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The Influence of Surfaces on Vapor Pressures

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Abstract: In the present paper I extend the analysis of the consequences of dynamic internal equilibrium in crystalline particles (A.W. Searcy, J. Chem. Phys., in press) to include the self-adsorption layer and vapor phase. Dynamic equilibrium results in a minimum Gibbs free energy for the particle-vapor system. The condition found for equilibrium is compatible with measurements of capillary rise, capillary condensation, and at least some data for particle-vapor equilibrium. New tests of the model are suggested.

Introduction

In the course of evaluating a conjecture of Gibbs¹ about the influence that the relatively weak attachments of molecules at crystal corners and edges may have on equilibrium crystal shapes, I showed that dynamic equilibrium between parts of a crystal, which have different bonding environments--for example, crystal edges and adjacent surfaces--creates a vacancy distribution different from that which is calculated on the assumption that the vacancy concentrations on each characteristic kind of site are independent.² I further showed that the dynamically determined vacancy distribution makes the total Gibbs free energy G_{sy} for the system comprised of the particle and its surface a minimum at constant temperature T , pressure P , and fixed number of each energetically distinguishable kind of site.

In the present paper I evaluate the pressure that would be established by dynamic equilibrium between a one-component particle which is at internal equilibrium and its vapor at constant temperature, and I show that the vapor pressure so derived makes G_{sy} a minimum for the system comprised of the particle, its surface, and its vapor. The predicted dependence of vapor pressure on particle size is significantly different from that of classical surface thermodynamic theory. The difference arises because the classical theory, as pointed out by Gibbs,¹ rests on two assumptions; one of these implicitly forbids the consequence of dynamic equilibrium which was demonstrated in Ref. 2. In the discussion section, I point out that recent experimental observations are incompatible with that classical assumption,^{3,4} and I suggest further experiments to test the model.

Theory

There is ample and persuasive evidence that, when crystals are undergoing net vaporization or condensation, surface features such as terraces, ledges, and kinks and nonequilibrium defects--especially screw dislocations--play important roles.⁵ But our present interest is in obtaining an expression for dynamic equilibrium for a crystal which may have perfectly faceted surfaces and which has as its only defect its equilibrium distribution of vacancies.

It has long been accepted that equilibrium between a one-component condensed phase and its vapor is maintained by a balance of molecular fluxes between the self-adsorption layer of the condensed phase and its vapor.^{5,6} Therefore, we can evaluate dynamic equilibrium between a particle and its vapor by first obtaining an equation for the equilibrium flux exchange between the self-adsorption layer and the remainder of the crystal, and by then incorporating the accepted relation for adsorption layer-vapor equilibrium.

In Ref. 2, the molecular flux J'_{ij} from n'_i lattice sites of one characteristic bonding environment to n'_j adjacent sites of a different characteristic bonding environment was described by the equation

$$J'_{ij} = n'_i v_{ij} g'_{ij} \exp[-(G^* - G_i^t - G_{vj}^t)/kT] X_i X_{vj}, \quad (1)$$

where v_{ij} is the frequency with which a molecule on an n'_i site and a vacancy on an adjacent n'_j site are excited to the thermal (i.e., nonconfigurational) transition state free energy G^* , g'_{ij} is a geometrical factor, G_i^t is the thermal free energy per i molecule, G_{vj}^t is the thermal free energy per j -site vacancy, k is the Boltzman

constant, X_i is the mole fraction of occupied i -sites, and X_{vj} is the mole fraction of vacant j -sites. When J'_{ij} of Eq. (1) is set equal to J'_{ji} , which is described by the same terms with reversed subscripts, the nonthermodynamic terms cancel and the relation then found is²

$$G_i^t - G_{vi}^t - kT \ln(X_{vi}/X_i) = G_j^t - G_{vj}^t - kT \ln(X_{vj}/X_j) \quad (2)$$

As demonstrated in Ref. 2, Eq. (2) can also be derived by minimizing the free energy of an i - j system with respect to the distribution of vacancies among the total number of sites that would be formed by independent minimization of the free energies of the i - and j -collections of molecules with respect to vacancy formation.

In Ref. 2, the self-adsorption layer was not considered. But both the kinetic and the thermodynamic analyses should apply to the exchange of molecules and vacancies between any two collections of molecules (including the collections formed by bulk molecules and a surface) for which the regular solution approximation can be used. A self-adsorption layer usually has a low concentration of molecules so that the regular solution assumption implicit in Eq. (1) is valid for the self-adsorption layer, as it is for parts of a crystal with low vacancy concentrations. The extent to which the conclusions reached in this section depend on modeling assumptions is discussed later.

When a identifies the dilute adsorption layer on an outermost surface layer s in Eq. (2), the equation written in exponential form is

$$(X_a/X_{va}) \exp(G_a^t/kT) = (X_s/X_{vs}) \exp[(G_s^t - G_{vs}^t)/kT] \quad (3)$$

Because for a dilute adsorption layer $G_{va}^t = 0$, it does not appear in Eq. (3). The left side of Eq. (3) is identical to the partition function calculated for an adsorption layer from statistical mechanics.^{7,8} If the equilibrium crystal has more than one kind of surface facet, for example (111) and (100) facets for a face centered cubic crystal, each kind of surface and its adsorption layer will establish an equilibrium like that described by Eq. (3). The mole fraction of occupied sites and the value of G_a for a (100) self-adsorption layer are different from the value for a (111) self-adsorption layer, but the equilibrium value of $(X_a/X_{va})\exp(G_a/kT)$ is the same for both, just as the right side of Eq. (2) has the same value if collections $k, 1, \dots$ etc. are substituted for collection j .

We will make use of the equilibrium relations between the self-adsorption layer on a particular surface, and the outermost complete layer (except for dilute vacancies) of that surface, and the bulk crystal for which

$$(X_s/X_{vs})\exp[(G_s^t - G_{vs}^t)/kT] = (X_b/X_{vb})\exp[(G_b^t - G_{vb}^t)/kT] \quad (4)$$

If an adsorption layer on an ordered solid is dilute enough so that interactions between the adsorbed species can be neglected, the desorption flux is

$$J_{ag} = P^0 X_a A \exp[-(G_a^* - G_a^t)/kT] / (2 \pi mkT)^{1/2} \quad (5)$$

where J_{ag} is the molecular flux from the adsorption layer to the gas phase, P^0 is the standard pressure, A is the surface area, and m is the

molecular mass. The corresponding flux from the gas phase that traverses any activation energy barrier to adsorption is when the pressure is equal to the fugacity

$$J_{ga} = P_g X_{va} A \exp[-(G^* - G_g^0)/kT] / (2 \pi mkT)^{1/2}, \quad (6)$$

where P_g is the pressure of the gas and G_g^0 is the free energy per gas molecule when the gas is at its standard state pressure P^0 . When J_{ag} is set equal to J_{ga} , the result can be put in the form

$$(X_a/X_{va}) \exp(G_a^t/kT) = (P_g/P^0) \exp(G_g^0/kT). \quad (7)$$

This same relation can be derived by setting the derivative of the total free energy of the gas with respect to the number of gas molecules equal to the derivative of the total free energy of molecules adsorbed on a fixed number of surface sites with respect to the number of adsorbed molecules.

Equations (2), (4), and (7) show that at dynamic equilibrium

$$(P_g/P^0) \exp(G_g^0/kT) = (X_i/X_{vi}) \exp[(G_i^t - G_{vi}^0)/kT] = \dots \quad (8)$$

The particle shape that, for a constant total number of constituent molecules, gives the lowest values of the quantities separated by equal signs is the equilibrium shape; other shapes that satisfy Eq. (8) are metastable.

Equation (8) was derived for a particle formed with ordered bulk and surface sites and with either the vacancy concentration or, for the

self-adsorption layer, the molecular concentration on each characteristic kind of site low enough so that the regular solution model could be used to calculate configurational entropies. For edges, surfaces, and self-adsorption layers at high temperatures, concentrations of the minor equilibrium defect may become high and the distributions may become nonrandom. But the conclusion that dynamic equilibrium produces a vacancy distribution which minimizes the particle free energy can be expected to remain valid. For liquids, the vacancy model is inadequate,⁹ but the equilibrium distribution of molecules and free volume between a liquid and its surface can be expected to be an exponential function of the bonding energies in the liquid and surface, like that found in Eq. (8).

We can obtain from Eq. (8) an equation which reveals the influence of particle size when edge and corner effects are neglected. To do so we assume that all molecules near enough to the surface to have average molecular free energies significantly greater than the free energies of bulk molecules form a single collection of n_s molecules of the same thermal free energy per molecule G_s^t . The reference state is P_b , the vapor pressure for the solid when the ratio of surface area to bulk volume approaches zero. For such a particle, the vapor pressure depends on the relation

$$G_g^o + kT \ln(P_b/P^o) = G_b^t - G_{vb}^t - kT \ln(X_{vb}^o/X_b^o) \quad (9)$$

where the superscripts on the mole fractions identify them as those for the solid in its standard state. When surface effects are negligible, $G_{vb}^t = kT \ln X_{vb}^o$, and Eq. (9) becomes

$$G_g^0 + kT \ln(P_b/P^0) = G_b^t + RT \ln X_b^0 = G_b^0, \quad (10)$$

where G_b^0 is the standard free energy of the bulk solid.

For a particle of significant surface area,

$$G_g^0 + kT \ln(P_g/P^0) = G_b^t - G_{vb}^t - kT \ln(X_{vb}/X_b) \quad (11)$$

Combining Eqs. (9) and (11) gives, because $X_b \cong X_b^0 \cong 1$,

$$P_g/P_b = X_{vb}^0/X_{vb} \quad (12)$$

The equilibrium mole fraction of vacancies in an isolated collection of i molecules in identical bonding environments is $X_{vi} = \exp[-G_{vi}^t/kT]$. Therefore, the total number of vacancies, generated on bulk and surface sites n_{vt} , if the difference between mole fraction of vacancies and their mole ratio is neglected, is

$$n_{vt} = n_b \exp[-G_{vb}^t/kT] + n_s \exp[-G_{vs}^t/kT] \quad (13)$$

Dynamic equilibrium redistributes these vacancies according to Eq. (2), and leads in the same approximation used in writing Eq. (13) to

$$(n'_{vs}/n_s) \exp[(G_{vs}^t - G_s^t)/kT] = (n'_{vb}/n_b) \exp[(G_{vb}^t - G_b^t)/kT] \quad (14)$$

where the primes indicate that Eq. (14) describes the changed numbers of vacancies established by dynamic equilibrium. Combining Eqs. (13) and (14) with $X_{vb} \cong n_{vb}/n_b$ and $n_{vt} = n'_{vb} + n'_{vs}$ gives

$$n'_{vb} = \frac{n_b \exp[-G_{vb}^t/kT] + n_s \exp[-G_{vs}^t/kT]}{1 + (n_s/n_b) \exp[(G_{vb}^t - G_b^t - G_{vs}^t + G_s^t)/kT]} \quad (15)$$

Thus, because when $n_s/n_b \rightarrow 0$, Eq. (15) reduces to $n_{vb}^0 = n_b^0 \exp[-G_{vb}^t/kT]$,

$$P_g/P_b = \frac{1 + (n_s/n_b) \exp[(G_s^t - G_{vs}^t - G_b^t + G_{vb}^t)/kT]}{1 + (n_s/n_b) \exp[(G_{vb}^t - G_{vs}^t)/kT]} \quad (16)$$

For $n_s/n_b \ll 1$, Eq. (16) can be put in the form

$$\ln(P_g/P_b) = (n_s/n_b) \{ \exp[(G_s^t - G_{vs}^t - G_b^t + G_{vb}^t)/kT] - \exp[(G_{vb}^t - G_{vs}^t)/kT] \} \quad (17)$$

But a sample calculation in the Discussion section shows that this approximation is unsatisfactory even for particles of $\sim 10 \mu\text{m}$ cross section.

The dependence of vapor pressure on particle size found in Eq. (16) is a consequence of either of the alternate assumptions: (a) from kinetics, that molecular fluxes are balanced between surface and bulk, or (b) from thermodynamics, that the total number of vacancies

formed in the surface and in the bulk must be so distributed as to minimize the total particle free energy. Classical thermodynamic theory for particle-vapor equilibrium is a consequence of two assumptions which are particular to surface thermodynamics.

The first assumption, as stated by Gibbs,¹ is that masses of two phases separated by a surface S can "be divided into three parts by two surfaces, one on each side of S and very near to that surface, although at such a distance as to lie entirely beyond the influence of the discontinuity in its vicinity." This assumption implicitly denies the possibility that a surface can influence the properties of adjacent phases by means of molecular motions. But it was shown in Ref. 2 that dynamic equilibrium in a crystalline particle makes the vacancy concentration in any part of the particle dependent upon the bonding environment of all other parts. The molecules of a liquid are more mobile than molecules of the solids from which the liquids are formed, so that molecular motions in liquids must produce a similar effect of surfaces on the bulk liquid. Unless the demonstrations of Ref. 2 are faulty, this first special assumption of classical surface thermodynamics must be invalid.

The second assumption identified by Gibbs was that because his Eq. (499),

$$\sigma \delta s - p' \delta v' - p'' \delta v'' = 0 ,$$

where δs is the change in surface area and p' and p'' are the pressures in the adjacent phases which are subject to the differential volume changes $\delta v'$ and $\delta v''$, "has evidently the same form as if a membrane

without rigidity and with a tension σ , uniform in all directions, existed at the dividing surface," the surface should be treated as if in tension. As long as it is supposed that a plane surface has no significant influence on the properties of adjacent bulk phases, some such assumption as this one is necessary in order to explain the experimental fact that surfaces do influence chemical and physical behavior. But as shown below, such an assumption may be unnecessary when molecular motions are taken into account.

Discussion

The derivation of the condition for maximum stability of a crystalline particle which was presented in Ref. 2 is consistent with the classical analysis of Gibbs. Gibbs assumed that the most stable shape for a crystalline particle of fixed total number of constituent molecules n_p is the shape which requires the minimum work to form the surface, and in a footnote following Eq. (665) he suggested that his solution is inexact because it neglects the fact that molecules in edge sites are less strongly bonded than molecules in parts of the surface away from edges. In making this suggestion, he clearly anticipated the concept of dynamic equilibrium. In Ref. 2, I used that concept to obtain the conditions for internal particle equilibrium and showed that these conditions minimize the Gibbs free energy of formation of a particle of fixed n_p and fixed number of various kinds of sites with the absolute minimum work for a particle of fixed n_p being given by the shape that minimizes $\Sigma(n_i G_i + n_{vi} G_{vi} + n_i kT \ln X_i + n_{vi} kT \ln X_{vi})$.

In the present paper I have shown that when the principle of dynamic equilibrium is extended to include with the particle its

self-adsorption layer and its vapor, the equilibrium corresponds to a minimum in the free energy of the defined particle-vapor system.^F This extension of the analysis of Ref. 2 is necessarily at variance with the classical theory because the classical theory rules out the possibility that a surface can influence the bulk properties of the phases it separates.

The classical theory has nearly universal acceptance, and some of its predictions are markedly different from those of the dynamic model. Nonetheless, much of the present data do not appear to be incompatible with the dynamic model. The most direct tests of surface thermodynamic theory are based on experiments of three general kinds: measurements of capillary rise, measurements of the influence of capillary condensation on vapor pressures, and measurements of particle-vapor equilibrium. These kinds of experiments will be considered in turn.

Capillary rise experiments are equally consistent with the classic and the dynamic model. In a gravitational field gradient, any gas phase must approach a steady state distribution in which the field gradient is balanced by a gas pressure gradient.¹¹ Consequently, the vapor pressure of a liquid is a (very weak) function of height in the field. The height to which a liquid will rise (or fall) from the level

^F Equilibrium between a vapor and a liquid particle at constant pressure of the vapor is always unstable in the sense that any increase in n_p that results from a statistical fluctuation yields a particle of differentially lower vaporizing flux than that of the parent particle. But the explanation given elsewhere for the long persistence of crystalline particles of metastable shapes¹⁰ also implies that those particles which have favorable ratios of constituent molecules to low-energy bonding sites can be locally stable to growth as well as to shape change.

of a reservoir can be predicted by minimizing the liquid surface free energy with respect to height in the field.¹² In the dynamic model, the liquid in a reservoir and capillary system would constitute a subsystem which is at internal equilibrium. Because the number of surface molecules in the liquid in such a system is usually very much less than the number of bulk molecules, the vapor pressure throughout the liquid would be essentially unchanged from that of the bulk liquid. But that vapor pressure is a function of height and must be lower at the meniscus than at the reservoir surface by the amount observed. If an identical reservoir and capillary system were placed so that its reservoir surface stood at the level of the top or bottom of the meniscus, the vapor pressure of that second reservoir at its surface would be the same as that at the top or bottom of the meniscus of the first reservoir.

For capillary condensation the classical theory is clearly inadequate. The long-standing evidence by Shereshefsky¹³ that vapor pressure reductions for liquids condensed in $\sim 1 \mu\text{m}$ capillaries are as much as 90 times those predicted by the classical theory has been doubted but never disproved, and similar results have been obtained in additional studies.¹⁴ It seems now to be widely accepted that in small capillaries the vapor pressure lowering must be related not to the capillary radius but to an effective radius corrected for the thickness of the film of liquid adsorbed on the capillary walls,^{4,5} and perhaps for an additional contribution to the reduction from the adsorption layer.⁴ What is particularly interesting about two concordant studies is that they provide evidence that the vapor pressure of a layer of liquid adsorbed on a plane surface is measurably reduced from that of the bulk phase when the liquid is as much as $0.1 \mu\text{m}$ thick. This is

direct evidence that the thermodynamic influence of a plane interface or of an adjacent phase extends over distances great enough to make the first assumption of classical surface thermodynamic theory inadequate for analysis of many phenomena now under active study--for example, the properties of semiconductor films or of the sintering of submicron particles. The dynamic equilibrium model is qualitatively consistent with the observations for capillary condensation and adsorption. For a solid film on a massive substrate equilibrium between successive layers would be characterized by equations like Eq. (2), and if interactions with the substrate are strong, its influence could be important in relatively thick films regardless of the shape of the interface. I plan to develop a quantitative model for dynamic equilibrium in liquids condensed on surfaces and/or in capillaries.

Several studies of particle-vapor equilibrium have been considered to confirm the very small increases in vapor pressure predicted by the Kelvin equation,^{16,17} but the experiments have required interpretations of kinetic measurements or of the nature of approach to equilibrium which make the changes calculated in vapor pressure sometimes only lower limits and sometimes of problematic value.

Woodland and Mack¹⁸ and Shereshefsky and Steckler¹⁹ measured the rates of vaporization of suspended droplets in air. Fits to the Kelvin equation were obtained by assuming that the rate-limiting process was diffusion into air from a vapor cloud that was significantly larger than the droplets themselves. That diffusion was rate limiting is unproved. If it is limiting, a more conventional interpretation would be that the equilibrium diffusion source is the particle surface, so that the

dependence of vapor pressure on $1/\text{radius}$ in the experiments of Woodland and Mack are 10^3 times the prediction of the Kelvin equation.

Interpretation of the experiments of La Mer and Gruen²⁰ involved the assumption that droplets of a nonvolatile liquid which were initially too small to scatter light grew by condensation of a more volatile liquid to observable dimensions. The droplets were introduced into a flask containing a master solution of the two liquids. When the flask was shaken, the intensity of light scattering "immediately" increased. It is possible that the droplets grew in large part by agglomeration and may have contained a much lower concentration of the volatile component than has been assumed.

The interpretation of measurements of the rates of vaporization of very small metal particles in an electron microscope by Sambles, Skinner, and Lisgarten²¹ require some assumptions that cannot be verified, in particular that the vaporization coefficient is independent of particle size. It is possible that as the particles grow smaller minor impurities build up on their surfaces to reduce their vaporization rates and to make the apparent dependence of vapor pressures on radius smaller than the true value. But it is hard to conceive of systematic errors large enough to reconcile these particular experiments with the predictions of the dynamic model, so they must be considered in fundamental disagreement with it.

Because in the dynamic model vapor pressure changes are exponential functions of n_s/n_b , much greater changes are predicted with decreasing radius than are predicted by the Kelvin equation. The approximate magnitudes can be illustrated with data for metals. For several metals, the enthalpies of formation of vacancies average about

$0.28 \Delta H_g$, and the enthalpy of formation per monolayer of surface average about $0.25 \Delta H_g$, where ΔH_g is the enthalpy of vaporization.²² The entropy of surface formation per mole of monolayer is about 2 k, and the entropy of formation of defects in the bulk and surface must be nearly equal. The enthalpy of formation of vacancies in metal surfaces is probably 2/3 to 3/4 this value, say $0.20 \Delta H_g$. Using these values in Eq. (16) with $\Delta G_g/kT = 31.8$, which is approximately the value for gold at 1300°K, leads to a predicted increase in vapor pressure of $\sim 3.7 \times 10^4 n_s/n_b$. This result implies that particles of 0.1 mm to 1 mm diameter would have vapor pressures of the order of 10% higher than particles 1 cm or greater in diameter. If such a large effect exists, and if it were expected by experimenters, it should of course have long ago been discovered. But my own experience has been that when confronted with the results of very careful measurements of relative vaporization rates for which the measured internal consistency appeared to justify a claim of only 4% systematic error, I concluded that well-established theoretical principles fixed the actual error as at least 11%.²³ Others may have reached similar conservative conclusions.

It is probably much harder to hold errors in relative pressures to the order of 10% in most experiments than the investigator usually recognizes. Tests of whether the dynamic model is tenable for particles should be based on experiments with particles of 1 μm or smaller for which the expected pressure increase is more than a factor of ten and for which the classical theory predicts less than a 10% increase. Sintering of the particles would have to be avoided. An alternate approach would be to measure the relative vapor pressures of thin unsupported metal sheets. The classical theory predicts that their

vapor pressures should be independent of thickness; the dynamic equilibrium model predicts that their vapor pressures should increase with n_s/n_b . The problem with such an experiment is likely to be that the sheets would prove unstable to shape changes.

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