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TRANSITION STATE THEORY FOR VAPORIZATION AND CONDENSATION

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ABSTRACT

A theory of Langmuir exactly predicts the rates of many vaporization reactions as functions of temperature. For these reactions his theory is shown to be superior to absolute reaction rate theory, which can be made to yield the same rate equation, in requiring fewer and more general hypotheses and in utilizing a kinetic factor that has been directly verified by experiment. Langmuir's theory is extended to provide an exact description of the kinetics of some dissociative vaporization reactions.

It is pointed out that Langmuir's gas-like kinetic factor has been experimentally verified for the desorption step of two substances that undergo retarded vaporization. It is argued that the transition state particles for desorption are free gas molecules and for surface diffusion in the self-adsorption layer are particles with gas-like velocities parallel to the surface. Rate equations which utilize gas-translation kinetic factors are derived for substances that vaporized with non-equilibrium distributions of electronic states and for substances with vaporization rates limited by separation of self adsorbed particles from

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catalytic surface sites or particles. The equations for dissociative vaporization reactions require that the concept of the transition state be broadened to recognize that transition state particles consist sometimes of a coupled flux of particles of two or more different kinds.

INTRODUCTION

Vaporization reactions are exceptional among chemical processes in that they are characterized by maximum possible rates that can be precisely predicted for any substance from thermodynamic data and from the kinetic theory of gases.[1-3] Furthermore, many substances have been found to vaporize into vacuum at their maximum possible rates--a result predicted by Langmuir[1] by means of a theoretical analysis that included the first explicit formulation of what is now usually called the principle of microscopic reversibility.[4] Vaporization at this maximum possible rate can be called unretarded vaporization, as distinct from retarded vaporization, a term which can be applied to describe vaporization at any lower rate.[5]

The rate of unretarded vaporization J in vacuum in moles per unit time per unit area is given for a substance which has only one major vapor species by the Hertz-Knudsen-Langmuir (HKL) equation:

$$J = (2\pi MRT)^{-1/2}P \tag{1a}$$

where M is the molecular weight of the vapor, R the gas constant, T the temperature and P is the equilibrium vapor pressure. Elimination of P by means of the Clausius-Clapyron relation yields the HKL equation in terms of the standard pressure P^o of the vapor, the standard enthalpy of vaporization, ΔH_v^o, and the standard entropy of vaporization, ΔS_v^o:

$$J = (2\pi MRT)^{-1/2}\ P^o \exp\ (\Delta S_v^o/R)\ \exp\ (-\Delta H_v^o/RT) \tag{1b}$$

This equation is readily generalized for dissociative congruent vaporization reactions (e.g. $A_mB_n = mA(g) + nB(g)$) in which the individual vapor molecules do not have the same composition as the condensed phase.[3,6]

It has been claimed[3] for substances that obey Eq. (1), that (a) the activated complex is identical to the vapor molecule produced in the reaction and that (b) the product of the frequency factor ν and transmission coefficient κ, as ordinarily defined in transition state theory[7,8] is identified with the numerical value of $(KT/2\pi m_g)^{1/2}$ Q^t where Q^t is the standard translational partition function of the vapor molecules. A substantiation of these claims is of considerable importance because in most types of chemical reactions the activated complex cannot be directly studied; its composition and properties must be inferred from the dependence of the reaction rate on system variables, and its inferred thermodynamic properties depend upon an estimated value of the frequency of decomposition of the presumed activated complex. In this paper the assumptions made by Langmuir in deducing Eq. (1a) are compared to the assumptions that lead through the theory of absolute reaction rates[9] to an equivalent relation, and it is then shown that experimental data for several substances that undergo unretarded vaporization confirm the kinetic factor and thermodynamic factor assumed by Langmuir rather than those of absolute reaction rate theory.

The analysis of unretarded vaporization provides insights into the nature of diffusion in the self-adsorbed layer. It will be argued that the product of the frequency factor and transmission coefficient for movement in the self-adsorption layer can be evaluated by means of the assumption that the activated complex is a two-dimentional gas, whether

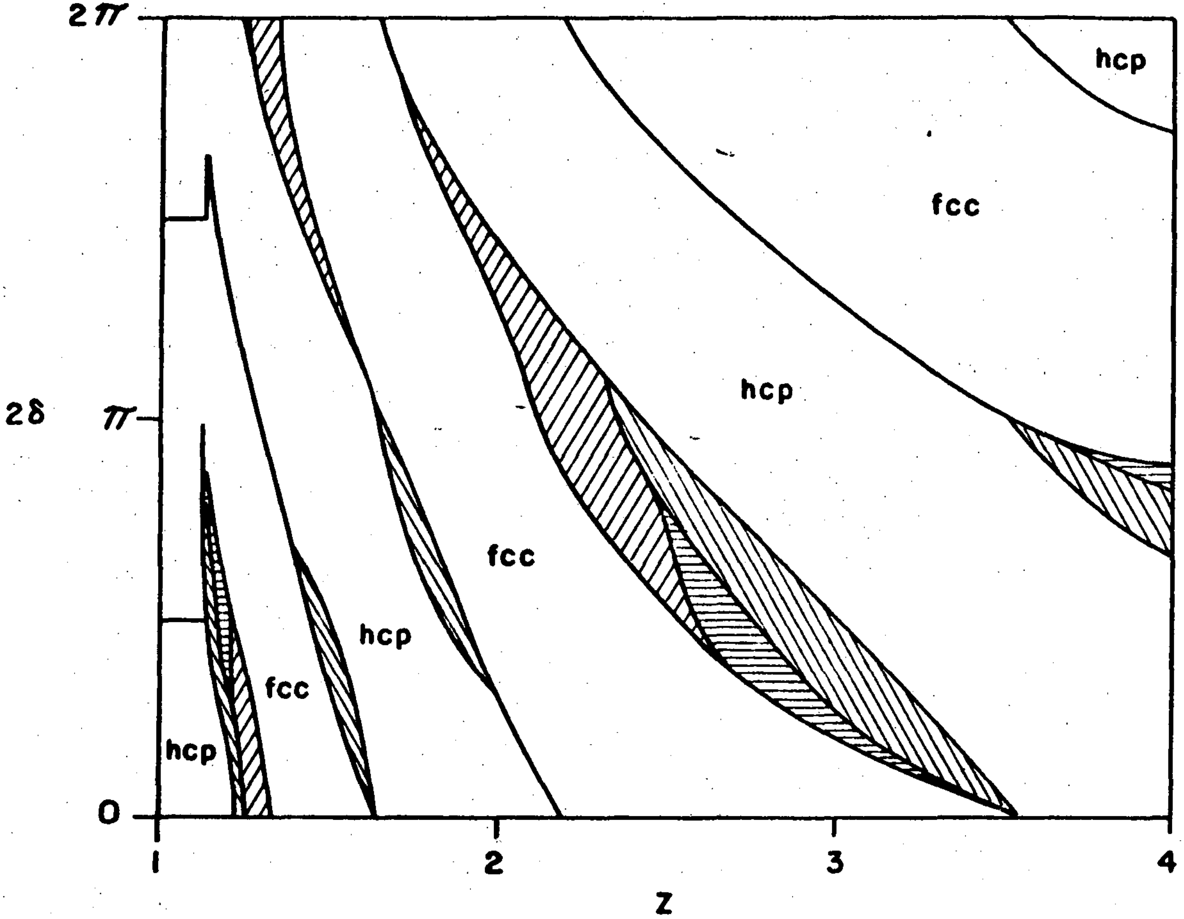

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Fig. 6

the vaporization process is retarded or not. This conclusion is used in simplifying a rate equation which is derived for vaporization when the rate is retarded by the availability of catalytic reaction sites or of catalytic adsorbed particles.

The paper concludes with a discussion of experiments that might test whether the rate limiting step in vaporization reactions is the desorption of excited molecules, whether it is the catalyzed dissociation of molecules from active sites or particles, or whether it is some other surface step of the vaporization process.

UNRETARDED VAPORIZATION AND CONDENSATION WITHOUT DISSOCIATION

Langmuir's prediction[1] that vaporization rates would obey Eq. (1a) was derived from three postulates: (1) Molecules of the equilibrium vapor come to complete equilibrium with the condensed phase upon every collision. (2) Vaporization equilibrium is maintained by detailed balancing of independent fluxes of vaporizing and condensing molecules. (A generalized form of this postulate, microscopic reversibility, has been proved for equilibrium processes by methods of statistical mechanics.)[10] (3) The flux of molecules that escape from the condensed phase to the vapor is unchanged during vaporization into vacuum from its value under equilibrium conditions. This kind of postulate is also commonly made in transition state theory.[8] Such postulates are expected sometimes to fail because any changes in the reaction environment can influence the reaction paths.

The first of Langmuir's postulates asserts that there is no thermodynamic barrier to condensation at equilibrium, so that the rate of condensation is a function of the equilibrium properties of the vapor molecules and of their dynamics of movement under equilibrium conditions. The second and third postulates then lead to the prediction that vaporization in vacuum occurs by exactly the reverse of the path(s) defined for condensation under equilibrium conditions.

Langmuir's theory, which he developed primarily to describe the vaporization of metals, predated transition state theory. But it can be viewed as equivalent to the special case in transition state theory in which the activated complex is identical to the reaction product.

For consideration of Langmuir's theory as a form of transition state theory, it is convenient to substitute different thermodynamic variables into the temperature-dependent form of Langmuir's rate equation. No new assumptions or approximations are required for the substitutions, which yield

$$j = \left(\frac{kT}{2\pi m_g}\right)^{1/2} [X_g^o] \left[\frac{2\pi m_g kT^{1/2}}{h} \ell\right] \frac{\pi Q_g^{\ell}}{\pi Q_c} \exp\left(-\Delta E_o^o/kT\right) \qquad (2)$$

Here j is the number of molecules that vaporize per unit area per second, m_g is their mass, k is the Boltzmann constant, h is Planck's constant, $[X_g^o]$ is the standard concentration of vapor, and ΔE_o^o is the energy difference per molecule at absolute zero between the vapor and the condensed phase. The term $(kT/2\pi m_g)^{1/2}$ is the velocity of a thermally equilibrated gas, while the quantity $(2\pi m_g kT)^{1/2} \ell\, h^{-1}$ is the standard translational partition function of the vapor in dimension ℓ normal to the surface. This quantity has been separated from the remainder of the total partition function of the vapor, which is symbolized by πQ_g^{ℓ}, for subsequent comparison with the equation of absolute reaction rate theory. The quantity πQ_c is the total partition function of the condensed phase.

The general rate equation for vaporization in terms of absolute reaction rate theory is[9]

$$j = \kappa \frac{kT}{h} [Z^{*}o] \frac{\pi Q^{*}}{\pi Q_c} \exp\left(- \Delta E_o^{*}/kT\right) \tag{3a}$$

For comparison of Eq. (3a) with the Langmuir equation (2), the term kT/h, which is viewed as a universal frequency term, can be interpreted as the product of the average velocity of the activated complex particles moving in one direction over the potential energy barrier of length δ times the translational partition function corresponding to the motion of a particle of mass m^* in a one-dimensional box of length δ.[9] When this procedure, which is equivalent to other derivations accepted for the general rate Eq. (3),[7] is followed Eq. (3) becomes:

$$j = \kappa \left(\frac{kT}{2\pi m^{*}}\right)^{1/2} \frac{1}{\delta} \cdot \frac{(2\pi m^{*} kT)^{1/2}}{h} \delta [Z^{*}o] \frac{\pi Q^{*}}{\pi Q_c} \exp\left(- \Delta E_o^{*}/kT\right) \tag{3b}$$

The transmission coefficient, κ, is introduced in transition state theory to account for possible reflection of molecules that have crossed the potential energy barrier to reaction. The term πQ^* is the partition function for the activated complex, as defined by Glasstone and coworkers;[9] πQ_c is the total partition function for the condensed phase and ΔE_o^* is the energy of formation of the activated complex from the condensed phase at absolute zero.

To derive the Langmuir Eq. (2) from the rate Eq. (3b)[11,12] requires some further assumptions beside the basic ones made in transition state theory. It is assumed that πQ^* is the same as the partition function for the gas, aside from the omitted translational motion away from surface.[11] The energy of activation ΔE_o^* is assumed to be identical to the energy of the equilibrium vaporization reaction, the transmission coefficient κ is assumed to have unit value, and the mass of the activated complex is assumed to be equal to the mass of the vapor modules. Equation (3b) then becomes identical to Eq. (2), the Langmuir rate equation, because $\mathcal{E} = 1$, and the quantity $[Z^{*o}]$ and $[X_g^o]$, which are the standard concentrations of the assumed activated complex and of the vapor molecules which impinge on the surface, are chosen, as is usual, to be one particle per cm^2 and therefore can be omitted from both equations.

While the expression for the molecular flux thus derived from absolute reaction rate theory is identical to that in Langmuir's theory, the kinetic and thermodynamic contributions which are assumed to enter the rate equation are different. In absolute reaction rate theory the activated complex is assumed to have a smaller total partition function than the vapor molecules, which implies a lower concentration. And each activated complex is assumed to be converted to vapor (if the complex was formed by equilibration of the condensed phase) or to the condensed phase (if the complex was formed from the vapor) with the frequency kT/h. Langmuir's theory views the rate of condensation as governed only by the rate of arrival of vapor molecules at the surface, and the rate of vaporization in consequence of his postulates is the identical rate at which thermal equilibration on the condensed phase surface generates a

Maxwell-Boltzmann flux of vapor molecules leaving the surface.

It is well established that molecules of an equilibrium vapor impinge on surfaces at the rate given by kinetic theory, which is the rate assumed by Langmuir in considering the condensation of vapors. Since by the definition of unit condensation coefficient, each collision of a vapor molecule with the surface must result in condensation, Langmuir's postulated kinetic factor is appropriate for unretarded condensation processes. But since when the condensation coefficient is unity, every vapor molecule that strikes the surface must condense, the concept that the reaction rate is governed in any fundamental sense by the rate at which the vapor molecules pass through a postulated intermediate state at a frequency kT/h is contradictory.

Direct measurements by the torsion-Langmuir method[13] of the forces produced in free surface vaporization confirm for several solids[3] the Langmuir hypothesis that molecules which leave a surface in free surface vaporization have a kinetic energy distribution identical to a flux of the equilibrium vapor. But the fact that an equilibrium energy distribution is found conflicts with the hypothesis of absolute reaction rate theory that activated complexes which move away from the surface along the reaction coordinate normal to the surface should each have a negligible translational partition function along that coordinate.[11]

Unretarded Congruent Dissociative Vaporization and Condensation

Just as a maximum possible rate can be calculated for simple vaporization processes such as those of interest to Langmuir, a maximum possible rate can be calculated for vaporization of substances that undergo dissociative congruent vaporization, that is, vaporization according to the general equation

$$A_mB_n(s) = mA(g) + nB(g) \tag{4}$$

where A or B may represent either atoms or molecules such as O_2 or S_2. The maximum possible rate for congruent vaporization is given by[3,6]

$$(J_A)^m(J_B)^n = (2\pi RT)^{-(m+n)/2} (M_A)^{-m/2} (M_B)^{-n/2} (P_A^o)^m (P_B^o)^n$$
$$\exp (\Delta S_v^o/R) \exp (- \Delta H_v^o/RT) \tag{5}$$

where J_A and J_B are the molar fluxes of the two vapor species, M_A and M_B are their molecular weights, and ΔH_v^o and ΔS_v^o are the standard enthalpy and entropy of the equilibrium reaction (4).

Equation (5) can be readily transformed into a more conventional rate equation which gives the flux of A_mB_n that vaporizes or condenses, but the form given in (5) has the advantage of emphasizing the essential connection between the rate equation for unretarded vaporization and the equation for flux through the orifice of an effusion cell inside which the equilibrium pressures of the vapor species have been established: The kinetic expression that describes free surface vaporization for any particular vaporization reaction and the expression for the rate of effusion from a cell of the equilibrium vapors from that reaction are identical functions of heat and entropy of the equilibrium reaction and of the kinetics of vapor movement.

It is an important experimental fact that the rate of at least two substances that vaporize dissociatively, cadmium telluride[14] and cadmium selenide,[15] have been demonstrated to be unretarded or nearly unretarded (vaporization coefficients 0.8 ± 0.2 and 0.7). Furthermore, since both demonstrations were made by means of the torsion-Langmuir method, they also showed that the vapor species leave the surface with a distribution of kinetic energies that must be close to Maxwellian normal to the surface.

To extend Langmuir's theory to unretarded dissociative reactions, it is only necessary to generalize the first of Langmuir's postulates while retaining the postulates of microscopic reversibility and independence of fluxes. We assume that molecules of A and B at equilibrium in the vapor of near stoichiometric composition always come to complete equilibrium with their solid upon striking the surface. Then by the postulates of microscopic reversibility and independence of fluxes, free surface vaporization in vacuum must yield a flux of molecules directed away from the surface which is indistinguishable in energy distribution and angular distribution from the flux of molecules that would pass through a plane in the equilibrium vapor.

To derive Eq. (5) from transition state theory and at the same time to predict correctly the experimentally observed pressure exerted against the surface by the vaporizing molecules, the transition state particles must be assumed to be identical in thermodynamic properties and in kinetic energy and energy distribution to the A and B molecules which pass through a plane in the equilibrium vapor. Such a transition state is of an unfamiliar kind in that the A and B molecules which together constitute the transition state particles are not even loosely bonded to each other. The unfamiliar nature of the transition state is a consequence of the fact that the highest potential energy along the reaction path in unretarded vaporization or condensation is coincident with the potential energy of the separated gas molecules.

To summarize the conclusions that can be drawn from what we have discussed up to this point for unretarded vaporization processes, Langmuir's theory is more satisfactory than transition state theory in that it requires fewer and more general postulates with no subsequent approximations. Furthermore, Langmuir's theory is superior to transition state theory in that it assumes, instead of a single average velocity for all transition state particles along the reaction coordinate, a Maxwellian velocity distribution normal to the surface of vaporization, an assumption which has been tested and proved correct for some vaporization processes. Dissociative unretarded vaporization can be understood by extending Langmuir's original assumptions to both (or all) vapor species that leave the surface. Langmuir's theory is inadequate to describe retarded vaporization reactions, but in the next section, modifications of transition state theory that adopt two of Langmuir's three hypotheses are developed. The resultant equations should provide an improved basis for analyses for some retarded vaporization processes.

TRANSITION STATES FOR SOME RETARDED VAPORIZATION PROCESSES

Several substances that undergo retarded vaporization have apparent enthalpies of activation which are greater than the enthalpy of the equilibrium reaction and apparent entropies of activation, when Langmuir's frequency factor is assumed, which are close to the entropy of the equilibrium reaction. It has been suggested that for such substances the rate limiting vaporization process may probably be either (1) desorption of the reaction products in excited states, or (2) desorption of equilibrium products to leave excited particles on the surface.[3]

The second of these suggested processes requires more detailed analysis because direct desorption of vapor molecules, like direct vaporization from ledge or kink sites, must be a higher energy and therefore probably a less important process than is dissociation from the catalytic sites of particles to non-catalytic adsorption sites of the surface, followed later by desorption.[16,17] A model for vaporization by this more probable sequence of steps can be developed by considering first the condensation process.

It will be assumed that the vapor molecules can be brought to complete equilibrium with the bulk condensed phase (a) only if they encounter thermally activated surface sites or molecules of the self adsorbed layer whose equilibrium mole fraction of total surface sites X_s is given by $X_s = \exp(-\Delta G_s^*/RT)$, and (b) a fraction of the encounters of vapor molecules with these sites or molecules given by $\exp(-\Delta G_e^*/RT)$ results in complete equilibration. If ΔG_e^* is small relative to RT, $\exp(-\Delta G_e^*/RT) \cong 1$, and essentially all encounters with the catalyst sites or molecules will cause equilibration. But in general, the fraction of the collisions of the vapor that result in immediate equilibration is given by $\exp(\Delta G_e^*/RT) \times \exp(-\Delta G_s^*/RT) = \exp(-\Delta G_r^*/RT)$.

The equation for the net molar flux J_n of the vapor which not only strikes the surface, but comes to equilibrium with the bulk condensed phase at a catalytic site or molecule can be written

$$J_n = (2\pi MRT)^{-1/2} P \left[\exp(-\Delta G_r^*/RT) + \right.$$

$$\left. \frac{\{1-\exp(-\Delta G_r^*/RT)\} \gamma_m \exp(-\Delta G_m^*/RT) \exp(-\Delta G_r^*/RT)}{\gamma_m \exp(-\Delta G_m^*/RT) \exp(-\Delta G_r^*/RT) + \gamma_d \exp(-\Delta G_d^o/RT)} \right] \qquad (6a)$$

The terms outside the bracket constitute the Langmuir expression for the total number of moles that strike the surface. The first term inside the bracket expresses the probability for direct reactive collisions of vapor molecules with the thermally activated catalytic sites. The quantity $\{1-\exp(-\Delta G_r^*/RT)\}$ expresses the probability that molecules of the vapor will make non-reactive collisions with the surface. These molecules that make non-reactive collisions can be assumed, in agreement with Langmuir's original hypothesis, to come to equilibrium with the surface with respect to their kinetic energies and rotational, and vibrational states. But some process necessary for complete equilibration such as a change in electronic state or a bond breaking and molecular rearrangement is assumed not to be possible except at the catalytic sites.

The adsorbed vapor molecules will still come to complete equilibrium if they make a reactive collision with an active site before desorbing. The remainder of the second term inside the brackets is an expression for the fraction of those molecules that initially adsorb without reaction, but that, rather than desorbing, undergo reactive collisions as a result of surface diffusion. The fraction is formed of a numerator that describes the frequency of reactive collisions by molecules that were initially adsorbed without reaction and a denominator that consists of the sum of the frequencies with which molecules either desorb or react. Here ΔG_d^o is the standard molar free energy for desorption of self-adsorbed vapor molecules, ΔG_m^* is the standard molar free energy of activation for surface diffusion, and the term $\exp(-\Delta G_r^*/RT)$, as before, gives the probability that those molecules which move to a new surface site will there undergo a reactive collision. The constants γ_d and γ_m are the molar frequencies with which molecules pass through the transition states for desorption and surface diffusion.

DeBoer has concluded that the frequency terms for surface jumps and for desorption are of the same magnitude.[18] There appears good reason for concluding they are often essentially equal. As noted above, the demonstration of unretarded vaporization by direct measurements of the force exerted by the vapor which leaves the surface proves a Maxwellian distribution of kinetic energies for molecules which acquire sufficient energy to escape. Furthermore, by comparing the mass flux and pressure for the vaporization of gallium nitride by the reaction $2GaN(s) = 2Ga(g) + N_2$, Mar and Searcy[19] demonstrated the kinetic energy of the products of this retarded reaction to also be Maxwellian, and Stickney[20] proved the kinetic energy and angular distribution of As_4 produced in retarded vaporization of arsenic both to be Maxwellian.

Surface diffusion is often interpreted in terms of random walk models for movement in near-surface crystal layers and in the self-adsorption layer. Observations such as those which have just been mentioned suggest that both desorption and diffusion in the self-adsorption layer can be viewed as manifestations of what might be called a random rocket launch model for movement of molecules of the adsorbed layer.

If a large number of rockets were randomly loaded with a relatively small amount of fuel and randomly pointed for launching without any limit to the minimum amount of fuel assigned to any rocket, relatively few rockets would have sufficient energy to escape from a gravitational field. Many rockets would fall back to the surface at various distances from their launching sites. Still more of the rockets would have insufficient energy to lift clear of the launching sites at all and would fall back on those sites. If the launches were from a stationary source into a frictionless atmosphere, components of movement parallel to the launching surface could be viewed as unrestrained translation, even though gravity acted on the rocket in a direction normal to the surface of the launching site.

Similarly, those molecules which vaporize are known to escape from the field of attraction of the condensed phase with kinetic energy distributions in all three coordinates that are random, that is with equilibrium or near equilibrium kinetic energy distributions for free gas molecules. More molecules must leave adsorption sites with insufficient kinetic energy normal to the surface for escape, but with energies and directions which can carry them out of the potential energy well formed by the surface particles that lie immediately adjacent to their adsorption sites. Those molecules which have left their potential energy wells would experience negligible forces in the plane parallel to the surface, and could in that plane achieve essentially gas-like velocity distributions. If motions in the two dimensions parallel to the surface are gas-like, the kinetic factor for surface diffusion in the self-adsorption layer γ_m should approach that for desorption.

A quantitative evaluation of the contribution to surface diffusion of particles moving by the random rocket launch mechanism requires complex summations,[21] which we hope to complete in our laboratory. Fortunately, the model for catalyzed vaporization does not require solution of this problem; the probability of a reactive collision by surface diffusion should depend mainly on the number of jumps before desorption and should be insensitive to the distance of movement in a single jump. This conclusion follows because molecules, viewed as projectiles launched from the surface, will encounter catalytic sites of the surface layer only at their points of impact and will seldom encounter other adsorbed particles in midjump.

When we accept the argument that $\gamma_d \cong \gamma_m$, use Langmuir's conclusion that vaporization in vacuum will occur by just the reverse of the steps followed for condensation in the equilibrium vapor, and make the substitution $P_{eq} = P^o \exp(-\Delta G_v^o/RT)$ we obtain from Eq. (6a)

$$J_v = \frac{P^o \exp(-\Delta G_v^o/RT)}{(2\pi MRT)^{1/2}} \left[\exp(-\Delta G_r^*/RT) + \frac{\{1-\exp(-\Delta G_r^*/RT)\}\exp\{-(\Delta G_m^* + \Delta G_r^*)/RT\}}{\exp\{-(\Delta G_m^* + \Delta G_r^*)/RT\} + \exp(-\Delta G_d^o/RT)} \right] \qquad (6b)$$

where ΔG_v^o is the standard free energy of vaporization.

If ΔG_r^* is small relative to RT or is small relative to $\Delta G_d^o - \Delta G_m^*$, the expression inside the square brackets of Eq. (6b) reduces to unity, and Eq. (1b), the temperature-dependent form of Langmuir's equation for vaporization in vacuum, is recovered. This result is consistent with the arguments that led to Eq. (6b) because at temperatures high enough so that ΔG_r^* is small compared to RT, all surface sites should be active in causing complete equilibration of vapor particles.

If ΔG_r^* is greater than RT so that $0 < \exp\left(-\frac{\Delta G_r^*}{RT}\right) \ll 1$, Eq. (6b) can be approximated

$$J_v = \frac{P^o \exp(-\Delta G_v^o/RT)}{(2\pi MRT)^{1/2}} \left[\frac{\exp\{-(\Delta G_m^* + \Delta G_r^*)/RT\}}{\exp\{-(\Delta G_m^* + \Delta G_r^*)/RT\} + \exp(-\Delta G_d^o/RT)}\right] \quad (7)$$

The physical meaning of this equation is that the vapor molecules commonly reach complete equilibrium with the condensed phase only after undergoing surface diffusion. For ΔG_r^* much greater than $\Delta G_d^o - \Delta G_m^*$, the first term of the denominator inside the square brackets of Eq. (7) is negligible in comparison to the second, and Eq. (7) becomes:

$$J_v = \frac{P^o \exp(-\Delta G_v^o/RT)}{(2\pi MRT)^{1/2}} \left[\exp -(\Delta G_m^* + \Delta G_r^* - \Delta G_d^o)/RT\right] \quad (8)$$

But $(\Delta G_v^o - \Delta G_d^o + \Delta G_m^*)$ is just the standard molar free energy difference ΔG_a^* between molecules in the two dimensional gas transition state for surface diffusion and in the bulk condensed phase. Accordingly, Eq. (8) becomes

$$J_v = \frac{P^o \exp\{-(\Delta G_a^* + \Delta G_r^*)/RT)}{(2\pi MRT)^{1/2}} \qquad (9)$$

Equation (9) differs from the result for a model which assumes that direct desorption occurs from active sites in that Eq. (9) has ΔG_a^* where the direct desorption model would place ΔG_v^o.

Equation (9) can be generalized to describe the steady state coupled fluxes of molecules in catalyzed dissociative vaporization. As an example, suppose for reaction 4, $A_mB_n(s) = mA(g) + nB(g)$, vaporization of A atoms or molecules is unretarded, but B atoms or molecules vaporize at a rate limited by their dissociation from thermally activated surface sites. Then

$$J_A = \frac{P_A^o \exp\,(-\overline{\Delta G_A^o}/RT)}{(2\pi M_A RT)^{1/2}} \qquad (10)$$

and

$$J_B = \frac{P_B^o \exp\,(-\overline{\Delta G_B^*}/RT)}{(2\pi M_B RT)^{1/2}} \qquad (11)$$

where $\overline{\Delta G_A^o}$ is the partial molar standard free energy of vaporization of A in the equilibrium reaction and also the partial molar free energy of activation of A to the transition state for vaporization; $\overline{\Delta G_B^*}$ is the partial molar free energy of activation for the retarded process that involves dissociation of B molecules from catalytic sites or particles.

With the standard pressures chosen as 1 atm,

$$J_A^m \cdot J_B^n = (2\pi RT)^{-(m+n)/2} (M_A)^{-m/2} (M_B)^{-n/2} \exp\left(-\Delta G^*/RT\right) \qquad (12)$$

where $\Delta G^* = m\overline{\Delta G}_A^o + n\overline{\Delta G}_B^*$. Note that Eq. (12) is identical to Eq. (5) which describes unretarded dissociative vaporization except that $\Delta G^* > \Delta G_v^o = \Delta H_v^o - T\Delta S_v^o$.

DISCUSSION

As pointed out in earlier papers, plots of the logarithm of pressures in free surface vaporization against the reciprocal of the temperature provide useful tests of the nature of the probable rate limiting step.[3,6] Three of the conclusions of the earlier papers are: (1) When the apparent enthalpy of activation for the reaction, which can be calculated from the slope of the plot, is smaller than the enthalpy of the equilibrium reaction, the rate limiting step must be a surface step rather than desorption. (2) The apparent activation enthalpy should be the same to within expected experimental error as the enthalpy of the equilibrium reaction, if the free angle ratio theory, which has been used to explain retarded vaporization for polar molecular substances[12,22] is applicable. (3) Non-linearity in the plot is evidence that two successive steps of different activation enthalpies have comparable rates in the range of study.[17]

It was argued in previous papers that when the Langmuir equation or its generalization for dissociative vaporization is used for a substance with retarded vaporization to calculate the apparent entropy of activation and that entropy is found to be nearly identical to the entropy of the corresponding equilibrium vaporization reaction, the near identity constitutes strong, but not conclusive, evidence that the rate limiting process is either desorption of vapor in excited states or desorption of vapor molecules in a process that leaves excited surface sites or surface particles behind.[3,6] We wish to discuss here in more detail and on the grounds of the analysis made in the previous section, the vaporization of such substances.

We can conveniently discuss in terms of Eq. (9) the range of possible apparent enthalpies and entropies of activation for vaporization when its rate is limited by dissociation from catalytic sites or particles, since the generalization for congruent dissociative vaporization follows directly. The entropy contributions to $\Delta G_a^* + \Delta G_r^*$ of Eq. (5) or Eq. (9) are ΔS_a^*, the entropy of formation of a two dimensional gas transition state, ΔS_s^* the entropy of formation of the activated site or surface particle, and ΔS_e^*, which would represent an extra thermal entropy of excitation if not all collisions between the two dimensional gas molecules and catalytic sites or particles are reactive.

The entropy of formation of a two dimensional gas from a bulk condensed phase should be less than for formation of the corresponding three dimensional gas by the difference between the entropy contribution of one translational degree of freedom and the low frequency vibrational entropy that acts on the two-dimensional gas normal to the surface. For a gas molecule of molecular weight 100 at 1000°K, the difference between ΔS_d^*

and ΔS_v^o the entropy of vaporization lies between -16 and 0 cal per mole per deg. The molar entropy of formation of surfaces for metals can be calculated from the temperature dependence of their surface tensions to range from 1 to 6 cal per mole of surface atoms per deg. Entropies of formation of special surface sites such as kinks in ledges must be more positive than the average for surface formation, and the entropies associated with extra thermal excitations for reactive collisions are also positive.

A range of apparent activation entropies from perhaps 15 cal per mole per degree less than the entropy of the equilibrium reaction to perhaps 6 cal per mole per deg. more could be consistent with a catalyzed vaporization process of the kind considered in this paper.

But the apparent activation free energy for any retarded process must exceed the standard free energy of the equilibrium reaction. Consequently, when apparent activation entropies for vaporization are equal to or greater than the entropies of the equilibrium reaction, the apparent activation enthalpies for retarded vaporization must be greater than the enthalpies of the equilibrium reactions. This means that measurements of vaporization fluxes and of their temperature dependence do not yield sufficient evidence to distinguish vaporization reactions which yield vapor species in activated states from reactions which are retarded by catalyzed reactions in the self adsorption layer.

Fortunately, the properties of the vapor molecules that leave the surface can be studied to further delineate the probable rate limiting step: The saddle point potential energy for the desorption step must coincide with the energy of the molecules that escape from the surface so that those molecules must be the transition state particles for the desorption step of the vaporization process whether or not the overall reaction rate is limited by desorption.

Unless high energy encounters with catalytic sites or particles is rate limiting for condensation, the assumed reversibility of paths makes it unlikely that molecules would vaporize with significant excess kinetic energy. Consequently, an experimental observation of excess kinetic energy or of a non-equilibrium angular distribution of spacial trajectories of molecules that leave the surface would constitute evidence for a catalyzed surface step.

However, the observation of an equilibrium distribution of energies does not prove that a catalyzed surface step can be ruled out as rate limiting. Excess kinetic energy may be lost to the surface after a molecule separates from a catalytic site. Brumbach and Rosenblatt[23] have used a Lennard-Jones 9-3 potential to calculate for As_4 the extent to which gaseous and evaporating molecules should equilibrate with the surface for various assumed potential energy wells. Our Eq. (9), when only a fraction of gas molecule encounters with catalytic sites given by $\exp(-\Delta G_e^*/RT)<1$ results in equilibration, corresponds with their assumed conditions. They conclude that some detectable fraction of evaporating As_4 molecules may leave the surface thermally excited, but that a significant fraction would attain equilibrium.

Some vaporization processes may be retarded because the formation of vapor molecules in their ground electronic states from atoms adsorbed on the condensed phase surface requires forbidden spectroscopic transitions. The products of free surface vaporization may then include a lower than equilibrium concentration of molecules in ground electronic states. Whether or not a non-equilibrium concentration of ground state molecules is formed in free surface vaporization should be determinable by spectroscopic means. In our laboratory an inhomogeneous field electromagnet coupled with a quadrupole detector will be used to seek evidence of non-equilibrium singlet state/triplet state ratios for S_2 molecules produced in a retarded dissociative vaporization reaction.

CONCLUSIONS

It has been shown that the prediction of Langmuir that molecules should leave a surface in free surface vaporization with an equilibrium distribution of kinetic and internal energy states has been confirmed experimentally for a number of substances, including two that undergo congruent dissociative vaporization. To reconcile transition state theory to the experimental observations for these unretarded vaporization reactions requires that the kinetic term of the rate expression be derived from the average velocity of the equilibrium gas molecule normal to the surface. And to predict rates of unretarded dissociative vaporization from transition state theory requires that the transition state particles be identified, not as clusters of a single kind of particle, but as the separated molecular products of the equilibrium vaporization reaction.

Those substances that experience a potential energy barrier to complete equilibration when their vapor molecules strike their surfaces need not vaporize to molecules that are equilibrated with respect to translational and internal excitations. Experimental data for two such substances, however, show that their translational states are equilibrated.

These observations make it appear probable that particles of the self-adsorption layer of substances which undergo retarded vaporization often almost fully equilibrate with respect to vibrational, rotational, and translational degrees of freedom, though they may not be at equilibrium with the bulk condensed phase with respect to forbidden electronic transitions or with respect to bond-breaking and rearrangement processes. An expression for catalyzed vaporization that assumes the rate of arrival at catalytic sites to depend upon gas-like translation in the self-adsorption layer parallel to the surface was derived to accord with these inferences. The model is generally consistent with the extensive experimental observations and the theoretical conclusions formed by Rosenblatt and co-workers as to the critical rate of sites associated with ledges in arsenic vaporization.[24,25]

It should be emphasized that we do not consider that the postulates that we have described need be appropriate to all retarded vaporization reactions. In particular, for vaporization that occurs with an activation energy much lower than the energy of the equilibrium reaction, such as amonium chloride dissociative vaporization,[26-28] rate equations that employ a frequency factor such as that used in absolute reaction rate theory may well be superior. But the kinetic factor for the desorption step, whether or not that step is maintained at equilibrium with the bulk condensed phase, is better derived from the average translational velocities of the equilibrium products of the desorption process. Fortunately, as pointed out above, this assumption is subject to direct experimental test.

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