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THE KINETICS OF PARTICLE VAPOR EQUILIBRIUM (1)

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ABSTRACT

A standard formulation of reaction kinetics is used to derive the condition for dynamic equilibrium between a crystalline particle and its self-adsorption layer. The result, when combined with the well-known condition for adsorption layer-vapor equilibrium, yields an expression for the relationship between the equilibrium vapor pressure and a vacancy-molecule distribution function for the particle. The effects of particle shape and size on vapor pressures are different from those of the Kelvin equation, but are consistent with the thermodynamic requirements that the internal free energy of the particle be a minimum at constant T and P. The classical theory, which neglects vacancies, is not.

Equilibrium between a one-component condensed phase and its vapor is maintained by a microscopically reversible exchange of molecular fluxes between the self-adsorption layer of the condensed phase and its vapor. (2) Therefore, dynamic equilibrium between a particle and its

vapor can be evaluated if an expression is also found for the equilibrium flux exchange between the self-adsorption layer and the remainder of the crystal.

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 is described by the equation (3),

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

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_i^* , 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 Boltzmann 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 is (3)

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

The molecular flux from a dilute self-adsorption layer to its underlying outer surface layer and the reverse flux from the surface layer to the self-adsorption layer can be described by expressions of

the same form as Eq. 1, and when the two fluxes are equal the ratio of mole fractions of occupied to unoccupied self-adsorption sites X_{a1}/X_{val} on surface 1 must be given by

$$G_{a1}^t - G_{val}^t - kT \ln(X_{val}/X_{a1}) = G_1^t - G_{v1}^t - kT \ln(X_{v1}/X_1) \quad (3)$$

But equalities of the same form are required by dynamic equilibrium for all subparts of the crystal, (3) so Eq. 3 assures dynamic equilibrium between the self-adsorption layer on each characteristic surface with the entire crystal.

When the left hand side of Eq. 3 is rewritten in exponential form, it is seen that the partition function that assures equilibrium between the self-adsorption layer of any crystal face and the remainder of the crystal is the same partition function that has been shown to be consistent with dynamic equilibrium between gases and dilute adsorption layers.(4)

$$(P_g/P^0) \exp(G_g/kT) = (\theta_1/(1 - \theta_1)) \exp(G_{alc}^t/kT) \quad (4)$$

Here the familiar symbol θ_1 is substituted for X_{a1} and the partial molecular thermal free energy of the component replaces $G_{a1}^t - G_{val}^t$ for the species. Thus dynamic equilibrium of a particle with its vapor is a function through the equalities of Eqs. 2, 3, and 4 of the vacancy distribution in all parts of the particle. The vapor pressure increases with decreasing particle size because an increase in the fraction of surface, near-surface, and edge sites increases the equilibrium value of each of the equal terms. This result is inconsistent with classical surface thermodynamic theory, but

consistent with the requirement that the internal free energy of a particle be a minimum for its size and shape when it is at equilibrium with its vapor.(3)

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