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Studies on Pore Systems in Catalysts

IX. Calculation of Pore Distributions from the Adsorption Branch of Nitrogen Sorption Isotherms in the Case of Open Cylindrical Pores

A. Fundamental Equations

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A study is made of the possible cause for sorption hysteresis in the case of cylindrical pores of uniform diameter, open at both ends. By means of simple thermodynamic reasoning, the equation of Cohan for capillary condensation in open cylinders during adsorption, is shown not to be suitable for quantitative work. After the introduction of the *t* curve of multimolecular adsorption, a model is given for the occurrence of hysteresis in this special case. From this model, quantitative relations are derived for the spontaneous filling of pores during adsorption, as well as for the evaporation of capillary condensate on desorption, in dependence of the pore radius. The relation between these equations and the work of Foster and Derjaquin is discussed.

1. INTRODUCTION

In Article V of this series (*1*), it was shown that on plotting the adsorption branch of the nitrogen sorption isotherm according to the *t* method, valuable indications may be obtained with respect to the characteristics of the pore system present. In many cases the picture formed from the information given by the *t* plot may be substantiated by a study of the form of the hysteresis loop exhibited by the nitrogen sorption isotherm (*2*). The combination of *t* plot and characterization of the hysteresis loop often leads to a clear picture of the pore system present. Thus, for slit-shaped pores, a linear *t* plot is to be expected for *t* values smaller than half the pore width of the pores present. When the thickness of the adsorbed layer exceeds this value for a certain fraction of the pores present, a downward deviation of the *t* plot is to be expected. On desorption, slit-shaped pores will give rise to the existence of a distinct hysteresis loop. For pores, consisting of inwardly curved walls, at a certain pressure capillary condensation during adsorption will set in, initially resulting in an upwardly curvature of the *t* plot.

Different models may be set up for pores exhibiting curved walls. If the hysteresis loop exhibits an A-type behavior, the pores —as an idealization—may be pictured as consisting of open cylindrical pores of uniform radius. On the other hand, pores may be pictured to consist of wide bodies, closed on all sides but for a certain number of narrow necks. It may be expected that the corresponding hysteresis loop is of the B type [see Part II of this series (*3*)]. In practice combinations of several types may be found, although examples of both types have been found, as was shown in Part IV of this series (*4*).

Additional information may be obtained from the calculation of pore distributions according to one of the models selected (*2*, *3*). If the model chosen is a realistic one, the calculated cumulative surface area, under certain restrictions, becomes equal to the surface area calculated from the initial part of the isotherm either by means of the BET equation or by the t method (*4*).

There is, however, some ambiguity with respect to the calculation of pore distributions from the adsorption branch. For isotherms exhibiting the A type of hysteresis loop, we may assume the model of open cylindrical pores (*2*). In such a case, the adsorption branch is only metastable with respect to the desorption branch, and the classical Kelvin equation may not be applied to it in calculating the pore distribution. In the present article, it will be shown that certain thermodynamic corrections may be applied to enable the calculation of pore distributions for the model of open cylindrical pores.

2. THEORIES OF COHAN AND OF FOSTER

Already in 1932, Foster (*5*), after a critical analysis of a number of isotherms of benzene and alcohol adsorbed on silica or on ferric oxide gel at different temperatures, showed that the adsorption branch in the case of hysteresis does not conform to analysis by means of the Kelvin equation. Foster supposed that the adsorption branch is governed by the formation of a multimolecular adsorption layer, until the narrow parts of the pores are blocked and a meniscus is formed, resulting in capillary condensation.

In 1938, Cohan (*6*) proposed a different approach. He assumed that the Kelvin equation may be applied to the cylindrical meniscus, formed by the gas-adsorbed layer interface present in a cylindrical pore. According to the Kelvin equation, the vapor pressure corresponding to such a cylindrical meniscus is given by

$$p/p_0 = \exp\left[-\gamma V_m/RT(r - t)\right] \qquad (1)$$

where γ is the surface tension (assumed to be equal to that of the bulk condensed phase); V_m, the molar volume of the adsorbate; R, the gas constant; r, the pore radius; and t, the thickness of the adsorbed film. If the vapor pressure exceeds the value given by (1), Cohan supposes capillary condensation to take place at the cylindrical film at the walls of the pores and consequently the pores to be filled by capillary condensate.

During desorption it may be assumed that a hemispherical meniscus is present at the mouth of the pore, its vapor pressure being given by

$$p/p_0 = \exp\left[-2\gamma V_m/RT(r - t)\right] \qquad (2)$$

If the vapor pressure is decreased below the value given by (2), capillary evaporation takes place and the pore is emptied except for a certain thickness of the adsorbed layer. From a comparison of (1) and (2), it is evident that this viewpoint immediately gives an explanation for the existence of hysteresis, as well as for the connection between the model of open cylinders and the A-type hysteresis loop.

In 1952, Foster (*7*) tried to combine his original viewpoint with that of Cohan, by taking the multilayer and the cylindrical meniscus effect together, resulting in the picture of a curved multilayer, only stable up to certain relative pressures, thereafter leading to capillary condensation. Foster tried to explain sorption hysteresis as well as the existence of a pressure where hysteresis is no longer observed. This last viewpoint is certainly not correct, as Foster neglected the adsorption effect in analyzing the desorption branch. When this is done, the existence of hysteresis interception may no longer be explained in this way. Nevertheless, Foster's viewpoint is suitable for a quantitative application to the analysis of the adsorption branch of isotherms in the case of open cylindrical pores. Before we do this, it is worthwhile to incorporate Foster's viewpoint into a general thermodynamic picture for the combined multilayer adsorption and capillary condensation in open cylinders.

3. THERMODYNAMIC TREATMENT OF CAPILLARY CONDENSATION IN OPEN CYLINDRICAL PORES

The vapor pressure of a cylindrical film of thickness t, present on the walls of an open cylindrical pore of radius r, is governed by the requirement of equilibrium with respect to mass transfer between the vapor phase and the adsorbed film at constant temperature and pressure. This may be exemplified by considering changes in the total free enthalpy of the system (including pore as well as vapor phase) at constant temperature and pressure (*8*), with respect to the transfer of dN moles of vapor to the adsorbed film

$$dG_{p,T} = \mu_c dN - \mu_g dN + \gamma dA \qquad (3)$$

where μ_c and μ_g are the thermodynamic potentials of the condensed phase and the gaseous phase, respectively, and dA is the change in free surface area of the condensed film upon condensation of dN moles of vapor. There exists a very simple relationship between dN and dA, viz.,

$$dA/dN = -V_m/(r - t) \qquad (4)$$

where t is the thickness of the condensed phase at the walls of the pore and V_m, the molar volume of the condensed phase.

In equilibrium, the following relation holds at constant temperature and pressure:

$$dG_{p,T} = 0 \qquad (5)$$

Combination of (3), (4), and (5) leads to

$$\mu_c - \mu_g = \gamma V_m/(r - t) \qquad (6)$$

When the vapor phase obeys the ideal gas law and the condensed phase is identical to that of the bulk liquid, Eq. (6) is identical to Eq. (1), as derived by Cohan, viz., the Kelvin equation applied to the cylindrical meniscus of the adsorbed layer.

As may be clear, it is assumed that the properties of the adsorbed layer are identical to those of the bulk liquid. This, however, leads to inconsistencies, which make the application of Eq. (1) questionable. To show this, it is well to realize that for the equilibrium to be stable, the free enthalpy of the whole system has to be a minimum with respect to virtual changes in the amount condensed from the gaseous phase at constant temperature and pressure. Equation (5) may correspond to a minimum as well as to a maximum. To determine the nature of the extreme in the free enthalpy, corresponding to (6), we have to determine the sign of the second derivative of the free enthalpy with respect to N, the number of moles present as a condensed phase. For stable equilibrium,

$$d^2G/dN^2{}_{p,T} \geq 0 \qquad (7)$$

Under the conditions underlying Cohan's equation, viz., μ_c constant and equal to that of the bulk liquid at the same temperature, the second derivative of G with respect to N is calculated to be equal to

$$d^2G/dN^2{}_{p,T} = -\gamma V_m/(r - t)^2 dt/dN \qquad (8)$$

As dt/dN is always positive, the second derivative is seen to be always negative, corresponding to an unstable equilibrium, and to a maximum in the free enthalpy.

To illustrate what this means exactly, the total change in free enthalpy of the system has been calculated, when the thickness of the condensed phase is increased from a certain value t_i, the thickness of the adsorbed layer,to an arbitrary value $t \leq r$ at a constant temperature and pressure. In principle, such a change in free enthalpy of the system is given by

$$\Delta G = \int_{N_i}^{N} (\mu_c - \mu_g) dN + \int_{A_i}^{A} \gamma dA$$
$$= \frac{\pi L_p}{V_m}\left[\int_{t_i}^{t} 2(\mu_c - \mu_g)(r - t)dt - 2\gamma V_m(t - t_i)\right], \qquad (9)$$

where L_p is the length of the pore under consideration.

Under the conditions corresponding to Eq. (8), where $\mu_c - \mu_g$ is constant and equal to $RT \ln[(p_0/p)]$, this simply is equal to

$$\Delta G = \frac{\pi L_p}{V_m}\left[RT \ln\left(\frac{p_0}{p}\right)(2rt - 2rt_i - t^2 + t_i^2) - 2\gamma V_m(t - t_i)\right] \qquad (10)$$

The function $\Delta G - t$ as plotted according to Eq. (10), is represented in Fig. 1 for different pressures. There are two singular curves to be distinguished in this figure. At pressures lower than p_D filling of the pores corresponds to an increase of the free enthalpy of the system and filling will not occur. At pressures equal to or higher than p_D filling is thermodynamically possible, but corresponds to the crossing of a free enthalpy barrier. Filling on account of the existence of the barrier will not occur spontaneously, although the process would lead to a thermodynamically more stable state. At the pressure p_D itself, the filled pore is thermodynamically just stable with respect to the pore only carrying an adsorbed film, and ΔG is exactly zero for complete filling. If, in Eq. (10), r is put equal to t, and ΔG is taken to be equal to zero, then the corresponding value of p/p_0 is seen to be exactly that given by Eq. (2) for desorption. At lower pressures, desorption takes places. In this case, there is no potential barrier, as the desorption takes place by gradually emptying of the pores by evaporation from the hemispherical meniscus present at the mouth of the pore.

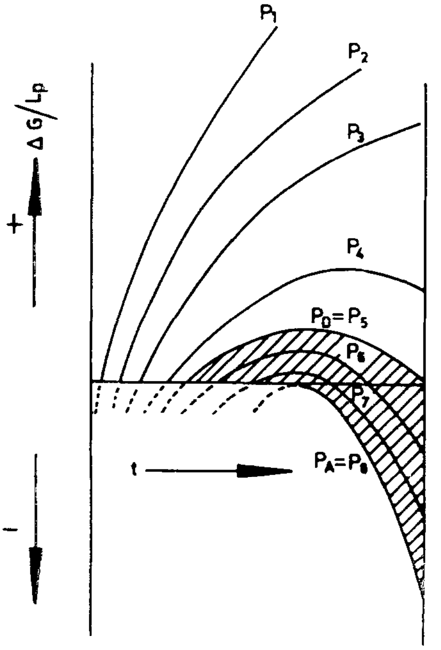

FIG. 1. ΔG as a function of t, the thickness of the condensed layer in a cylindrical pore, for different pressures, according to Eq. (10). The relative pressure is increasing from P_1 to P_8. The region of sorption hysteresis is hatched.

At the pressure p_A, every increase in thickness of the adsorbed layer corresponds to a decrease in the free enthalpy of the system, and spontaneous filling will take place. From the figure, the occurrence of hysteresis finds a very simple explanation. The value of p_A, at which spontaneous filling will occur, is clearly given by the requirement that $d(\Delta G)/dt$ for $t = t_i$ is equal to zero. Upon differentiating (10), Eq. (1) is recovered, being the equation of Cohan.

At the same time, Fig. 1 shows why this picture is definitely unrealistic. For the value t_i, the thickness of the adsorbed layer, the free enthalpy of the system exhibits no minimum. In principle, the free enthalpy of the system at constant temperature and pressure would be lowered by lowering the value of t, the thickness of the adsorbed layer, beyond the value t_i. The adsorbed layer cannot exist as a stable phase at any pressure unless it is assumed that the properties of the layer are different from those of the phase condensed on top of this layer. This is the meaning of Eq. (8). In the picture of Cohan, there is a discontinuity between the adsorbed layer present in the pore at a certain pressure and the phase condensed on this layer upon increase of the thickness t. There is a sharp change in properties, occurring in the condensed phase at a distance t_i from the pore wall, from adsorbed phase to bulk liquid. The distance at which the change takes place is assumed to be dependent on pressures, but not on the pore radius.

This picture is incompatible with the existence of a continuous multilayer with a thickness probably approaching infinity as the saturation pressure is reached. There are no indications of an abrupt breaking off of the influence of the pore wall on the condensed layer in the case of nitrogen multilayer adsorption, as implicitly required by Cohan's treatment. This means that in all Eqs. (3) to (9), the thermodynamic potential μ_a of the adsorbed layer has to be regarded as dependent on the distance t from the pore wall, and only approaching μ of the bulk liquid for infinite layer thickness. For quantitative work the function μ_a as dependent on the thickness of the adsorbed layer, has to be evaluated from experimental data and inserted in the formulas (3) to (9) in order to evaluate the thickness of the adsorbed layer and the pressure at which a cylindrical pore fills or empties, which depends on the pore radius. This is possible by making use of the concept of the universal t curve [see Part VI of this series (*9*)].

4. THE INTRODUCTION OF THE UNIVERSAL t CURVE

In Part VI of this series (*9*), it was shown that the amount adsorbed per unit of area surface present for a large group of adsorbents could be represented by one universal curve, giving a relation of the form:

$$V_a/V_m = f(p/p_0).$$

If it is assumed that the density of the adsorbed layer is constant and equal to that of the bulk liquid at the same temperature, an approximation probably admittable for not too small layer thicknesses, the thickness of the adsorbed layer may be evaluated, e.g., in the case of the adsorption of nitrogen at 78°K, by means of

$$t = 3.54\ V_a/V_m.$$

These t values hold for surfaces, which, although energetically nonhomogeneous, may be considered to have a negligible curvature with respect to the thickness of the adsorbed layer. For such a "flat" surface, it is possible to plot these experimental t values as a function of $RT \ln (p_0/p)$:

$$RT \ln (p_0/p) = F(t) \qquad (11)$$

As for such a "flat" surface and for an ideal vapor, the function $RT \ln(p_0/p)$ is equal to the difference in thermodynamic potential between the "bulk" liquid at the same temperature and the adsorbed phase of thickness t, it is possible to evaluate the thermodynamic potential of an adsorbed layer of thickness t in the form

$$\mu_a(t) = \mu_L - F(t) \qquad (12)$$

Strictly speaking, Eq. (12) only holds for layers adsorbed at "flat" surfaces. We now assume that the thermodynamic potential of the adsorbed layer is primarily determined by its distance from the pore wall and that the influence of the curvature of the pore wall on thermodynamic potential of the adsorbed layer, in the case of cylindrical pores, is negligible. As long as this approximation is admitted, Eq. (12) may also be used as a relation between the thermodynamic potential of the adsorbed layer in cylindrical pores and the thickness of this adsorbed layer. However, the vapor pressure of an adsorbed layer of thickness t, present in a cylindrical pore of radius r, is no longer solely dependent on the thermodynamic potential of the layer, as in the case of a "flat" surface, but also on the curvature of the interface between the adsorbed layer and the vapor phase. Consequently, although Eq. (12) may be used for predicting the dependence of the thermodynamic potential of an adsorbed layer on its thickness, Eq. (11) may not be used for calculating the vapor pressure of an adsorbed layer of thickness t_e in a cylindrical pore of radius r. In this last case, the relation between the equilibrium vapor pressure, the equilibrium thickness t_e, and the pore radius may be calculated by inserting relation (12) in Eqs. (3) and (5) of Section 3. By making use of (4), and of the fact that in each case $RT \ln(p_0/p)$ is equal to $\mu_L - \mu_g$, the following relation, which in the case of cylindrical pores is the equivalent of (11), is obtained:

$$RT \ln (p_0/p) - F(t) = \gamma V_m/(r - t) \qquad (13)$$

If $F(t)$ is known and expressed as an analytical function of t, t_e may be solved as a function of p/p_0 for different values of r. Whether this equation for the film thickness corresponds to a *stable* equilibrium, may be determined with the aid of Eq. (7), which takes, for $t = t_e$, the form

$$-dF(t)/dt - V_m/(r - t)^2 \geq 0 \qquad (14)$$

When for a certain pore radius, the left side of (14), evaluated with the aid of the t_e value calculated by means of Eq. (13) as a function of (p/p_0), exactly equals zero, then this value of t_e is a critical thickness, which we shall denote by t_{cr}. An infinitely small increase in pressure increases t_{cr} discontinuously, the equilibrium becomes unstable, and the whole pore fills spontaneously with capillary condensate. The pressure corresponding to this critical thickness is the pressure of spontaneous capillary condensation during adsorption.

For a given pore radius, r, and a given relative pressure p/p_0 the total change in free enthalpy of the whole system (pore + vapor phase) corresponding to an increase in the thickness of the condensed phase in the pore from t_e to a certain value $t \leq r$, may be calculated with the aid of Eq. (9), which takes the form

$$\Delta G_{p,T} = \frac{\pi L_p}{V_m}\left[\int_{t_e}^{t} 2\left(RT\ln\left(\frac{p_0}{p}\right) - F(t)\right)(r-t)\,dt - 2\gamma V_m(t-t_e)\right] \quad (15)$$

With the aid of (15), lines representingΔG as a function of t at constant temperature and pressure may be calculated for different values of (p_0/p_0). This is schematically represented in Fig. 2.

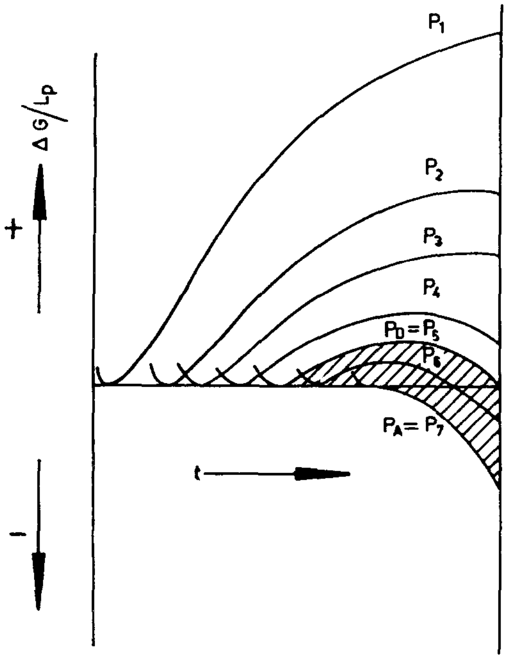

FIG. 2. ΔG as a function of t, the thickness of the condensed layer in a cylindrical pore, for different pressures, according to Eq. (15). The relative pressure is increasing from P_1 to P_7. The region of sorption hysteresis is hatched.

Again, two singular lines may be distinguished, bounding the region of sorption hysteresis, and corresponding to the pressure p_D, the pressure of capillary evaporation during desorption, and the pressure p_A, corresponding to the spontaneous filling of pores during adsorption. The pressure p_D is given by the equality

$$\Delta G_{p,T} = 0 \qquad \text{for } t = r$$

which corresponds to a pressure determined by the following relation:

$$RT\ln\left(\frac{p_0}{p}\right)(r-t_e)^2 = 2\gamma V_m(r-t_e) + \int_{t_e}^{r} 2F(t)(r-t)\,dt,$$

which may be written as

$$r - t_e = \frac{2\gamma V_m}{RT\ln(p_0/p)} + \frac{\int_{t_e}^{r} 2F(t)(r-t)\,dt}{(r-t_e)RT\ln(p_0/p)}. \quad (16)$$

5. A COMPARISON WITH THE KELVIN EQUATION

Equation (16) is reminiscent of the Kelvin equation. In fact this equation may be shown to be the analog for cylindrical pores of an equation derived by Derjaguin for slit-shaped pores (*10*), and it resembles an equation already derived by the same author in 1940 along different lines of reasoning, making use of the concept of disjoining pressure (*11*). When an analytic expression for $F(t)$ as a function of t is known, t_e may be solved for r, where it must be borne in mind, however, that $RT \ln (p_0/p)$ has to satisfy Eq. (13) simultaneously. When this is taken into account, Eq. (16) may be used for the calculation of pore distributions from A-type sorption isotherms, making use of the model of cylindrical pores. We hope to publish the results in a forthcoming paper.* For the present, we will restrict ourselves to the calculation of the pressure where spontaneous capillary condensation takes place during adsorption. This pressure corresponds to the line p_A of Fig. 2. The function ΔG exhibits a point of inflection for $t = t_e$ for this pressure, corresponding to $(d^2\Delta G/dt^2)_{t=t_e} = 0$.

Of course, this value for t_e is given by the left-hand side of Eq. (14) when put equal to zero, and thus is equal to t_{cr}. For a certain pore radius, each pressure between p_D and p_A corresponds to a metastable state, giving rise to hysteresis. The filled pore corresponds to a more stable situation than the pore equipped with a cylindrical adsorbed layer of thickness t_e, as given by Eq. (13). Both states are separated by a free enthalpy barrier. From Fig. 2, it is clear that the

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*This will be Part XII of this series.

explanation of Foster for the phenomenon of so-called hysteresis inception, the existence of a minimum pressure for which hysteresis may be observed, is not the right one. The values for capillary condensation during adsorption, as determined by (14), are in accordance with the basic ideas of Foster (7). The desorption pressure, however, is not given by the classical Kelvin equation, but by an equation of the type of Eq. (16), which is in concordance with the general ideas of Derjaguin *(10)*. In the present treatment, both theories are logically connected through the systematic application of Eq. (9). Also, the existence of the phenomenon of hysteresis finds a logical explanation from the consideration of Fig. 2. At the moment, there is no fully satisfactory explanation for the phenomenon of hysteresis inception. A possible explanation could be offered by the "narrowness" of the free energy barrier in very narrow pores, making the crossing of this barrier towards a stable state more easy. As it is questionable, however, whether the thermodynamic treatment given here, where the adsorbed layer is pictured as being continuous, is applicable to the situation in very narrow pores, viz. for total thicknesses of the adsorbed layer close to the dimensions of the adsorbate molecules, this point will not be elaborated here.

As will be shown in Article X of this series, which is Part B of this paper (following), equations (13) and (14) may be applied to the calculation of pore distributions from the adsorption branch of A-type sorption isotherms, after the introduction of a mathematical expression for the t curve of multimolecular adsorption.

6. CONCLUSIONS

The assumptions underlying the formulas of Sections 3 and 4 of this paper are as follows:

(1) The density of the adsorbed phase is constant and equal to that of the bulk phase.

(2) The same applies to the surface tension of the interface between the condensed phase in the pore and the vapor phase. Moreover, the surface tension is assumed to be independent of the radius of the meniscus.

(3) Thermodynamic reasoning along the lines of Sections 3 and 4 is applicable to the condensed film in the pore. This may not be true for small thicknesses of the adsorbed film, viz., for very narrow pores or for very low pressures.

(4) The thermodynamic potential of the adsorbed layer is not altered significantly by the curvature of the pore walls.

Introducing the universal t curve, the following conclusions may be drawn:

(1) In a cylindrical pore, the thickness of the adsorbed layer is different from that on a flat surface at the same pressure.

(2) Filling of open cylindrical pores by capillary condensation occurs on behalf of the lack of stability of the adsorbed layer when a certain pressure is reached, depending on the pore radius.

(3) The pressure at which capillary evaporation takes place is seen to be different from that of the Kelvin equation. The pressure at which desorption takes place may be expected to be lower than the pressure at which spontaneous filling takes place during adsorption. This may not be true for very narrow pores.

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