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Studies on Pore Systems in Catalysts

XII. Pore Distributions from the Desorption Branch of a Nitrogen Sorption Isotherm in the Case of Cylindrical Pores

A. An Analysis of the Capillary Evaporation Process

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A refinement is given of the classical Kelvin equation in pores, which takes into account the influence of adsorption forces on the shape of the liquid–vapor meniscus. It is shown that the curvature of the meniscus is dependent on the distance to the walls of the pores and that taking into account this dependence leads to a different shape of the meniscus from the hemispherical shape generally assumed for cylindrical pores. The influence of adsorption forces on the liquid–vapor equilibrium is shown to result in a stabilizing of the capillary-condensed liquid in the pore, as well as in a mechanism for the evaporation process which is different from that which is based on the application of the classical Kelvin equation in cylindrical pores.

1. INTRODUCTION

In the preceding three articles of this series (*1*, *2*, *3*) it was shown that the adsorption branch of a nitrogen sorption isotherm may be used for the calculation of pore distributions in the case of A-type and E-type hysteresis loops, provided the necessary corrections are applied to Kelvin's equation in order to take into account the influence of adsorption on the stability of the liquid–gas interface* present during adsorption in a cylindrical or spherical cavity. These corrections may be calculated according to the method given in Part IX of this series (*1*).

The discussion of the process of capillary condensation given in Part IX led to the conclusion that it is not justified to apply the uncorrected Kelvin equation to the analysis of capillary condensation during adsorption and, moreover, that similar corrections have to be applied to the Kelvin equation when it is used for the analysis of the desorption branch of an isotherm measured at a porous adsorbent, at least in the case of cylindrical pores.

The last-mentioned necessity, viz., a correction of the Kelvin equation used for the desorption branch, in order to take into account the influence of adsorption on the equilibrium between the capillary-condensed phase and the gas phase, was already pointed out several years ago by B. V. Derjaguin (*4*), who gave a complete and consistent treatment of the desorption from slit-shaped pores filled with capillary-condensed liquid (*5*).

To our knowledge, the formula of Derjaguin has not yet been systematically applied to the analysis of the desorption branch of sorption isotherms, although we will show in Part XIV of this series that such may be done quite easily with the aid of the concept of the common t curve of multimolecular adsorption. In the present paper we discuss in some detail the shape of the meniscus, which is consistent with the in-

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* The condensed phase may be a supercritical two-dimensional N_2 layer, or perhaps an already three-dimensional N_2 layer formed by capillary condensation; this question will be treated in one of the following articles of this series.

fluence of the adsorption forces emanating from the walls of the pore in the case of cylindrical pores. We show that the same criterion for desorption given in Part IX of this series may be obtained along a different line of reasoning, viz., by modifying the classical geometrical picture, commonly connected with Kelvin's equation (*6*, *7*), by taking into account the influence of the adsorption forces.

2. GENERALIZATION OF KELVIN'S EQUATION

In Part IX of this series it was shown that the essential assumptions underlying the classical application of Kelvin's equation to the condensation in and evaporation from pores—namely, the constancy of the thermodynamic potential of the phase condensed in the pores, taken as being equal to that of the bulk liquid at the same temperature and thus taken to be independent of the distance to the pore walls—led to some inconsistencies, which could only be discarded by taking into account explicitly the dependence of the thermodynamic potential of the liquid condensed in the pores upon the distance to the pore walls.

The same refinement may be incorporated in the usual derivation of Kelvin's equation, where on geometrical grounds a connection is made between the curvature of the meniscus of the liquid and its vapor pressure. Although in principle it is not strictly necessary to assume the density of the capillary-condensed liquid to be constant and independent of the distance to the pore wall, nor is it necessary to take the surface tension of the liquid–vapor interface as a constant and independent of the curvature of the interface, in general the density of the adsorbed and capillary-condensed phase is supposed to be equal to that of the bulk liquid at the same temperature, whereas there are arguments to suppose that the curvature of an interface has only a very small influence on the magnitude of the surface tension (*8*, *9*). In the present discussion we will assume both parameters to be constant and equal to those of the bulk liquid.

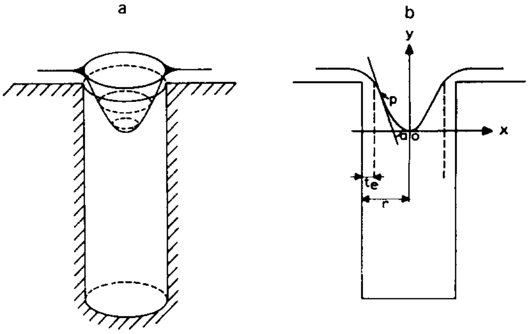

FIG. 1. (a) The shape of the meniscus present during desorption from a cylindrical pore. (b) Axial section through the pore of Fig. 1a.

Consider a meniscus present in a cylindrical pore of radius r at a certain relative pressure p/p_0 (see Fig. 1a). Edge effects will be neglected. A plane section through the axis of the cylindrical pore of Fig. 1a is shown in Fig. 1b. A reference coordinate framework is shown in the same figure, the y axis being parallel to the pore walls and the x axis being perpendicular to it. For the meniscus to be in equilibrium with the vapor phase, it is necessary that each particular point of the meniscus independently is in equilibrium with the vapor phase. For a transfer of dN moles of vapor to a point of the meniscus, the change in free enthalpy is given by

$$dG_{p,T} = (\mu_t - \mu_g)\, dN + \gamma dA \qquad (1)$$

where the thermodynamic potential of the vapor is denoted by μ_g, that of the capillary condensed phase at a distance t of the pore wall by μ_t and the surface tension of the liquid–vapor interface by γ; dA represents the change in free interface area upon transferring these dN moles to that part of the meniscus situated at a distance t from the wall. It will be clear that dA is related to dN through the curvature of the meniscus at a distance t from the pore wall by (*10*)

$$\frac{dA}{dN} = -V_m\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad (2)$$

where R_1 and R_2 are the main radii of curvature of the meniscus at a distance t from the wall, or, according to Euler's theorem, any two radii of curvature normal to each other. Accordingly, (1) may be written as

$$\frac{dG}{dN_{p,T}} = \mu_t - \mu_g - \gamma V_m\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \quad (3)$$

In equilibrium for every part of the meniscus the relation

$$dG/dN_{p,T} = 0 \quad (4)$$

must hold and, consequently, for the case of equilibrium Eq. (3) may be written as

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{(\gamma V_m)}(\mu_t - \mu_g) \quad (5)$$

As μ_t is a function of the distance from the pore wall, the radius of curvature of the meniscus is seen to be dependent on that same distance. Relation (5) thus is a sort of generalization of Kelvin's equation, relating the curvature of the meniscus to the thermodynamic potential in the case that this thermodynamic potential depends on the coordinates of the system. In order to derive from (5) the shape of the meniscus in a particular case, it is necessary to connect the radii of curvature to the equation describing the meniscus analytically with respect to the reference frame.

In Fig. 1b the meniscus is considered to be convex, so R_1 and R_2 are both positive. Let us denote the radius of curvature of the section through the meniscus shown in Fig. 1a by R_1. The other radius of curvature, R_2, is perpendicular to R_1, and is situated in a plane perpendicular to the x–y plane of Fig. 1b.

In a certain point P of the section through the meniscus shown in Fig. 1b a tangent is drawn to the meniscus and the angle between this tangent and the x axis is denoted by (a). For the meniscus, $y' = \tan\,(a)$, whereas $y'' = 1/\cos^2(a) \times d(a)/d(x)$. According to elementary geometrics, R_1 may be related to the coordinates x and y of the meniscus by *(11)*

$$R_1 = (1 + y'^2)^{3/2}/y'' \quad (6)$$

whereas, as a consequence of the symmetry of the meniscus around the cylinder axis, R_2 is related to R_1 by *(12)*

$$R_2 = x/\sin(a) \quad (7)$$

By substituting $\tan(a)$ for y', (6) may be written as

$$R_1 = [1/\cos(a)][d/(x)/d(a)] \quad (8)$$

and by substituting (7) and (8) into (5), we obtain

$$\frac{\cos(a)\,d(a)}{d(x)} + \frac{\sin(a)}{x} = \frac{d\sin(a)}{d(x)} + \frac{\sin(a)}{x} = \frac{1}{(\gamma V_m)}(\mu_t - \mu_g) \quad (9)$$

If μ_t is expressed as a function of x, the distance from the axis of the pore, then (9) is a simple first order linear differential equation in $\sin(a)$ and x. The general solution of this equation is *(13)*

$$\sin(a)x = 1/(\gamma V_m)\int x(\mu_t - \mu_g)\,dx + \text{integration constant} \quad (10)$$

According to Fig. 1b, x is related to r, the pore radius, and t, the distance to the pore wall, by

$$x = -(r - t) \quad (11)$$

Integration of (10) between the boundaries 0 and $-(r - t)$, i.e., from the center of the pore to a distance t from the pore wall, results in the following expression for the slope of the meniscus at a distance t from the pore wall

$$\begin{aligned} -\sin(a)(r-t) &= \frac{1}{(\gamma V_m)}\int_0^{-(r-t)}(r-t)(\mu_t-\mu_g)\,d(r-t) \\ &= \frac{-1}{(\gamma V_m)}\int_r^t (r-t)(\mu_t-\mu_g)\,dt \\ &= \frac{1}{(\gamma V_m)}\int_t^r (r-t)(\mu_t-\mu_g)\,dt \quad (12)\end{aligned}$$

the integration constant of (10) vanishing on account of the obvious boundary condition

$$\sin(a) = 0, \text{ for } t = r \quad (13)$$

With the aid of Eq. (12) the shape of the meniscus may be determined as a function of t, the distance from the pore wall, provided μ_t is known in dependence of t. In Part IX of this series, it was proposed to express μ_t formally as

$$\mu_t = \mu_L - F(t)$$

and it was shown that $F(t)$ may, in principle, be obtained from the universal t curve of multimolecular adsorption, on the assumption that the influence of the wall curvature of the solid material constituting the pores, on μ_t, may be neglected. Consequently, (12) may formally be written as

$$-\sin(a)(r-t) = \frac{1}{(\gamma V_m)} \int_t^r \left[RT \ln\left(\frac{p_0}{p}\right) - F(t) \right] (r-t)\, dt \qquad (14)$$

3. ANALYSIS OF THE SHAPE OF THE MENISCUS

From (14), for a certain value of r and p/p_0, $\sin(a)$ may be calculated as a function of t, the distance to the pore wall. Of course, $\sin(a)$ is related to y' by

$$y' = \sin(a)/[1-\sin^2(a)]^{1/2}$$

Thus, the whole shape of the meniscus shown in Fig 1b is determined by the equation

$$y = \int_t^r \frac{\sin(a)}{[1-\sin^2(a)]^{1/2}}\, dt \qquad (15)$$

which may be integrated upon substitution of (14) for sin (a).

Actually, an analytical solution of (15) may only be found in very simple cases.

(A) In the classical theory of capillary evaporation, where the state of the condensed phase is considered to be equal to that of the bulk liquid, $F(t)$ equals zero for every value of t, and (12) reduces to

$$-\sin(a)(r-t) = \frac{1}{(\gamma V_m)} RT \ln\left(\frac{p_0}{p}\right) \frac{(r-t)^2}{2}$$

viz.

$$\sin(a) = \frac{-RT \ln(p_0/p)}{2\gamma V_m} (r-t) \qquad (16)$$

If we denote $2\gamma V_m/[RT\ \ln(p_0/p)]$ by R_k, then in the classical case (15) reduces to

$$y = -\int_t^r \frac{(r-t)/R_k}{\{1-[(r-t)/R_k]^2\}^{1/2}}\, dt$$

which is equal to

$$y = R_k - [R_k{}^2 - (r-t)^2]^{1/2} \qquad (17)$$

This is the equation of a circle with radius R_k. The radius of the circular meniscus (which is the section of the meniscus by the x–y plane of Fig. 1b, if, as is assumed in the application of the Kelvin equation, this meniscus is hemispherical and not conical as already shown in the figure) decreases with decreasing p/p_0. In order that the meniscus covers the whole diameter of the pore, it is evidently necessary that

$$R_k \geq (r - t_a)$$

where t_a is the thickness of the adsorbed layer belonging to the relative pressure p/p_0. This immediately leads to the well-known Kelvin equation for desorption from cylindrical pores

$$r - t_a = \frac{2\gamma V_m}{RT^1 \ln(p_0/p)} \qquad (18)$$

The shape of the meniscus according to the classical picture is sketched in Fig. 2a for different relative pressures. The desorption condition eq. (18) is equivalent to the requirement that the hemispherical meniscus in the pore just touches the adsorbed layer at the walls of the pore for $p = p_D$, viz.,

$$\sin(a) = -1 \text{ for } t = t_a \text{ and } p = p_D \qquad (19)$$

(B) For the adsorption of nitrogen in not too narrow pores present in inorganic oxides and related substances, it was shown in Part X that $F(t)$ is not negligible, but may be expressed as a mathematical function of t. Integration of (15) then is not simple and in general is not analytically possible, although a numerical solution of (15) may always be obtained for stable meniscii. Information about the shape of the meniscus in this last case may be obtained by investigating the behavior of the radii of curvature of the meniscus as a function of the distance from the pore walls. According to (8), the first principal curvature may be denoted by $d \sin(a)\ /\ dt$, so from (14) the first principal curvature may be calculated to be equal to

$$\frac{1}{R_1} = \frac{RT \ln(p_0/p)}{2\gamma V_m} - \frac{F(t)}{\gamma V_m} + \frac{\int_t^r (r-t)F(t)\, dt}{(r-t)^2 \gamma V_m} \qquad (20)$$

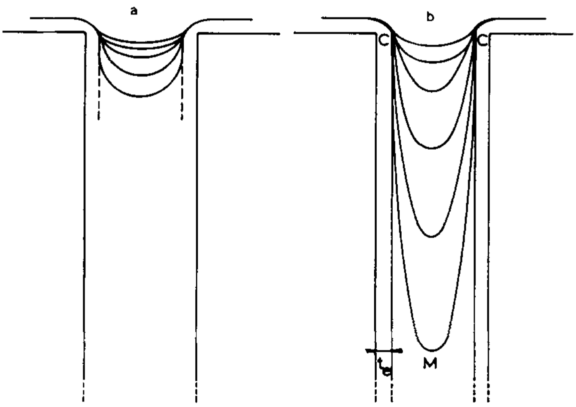

FIG. 2. (a) The shape of the meniscus in a cylindrical pore according to the classical picture for different relative pressures. For the sake of clarity, the change in thickness of the adsorbed layer as a function of pressure is not shown. (b) The shape of the meniscus in a cylindrical pore according to the present treatment for different pressures. For the sake of clarity the variation of the thickness of the adsorbed layer with pressure is not shown.

It is seen that the effect of $F(t)$ is to reduce the curvature of the meniscus, although this effect is counteracted by the integral term at the right-hand side of (20), and that the curvature is nowhere a constant but diminishes towards the walls of the pore, where $F(t)$ increases. Even in the center of the pore the curvature is smaller that the curvature corresponding to the application of the classical Kelvin equation, by an amount $F(t)/(\gamma V_m)$.

The second principal curvature $1/R_2$, which is given by (7), may be calculated to be equal to

$$\frac{1}{R_2} = \frac{RT\ln(p_0/p)}{2\gamma V_m} - \frac{\int_t^r (r-t)F(t)\,dt}{(r-t)^2\gamma V_m} \tag{21}$$

In the center of the pore this second curvature equals that of the meniscus corresponding to the classical Kelvin equation, but again the curvature is not constant but decreases towards the walls of the pore. Thus, in not very wide pores, the meniscus is not hemispherical but rather more conical in character, resembling the shape represented in Fig 1a. Upon decreasing relative pressure the curvature at each point of the meniscus increases and qualitatively the shape of the meniscus as a function of relative pressure may be represented by the lines of Fig. 2b. When the vapor pressure in the system is decreased to a value p_D, the meniscus just touches the adsorbed layer of thickness t_e, corresponding to $\sin(a) = -1$ for $t = t_e$, which is equivalent to condition (19) for desorption. Upon a further decrease in relative pressure the meniscus detaches itself from the adsorbed layer at the walls of the pore and emptying of the pore, except for the equilibrium adsorbed layer at the walls of the pore, occurs.

Integrating (14) from t_e to r and putting $\sin(a)$ equal to -1, yields the desorption condition

$$-1 = \frac{-\int_{t_e}^r (r-t)[RT\ln(p_0/p_D) - F(t)]\,dt}{\gamma V_m(r-t_e)}$$

viz.

$$r - t_e = \frac{2\gamma V_m}{RT\ln(p_0/p_D)} + \frac{\int_{t_e}^r 2(r-t)F(t)\,dt}{(r-t_e)RT\ln(p_0/p_D)} \tag{22}$$

Relation (22) has already been derived in Part IX of this series along a different line of reasoning. Just as was pointed out there it is to be realized that according to the present treatment t_e is no longer only dependent on the relative vapor pressure in the system, but also on the pore radius. In Part IX of this series it was shown that for t_e to be an equilibrium the thickness corresponding to a minimum in the free enthalpy of the system the following relation must hold

$$RT \ln(p_0/p_D) - F(t_e) = \gamma V_m/(r - t_e) \quad (23)$$

This equation is consistent with the present treatment, as may be seen from the realization that for the adsorbed layer, which essentially is a cylindrical meniscus, R_1 must be zero and R_2 is equal to $(r - t_e)$. By adding the relations (20) and (21), for the pressure p_D, (23) is readily obtained.

If $F(t)$ is known as a function of t, the desorption pressure p_D corresponding to a certain pore radius r, may be found by eliminating t_e from (24) and (25) and solving for p_D.

The present discussion confirms, on a geometrical basis, the views forwarded by Derjaguin in 1940 (*3*), on capillary evaporation from nearly cylindrical pores. Along a different line of reasoning, by making use of the concept of disjoining pressure, this author arrived at an equation essentially equivalent to relation (22), though the correction (23) to the thickness of the adsorbed layer was not taken into account before. As was shown in Part IX of this series, it is exactly this equation that leads to the concept of capillary condensation in open cylinders and to the concept of sorption hysteresis connected with the just mentioned model. Nevertheless, it is somewhat surprising that the ideas of Derjaguin have up till now found no practical application in the calculation of pore distributions from sorption isotherms.

4. MECHANISM OF CAPILLARY EVAPORATION

Consider again Fig. 2b. It is seen that the meniscus shown in that figure gradually deepens upon decreasing the relative pressure, until below the pressure p_D, corresponding to (22) and (23), the meniscus ceases to exist. It is important to investigate whether, for the pressure p_D, the distance between the minimum of the meniscus, m, situated at the center of the pore with coordinates $x = 0$ and $y = 0$ (see Fig. 1b) and the point of contact, c, between the meniscus and the adsorbed layer, situated at $x = -(r - t_e)$, has a discrete, well-defined value. Because of the mathematical difficulty in integration of (15) analytically in the case of nonzero $F(t)$, the problem has to be solved in an indirect way. From (14) it is evident that for $p = p_D$ the tangent to the meniscus is infinite at the point c, where $t = t_e$. From (20), (22), and (23) it may be easily verified that at this pressure the curvature of the section of the meniscus with the x–y plane is exactly equal to zero in the point $t = t_e$.

Now it is a general feature of lines exhibiting at a certain point a vertical slope, combined with zero curvature, that the y coordinate of such a point is situated at an infinite distance from any other y coordinate of any other point of such a line. In fact this property of the lines of the class just discussed may be proved strictly whenever it is possible to express the tangent to the lines as a polynomial in t or a fraction of polynomials in t. As the empirical representations for $F(t)$, discussed in Part X of this series, may be shown to possess these properties, it is to be expected that the y coordinate of the meniscus in the point $t = t_e$ is situated at an infinite distance from the minimum of the meniscus in the center of the pore whenever p has just reached the critical pressure p_D of (22) and (23). This property of the model of the meniscus presented here was confirmed by numerical integration of (15) for the functions $F(t)$ representing the adsorption of nitrogen at its normal boiling point.

This leads us to an interesting conclusion concerning the emptying of pores filled with capillary condensate. In the classical picture, the meniscus always is hemispherical, its radius of curvature never being infinite. Consequently, the depth of the meniscus is restricted, attaining its maximum value at $p = p_D$. In accordance with Fig. 2a the depth of the meniscus below the mouth of the pore reaches a value of $(r - t_a)$ for $p = p_D$. On lowering the relative pressure below p_D/p_0, the meniscus vanishes and capillary desorption takes place as a *discontinuous* process, resulting a *sudden* release of capillary condensate.

When, however, the influence of the wall on the state of the capillary-condensed

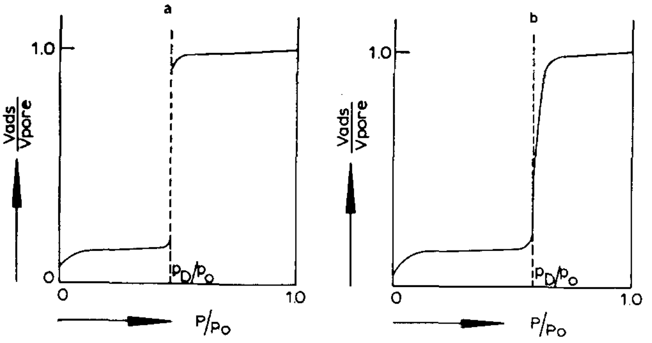

FIG. 3. (a) Volume of capillary condensate, V_a, as a function of pressure, in a cylindrical pore according to the classical picture. Sudden evaporation, except for the adsorbed layer, takes place at the pressure p_D. (b) Volume of capillary condensate, V_a, as a function of pressure, in a cylindrical pore according to the present treatment. At the pressure p_D, the pore is just empty except for the adsorbed layer of thickness t_e.

liquid in the pore is taken into account, by means of $F(t)$, the picture is completely changed. On lowering the relative pressure from saturation downwards the meniscus gradually deepens, until at the pressure p_D, the depth of the meniscus has become infinite. In other words, at the pressure $p = p_D$ every pore of radius r and of finite length is completely empty, except for an adsorbed layer of thickness t_e. The emptying of pores is seen to be a *continuous* process and the pressure p_D is seen to be a limiting value for the presence of capillary condensate, the capillary-condensed phase being *gradually* released from the pore. In Fig. 3a and 3b both mechanisms of desorption from cylindrical pores—the discontinuous process that would follow from the application of Kelvin's equation, and the continuous process that follows from the treatment leading to the corrected Kelvin equation (22)—are represented schematically.

Whereas the preceding discussion may be of theoretical interest, its practical consequences are limited. Only in the neighborhood of p_D is the extension of the meniscus of quantitative significance for the function $F(t)$, discussed in Part X of this series, so for practical purposes the continuous desorption process connected with the discussion of the present model of capillary evaporation may be replaced by a practically discontinuous emptying at the pressure $p = p_D$ corresponding to (22) and (23). It is to be stressed, however, that the desorption process from cylindrical pores is seen to differ basically from the adsorption process in open cylindrical pores. As was shown in Part IX of this series, capillary condensation during *adsorption* in *open* cylinders is a discontinuous process, resulting from the transition of a metastable adsorbed layer at the walls of the pores to an unstable adsorbed layer. This is in accordance with the essential metastable character of the adsorption branch in open cylinders, as compared to the completely stable character of the desorption branch of cylindrical pores.

In the case of ideal cylinders closed at one end, the adsorption branch and the desorption branch will coincide because, as soon as p_D is reached during adsorption, a meniscus will be formed at the bottom of the cylinder (this meniscus essentially is already present in the form of an adsorbed layer at the bottom of the pore), and increasing the pressure above the value p_D will result in a complete filling of the pore, exactly in the reverse direction from the desorption process in the neighborhood of p_D. Thus, adsorption and desorption are essentially reversible processes, neither of them being stepwise in character, and complete equilibrium exists over the whole isotherm.

In the case of Type II ink bottles (*3*) a narrow neck at the open side of the pore prevents equilibrium evaporation during desorption as long as the neck of the pore is completely filled with capillary condensate. In this case the adsorption branch is the stable branch, at least with regard to the wide cylindrical part of the ink bottle, whereas the desorption branch is only stable with respect to the narrow necks of the pores. Very short necks may behave differently. According to the present discussion the exact pressure at which a cylindrical pore empties, to some extent is dependent on the length of the pore, the pore being empty the moment the depth of the meniscus exceeds the length of the pore. For not very short pores this effect may be neglected and the pressure of complete emptying essentially coincides with p_D, but with very short necks this effect might result in a more narrow hysteresis loop than would actually be expected from the radius of the ink-bottle necks, making the analysis of the desorption branch in the case of ink-bottle-type pores even more complicated.

5. Conclusions

In the preceding sections of this paper we have given independent arguments for the viewpoint developed several years ago by Derjaguin that the curvature of a liquid–gas meniscus present in a narrow pore must be dependent not only on the relative vapor pressure (as it would be according to Kelvin's equation), but also on the magnitude of the interaction between the solid pore walls and the capillary-condensed liquid. By giving a refined derivation of Kelvin's equation, while taking into account the dependence of the thermodynamic potential of the capillary-condensed phase on the distance to the pore walls, we were able to establish the connection between curvature of the meniscus and the interaction between the capillary-condensed phase and the solid walls. As a result of this analysis it has been shown that, when the influence of the wall interaction is taken into account, the two main curvatures of the meniscus no longer are constant and equal in magnitude. Consequently, in an actual pore the shape of the meniscus may not be expected to be hemispherical any more. Moreover, if the dependence of the curvature of the meniscus on relative pressure and distance to the pore walls is regarded in more detail, it has to be concluded that the actual mechanism of capillary evaporation is somewhat different from that consistent with the classical views on capillary evaporation resulting from the application of Kelvin's equation in its uncorrected form. In the present point of view capillary evaporation no longer consists of two equilibrium stages, viz., the pore completely filled with capillary condensate on the one hand and the pore only carrying an adsorbed layer on the other hand, interconnected through a series of nonequilibrium stages corresponding to the sudden emptying of the pore, but the actual process of capillary evaporation is pictured as a series of equilibrium stages of emptying, connected with a progressively increasing overall curvature of the meniscus, reaching a critical value at the pressure p_D, just corresponding to an empty pore except for the presence of an adsorbed layer.

In the next article in this series (following in this issue) we will show how, with the aid of the common t curve of multimolecular adsorption for oxidic substances, the pressure at which desorption occurs from a pore of certain radius, may be calculated. It must be realized, however, that the present discussion is still essentially a nonmolecular one, and that the validity of the present method for pores with radii of only a few molecules diameters, viz., for submicropores, certainly is questionable.

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