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Effect of Incident Flux on Surface Concentrations and Condensation
Coefficients when Growth and Vaporization Involve
Mobile Surface Species

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Running Head: Surface Concentrations and Condensation Coefficients

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ABSTRACT

Kinetic analysis of condensation and vaporization processes which proceed through a mobile, adsorbed precursor state shows that the relative concentration c_s/c_{se} of mobile surface molecules depends upon both the vapor saturation ratio P/P_e and the condensation or vaporization coefficient α : $c_s/c_{se} = \alpha + (P/P_e)(1 - \alpha)$. The result may affect previous treatments of two-dimensional nucleation and of spiral ledge dynamics in which it was assumed that $c_s/c_{se} = P/P_e$. When condensation or vaporization proceeds through a mobile surface layer, condensation coefficients of unity may be approached, but not attained. If surface migration is rapid, the condensation-vaporization coefficient α will change with vapor saturation only if there is a change in the concentration of surface sites at which mobile molecules are incorporated, in the rate constant for incorporation of mobile molecules at these sites, or in the surface residence time. When α is small, the temperature dependence of α yields information on the difference between the activation energy for incorporation and the depth of the molecule-surface potential well. If condensation or vaporization occurs primarily from spiral ledges originating at screw dislocations, condensation and vaporization coefficients will decrease as the system is taken from large oversaturations or large undersaturations towards equilibrium. The slopes of hillocks or pits formed at screw dislocations will decrease concurrently. The results are applied to vaporization and condensation of arsenic and antimony.

Many gas-surface experiments and technological processes involve the transition from a rarefied gas through a mobile, adsorbed surface layer to a chemisorbed or immobile condensed state. Examples include molecular beam deposition experiments, epitaxial growth of thin films, and heterogeneous catalysis. The reverse transition occurs upon vaporization of single crystals or evaporation of adsorbed layers. The present paper examines the kinetics of surface reactions which proceed through a mobile surface state in an attempt to clarify some of their overall characteristics.

The first part of the paper is a generalized analysis of the variation of condensation coefficients, and of the concentrations of mobile adsorbed molecules, with the degree of vapor saturation for such processes. The results imply that, when condensation or vaporization occurs via a mobile precursor state, condensation and vaporization coefficients of unity can be approached but not attained. A condensation coefficient of unity requires that the concentration of mobile surface molecules be independent of the degree of vapor saturation. For any value of the condensation coefficient, if the number of incorporation sites is independent of the incident flux, the condensation coefficient will be independent of the rate of vapor impingement upon the surface.

The second part of the paper examines the variation of vaporization and condensation coefficients with the degree of vapor saturation under those conditions where vaporization and condensation occur primarily at monomolecular ledges emanating from screw dislocations. Under these circumstances, the number of condensation sites, which depends upon the total length of monomolecular ledge on the surface, may vary with the incident flux. In this case vaporization coefficients and condensation

coefficients will decrease as one proceeds from large undersaturations or supersaturations towards equilibrium.

I. Steady-State Kinetics of Molecular Condensation and Vaporization

A. The model

We assume throughout that condensation (or evaporation), occurs by the following steps, each of which is reversible.

(1) A fraction δ of the molecules incident upon the surface from the vapor (incident flux J_i) are "trapped", thermally accommodated, and are mobile. The concentration of migrating surface molecules is c_s molecules per unit area.

(2) Growth of single-crystal substrate or chemisorption requires that the migrating surface molecules become attached to the substrate at specific condensation sites, concentration c_c . For clarity, in the present discussion, the term condensation will be restricted to this latter process.¹ Thus, only these molecules which become incorporated in the substrate crystal lattice (or which chemisorb) are considered condensed. With this definition, both vaporization and condensation require complete, but reversed, traversal of the same series of stepwise processes. Attachment of migrating surface molecules at condensation sites is assumed to be a first-order process which occurs at a rate $k_c c_c c_s$.

(3) In addition to condensing in step (2), migrating surface molecules can desorb into the vapor phase. Desorption is a first-order process characterized by a surface residence time τ , so the desorption rate is c_s/τ .²

The overall kinetic process is diagrammed below:

The model is similar to those used to discuss specific molecular beam condensations.³

In many, possibly most, examples of practical interest the "trapping coefficient" δ is equal or close to unity and essentially all incident molecules thermally accommodate and become part of the mobile adsorbed layer.^{4,5} A trapping coefficient of unity implies that the condensation coefficient α_c is independent of the temperature T_v of the impinging vapor. This has been observed experimentally.⁶ Here, although δ is included, it will be assumed that the trapping coefficient is independent of the incident flux. Although this appears reasonable for the low surface-coverages characteristic of the low-pressure conditions (in the molecular-flow regime) under which the processes being considered are often carried out, it may not hold under conditions where the concentration of mobile surface molecules becomes an appreciable fraction of a monolayer. The rate constants k_c and k_s and the characteristic surface residence time τ are also assumed to be independent of the incident flux and, therefore, of the concentration of mobile surface molecules.

The model further assumes that the surface coverage described by c_s is uniformly distributed over the surface in the sense that the rate of incorporation (condensation) of mobile molecules is assumed proportional to the concentration c_s of those molecules. Thus, the model implicitly assumes that surface migration or diffusion is sufficiently rapid, or that condensation sites are distributed sufficiently uniformly, that no significant concentration gradient becomes established between mobile molecules on surface adjacent to condensation sites and those a maximal distance away from condensation sites. This assumption appears inherently

likely to be realized closely when surface migration proceeds with little hinderance, in a fashion approaching a two-dimensional gas.^{3,5,7} In contrast, the assumption might seem questionable for vacuum vaporization of a single crystal on which adatoms migrate by site-to-neighbor site surface diffusion. However, even in that case, Surek, Hirth, and Pound⁸ show that the interaction between condensation sites (ledges) and surface-diffusion gradients causes the concentration of condensation sites to increase to the point where steady-state vaporization coefficients become essentially unity. Thus, the assumption may also be reasonable under what appear to be inauspicious circumstances.

Even under circumstances where these assumptions do not apply (for example, analysis of transient behavior before steady-state is attained⁹), examination of the above model imposes limiting generalizations.

B. Kinetic analysis

Net vaporization and condensation fluxes (J_v and J_c , respectively), in the molecular-flow regime may be described by the Hertz-Knudsen-Langmuir equation.^{1,2} To describe the whole range of saturation from vacuum to very large supersaturation, this may be written in the form,

$$J_c = \alpha(P - P_e)(2\pi mkT)^{-\frac{1}{2}} \quad (1)$$

Here P_e is the equilibrium vapor pressure (of the condensate) at temperature T and P is the effective pressure of ambient, or incident, vapor. When $P > P_e$, net condensation occurs and α is the condensation coefficient α_c .¹ When $P < P_e$, net vaporization occurs with a vaporization flux $J_v = -J_c$ and α is the vaporization coefficient α_v .¹ The condensation-vaporization coefficient α in Eq.(1) may vary with saturation, i.e., $\alpha = \alpha(P)$.

It is convenient to define an equilibrium flux J_e as the vapor flux incident upon the substrate when these are in equilibrium,

$$J_e = P_e (2\pi mkT)^{-\frac{1}{2}} . \quad (2)$$

Under other conditions the incident flux J_i is^{1,2}

$$\begin{aligned} J_i &= P_v (2\pi mkT_v)^{-\frac{1}{2}} \\ &= P (2\pi mkT)^{-\frac{1}{2}} . \end{aligned} \quad (3)$$

Here, T is the substrate temperature and T_v is the temperature of the vapor source. The pressure $P = P_v (T/T_v)^{\frac{1}{2}}$ is the flux-equivalent pressure on the substrate caused by a pressure P_v of vapor from an equilibrium source at T_v .²

The Hertz-Knudsen-Langmuir equation may now be written as,

$$J_c = \alpha (J_i - J_e) . \quad (4)$$

Note that

$$J_i/J_e = P/P_e . \quad (5)$$

At steady-state the concentration of mobile adsorbed molecules is constant.

$$\frac{dc_s}{dt} = 0 = \delta J_i + k_s c_c - \frac{c_s}{\tau} - k_c c_c c_s . \quad (6)$$

But, by definition, the net rate of condensation is given by the net rate at which molecules are incorporated into the condensed phase.

$$J_c = k_c c_c c_s - k_s c_c . \quad (7)$$

From Eqs.(6) and (7) it can be seen that the net condensation flux is equal to the difference between the number of molecules entering the mobile adsorbed layer from the vapor and the number of molecules from the mobile layer which are re-emitted to the vapor phase.

$$J_c = \delta J_i - c_s/\tau . \quad (8)$$

Equation (8) is independent of the kinetic form of the rate expression for condensation from the mobile adsorbed layer and could have been written down directly.

When substrate and vapor are at equilibrium, the net condensation flux is zero, $J_c = 0$. At equilibrium, the incident flux is J_e and the concentration of mobile, adsorbed molecules is c_{se} . From Eq.(8),

$$\delta J_e = c_{se}/\tau \quad (9)$$

and from Eq.(7),

$$k_c c_{se} = k_s \quad (10)$$

Dividing Eqs.(4), (7), and (8) by J_e , making use of Eqs.(5), (9), and (10), leads to

$$J_c/J_e = \alpha[(P/P_e) - 1] \quad (11)$$

$$J_c/J_e = \delta[(P/P_e) - (c_s/c_{se})] \quad (12)$$

$$J_c/J_e = \delta \tau k_c c_c [(c_s/c_{se}) - 1] \quad (13)$$

The quantity $(P/P_e) - 1$ in Eq.(11) is often called the relative degree of supersaturation. Combination of Eqs.(11) and (12) gives the variation in the concentration of mobile surface molecules with the ambient pressure.

$$\frac{c_s}{c_{se}} = \frac{\alpha}{\delta} + \frac{P}{P_e} \left(1 - \frac{\alpha}{\delta}\right) \quad (14)$$

Equation (14) can be written equally well in terms of the incident flux J_i by making use of Eq.(5). Because Eq.(14) does not depend upon Eqs.(7), (10), and (13), it is independent of the kinetic form of the rate expressions for exchange of mobile molecules between the immobile condensed phase and the mobile layer. The relative concentration c_s/c_{se} depends only upon α/δ and the saturation ratio P/P_e . It is plotted in Fig. 1. Equation (14)

is discussed further below, but it should be pointed out here that the ratio c_s/c_{se} is not, in general, simply P/P_e in condensation nor α_v in vaporization as has been assumed previously.²

Combination of Eqs.(11) and (13), using Eq.(14), yields after some manipulation:

$$\alpha = \delta \tau k_{cc} / [1 + \tau k_{cc}] \quad . \quad (15)$$

C. Implications of Eqs.(14) and (15)

Although the model leading to Eqs.(14) and (15) is undoubtedly oversimplified, the results have implications which may not have been obvious in advance. Some of these appear to have been overlooked in previous treatments of specific aspects of condensation, crystal growth, and vaporization phenomena.

(1) The value of α . Equation (15) shows that, under the assumed conditions, the condensation-vaporization coefficient α must be less than the trapping coefficient δ . It can closely approach, but not equal, δ . Physically, the result says that, in any condensation process requiring surface migration, some of the "trapped" mobile molecules will desorb before they can condense at active crystal sites. Since most single-crystal growth mechanisms assume some surface migration²⁻⁶ the result implies that, even though the trapping coefficient δ may well be unity, the condensation coefficient will be less than exactly one. This has been observed in recent experiments at moderate supersaturations.³

(2) Requirements for $\alpha \approx 1$. A high condensation-vaporization coefficient α (approaching either unity or δ) means that $c_s = c_{se}$ both in vaporization and in condensation at moderate supersaturations. At high

supersaturations, from Eq.(14), c_s/c_{se} exceeds unity but is significantly below P/P_e (See Fig. 1). In physical terms, the present model shows that $\alpha \approx \delta$ only when surface-crystal processes are sufficiently rapid that there is essentially no change in the concentration of c_s of mobile surface molecules from vacuum to supersaturations such that $P/P_e \gtrsim [1 - (\alpha/\delta)]^{-1}$.

If c_s is to exceed c_{se} in a vapor deposition experiment then the condensation coefficient must be measurably below unity or the saturation ratio must be high. The present results indicate that, when α approaches δ , some modification is required in the common assumption that $c_s/c_{se} = P/P_e$ in condensation and growth processes.²

The present model does not include surface diffusion constraints.^{8,9} However, it does not appear that the results in Fig. 1. will be changed by surface concentration gradients since the mass-balance which leads to Eq.(14) is independent of the surface-molecule condensation mechanism described by Eqs.(7) and (10). Thus, the fact that c_s in Eq.(7), which describes the concentration of mobile surface molecules which are near condensation sites, might differ from c_s in Eq.(8), which is an average over the whole surface, does not affect Eq.(14). When surface concentration gradients are significant, c_s in Eq.(14) and Fig. 1 refers to the concentration of mobile molecules averaged over the entire surface.

In the present model, a high value of α (approaching unity, or δ) in both vaporization and condensation is favored by a long surface residence time τ , by a large rate constant k_c for capture of mobile molecules at condensation sites, and by a high concentration c_c of crystal condensation sites. Equation (15) shows that the product of these three factors must appreciably exceed one for a high value of α to be observed. If surface diffusion

played a significant constraining role in the condensation or vaporization process, a high value of α would also be favored by rapid surface diffusion.⁸

At very high supersaturations, the accumulated experimental results indicate that, for atomic vapors on clean metal surfaces,^{5,10} the condensation coefficient α_c is essentially unity. This is because, at the low substrate temperatures used experimentally to achieve high supersaturations, the characteristic surface residence time τ is relatively very large, so that "trapped" molecules have an extremely low probability of being re-emitted. As the substrate temperature increases, τ decreases in an Arrhenius, exponential fashion,^{2,7} so that, at the higher substrate temperatures used to achieve lower supersaturations, one expects $\alpha < 1$, as observed.³ Because observation of $\alpha < 1$ requires that the surface residence time not be unduly long, the kinetic process treated in the present model is sometimes described, when $\alpha < 1$, as having a "rate-limiting" desorption step.³ However, other authors^{1,19} have restricted this terminology to the situation where $\alpha = \delta$. As will be seen below, the present model can equally well correspond to the situation where incorporation at condensation sites is considered "rate-limiting", illustrating the ambiguities of attempting to name the "rate-limiting" step in sequential surface reactions.¹¹

(3) Variation of α with P . Equation (15) indicates that condensation and vaporization coefficients α will vary with saturation if the concentration of condensation sites c_c , or the rate constant k_c for incorporation at condensation sites, depends upon the incident flux of condensing molecules. One well-known condition under which the concentration c_c depends upon incident flux is when two-dimensional nucleation to form new growth sites

occurs upon collisions between mobile molecules.² Another condition, considered further below, under which the concentration of condensation sites depends upon ambient pressure may arise when incorporation of mobile molecules takes place at monomolecular spiral ledges originating at screw dislocations.^{2,8,12} In this case, the spacing between adjacent spiral ledges, and, hence, the density of sites c_c , may depend upon the ambient pressure. In chemisorption, it is the rule, rather than the exception, for the steady-state number of available chemisorption sites --- and, possibly, the probability of mobile molecules being caught by these sites¹³ --- to vary with the pressure and surface coverage.

However, if c_c and k_c , as well as τ and δ , are independent of the incident flux, then, regardless of its value, the condensation or vaporization coefficient $\alpha = \alpha_c = \alpha_v$ will be independent of saturation over the whole range of pressure from vacuum to high supersaturations.

(4) Relation between c_c and α when $\alpha \ll 1$. Equation (15) shows how the condensation-vaporization coefficient α depends upon the concentration c_c of condensation sites when these vary. When $(\alpha/\delta) < 0.1$, then α is essentially directly proportional to the concentration of crystal condensation sites:

$$\alpha = \delta \tau k_c c_c \quad (16)$$

Equation (16) applies to the retarded vaporization of arsenic¹⁴⁻¹⁷ and, to a large degree, of antimony.^{15,16} (See Section II).

(5) Temperature dependence of α . The temperature dependence of condensation and vaporization coefficients is often described as the difference between an activation enthalpy for vacuum vaporization ΔH^* and the equilibrium

enthalpy of vaporization ΔH° ,¹

$$-R \frac{d(\ln \alpha)}{d(1/T)} = \Delta H^* - \Delta H^\circ \quad (17)$$

(This formulation may be readily converted to other conventions).^{1,16}

When $\alpha \approx 1$, $\Delta H^* = \Delta H^\circ$, and, as Eq.(15) shows, the temperature dependence of α is independent of the temperature dependence of δ , τ , k_c , or c_c . Thus, when $\alpha \approx 1$, the temperature dependence of the vacuum vaporization flux does not depend explicitly upon the energies of individual steps in the vaporization process. Observation of $\alpha \approx 1$ does not imply that the energy required for one or another of these steps equals ΔH° .

However, when $\alpha \ll \delta$, Eq.(16) may be used to examine the temperature dependence of α . Assume that the "trapping" coefficient δ ¹⁸ and the concentration c_c of condensation sites vary only slowly or not at all with temperature. The rate constants k_c and τ may be considered to vary in Arrhenius fashion^{2,7}

$$k_c = A_c e^{-E_c/RT} \quad (18)$$

$$1/\tau = \nu_{\perp} e^{-E_a/RT} \quad (19)$$

where E_c is the activation energy for incorporation (condensation) and E_a is the depth of the gas-surface adsorption potential well. It follows, utilizing Eqs.(16) and (17), that, when α is small,

$$\Delta H^* - \Delta H^\circ = E_c - E_a \quad (20)$$

If δ or c_c have significant exponential temperature dependences these activation energies must be added to E_c in Eq.(20). Equation (2) leads to a number of corollaries which appear to be generally similar to the results of a transition-state-theory analysis of vaporization and condensation.^{19,20}

(a) Even when the concentration c_c of condensation sites is invariant, α will vary with temperature if $\alpha < 1$, since $\Delta H^* = \Delta H^\circ$ only in the fortuitous, and unlikely, circumstance that $E_c = E_a$.

(b) When $\alpha < 1$ and $E_c < E_a$, then $\Delta H^* < \Delta H^\circ$, in which case α decreases with increasing temperature. This is sure to be true when the activation energy E_c for condensation is essentially zero, as appears reasonable for adatom incorporation in metallic crystals. Under these circumstances α will decrease as T increases because τ will decrease. This situation might be described as having a "rate-limiting" desorption step,³ but the terminology should be applied with caution¹¹ since the kinetic limitation is not the same as that called rate-limiting desorption in Searcy's transition-state treatment.^{19,20}

(c) Suppose α is small because of a significant activation energy E_c for incorporation of mobile molecules. This means that $E_c > E_a$, in which case $\Delta H^* > \Delta H^\circ$ and α increases with temperature. This situation might be described as having a "rate-limiting" incorporation step and applies to arsenic and antimony.^{15,16}

(6) Limiting value of c_s in condensation when $\alpha \ll 1$. For condensation, and for vaporization at limited undersaturations $[(P/P_e) > 10(\alpha/\delta)]$ if, and only if, the condensation or vaporization coefficient is quite small ($\alpha/\delta < 0.1$), Eq.(14) simplifies to

$$c_s/c_{se} = P/P_e \quad . \quad (21)$$

An extreme case arises in physical adsorption where $\alpha = 0$ and Eq.(21) applies throughout the pressure range. On the other hand, in contrast to previous assumptions,² when the condensation coefficient is not small Eq.(21) does not apply (cf. Fig. 1) and Eq.(14) must be used.

(7) Free evaporation value of c_s . For vaporization into vacuum ($P = 0$), Eq.(14) reduces to

$$c_s^{\circ}/c_{se} = \alpha_v^{\circ}/\delta \quad (22)$$

where the superscripts indicate the restriction to vacuum conditions.

This is a well-known result.^{2,8} However the present discussion emphasizes that Eq.(22) no longer applies when $P \gtrsim 0.1\alpha_v P_e/\delta$ (see Fig. 1). Thus, the range of validity of Eq.(22) depends upon the value of the vaporization coefficient α_v . When α_v is significantly below one, Eq.(22) applies only over a quite restricted range of saturation. The implicit assumption that Eqs.(21) and (22) hold simultaneously may have thwarted some previous analytical efforts² to ascertain the pressure dependence of α_v .

(8) Further implications of Eq.(14). As has been pointed out above (see paragraph 2), Eq.(14) is independent of the surface reaction paths available to mobile, adsorbed molecules after they are trapped on the surface. Equation (14) requires only that desorption be a first-order process and that a (transient) steady-state be attained. Thus, Eq.(14) has application in more complex circumstances than those specifically considered here. Examples include analyses of the time-dependent changes occurring when surface-diffusion constraints or two-dimensional nucleation are involved.^{2,8,21} The present results suggest that some theoretical treatments^{2,8,9,21,22} of the back-force effect in ledge dynamics and of two-dimensional nucleations may have to be modified²³ so as to incorporate Eq.(14), if they assumed that Eqs.(21) and (22) hold outside their limited range of validity (see Paragraphs 6 and 7).

Theories of surface nucleation and of screw dislocation ledge spacings usually are based upon a calculation of the change in chemical potential

$\Delta\mu$ when a molecule is taken from the crystal to the surrounding medium.^{2,12,21,22} In early theoretical treatments^{2,12} it was assumed implicitly that Eq.(21) applies. Thus, the relative activity ratio corresponding to $\Delta\mu$ was taken interchangeably to be given by P/P_e or c_s/c_{se} . However, Eq.(14) makes it necessary to consider whether the relative activity ratio associated with $\Delta\mu$ is most closely approximated by the saturation ratio P/P_e or the surface concentration ratio c_s/c_{se} . It would appear that the change in chemical potential which is of interest in surface nucleation, and in dislocation surface effects, is the difference in chemical potential between mobile surface molecules and immobile, "condensed" molecules, $\Delta\mu = \mu_s - \mu_c$. At equilibrium, $\mu_{se} = \mu_{ce}$. If the chemical potential μ_c of molecules incorporated at condensation sites remains constant when the system is displaced from equilibrium so that $\mu_c = \mu_{ce}$, then $\Delta\mu = \mu_s - \mu_{se}$. Therefore,

$$\Delta\mu = kT \ln(c_s/c_{se}) \quad (23)$$

where c_s/c_{se} is given by Eq.(14). The activity ratio represented by Eq.(23) seems to have been adopted, in essence, in calculations of the "back-force" effect^{9,21,22} where one computes and utilizes local undersaturations on the surface which are reduced from those in the vapor.

II. Vaporization and Condensation Processes Dominated by Dislocation Spiral Sources

A. Development

Cabrera and Levine¹² showed that the average spacing λ between adjacent monomolecular ledges near the core of a screw dislocation, upon crystal growth or evaporation, is²

$$\lambda = -19\epsilon\Omega/\Delta\mu. \quad (24)$$

Here, ϵ is the surface free energy per unit area of vertical ledge, which often is taken to be equal to the surface free energy of unit area of crystallographic plane upon assuming interfacial free energies to be isotropic and unperturbed by edge effects. The quantity $\Delta\mu/\Omega$ represents the change in Gibbs free energy upon transport of unit volume of gaseous species from the ledge (which is in equilibrium with bulk solid) to the surrounding medium. The symbol Ω represents the volume of a vapor molecule in the crystal. The derivation of Eq.(24) is based upon thermodynamic surface-tension arguments stemming from those used by Kelvin and Gibbs to describe the variation in vapor pressure of a spherical liquid droplet with the droplet radius. There is some question whether the number 19 in Eq.(24) should be 19,¹² 4π ,^{9,24} or another number between 1 and 50.^{9,21} The number 19 appears particularly uncertain if Eq.(24) is to be applied to situations, such as those considered here, where equilibrium is not maintained near the ledge, since this was assumed in the original derivation.¹² However, as will be seen below, this uncertainty cancels out in a major part of the present development.

Of greater significance, in the present context, is the question considered in Paragraph 8 of the preceding section: Is the relative activity ratio

corresponding to $\Delta\mu$ in Eq.(24) most closely approximated by a vapor saturation ratio P/P_e , or by a surface concentration ratio c_s/c_{se} ? The question did not arise in the original paper because it was assumed^{2,12} implicitly that $P/P_e = c_s/c_{se}$, regardless of whether the restrictions pointed out in Paragraph 6 of the preceding section are applicable. With this assumption, Eqs.(23) and (24) lead to $\lambda \rightarrow 0$ in vacuum vaporization ($P = 0$), which corresponds to formation of infinitely steep vaporization pits centered at screw dislocations. This difficulty led to subsequent calculations of the "back-force" effect.^{9,22} These calculations examine the way that interactions between ledge incorporation processes and surface concentration profiles reduce the local undersaturation on the surface from that in the vapor.

Here we conclude (see Paragraph 8 of the preceding section), that the surface concentration ratio c_s/c_{se} determines the driving force for ledge curvature, as expressed in Eq.(23). Use of Eq.(23) appears similar in spirit to the approach taken in the back force calculations,^{9,21,22} However, the concentration ratios c_s/c_{se} given by Eq.(14) provide limits for λ at all saturations which do not require modification by further calculations of the "back force" in order to be reasonable. Eqs.(14) and (23) are most applicable under conditions, i.e., overlapping diffusion fields and small concentration gradients, where calculation of the back-force becomes a very complicated problem.^{21,22} Use of Eq.(14) may do away with the need for detailed back-force computations under some circumstances (e.g., rapid surface diffusion) and may lead to some modification (possibly simplification) in dislocation and nucleation theories under other circumstances. In the present paper no attempt will be made to expand upon or modify the detailed treatments.^{9,21}

The work is restricted to examination of the implications of the limiting model introduced in Section I.A.

Combination of Eqs.(23) and (24) gives

$$1/\lambda = -(kT/19\epsilon\Omega) \ln (c_s/c_{se}) \quad (25)$$

Equation (25) indicates that when $c_s \approx c_{se}$ (see Paragraph 2 of the preceding section and Fig. 1), the spacing λ between adjacent turns of a spiral ledge becomes very large. The result implies that neither vaporization pits nor condensation hillocks will form at screw dislocations when $\alpha \approx 1^a$ since, when α is close to unity, $c_s \approx c_{se}$ in vaporization, as well as in condensation at moderate supersaturations. At higher supersaturations other growth processes will dominate (Paragraph 2 of the preceding section). One infers that, when $\alpha \approx 1$, ledges from screw dislocations will not dominate the condensation or vaporization kinetics, a result which appears to accord with observation,^{3,6}

In contrast, when $\alpha < 0.1$,² Eqs.(14) and (25) suggest that pits and hillocks will appear at screw dislocations upon evaporation or growth, respectively. The pits and hillocks will disappear at saturations very near equilibrium and become steeper away from equilibrium. The pits and hillocks will have, neglecting further interactions,^{8,9,21} slopes θ near their centers given by $\tan \theta = h/\lambda$ where h is the height of a monomolecular ledge.

When $\alpha \leq 0.1$, in growth, as well as in vaporization at limited undersaturations where $P/P_e > 10\alpha$ (see Fig. 1), the relative concentration ratio c_s/c_{se} is closely approximated by P/P_e , as in Eq.(21).^a Under these

Footnote a. It will be assumed throughout this section that the trapping coefficient δ is unity. The results may be extended to circumstances where $\delta < 1$ simply by replacing α , whenever it occurs, by α/δ .

circumstances Eq.(25) reduces to the original form of the Cabrera-Levine equation.^{2,12} The change in sign of λ when $P > P_e$ from that when $P < P_e$ corresponds to a change in the sense of rotation of the spiral. Equation (25) implies that, as the saturation ratio increases, spiral dislocation hillocks will become steeper until the surface concentration c_s reaches the value required for two-dimensional nucleation. Above this concentration dislocations will no longer be the dominant ledge sources.² Of course, impurities, surface-diffusion gradients, or other effects not specifically considered here may also affect the ledge spacing.^{8,21,22}

Similarly, in evaporation, pits will become steeper as the saturation ratio decreases and will have limiting slopes determined by the vacuum ledge spacing^a

$$1/\lambda^0 = -(kT/19\epsilon\Omega) \ln \alpha_v^0 \quad . \quad (26)$$

The Cabrera-Levine prediction that spiral ledge spacings will vary with saturation has further implications for growth and vaporization processes which take place at spiral ledges. If incorporation of mobile surface molecules into substrate crystal takes place primarily at ledges from screw dislocations the concentration of condensation sites c_c will be proportional to the total length of spiral ledge on the surface. In the most obvious applications of this assumption the condensation sites would be presumed to be kinks.^{1,2} When α is significantly below one^a and all ledges contain, on the average, the same concentration c_c of incorporation sites (kinks), all ledges move at the same rate. Under these conditions the initial ledge spacing λ established near the dislocation line will be perpetuated and pits or hillocks will have constant slope.¹⁵ The

concentration c_c of condensation sites in the pitted or hillocked surface will be

$$c_c = 1/\ell_c \lambda \quad (27)$$

where ℓ_c is the average ledge length between condensation sites.

Unlike Eqs.(25) and (26), which depend only upon Eq.(14) and the Cabrera-Levine formulation, Eq.(27), and those which follow, depend upon the totality of assumptions underlying the model described in Section I.A. Specifically, it is assumed that surface migration is rapid enough that the spacing λ between ledges is unaffected by surface concentration gradients. (The effect of surface diffusion on spiral ledge spacings in vaporization has been considered in detail by Surek, Pound, and Hirth²¹). Also, when discussing vaporization and condensation coefficients, it will be assumed that the crystal has reached steady-state so that spiral ledges cover the whole crystal surface uniformly. This last assumption is not necessary when discussing pit or hillock slopes. The assumptions in the model appear applicable to the retarded vaporization of As_4 and Sb_4 from arsenic and antimony single crystals.

Introduction of Eq.(27) into Eq.(16) yields^a

$$\alpha = k_c' \tau / \lambda \quad (28)$$

with $k_c' = k_c / \ell_c$. Thus when $\alpha < 0.1$, the condensation-vaporization coefficient α is inversely proportional to the spiral ledge spacing λ :

$$\alpha / \alpha_v^o = \lambda^o / \lambda \quad (29)$$

Combination of Eqs.(14), (25), (26), and (29) indicates that over the saturation range where screw dislocations dominate as ledge sources:^a

$$\alpha(P) / \alpha_v^o = \log[\alpha + (P/P_e)(1 - \alpha)] / \log \alpha_v^o \quad (30)$$

The ratios in Eqs.(29) and (30) are independent of the questionable number 19 in the Cabrera-Levine theory, Eq.(24).^{9,21} The ratios $\alpha(P)/\alpha_v^\circ$ given by Eq.(30) are plotted in Fig. 2 as a function of the saturation ratio P/P_e for various values of α_v° . The plots in Fig. 2 also represent the ratio λ°/λ .

Equation (30) does not apply when $\alpha_v^\circ \geq 0.2$, but the vaporization and condensation kinetics are less likely to be dominated by screw dislocations under these circumstances. (The case where $\alpha_v^\circ \geq 0.5$ has been treated in detail by computer simulation by Surek, Hirth, and Pound.²¹) Equation (30) also becomes inapplicable at saturations such that $P \approx P_e$, where spiral ledges no longer predominate as ledge sources. The interesting cases arise when $\alpha \leq 0.1$ and $(P/P_e) > 0.1\alpha$,^a since at lower pressures α does not deviate significantly from the vacuum value α_v° (see Fig. 2). When $\alpha \leq 0.1$ and $P/P_e > \alpha$, the quantity in square brackets in Eq.(30) reduces to the saturation ratio P/P_e (see Paragraph 6 of the preceding section) and the plots of $\alpha(P)$ as a function of $\log(P/P_e)$ in Fig. 2 become straight lines.

As Fig. 2 indicates, Eq.(30) implies that, over the range of α and of saturation where ledges from screw dislocations dominate as condensation sites, α will be at a maximum in vacuum and at high supersaturations. As equilibrium is approached α and c_c will decrease until the concentration of condensation sites c_c approaches a value determined by sources other than spiral ledges. Although growth and vaporization processes are qualitatively similar, albeit reversed, the plots in Fig. 2 are not symmetric about $P = P_e$ because of the asymmetry in the surface concentration ratios shown in Fig. 1.

B. Discussion of Eqs.(25) and (30).

(1) Qualitative comparison with previous work. All published experiments reporting the dependence upon vapor saturation of vaporization and condensation coefficients α in systems for which these are significantly below unity appear to be in qualitative agreement with the expectation, Eq.(30), that α will increase as the conditions move away from equilibrium.^{2,14,25-31} A decrease in α_v as the conditions move from vacuum towards equilibrium has been reported for substances as diverse as alkali halides,^{25,27,30} organic crystals,^{26,28,29} sulfur,²⁷ arsenic,¹⁴ and antimony sulfide.²⁷ It also appears that, in the growth of iodine,² organic crystals,^{2,26} and contaminated NaCl,³¹ α_c increases with saturation. Associated observations on the vaporization etch pits which appear upon sublimation of alkali halides,²⁵ β -methylnaphthalene and p-toluidine,²⁸ and arsenic¹⁵ indicate that pit slopes θ decrease and spiral ledge spacings λ increase when the ambient pressure increases, as predicted by the Cabrera-Levine theory, Eq.(25). The agreement between the experimental results and those in Section II.A suggests that either screw dislocations are indeed important ledge sources in chemical systems showing "retarded" vaporization kinetics or that the density c_c of primary vaporization sites depends upon the incident vapor flux in a manner not dissimilar to that of spiral ledges.

It is not easy to compare the present results with those from detailed (rather complex) computer simulations of the time-evolution of ledges upon vaporization.^{8,9,21} Those calculations assume equilibrium at ledges, but include concentration gradients in c_s away from ledges. They apply most directly to unretarded vaporization processes, $\alpha_v^0 > 0.5$.²¹ In contrast, the

kinetic model described in Section I.A is not restricted to equilibrium at ledges, but it does not specifically consider gradients in the concentration c_s of mobile surface molecules. Equation (30) is limited to $\alpha_v^0 \lesssim 0.1$, although Eqs.(14) and (25) are not. It was pointed out in Part I that Eq.(14) would not be affected significantly by consideration of surface concentration gradients. However, combination of Eqs.(14) and (25) to compute the ledge spacing λ as a function of saturation when $\alpha_v^0 > 0.5$ first requires evaluation of α as a function of saturation, a complex problem²¹ beyond the scope of the present treatment. Both the present work and the computer simulations predict that α_v increases and λ decreases when the system is displaced further from equilibrium. The predictions of the two approaches do not appear to contradict each other under conditions where they converge and it is possible that the results are mutually consistent.

We turn now to somewhat more quantitative comparison of Eqs.(25) and (30) with experiment for systems, arsenic and antimony, to which the present model might be expected to apply. Experiments on these systems indicate that vaporization coefficients are small, equilibrium is not established at ledges, and surface migration is rapid.¹⁵

(2) Arsenic. Arsenic single crystals appear to vaporize almost exclusively from spiral ledges originating at screw dislocations.¹⁵⁻¹⁷ Dowell¹⁵ observed that As(111) wafers evaporated in vacuum form triangular vaporization pits with slopes in the range 9 to 13^a (average 11°), but that crystals vaporized in Knudsen cells at much higher saturations form pits with slopes ranging from less than 1° to 11°. The results concur with the expectation from Eqs.(29) and (30).

Assuming that arsenic vaporization pits are composed of monomolecular ledges with heights of $3.5 \text{ \AA}$, a pit slope of 11° corresponds to a ledge spacing of $18 \text{ \AA}$. This value can be substituted into Eq.(26) to compute a surface free energy ϵ of 78 ergs/cm^2 from the vacuum vaporization coefficient, $\alpha_v^o = 8.3 \times 10^{-5}$ at 550 K .³³ The value looks surprisingly reasonable upon comparison with surface tensions estimated from elastic moduli,³⁴ by comparison with krypton,³⁵ or by comparison with other metals¹⁶ (see Table I). The agreement may be fortuitous. On the other hand, it may suggest that the number 19 in the Cabrera-Levine equation is correct within a factor of two even for a system which deviates from the conditions assumed in the deviation as much as arsenic. Surface concentrations near ledges are far from equilibrium on arsenic.¹⁷ Also, arsenic surface energies are sufficiently anisotropic that ledges are straight (triangular pits)¹⁵ rather than curved (conical pits), although the ledges might not be straight in the pit center where the ledge spacing is established.

Brewer and Kane¹⁴ investigated the variation in the vaporization rate of arsenic powder with vapor saturation by measuring the apparent vapor pressure P from Knudsen cells with orifice areas a varying from very small to an open crucible. By using the (approximate) relation $P_e/P = 1 + (a/\alpha_v A')^{1/3}$,³² the product $\alpha_v A'$ can be computed from the results. If one assumes the effective vaporizing area A' ,³² to be independent of saturation and normalizes the results to the open crucible (vacuum) result for $\alpha_v A'$ one obtains the points plotted in Fig. 3. It has been assumed in the plot that the pressure P in the open crucible experiment is equal to the Langmuir vapor pressure¹ measured in that experiment. There is an inherent

Table I

Estimates of the Surface Tension of Arsenic and Antimony, $\epsilon(\text{ergs/cm}^2)$

	<u>As(111)</u>	<u>Sb(111)</u>
Vaporization pits, Eq.(26)	78	30
Growth hillocks, Eq.(25)	---	31 to 62
Elastic moduli, (Ref. 34)	41	---
Comparison with rare gas	81	127
Comparison with metal	110	215

uncertainty in comparing the points in Fig. 3 with predictions from Eq.(30) because the points come from powder samples with an unknown effective area. The effective area will vary with saturation if α varies with saturation.³² Rather than attempting to adjust each of the experimental data points Fig. 3 contains two lines based upon Eq.(30). The upper line is computed upon taking the vacuum vaporization coefficient to be that obtained from the powder measurements by assuming the vaporizing area to equal the projected, or cross-sectional area, of the powder. The lower line is computed upon taking α_v^o to equal the lower limit determined from single crystal measurements.³³ These two lines should give limits for the powder results. The upper line has to fit the open crucible experiment (the last point) since it is based upon that experiment.

(3) Antimony. The observation that antimony, which is isostructural with arsenic, forms shallower vaporization pits, average 5° , is qualitatively consistent with what one expects from Eq.(26) since antimony has a significantly larger vaporization coefficient.¹⁵ However, the quantitative agreement is less satisfactory. Assuming monomolecular ledge heights of $3.8 \text{ \AA}$, vacuum ledge spacings on antimony average $43 \text{ \AA}$. From this and $\alpha_v^o = 0.17$ at 650 K ,³⁶ one computes $\epsilon = 30 \text{ ergs/cm}^2$ from Eq.(26). As Table I indicates this value is a factor of four to seven below what one might expect from comparison with other crystals. The discrepancy may indicate that the factor 19 in the Cabrera-Levine formulation is not applicable or, equally likely, that the vaporization coefficient of antimony is sufficiently high that surface concentration gradients and impurity effects cannot be neglected when trying to compute ledge spacings.

Martin and Rosenblatt³⁵ measured the slopes of dislocation hillocks grown on Sb(111) at low supersaturations to be between 1 and 2°. From the supersaturation ratio in their experiments, $P/P_e = 1.8$, one computes from Eq.(25) that ϵ is between 31 and 62 ergs/cm. It is interesting that the ratio $\theta_{\text{hill}}/\theta_{\text{pit}} = \lambda_{\text{pit}}/\lambda_{\text{hill}} = \alpha_c/\alpha_v = 0.4$ which one computes from Eq.(30) is in agreement with the observed ratio of hillock and pit slopes. This last result tentatively suggests that changes in the limiting model considered here, which are introduced by surface concentration gradients, affect the factor $19 kT/\epsilon\Omega$ in Eq.(25) considerably more than they affect the logarithmic dependence upon c_s/c_{se} .

III. Conclusions

(1) In condensation and vaporization processes which proceed through a mobile surface layer, the relative concentration c_s/c_{se} of mobile surface molecules is not equal to the saturation ratio P/P_e under most conditions of interest but is, rather, given by Eq.(14). This result has a number of consequences which are discussed in section I.C. It also implies that previous calculations of the "back-force" effect might require some modification.

(2) When screw dislocations dominate as ledge sources in the vaporization or condensation of single crystals, vaporization and condensation coefficients α will decrease as one proceeds from large under- or over-saturation towards equilibrium. Pit or hillock slopes will decrease concurrently.

In contrast, if the concentration c_c of sites at which mobile adsorbed molecules are incorporated into the solid is independent of incident flux, vaporization and condensation coefficients will be equal and constant from vacuum through equilibrium up to supersaturations so large that c_c is no

longer constant. (This conclusion assumes rapid surface migration and is restricted to that limit.)

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Figure Captions

- Fig. 1. Plot of surface concentration ratio as a function of the saturation ratio for various values of α/δ . See Eq.(14) in text.
- Fig. 2. Variation of vaporization and condensation coefficients with saturation when screw dislocations dominate. See Eq.(30) in text. The lines correspond to different values of the vacuum vaporization coefficient α_v^0 , as labelled.
- Fig. 3. Variation of the vaporization coefficient with saturation for powdered arsenic at 575 K. The experimental points are from Ref. 14. The top line represents the values predicted from Eq.(30) using the apparent value of α_v^0 measured from the powder. The bottom line represents the values predicted from Eq.(30) using the single crystal value of α_v^0 .

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Fig. 1.

8 1 5 8 0 2 4 0 0 0 0

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Fig. 2.

Fig. 3.

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