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THE KINETICS OF EVAPORATION AND

CONDENSATION REACTIONS

Alan W. Searcy

The useful life of materials in a variety of high temperature applications may be limited by the rate at which the materials vaporize or react to form gaseous products. Some industrial processes for production of high purity single crystals and for production of specialized poly-crystalline refractories include condensation from the vapor or reaction of a vapor at a surface as a critical step.

The obvious practical importance of rate studies for vaporization reactions, condensation reactions, and gas-condensed phase reactions is matched by unusual theoretical importance as well. Evaporation and condensation reaction kinetics have commonly been considered less tractible to experimental study and theoretical analysis than have gas phase and solution reaction kinetics. But some evaporation processes lend themselves to simple mechanistic interpretations, and one of the objectives of this chapter will be to illustrate the significance of evaporation kinetic studies to the general theory of reaction kinetics.

The chapter begins with an analysis of evaporation reactions as two step processes in which either a surface or a desorption step may be rate limiting. Experimental kinetic data are compared with the model to establish whether for various types of reactions the nature of the rate limiting step can be identified. With this background, generalizations about rates of vaporization of different types of refractories are given, and the kinetics of condensation reactions are more briefly discussed. Space does not permit specific discussion of gas-condensed phase reactions but the means for extension of the analysis to such reactions should be consulted for additional information not included here (1-5). References

(1-3) in particular include excellent discussion of experimental techniques.

The Relationship of Evaporation Studies to Kinetic Theory

Pioneering investigations by Hertz, Langmuir and Knudsen established and exploited the relationship between the kinetic theory of gases and the rate of evaporation (6-8). The equations and conceptual approaches that they developed still remain central to most thermodynamic and kinetic studies of evaporation and condensation.

Hertz was the first to show that a consequence of the kinetic theory of gases and of the Maxwellian distribution of molecular velocities is that the flux J in moles of vapor molecules that strike a unit area of surface per unit time is given by the expression

$$J = P/(2\pi MRT)^{1/2} \qquad\qquad (1)$$

where P is the pressure, R is the gas constant, M is the molecular weight, and T is the absolute temperature.

Langmuir argued from an analysis of the energetics of the collision process that every molecule of vapor which strikes the condensed phase surface should be captured in the attractive field of the surface and be condensed. Equilibrium between the vapor and the condensed phase would be maintained by an equal flux of molecules evaporating from the condensed phase surface. Condensation and evaporation could then be viewed as two independent processes that are in balance at equilibrium. He further argued that the flux of evaporating molecules should remain unchanged from the equilibrium flux if evaporation occurs into a vacuum. As a consequence, the equilibrium pressure should be given by $P_{eq} = J(2\pi MRT)^{1/2}$, where J is

now the flux evaporating into vacuum. But the equilibrium pressure is
related to the standard entropy of vaporization ΔS_V° and to the standard
enthalpy of vaporization, ΔH_V° by the equation $P_{eq} = \exp(\Delta S_V^\circ/R) \exp(-\Delta H_V^\circ/RT)$,
so these thermodynamic quantities should be related to the flux during
free surface evaporation by the expression

$$J = (2\pi MRT)^{-1/2} \exp(\Delta S_V^\circ/R) \exp(-\Delta H_V^\circ/RT)$$

Knudsen showed, however, that pressures calculated from weight losses
may sometimes be orders of magnitude lower than pressures measured under
proved equilibrium conditions. He introduced into the Hertz-Langmuir
equation a factor α, so that it becomes

$$J = \alpha P_{eq} (2\pi MRT)^{-1/2} = \alpha(2\pi MRT)^{-1/2} \exp(\Delta S_V^\circ/R) \exp(-\Delta H_V^\circ/RT). \quad (2)$$

Then α has a value of unity when every molecule of vapor that strikes the
surface is condensed, but may take smaller values when equilibrium is not
established between the condensed phase and each vapor molecule which
strikes the surface.

Sometimes α is described as the factor that accounts for the number
of vapor molecules that are reflected upon collision with the surface.
But a vapor molecule may be adsorbed and yet fail to come to equilibrium
with the bulk condensed phase. It is preferable to define α as that
fraction of vapor molecules that upon striking the surface attain complete
thermodynamic equilibrium with the condensed phase.

An essential condition for equilibrium is that there be no net flux
between condensed phase and vapor. It is apparent, therefore, for
equilibrium conditions that if only a fraction α_c (the condensation coeffi-
cient) of the vapor molecules striking a surface come to equilibrium with

the condensed phase, the flux of molecules that evaporate is correctly

predicted from the equilibrium vapor pressure by the Hertz-Langmuir

equation only if a numerically identical factor α_v (the vaporization or

evaporation coefficient) is introduced. Under nonequilibrium conditions

α_c and α_v need not have equal values, and it has been argued that α_c and

α_v can be expected to be very different under usual conditions of experi-

mental study (10). But it will be shown here that α_v and α_c probably do

remain equal, or very nearly so, over a wide range of nonequilibrium con-

ditions.

To explain the experimental observation that α_v can be unity for

some condensed phases and at least as small as 10^{-6} for other, three

principal theoretical approaches have been used.

The approach that has reached the most sophisticated level of develop-

ment is the evaluation of α_v and α_c for solids in terms of the details

of movement of atoms through a series of reaction steps on the surface

to positions of successively lower binding energies: From bulk sites to

positions in ledges, to kink sites in ledges, to adsorption sites on

ledges, to surface adsorption sites. (Fig. 1) Notable contributors

to the theory have been Kossel, Stanski, Knacke, Burton, Cabrerra, Frank,

and Hirth and Pound. (See references 1-4).

The atomistic approach per se is recognized to be adequate only for

analysis of sublimation rates for metals and non-polar, molecular solids.

The quantitative prediction of the model as developed by Hirth and Pound

(3,11) for steady state sublimation of low index, single crystal planes

of such solids in vacuum is that α_v should be about 1/3. The prediction

for high index planes of any size, or for low index planes of small size

or with dislocation densities greater than 10^5 cm^{-2} is that $\alpha_v \simeq 1$.

Because dislocation densities less than 10^5 cm^{-2} are hard to attain and because free surface sublimation rates are difficult to establish unequivocally within a factor of three, conclusive experimental tests of the predictions have not been available (5,12). However, a recent experimental study appears rather definitely to prove that $\alpha_v \simeq 1$ for the (0001) plane of high purity zinc under conditions for which the theory predicts 1/3 (13).

The atomistic approach, therefore, while extremely useful in shaping our understanding of surface morphology and of the qualitative effects of impurities, vapor supersaturation, and other variables on crystal growth or evaporation, in its present form is wrong in its quantitative predictions. In any event the atomistic model does not direct itself to the analysis of the chemical processes that lead to the wide range of observed evaporation coefficients.

A second approach to theoretical evaluation of evaporation kinetics is through use of the formalism of irreversible thermodynamics (10). This approach will probably become an important one, but so far only very general predictions can be derived from it. The third approach, the adaption of transition state theory of reaction kinetics to the special conditions of the heterogeneous evaporation reaction, appears the most fruitful now available. This approach, which can be fused with the atomistic approach whenever it appears useful to do so (12), is explored in the remainder of the chapter.

The analysis here will differ in several important respects from previous analyses (2,12,14,15) of evaporation or condensation reactions in terms of transition state theory. First, a particular effort will be made to identify a surface step or the desorption step as the probable

rate limiting step in evaporation. Discussions of evaporation kinetics appear usually to tacitly assume that the activated complex for the slow step in evaporation is physically located on the reaction surface (1-5). It will be shown that for some evaporation reactions the activated complex is in the vapor phase. Second, a means (16) of evaluating the frequency factor ν and the transition probability κ of the desorption step will be used. In previous studies, ν was commonly assumed to be either the Debye frequency for the solid or kT/h per molecule where k is the Boltzmann constant and h is Planck's constant, and κ was assumed to be 0.5 or 1. Third, the temperature dependence of evaporation rates will be more fully used than has usually been done (the paper of Gregory (17) and recent reviews by Somorjai (5) are important exceptions) to evaluate apparent activation enthalpies and entropies for comparison with enthalpies and entropies of the equilibrium reactions and for prediction of the temperature dependence of the evaporation and condensation rates. Finally, the relationship between the kinetics of evaporation and of condensation will be more strongly emphasized and explicitly discussed than in other reviews.

The Rate Equation for a Two Step Evaporation Reaction

Analysis of the stepwise evaporation process for a particular example will demonstrate the general approach, which can be extended as necessary to more complex reactions. Suppose that a particular liquid or solid evaporates to a single important vapor species of the same elemental composition as the condensed phase, and further suppose that the evaporation takes place in two steps; the formation of a surface complex followed by desorption of the complex from the surface. If the condensed phase and vapor are at equilibrium, the two step process can be written as

$$n \; Y(b) \; \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \; Y_n(a) \qquad\qquad (3)$$

$$Y_n(a) \; \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \; Y_n(g) \qquad\qquad (4)$$
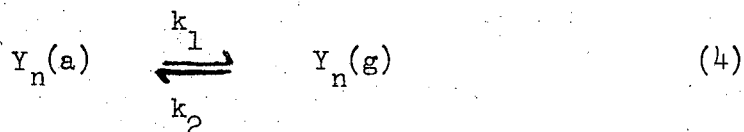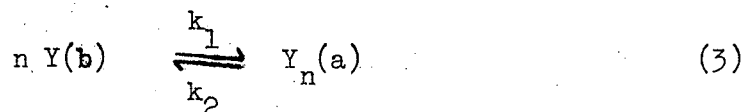
where $Y(b)$ is an atom or molecule in the bulk crystal, $Y_n(a)$ is a complex of n atoms or molecules adsorbed on the surface, and $Y_n(g)$ is the vapor molecule.

At equilibrium the net flux of molecules must be zero, with the material balance described by

$$k_1 \; = \; k_2 \qquad [\; Y_n(a) \;] \qquad\qquad (5)$$

and

$$k_3 \; [Y_n(a)] \; = \; k_4 \; [Y_n(g)] \qquad\qquad (6)$$

where the bracketed expressions indicate activities of the adsorbed and gaseous species relative to their respective standard states. The activity of the bulk molecules does not appear explicitly in Eq. (5) because it remains unity for all conditions of present interest.

If the concentration of vapor molecules is reduced by evacuating the system in which the solid is heated or by flushing the reaction chamber with a fast-moving stream of inert gas, the value of the expression $k_4 \; [Y_b(g)]$ can be made negligibly small. If we provisionally apply the usual hypothesis of chemical kinetics, that the specific rate constants are nearly independent of concentrations of the reactant and intermediate species, the flux of molecules J_{Y_n} which will now lease the surface can be described by

$$J_{Y_n} \; = \; k_3 \; [Y_n(a) \;] \qquad\qquad (7)$$

where k_3 is unchanged. If k_1 is much greater than $k_4[Y_n(g)]$, then $[Y_n(a)]$ will also be essentially unchanged. But if not, $[Y_n(a)]$ may decrease significantly below its equilibrium value.

For steady state sublimation in vacuum $[Y_n(a)]$ will have a time independent value so that $d[Y_n(a)]/dt = k_1 - k_2[Y_n(a)] - k_3[Y_n(a)] = 0$, and $[Y_n(a)] = k_1/(k_2 + k_3)$. Substitution of this expression into Eq. (7) yields

$$J_{Y_n} = k_1 k_3/(k_2 + k_3) \,. \tag{8}$$

While various approaches to the theory of reaction rates differ in details, there is general agreement that the specific rates constant, k_i, for an elementary reaction step, i, at constant pressure and temperature has the value $k_i = \kappa_i \nu_i \exp(-\Delta G_i^*/RT)$, where κ_i is the transmission coefficient, ν_i is the frequency factor, and ΔG_i^* is the Gibbs free energy of activation (17,18). Accordingly, Eq. (8) can be written in the form

$$J_{Y_n} = \frac{\kappa_1 \nu_1 \kappa_3 \nu_3 \exp\{-(\Delta G_1^* + G_3^*)/RT\}}{\kappa_2 \nu_2 \exp\{-\Delta G_2^*/RT\} + \kappa_3 \nu_3 \exp\{-\Delta G_3^*/RT\}} \tag{9}$$

and since from Eq. (2), $\alpha = J_{Y_n} (2\pi MRT)^{1/2}/P_{eq}$

$$\alpha = \frac{\kappa_1 \nu_1 \kappa_3 \nu_3 \exp\{-(\Delta G_1^* + \Delta G_3^*)/RT\}}{\kappa_2 \nu_2 \exp\{-\Delta G_2^*/RT\} + \kappa_3 \nu_3 \exp\{-\Delta G_3^*/RT\}} \times \frac{(2\pi MRT)^{1/2}}{\exp\{-\Delta G_V^\circ/RT\}} \tag{10}$$

where ΔG_V° is the standard Gibbs free energy of the evaporation reaction. Equation (10) is an expression, then, for α in terms of fundamental thermodynamic parameters for the overall reaction and of fundamental kinetic parameters for two elementary reaction steps either of which, we have tentatively assumed, may control the rate of evaporation.

The Significance of Unit Evaporation Coefficients

It is generally assumed, and probably correctly, that the evaporation coefficient is unity independent of temperature for clean liquid metals that evaporate to their atoms and for non-polar molecular liquids, though experimental evidence is available for only a few examples (3,5). Although the vaporization characterisitcs of solids are of more practical importance for materials applications, solid vaporization behavior is less well established. Table 1 lists solids which have been reported to have temperature independent evaporation coefficients of unity within estimated experimental uncertainities. From comparison of evaporation rates of the solid and liquid at the melting point, Burns, Jason, and Inghram conclude that solid copper, silver, gold, silicon and boron also have unit evaporation coefficients (26).

For several additional solid metals which are not included in the Table there are conflicting reports with some authors finding evaporation coefficients in the range from 0.1 to 0.5 and other finding values close to 1 (3). The correctness of measured evaporation coefficients is sometimes difficult to assess. But the author is convinced that the values reported in Table 1 are substantially correct and that the solids listed represent just a small sampling of those that will eventually be proved to have unit or near unit evaporation coefficients, including those metals for which the present evidence is conflicting.

For substances with unit evaporation coefficient, Eq. (10) leads directly and unambiguously to some important quantitative relationships between the kinetic parameters and thermodynamic parameters for evaporation. If α is unity the ratio of the kinetic terms in equation (10)

must reduce to $\exp(-\Delta G_v^\circ/RT)/(2\pi MRT)^{1/2}$. In other words when $a_v = 1$, the rate expression of equation 9 reduces to an expression characteristic of a single step process for which the free energy of activation is ΔG_v°, the standard free energy for the overall equilibrium reaction $nY(b) = Y_n(g)$, and for which $\kappa_v \nu_v = (2\pi MRT)^{-1/2}$.

Equation 10 will reduce to the correct single step expression only if $k_3 = \kappa_3 \nu_3 \exp(-\Delta G_3^*/RT)$ is small relative to $k_2 = \kappa_2 \nu_2 \exp(-\Delta G_2^*/RT)$. This condition $k_3 << k_2$ means that the intermediate reaction product (and any other reaction intermediate) remains for practical purposes at complete equilibrium with the bulk condensed phase during steady state sublimation in vacuum. The principle of microscopic reversibility then requires that $\kappa_1 \nu_1 = \kappa_2 \nu_2$ so $\kappa_3 \nu_3 = \kappa_v \nu_v = (2\pi MRT)^{-1/2}$, that is the product of the transmission coefficient and frequency factor for the disorption step must, when $\alpha_v = 1$, be $(2\pi MRT)^{-1/2}$. And $\Delta G_1^* + \Delta G_3^* - \Delta G_2^* = \Delta G_v^*$. When $\alpha_v = 1$, intermediates that remain at equilibrium with the bulk phase need not be explicitly introduced into the description of the reaction kinetics. Since for any reaction $\Delta G = \Delta H - T\Delta S$, it is apparent that for α to be unity over a range of temperatures implies the additional equalities $\Delta H_1^* - \Delta H_2^* + \Delta H_3^* = \Delta H_v^* = \Delta H_v^\circ$ and $\Delta S_1^* - \Delta S_3^* = \Delta S_v^* = \Delta S_v^\circ$.

In transition state theory for reaction kinetics, the acitvated complex is the aggregate of atoms at the saddle point free energy position of the rate determining step of the reaction (18,19). For an evaporation coefficient of unity, the saddle point enthalpy and entropy have here been shown to differ from the enthalpy and entropy of the bulk condensed phase by just the amounts necessary to produce a flux from the surface which is identical to the flux which would cross an imaginary plane in a given direction in the equilibrium vapor. From these facts it is apparent

that the rate determining step is $nY(b) = Y_n(g)$, and that the activated
complex is Y_n (g), the product of the equilibrium reaction. The saddle
point free energy position can be viewed as an imaginary plane drawn
parallel with the plane of evaporation at a distance above the surface
just sufficient to make neglibibly small the energy of interaction between
the surface and molecules that have sufficient energy to evaporate.

It can now be seen that reactions with unit evaporation coefficients
provide clear-cut verifications of several assumptions of transition state
theory. The importance of these verifications can be judged from the
comment in a recent monograph on reaction kinetics, "Unfortunately in
the case of transition-state theory, an adequate **experimental** test of the
theory is not possible at present, nor does it seem likely that this situa-
tion will change in the foreseeable future" (27).

In agreement with equilibrium transition state theory, the enthalpy
and entropy of formation of the activated complex if $\alpha = 1$ remain at their
equilibrium values when the reverse reaction becomes negligible. The
rate of formation of the activated complex from the reactant under non-
equilibrium conditions is identical with the maximum possible rate of
formation from the reactant under equilibrium conditions.

A point of some uncertainty in application of transition state theory
has been whether the transmission coefficient should be assumed to be
unity one-half, or some other value at the saddle point reaction coordinate,
Experimental values have not been available. For these reactions with
evaporation coefficients of unity, there is clearly nothing to reflect
molecules at the saddlepoint, so κ must be unity. And since $\kappa\nu$ has
been already shown to be $(2\pi MRT)^{-1/2}$ it follows that $\nu = (2\pi MRT)^{-1/2}$.

It is extremely important to recognize that every point on the
surface of a condensed phase that displays a unit evaporation coefficient

supplies a flux of molecules to the vapor that is the maximum predictable from equilibrium data. It follows that every point on the surface of a solid with unit evaporation coefficient must be at equilibrium with the bulk solid even when the solid is held in a vacuum. The difference in entropy between atoms on various kinds of surface sites and the entropy of atoms at bulk lattice sites is not negligible as commonly assumed (4,11). The activity of adsorbed atoms is the same as the activity of atoms of kink sites, in ledge sites or in the bulk. The lower bonding energies that hold adsorbed atoms are just compensated for by increased configurational and vibrational entropies (see Chapter 7 and 8 for discussion of these entropy terms). Thus the free energy change for transfer of an atom from a bulk to a kink site is not one-half the molar heat of sublimation as commonly assumed, but zero if $\alpha_V = 1$, and does not normally exceed $RT \ln \alpha_V$ if $\alpha_V < 1$. The idea (4) that special significance should be attributed to the kink positions in surface ledges because atoms at such positions are bound by energies that are approximately half the energies with which atoms are bound at bulk lattice sites is mistaken.

The Interpretation of Kinetics of Reactions When $\alpha_V < 1$.

The analysis in terms of equilibrium transition state theory of evaporation reactions with unit evaporation coefficients has led to unambiguous identifications of the composition, physical location, and enthalpy and entropy states of the activated complex and to the values of the transmission coefficient and frequency factor at the reaction saddlepoint. These unambiguous identifications are only possible because, when $\alpha_V = 1$, the equilibrium reaction product is itself the activated complex. There is no reason, however, why if the activated complex were

a gas molecule other than the equilibrium product, the values of κ and ν should be different from their values when $\alpha_V = 1$. We can assume that for all vaporation reactions $\kappa_3 \nu_3$ of reaction 4 will be equal to $(2\pi MRT)^{-1/2}$. This assumption will enable us to calculate from experimental values of vaporation rates as a function of temperature what the values of ΔS_3^* and ΔH_3^* would have to be if the desorption step is rate determining. From the plausibility of these calculated values of ΔS_3^* and ΔH_3^* we can decide whether the descrption step or a surface step is more likely to be rate determining for any particular evaporation reaction.

Figure 2 compares the temperature dependence of the flux for a substance with unit evaporation coefficient with the three different types of behavior which have been emperically observed for substances with low evaporation coefficients; Evaporation coefficients may remain essentially independent of temperature or increase or decrease with temperature. The flux for $\alpha_V = 1$ is, of course, identical to the flux that would escape through a small hole in the wall of a chamber in which the equilibrium pressure is maintained. If for example α increases with temperature, the slope of the ℓnJ versus $1/T$ plot is less than the slope of the plot for the equilibrium flux and the enthalpy of activation for evaporation ΔH_V^* is less than the enthalpy of the equilibrium vaporization reaction, ΔH_V°.

The displacement from the equilibrium shown for each of the curves of Fig. 1 is arbitrary. A substance for which the apparent enthalpy of activation ΔH_V^* is larger than ΔH_V° (type 1) may for example have a smaller α_V in the experimental range than do substances for which ΔH_V^* is smaller than ΔH_V° (type 3).

Table 2 includes data for reactions for which the apparent enthalpies of activation have been measured. The empirically measured activation

enthalpies should properly be called apparent enthalpies of activation because there is no assurance that the reaction assumed to be rate determining really is so.

The variation in evaporation rates with temperature may be fixed by the rates of two or more simultaneous reactions. Even if only a single reaction step is rate determining, the calculated enthalpies and entropies may not be the true values for the actual activated complex. All activation enthalpies and entropies reported in this chapter are calculated on the assumption that the activated complex has the same composition as the equilibrium reaction products. For dissociative sublimation reactions this procedure is different from that conventionally used for reporting activation energies. For example Somorjai (31) reports for CdS sublimation $\Delta H_v^* = 50.3$ kcal, which is the enthalpy calculated from the temperature dependence of the expression $J_{CdS(s)} = (2\pi MRT)^{-1/2} \exp(\Delta S_v^*/R) \exp(-\Delta H_v^*/RT)$, while the value in Table 2 is 150.9 kcal, the value of ΔH^* calculated from

$$[J_{Cd}(g)]^2 [J_{S_2}] = (2\pi RT)^{-3/2} M_{Cd}^{-1} M_{S_2}^{-1/2} \exp(\Delta S_v^*/R) \exp(-\Delta H_v^*/RT).$$

The values of ΔH^* and ΔS^* are then directly comparable to the enthalpies and entropies of the equilibrium reaction, which for CdS sublimation is obtained from $K_{eq} = P_{Cd}^2 \times P_{S_2} = \exp(\Delta S_v^\circ/R) \exp(-\Delta H_v^\circ/RT)$ so that $(J_{Cd}^\circ)^2$ $(J_{S_2}^\circ) = (2\pi RT)^{-3/2} M_{Cd}^{-1} M_{S_2}^{-1/2} \exp(\Delta S_v^\circ/R) \exp(-\Delta H_v^\circ/RT)$, where the J°'s are equilibrium (maximum) fluxes. Then for a substance for which $\alpha_v = 1$, $\Delta H_v^* = \Delta H_v^\circ$ and $\Delta S_v^* = \Delta S_v^\circ$, and for a subtance for which $\alpha_v < 1$, the relative magnitude of ΔH^* and ΔH_v° indicate immediately whether the flux for free surface evaporation has a greater or smaller temperature dependence than does the equilibrium flux.

Activation enthalpies calculated in this manner would be the true values if the rate limiting elementary stress is desorption. If in the

cadmium sulphide example, the rate limiting step were formation of a
[CdS (ads)] complex, the true activation enthalpy for the elementary step
of formation of this complex might be given by $J_{[CdS(ads)]} = \kappa \nu \exp(\Delta S^*/R)$
$\exp(-\Delta H^*/RT)$ for which ΔH^* would be 1/3 the value reported in Table 2, i.e.
the value reported by Somorjai.

If the rate determining step occurs on the condensed phase surface,
the frequency factor will no longer be $(2\pi MRT)^{-1/2}$, so that the calculated
entropies of activation cannot be correct even if the composition of the
activated complex has been correctly assigned.

The striking differences between the unit evaporation coefficients
for arsenolith modification of As_4O_6 and white phosophorous (see Table 1)
on the one hand and the very low evaporation coefficients for the claudetite
modification of $As(s)$ and for red phosphorous on the other, have been
attributed to the fact that the first two solids contain as distinct units
of the crystal the molecules which are the principal equilibrium vapor species,
while the second two solids are made up of atoms or ions linked into infi-
nite networks (21, 22). The equilibrium vapor molecules from red phos-
phorous can only be formed by a process of breaking and reforming of bonds,
a process that is unnecessary for vaproization of arsenolith or white phos-
phorous. Of course, whether a low evaporation coefficient will be found
when evaporation requires breaking and reforming of bonds depends not only
on bond strength but also on bond type and on the complexity of the struc-
tural change that is required to form the vapor molecules. Recent measure-
ments for barium fluoride, lanthanum fluoride, and praseodymium flouride
(23,24,16) show that ionic solids can vaporize with unit evaporation co-
efficent even though the vapor molecular units are not present in the solid.
Data are not yet available to demonstrate for metals whether vaporization

to vapor phase molecules such as the dimer Na_2 do or do not occur with low evaporation coefficients.

It is striking that several of the solids of Table 2 have apparent enthalpies of activation which are greater than the enthalpies of the equilibrium reactions but have apparent entropies that are close to those of the equilibrium reaction. Arsenic sublimation provides a good example to illustrate how the reactions of this type can be interpreted in terms of equation 10.

Rosenblatt, et al. (29) measured the rate of sublimation of $As_4(g)$ from the trigonal face of arsenic single crystals and report the apparent activation enthalpy at $550°K$ to be 43.8 ± 1.4 kcal per mole of As_4 compared to 33.1 kcal for enthalpy of the equilibrium sublimation reaction. They calculate the apparent entropy of activation to be 37.6 ± 2.7 eu per mole of As_4 compared to 38.0 eu for the equilibrium reaction.

Rosenblatt has presented ingeneous and very convincing evidence and arguements in support of the conclusion that the slow vaporization step is the formation of As_4 molecules at kink sites of crystal ledges (38). In particular, correlation of the approach to steady state conditions with the concentration, form, and size of thermal etch pits lends strong support to the interpretation that the rate of sublimation depends directly on the concentration of kink sites.

However, implicit in the calculation of the apparent activation entropy of the equilibrium reaction, is the assumption that $\kappa \nu = (2\pi MRT)^{-1/2}$ for the rate limiting step. Despite the very strong evidence of Rosenblatt, et al., the fact that the steady state value for $\kappa \nu \exp(\Delta S_V^*/R)$ is very close to $(2\pi MRT)^{-1/2} \exp(\Delta S_V^\circ/R)$ invites the alternate interpretation that desorption is the rate limiting step and that the activated complex is an excited As_4 gas molecules. The mechanism of Rosenblatt,

et al. is of a kind that is predicted from equation 8 when k_3 is large compared to k_2. For this condition equation 9 reduces to $J_{y_n} = \kappa \nu \exp\left(-\Delta G_1^*/RT\right)$. And substitution in equation 10, yields when the experimental behavior is that of arsenic

$$\kappa_1 \nu_1 \exp\left(\Delta S_1^*/R\right) \cong (2\pi MRT)^{-1/2} \exp\left(\Delta S_V^{\circ}/R\right) \tag{11}$$

In terms of Rosenblatt's model, ΔS_1^* would be the entropy of formation of As_4 complexes bound to only that small fraction of surface sites which are kink sites. Both the low thermodynamic probability of kink sites and the restriction in As_4 complex movement that results from the binding energy would reduce ΔS^* below ΔS_V°. The near equality of equation 11 could only be maintained if $\kappa_1 \nu_1$ were fortuitously to exceed $(2\pi MRT)^{-1/2}$ by an amount that just compensates for the entropy difference. Fortuitous compensation seems an unlikely explanation of the experimentally observed near equality of equation 11 for both arsenic and antimony.

The model developed in this chapter would be consistent with the concept of a mobile adsorption layer of arsenic atoms which occasionally cluster to As_4 units. Of any As_4 units only those which acquire the energy necessary to escape from the surface would be activated complexes for the evaporation reaction.

Since $\Delta H_V^* > \Delta H_V^{\circ}$ the molecules that escape may carry excess excitation energy. Confirmation of the mechanism might be obtained by demonstration that the molecules which leave the surface are in excited energy states not necessarily an easy task since lifetimes for excited states are some-times so short that spontaneous deactivation may occur before a beam of vapor can traverse the distance of the order of 10cm necessary to reach a detector. The fact that As_4 molecules from free surface sublimation have the same fragmentation pattern at various electron voltages in a mass

spectrometer as do As_4 molecules from a near equilibrium vapor beam implies that negligible excess internal energy is carried as far as 10cm by the molecules in the non-equilibrium free surface sublimations.

Even though their apparent activation enthalpies of sublimation are high, the rate limiting steps for gallium nitride and beryllium nitride sublimation may well be surface rather than desorption steps, because for each ΔS_v^* is much less than ΔS_v^o. If desorption to an activated complex that is a free vapor molecule is rate limiting, the experimentally determined activation entropy should be comparable to the entropy of equilibrium species of the same formula instead of much lower, as observed. For gallium nitride sublimation, mass spectrometric measurements (39) definitely show the particles that leave the surface to be gallium atoms and nitrogen molecules. For sublimation of these two nitrides, either a surface step must be rate determining or the desorption step must occur from only a severely limited number of surface sites.

Mar and Searcy have proved that the N_2 molecules and gallium nitride surface do not have excess kinetic energy (40). It had been hypothesized that molecules that evaporate by a process that has an activation energy greater than the enthalpy of the equilibrium reaction would be at a higher average temperature than the temperature of the surface (41). The experimental results show that the hypothesis is wrong for gallium nitride. The hypothesis could only be valid if desorption is rate determining but probably is not valid even then.

For the second class of evaporation reactions, those which have low, but temperature independent, evaporation coefficients, the simplest assumption is that evaporation is limited by the number of suitable sites for the desorption process or by the probability that atoms which form

a product gas molecule will collide in the adsorption layer. Cadmium
sulphide sublimation will be discussed as a prototype for this second class
of evaporation reactions. As a result of the outstanding studies of
Somorjai and coworkers, whose results are summarized in reference 5, more
is known about factors that influence cadmium sulphide sublimation than
is known for any other material. Somorjai and coworkers (5) not only mea-
sured the influence of temperature on cadmium sulfide sublimation, but
also the influence of a beam of sulphur, and cadmium vapor impinged on the
surface, the influence of changes in solid composition, and the influence
of light.

The observed effects of directing cadmium atom and S_2 molecule beams
against the surface are particularly interesting. When an S_2 beam flux
became comparable to the vaporization flux, the loss of cadmium sulfide
from the surface was found to vary inversely with the square root of the
sulphur vapor pressure. A cadmium beam, however, did not influence
the sublimation rate. This behavior appears to indicate rather clearly
that the sublimation rate is limited by availability of surface sites at
which sulphur atoms can react to form S_2 molecules. Since $\Delta H_v^* \cong \Delta H_v^\circ$
it can be hypothesized that the probability is low for sulphur atom colli-
sion on the surface except at a limited number of sites, but when collisions
occur between atoms at these, presumably adjacent, sites there is no
excess free energy barrier for S_2 gas desorption. If the number of sur-
face sites is in fact critical to the sublimation rate, some other non-
metal vapor beams should act like the S_2 beam in reducing the evaporation
rate.

It has been shown that for liquids and solids that contain polar molecular units the observed values of α_v are approximately equal to the ratios of the partition function for the condensed phase molecules to the partition function for the vapor molecules. The observed low values of α_v in the range from 0.01 to 0.5, have been interpreted, therefore, as arising because the rotational states do not equilibriate during the vaporization step with the result that the value of ΔS_v^* is smaller than ΔS_v° by the difference between the rotational entropies of the vapor and condensed phase molecules (14,42,43). It is argued that since the enthalpy of molecules that escape is little affected by the degree of rotational excitation, the vaporization coefficient reflects only the unfavorable entropy, and α_v is independent of temperature.

While this explanation is appealing, it should be noted that experimental values for evaporation of polar molecules are for the most part not firmly established, and most of the data to which this theory has been compared are for single temperatures, so that it is not known whether or not the evaporation coefficients are really temperature independent. Careful measurements of evaporation coefficients over substantial temperature ranges are needed to test this theory.

Not included in Table 2 are data for iodine and ferric choloride sublimation (17) because there is some question about the reliability with which activation enthalpies, and especially, activation entropies can be calculated from the dependence of measured Knudsen effusion pressures of effusion orifice area. There is no doubt, however, that solid iodine shows type 3 evaporation behavior (17,37). For a molecular solid like I_2, a unit evaporation coefficient is expected. Adsorbed impurities may explain the discrepancy.

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For the desorption step of evaporation to be rate determining with
an activation enthalpy lower than the equilibrium enthalpy of reaction
(type 3 of Fig. 1) would require that the activated complex have an average
bond energy per atom that is higher than that of the equilibrium reaction
product, but have an entropy that is enough lower than that of the equili-
brium product to make the activated complex a less stable gas species at
the temperature of study than is the equilibrium product. (At sufficiently
low temperatures the higher bond energy per atom of the activated complex
would make it more stable). Evaporation reactions for which these condi-
tions are met can be expected under certain circumstances. As one example,
if the vapor flux from free surface sublimation of a single crystal of
sulphur were measured with sufficient accuracy, the enthalpy of activation
should be found to be several percent below the equilibrium enthalpy of
sublimation. The only vapor molecule that is produced at a high flux level
during free surface sublimation, S_8 (44) has a bond energy per atom that
is slightly higher than the average bond energy per atom in the equili-
brium mixture of sulphur vapor species. The equilibrium mixture of mole-
cules of formulas varying from S_2 through S_8 is stable relative to pure S_8
gas because of entropy of the mixture is higher than that of S_8.

A related, but more subtle, possibility is that a condensed phase
might evaporate exclusively to its ground state vapor molecules rather than
to an equilibrium mixture of the ground state and low lying excited states.
Such behavior would be possible for substances for which the spectroscopic
selection rules forbid the transition between the ground state and the low
lying excited state as could be true, for example, if the ground state were
a singlet state and the low lying state were a triplet. In neither of the
cases just described would the experimentally measured enthalpy of activa-
tion be expected to lie more than ten percent below the enthalpy of the

equilibrium reaction, and if the composition of the vapor were determined in the first example and if the gaseous molecular energy states were determined in the second example, the expected discrepancy could be calculated for comparison with the experimental observations.

When the apparent enthalpy of activation is found to be considerably smaller than the enthalpy of the equilibrium reaction, as is found for the ammonium halides of Table 2, a desorption step cannot be rate limiting. Thus while some details of Spingler's analysis of his pioneering study of ammonium chloride (37) are probably wrong - - he made the usual assumptions that only enthalpy changes need be considered and that the kink poisition can be expected to have special mechanistic importance - - his central conclusions are correct. The rate limiting process occurs on the surface and it probably is the reaction of an ammonium ion with a chloride ion to produce adsorbed ammonia and hydrogen chloride.

The Dependence of Evaporation Coefficients on Other Variables.

In the discussion of evaporation kinetics to this point, congruent vaporization has been assumed. That is, it has been assumed that the gas phase produced by vaporization has a composition identical to that of the condensed phase. For dissociative reactions such as, for example the reaction $2CdS(s) = 2Cd(g) + S_2(g)$, deviations from congruent evaporation cause an increase in the equilibrium pressure of one vapor species and a decrease in pressure of the other. The changes in pressure of the two species are so related by the Gibbs-Duhem equation that there is a net pressure increase (45). An increase in the flux of vapor might therefore be expected for free surface vaporization when the composition is changed away from that for congruent evaporation.

But for both cadmium sulfide (5) and zinc oxide (46), the only solids
for which the effect of composition on sublimation rates appears to have
been studied, variations from the composition for congruent sublimation
give decreased sublimation rates. Both of these solids sublime by dissocia-
tion to metal atoms and a diatomic molecule of the non-metallic element.
It will be interesting to see if composition changes have similar effects
on sublimation rates when other types of vapor species are formed.

One factor that must influence the vaporization kinetics when the
condensed phase composition is altered is the rate of diffusion of the com-
ponent that is present in excess of its composition for congruent vaporiza-
tion. If a component that is present in excess can diffuse rapidly in the
condensed phase, and if there is no particular barrier to its vaporization,
that component should diffuse to the surface and evaporate preferentially
(47). Vaporization would then be characterized by a transient
period during which the composition of the condensed phase and vaporization
flux both vary continuously toward characteristic steady state values.
These steady state values would be the same for a particular phase regard-
less of the initial composition chosen, (unless as may occasionally happen,
there is more than one composition of congruent evaporation). But if
diffusion of the component in excess is slow relative to the rate of
vaporization, the rate of vaporization may have a different steady state
value characteristic of each particular composition. Such behavior might
be expected for some solid phases, since diffusion rates in solids are
slower than those in liquids.

Knudsen showed that the rate of evaporation of liquid mercury is
reduced by several orders of magnitude if the surface is dirty(48). Non-
volatile impurities might be expected to accumulate at the surface of
a solid as the surface recedes during sublimation, and the accumulation

of impurities might be expected to progressively lower the sublimation rate.

Most studies of sublimation kinetics have ignored the possibly significant effects of the residual pressures in the vacuum system, but Blank and Searcy showed that when nitrogen or argon gases were introduced into their system at pressures comparable to the pressures calculated from their Hertz-Langmuir data for magnesium nitride, the evaporation flux significantly decreased and its temperature dependence changed (49).

Somorjai and Lyon have shown that small concentrations of copper will slightly reduce the rate of cadmium sulfide sublimation (5,50). But the data indicate that the copper can diffuse in cadmium sulfide at a rate that is high relative to the rate of sublimation, and the copper apparently does not concentrate preferentially at the sublimation surface, Copper appears to diffuse away from the surface during sublimation to maintain a relatively uniform concentration throughout the solid.

Mar (13) has calculated that in a system which has a residual pressure of 10^{-6} torr the zinc oxide formed on a zinc metal surface by reaction with the residual oxygen should produce serious impedence to zinc sublimation if the oxide formed as a protective coating. He observed, however, that the oxide appeared to collect in fluffy and loosely bound particles which impeded sublimation only in very local areas.

Properly chosen reagents may catalyze rather than impede sublimation reactions. Brewer and Kane (21,28) showed that the rate of sublimation of red phosphorous or of arsenic was increased two to three orders of magnitude in the presence of liquid thallium. Schoonmaker, Buhl, and Lemley (5,1) have shown that the rate of dissociative sublimation of gallium nitride is increased by either liquid indium or liquid gallium. In each

case the liquid phase is believed to provide a solvent that reduces the
activation enthalpy for the rate determining reaction step. A catalyzed
reaction will usually have a lower activation enthalpy than an uncatalyzed
reaction. As a consequence the effectiveness of catalysis usually will
decrease with increasing temperature.

Since the evidence is strong that for certain vaporization reactions
the rate at which bonds can be broken or the rate at which electrons can
be transferred is rate determining, it is not surprising that the activation
energy for sublimation of the claudetite modification of arsenous oxide
can be reduced more than 20% by neutron irradiation (52). Presumably the
reduction reflects assistance provided by the radiation in the bond rup-
turing step necessary to sublimation of claudetite.

Photons of energy high enough to excite electrons across the band gap
in cadmium sulfide increases the rate of sublimation for that material at
certain composition but depresses the rate of sublimation of cadmium doped
cadmium sulfide (53,54). Somorjai explains that for the cadmium-doped
solid, the effect of light in reducing the rate of out-diffusion of the
excess cadmium is apparently more important than its effect in increasing
the already high free carrier concentration. It is interesting that the
composition for steady state sublimation in light is slightly different
from the composition in the dark.

In concluding this brief discussion of the effects of other variables
on the evaporation coefficient, the effect of surface roughness or porosity
should be mentioned. Roughening the surface will not, of course, affect
the true evaporation coefficient except insofar as the evaporation co-
efficients for different crystal planes may differ from each other, and
differences in α_v for different planes of a given crystal are probably
usually small unless the crystals are highly anisotropic. Rideal and

Wiggins report slightly different evaporation coefficients for four differ-
ent crystal faces of rhombic sulphur (55).

However, surface roughness and, especially, sample porosity can
greatly increase the flux of vapor that escapes from a sample, if the
material has a low evaporation coefficient. In the limit of a very low
evaporation coefficient, almost all the molecules that evaporate within
sample pores as well as the molecules from the sample surface will contri-
bute to the flux that leaves the sample. This behavior follows because,
as will be shown in the next section, samples with low evaporation coefficients
will usually also have low condensation coefficients, so that molecules
which evaporate within a pore can strike the pore walls many times without
recondensing. Once evaporated, therefore, there is a relatively high prob-
ability that molecules from substances with low-evaporation coefficients
will escape from the mouth of a pore rather than recondense on the pore
wall.

For a substance that has a unit evaporation coefficient, on the other
hand, the flux leaving a body of a particular geometric shape will not be
increased by the introduction of pores into the sample. The pressure
inside the pores cannot exceed the equilibrium vapor pressure, so that the
flux emitted from the mouth of any pore is identical with that from a
sample surface. A number of authors have contributed to our understand-
ing of how the evaporation coefficient (7,56-59) and its temperature (32)
dependence are related to rates of vapor effusion from a Knudsen cell or
from a porous solid.

Generalizations About Evaporation Coefficients for Various Classes of Solids

We have seen that rates of sublimation vary widely from material to
material and are influenced by the same kinds of variables that influence

other surface reactions: the activities of the reactants, the surface structure and area, adsorbed catalysts or poisons, light, and nuclear radiation. Because systematic studies of the effects of these variables have been made for only a few materials, generalizations about rates of sublimation can only be tentative. But it may be helpful to summarize the generalization that can be made about sublimation behavior of various classes of inorganic solids as a result of the experimental data and the analysis of this chapter. Predictions are guided by the observation that, in the absence of protective coatings, many classes of substances evaporate at rates close to those predicted from equilibrium data by means of the uncorrected Hertz-Langmuir equation. Furthermore, various broad classes of reactions tend to show similar deviations from the predictions of the Hertz-Langmuir equation.

For steady state sublimation of pure metals and molecular cyrstals into vacuum, α_v is unity for the metal atoms and the molecular units of the crystal. For other equilibrium species, such as S_7 from rhombic sulfur for example (44), α_v may be orders of magnitude less than unity. How far below unity the evaporation coefficient will be depends on the complexity of the rearrangement reaction necessary and the strength of the bonds that must be broken to effect the rearrangement.

For vaporization of elemental solids such as sulphur, carbon, or white phosphorous that yield polyatomic vapor species, the smaller the the value of α_v for a given species the more rapidly α_v for that species can be expected to increase with temperature. This conclusion follows because for these reactions a high enthalpy barrier usually governs the value of α_v and the higher the barrier is, the greater is its temperature dependence.

For condensed phases made up of dipolar molecular units, evaporation coefficients have been found to range from 0.01 to 0.5. The hypothesis that these values reflect the difference in rotational partition functions between liquid and condensed phases (4,42,43) has not been adequately tested by measurement of the temperature dependence of α_v. If the hypothesis is correct (42,43) values of α_v for polar molecules should be independent of temperature.

For two rare earth trifluorides and one alkaline earth difluoride of unknown dislocation densities, the evaporation coefficients have been shown to be unity to within a small estimated experimental error over a range of temperatures. For the monomer, dimer and trimer of LiF the measured evaporation coefficients have been shown to lie in the range between .5 and 1 (60). For sodium chloride an increase in the dislocation density from about 10^{-6} per cm^2 to about 10^{-7} per cm^2 raised the value of α_v from .5 to 1. (25). The evaporation coefficient for vaporization $Fe_2Cl_{6(g)}$ from solid $FeCl_3$, however appears to be less than 10^{-2} (17). It would be of value to investigate whether or not the low value reflects poisoning of the surface by some impurity.

Evaporation coefficients for solids that sublime by dissociative sublimation reactions tend to be smaller than evaporation coefficients for similar solids that sublime to vapor species of the same simplest formulas as the solid phase. Ferric chloride which evaporates by both kinds of reaction illustrates this point (17). For $2FeCl_3(s) = (FeCl_3)_2$ (g), α_v is 7×10^{-3}, while for $FeCl_3(s) = FeCl_2(g) + 1/2Cl_2(g)$, α_v is about 10^{-6}.

Sublimation kinetic data are available for several solid oxides in addition to those listed in Table 2 which dissociate to two or more gas species on sublimation Stannic oxide (62) and gallium sesquioxide (63) have nearly temperature independent evaporation coefficients of 10^{-1} and 0.3

respectively below their melting points. For solid aluminum oxide and solid indium oxide the vaporation coefficients of the principal evaporation reactions increase with temperature. The values at the melting points are 0.3 and 0.03 respectively. It seems probable that evaporation coefficients for most dissociating solid oxides will lie in the range 10^{-3} to 0.5.

For cadmium sulphide and selenide the sublimation reaction products are metal atoms and $S_{2(g)}$ or $Se_{2(g)}$. Both have evaporation coefficients of about 10^{-5} (5). Blank (61) finds $\alpha_v = 0.3$ for ZnS and $\alpha_v = 0.9$ for CdTe. Values of the order of 0.01 to 1 can be expected for most sulphides, selenides, and tellurides. Metal nitrides which yield the metal atoms and N_2 molecules as gaseous products have evaporation coefficients lying in the range from 10^{-2} to 10^{-6}.

No clear regularities in the temperature dependence of the evaporation coefficients of the oxides, sulfides, and nitrides is apparent. Some values increase, some decrease, and some are nearly constant with temperature. Perhaps for some of these solids selective adsorption of one of the sublimation reaction products or of foreign substances significantly affected the reported values of α_v. An effect of atmosphere has been demonstrated for magnesium nitride dissociation sublimation (49). The evaporation coefficients of aluminum oxide and gallium oxide increase discontinuously apparently to unity, when the solids melt (63). It is probable that most relatively ionic salts have unit or near unit evaporation coefficients for congruent vaporization above the melting points even when vaporization is by dissociative reactions.

The Relationship of Condensation Coefficients to Evaporation Coefficients

The principle of microscopic reversibility requires that even if a reaction occurs by more than one path, under equilibrium conditions the flux of molecules which cross a saddle point free energy barrier between

reactants and products of a given reaction be identical in the two directions. The arguments of this chapter demonstrate that the saddle point free energies for reactions with $\alpha_v = 1$, remain unaltered when the flux of vapor that impinges on a condensed phase surface is reduced from the equilibrium flux to zero. It seems most probable that the saddle point free energy will also not be altered when the flux of vapor is increased above the equilibrium flux so that condensation predominates over evaporation. Substances that have unit evaporation coefficients, therefore, can be expected to have unit condensation coefficients, at least at relatively modest supersaturations.

In the more general case of evaporation coefficients less than unity, if a single reaction step is predominantly responsible for limiting the evaporation rate, Eq. (10) reduces to the ratio of $\kappa v \exp(-\Delta G^*/RT)$ for that step to $\exp(-\Delta G_v^\circ/RT)/(2\pi MRT)^{1/2}$. At equilibrium, the flux of molecules that condense must equal the flux of evaporating molecules so that this same ratio must also give the value of the condensation coefficient α_c.

When the flux of vapor molecules that strike the condensed phase surface is increased above the equilibrium value, the normal assumption of reaction kinetics can be applied, i.e., that the free energy barrier height is not changed by the change in flux. The expectation is then, at least for modest supersaturation, α_c will remain equal to α_v and have the same temperature dependence. If k_4 of equation 4 is small compared to k_2 the adsorption step would be rate determining. But at high supersaturation, the flux of molecules that adsorb can become large compared to the flux for the $Y_n(a) = nY(b)$ step under equilibrium conditions and transfer of matter from the adsorption sites to bulk lattice sites could then be

rate determining. As a result α_c would become smaller than predicted from evaporation data. Alternately at high supersaturations the vapor may continue to condense at about the predicted rate but produce a non-equilibrium condensed phase material.

The extent to which the evaporation and condensation coefficients can be expected to differ has sometimes been overstressed. For example, Ackermann, Thorn, and Winslow (10) have posed an amusing pair of paradoxes which they say could result from an incomplete understanding of the distinction between evaporation and sublimation coefficients: "One can show that at equilibrium the vaporization coefficient must equal the condensation coefficient. Therefore (one might argue), if the vaporization coefficient decreases monatonically with decreasing temperature [the condensation coefficient must also decrease, and] the substance cannot be condensed by decreasing the temperature. Or, if the vaporization coefficient increases monatonically with decreasing temperature - it must approach unity at low temperatures and zero at high temperatures. Then a (high) temperature will be attained at which vaporization ceases."[*]

Ackermann, et al. consider that the resolutions of these paradoxes lie in the fact that for the non-equilibrium conditions under which evaporation and condensation coefficients are studied, α_v need not equal α_c. Since Ackermann, et al. do not identify and discuss the kind of non-equal values of α_v and α_c which would resolve the paradoxes, it is difficult to assess the results of their approach, but any appeal to non-equal values of α_v and α_c is unnecessary.

The paradoxes are easily resolved when α_c and α_v are identified as functions of the excess free energy barrier to the condensation and sublimation processes. A substance for which α_v decreases with temperature

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[*] Parentheses were in original, the bracketed phrase was added for clarity.

will be found to have, as the liquid-vapor critical point is approached, a temperature dependence of the form $\exp [-(\Delta H_v^* - \Delta H_v^\circ)/RT]$ where $\Delta H_v^* < \Delta H_v^\circ$. But ΔH_v^* will always be greater than zero, and even though α_v decreases with temperature, the rate of evaporation nonetheless increases exponentially with temperature according to the expression $\kappa_v \nu_v \exp (\Delta S_v^*/R) \exp (-\Delta H_v^*/RT)$. The value of α_v at the critical point may be small, but can never be zero as concluded in the statement of the paradox.

Since at the critical point the properties of liquid and vapor become identical, the values of α_v and α_c, even if different under other conditions, must approach the critical point values. A low evaporation coefficient at the critical point would reflect a finite free energy barrier to trans- fer of a molecule or atom from one cluster of fluid particles to another. Above the critical point, α_c and α_v have no physical significance except that the rate of transfer of particles between clusters in the fluid above the critical point might be predictable from measurements of α_c or α_v near the critical point.

The paradox concerning the prediction of non-condensation at low temperatures with gases for which α_c decreases with decreasing temperature has a simple, but more dramatic resolution. The vapor will in fact not condense at low temperatures to the equilibrium solid. It will, however, condense. The product will be a metastable condensed phase which can be produced from the vapor without passage over a high free energy barrier.

The predicted behavior has been observed. For example, α_c becomes very small at low temperatures for condensation of $P_{4(g)}$ molecules to red phosphorous because there is a high enthalpy barrier to breaking bonds of the P_4 molecules in order to free atoms for formation of the three dimensional bonding network of red phosphorus. White phosphorus, which is thermodynamically unstable relative to red phosphorous, is the product

obtained when P_4 vapor is condensed at low temperatures. Because white phos-
phorous is a molecular lattice formed of P_4 units there is a negligible free
energy barrier to its formation from P_4 vapor.

As this example illustrates, if conditions are shifted far enough
from equilibrium, the assumption that condensation occurs by simply the
reverse of the path for vaporization completely breaks down. But even so,
the analysis of kinetics of the evaporation reaction in terms of transition
state theory was helpful in understanding the kinetics of the condensation
reaction. The same high enthalpy barrier that reduces the rate of the red
phosphorus sublimation reaction is responsible for the failure of P_4 vapor
to condense to red phosphorus when P_4 is condensed at low temperature.

Furthermore, it is highly probable that at moderate supersaturations
and relatively high temperatures P_4 vapor could be recondensed to red phos-
phorus at a rate predicted from the assumption that $\alpha_v = \alpha_c$ or the equi-
valent assumption, that $J_c = P \exp [-(\Delta G_v^* - \Delta G_v^\circ)/RT]/(2\pi MRT)^{1/2}$ where J_c
is the flux of molecules from the vapor that condense to the equilibrium
reaction product and P is the pressure maintained for the vapor reactant.
The net rate of condensation is predicted to be the difference between
this expression and the rate of evaporation $J_v = \exp (-\Delta G_v^*/RT)/(2\pi MRT)^{1/2}$.

For any kind of a reaction the rate determining steps may be differ-
ent for the forward and reverse directions when the reaction is not at
equilibrium. But they also may be the same, and the reaction steps traced
by the reverse reaction usually will be the same as the steps traced by
the forward reaction. In studying the rates of condensation and evapora-
tion reactions, the working hypothesis should be that the reaction paths
and rate determining step for evaporation and condensation are related
until experimental or theoretical information is developed that indicates
the hypothesis is invalid.

ACKNOWLEDGEMENTS

REFERENCES TO CHAPTER 6

1. "The Characterization of High Temperature Vapors," J. L. Margrave, Ed. John Wiley and Sons, Inc., New York (1967).

2. "Condensation and Evaporation of Solids," E. Rutner, P. Goldfinger, and J. P. Hirth, Editors, Gordon and Breach, New York (1964).

3. Hirth, J. P, and Pound, G. M., "Condensation and Evaporation - Nucleation and Growth Processes," Progress in Materials Science Monograph-Pergamon Press, New York (1963).

4. Knacke, O., and Stranski, I. N., Progress in Metal Physics 6, Pergamon Press, New York (1956) p. 202.

5. Somorjai, G. A. and Lester, J. E., Progress in Solid State Chemistry 4, H. Reiss, Editor (1968); Somorjai, G. A., Science 162, 755 (1968).

6. Carlson, K. D., Chapter 5 or Ref. 2 and Paule, R. C. and Margrave, J. L., Chapter 6 of Ref. 1.

7. Paule, R. C. and Margrave, J. L., Chapter 6 of Ref. 1.

8. Knudsen, M. "The Kinetic Theory of Gases," Methuen and Co., London (1950).

9. Hirth, J. P. and Pound, G. M., J. Phys. Chem. 64, 619 (1960).

10. Ackermann, R. J., Thorn, R. J., and Winslow, G. H., Chapter 14 of Ref. 1.

11. Hirth, J. P. and Pound, G. M., J. Chem. Phys. 26, 1216 (1957).

12. Hirth, J. P., Ref. 1, Chapter 15.

13. Mar, R. W., UCRL-18257 (Ph.D. Thesis), University of California (1968).

14. Eyring, H., Wanlass, F. M., and Eyring, E. M., Ref. 2, p. 3.

15. Hirschwald, W. and Stranski, I. N., Ref. 2, p. 59.

16. Skinner, H. B. and Searcy, A. W., J. Phys. Chem. 72, 3375 (1968)

17. Gregory, N. W., J. Phys. Chem. 67, 618 (1963).

18. Benson, S. W., "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York (1960).

19. Johnston, H. S., "Gas Phase Reaction Theory," The Ronald Press Co., New York (1966).

20. Winterbottom, W. L. and Hirth, J. P., Ref.2, p. 347.

21. Brewer, L. and Kane, J. S., J. Phys. Chem. 59, 105 (1955).

22. Karutz, I. and Stranski, I. N., Z. Anorg. Allg. Chemie 292, 330 (1957).

23. Hart, P. E. and Searcy, A. W., J. Phys. Chem. 70, 2763 (1966).

24. Mar, R. W., and Searcy, A. W., J. Phys. Chem. 71, 888 (1967).

25. Lester, J. E. and Somorjai, G. A., UCRL-17794 Revised, March, (1968).

26. Burns, R. P., Jason, A. J., and Inghram, M. G., J. Chem. Phys. 40, 2739 (1964); 46, 394 (1967).

27. Amdur, I. and Hammes "Chemical Kinetics: Principle and Selected Topics," McGraw-Hill Book Co., New York (1966), p. 58.

28. Kane, J. S., Ph.D. Dissertation, University of California, Berkeley (1955).

29. Rosenblatt, G. M., Lee, P., and Dowell, M.B., J. Chem. Phys. 45, 3454 (1966).

30. Hoenig, C.L., UCRL-7521 (Ph.D. Dissertation) University of California (1964).

31. Somorjai, G. A., ref. 2, p. 417.

32. Hoenig, C. L. and Searcy, A. W., J. Am. Ceram. Soc. 50, 460 (1967).

33. Munir, Z. A. and Searcy, A. W., J. Chem. Phys 42, 4223 (1965).

34. Chaiken, R. F., Sibett, D. J., Sutherland, J. E., Van De Mark, D. K. and Wheeler, A., J. Chem. Phys. 37, 2311 (1962).

35. Spingler, H. Z., Physik Chem. (Frankfurt) B52, 90 (1942).

36. Schultz, R. D. and Dekker, A. O., J. Phys. Chem. 60, 1095 (1956).

37. Stern, J. H. and Gregory, N. W., J. Phys. Chem. <u>61</u>, 1226 (1957).

38. Rosenblatt, G. M. preprint of a paper for a symposium (to be published) on "Materials Research Problems and Prospectives, University of Missouri, Rolla, Oct. 30 and 31, 1967.

39. Bedford, R. G., unpublished work, University of California, 1967.

40. Mar, R. W. and Searcy, A. W., J. Chem. Phys. <u>49</u>, 182 (1968).

41. Cf. Ref. 3, page 5.

42. Wyllie, G., Proc. Royal Soc. (London), <u>A197</u>, 383 (1949).

43. Mortensen, E. M. and Eyering, H., J. Phys. Chem. 64, 846 (1960).

44. Berkowitz, J. in "Elemental Sulphur," B. Meyer, Ed., Interscience, 1965.

45. The variation of partial pressures of In_2S and S_2 with composition of the solid indium sesequisulphide phase illustrates the equilibrium behavior. See Miller, A. R. and Searcy, A. W., J. Phys. Chem. <u>69</u>, 3826 (1965).

46. Leonard, R. B., UCRL-17108 (M.S. Thesis), Dec, 1966.

47. Somorjai, G. A., and Jepson, G. W., J. Chem. Phys. <u>41</u>, 1394 (1964).

48. Knudsen, M., Ann Phys. <u>47</u>, 697 (1915).

49. Blank, B. A. H., and Searcy, A. W., J. Phys. Chem. <u>72</u>, 2241 (1968).

50. Somorjai, G. A. and Lyon, H. B., J. Chem. Phys. <u>43</u>, 1456 (1965).

51. Schoonmaker, R. C., Buhl, A. and Lemley, J., J. Phys. Chem. <u>69</u>, 3455 (1965).

52. Iwamoto, A. and Stranski, I. N., Diplomarbeit T. U. Berlin (1962).

53. Somorjai, G. A., Surface Sci. <u>2</u>, 298 (1964).

54. Somorjai, G. A. and Lester, J. E., J. Chem. Phys. <u>43</u>, 1450 (1965).

55. Rideal, E. R. and Wiggins, P. M., Proc. Roy. Soc. (London) <u>A210</u>, 291 (1952).

56. Speiser, R. and Johnston, H. L., Trans. Amer. Soc. Metals 42, 283 (1950).

57. Whitman, C. I., J. Chem. Phys. 20, 161 (1952).

58. Motzfeld, K., J. Phys. Chem. 59, 139 (1955).

59. Rosenblatt, G. M., J. Electrochem. Soc. 110, 563 (1963).

60. Kusch, P., Ref. 2, p. 87.

61. Blank, B. H. H., unpublished work, University of California, 1966.

62. Hoenig, C. L. and Searcy, A. W., J. Am. Ceram. Soc. 49, 128 (1966).

63. Burns, R. P, J. Chem Phys. 44, 3307 (1966).

TABLE 1

Sublimation Reactions for Which Evaporation Coefficients Are Unity

Reaction	Remarks	Evaporation Coefficient	References
$Ag(s) = Ag(g)$	single crystal, high dislocation density		20
$Zn(s) = Zn(g)$	(0001) face, low dislocation density, (00$\bar{1}$0) face	$1.1_0 \pm 0.1$	13
$P_4(s) = P_4(g)$	polycrystalline	~1	21
$As_4O_6(s) = As_4O_6(g)$	polycrystalline arsinolith	~1	22
$BaF_2(s) = BaF_2(g)$	(111) face	0.9 ± 0.1	23
$LaF_3(s) = LaF_3(g)$	(0001) face	0.95 ± 0.1	24
$PrF_3(s) = PrF_3(g)$	(0001) face	0.9 ± 0.1	16
$NaCl(s) = NaCl(g)$	(100) face, high dislocation density	1	25
$2NaCl(s) = Na_2Cl_2(g)$	(100) face, high dislocation density	1	

TABLE 2

Activation Enthalpies For Reactions With Low Evaporation Coefficients

Reaction	Enthalpy of Reaction (Kcal/mole)	Entropy of Reaction (eu)	Apparent Enthalpy of Activation (Kcal/mole)	Apparent Entropy of Activation	Average Evaporation Coefficient	Average Temperature (Deg. K)	Reference
$2As_2O_3(s) = As_4O_6(s)$	24.2	50	55.5	~74	$\sim 10^{-6}$	475	21
$4P(s) = P_4(g)$	28	49.4	52		$\sim 10^{-6}$	-600	21,28
$4As(\overset{*}{s}) = As_4(g)$	33.1	38.0	43.8	37.6	5.10^{-5}	550	29
$4Sb(\overset{*}{s}) = Sb_4(g)$	47.4	35.7	49.5	35.5	2.10^{-1}	650	29
$2ZnO(s) = 2Zn(g)+O_2(g)$	222	96	264	90	$\sim 10^{-3}$	1400	30
$2CdSe(s) = 2Cd(g)+Se_2(g)$	144.6	92.8	167.7	~94	$\sim 10^{-1}$	1000	31
$Be_3N_2(s) = 3Be(g)+N_2(g)$	361	124	408	~60	$\sim 10^{-5}$	1800	32
$2GaN(s) = 2Ga(g)+N_2(g)$	(173)	(101)	219	74	$< 10^{-3}$	1300	33

Type 2

$2CdS(\overset{*}{s}) = 2Cd(g)+S_2(g)$	150.4	90.8	150.9	77	10^{-1}	1000	31

Type 3

$NH_4F(s) = NH_3(g)+HF(g)$	36	(63)	24.4	21	3.10^{-3}	600	34
$NH_4Cl(s) = NH_3(g)+HCl(g)$	39.5	61	27.0	4	3.10^{-5}	600	34,35,36
$NH_4Br(s) = NH_3(g)+HBr(g)$	43.3	61	30.0	8	3.10^{-5}	600	34
$NH_4I(s) = NH_3(g)+HI(g)$	44	(62)	33.2	14	3.10^{-5}	600	34

* Single Crystal

FIGURE CAPTIONS

Fig. 1   Kossel-Stranski model of a close-packed surface. $\underline{A}$ is an

atom in the surface; $\underline{B}$ is an atom in a ledge; $\underline{C}$ is at kink;

$\underline{D}$ is at a ledge; $\underline{E}$ is an adsorbed atom; $\underline{F}$ is in the vapor.

Fig. 2   Three observed types of temperature dependence for rates

of evaporation.
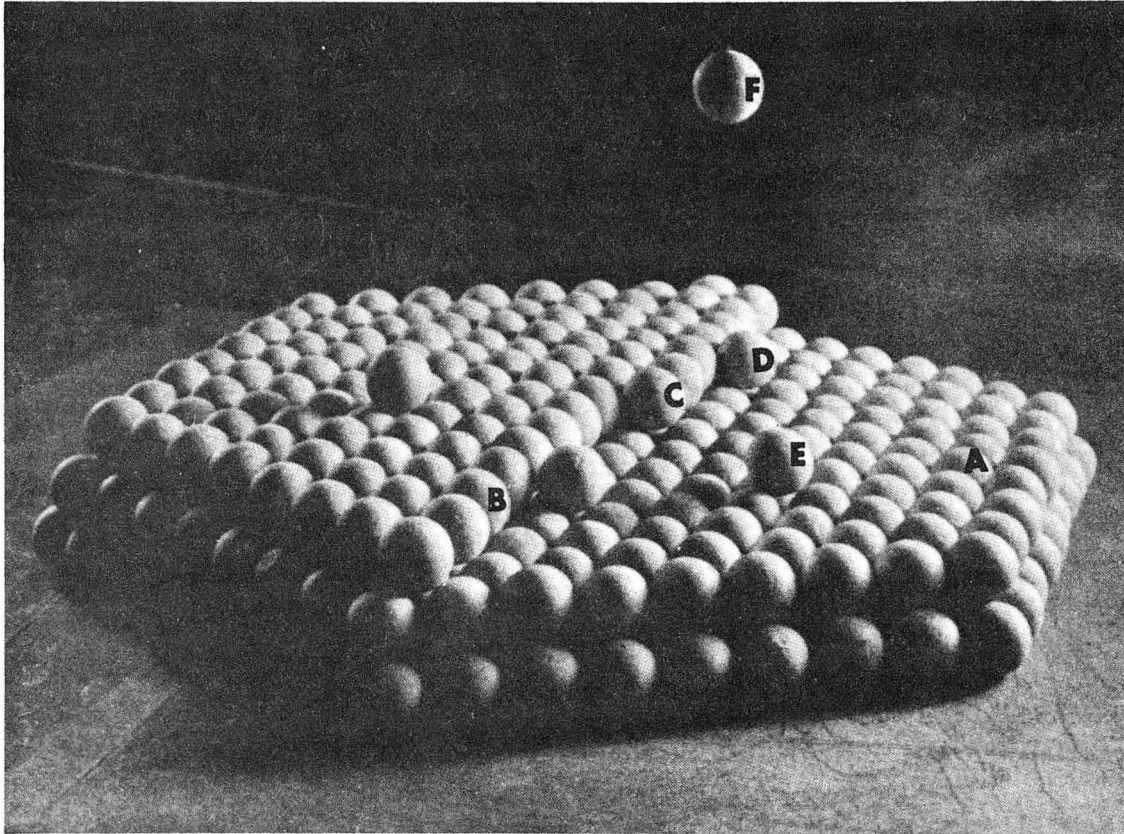
XBB 687-4159

A - atom in surface

B - atom in ledge

C - atom in kink

D - atom at ledge

E - adsorbed atom

F - vapor atom

Fig. 1
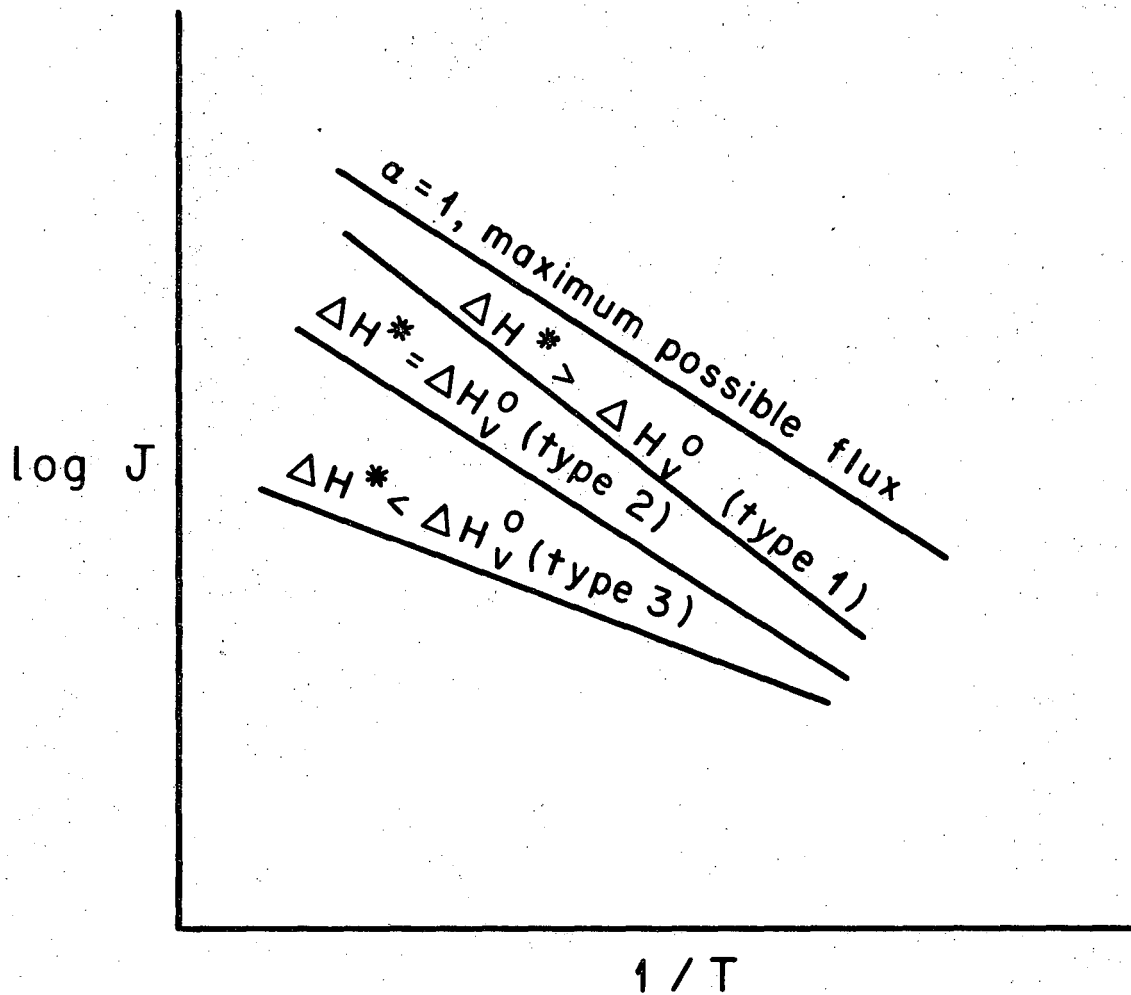
Three types of experimentally observed
sublimation behavior in vacuum. J is the
flux of molecules from a sample surface.

XBL688-3520

Fig. 2