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THE KINETICS OF DISSOCIATIVE VAPORIZATION REACTIONS

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ABSTRACT

Chemical kinetics of sequential reactions and transition state
theory are applied to the terrace-ledge-kink model for the vaporization
of solids and more specifically to compounds which vaporize according
to the reaction

\[ 2AB(s) = 2A(g) + B_2(g). \]

The variation of vaporization rate with temperature depends on the
difference in enthalpy between the activated complex of the rate deter-
mining step and the enthalpy of the bulk solid can thus be used as a
guide in ascertaining which of the sequential steps is rate determining.
This is illustrated with respect to the above vaporization reaction by
comparing the case in which kink-pair nucleation is rate determining
with that in which desorption is rate determining.

For a temperature range in which two steps are rate determining,
the plot of the logarithm of the "apparent" equilibrium constant \( K \)
versus the inverse of the temperature will usually show a curvature.
Experimental evidence of this effect in the vaporization of ice and of
sodium chloride are cited.

Vaporization studies of II-VI compounds are discussed and the data
are found to be consistent with a model in which desorption or dis-
sociation from catalytic surface sites is rate limiting.
INTRODUCTION

Experimental data for vaporization and condensation of crystalline solids appear to be very well described by the terrace-ledge-kink model of Kossel and Stranski (1,2). That model conceives of vaporization as occurring by a sequence of steps in which ledges first form at a crystal edge or an imperfection such as a dislocation. Kinks form in the ledges, and atoms move from kink sites to adsorption sites at ledges, diffuse away from the ledges onto the crystal surface, and finally desorb from surface sites. Condensation occurs by the reverse of these steps.

It has been recognized that an activation energy barrier to any of the sequential steps might influence the rate of the vaporization or condensation process (2), but the clear experimental fact that the vaporization and condensation processes are correlated with the dynamics of ledge formation and movement has led most investigators to interpret vaporization and condensation behavior primarily in terms of ledge dynamics and to assign relatively little attention to interpretation of experimentally determined apparent activation energies or entropies.

The most exhaustive recent monograph (3) on the kinetics of vaporization and condensation processes, for example, in its treatment of the steady state vaporization process, concentrated attention on the development of theoretical explanations for measured values of $\alpha_v$, the vaporization coefficient, which can be defined as the ratio of the measured flux of matter from a surface to the total flux that must leave the surface when it is in equilibrium with its vapor. Comparison of the temperature dependence of $\alpha_v$ to the dependence predicted by means of different theoretical models was not, however, exploited.
The fact that the temperature dependence of measured vaporization rates can provide useful tests of theories of vaporization is easily illustrated. Kane and Brewer (4) have shown that when the rate of vaporization is limited by a single slow step (assumed to have a frequency factor identical to that for desorption), the vaporization coefficient is identified as

\[ \alpha_v = \exp \left[ - \frac{\Delta G^* - \Delta G_v^0}{RT} \right], \]

where \( \Delta G^*_v \) is the standard free energy of activation for vaporization and \( \Delta G_v^0 \) is the standard free energy of the vaporization reaction. Since activation entropies and the frequency factors of rate processes are insensitive to temperature, the temperature dependence of \( \alpha_v \) is a measure of \( \Delta H^*_v - \Delta H_v^0 \), the difference between the enthalpy of activation for the rate limiting step and the enthalpy of the overall vaporization reaction. This interpretation of the temperature dependence for \( \alpha_v \) remains valid whether or not desorption is rate limiting (5). Searcy pointed out, as one example of the value of comparing apparent activation enthalpies and entropies calculated from experimental data with theory, that a theory (6) which relates some low vaporization rates to non-equilibration of rotational states, could be tested by measuring the temperature dependence of \( \alpha_v \) (5). The theory (6) would require \( \alpha_v \) to be essentially independent of temperature.
The model which has so far been presented for use in comparison of experimental and theoretical values of apparent activation enthalpies and entropies of vaporization has assumed a relatively simple vaporization reaction and a simple two step reaction sequence—an unspecified surface step followed by desorption (7). In the present paper the sequential theory of chemical reactions is extended to a more complex reaction,

$$2AB(s) = A(g) + B_2(g)$$  \hspace{1cm} (1)

and is formulated to be explicitly consistent with the terrace-ledge-kink model for vaporization. Comparison of the predictions derivable from the analysis to representative experimental data is illustrated in the discussion section. The expressions derived can also be applied to a solid that undergoes net condensation by introducing the appropriate flux of vapor against the solid surface.

**MATHEMATICAL DEVELOPMENT**

According to the terrace-ledge-kink (TLK) model, two likely reaction sequences which would yield the overall reaction of Eq. (1) are the following:

**Sequence I**

$$AB(\text{kink}) \to AB(\text{ledge})$$
$$AB(\text{ledge}) \to A(\text{ads}) + B(\text{ads})$$
$$2B(\text{ads}) \to B_2(\text{ads})$$
$$A(\text{ads}) \to A(g)$$
$$B_2(\text{ads}) \to B_2(g)$$
Sequence II

\[
\begin{align*}
AB(kink) &\rightarrow AB(\text{ledge}) \\
AB(\text{ledge}) &\rightarrow AB(\text{ads}) \\
AB(\text{ads}) &\rightarrow A(\text{ads}) + B(\text{ads}) \\
2B(\text{ads}) &\rightarrow B_2(\text{ads}) \\
A(\text{ads}) &\rightarrow A(g) \\
B_2(\text{ads}) &\rightarrow B_2(g)
\end{align*}
\]

In these sequences (ledge) denotes a molecule adsorbed at a ledge, and (ads) denotes a molecule or atom adsorbed on the surface. The difference between these two sequences lies in the step at which the dissociation is considered to take place.

To facilitate comparison between sequences I and II it is convenient to adopt a standardized system of notation. Reactions in the forward direction will be given even numbers, and those in the backward direction odd numbers. Following is a list of reactions with the assigned numbers indicated immediately above or below the appropriate arrow.

\[
\begin{align*}
0 &\quad AB(kink) \xrightarrow{*} AB(\text{ledge}) \\
1 &\quad \quad \\
2 &\quad AB(\text{ledge}) \xrightarrow{*} AB(\text{ads}) \\
3 &\quad \quad \\
4 &\quad AB(\text{ads}) \xrightarrow{*} A(\text{ads}) + B(\text{ads}) \\
5 &\quad \quad \\
24 &\quad AB(\text{ledge}) \xrightarrow{*} A(\text{ads}) + B(\text{ads}) \\
35 &\quad \end{align*}
\]
Reaction 0, with back reaction 1, is the movement of a molecule from a kink position to a ledge position. Reaction 2 carries the molecule from the ledge to the open surface, and dissociation on the surface occurs in reaction 4. Reaction 24 is a combination of reactions 2 and 4, i.e., movement from the ledge to the surface and dissociation. Reactions 3, 5, and 35 respectively are the back reactions for reactions 2, 4, and 24. Reaction 6, with back reaction 7, is the association of two B atoms to form the B2 molecule. Finally, reactions 8 and 10 are the desorption of A and B2, with back reactions 9 and 11.

Two kinds of concentrations are of interest in these sequences: the concentration of species adsorbed on the surface and the concentration of species adsorbed at a ledge. Adsorption on the surface will be indicated by means of square brackets, [ ], and at a ledge by a parenthesis, ( ). For instance, [A] and (AB) will denote the concentration of A adsorbed on the surface and the concentration of AB adsorbed at a ledge, respectively.

Except for the additional complications of the dissociation of AB and the formation of B2, these steps correspond to those of the typical TLK model (2,3). In fact, the two sequences considered are essentially
identical with those suggested by Munir, Seacrist and Hirth (8) for the vaporization of cadmium selenide. It will be noted that diffusion is not explicitly treated in these sequences. If the surface steps of the TLK model for vaporization are to have much significance, the energy for desorption must be considerably greater than that associated with the movement of the species away from the kink position onto the surface (9). Hence it seems unlikely that surface diffusion can be as slow as desorption in any vaporization process accurately described by the TLK model. Accordingly, it will be assumed that concentration gradients on the surface are negligible, that is, that the mean free path of the various species on the surface is at least as large as the interledge spacing. Experimental evidence that the assumption is appropriate for CdSe and other II-VI semiconductors is presented in the discussion.

Reaction steps 0 and 1, which have to do with movement of a molecule between a kink and a position adsorbed at a ledge, differ from later steps in that steps 0 and 1 depend upon the concentration of kinks per unit area of surface, which will be denoted by n. The quantity n is in turn dependent on the length of ledge per unit area and thus on the dislocation density, which is not an equilibrium property of the crystal.

Under equilibrium conditions the surface concentrations of the various species should be essentially independent of n, since otherwise the equilibrium vapor pressure would depend on the dislocation density and so be a function of the history of the crystal rather than a state function. This criterion is satisfied if the rate of the forward reaction 0 is taken as being equal to nk, and the rate of the back
reaction 1 to \( n_{k1}(AB) \), where \( k_0 \) and \( k_1 \) are the rate constants and \( (AB) \) is the concentration of AB at a ledge as defined above. The rate expression for reaction 1 depends upon the fact that it can be written in the alternate form

\[
AB(\text{ledge}) + (\text{kink site}) = AB(\text{kink}),
\]

and that the concentration of kink sites as well as the concentration of kinks is equal to \( n \). At equilibrium, the rates of reactions 0 and 1 are equal so that

\[
nk_0 = nk_1(AB)_{\text{eq}}
\]  \hspace{1cm} (2)

or

\[
(AB)_{\text{eq}} = k_0/k_1.
\]

For sequence I the set of rate expressions are as follows, with \( J \) being the net flux in moles per unit area per unit time:

\[
J = nk_0 - nk_1(AB)
\]  \hspace{1cm} (3)

\[
J = k_{24}(AB) - k_{35}[A][B]
\]  \hspace{1cm} (4)

\[
J = 2k_6[B]^2 - 2k_7[B_2]
\]

\[
J = k_9[A]
\]

\[
J = 2k_{10}[B_2].
\]
For sequence II the set of equations is the same except that Eq. (4) is replaced by the following two equations:

\[ J = k_2(AB) - k_3[AB] \]

\[ J = k_4[AB] - k_5[A][B]. \]

Back reactions 9 and 10 are assigned zero flux because attention is restricted to Langmuir or free-surface evaporation into a vacuum.

For both sequences it is possible to express the various concentrations in terms of the net flux \( J \) and the rate constants so that the final equation involves only these quantities. For sequence I the equation is

\[ J^3 = \frac{2k_2^2k_5k_6k_8k_{10}}{k_4^2k_5^2(k_7 + k_{10})} \left( 1 - \frac{nk_1 + k_2}{nk_5k_4} \right)^2 \]

and for sequence II

\[ J^3 = \frac{2k_2^2k_5^2k_6k_8k_{10}}{k_4^2k_5^2(k_7 + k_{10})} \left( 1 - \frac{nk_1 + nk_4 + k_5}{nk_0k_2k_4} \right)^2. \]

If equilibrium is assumed for all reactions save 0, 1, 8 and 10, that is, those reactions affected by kink nucleation and desorption, then the equations become simpler:

\[ J^3 = \frac{2k_2^2k_5^2k_6k_8k_{10}}{k_4^2k_5^2k_7} \left( 1 - \frac{J}{nk_0} \right)^2. \]
and

\[ J^3 = \frac{2k_8^2k_6^2k_7^2}{k_1^2k_3^2k_5^2k_7} \left( 1 - \frac{J}{nk_0} \right)^2. \]

These expressions can be solved exactly for \( J \). For example,

\[ J = nk_0 \left[ \frac{y^3}{27} - \frac{y^2}{3} + \frac{y}{2} + \frac{y}{2} \left( 1 - \frac{4}{27} y \right)^{1/2} \right]^{1/3} \]

\[ + nk_0 \left[ \frac{y^3}{27} - \frac{y^2}{3} + \frac{y}{2} - \frac{y}{2} \left( 1 - \frac{4}{27} y \right)^{1/2} \right]^{1/3} + nk_0 \frac{y}{3} \]

where

\[ \gamma = \frac{2k_8^2k_6^2k_7^2k_{10}}{nk_0k_1^2k_3^2k_5^2k_7} \]

for sequence I, and

\[ \gamma = \frac{2k_8^2k_6^2k_7^2k_{10}}{nk_0k_1^2k_3^2k_5^2k_7} \]

for sequence II. However, the complexity of these solutions obscures much of their significance. A more instructive and easier approach is to solve the rate equations for two extreme conditions which are of interest: (a) the condition in which kink nucleation is the rate limiting step, and (b), the condition in which desorption is rate limiting.

Condition (a) implies that \( n \), the concentration of kinks is small compared to the concentration necessary to maintain adsorbed surface
species at near equilibrium values during sublimation in vacuum. Munir and Hirth, in their experiments with zinc sulfide, have noted that the surface morphology changed according to the degree of saturation of the vapor and present this as evidence in favor of kink nucleation as the rate determining step (10). The low value of $n$ would then mean that reactions 0 and 1 would both be inhibited.

From Eqs. (2) and (3),

$$J = n k_0 - n k_1(AB),$$

$$= n k_1(AB)_\text{eq} - n k_1(AB),$$

$$= n k_1[(AB)_\text{eq} - (AB)].$$

(5)

The flux $J$ is then seen to be proportional to the undersaturation of $AB$ adsorbed at the ledges. If reaction 0 proceeds slowly relative to subsequent reactions, as is consistent with the supposition that kink nucleation is the rate determining step, then the undersaturation would be quite severe, so that $(AB) \ll (AB)_\text{eq}$, and the net flux $J$ can be approximated by means of Eqs. (5) and (2):

$$J = nk_1[(AB)_\text{eq} - (AB)] = nk_1(AB)_\text{eq} = nk_0.$$  

(6)

In accordance with the mechanism proposed by Munir, Seacrist and Hirth (8), it can be assumed that the intermediate reactions are in equilibrium. This assumption requires that the desorption reactions 8 and 10 be considerably slower than the intermediate reactions, though
not as slow as reactions 0 or 1. Then it is easy to calculate the concentrations of the intermediate species for both sequences by means of Eq. (6) and the relations

\[ k_6[A] = J \]  \hspace{1cm} (7)

\[ 2k_{10}[B_2] = J \]  \hspace{1cm} (8)

\[ k_6[B]^2 = k_7[B_2] \]  \hspace{1cm} (9)

\[ k_{24}(AB) = k_{35}[A][B] \]  \hspace{1cm} (10)

for sequence I, and substituting

\[ k_2(AB) = k_3[AB] \]  \hspace{1cm} (11)

and

\[ k_4[AB] = k_5[A][B] \]  \hspace{1cm} (12)

for Eq. (10) in sequence II.

Then, for sequence I

\[ [A] = \frac{nk_0}{k_8} \]

\[ [B] = \left( \frac{nk_0k_7}{2k_6k_{10}} \right)^{1/2} \]

\[ [B] = \frac{nk_0}{2k_{10}} \]
and for sequence II

$$(AB) = \frac{n k_0 k_3 k_5}{k_2 k_4 k_8} \left( \frac{n k_0 k_7}{2 k_6 k_{10}} \right)^{1/2}$$

$$[AB] = \frac{n k_0 k_5}{k_4 k_8} \left( \frac{n k_0 k_7}{2 k_6 k_{10}} \right)^{1/2}.$$  

The quantities \([A], [B] \text{ and } [B_2]\) are the same as for sequence I.

Using these values, a better approximation for \(J\) may be obtained by substituting the appropriate expression for \((AB)\) in Eq. (3):

sequence I

$$J = n k_0 \left[ 1 - \left( \frac{n^3 k_0 k_1^2 k_3^2 k_7}{2 k_4^2 k_6 k_8^2 k_{10}} \right)^{1/2} \right]$$

sequence II

$$J = n k_0 \left[ 1 - \left( \frac{n^3 k_0 k_1^2 k_3^2 k_7}{2 k_4^2 k_6 k_8^2 k_{10}} \right)^{1/2} \right].$$

For the present purpose, it will suffice to note that the flux \(J\) is approximately equal to \(n k_0\), the rate of reaction 0, and that succeeding reactions have little effect on it.

If, instead of kink nucleation, condition (b) applies and desorption is taken as the rate determining step, then again the various species on the surface are essentially in equilibrium with each other, but in this case their concentrations are very nearly the same as they would be if the solid were in equilibrium with the vapor. As before,
it is simple to find the approximate concentrations of these species. The relation \( nk_1(AB) = nk_0 \) is used together with Eqs. (7) through (12) to give

\[
J = \left( \frac{2k_8^2k_2^2k_6^2k_8k_{10}}{k_1^2k_3^2k_5k_7} \right)^{1/3}.
\]

For sequence I then

\[
(AB) = \frac{k_0}{k_1}
\]

\[
[A] = \left( \frac{2k_8^2k_2^2k_6k_{10}}{k_1^2k_3^2k_5k_7} \right)^{1/3}
\]

\[
[B] = \left( \frac{k_0k_2^4k_7k_8}{2k_1k_3^5k_6k_{10}} \right)^{1/3} = \left( \frac{k_7}{2k_6k_{10}} \right)^{1/2} J^{1/2}
\]

\[
[B_2] = \left( \frac{k_8^2k_2^2k_6k_8^2}{4k_1^2k_3^5k_7k_{10}} \right)^{1/3} = \frac{J}{2k_{10}}.
\]

For sequence II the results are the same except that, in the expressions above, \( k_{24} \) is replaced by the product \( k_2k_4 \) and \( k_{35} \) by \( k_3k_5 \). In addition,

\[
[AB] = \frac{k_0k_2}{k_1k_3}.
\]
As before, more accurate values can be obtained by means of a recursion technique, but it is obvious even from these approximate solutions that the flux $J$ is a function of all the rate constants but is not significantly dependent on $n$ for the case where desorption is the rate limiting step.

**ENERGETICS**

The energetics and temperature dependence of the flux and of the various steps in the vaporization process become more obvious when the rate constants are written as products of a pre-exponential frequency factor and an exponential in the usual manner, that is

$$k_i = v_i \exp(-\Delta G_i^*/RT).$$

Here $v_i$ is the frequency factor and $\Delta G_i^*$ is the standard Gibbs free energy of activation for the formation of the activated complex for the $i$th step.

It should be noted at this point that $\Delta G_0^*$, the free energy of activation for movement of a molecule from a kink position to a position adsorbed at a ledge, is the difference in free energy between the activated complex for this step and the bulk solid. This is true because the net effect of the step is to transfer a molecule from the bulk solid to the ledge position. The number of kink positions remains the same, as does the length of ledge and surface area. For all other reaction steps the relevant $\Delta G_i^*$ is the difference in free energy between the activated complex of the step in question and the product of the preceding step.
Expressed in these terms, the flux for the case where kink nucleation is rate limiting is simply

$$J = n v_0 \exp(-\Delta G^*/RT).$$

(13)

If desorption is rate limiting, the principle of dynamic reversibility would require that, for those reaction steps which are considered to be effectively in equilibrium, the frequency factors for the forward and back reactions be equal, that is, $v_0 = v_1, v_{24} = v_{35}, v_2 = v_3, v_4 = v_5$ and $v_6 = v_7$. Then

$$J = \left(2v_8^2v_{10}\right)^{1/3}$$

$$x \exp \left(-\frac{2\Delta G_0 - 2\Delta G_1 + 2\Delta G_2 - 2\Delta G_3 + \Delta G_4 - \Delta G_5 + \Delta G_6 - \Delta G_7 + \Delta G_8 + \Delta G_{10}}{3RT}\right)$$

and

$$J = \left(2v_8^2v_{10}\right)^{1/3}$$

$$x \exp \left(-\frac{2\Delta G_0 - 2\Delta G_1 + 2\Delta G_2 - 2\Delta G_3 + 2\Delta G_4 - 2\Delta G_5 + \Delta G_6 - \Delta G_7 + 2\Delta G_8 + \Delta G_{10}}{3RT}\right)$$

for sequences I and II, respectively.

Equation (13) contains $n$ as a factor which must itself be dependent on an energy and on temperature. It is useful at this point to introduce an expression for $n$ which is derived in the appendix for the case
were kink nucleation is rate limiting:

\[ n = (2k_f/k_0)^{1/2} \lambda, \]

where \( k_0 \) is defined as before, \( k_f \) is the rate constant for nucleation of a kink in a ledge, and \( \lambda \) is a parameter proportional to the length of ledge per unit area of crystal surface. If this expression is now substituted in Eq. (13), the expression for \( J \) becomes the following:

\[
J = \left( \frac{2k_f}{k_0} \right)^{1/2} \lambda v_0 \exp(-\Delta G^*/RT) \\
= \lambda (2v_f v_0)^{1/2} \exp \left( -\frac{\Delta G^*_0 + \Delta G^*_f}{2RT} \right). 
\]

Thus the effective free energy of activation for the overall reaction in either of the sequences when kink nucleation is rate limiting is equal to half the free energy of activation for movement of a molecule from a kink position to a position adsorbed at a ledge plus half the free energy of activation for nucleation of a kink-pair.

For both rate limiting cases then, the flux \( J \) can be written in the form

\[
J = v_j \exp(-\Delta G^*_j/RT) \tag{14}
\]
where \( v_J \) is a frequency factor, which, if kink nucleation is rate limiting, is equal to \((2v_f v_0)^{1/2}\), and if desorption is rate limiting, 
\( v_J = (2v_f^2 v_{10})^{1/3} \). Similarly \( \Delta G_J^* \) depends on the case:

\[
\Delta G_J^* = \frac{\Delta G_x^* + \Delta G_y^*}{2},
\]

for the kink nucleation limited case, and

\[
\Delta G_J^* = 2\Delta G_0^* - 2\Delta G_1^* + 2\Delta G_2^* - 2\Delta G_3^* + \Delta G_4^* - \Delta G_5^* + 2\Delta G_6^* + \Delta G_10^*,
\]

or

\[
\Delta G_J^* = 2\Delta G_0^* - 2\Delta G_1^* + 2\Delta G_2^* - 2\Delta G_3^* + 2\Delta G_4^* - 2\Delta G_5^* + \Delta G_6^* - \Delta G_7^* + 2\Delta G_8^* + \Delta G_10^*,
\]

for the sequences in which desorption is rate limiting. An analysis of these expressions for \( \Delta G_J^* \), the free energy of activation for the overall vaporization process, will show that it is equal to the difference in standard free energy between the activated complex of the rate determining step and the bulk solid.

The evaporation coefficient \( \alpha_v \) for the overall reaction of Eq. (1) can be written in terms of the flux \( J \) as follows (11):

\[
\alpha_v = \frac{(2\pi \mu RT)^{1/2}}{(2K)^{1/3}} J,
\]

Here \( \mu \) is equal to \((2M_A^2 M_B^2)^{1/3}\), where \( M_A \) and \( M_B \) are, respectively, the atomic weights of \( A \) and \( B \), and \( K \), the equilibrium constant for the vaporization reaction, is equal to \( P_{A_B}^2 \) at equilibrium.
Although in the present case the crystal is considered to be evaporating into a vacuum, it is possible to talk of pressures of A and B$_2$ gases where these pressures are defined by means of the relations,

\[ P_A = (2\pi M_A RT)^{1/2} J; \quad P_{B_2} = (4\pi M_{B_2} RT)^{1/2} J/2. \]

The sum of these pressures would be the pressure measured in Langmuir or free-surface torsion-effusion studies such as those conducted by Munir and Seacrist (12) and by Galluzzo and Searcy (13).

To facilitate comparison with equilibrium data, an apparent equilibrium constant $\hat{K}$ is defined by the expression

\[ \hat{K} = \frac{P_A^2}{P_{B_2}} = \alpha_v^3, \]

and its logarithm plotted against the inverse of the temperature. This can then be compared with the logarithm of the true equilibrium constant K plotted in the same way.

By analogy to the true equilibrium constant, an "apparent" Gibbs free energy change $\Delta G_v^\ast$ can be associated with $\hat{K}$, defined by means of the relations,

\[ \Delta G_v^\ast = -RT \ln \hat{K} \]

\[ = \Delta G_v^0 - 3RT \ln \alpha_v. \]

If $\hat{K}$ is expressed in terms of the flux J,
Then

\[ \ln K^* = \ln \left( \frac{v_J}{v_g} \right) - 3\Delta G_J^*/RT \]

\[ = -\Delta G_v^*/RT \]

\[ = 3 \ln \alpha_v - \Delta G_v^*/RT, \]

when \( J \) is expressed in terms of Eq. (14), and \( v_g \), defined as \( 2^{1/3}/(2\pi\mu RT)^{1/2} \), is a frequency factor for the gas phase.

The slope of the plot is given by the derivative:

\[ \frac{3 \ln K^*}{\partial 1/T} = 3 \frac{\partial}{\partial 1/T} \ln \left( \frac{v_J}{v_g} \right) - \frac{3\Delta H_J^*}{R} = 3 \frac{\partial \ln \alpha_v}{\partial 1/T} - \frac{\Delta H_v^*}{R} = -\frac{\Delta H_v^*}{R}. \]  

If desorption is rate limiting \( v_J \) is equal to \( v_g \) (14), and Eqs. (15) and (16) give the results \( \Delta G_v^* = 3\Delta G_J^* \) and \( \Delta H_v^* = 3\Delta H_J^* \). It follows that the apparent entropy is also equal to three times the entropy of the activated complex. Thus the enthalpy and entropy of the activated complex can be derived from the slope and intercept, respectively, of the plot of \( \ln K^* \) if desorption is the rate limiting step.

Even in the case where some surface step prior to desorption is rate limiting, the ratio \( v_J/v_g \) is only weakly dependent on temperature so that \( \Delta H_v^* \) will still be approximately equal to \( 3\Delta H_J^* \), but the intercept of the plot will be equal to \( 3\Delta S_J^*/R + \ln \left( \frac{v_J}{v_g} \right) \) rather than
DISCUSSION

Because the expressions that have been derived in the present analysis are complex, their physical significance can best be seen from their application in specific cases.

It is important to emphasize that the sequential reaction step analysis demonstrates that the measured apparent activation enthalpy is not the activation enthalpy for a single step in the assumed reaction sequence, but is always a measure of the difference in enthalpy content between the activated complex of the rate determining step and the enthalpy content of the bulk solid.

A recent study by Davy and Somorjai (15) of the kinetics of vaporization of ice provides particularly interesting data with which to illustrate the application of sequential reaction kinetic equations. Two distinct ranges with different kinetic behavior were found. Below about 190°K the vaporization coefficient was found to be unity independent of temperature. At higher temperatures the vaporization coefficient decreased and a plot of the logarithm of $K^*$ versus reciprocal temperature showed a lower slope (Fig. 1).

The concentration in the self-adsorption layer can approximate its equilibrium value in the absence of a flux of vapor against the surface only if the flux of molecules traversing any prior steps in the reaction sequence in each direction is large compared to the net flux desorbing from the surface, that is, the molecules in each state of the reaction sequence must also be essentially at equilibrium with the bulk solid.
Under these circumstances the apparent activation enthalpy measured from the slope of the plot is simply the difference in enthalpy between the species that desorb from the surface, i.e., \( H_2O \) gas with equilibrium properties, and the bulk condensed phase.

On the other hand, in the temperature range for ice vaporization with the lower temperature dependence, some step prior to desorption must be rate limiting. Desorption cannot be rate limiting in that range because the experimental activation enthalpy is less than the minimum enthalpy necessary to produce any possible vapor species from the bulk solid (5). The apparent activation enthalpy in this range of temperatures is again a measure of the difference in enthalpy between water molecules in the activated complex of the slow step for that temperature range and the enthalpy of the molecules in bulk ice. The measurements of flux as a function of temperature thus provide information on the extent of bonding of the activated complex with the surface but do not give information about the path or paths by which molecules of the bulk solid reach the activated state.

Davy and Somorjai estimate that the limiting value of their apparent activation enthalpy at the high end of the experimental range is about one half the enthalpy of sublimation. If we use this estimate we can infer that the activated complex is held to the surface by half as many hydrogen bonds per molecule as in the bulk solid.
It is interesting to note that the free angle ratio theory (6) which has been suggested to explain the kinetics of vaporization of water cannot explain the vaporization of ice in either temperature range because that theory assumes non-equilibration of rotational states, but essentially normal enthalpy changes. The theory therefore requires a plot of $\log k$ versus $1/T$ to lie below the plot of $\log K$ by an amount which would remain approximately constant throughout the temperature range.

More recently, results very similar to those described above for water have been obtained by Ewing and Stern in their work with sodium chloride (16). From 530° to 660°C the plot of the flux versus $1/T$ was linear and parallel to the plot of the maximum flux obtained from equilibrium data. Above 660°C the slope gradually became less, indicating a change in the rate determining step. Ewing and Stern interpret their results to mean that at lower temperatures the rate determining step is desorption, but that at high temperatures a prior surface step becomes rate determining.

Recent studies of vaporization of single crystals of cadmium sulfide (17), cadmium selenide (8)(12), zinc sulfide (10) and zinc oxide (13) reveal temperature dependencies for vaporization coefficients that differ markedly from that found for ice. The vaporization coefficients of each of these four II-VI semiconductors increases with temperature. The apparent activation enthalpies calculated from plots of $\log K$ versus $1/T$ are greater than the enthalpy of the equilibrium congruent vaporization reaction, and the apparent activation entropies, calculated under the assumption that the frequency factor for the rate limiting process is equal to $v_g$ as defined earlier, are identical with
the standard entropies of the equilibrium vaporization reactions to within the probable experimental error.

From interpretation of the observed structure of the steady state surfaces in terms of the dynamics of ledge movement, Munir, Seacrist and Hirth (8)(10) recently concluded that the rate of vaporization of these semiconductors is probably partially controlled by double kink nucleation or by dissociation at kinks and partially controlled by desorption. The analysis presented in this paper shows, however, that if any two of the sequential steps in the overall vaporization path are slow enough to influence the rate of vaporization, the product of the frequency factor and exponent raised to $\Delta G^*/RT$ ($\Delta G^*$ being the free energy of formation of the activated complex) must be of comparable magnitude for both of the steps in question. The result then usually would be a curvature of the plot of $\log K^*$ versus $1/T$ such as is observed for ice in the temperature range for which both steps influence the rate. For
both of two sequential steps to influence significantly the vaporization rate over a range of temperatures in which the plot of log K versus 1/T remains linear would require that the activated complexes of each of the two steps have nearly identical enthalpies of formation from the bulk solid. To reconcile the conclusion of Munir, Hirth et al. that each of two sequential steps significantly influence kinetics of vaporization of II-VI semiconductors with the analysis of sequential reactions thus would require that the partially rate determining step associated with ledges not be a step of low activation energy but one in which the activated complex is in a very high energy state, for example, a molecule or atom directly desorbed from a ledge site. Such an interpretation would be incompatible with the accepted view of the TLK model that the process of movement of species from ledge sites to adsorption sites at ledges is a much more probable process than direct desorption from ledges (2)(3).

An alternate suggestion that either desorption of excited molecules or desorption of equilibrium state molecules to leave excited particles on the surface may be rate limiting in the vaporization of these II-VI semiconductors is consistent with the sequential reaction analysis in that activation enthalpies and entropies predicted when these processes are assumed to be rate limiting agree well with the experimental data (13). Dissociation of one or more of the eventual vapor species from catalytic surface sites into a two dimensional gas state of the self-adsorption layer might also give rise to the observed reaction kinetics (18).
The conclusion of Munir, Seacrist and Hirth that the rate of vaporization of the II-VI semiconductors is influenced partially by a process at the ledges appears to depend crucially on the assumption that the self-adsorbed molecule concentrations on crystal surfaces are determined by local equilibrium with the ledges (19). We suggest that the spacing between ledges during free surface vaporization may reflect mainly the development of surface planes of decreased energy rather than gradients in the concentration of self-adsorbed molecules between ledges. The mean free path of self-adsorbed species prior to desorption for these particular surfaces may not be of the order of the inter-ledge spacings as assumed in applying the TLK model to vaporization kinetics (8)(19), but may be a much greater distance. In consequence, local ledge spacings may have no direct correlation with local self-adsorbed molecule concentrations. Two lines of experimental evidence support this suggestion:

(1) The (0001) surface of cadmium sulfide is reported to develop steep sided walls of high ledge concentrations which surround an approximately equal area of flat-bottomed pits where ledge concentrations are negligible small (17). Munir and Hirth (10) assumed that these flat surfaces of cadmium sulfide crystals have negligible concentrations of self-adsorbed molecules. But for the steady state surface to maintain such features requires that the average rate of recession of flat portions of the surface be the same as for ridged sections, which requires that the overall steady state process of vaporization proceed at the same rate in flat and ridged regions of the surface.
(2) While the rates of many reactions that are catalyzed by surfaces are very sensitive to surface impurities, and while vaporization reactions are known that are moderately influenced by adsorbed impurities (20), Winterbottom (21) found that even when the concentration of adsorbed gases on silver was great enough to affect the morphology of the crystal surface, no effect was noticeable in the vaporization rate. Adsorption of gases on zinc oxide also had a negligible effect on its rate of vaporization (17). Since impurities are likely to adsorb preferentially at ledges and impede their movement, the insensitivity to impurity levels argues that the rate of steady state vaporization of II-VI semiconductors is insensitive to ledge concentrations, at least in the temperature ranges so far studied.

A point that we wish to emphasize in conclusion is that the analysis of the kinetics of vaporization in terms of sequential chemical reactions that we have illustrated is complementary rather than contradictory to the analysis of vaporization in terms of the dynamics of ledge and molecule movement. Interpretations of the physical structures of surfaces in terms of ledge and particle dynamics is a powerful tool for reaching a qualitative understanding of the details of the path followed in vaporization and condensation processes. The interpretation of apparent activation enthalpies and entropies in terms of sequential reaction analysis provides no direct information on details of the path followed by vaporizing or condensing molecules, but identifies the enthalpy difference (and, with an assumed frequency factor, an entropy difference) between the activated complex of the slowest step in the reaction sequence and the bulk solid. Our understanding of vaporization
and condensation kinetics can best be advanced by use of the two approaches in concert.

APPENDIX

EVALUATION OF KINK DENSITY IN THE CASE WHERE KINK NUCLEATION IS RATE LIMITING

For Langmuir or free-surface evaporation in the case where kink nucleation is rate limiting, it has already been argued that the concentrations of the adsorbed species on the crystal surface are considerably below those of a crystal in equilibrium with its vapor. Under these conditions the primary mechanism of kink nucleation or formation would consist of a molecule moving from a position in a ledge to a position where it is adsorbed on the surface or at the ledge. The rate of creation of kinks by this mechanism can be set equal to $2k_\text{f}A$ where $k_\text{f}$ is the rate constant and $A$ is a parameter equal to the number of moles of molecules in ledges per unit area of surface, that is, the number of molecules in ledges per unit area divided by Avogadro's number. The factor of two results from the fact that removal of a molecule from the ledge produces two kinks of opposite orientation (A in Fig. 2). Once formed, a kink can reasonably be expected to persist until it encounters another kink of opposite orientation or an edge. To judge from the surface morphology of the materials which have been studied, edges would not play an important role as sinks for kinks (8)(10)(16), so that the annihilation of kinks will result predominantly from the merging of two kinks of opposite orientation as the intervening molecules move out from the kink position.
Figure 2 schematically represents a variety of kinks as they might exist. The pair of kinks of opposite orientation labelled B and C represent what will be called a "simple" pair, that is, they are separated by a straight ledge with no other kinks in it. The pair of kinks labelled D and E, on the other hand, are separated by sections of ledges containing other kinks. These will be called a "compound" pair. Obviously the simple pair of kinks must disappear before the compound pair can disappear. In fact, once the simple pair has disappeared, then the compound pair D and E will become a simple pair.

Consider a unit area of crystal surface characterized by A and with n kinks. The mean number of molecules between kinks will be equal to $N\Lambda/n$ where $N$ is Avogadro's number. According to probability theory, half of the kink pairs will be of the simple variety. From each kink $Nk_0$ molecules will be lost per unit time, so the mean lifetime $\tau$ of a simple kink pair will be given by

$$\tau = \frac{N\Lambda}{2Nk_0n} = \frac{\Lambda}{2nk_0}.$$ 

The rate of kink annihilation is then equal to the number of simple kinks divided by their lifetime:

$$\frac{n}{2\tau} = \frac{n^2k_0}{\Lambda}.$$ 

At steady state this must be equal to the rate of kink formation:
Solving for \( n \),

\[
2k_f \Lambda = \frac{n^2 k_0}{\Lambda}.
\]

For the case where kink nucleation is rate limiting, then, the flux \( J \) will be given by the relation

\[
J = nk_0 = \left(\frac{2k_f k_0}{k_0}\right)^{1/2} \Lambda.
\]

This simple model has been checked by calculations of the Monte Carlo type for small values of \( \Lambda \), \( k_f \), and \( k_0 \) and found to be valid within limits of about 10%.

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Undoped ice single crystals (warm chamber), Average of 5

\[ \Delta H_s^* = 6.1 \text{ kcal/mole} \]

\[ \Delta H_s^0 = 12.2 \text{ kcal/mole} \]

Fig. 1
Fig. 2. Kinks and Ledges.
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