions in accord with a complicated procedure. Because it was tedious and time-consuming, repeated fractional crystallization was never widely adopted as a purification procedure.

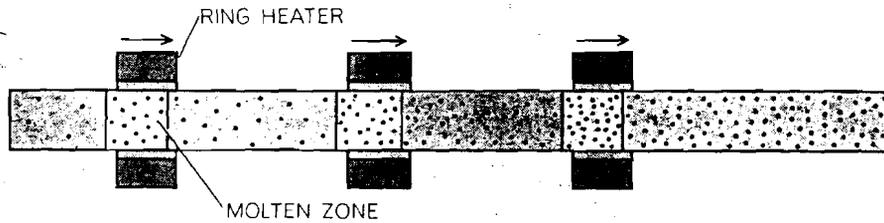
By means of zone refining, the old idea of repeated fractional crystallization

is converted from a cumbersome process into an extremely simple one. With little difficulty several molten zones can be passed through an ingot, one behind the other, with each zone-pass comprising a step of crystallization. Moreover, the ingot can be subjected to as many zone-passes as desired, increasing its purity each time, without the troublesome handling of fractions. This is the main advantage of zone refining. The charge does not have to be touched, or even moved, until the process is finished.

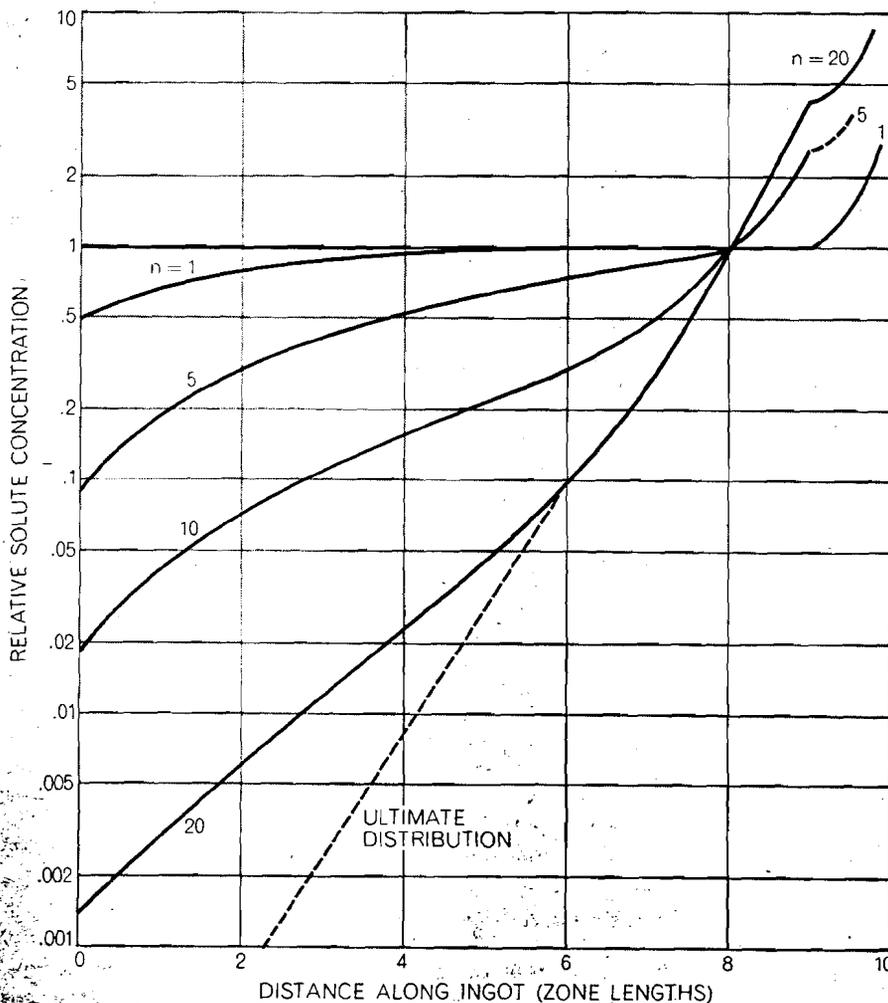
The effect of multizone passes can readily be appreciated. Suppose the original ingot contains 1 percent of some

impurity and that the distribution coefficient  $k$  is .5. The first solid to freeze behind the first pass of a molten zone will contain .5 percent of impurity. If  $k$  remains .5, the first solid to freeze behind the second pass will contain .5 times the average concentration of impurity in the first zone length. It is easy to compute that 10 passes through a charge 10 zone lengths long will reduce

the initial concentration of a given impurity by 98 percent and that 20 passes will reduce the concentration by about 99.85 percent [see lower illustration below]. The ultimate distribution varies exponentially with the distance from the beginning of the charge and thus appears as a straight line when plotted on semilog paper. Such calculations have been verified experimentally.



**MULTIPASS ZONE MELTING**, more commonly called zone refining, was first described by the author in 1952. For speed and convenience several molten zones are passed through an ingot simultaneously. Each is as effective as a single molten zone traveling alone.



**PURIFICATION ATTAINABLE BY ZONE REFINING** is shown in this family of curves for one, five, 10 and 20 passes of a molten zone through an ingot 10 zone lengths long. The purification is for a distribution coefficient of .5. The ultimate distribution is the one theoretically attainable after many zone passes. Although the curves were generated by a computer, they have been confirmed in actual practice. In germanium and silicon ingots used for making transistors, harmful impurities are routinely reduced to less than one part in 10 billion.

The ultimate distribution represents the maximum purification attainable. It is something like piling sand against a wall. There is a maximum height for a given amount of sand. In zone refining the ultimate distribution is the steady state reached by two opposing fluxes. The first is the ability of the freezing interface to reject solute, roughly proportional to the absolute value of  $1 - k$ . The second is the rapid mixing effect, proportional to the square of the length of the zone, which causes freshly dissolved solute to migrate backward from the melting interface to the freezing interface of the zone. The purification represented by the ultimate distribution is roughly proportional to (and very sensitive to) the number of zone lengths in the charge and to the value of  $k$  [see illustration on opposite page].

I mentioned earlier that impurities sometimes travel opposite to the direction of zone travel and accumulate at the front of the charge. How is that possible? This happens when  $k$  for a particular solute is greater than unity. In the case of an ordinary solute, which lowers the melting point of the solvent,  $k$  is less than unity. But in the typical phase diagram showing liquidus and solidus curves it is also possible to select a composition at the far right where the major component (B) is regarded as the solvent and the minor component (A) as the solute (whereas at the left of the diagram the roles are reversed). In this region of the diagram the concentration of the solute (A) in the freezing-out solid is greater than in the liquid; hence  $k$  is greater than unity. Such a solute also raises the freezing point of the solvent. In both normal freezing and in zone refining such solutes travel backward and become concentrated at the front of the ingot.

To achieve zone leveling, so important in producing single crystals of germanium and silicon with a uniform concentration of desired impurities, one exploits the characteristics of a solute with a very low distribution coefficient (a  $k$  of about .005). The simplest procedure is to use a seed crystal of desired orientation and to place a pellet of low- $k$  solute at the beginning of a charge of pure germanium or silicon. This may seem paradoxical because in normal freezing low- $k$  solutes produce the greatest segregation. When used in zone leveling, however, low- $k$  solute stays predominantly in the molten zone, so that the concentration in the melt is typically some 200 times higher than it is in the solid freezing out at the trailing interface. The net effect

that a slight and virtually uniform amount of solute is left behind in the solution as the zone travels through the ingot. Germanium was the first element to be ultrapurified by zone refining. Except for the addition of automatic controls, the present-day commercial process [see illustration on next page] hardly differs from the original laboratory one. An ingot of germanium is placed in a "boat" of high-purity graphite and subjected to repeated zone meltings in an inert atmosphere of nitrogen.

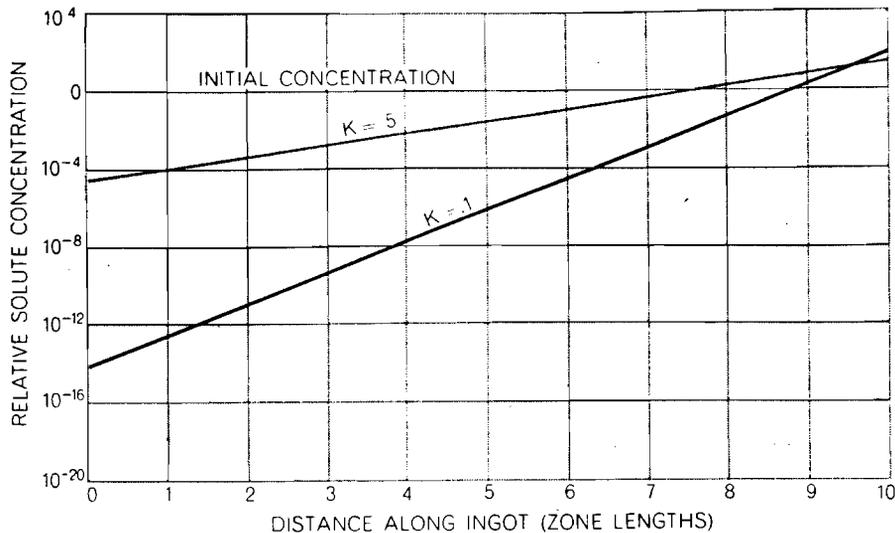
### A Zone That Floats

When the same technique was tried with silicon, however, problems developed. The silicon became contaminated because no boat could be found that was not wetted by the molten silicon. The problem was solved, and a wide area of investigation was opened, when my colleague Henry C. Theuerer invented the floating-zone technique. The technique was subsequently discovered by others: by the late Paul H. Keck and Marcel J. E. Golay of the U.S. Army Signal Corps Laboratories in Fort Monmouth, N.J. (who published first and gave the technique its name), and by R. Emeis of Siemens and Halske.

In this refining method a rod of silicon is clamped in a vertical position, held only at the ends. An unsupported, or floating, molten zone extending through the cross section is produced by a water-cooled induction heating coil. Refining is accomplished by moving the floating zone repeatedly from one end of the rod to the other. Today industry routinely turns out float-zoned single crystals of silicon about four centimeters in diameter and about 30 centimeters long [see bottom illustration on next page].

Since a transistor today uses less than a milligram of silicon, such a crystal represents many tens of thousands of devices.

It is perhaps obvious that only one molten zone can be passed through an ingot at a time in the float-zone technique. If two zones were introduced, the solid region between the two—being unsupported—would simply collapse the lower zone. It may be surprising, nevertheless, that surface tension is quite adequate to support a single molten zone, provided that a certain height is not exceeded. In this regard nature has been kind. The highest-melting metals, being extremely reactive when molten, are most in need of the float-zone technique for refining. Fortunately surface tension increases with melting temperature and thus allows a large molten zone. Certain



ULTIMATE DISTRIBUTION CURVES are critically dependent on the effective distribution coefficient,  $k$ , and on the length of the ingot, measured in zone lengths. Here for an ingot of 10 zone lengths are the ultimate distribution curves when  $k$  is .1 and when  $k$  is .5.

very stable inorganic compounds also lend themselves to float-zone treatment. Water, because of its anomalously high surface tension and its low density, could also be purified by the float-zone method if one wished.

At very high temperatures, say above 1,500 degrees centigrade, float-zone purification occurs partly by volatilization of impurities and partly by zone refining. An effective way to create a floating molten zone in a high-melting metal is to place a ring-shaped cathode around the rod to be refined, which serves as the anode. Electrons from the cathode bombard the rod and melt it. An electron-beam refiner of this kind, built by the Materials Research Corporation, appears on the cover of this issue of *Scientific American*. The ingot in the photograph is titanium.

Mechanical, chemical, electrical and magnetic properties of a metal often change strikingly when it is made really pure. For example, Raymond L. Smith and John L. Rutherford, then at the Franklin Institute, showed that float-zone-refined iron remained ductile even when cooled to the temperature of liquid helium (4.2 degrees C. above absolute zero). In the laboratory of Georges Chaudron at Vitry-sur-Seine in France it has been found that in zone-refined iron the solubility of oxygen and hydrogen falls below the limits of detection and that resistance to oxidation increases.

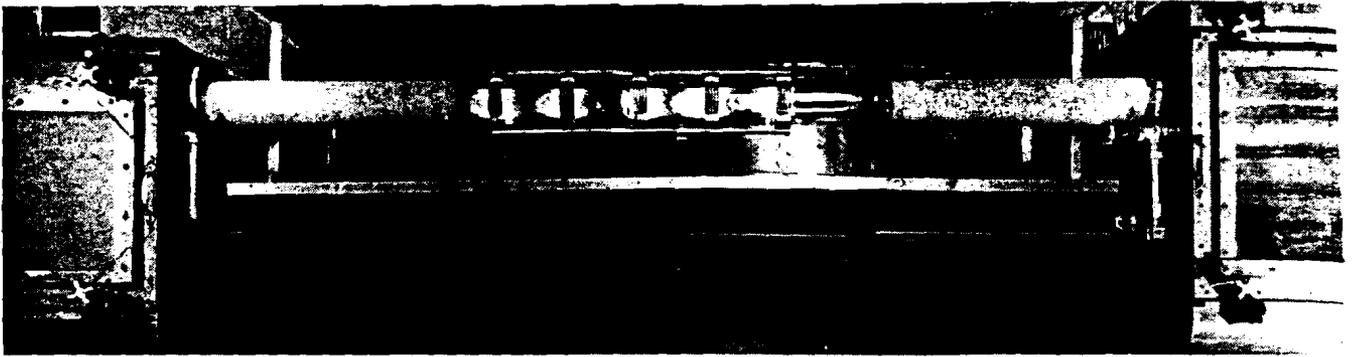
Ductility in general increases remarkably when metals are made very pure. Beryllium is ordinarily an extremely hard and brittle metal at room temperature. Yet a crystal rod of beryllium 1.5

centimeters in diameter, purified by float-zoning in a high vacuum, turned out to be so ductile that it could be bent by hand into a complete circle. The purification was done at the Nuclear Energy Research Institute at Grenoble by B. Schaub.

Not many years ago the phenomenon of superconductivity—the ability of a metal to carry an electric current without resistance at very low temperatures—was thought to be restricted to a modest group of metals and not particularly sensitive to the metal's purity. But recently molybdenum and tungsten were shown to be superconductors when the magnetic impurity iron was reduced to a very low level. Highly purified beryllium has similarly proved to be a superconductor; the critical impurity remains to be established.

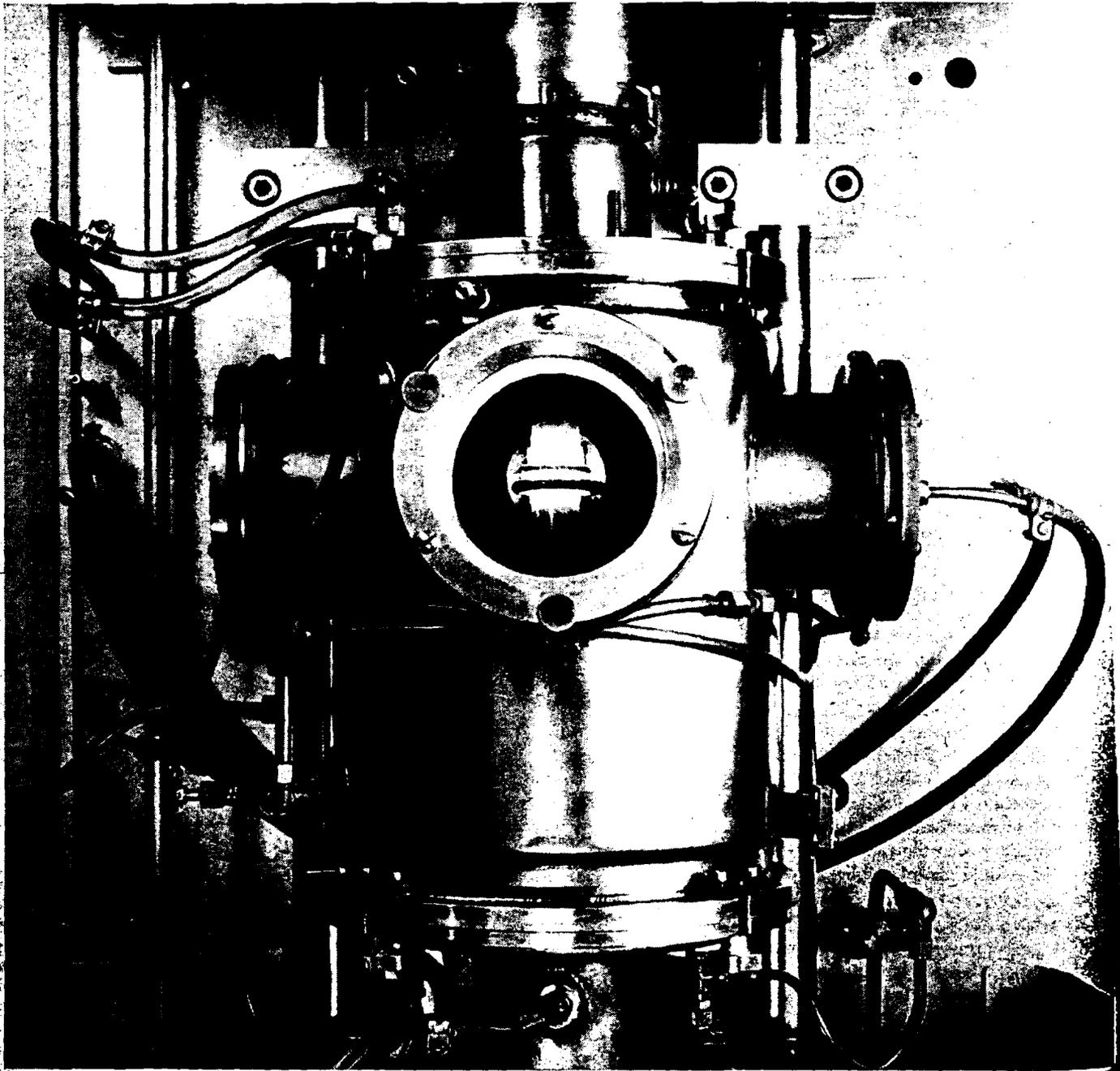
The actual velocity of grain-boundary migration in zone-refined lead of extreme purity was measured by J. W. Rutter and K. T. Aust of the General Electric Research Laboratory. They found that as little as three parts per million of silver reduced the velocity of migration by a factor of a thousand.

The General Electric Company has recently described how it employs zone refining to produce copper of exceptional purity for use in vacuum circuit breakers. For heavy-duty service these devices require electrode faces that are extremely free of gas, otherwise undesirable arcing occurs when the circuit is broken. Zone refining enables General Electric to produce copper with the necessary low gas content: less than one atom of gas per 10 million atoms of copper. Too low



**PRODUCTION ZONE REFINER** at the plant of the Western Electric Company in Allentown, Pa., is shown from above. Ingots of

germanium feed in automatically from the right, are refined passing through five induction heating coils and emerge at the le



**FLOAT-ZONE REFINER**, also at Western Electric, converts ingots of silicon into single crystals of controlled purity by passing them vertically through an induction heating coil. The molten zone is

held in place by surface tension. By adding trace amounts of desirable impurities to the controlled atmosphere surrounding the ingots, the properties of the finished silicon can be varied

measure analytically, the gas content can be inferred by building a circuit breaker and testing it under operating conditions.

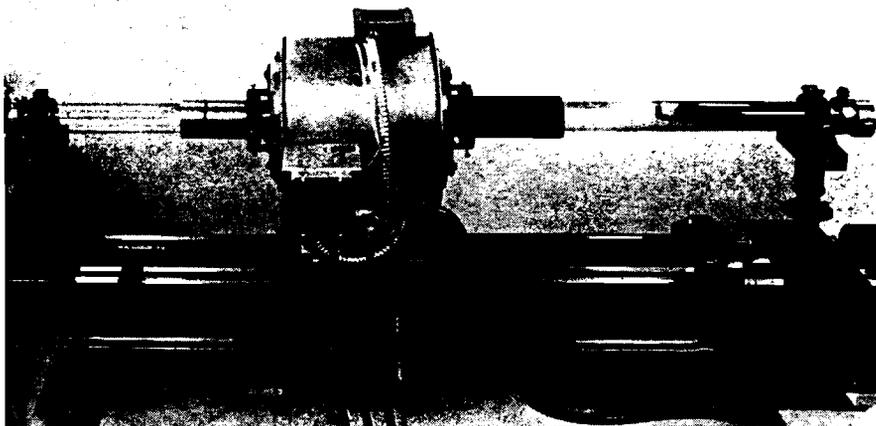
### Some Special Zone Refiners

In any zone refining operation, time is saved if the zones are short and close together. Shortening the zone length, moreover, results in greater purity in a given length of ingot. The problem of achieving short zone length and short interzone spacing is particularly difficult for organic compounds. On the whole their thermal conductivity is very low, about a thousandth that of metals, so that it is difficult to remove the heat of fusion liberated at the rear, or freezing, interface of the zone. If the heat of fusion is not removed efficiently, the zone gets longer.

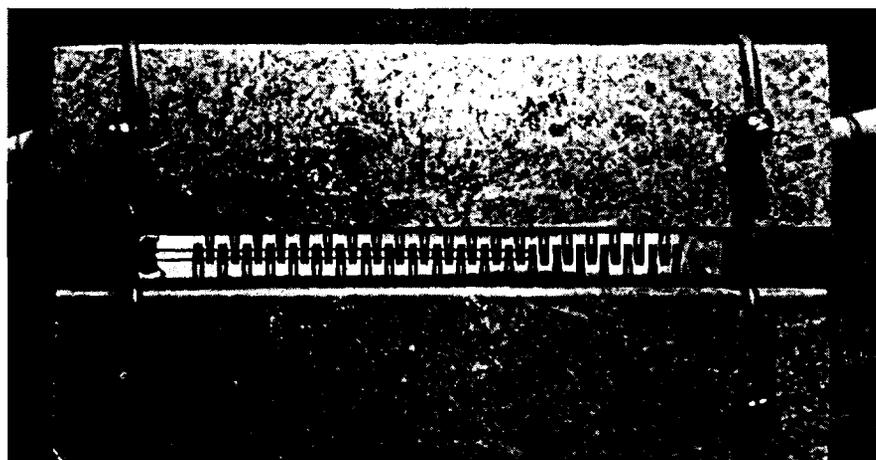
Ideally the zone refiner should have closely spaced, alternate arrays of heat sources and heat sinks. A beautiful example of such apparatus is a microscale zone refiner developed by Hermann Schildknecht and H. Vetter at Erlangen University. The refiner, which handles ingots weighing only a few milligrams, compresses 20 hot zones and 20 cold zones in a distance of six centimeters [see lower illustration at right]. Schildknecht and Klaus Maas have since built an even smaller zone refiner that can treat less than 100 micrograms of material. His group, now at the University of Heidelberg, has become the leader in the zone refining of organic compounds. For example, Schildknecht's group determined for the first time the true melting points of the homologous series of fatty alcohols ( $C_nH_{2n+1}OH$ ) from  $C_{19}$  through  $C_{30}$  using samples that had received as many as 200 zone passes. The study removed an anomaly in the relation of melting point to number of carbon atoms in the homologous series.

Organic compounds are multitudinous and notoriously impure. I think small-batch zone refining will make a major contribution in establishing the true properties of such compounds. Some recent accomplishments are noteworthy. Zone refining showed that the objectionable odor always associated with skatole (a constituent of feces) was due to impurities. Similarly, the insecticide lindane lost its musty odor after zone refining. Ortho-nitrophenol, like many similar compounds, had been thought to be self-oxidizing on exposure to air. It has now been shown that the zone-refined compound does not so oxidize.

Chemists, with the exception of Schild-



ZONE-LEVELING APPARATUS is used to distribute a uniform amount of a desirable impurity throughout a previously purified ingot of germanium. The concentration of such impurities is typically about one part in  $10^7$ . The distribution is accomplished by one slow traverse of the heating element. This photograph was also made at Western Electric.

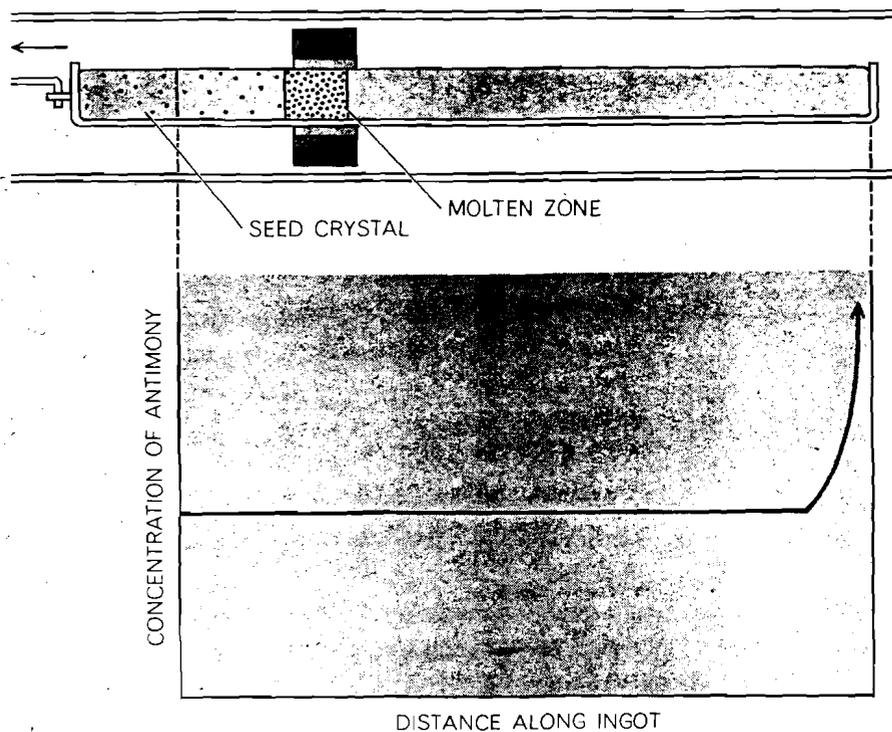


MICROSCALE ZONE REFINER for purifying milligram quantities of organic compounds was built by Hermann Schildknecht and H. Vetter at Erlangen University. It compresses some 40 molten and solid zones in a length of about six centimeters. The heaters and coolers are copper coils connected to an insulated heat source (top) and a heat sink (bottom).

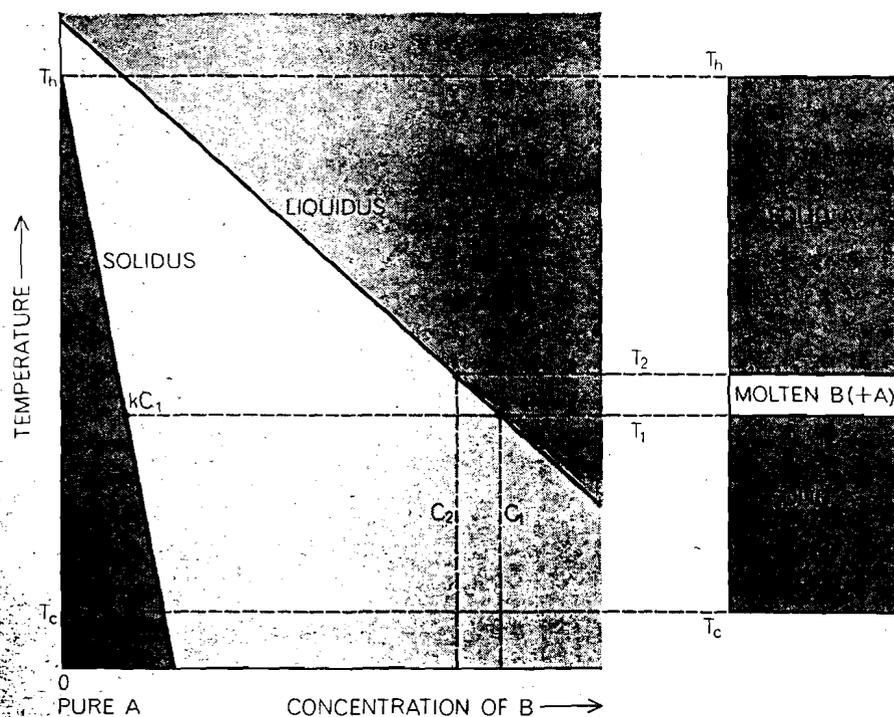
knecht and a few others, have shown surprisingly little imagination in the design of zone refining apparatus. Most of their zone refiners, as described in the literature, have long zone lengths and long interzone spacings. Recently Charles E. Miller, J. D. Hunt and I developed a zone refiner for chemical compounds that goes a long way toward eliminating these deficiencies. We call it a rotation-convection refiner [see illustration on page 62]. The zones are about .6 centimeter long, 2.5 centimeters in diameter and about two centimeters apart. The close spacing is achieved by having cooling water pass between a series of loose-fitting brass rings and the surface of the glass tube containing the sample. Surface tension confines the water to the space between ring and tube. The re-

gions between the rings are heated by single loops of resistance wire. Slow rotation of the sample tube produces alternate molten and solid zones whose interfaces are practically flat and perpendicular to the surface of the tube.

Thus far I have discussed zone refining as a batch process. For purifying commercial quantities of organic compounds I believe large-scale batch and also continuous zone refiners will become commercial. Three different continuous methods have been conceived and worked on experimentally. In a continuous zone refiner impure feed-liquid enters somewhere near the middle of the apparatus, while purified product leaves at one end and concentrated waste leaves at the other end. These flows of feed, product and waste have to be su-



**ZONE-LEVELING PRINCIPLE** was thought of by the author about a dozen years before he conceived of zone refining. The ingot to be leveled rests in a "boat" (top) of fused silica. At the left of the ingot is a seed crystal, placed in the desired orientation, together with a measured amount of a solute, such as antimony, that has a very low distribution coefficient ( $k \sim .005$ ). The boat is pulled slowly through a heating coil. The curve (bottom) shows how antimony is distributed uniformly throughout most of an ingot of germanium.



**TEMPERATURE-GRADIENT ZONE MELTING**, as the name implies, depends on a temperature gradient to move a zone of molten material through a solid matrix. In the simplest case a layer of *B* is sandwiched between two blocks of solid *A*. The temperature range is below the melting point of *A* but above the melting point of liquid solutions of *B* containing *A*. Thus *B* begins to dissolve some *A* at both interfaces. Solution of *A* at the cooler interface ceases at  $T_1$  but continues at the warmer ( $T_2$ ) interface. Diffusion then carries *A* from the richer (warmer) to the leaner (cooler) interface. As a result a layer of *A* containing concentration  $kC_1$  of *B* finally freezes. In this way the molten zone climbs steadily.

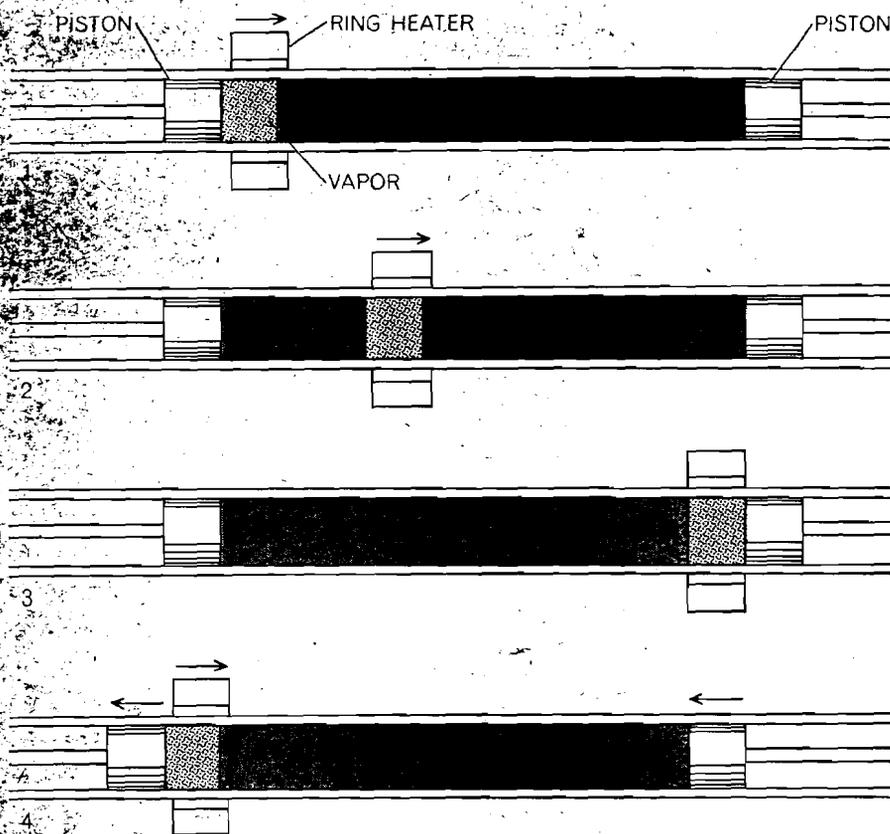
perimposed on the movements of the molten zones that provide the purification.

The final variation of zone melting that I shall describe in detail is fascinating, to my mind, because it must be happening all the time in nature and conceivably, over aeons, could lead to profound geologic segregation effects. Because it depends simply on the presence of a temperature gradient, it is known as temperature-gradient zone melting. As practiced in the laboratory it differs from other zone melting methods in the relatively small size of the molten zones, in the manner of moving the zones, and in the amount of solute in the zones. The zones are usually very small: sheets, wires or dots whose smallest dimension is of the order of thousandths of an inch. The zones have a high solute content, which means that they remain liquid well below the melting point of the solid through which they travel. Finally, the zones are made to move not by a traveling heat source (although this is possible) but by a stationary temperature gradient impressed across the entire charge.

These features have led to unusual applications that include fabrication of junction transistors of unusual form, joining of solid bodies with a solder that is then caused to migrate out of the joint, purifying and cleaning, measuring the diffusivity of liquids and measuring rates of dissolution and freezing. Beyond this understanding of temperature-gradient zone melting has made technical people aware that it is a widespread phenomenon and that it must occur, often unrecognized, in many laboratory experiments, whenever a temperature gradient is present.

The phenomenon is most easily understood by examining a simple case. Imagine a system in which a thin layer of solid *B*, regarded as the solute, is sandwiched between two blocks of solid *A*, the solvent [see bottom illustration at left]. The sandwich is now placed in a temperature gradient so that the temperature of *B* falls somewhere between the two extremes. The temperature must be high enough to form a liquid solution of *B* containing *A* but not so high as to melt the blocks of *A*.

When the process is started, *B* immediately begins to dissolve some *A* at both interfaces, forming a liquid layer. As a result the concentration of *B* in the layer is reduced. At some point the concentration of *A* in the layer becomes high enough to cause the solution to freeze at the interface nearest the cooler end of the gradient. At the hotter interface



**SOLID-VAPOR ZONE REFINING** is one of several variations of the zoning technique. The charge is held in a tube between movable end pistons. At the start (1) a void is created at the left and the heater begins moving to the right. The material vaporized by the heater re-solidifies to the left, behind it (2). When the heater reaches the right end of the tube (3), it is quickly moved back to the left. Simultaneously (4) the two pistons are moved to the left to create a new void at the left and to fill the void at the right. The process is then repeated.

meanwhile, A continues to dissolve in the layer. Thus within the layer a concentration gradient of A is created: the highest concentration near the warmer interface and the lowest near the cooler interface. The net effect is that the molten layer migrates through the block from the cooler end to the warmer end of the temperature gradient, leaving behind a solid in which the concentration of B is usually small.

One potentially widespread use of temperature-gradient zone melting is the removal of particles or droplets of an unwanted impurity that have become trapped during the growth of a crystal or the freezing of an alloy. If the crystal or alloy is placed in a temperature gradient, and if the temperature is high enough to cause the impurity particles to form tiny liquid droplets by dissolving the matrix, the droplets will migrate to the hotter surface, where they can be removed, thereby cleaning the main crystal.

A most useful twist of this idea was recently exploited by my colleague Richard S. Wagner. He used the method

to clean the droplets rather than the matrix. He was studying the undercooling of droplets of gold-silicon alloy, which rested on the upper surface of a silicon crystal. He wanted to see how far a really clean sample of this alloy could be undercooled below its equilibrium freezing temperature. In spite of all precautions, there were always microscopic insoluble particles in the droplets that nucleated crystal growth and prevented substantial undercooling. Wagner succeeded in cleaning the droplets by applying a temperature gradient parallel to the crystal face, causing the droplets to migrate along the surface and leave the particles behind. Only then were consistent—and very large—undercoolings obtained.

#### Other Kinds of Zoning

So far I have discussed only those forms of zone refining that use the liquid-to-solid transformation, that is, melting and freezing. There are other useful transformations to which the zoning principle can be applied. Thus

it is possible to use solid-solid zoning, solid-vapor zoning and liquid-vapor zoning.

The first was demonstrated for a mixture of lithium sulfate and silver sulfate by A. Lundén and his co-workers in Sweden. This technique exploits the fact that solid solutions of two substances often show a tendency to segregate at different proportions at different temperatures. The drawback to this method is that diffusion in solids tends to be slow.

Solid-vapor zoning was introduced by Leonard R. Weisberg and Fred D. Ross of the Radio Corporation of America to purify arsenic. In this technique a solid ingot is vaporized and solidified in zone fashion [see illustration at left]. By further perfecting the technique Gilbert J. Sloan of E. I. du Pont de Nemours & Co. has obtained pure tetracene from a charge containing about 30 different impurities.

The third of these unusual techniques, liquid-vapor zoning, sounds like ordinary distillation but isn't. Although to my knowledge it has not yet been demonstrated in a practical apparatus, I have diagrammed and described a hypothetical system in the second edition of my book *Zone Melting*. Liquid-vapor zoning would employ vapor zones of high diffusivity separated by liquid zones of low diffusivity. In ordinary distillation, diffusivity is high in both liquid and vapor.

There are many other variations of zone melting—some in use, some potentially useful, all interesting. I cannot describe them all in this article. To quote from my first paper on the subject in 1952: "Possibly the most significant feature of zone melting is its flexibility. The charge may be regarded as a medium, and the molten zone as a distributor of solutes in the medium. . . . An operator can produce a large variety of useful distributions of solute in the medium. Among the tools at his disposal are the arrangement of the starting charge and the size, number, and direction of travel of the molten zones."

To end on a personal note, if I may I regard the conception and development of zone melting as an exciting scientific advance. And I cannot help being saddened to hear it occasionally referred to as simply a technical innovation that was mysteriously evoked by the need for transistor-grade germanium and silicon. I regard zone melting as elegant both in its simplicity and in its surprising complexity. I also regard it to this day as a wonderful adventure, filled with surprise and joy.