Physicochemical Principles of the Theory Concerning Polymolecular Adsorption Films and Capillary Condensation of Polar Liquids

I. Basic Thermodynamics of Sorption Films of Polar Liquids

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Analyzed are the general conditions of thermodynamic equilibrium in polymolecular adsorption films of polar liquids. Thermal equations of adsorption and a capillary condensation are derived for systems with a developed interphase boundary.

1. General Conditions of Equilibrium in Polymolecular Adsorption Films. The existence of polymolecular films in thermodynamic equilibrium at the surface of a solid has been demonstrated in numerous experimental and theoretical studies by B. V. Deryagin and his students [1-4]. An adsorption film of polar liquid has a sharply defined interphase boundary with its vapor as well as with the bulk liquid and, therefore, formally may be treated as a separate phase [4]. It differs from the bulk liquid in that it is located in the potential field of the solid surface and, as a result, acquires a more ordered (oriented) structure.

If the adsorbent surface is regarded as an "extraneous wall" and its effect on the film is accounted for in terms of the potential field of the surface, then the adsorption film together with its vapor can be viewed as a thermodynamic system in a nonuniform external field.

When the field of the adsorbent surface is nonuniform, then the adsorbate molecules exist under unequal conditions and the equilibrium distribution of particles in the field, while their total number in the system remains unchanged, follows the equation:

$$\mu + N = \text{const.} \quad (1)$$

Owing to the nonhomogeneous electrical topography of the adsorbent surface, polymolecular adsorption will occur in discrete domains of rather small dimensions (of the order of $10^{-7}$-$10^{-5}$ cm). In films of such small dimensions the thermodynamic potentials cease to be additive over the mass, becoming functions of the film thickness and of the domain size. From a strictly phenomenological viewpoint, this situation may be regarded as evidence of certain characteristics which distinguish an adsorption film from the bulk liquid.

The thickness of an adsorption film and the dispersivity of the adsorbent can both vary over wide ranges and, therefore, the applicability of the thermodynamic method to an analysis of adsorption films may be limited. Gibbs' fundamental adsorption equation [5], which relates the variations in surface tension in the chemical potential of a film to its thickness, remains valid for a plane interphase boundary until the system has become completely homogenized [6], inasmuch as all parameters in this equation do not depend on the location of this interphase boundary. In the case of very curved interphase boundaries the tension surface may degenerate and the surface tension of the film will then depend on their location. As has been shown in [6, 7], the thermodynamic (quasithermodynamic) method, which yields not only good qualitative but also quantitative results, may be applied to an analysis of thin objects like films. If the equimolecular interface is regarded as the geometrical boundary, then variations in surface tension will correspond to actual variations in the interface curvature and in the film thickness [8].

With all this in mind, we will now analyze the conditions of mechanical equilibrium in a single-component two-phase system: a polymer adsorption film ($^1$) and its vapor ($^2$). We will assume that the

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adsorbent does not react chemically with the film, dissolves neither in the film nor in the surface layer, and constitutes part of the shell which contains the system. Let the system be thermally insulated and mechanically isolated from the ambient medium. If the sum of the mass of both phases remains constant, then the internal energy of the system will also be constant. This internal energy will represent here the thermodynamic potential. The equilibrium condition, which implies that all possible work of the system is equal to zero (the energy of the system is minimum) can be written as

$$\delta U = \delta U' + \delta U'' + \delta U_F = 0.$$  

Inasmuch as the system is under the influence of a nonuniform external field and the interphase boundary can generally have various curvatures, Eq. (2) will now be rewritten in integral form. Since for a small part of the system

$$dU = TdS - PdV + (\mu + \Pi) dN + \sigma dF,$$

hence

$$\delta U' = \int T \delta (dS') - \mu' \delta (dV') + \Pi' \delta (dN') + \sigma' \delta (dF),$$  

$$\delta U'' = \int T \delta (dS'') - \mu'' \delta (dV'') + \Pi'' \delta (dN'') + \sigma'' \delta (dF),$$  

$$\delta U_F = \int \sigma \delta (dF).$$  

Integral (4c) with respect to the interphase boundary area may vary due to a variation either in the boundary shape or in its size. Therefore, the total possible variation of $U_F$ is

$$\delta U_F = \int \sigma \delta (dF) + \int \delta \sigma \delta (dF).$$  

Furthermore, the integrals with respect to potential energy may vary due to either a variation in the magnitude of the masses or a variation in the location of constant masses in the potential field

$$\delta \int \Pi' dN' = \int \Pi' \delta (dN') + \delta \Pi' dN',$$  

$$\delta \int \Pi'' dN'' = \int \Pi'' \delta (dN'') + \delta \Pi'' dN''.$$  

A simultaneous solution of Eqs. (2), (4), (5), (6) and the additional conditions of constant entropy, constant volume, and constant mass of the total system will yield the following conditions of equilibrium between an adsorption film and its vapor:

$$T' = T'' = T = \text{const},$$  

$$\mu' + \Pi' = \mu'' + \Pi'' = \mu_p = \text{const},$$  

$$P' - P'' = \sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{\partial \sigma}{\partial n}.$$  

2. Thermodynamic Parameters of an Adsorption Film. All quantities in expressions (7b), (7c) are functions of the film thickness $h$, all other conditions remaining unchanged. Let us differentiate these quantities with respect to $h$, with $T = \text{const}$. Considering that $\partial \mu / \partial P = v$, we have

$$\sigma \left( \frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{\partial \sigma}{\partial n}.$$  

$$\frac{\partial P'}{\partial h} - \frac{\partial P''}{\partial h} = \frac{\partial \sigma}{\partial h} \left[ \frac{1}{R_1} + \frac{1}{R_2} \right].$$  

A simultaneous solution of these equations and a subsequent integration from $\infty$ to $h$ yields (the vapor assumed a nearly ideal gas):

$$P = P_0 \exp \left[ \frac{\Pi'}{kT} + \frac{v'}{kT} \left( C \sigma + \frac{\partial \sigma}{\partial n} \right) \right].$$