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Mechanism of Sublimation

Structural and chemical rearrangements at the vaporizing surface control the rate of sublimation.

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Studies of sublimation mechanisms reveal the reaction steps by which atoms break away from their neighbors in the crystal lattice and are removed into the gas phase. Detailed understanding of these steps should allow us to control vaporization and to increase or suppress its rate by suitable adjustment of the conditions of sublimation. This may have great importance in several fields of science and technology. For example, the useful life of materials at high temperatures may depend on their sublimation rates. The growth of high-purity crystals may be aided by investigation of their vaporization mechanisms. Understanding the sublimation mechanism of ice may allow us to control rainfall or the loss of water by vaporization.

Most previous studies of sublimation were carried out under conditions of equilibrium between the solid and vapor in order to obtain thermodynamic data (vapor pressure, enthalpy, free energy) for the vaporization reaction. Vaporization experiments of this type, however, do not yield information about the reaction path. Little attention has been paid to the kinetics of vaporization which are carried out far from equilibrium, although these studies should provide information about the mechanism of sublimation. Such investigations have been carried out on a relatively small number of solids in a few laboratories (*1*).

I shall discuss here some of the principles and techniques associated with studies of sublimation kinetics and describe the present physical picture of the vaporization process. I shall also discuss the sublimation mechanisms of four solids which may be taken as representatives of larger groups of materials.

Consider the vaporization of one crystal face of a monatomic solid A. If we assume that the overall vaporization reaction is

$$\mathrm{A(solid)} \underset{k'}{\overset{k}{\rightleftarrows}} \mathrm{A(vapor)}$$

the net rate of vaporization J may be expressed as

$$J(\text{mole cm}^{-2}\text{sec}^{-1}) = k[\mathrm{A}]_s - k'[\mathrm{A}]_v \qquad (1)$$

where k and k' are the rate constants for vaporization and condensation, respectively; $[\mathrm{A}]_s$ is the concentration of molecules in the surface sites from which vaporization proceeds; and $[\mathrm{A}]_v$ is the vapor density. For studies of the kinetics of vaporization the condensation rate, $k'[\mathrm{A}]_v$, must be smaller than the rate of sublimation, $k[\mathrm{A}]_s$. In such investigations the evaporation rate of the solid is measured under nonequilibrium conditions, most frequently in a vacuum (*1*). For sublimation into a vacuum or, as it is frequently called "free vaporization," the rate of condensation may be taken as zero and Eq. 1 can be simplified to

$$J_v(\text{mole cm}^{-2}\text{sec}^{-1}) = k[\mathrm{A}]_s = k_0[\mathrm{A}]_s \exp(-E^*/RT)$$

where k_0 is a constant related to the frequency of attempted motion of vaporizing molecules over the energy barrier E^*, R is the gas constant, and T is the temperature.

The maximum theoretical rate of vaporization from the surface $J_{\max}$ would be attained at a given temperature if the solid were in dynamic equilibrium with the vapor ($k[\mathrm{A}]_s = k'[\mathrm{A}]_v$). Under these conditions the net rate J is zero. However, the vaporization experiment may be carried out in a cell (Knudsen cell) with a very small orifice in which one may sample the vapor phase without significantly perturbing the solid-vapor equilibrium. Thus, from equilibrium (Knudsen cell) studies one can determine the maximum evaporation rate of most substances. The vacuum sublimation rate, on the other hand, may have any value depending on the mechanism of vaporization, but its upper limit is that which is obtainable under conditions of dynamic equilibrium at a given temperature. It is customary to express the deviation of the vacuum evaporation rate J_v from the maximum equilibrium rate $J_{\max}$ in terms of the evaporation coefficient α which is given (*1*) by

$$\alpha(T) = J_v(T)/J_{\max}(T)$$

For some substances the vacuum evaporation rate equals the maximum rate [$\alpha(T) \simeq 1$] whereas for others it may be orders of magnitude smaller than the maximum rate [$\alpha(T) \ll 1$].

Strong experimental evidence (*2, 3*) indicates that the surface of the solid is heterogeneous. One can distinguish several atomic positions which differ in the number of neighbors surrounding them. Figure 1 depicts some of these positions. Atoms in different surface sites have different binding energies. Vaporization is considered to be a multistep process in which atoms break away from a kink site and may diffuse on the surface until they are ready to

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vaporize, most likely from an adsorbed state. This simple sequence of reaction steps becomes more complicated if the surface atoms or ions must undergo rearrangements such as association, dissociation, or charge transfer prior to desorption from the vaporizing surface (*1*). The rate of any one of these reaction steps may control the overall sublimation process. Certain solids may vaporize by two different reaction paths which can operate simultaneously at different surface sites (*4*).

During vaporization the structure of the surface adjusts to the particular conditions of sublimation. During these rearrangements in the surface structure there is an initial, transient evaporation rate (*5*). After a short induction period, however, a steady-state vaporization rate is obtained which can then be maintained at a given temperature.

Studies of sublimation mechanisms may be divided into two categories: (i) chemical studies which are carried out to uncover the chemical rearrangements (association, dissociation, charge transfer) which take place during vaporization; and (ii) studies of surface topology that reveal the surface structure (arrangement and concentration of atomic steps, ledges, and dislocations) to give the optimum sublimation rate under different experimental conditions. The sublimation of substances which undergo marked chemical rearrangements during vaporization is, in general, controlled by the rate of a chemical reaction that takes place at a particular surface site. For solids which do not undergo marked atomic rearrangements during sublimation, the surface structure plays a more dominant role in determining the rate of vaporization.

Studies of sublimation mechanisms should, in general, be carried out with "stable" single-crystal surfaces (*1*). (The surface area of a stable crystal face remains constant throughout the vaporization.) The use of polycrystalline samples can lead to serious difficulties in the interpretation of experimental results (*6*). The measuring techniques are of two types. (i) Total weight loss measurements which are carried out by vacuum microbalance techniques (*7*) (such studies give reliable absolute evaporation rates but do not provide information about the composition of the vapor). (ii) The vapor composition and its temperature dependence can be monitored with a mass spectrometer (*8*). This technique should certainly be used if the vapor is composed of more than one species. In this way the vapor constituents are identified and their activation energies of vaporization are determined separately. Mass spectrometric measurements, in general, yield only relative evaporation rates. Both these techniques should be used to obtain complete information about the sublimation mechanism (*4, 8*). Since sublimation is an endothermic reaction, heat has to be supplied to the vaporizing surface continuously in order to avoid surface cooling. For the same reason vacuum sublimation studies should be restricted to temperatures at which the flux of vaporizing molecules is small in order to avoid introducing any temperature gradient between the bulk of the crystal and its vaporizing surface (approximately $J \leq 5 \times 10^{-5}$ mole cm^{-2} sec^{-1}) (*1*). Studies of the velocity distribution of the vapor fluxes indicate that thermal equilibrium between the solid surface and the vaporizing molecules can be easily maintained (*9*).

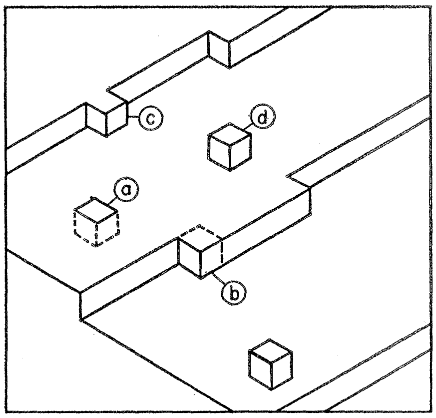

Fig. 1. Model of a surface depicting atoms in the following positions: (*a*) in surface, (*b*) kink, (*c*) at ledge, and (*d*) adsorbed on the surface.

From measurements of the vacuum evaporation rates at different temperatures from one face of a clean single crystal, one can determine the activation energy of vaporization. These data, however, do not tell us the mechanism of the vaporization reaction. Suitable complementary experiments should be performed to determine the reaction steps which control the desorption rate of the vaporizing species. Here I list some of the experiments which, for certain solids, were found useful in identifying the reaction steps of the complex vaporization reaction: (i) measurements of the sublimation rate of crystals doped with impurities (*4, 10*); (ii) study of the sublimation rate of crystals with defects (vacancies or dislocations) in excess of their steady-state concentration (*11, 12*); (iii) sublimation rate measurements as a function of the surface concentration of the vaporizing species (*13*); (iv) measurement of the sublimation rates in a temperature range where phase transitions occur or in the presence of a liquid phase (*14, 15*); and (v) illumination of the vaporizing surface by light of suitable wavelength and intensity (*16*).

As the conditions of sublimation are changed, the rate-controlling reaction step may change as well. Thus, the evaporation rate $\alpha(T)$, the activation energy, or even the vapor composition may differ from that observed during vacuum vaporization of the clean single-crystal surface.

I shall now discuss the sublimation mechanisms of single-crystal surfaces of sodium chloride, silver, arsenic, and cadmium sulfide. The first two solids show evaporation rates which, under suitable conditions, are nearly equal to the maximum rate. Arsenic and cadmium sulfide, however, are representatives of a large group of solids which undergo marked chemical rearrangements during sublimation. These materials have sublimation rates which are appreciably smaller than the maximum equilibrium rate.

Sublimation Mechanism of Sodium Chloride

The sublimation mechanism of sodium chloride has been investigated using the (100) face of the single crystal in the temperature range from 450° to 650°C (*8*). The sodium chloride vapor is composed mostly of monomer (NaCl) and dimer (Na_2Cl_2) molecules with the dimer concentration increasing with increasing temperature (5 to 30 mole percent).

The activation energies of vaporization of the monomer and dimer molecules in a vacuum are $E^*(\mathrm{NaCl}) = 52.6$ kcal per mole of vapor and $E^*(\mathrm{Na_2Cl_2}) = 62.1$ kcal per mole of vapor (*4, 8*); these values are nearly equal to the equilibrium heats of sublimation [$\Delta H_v(\mathrm{NaCl}) = 52.1$ kcal per mole of vapor and $\Delta H_v(\mathrm{Na_2Cl_2}) = 59.5$ kcal per mole of vapor] (*17*). The vacuum evaporation rate is dependent on the dislocation density in the clean single crystals. Samples with few (approximately $\sim 10^6$) dislocations per square centimeter have evaporation rates equal to one half of the maximum evaporation rate (Fig. 2). Other crystals which were strained to introduce high dislocation densities (approximately 10^7 cm^{-2}) vaporized with the maximum rates (Fig. 2) (*11*). The activation energies of vaporization and the relative concentrations of monomer and dimer sodium chloride molecules in the vapor remained unchanged for crystals with different dislocation density. When the samples were doped with approximately 200 parts per million of calcium, the vacuum evaporation rate of the (100) face decreased markedly to about one-tenth of the maximum rate of sublimation (Fig. 2). Furthermore, the activation energies of vaporization for the doped crystals increased by several kilocalories. Calcium enters the crystal lattice of sodium chloride as a divalent ion, and simultaneously excess sodium-ion vacancies are created. Monovalent ion impurities, such as Br^-, OH^-, or O_2^-, on the other hand, had no apparent effect on the sublimation rates of single crystals of sodium chloride.

Increasing the dislocation density seems to increase the concentration of surface sites (kinks in ledges) from which vaporization can proceed. This is a surprising result, for most other solids which have been investigated show a constant evaporation rate (after a short induction period) at a given temperature, independent of the dislocation density. It appears that for alkali halides the mean free path X of molecules away from the ledges is short; hence, molecules must vaporize near the ledges so that surface diffusion cannot contribute significantly in the vaporization reaction. The mean free path can be estimated by the equation

$$X = a \exp(E^*_{\text{des}} - E^*_{\text{diff}})/2kT$$

where a is the interatomic distance and E^*_{diff} and E^*_{des} are the activation energies of surface diffusion and of desorption from the free surface, respectively. Calculations (*18*) indicate that $X \approx a$; thus the mean free path is of the order of a few lattice spacings. The lack of any appreciable surface diffusion inhibits the establishment of a steady-state ledge concentration for crystals with low dislocation density. Therefore, greater ledge density and kink concentration could be created around dislocations. This gives rise to an increase in the sublimation rate with increasing dislocation density.

The observation that the ratio of monomer and dimer sodium chloride molecules remains constant for the crystals of different dislocation density, even though the total evaporation rate changes markedly, indicates that there is no equilibrium on the surface between these two species (*4, 8*). If the dimers formed by an equilibrium association of two monomer molecules adsorbed on the surface, then the monomer-to-dimer ratio should decrease as a function of the increasing monomer concentration, that is

$$(\text{NaCl})/(\text{Na}_2\text{Cl}_2) \propto 1/(\text{NaCl})$$

This does not happen. Reaction paths of the monomer and dimer which lead to sublimation appear to be independent of each other. This result gives additional evidence in support of the short residence time of the adsorbed molecules on the vaporizing surface prior to desorption into the vacuum.

For undoped sodium chloride crystals the availability of surface sites (concentration of kinks in ledges) from which vaporization may proceed seems to control the sublimation rate. Therefore, variation of the dislocation density which changes the ledge concentration has a marked effect on the rate. The marked decrease of the sublimation rate for crystals doped with calcium indicates that the removal of a sodium chloride molecule from a surface site becomes the rate-controlling step in the presence of neighboring divalent ions or sodium-ion vacancies. Several complementary vaporization studies have been carried out on other alkali halide crystals (*19, 20*).

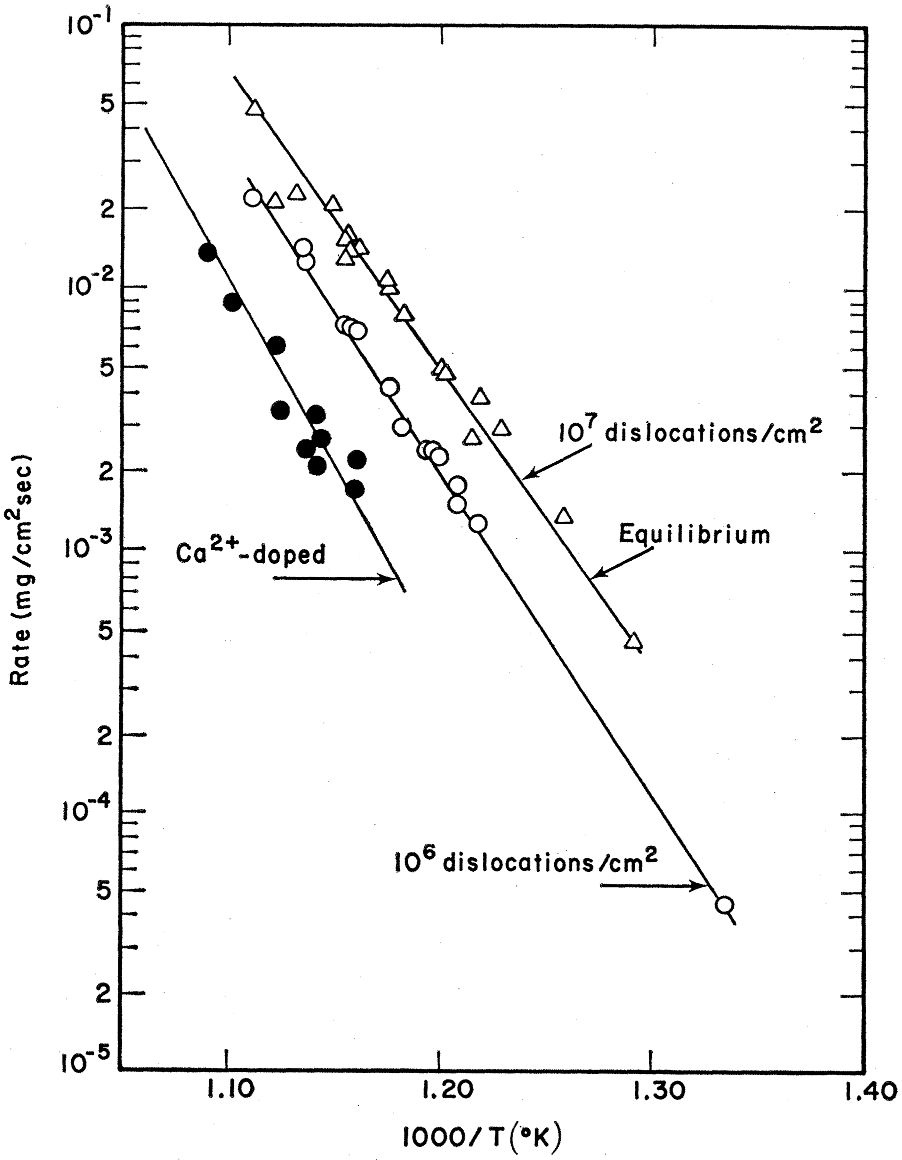

Fig. 2. Vaporization rates of clean single crystals of sodium chloride with different dislocation densities and of samples doped with calcium.

Sublimation Mechanism of Metals

The vapor of most metals is composed primarily of monatomic gaseous species. Vaporization studies based on the use of single-crystal metal surfaces are scarce; such studies have been carried out on silver (*21*) and zinc (*22*) surfaces. The results indicate that the evaporation rates, after a short induction period, reach the maximum sublimation rate within the accuracy of the experiments. Furthermore, the activation energy for vacuum vaporization is equal to the heat of sublimation determined from equilibrium vapor-pressure measurements ($E^* \simeq \Delta H_v$). It appears that equilibrium can be established in all the surface reaction steps which lead to vaporization and that the desorption of metal atoms from the vaporizing surface requires no extra activation energy.

If we assume that the surface area of the vaporizing crystal face is equal to the geometrical surface area, the large vacuum evaporation rate J_{max} implies that every surface atom should be available for sublimation with equal probability. However, this is very unlikely, considering the heterogeneous nature of the surface (many different atomic sites with varying atomic binding energies). Closer inspection of the metal surfaces (with an electron microscope) reveals a considerable roughness and a markedly increased surface area. The larger total surface area with respect to the geometric area may be responsible for the fact that only a fraction of the total surface atoms, which are in suitable atomic positions and have sufficient energy, would vaporize per unit area; thus the maximum sublimation rate could still be maintained. Melville (*23*) and Winterbottom (*24*) have shown that, no matter how rough the surface becomes, the evaporation rate may never be larger than the maximum sublimation rate from a crystal having a smooth, geometrical surface area (for a condensation coefficient near unity).

At the onset of the vaporization experiments, the sublimation rates were lower for single crystals of both zinc and silver and only slowly approached the higher steady-state rate at a given temperature. It appears that during this induction period the vaporizing surface area or the concentration of surface sites from which sublimation occurs gradually increases until the limiting maximum rate is obtained.

Using a model with a probable series of surface reaction steps, Hirth and Pound (*25*) have derived an equation for the evaporation rate of monatomic solids. For small crystals the maximum sublimation rate was predicted for their model crystal. For large low-index crystal planes a limiting evaporation rate, which is one-third of the maximum rate, was obtained from their theory, as a result of the limiting velocity of ledge motion. There is as yet no experimental confirmation of this latter result. It is possible that because of the imperfect structure of real crystal surfaces, which always contain a large concentration of ledge sources (like dislocations), the maximum evaporation rate will be obtained in the steady state for metal crystals of any size. More experiments with clean metal single-crystal surfaces must be carried out to ascertain the sublimation mechanism of monatomic solids.

Clean single crystals of sodium chloride, silver, and zinc under proper experimental conditions show nearly maximum sublimation rates and activation energies which are approximately equal to that of the equilibrium heat of sublimation. For these clean materials the structure of the vaporizing surface (dislocations, step, or ledge concentrations) plays a dominant role in determining the sublimation rate. Impurities of certain types (for example, calcium in sodium choride or oxygen in silver) introduced in the crystal lattice, could also markedly change the vaporization characteristics. It appears, however, that for these materials equilibrium can be achieved in all steps of the surface reaction, and that desorption of the vaporizing species from the solid surface requires no additional activation energy. This is certainly not the case for the sublimation of solids which undergo pronounced chemical changes such as association or dissociation upon vaporization.

Sublimation Mechanism of Arsenic

The vaporization of polycrystalline and single-crystal arsenic has been studied by Brewer and Kane (*14*) and by Rosenblatt (*5*) in the temperature range from 270° to 370°C. The vapor over the rhombohedral crystal is composed mainly of tetrahedral gaseous molecules (As_4). Evaporation studies on the (111) crystal face revealed vacuum evaporation rates which were five to six orders of magnitude smaller than the maximum sublimation rates ($\alpha = 5 \times 10^{-5}$ at 277°C). The activation energy of vaporization is $E^* = 43.8$ kcal per mole of vapor, whereas the equilibrium enthalpy of sublimation is much lower ($\Delta H_v{}^\circ = 33.1$ kcal per mole of vapor). Crystals of low dislocation density show initially low evaporation rates which gradually rise to a higher steady-state value. Studies of the surface topology reveals that most of the vaporization occurs from shallow triangular pits which appear at the point of emergence of spiral dislocations. The rate of vaporization increases as the pits grow, until they intersect. Once the whole surface is covered by pits, a constant vaporization rate is obtained.

The evaporation rate of arsenic can be increased by several orders of magnitude if liquid thallium is placed in intimate contact with the vaporizing surface (*14*). It appears that the formation of As_4 molecules is catalyzed by the presence of the liquid metal. The sublimation characteristics of antimony (*5*) and red phosphorus (*14*) are similar to those of arsenic.

These experimental results appear to be consistent with a mechanism in which the slow reaction step in the vaporization process is associated with the formation of the tetrahedral As_4 molecule at a kink on a spiral ledge [4 As(surface) $\rightarrow$ As_4(surface)]. These adsorbed molecules then diffuse rapidly on the surface and are subsequently desorbed into the vacuum.

As in any complex multistep reaction, changing the conditions of the experiment is likely to change the reaction rate. The greatly enhanced vaporization rate of arsenic in the presence of a liquid metal (thallium) demonstrates this clearly. Sublimation catalysis has been also observed for other solids such as gallium nitride (*26*) and gallium arsenide (*27*). Both these compounds show markedly increased sublimation rates in the presence of liquid gallium. This effect may be due to the dissolution of the vaporizing crystal in the liquid metal, thereby providing an alternate reaction path for sublimation (*14*).

For sodium chloride crystals the steady-state evaporation rate is dependent on the initial density of dislocations, whereas for arsenic the same steady-state evaporation rate is reached at a given temperature regardless of changes in dislocation density (after a short induction period). This difference in vaporization behavior is thought to result from the much shorter mean free path for the surface diffusion of ion pairs of sodium chloride by comparison with arsenic atoms.

Sublimation Mechanism of Cadmium Sulfide

There are large groups of substances which dissociate to their atomic constituents or to molecular aggregates of their constituents. For diatomic substances of this type the dominant vaporization reaction can be written as

$$AB(\text{solid}) \rightarrow A(\text{vapor}) + (1/y)\, B_y(\text{vapor})$$

where y has the value 1, 2, or 4 in most cases. If the vaporizing substance retains a nearly constant composition during vacuum vaporization the sublimation is said to be "congruent." Some dissociating materials which vaporize congruently exhibit partly ionic character [NH_4Cl (*28*), ZnO (*29*), CdS (*1*)] or more covalent bonding [SnO_2 (*30*), GaN (*26*), GaAs (*27*)]. I shall discuss the sublimation mechanism of one of these substances, cadmium sulfide, which has been investigated in detail.

The vapor emanating from the (111) face of the hexagonal single crystal of cadmium sulfide is composed mainly of cadmium atoms (Cd) and diatomic sulfur molecules (S_2). The vacuum evaporation rate is approximately an order of magnitude smaller ($\bar{\alpha} \leqq 0.1$) than the maximum sublimation rate in the temperature range from 650° to 800°C. The activation energy of vaporization is $E^* = 50.3$ kcal per mole of solid, much smaller than the heat of sublimation, $\Delta H_v{}^o = 75.2$ kcal/mole, of the vaporizing solid (*1*). (The value of E^* for the rate-limiting sublimation step may be either larger or smaller than the equilibrium heat of sublimation since the rate of the slow reaction step depends on the product $k[A]_s$ and not on k alone. Thus, even if E^* is less than $\Delta H_v{}^o$, either the surface concentration of vaporizing species or the pre-exponential factor might be small, which can make that particular vaporization step rate-determining.) In order to explore the mechanism of sublimation of cadmium sulfide, four alternative techniques were used.

The vaporizing surface was illuminated by light of energy greater than band-gap [$E_{\text{gap}}(25°C) = 2.41$ electron volts] in order to increase the charge carrier concentration (holes and electrons) at the surface of the semiconductor crystal (*16*, *31*). For crystals with high resistivity the vacuum evaporation rate increases linearly with light intensity.

Cadmium sulfide crystals were doped with copper and then vaporized (*10*); copper is an acceptor in CdS, which reduces the free carrier concentration of the pure crystals by several orders of magnitude. Copper doping reduces the vacuum evaporation rate by more than 50 percent from that of the undoped sample.

Crystals were doped with excess cadmium or sulfur (*12*). These treatments reduced the initial evaporation rates of crystals doped with both cadmium and sulfur by almost an order of magnitude with respect to the undoped crystal at the same temperature. The excess cadmium or sulfur, however, diffuses out of the crystal during vaporization. When all the excess crystal constituents are removed and the crystal attains its steady-state composition, the evaporation rate increases sharply and returns to the higher steady-state rate characteristic of the undoped samples.

The surface concentration of the vaporizing species was varied by an atomic beam of cadmium or a molecular beam of sulfur which was allowed to impinge on the vaporizing surface at a given temperature (*13*). The evaporation rate of cadmium sulfide is proportional to the $-\frac{1}{2}$ power of the sulfur flux and is independent of the cadmium flux incident on the vaporizing surface.

From these experiments the detailed mechanism of vaporization of cadmium sulfide can be deduced (*1*). The concentration of charge carriers, electrons, and holes plays an important role in determining the sublimation rate. The vaporization reaction steps which can be deduced from the available experimental data are (i) diffusion of excess cadmium or sulfur from the bulk of the crystal to the vaporizing surface; (ii) electron transfer to convert the cadmium ions at the surface to neutral atoms; (iii) hole transfer to neutralize the sulfur ions at the surface; (iv) association of sulfur atoms; (v) desorption of diatomic sulfur molecules; and (vi) desorption of cadmium atoms.

Under conditions of vacuum sublimation for undoped crystals, reaction steps (ii) and (iii) are indistinguishable and rate-limiting. For crystals doped with sulfur and cadmium, step (i) controls the rate. For copper-doped samples, step (ii) is the possible slow step.

The crystal composition of cadmium sulfide which produces the optimum evaporation rate at a given temperature is established when the steady-state sublimation rate is reached. Any deviation from this solid composition decreases the rate and is self-corrected by the diffusion out of the crystal of the excess during vaporization. Similar results have been obtained for zinc oxide crystals doped with oxygen (*29*). This self-correcting change in composition indicates that, although the compound dissociates upon vaporization, the vaporizations of cadmium and sulfur species are not independent but must be controlled by the same slow reaction step (charge transfer) at the vaporizing surface (*1*, *16*).

Most oxides (Al_2O_3, Ga_2O_3, SnO_2, and so forth) vaporize dissociatively while remaining congruent during vaporization. For all these substances the vacuum evaporation rates are markedly smaller than the maximum rates which were determined from equilibrium vaporization studies. Several oxides exhibit a marked discontinuity in the evaporation rate at the melting point where the rates show a sudden (threefold) increase as the crystal lattice collapses (*15*).

Noncongruent Vaporization

Substances which belong to this group of solids have constituents with greatly different evaporation rates. Thus, the solid composition may change markedly during vaporization, which indicates that the compound constituents vaporize by independent reaction paths (*32*). A large number of metal nitrides, carbides, borides, and silicides vaporize in this manner.

Compounds composed of elements from groups IIIA to VA of the periodic table exhibit an interesting transition from congruent to noncongruent vaporization. These compounds vaporize dissociatively; both gallium nitride and gallium arsenide appear to vaporize congruently, although liquid gallium droplets are readily discernible on the surface of the gallium arsenide crystals. Boron nitride, on the other hand, shows noncongruent vaporization. Solid boron condenses at the vaporizing surface, and further vaporization is limited by diffusion out of the crystal nitrogen through the boron layer (*32*). Studies of the sublimation mechanisms which lead to noncongruent vaporization have not as yet been reported.

Summary

Studies of sublimation rates which are carried out far from equilibrium provide information about the mechanism of sublimation. The activation energy of sublimation is obtained from measure-

ments of the vacuum evaporation rate of single-crystal surfaces as a function of temperature. Complementary studies of vaporization are carried out to determine the reaction steps leading to the desorption of the vaporizing species. The rates of vacuum sublimation of solids, which undergo marked chemical rearrangements (association or dissociation) upon vaporization, are lower ($\alpha \ll 1$) than the maximum equilibrium sublimation rate. For these solids a particular chemical reaction is the rate-controlling vaporization step. Solids which do not exhibit appreciable structural rearrangements during sublimation may have vacuum evaporation rates equal to the maximum rate. For clean materials of this type, the structure of the vaporizing surface (dislocations, atomic steps, ledge concentrations) plays a more dominant role in determining the rate of vaporization. Once the reaction steps which lead to sublimation are known, the sublimation rates can be changed by several orders of magnitude by a suitable adjustment of the conditions of sublimation, such as the addition of impurities, illumination, and the introduction of dislocations or vacancies.

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The Optics of Insect Compound Eyes

Microcomponents with dimensions near a wavelength of light cause observable optical effects.

W. H. Miller, G. D. Bernard, and J. L. Allen

In the 1800's, when Müller (*1*) and Exner (*2*) made the first important advances toward understanding the optical function of compound eyes, their theories of function were based on only the most obvious anatomical details. Nevertheless, these theories are widely respected even now. Müller proposed that the radially arranged facets of compound eyes are stimulated principally by light coming from the directions they face. If each ommatidium acts as a unit, the eye sees an erect mosaic image comparable to a newspaper halftone, but about 100 times coarser. Exner agreed with this theory for the eyes of diurnal insects, but for certain nocturnal insects in the dark-adapted condition he found evidence that a large part of the dioptrics functions to project a coarse erect image on the photoreceptors. This finding differed from that predicted by Müller's mosaic theory in which the individual facets are held to transmit light only to their own photoreceptors.

In recent years it has become evident that the dioptrics of insect eyes are more complex than early investigators had thought. In fact, as better microscopes and microscopic techniques have evolved, numerous additional dioptric components, characterized by dimensions of the order of a wavelength of light, have been discovered. Some of these components, such as the crystalline tracts and rhabdomeres, by their very existence have forced examination of Müller's and Exner's theories. The finding of other structures, such as the corneal nipples and various periodic layered structures, have called attention to the possibility of more subtle optical processes. All these microcomponents pose interesting problems about the nature of their interaction with light and the consequences of this interaction for the function of the eyes and for other biological processes of the animal. Before turning to these problems, we will review the basic construction of the compound eye (*3*).

Gross Anatomy of the Compound Eye

The compound eyes of insects are composed of a large number of ommatidia (little eyes). The ommatidia are hexagonally or rectangularly packed over portions of the insect's head (Fig. 1). The outermost part of each ommatidium, the cornea, is an extension of the

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