PHYSICAL 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:

$$\mu + \Pi = \text{const.} \tag{1}$$

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 (') and its vapor ("). We will assume that the

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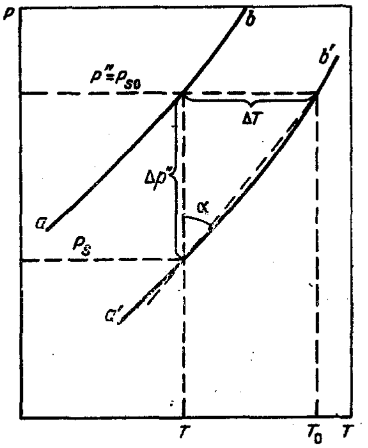

Fig. 1. Vapor equilibrium P–T diagram.

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

$$\delta U = \delta U' + \delta U'' + \delta U_F = 0. \tag{2}$$

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

$$dU = TdS - PdV + (\mu + \Pi)\, dN + \sigma dF, \tag{3}$$

hence

$$\delta U' = \int T\delta(dS') - \int p'\delta(dV') + \int \mu'\delta(dN') + \int \Pi'\delta(dN'), \tag{4a}$$

$$\delta U'' = \int T\delta(dS'') - \int p''\delta(dV'') + \int \mu''\delta(dN'') + \int \Pi''\delta(dN''), \tag{4b}$$

$$\delta U_F = \int \sigma\delta(dF). \tag{4c}$$

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

$$\delta U_F = \delta \int \sigma dF = \int \sigma\delta(dF) + \int \delta\sigma dF. \tag{5}$$

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

$$\delta \int \Pi' dN' = \int \Pi'\delta(dN') + \int \delta\Pi' dN', \tag{6a}$$

$$\delta \int \Pi'' dV'' = \int \Pi\delta(dN'') + \int \delta\Pi'' dN''. \tag{6b}$$

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:

$$T' = T'' = T = \text{const}, \tag{7a}$$

$$\mu' + \Pi' = \mu'' + \Pi'' = \mu_p = \text{const}, \tag{7b}$$

$$P' - P'' = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{\partial\sigma}{\partial n}. \tag{7c}$$

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 = const. Considering that $\partial\mu/\partial P = v$, we have

$$v' \frac{\partial P'}{\partial h} + \frac{\partial \Pi'}{\partial h} = v \frac{\partial P}{\partial h}, \tag{8a}$$

$$v'' \frac{\partial P''}{\partial h} + \frac{\partial \Pi''}{\partial h} = v \frac{\partial P}{\partial h}, \tag{8b}$$

$$\frac{\partial P'}{\partial h} - \frac{\partial P''}{\partial h} = \frac{\partial}{\partial h}\left[\sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) + \frac{\partial\sigma}{\partial n}\right]. \tag{8c}$$

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

$$P = P_s \exp\left[\frac{\Pi'}{kT} + \frac{v'}{kT}\left(C\sigma + \frac{\partial\sigma}{\partial n}\right)\right], \tag{9a}$$

$$P' \simeq P_s + \left(C\sigma + \frac{\partial\sigma}{\partial n}\right), \tag{9b}$$

$$P'' = P_s \exp\left[\frac{\Pi' - \Pi''}{kT} + \frac{v'}{kT}\left(C\sigma + \frac{\partial\sigma}{\partial n}\right)\right], \tag{9c}$$

where $C = 1/R_1 + 1/R_2$.

From the equilibrium conditions (7) one can derive the Clapeyron—Clausius equation, which will relate the heat of phase transformation, the jump in specific volume and in pressure, and the slope of the equilibrium curve at the transition point. Transition from one equilibrium state to a state infinitesimally close to equilibrium occurs in accordance with the following relations:

$$d\mu'(P', T) + d\Pi' = d\mu''(P'', T) + d\Pi'', \tag{10a}$$

$$dP' - dP'' = d\left(C\sigma + \frac{\partial\sigma}{\partial n}\right). \tag{10b}$$

For a variation in the chemical potential we have

$$d\mu = -SdT + vdP. \tag{11}$$

Considering that $(S'' - S')T = \eta$ and solving (10), (11) simultaneously, we obtain

$$\frac{dP''}{dT} = \frac{\eta + T\frac{d}{dT}\left[\Pi' - \Pi'' + v'\left(C\sigma + \frac{\partial\sigma}{\partial n}\right)\right]}{T(v'' - v')}. \tag{12}$$

Expression (12) is the Clapeyron—Clausius equation, extended to two-phase systems with a developed interphase boundary. Curve ab denoting the equilibrium between an adsorption film and its vapor on the P—T diagram (Fig. 1) is shifted here upward from its position for the bulk liquid and its vapor (curve $a'b'$) so that the phase-transformation temperature for the surface phase T lies below the phase-transformation temperature for the bulk liquid T_0 under the same pressure. This drop in the phase-transformation temperature (Fig. 1) is

$$\Delta T = T_0 - T = (P'' - P_s)\operatorname{tg}\alpha. \tag{13}$$

Owing to the small curvature of line $a'b'$, one may let

$$\operatorname{ctg}\alpha \simeq \frac{dP_s}{dT}. \tag{14}$$

Treating the vapor as an ideal gas, approximately, and disregarding $Pv' \ll kT$, we obtain

$$\operatorname{ctg}\alpha = \frac{P_s\eta_s}{kT^2}. \tag{15}$$

A simultaneous solution of Eqs. (9c) and (15) yields the expression

$$\Delta T = \frac{kT^2}{\eta_s}\left\{\exp\left[\frac{\Pi' - \Pi''}{kT} + \frac{v'}{kT}\left(C\sigma + \frac{\partial\sigma}{\partial n}\right)\right] - 1\right\}. \tag{16}$$

The differential heat of phase-transformation for systems with a developed interphase boundary is not equal to the corresponding value η_s for the bulk liquid. In order to determine $\eta(P'', T)$, we differentiate the complete derivative

$$\frac{d}{dT}\left[v'\left(C\sigma + \frac{\partial\sigma}{\partial n}\right) + \Pi' - \Pi''\right] = \frac{d}{dT}\left(kT\ln\frac{P''}{P_s}\right)$$

with respect to P and T, then insert into (12). After necessary operations, we obtain

$$\eta = \eta_s - (1 - \alpha_t' T)\, kT \ln\frac{P''}{P_s}. \tag{17}$$

The differential heat of adsorption can be easily found from expression (17). Noting that for an ideal gas $S - S'' = k\ln(P''/P)$, we have

$$\lambda = (S - S')T = \eta - \Pi'' = \eta_s + kT\ln\frac{P_s}{P} + \alpha_t' kT^2 \ln\frac{P''}{P_s}. \tag{18}$$

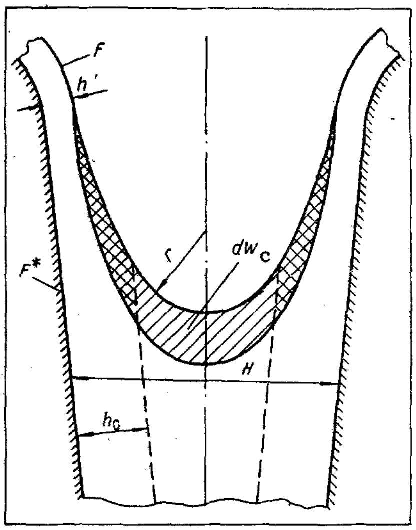

Fig. 2. Schematic diagram of an equivalent sorbent capillary.

Capillary effects of the second kind, which appear when the film dimensions are small, cause the surface tension to depend on the film geometry. In order to determine σ, we will use the equilibrium condition (7c) and the well known differential equation in [9] relating the surface tension σ, the difference between the phase pressures P'—P", and the nominal thickness of the transition layer δ

$$\left[\frac{\partial\sigma}{\partial(P'-P'')}\right]_T=-\delta. \tag{19}$$

In order to render the problem determinate, we let C = 2/R. If $\delta \ll R$, then δ may be assumed independent of R, to the first approximation, and equal to δ_s for the bulk liquid [8]. At a constant temperature δ_s = constant. Differentiating Eq. (7c) with the temperature constant along the normal n yields

$$\frac{\partial(P'-P'')}{\partial n}=\frac{\partial}{\partial n}\left(\frac{2\sigma}{R}+\frac{\partial\sigma}{\partial n}\right). \tag{20}$$

A simultaneous solution of (19) and (20) for the boundary conditions

$$\sigma|_{h=0}=0,\ \sigma|_{h=\infty}=\sigma_\infty,\ \left.\frac{\partial\sigma}{\partial n}\right|_{h=\infty}=0,$$

yields

$$\frac{\partial\sigma}{\partial n}=\frac{1}{\sigma}\left[\sigma_\infty-\sigma\left(1+\frac{2\delta}{R}\right)\right],$$

or

$$\frac{2\sigma}{R}+\frac{\partial\sigma}{\partial n}=\frac{1}{\delta}(\sigma_\infty-\sigma), \tag{21}$$

$$\sigma=\exp\left[-\int\left(\frac{1}{\delta}+\frac{2}{R}\right)dn\right]\left\{\frac{\sigma_\infty}{\delta}\int\exp\left[\int\left(\frac{1}{\delta}+\frac{2}{R}\right)dn\right]dn+C_1\right\}. \tag{22}$$

The solution to Eq. (22) with these boundary conditions yields the following expressions for the surface tension σ as a function of the curvature radius R and of the film thickness h = n · cos α.

$$\begin{aligned}\sigma=\sigma_\infty&\left\{1-\frac{2\delta}{R}+\left(\frac{2\delta}{R}\right)^2\left(1-\frac{1}{2}\frac{\partial R}{\partial n}\right)-\left(\frac{2\delta}{R}\right)^3\right.\\&\times\left[1-\frac{3}{2}\frac{\partial R}{\partial n}+\frac{1}{2}\left(\frac{\partial R}{\partial n}\right)^2-\frac{1}{4}R\frac{\partial^2 R}{\partial n^2}\right]+\cdots\\&-\exp\left[-\frac{n}{\delta}-\frac{2n}{R}-\left(\frac{n}{R}\right)^2\left(\frac{\partial R}{\partial n}-\frac{1}{3}n\frac{\partial^2 R}{\partial n^2}\right.\right.\\&\left.\left.\left.+\frac{1}{12}n^2\frac{\partial^3 R}{\partial n^3}-\cdots\right)-\cdots\right]\right\}.\end{aligned} \tag{23}$$

For thin films $R \gg h$, and for thick films the entire exponential term tends to zero. Therefore, retaining only the first two terms in the exponent will be sufficiently accurate. Then, with the terms of higher-order smallness omitted, we have

$$\sigma = \sigma_\infty \left[1 - \frac{2\delta}{R} - \exp \frac{-h}{\delta \cos \alpha} \left(1 + \frac{2\delta}{R} \right) \right]. \tag{24}$$

Equation (24) is analogous to the closed Gibbs–Tolman–Koenig–Baff equation [8] derived for small droplets or bubbles, except that its exponential term accounts also for capillary effects of the second kind associated with thin films (small values of h) [10].

<u>3. General Equations of Adsorption and Capillary Condensation.</u> Expression (9a) can, with the aid of (21), be rewritten as

$$kT \ln \frac{P_s}{P} = -\Pi' - \frac{v'}{\delta} (\sigma_\infty - \sigma). \tag{25}$$

Equation (25) is the thermal equation of adsorption, extended to systems with a developed interphase boundary. If capillary effects are disregarded, then the second term on the right-hand side of (25) becomes zero and we have the conventional Polani equation of adsorption [11]. An analysis of (25) shows that, under certain conditions (for example, for the adsorption of polar molecules), the right-hand side of Eq. (25) becomes zero at a finite thickness h_0 of the adsorption film, which has been confirmed experimentally by several authors [3, 12, 13]. For this condition of equilibrium between a polymolecular adsorption film and its saturated vapor (saturated relative to the bulk liquid) P_s is determined from (25)

$$-\Pi' = \frac{v'}{\delta} (\sigma_\infty - \sigma). \tag{26}$$

In the majority of hygroscopic materials over a wide range of moisture level, characteristically, the processes of adsorption and capillary condensation occur simultaneously, which significantly reduces the applicability of Eq. (25). The applicability of the Kelvin–Thompson equation of capillary condensation becomes limited for the same reason, as has been confirmed in many experimental and theoretical studies [14-16].

The effect of polymolecular adsorption films on capillary condensation in wide pores has been explored thoroughly enough by B. V. Deryagin [17, 18], where he has shown that the hydraulic radius of an equivalent pore at the meniscus level is equal to the thickness of the adsorption film plus the thickness of the variable-curvature transition layer plus the thickness of the constant-curvature capillary condensate layer (Fig. 2). Such a model of sorption phenomenon is characteristic of wide pores, where the effective ranges of surface forces on opposite walls do not overlap. In narrow pores the adsorption potentials overlap and the total potential at the pore axis is not zero, inasmuch as the dispersion forces are adding here. A constant-curvature region of capillary condensate, with parameter values other than the corresponding parameter values for the bulk liquid, may be missing in narrow pores.

On this basis, then, we will examine the general conditions of equilibrium between the adsorption film and its vapor, assuming that there is no capillary condensate present in narrow pores. For simplicity, we will consider a single capillary (Fig. 2) whose wall length and wall slope are determined by the total volume of pores in a given sorbent. The free energy of the sorbed liquid (we assume that the constant-curvature meniscus exists) is

$$F = \omega F + \omega_0 (F^* - F) + f_c \cdot N_a \cdot W_c + s\sigma_s + F_0. \tag{27}$$

By analogy with [18], we consider the virtual desorption of dW_c moles at p = const. and h = const. (the entire shaded area in Fig. 2) by isothermal reversible distillation into the bulk liquid under pressure P_s. We then have

$$-(\mu_s - \mu_p) N_a dW_c = (\omega - \omega_0) dF + N_a f_c dW_c + \sigma_s ds. \tag{28}$$

The walls of the equivalent capillary slope only slightly, and it may be assumed that they remain parallel within every cross section at the meniscus level. Then $ds \simeq 0$ and

$$dW_c = -\left(\frac{H}{2} - h \right) \frac{dF}{v'_\mu}. \tag{29}$$

Furthermore, by definition

$$f_c = \mu_c - \mu_s. \tag{30}$$

With (29) and (30), expression (28) becomes

$$\frac{H}{2} = h + v' \frac{\omega - \omega_0}{\mu_c - \mu_p}. \tag{31}$$

For determining ω we use B. V. Deryagin's generalization of the chemical potential of a layer [4]:

$$\mu' + v' \frac{\partial \omega}{\partial h} = \mu_p. \tag{32}$$

In the general case, the boundary surface between an adsorption film and its vapor is curved and, therefore, $\mu' \neq \mu_s$. The value of μ' can be found from the equilibrium condition (7b). Solving simultaneously (32) and (7b) yields, after integration,

$$\omega = \omega_s - \int_\infty^h (\mu' - \mu_p)\, dh = \omega_s + \int_\infty^h \Pi' dh. \tag{33}$$

Considering that

$$\omega_s = \omega_0 + \sigma_s \cos\theta_s, \tag{34}$$

and inserting (33) as well as (34) into (31), we obtain the correct equation of capillary condensation for systems with a developed interphase boundary:

$$\frac{H}{2} = h + \frac{v'\sigma_s \cos\theta_s - \int_\infty^h (\mu' - \mu_p)\, dh}{\mu_c - \mu_p}. \tag{35}$$

Equation (35) applies to pores of any width. With the adsorption potential disregarded here, (35) becomes the simple Kelvin–Thompson equation. For sufficiently wide flat pores (where the effective ranges of forces on opposite walls do not overlap) one may assume that $\mu' = \mu_c = \mu_s$, and (35) becomes the Deryagin equation. In both cases the limiting width of an equivalent capillary tends to infinity. The physical pattern is different during sorption in narrow capillaries. Assuming that $\mu_c \simeq \mu'$ and using relation (7b), for example, we thus obtain

$$\frac{H}{2} = h - \frac{v'\sigma_\infty \cos\theta_\infty + \int_\infty^h \Pi' dh}{\Pi'}. \tag{36}$$

For sorbed molecules with high potential energies (for sorption of polar molecules by a fine dispersion) the limiting value H_0 (as well as the limiting thickness h_0 of the adsorption film) becomes finite and dependent on the temperature, on the kind of sorbent, and on the kind of sorbate material. The fact may explain the temperature dependence of the maximum moisture content, established in many experiments during the sorption of water.

NOTATION

Π is the potential energy of a molecule in the field of surface forces;
μ is the chemical potential of a molecule;
μ_P is the chemical potential of vapor at pressure P;
U is the internal energy;
F is the free energy;
S is the entropy;
V is the volume;
P is the pressure;
T is the temperature;
σ is the surface tension of adsorption film, referred to the film-vapor interphase boundary;
σ_∞ is the surface tension of film of infinite thickness;
F is the surface area;

F^*	is the total surface area of sorbent;
R_1, R_2	are the principal radii of the film-vapor interface;
n	is the normal to the surface;
α	is the angle between a normal to the interface and the z-axis;
h	is the thickness of adsorption film;
v	is the volume per molecule;
v_μ	is the molar volume;
k	is the Boltzmann constant;
N_A	is the Avogadro number;
η	is the heat of phase transformation;
λ	is the heat of adsorption;
α_t^1	is the true volume expansivity of adsorption film;
δ	is the nominal thickness of transition layer, referred to the density of adsorption film;
ω	is the excess free energy per unit area of interphase boundary between sorbent (including the adsorption film) and vapor at pressure P [18];
ω_0	is the excess free energy per unit area of interphase boundary between sorbent and capillary condensate;
f_c	is the excess of bulk free energy (exclusive of ω_0) of capillary condensate;
W	is the quantity of sorbed liquid, in moles;
s	is the total surface area of menisci;
H	is the width of equivalent pore at the meniscus level;
θ	is the critical wetting angle.

Subscripts

s	refers to bulk liquid;
c	refers to capillary condensate;
(')	refers to adsorption film;
(")	refers to vapor.

LITERATURE CITED

1. B. V. Deryagin and E. Obukhov, Kolloid. Zh., No. 1 (1935).
2. B. V. Deryagin and M. Kusakov, Izv. Akad. Nauk SSSR Ser. Khim., No. 5, (1935).
3. B. V. Deryagin and Z. M. Zorin, Zh. Fiz. Khim., 29, (1955).
4. B. V. Deryagin and L. M. Shcherbakov, Kolloid. Zh., 23, No. 1, (1961).
5. J. W. Gibbs, Thermodynamic Studies [Russian translation], Gostekhizdat, Moscow (1950).
6. A. I. Rusanov, Thermodynamics of Surface Phenomena [in Russian], Izd. Leningradsk. Gosud. Univ., Leningrad (1960).
7. R. C. Tolman, J. Chem. Phys., 16, 758 (1948).
8. S. Ono and S. Kondo, Molecular Theory of Surface Tension in Liquids [in Russian], Izd. Inostr. Lit., (1963).
9. J. Keenan, Thermodynamics [Russian translation], Gosénergoizdat, Moscow—Leningrad (1963).
10. L. M. Shcherbakov, Kolloid. Zh., 22, No. 1, (1960).
11. M. M. Dubinin, Physicochemical Principles of Sorption Technology [in Russian], Goskhimtekhizdat, Moscow—Leningrad (1932).
12. J. W. Whalen, J. Phys. Chem., 65, No. 10, 1676 (1970).
13. V. D. Perevertaev and M. S. Metsik, Kolloid. Zh., 28, No. 1, (1966).
14. K. S. Lyalikov, Dokl. Akad. Nauk SSSR, 15, 329 (1937).
15. K. V. Chmutov, Kolloid. Zh., No. 11, 14 (1949).
16. L. M. Shcherbakov, Trudy Tulsk. Mekhan. Inst., 7, 117 (1958).
17. B. V. Deryagin, Zh. Fiz. Khim., 14, No. 2, (1940).
18. B. V. Deryagin, Dokl. Akad. Nauk SSSR, 113, No. 4, (1957).
19. L. M. Nikitina, Thermodynamic Parameters and Mass Transfer Coefficients of Moist Materials [in Russian], Izd. Énergiya, Moscow (1968).