THE INFLUENCE OF DISPERSION FORCES
ON THE MERCURY INTRUSION INTO PORES OF SOLIDS

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On the basis of the Gibbs condition of thermodynamic equilibrium of heterogeneous system occurring in a force field, a general expression is derived for the dependence of the liquid mercury pressure on an equivalent radius of pores volume-filled on its intrusion. For the equivalent radius r of pores greater than 30 nm, this equation turns into the well-known Washburn equation. It is shown that for pores of equivalent radii smaller than 5 nm, the presence of dispersion forces is the reason of considerable deviations from the classical Washburn equation. The effect of the liquid mercury pressure on the contact angle θ of intruded mercury with pore walls is also discussed.

To study the porous structure of solids, the adsorption methods and the method of mercury porosimetry are usually used. Calculations of the pore distribution on the basis of the data obtained by these methods are based on equations of capillarity and require an assumption of the pore shape. The calculated pore distributions do not correspond to the real porous material but to an equivalent porous material with a common (as a rule cylindrical) shape of pores whose desorption branch of isotherm and dependence of volume of the intruded mercury on the mercury hydrostatic pressure are identical with the respective dependences for the real porous structure. The calculated pore radii for the model porous systems are effective radii for real porous materials. The identity of results of the pore structure analysis by both the methods applied to a real porous material consists in the fact that both methods are not entirely independent because they are based on capillary phenomena whose basic prerequisite is the existence of a so-called meniscus (liquid–gas interface) of a defined curvature $J = 1/R_1 + 1/R_2$, where R_1 and R_2 are the principal radii of curvature. By convention, when liquid–vapour interfaces are discussed, a radius of curvature is given a positive sign when its centre of curvature lies on the liquid side of the interface. The main difference of both methods lies in the conditions of wetting of the pore walls by the liquid. In case of the adsorption methods, the condition of the wetting of the pore walls with a liquid adsorbate leads to the necessity of introducing corrections for the thickness of adsorption layer whose presence is the fundamental condition of capillary condensation.

It was shown in a number of papers that the dependences of pore volumes on effective radii measured by the capillary condensation method and by the mercury porosimetry are identical[1,2]. However, it is not possible to ascribe general meaning to those results, valid for all porous substances of varying nature. So, *e.g.*, in the case of active carbons obtained by the method of inorganic activating agents ($ZnCl_2$) both methods yield different results when analyzing mesopores. The total volumes of mesopores as determined by the method of mercury porosimetry are several times larger than those determined by the method of capillary condensation[3,4]. To

explain these differences, an assumption was expressed of the presence of the ink-bottle shaped macropores with narrow necks of dimensions corresponding to mesopores. These pores will manifest themselves during the mercury porosimetry as mesopores whereas the method of capillary condensation is not able to prove their presence for, as it is well-known, the macropores are not volume-filled with condensed adsorbate even at relative vapour pressure equal unity. The presence of similar macropores, however, was not proved by the specially developed method of a so-called forced capillary condensation[5] in the above-mentioned samples of active carbons. This method consists in lowering the value of saturated vapour pressure p_0^g of adsorbate by the impregnation of the sample with a small amount of nonvolatile salt soluble in the adsorbate. By using this method, the whole porous structure is filled by condensed adsorbate at relative vapour pressure equal to unity. The problem of the origin of different results of the mesopore analysis of active carbons prepared by chemical activation has therefore remained hitherto unsolved.

The ways of evaluating the experimental data of porosimetric analysis are developed continuously to be more precise, $e.g.$ by introducing various corrections for the thickness of adsorption layers, for the dependence of surface tension σ^{lg} of liquid on the pore radius, $etc.$ The question is whether similar improvements may not contribute to the elucidation of the above-mentioned discordance of both the main methods used to analyse the mesopores of chemicaly activated active carbons. It is quite possible that they can be, in a certain range of pore radii, of basic significance. As it is apparent from the example given above, the methods of pore analysis and of evaluation of experimental results have to be further refined.

In the mesopores of radii lower than 7 nm, the capillary phenomena may be substantially influenced by the presence of dispersion forces. In case of the capillary condensation of vapours, this effect has already been studied[6,7], and an equation was proposed expressing the relation between the relative vapour pressure $x = p^g/p_0^g$ and the effective pore radius comprising the effect of dispersion forces[8]. This work presents a theoretical study of the effect of dispersion forces on the mercury intrusion into meso- and micropores.

The effect of adsorption forces on the intrusion of liquid mercury into pores may manifest itself also indirectly with pores whose radius is greater than 30 nm. A change in the liquid mercury pressure brings about a change of pressure of the supersaturated mercury vapours in volume-unfilled pores. The adsorption forces on the pore surface are the reason of a certain extent of the Gibbs adsorption of mercury vapours. The change in this adsorption due to a change in the pressure of supersaturated mercury vapours must be the cause of changes of values of the contact angle of mercury θ with a change in the liquid mercury pressure p_f^l corresponding to the filling-up of pores of the given dimensions. An approximate method is proposed which makes it possible to evaluate the effect of the liquid mercury pressure p_f^l on the contact angle θ.

Application of the derived general equation, expressing the dependence of pressure p_f^l of intruded mercury on the effective radius r of pores, to real porous systems will be given in a forthcoming paper.

THEORETICAL

General Equation for the Mercury Intrusion into Porous Materials

When deriving a general relation for pressure of liquid mercury, allowing for the volume filling of pores of the given shape and radius, we start from the Gibbs thermodynamic condition of equilibrium of heterogeneous system in a field of force. Accordingly, the sum of the chemical potential μ of the component in question and its potential of intermolecular forces ϕ has the same value at any point of the pore space under equilibrium conditions

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

Henceforth we shall designate the thermodynamic quantities (chemical potential μ, molar volume v, pressure p and surface tension σ) corresponding to the liquid and gas phases by superscripts l and g, the adsorbed liquid and gas phases by superscripts al and ag and further simultaneously, the quantities corresponding to the standard state by subscript o and the quantities corresponding to filling-up and emptying (extruding) the pores by subscripts f and e, respectively. The condition of thermodynamic equilibrium with respect to mass transfer (1) for the one-component system (mercury) under the conditions of filling-up of the pores leads to the relation

$$\mu_f^{al} + \phi = \mu_f^{l}, \tag{2}$$

where μ_f^{al} is the chemical potential of mercury intruded into pores occurring in a force field and μ_f^{l} the chemical potential of liquid mercury outside the adsorbent where the potential of adsorption forces θ has the zero value.

The chemical potential of liquid μ_f^{l} is determined at a given temperature T by the hydrostatic pressure in the liquid phase p_f^{l} with respect to the chosen standard pressure p_0^{l}:

$$\mu_f^{l} = \mu_0^{l} + \int_{p_0^{l}}^{p_f^{l}} v^l \, dp = \mu_0^{l} + \bar{v}^l(p_f^{l} - p_0^{l}), \tag{3}$$

where v^l is the liquid molar volume and $\bar{v}^l$ is its average value in the pressure range from p_0^{l} to p_f^{l}, and μ_0^{l} is the chemical potential of liquid in the standard state. As usual, as the standard state a state is chosen at which the pressures in the liquid and vapour phases are equal to each other $(p_0^{l} = p_0^{g})$, *i.e.* they are equal to the pressure of saturated vapours of liquid mercury above the interface whose curvature J equals zero.

The chemical potential of mercury in the force field μ_f^{al} is determined by the relation

$$\mu_f^{al} = \mu_0^{l} + \int_{p_0^{l}}^{p_f^{al}} v^{al} \, dp + \mu^* = \mu_0^{l} + \bar{v}^{al}(p_f^{al} - p_0^{l}) + \mu^*, \tag{4}$$

where p_f^{al} is the mercury pressure in the force field (in pores being just filled), and μ^* the change in the chemical potential of mercury corresponding to the change of its structure in the force field. The symbol $\bar{v}^{al}$ denotes the average value of the molar volume of liquid mercury occurring in the force field in the pressure range of p_0^l to p_f^{al}.

By inserting Eqs (3) and (4) into condition (2) we get after rearranging the expression for the pressure of intruded mercury

$$p_f^l = \frac{\bar{v}^{al}}{\bar{v}^l}\left(p_f^{al} - p_0^l\right) + p_0^l + \frac{\phi}{\bar{v}^l} + \frac{\mu^*}{\bar{v}^l}. \tag{5}$$

With regard to a small mercury compressibility, it holds that $\bar{v}^{al} \approx \bar{v}^l$, and consequently Eq. (5) may be, as a rule, simplified to the form

$$p_f^l = p_f^{al} + \frac{\phi}{\bar{v}^l} + \frac{\mu^*}{\bar{v}^l}. \tag{6}$$

If there exists the mercury meniscus in pores, it is possible to insert into Eq. (6) the expression following from the Laplace–Young equation

$$p_f^{al} - p_f^{ag} = \sigma^{lg} J^{lg} = \frac{-2\sigma^{lg}\cos\theta}{r}, \tag{7}$$

for a cylindrical pore of radius r. The mercury vapour pressure p_f^{ag} may then be neglected in comparison with the pressure p_f^{al}, and the expression for pressure p_f^l is so obtained in the form

$$p_f^l = \frac{-2\sigma^{lg}\cos\theta}{r} + \frac{\phi}{\bar{v}^l} + \frac{\mu^*}{\bar{v}^l}. \tag{8}$$

The dispersion forces form, as a rule, a substantial part of adsorption forces. Therefore it is possible to express the potential ϕ through the relation derived in our previous paper[9] for the dependence of the potential of dispersion forces in the centre of pores of different shapes on their dimensions:

$$\phi = -NC_A\pi\left\{f_A\frac{1}{q^3} - \frac{r_0^6}{2}f_B\frac{1}{q^9}\right\} = -\frac{k_A}{q^3} + \frac{k_B}{q^9}, \tag{9}$$

where N is the number of atoms in unit volume of solid, C_A is the Kirkwood–Müller constant, r_0 is the equilibrium distance of the adsorbed molecule (atom) from the solid surface, and the values of parameters f_A and f_B, which depend on the pore

shape, are tabulated[9]. The parameter q characterizes the pore dimensions, and for the cylindrical pores is equal to pore radius r. For cylindrical pore shapes we obtain, by inserting Eq. (9) into (8), the expression for p_f^l in the form

$$p_f^l = \frac{-2\sigma^{lg}\cos\theta}{r} + \frac{1}{\bar{v}^l}\left(\frac{-k_A}{r^3} + \frac{k_B}{r^9}\right) + \frac{\mu^*}{\bar{v}^l} \, . \tag{10}$$

The first term on the right-hand side of Eq. (10) is connected with the existence of meniscus. This term may acquire a more complex form in more precise calculations, partly for that reason that both the surface tension σ^{lg} and the contact angle θ, as it will be shown below, depend on the pore dimensions. Further it is well-known that in micropores the capillary phenomena are loosing their physical meaning. The reason is that a small number of liquid atoms or molecules in these pores does not make it possible to form the meniscus. The first term on the right-hand side takes the zero value in micropores. This fact can be expressed by multiplying the first term of Eq. (10) by a function $\gamma(r)$ which determines the degree of possibility of applying the capillary phenomena. For micropores $\gamma(r) = 0$ and for meso- and macropores $\gamma(r) = 1$. In the transient region, the function $\gamma(r)$ does not change in steps[8], and can be expressed by the empirical function

$$\gamma(r) = \exp\left[-(r_k/r)^{\tau}\right], \tag{11}$$

where r_k is the pore radius characterizing the range of pore radii in which the capillary phenomena cease manifesting themselves, and τ is a parameter determining the range of pore radii in which the function $\gamma(r)$ changes from zero to one. The function $\gamma(r)$ can be expressed in the first approximation on using the parameters $r_k = 0.7$ nm and $\tau = 6$.

For the dependence of surface tension σ^{lg} on the radius of curvature R of spheric interphase, Tolman[10] derived, on the basis of quasithermodynamic approach, the relation

$$\sigma^{lg} = \sigma_\infty^{lg} \left/ \left(1 + \frac{2d}{R}\right)\right., \tag{12}$$

where σ_∞^{lg} is the surface tension of a flat surface. Later on, Ahn and coworkers[11] starting from the statistical theory of liquids, derived the Tolman equation (12) and an actual expression for the coefficient d in the form

$$d = 0.9165(v^s/N_A)^{1/3}, \tag{13}$$

where v^s is the molar solid–like volume, and N_A is the Avogadro number. Providing that $v^s \doteq v^l$, then at 20°C $2d = 0.533$ nm. Further, inserting relation (14) between

the radius of curvature of spherical meniscus and the radius of cylindrical pore r

$$R_s = -r/\cos\theta \tag{14}$$

into Eq. (12), we obtain the relation for the dependence of surface tension σ^{lg} on the radius of cylindrical pore r

$$\sigma^{lg} = \sigma^{lg}_\infty \left/ \left(1 - \frac{2d\cos\theta}{r}\right)\right. . \tag{15}$$

On inserting relation (15) into Eq. (10) and multiplying the first term on the right-hand side by function (11), we obtain, for dependence of pressure of liquid mercury p_f^l on the radius r of filled-up pores, the general equation

$$p_f^l = \frac{-2\sigma^{lg}_\infty \gamma(r)\cos\theta}{r - 2d\cos\theta} + \frac{1}{\bar{v}^l}\left(\frac{-k_A}{r^3} + \frac{k_B}{r^9}\right) + \frac{\mu^*}{\bar{v}^l}. \tag{16}$$

Still it is necessary to mention the last term on the right-hand side of Eq. (16). A change of chemical potential μ^* of liquid, connected with the change of its structure in pores, is to be expressed as the work of its transfer from the standard state to a hypothetical pressure p_ω by the relation

$$\mu^* = RT \ln \left(f_\omega/f_0^g\right), \tag{17}$$

where f_ω and f_0^g are the fugacities corresponding to the hypothetical pressure p_ω and the standard pressure p_0^g; p_ω is the pressure, the modified liquid would have, were it free of the adsorption potential field but not otherwise changed. In typical micropores, e.g. in active carbons, of radii 0·6 to 0·7 nm (ref.[7]), mercury loses its metallic character, and the quantity μ^* acquires in them considerable positive values. It is well-known that these micropores are volume-filled with mercury only at pressures p_f^l greater than 500 MPa. From Eq. (9) follows the value $\phi = -18\cdot55$ kJ mol^{-1} for the potential of dispersion forces in the centre of micropore of radius $r = 0\cdot6$ nm. On the basis of Eq. (16), and on the assumption that $\gamma(r) = 0$, it is possible, on the basis of the above-mentioned values of ϕ and p_f^l, to estimate the value μ^* to be greater than 26 kJ mol^{-1}. Therefore at 20°C, $v = f_\omega/f_0^g$ is greater than $5 . 10^4$ in micropores of radii $r = 0\cdot6$ nm. In supermicropores, mesopores and macropores, mercury keeps its metallic character, and $\mu^* \doteq 0$.

Dependence of Contact Angle on the Equilibrium Pressure of Liquid Mercury

The contact angle θ of the mercury with the solid used in mercury porosimetry is determined, as a rule, by a macroscopic measurement, and it is assumed that it does

not depend on the pressure of intruded mercury p_f^l. This assumption is not quite correct. In fact, the contact angle θ depends on pressure p_f^l. We present a way enabling an approximate estimate of this dependence. For this purpose we determine first the equilibrium vapour pressure of mercury in pores p_f^{ag}.

When calculating the expression for supersaturated vapour pressure of mercury p_f^{ag}, corresponding in equilibrium to pressures of liquid mercury p_f^l greater than the standard pressure p_0^l, we start again from the thermodynamic condition of equilibrium of heterogeneous liquid–vapour system in a force field. According to this condition (1), the chemical potential of liquid mercury μ_f^l occurring outside adsorbent is in equilibrium equal to the sum of the chemical potential of mercury vapours μ_f^{ag} present in pores and the potential of adsorption forces ϕ

$$\mu_f^l = \mu_f^{ag} + \phi . \tag{18}$$

The chemical potential μ_f^{ag} can be expressed by the relation

$$\mu_f^{ag} = \mu_0^g + RT \ln \left(p_f^{ag}/p_0^g\right) , \tag{19}$$

where μ_0^g is the chemical potential of mercury vapours in the standard state. On inserting Eqs (3) and (19) into Eq. (18), considering the equality of chemical potentials of liquid and vapour in the standard state, $\mu_0^g = \mu_0^l$, we obtain after rearranging the expression for the vapour pressure of mercury in pores p_f^{ag}

$$p_f^{ag} = p_0^g \exp \left\{ \left[\bar{v}^l(p_f^l - p_0^l) - \phi\right]/RT \right\} . \tag{20}$$

It follows from relation (20) that increasing the pressure p_f^l at 20°C, e.g., from the value p_0^l to 500 MPa, then the pressure p_f^{ag} will increase approximately twentyfold. This change in the pressure of supersaturated mercury vapours will be the reason of a certain change in mercury adsorption on the pore surface and consequently also the reason of a change of the value of contact angle θ. This change can be determined approximately on the basis of relations between the adsorption isotherm and contact angle θ proposed by Adamson[12].

The shape of mercury isotherms differs substantially from the isotherms of type I to V of the Brunauer classification[13]. The structure of mercury in adsorption layer differs considerably from the structure of liquid mercury $(\mu^* \gg 0)$, and the isotherms of mercury on nonmetallic substances are therefore to be characterized by the types VI and VII of isotherms illustrated schematically in Fig. 1a. As it has been shown by Adamson[12], the integration of the isotherms of the type VI and VII with respect to ln p up to a point of the first intersection of the line p_0^g, gives the equilibrium two-dimensional pressure π_0^{sg} of the adsorbed film

$$\pi_0^{sg} = \sigma^s - \sigma^{sg} = RT \int_{\Gamma=0}^{\Gamma_0} \Gamma \, d\ln p \,, \tag{21}$$

where Γ stands for the Gibbs adsorption (mol cm^{-2}). By integrating the isotherm to an infinite thickness of layer (as a rule, it is sufficient to do it over two monolayers), we obtain

$$\sigma^s - (\sigma^{sl} + \sigma^{lg}) = RT \int_{\Gamma=0}^{\infty} \Gamma \, d\ln p \,. \tag{22}$$

Subtracting Eq. (21) from (22), we obtain

$$\sigma^{sg} - (\sigma^{sl} + \sigma^{lg}) = RT \int_{\Gamma=\Gamma_0}^{\infty} \Gamma \, d\ln p = \Delta I \,. \tag{23}$$

The integral ΔI corresponds to the hatched area in Fig. 1a and is in a relation to the contact angle θ which can be expressed by inserting the Young–Dupre equation (24) into Eq. (23), viz.

$$\sigma^{sg} - \sigma^{sl} = \sigma^{lg} \cos \theta \tag{24}$$

in the form

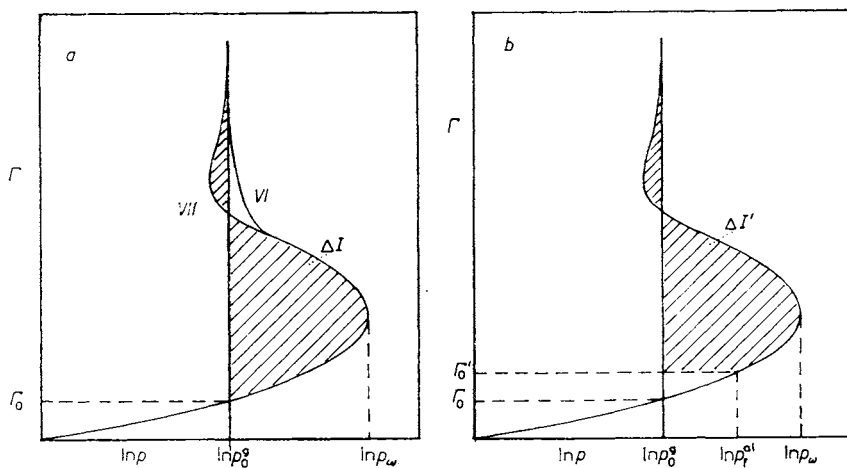$$\cos \theta = \frac{\Delta I}{\sigma^{lg}} + 1 \,. \tag{25}$$

FIG. 1

Schematic adsorption isotherms of the type *VI* and *VII*. The hatched areas correspond to integrals ΔI and $\Delta I'$. *a* Wetting of flat surface, *b* wetting of surface of pores

For liquids which wet the solid surface with a non-zero contact angle, the integral ΔI takes negative values.

Analogous relations to Eqs $(21)-(25)$ hold for the quantities σ^{sg}, Γ_0, ΔI and θ corresponding to the filled pores under the liquid mercury pressure p_f^1 which will be denoted henceforth $\sigma^{sg\prime}$, Γ_0', $\Delta I'$ and θ'. The integral $\Delta I'$ corresponds to the hatched area in Fig. 1b. Even from the graphical comparison given in Figs 1a and 1b it is apparent that the absolute values of the integral $\Delta I'$ are smaller than those for the integral ΔI. Since this integral takes negative values[12], $\Delta I' > \Delta I$. Then it follows from Eq. (25) that $\theta' < \theta$.

The value of the integral $\Delta I'$ and consequently of the angle θ', too, depends on the pressure p_f^1. The change of contact angle with pressure can be expressed as the dependence of θ on the equivalent pore radius $\phi(r)$ because the function $p_f^1(r)$ is determined uniquely by Eq. (16). It follows from this consideration that the contact angle of non-metallic porous materials with mercury decreases with decreasing equivalent pore radius. Calculation of this dependence, requiring the knowledge of parameters of the mercury isotherm, will be given in forthcoming paper.

The discussed dependence of the contact angle θ on the equivalent pore radius r is as well a result of effect of the presence of adsorption forces on the pore surface of solids. Their presence is the reason for adsorption of supersaturated mercury vapours which, though small in extent[14], influences the conditions of wetting the pore walls.

Calculation of the Dependence of Pressure of the Intruded Mercury on the Pore Radius for a Carbonaceous Porous Material

To assess the effect of dispersion forces on the intrusion of mercury, a calculation will be carried out of the dependence of $p_f^1(r)$ for a carbonaceous substance (graphite). For this purpose it is necessary to determine firstly the values of the Kirkwood–Müller constant C_A and of the constants k_A and k_B. The constant C_A was established on the basis of the well-known relation

$$C_A = -6m_e c^2 \alpha \alpha_s \Big/ \left(\frac{\alpha}{\chi} + \frac{\alpha_s}{\chi_s} \right), \tag{26}$$

where m_e is the mass of electron $(9 \cdot 109534 \,.\, 10^{-28} \text{ g})$, c is the light velocity in vacuum $(2 \cdot 997925 \,.\, 10^8 \text{ m s}^{-1})$, α is the polarizability of mercury $(51 \cdot 10^{-25} \text{ cm}^3$, see ref.[15]$)$, α_s is the polarizability of carbon $(9 \cdot 6 \,.\, 10^{-25} \text{ cm}^3)$, χ is the molar diamagnetic susceptibility of mercury $(-41 \,.\, 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, see ref.[16]$)$ and χ_s is the molar diamagnetic susceptibility of carbon $(-6 \,.\, 10^{-6} \text{ cm}^3 \text{ mol}^{-1})$. The calculated value of the Kirkwood–Müller constant is $C_A = 8 \cdot 511 \text{ J nm}^6 \text{ mol}^{-1}$. On its basis, on using Eq. (9), the constants k_A and k_B were calculated. For this purpose, the value corresponding to graphite, *i.e.* $1 \cdot 127 \,.\, 10^2 \text{ nm}^{-3}$ was used for N, the value $r_0 = 0 \cdot 3 \text{ nm}$, and the

parameters f corresponding to cylindrical pores are $f_A = 1.333$ and $f_B = 0.444$. Consequently, for the system mercury–carbon, $k_A = 4.017 \, kJ \, nm^3 \, mol^{-1}$ and $k_B = 4.877 \cdot 10^{-4} \, kJ \, nm^9 \, mol^{-1}$. The molar volume of mercury at 20°C is $14.808 \, cm^3 \, mol^{-1}$.

Calculation of the first term of Eq. (16) is similar to the procedure applied in the case of the Washburn equation. For the surface tension of mercury σ_∞^{lg} the value $0.474 \, N \, m^{-1}$ (ref.[17]) was used and for the contact angle the value $142°$ (ref.[1]). On the assumption that $\gamma(r) = 1$, $\mu^* = 0$ and $\theta = 142° = const.$, it is possible, for the carbonaceous porous material with cylindrical shape of pores, to express Eq. (16) in the form

$$p_f^l = \frac{747.0}{r + 0.42} - \frac{271.3}{r^3} + \frac{0.033}{r^9}, \qquad (27)$$

where p_f^l is in MPa and r in nm.

Table I (the second column) presents the calculated dependence of pressures p_f^l on the pore radius r on the basis of Eq. (27) and the dependence calculated when omitting the second and third terms on the right-hand side of this equation, *i.e.* on the basis of the Washburn equation (considering the dependence of σ^{lg} on r).

RESULTS AND DISCUSSION

As it follows from Table I, the dispersion forces influence substantially the value of the pressure p_f^l of the mercury intruded into the pores of radii smaller than 5 nm. For a mercury pressure, *e.g.* 308.68 MPa, the pores of radii 1.5 nm are filled-up, whereas the Washburn equation for this pressure p_f^l gives the value $r = 2 \, nm$. For the pores of radii close to 1 nm, the values of pressures p_f^l are lower than those corresponding to filling typical mesopores. This fact makes it possible to explain the above-mentioned contradictory results, obtained by the capillary condensation and mercury porosimetry methods of the analysis of mesopores of active carbons containing supermicropores.

The active carbons prepared by the method of inorganic activating agents contain besides typical micropores of radii r from 0.6 to 0.7 nm (refs[5,18]) also so-called supermicropores of radii r from 0.8 to 1.4 nm (ref.[8]). As it is apparent from Table I, these supermicropores are volume-filled by mercury at pressures p_f^l from about 80 to 300 MPa similarly to mesopores of radii from 1.6 to 10 nm. This volume filling of supermicropores during mercury intrusion simultaneously with filling-up of the mesopores of substantially greater dimensions is made it possible by reducing the value of pressure p_f^l due to the presence of dispersion forces. It is evident that in this way, only those supermicropores are filled-up with mercury which mutually communicate with the system of filled-up meso- and macropores. A scheme of such a system of supermicropores and mesopores partly filled with mercury is given in

TABLE I

Comparison of the dependence of liquid mercury pressure p_f^l on the radius r of cylindrical pores of carbonaceous material calculated on the basis of Eq. (27) and on the basis of the Washburn equation (Eq. (27) without the second and third terms on its right-hand side)

r nm	$(p_f^l)^a$ MPa	$(p_f^l)^b$ MPa
0·7	− 123·18	666·96
0·8	82·66	612·30
0·9	193·84	565·91
1·0	254·79	526·06
1·2	304·12	461·11
1·5	308·68	389·06
1·8	289·97	336·49
2·0	274·77	308·68
2·5	238·46	255·82
3·0	208·37	218·42
5·0	135·65	137·82
7·0	99·88	100·67
10·0	71·42	71·69
30·0	24·55	24·56
35·0	21·08	21·09
40·0	18·48	18·48

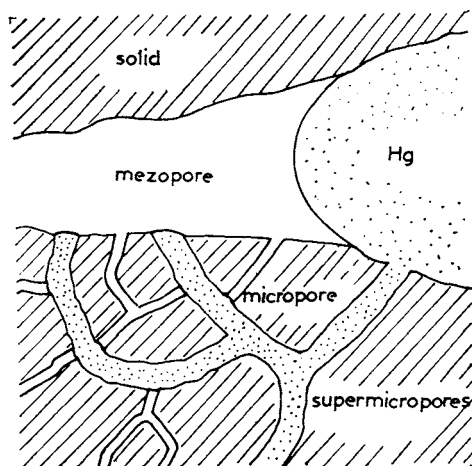[a] In terms of Eq. (27); [b] in terms of the Washburn equation.

FIG. 2

Sketch of a porous system partly filled with mercury, during its intrusion. Supermicropores of radii close to 0·8 nm are filled sooner than mesopores smaller than 10 nm. If the entire pore surface is not completely wetted (*i.e.* the meniscus exists), and the contact angle does not show hysteresis, the pores are filled reversibly

Fig. 2. The method of mercury porosimetry yields in these cases, as a rule, substantially higher values of the mesopore volumes than those actually present in samples. In such a way, the capillary condensation methods enable to describe the real mesopore structure. The difference of the mesopore volumes determined by the method of mercury porosimetry and by the adsorption methods corresponds to the volume of supermicropores.

The correctness of the above-mentioned explanation of contradictions of the porosimetric and adsorption methods of the mesopore analysis is proved by further experimental facts. So, *e.g.*, the total volumes of pores determined on the basis of the adsorption and porosimetric methods are just the volumes of supermicropores larger than the total volumes of pores of active carbons activated chemically, as determined on the basis of the mercury and helium densities[19]. In case of active carbons prepared by activation of carbonized wood material with steam, whose microporous system contains only typical micropores, the total pore volumes determined by different methods are identical[20].

It is necessary to emphasize that the mentioned "inverse" filling-up of supermicropores with mercury at pressures p_f^1 lower than the pressures corresponding to the filling-up of typical mesopores is apparently made possible, among others, by the fact that in supermicropores mercury does not yet lose its metallic character. The values of perturbation chemical potential μ^* are in supermicropores still small for mercury. Another situation, however, occurs in the case of filling-up the typical micropores of radii r from 0·6 to 0·7 nm. For these micropores, Eq. (27) gives already unreal negative values of pressures p_f^1. It is caused by the fact that the last term on the right-hand side of Eq. (16), containing the expression μ^*, was neglected. This omission is unacceptable for typical micropores since, owing to a small number of mercury atoms in micropores, mercury loses its metallic character, and the chemical potential corresponding to the change of mercury structure μ^* takes, as it has been shown above, considerable positive values $(\mu^* > 26 \text{ kJ mol}^{-1})$.

For the pores of radii greater than 1 nm it is possible to assume that $\gamma(r) \doteq 1$ and $\mu^* \doteq 0$. The extent of the mercury vapour adsorption on the surface of solids is at ambient temperatures, as a rule, small[14]. Therefore it is to be assumed that the effect of the dependence of contact angle θ on the radii of volume-filled pores r will represent the correction of the second order. An equation of the type of Eq. (27) thus describes well the intrusion of mercury into pores of equivalent radii r greater than 1 nm.

In connection with the discussed effect of adsorption forces we mention in addition the question of hysteresis during intrusion and extrusion of mercury. Lowell[21] suggested an elucidation of this hysteresis by the presence of adsorption forces in pores as an alternative of the usually presented ink-bottle effect. The question of occurrence of this hysteresis is, however, rather more complicated than the explanation due to Lowell. As far as there exists a meniscus in pores and hysteresis of contact angle θ is not considered, the function $p_e^1(r)$ for a model system of cylindrical

pores is the same as the function $p_f^l(r)$ given by Eq. (16) even though the potential ϕ in pores takes considerable negative values. Here p_e^l is the pressure of liquid mercury at which the extrusion of mercury from pores of radii r takes place. This fact is connected with the existence of reversible equilibrium in pores which is expressed by condition (2). Even in the case of the presence of supermicropores, if a meniscus in pores exists, a reverse sequence during extrusion occurs than that taking place during intrusion. The extrusion of mercury will take place first in mesopores and only at a lower pressure p_e^l in communicated supermicropores.

However, another situation occurs when the mercury is completely intruded into the single-ended pores so that the full wetting of the pore walls and the disappearance of the menisci take place. The prerequisite of this thorough wetting of full pore surface is a thorough sample evacuation. In this case, it is necessary to use a negative pressure p_e^l $(p_e^l < 0)$ to separate (to detach) mercury from pore walls and to recreate menisci. Then $p_e^l < p_f^l$ holds, which leads directly to hysteresis. This phenomenon occurring as well in glass capillaries is well-known to experimentalists. When measuring gas pressures by the McLeod manometer, providing that a so-called sticky vacuum is reached, mercury sticks on the capillary walls, and a negative pressure p_e^l of liquid mercury is needed to detach it and to recreate the mercury meniscus. The reason of this phenomenon consists in the adhesion of mercury to the walls of the capillary (pores), the nature of the adhesion consisting in the presence of adsorption forces. In the case when the wetting of all the pore surface takes place, the Lowell explanation of the intrusion-extrusion hysteresis is therefore correct. On the basis of the above--mentioned knowledge, it is to be expected that the extent of this hysteresis will depend on the conditions and the depth of degassification of samples.

Equation (16) can be considered as a general equation of mercury porosimetry. It is evident that the application of this equation can start from different methods of calculating the potential of adsorption forces proceeding, *e.g.* from the macroscopic theory of intermolecular forces[22], taking into consideration also the effect of the electron gas of mercury. It is to be expected that general equation (16) will prove to be useful in future as well in analysis of micropores. On its basis is is possible to expect that at temperatures $250-350°C$, a considerable decrease in the pressure p_f^l will take place corresponding to the intrusion into micropores owing to the decrease in value of μ^*. During an increase of temperature, the saturated vapour pressure of mercury p_0^g grows probably more rapidly than the hypothetical vapour pressure p_ω because the heat of vaporization of mercury is considerably higher than the hypothetical heat of vaporization of mercury whose atoms are not bound by electron gas. It is probable that this effect predominates the effect of increasing the term of RT in Eq. (17) with increasing temperature.

From the above-mentioned follows that the consideration of the effect of adsorption forces in mercury porosimetry does not mean only a mere introduction of refining corrections but has an essential significance, *e.g.* in analysis of mesopores. It makes

it possible to explain the differences of values of total volumes of mesopores determined by porosimetric and adsorption methods which reach in case of the porous substances containing supermicropores as many as several hundred percent.

LIST OF SYMBOLS

N_A Avogadro number

C_A Kirkwood–Müller constant [kJ nm^6 mol^{-1}]

c light velocity in vacuum [m s^{-1}]

d coefficient in Eq. (12) [nm]

f_A, f_B parameters of Eq. (9) dependent on pore shape

f fugacity [Pa]

f_ω fugacity corresponding to pressure p_ω [Pa]

J^{lg} curvature of the liquid–gas interface (of meniscus) [nm^{-1}]

k_A, k_B parameters in Eqs (9) and (10) [kJ nm^3 mol^{-1}] and [kJ nm^9 mol^{-1}]

m_e electron mass [g]

N number of atoms in unit volume of solid [cm^{-3}]

p pressure [Pa]

p_ω hypothetical saturated vapour pressure of mercury corresponding to its structure in force field but taken out of reach of adsorption forces [Pa]

q parameter characterizing pore dimensions (for cylindrical pores $q = r$) [nm]

R gas constant [kJ mol^{-1} K^{-1}]

R_1, R_2 principal radii or curvature of meniscus [nm]

R_s radius of curvature of spherical meniscus [nm]

r effective pore radius [nm]

r_0 equilibrium distance of adsorbed molecule (atom) from the solid surface [nm]

r_k pore radius characterizing the range of radii in which the capillary phenomena cease acting [nm]

T absolute temperature [K]

v molar volume [cm^3 mol^{-1}]

v^s molar solid–like volume [cm^3 mol^{-1}]

$x = p^g/p_0^g$ relative vapour pressure

α polarizability of mercury [cm^3]

α_s polarizability of adsorbent (carbon) [cm^3]

Γ adsorbed amount according to Gibbs [mol cm^{-2}]

Γ_0 adsorbed amount according to Gibbs corresponding to the relative pressure $x = 1$ [mol cm^{-2}]

Γ_0' adsorbed amount according to Gibbs corresponding to vapour supersaturation [mol cm^{-2}]

$\gamma(r)$ function determining the degree of possibility of occurrence of capillary phenomena

ΔI integral in Eq. (23)

$\Delta I'$ integral in Eq.(23) corresponding to the supersaturated vapour pressure p_f^{ag}

θ contact angle of pore walls with mercury [deg]

θ' contact angle of pore walls with mercury under conditions of supersaturation [deg]

μ chemical potential of mercury [kJ mol^{-1}]

μ^* chemical potential corresponding to a change of structure of mercury in force field [kJ mol^{-1}]

$v = f_\omega/f_0^g$ relation of the fugacity f_ω to the standard fugacity f_0^g

σ	surface tension, surface energy, interfacial energy [N m^{-1}], [J m^{-2}], respectively
π_0^{sg}	equilibrium two-dimensional pressure of adsorbed film [N m^{-1}]
σ^{sg}	solid-gas interfacial energy [J m^{-2}]
τ	parameter determining the range of pore radii in which the function $\gamma(r)$ changes from zero to unity
ϕ	potential of dispersion forces [kJ mol^{-1}]
χ	molar diamagnetic susceptibility [cm^3 mol^{-1}]

Superscripts

ag	adsorbed vapour–like phase
al	adsorbed liquid–like phase
g	gas phase
s	solid phase
sg	solid–gas interface
sg′	solid–gas interface corresponding to supersaturation ($p_f^l > p_0^l$)
sl	solid–liquid interface
l	liquid phase
lg	liquid–gas interface

Subscripts

e	pore emptying (extrusion)
f	pore filling
s	solid phase-adsorbent (carbon)
0	standard state

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Note added in proof: The Tolman equation in the form (*15*) was applied for mercury porosimetry in[24].