

# LITERATURE CITED

1. P. P. Zolotarev and V. I. Ulin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 500 (1977).
2. T. Gudmen, in: *Heat Exchange Problems*, Atomizdat (1967), Part 1, p. 41.
3. P. P. Zolotarev, *Izv. Akad. Nauk SSSR, Khim.*, 711 (1969); 526 (1972).
4. V. A. Ditkin and A. P. Prudnikov, *Handbook on Operational Computations* [in Russian], Vysshaya Shkola (1965).
5. A. M. Voloshchuk and M. M. Dubinin, *Dokl. Akad. Nauk SSSR*, **212**, 649 (1973).
6. A. M. Voloshchuk, M. M. Dubinin, and I. T. Erashko, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 517 (1975).
7. M. M. Dubinin, I. T. Erashko, O. Kadlec, V. I. Ulin, A. M. Voloshchuk, and P. P. Zolotarev, *Carbon*, **13**, 193 (1975).

## CAPILLARY EFFECTS AND INFORMATION CONCERNING THE PORE STRUCTURE OF ADSORBENTS

### 1. ADSORPTION AND CAPILLARY VAPORIZATION OF NITROGEN FROM ADSORBENT MESOPORES

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Capillary vapor condensation, the depression of mercury, and similar capillary effects are widely used to characterize and describe the mesopore and macropore structures of adsorbents and catalysts. Since the theory of these effects has been developed for certain simple geometrical pore forms (cylindrical, slotted, etc.), porous structures are described in terms of some previously selected geometrical pore model. Calculated integral and differential curves showing the distribution of pore volumes and surface areas over pore radii therefore apply, not to the actual adsorbent or catalyst but, rather, to an equivalent model porous body with arbitrarily chosen pore form [1].

The principal steps involved in the development of methods for determining adsorbent and catalyst mesopore volume distributions from experimental data on the capillary condensation of vapors have been outlined in [1]. The trend of recent years has been to combine highly precise calculations based on the cylindrical pore model [2], with study of the adsorption field arising from the pore walls, its effect on the thermodynamic potential of the adsorbate, and the resulting modifications of the Kelvin equation [3-5], a program initiated in the earlier papers of Deryagin [6-8].

Work with the cylindrical pore model [1, 9] has shown that the approximation methods of [1, 9, 10] and the more exact treatment of [11] lead to essentially the same results in the case of bodies containing intrinsic mesopores with radii in excess of 16 Å. Marked differences in the results obtained by these methods are obtained only in formal calculations on supermicroporous bodies with pore radii ranging from 16 to 7 Å [12], where the concept of capillary vapor condensation no longer has physical significance.

The present work has extended the Deryagin-Broekhoff-de Boer method to allow for variation of the surface tension with the mean radius of meniscus curvature in the model cylindrical pore body, giving pore-volume distribution curves which can be compared with those obtained from approximation and exact classical calculations on the equivalent model adsorbent. Treatment is limited here to the sorption of nitrogen (bp ~ 77°K), experimental data from the region of polymolecular adsorption having shown the mean statistical depth of the adsorbed layer of this gas to be essentially independent of the chemical nature of the adsorbent.

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1. The classical analysis of the capillary condensation of nitrogen in the mesopores of adsorbents and catalysts is based on an application of the Kelvin equation

$$r_c = \frac{2\sigma v}{RT \ln(p_s/p)} = \frac{4.05}{\lg(p_s/p)}, \text{ \AA} \quad (1)$$

to the desorption branch of the adsorption isotherm for the cylindrical pore model adsorbent. Equation (1), an expression for  $r_c$ , the radius of curvature of the spherical meniscus at  $T = 77.3^\circ\text{K}$ , was obtained by treating nitrogen as a normal liquid with surface tension  $\sigma = 8.72 \text{ dyn/cm}$  and molar volume  $v = 34.68 \text{ cm}^3/\text{mole}$  [5]. Here it was assumed that the liquid-nitrogen meniscus is established between adsorbed films,  $t$ , the mean statistical film depth being determined by  $p/p_s$ , the relative pressure alone, regardless of the pore surface curvature. The adsorption layer depth is described by a standard  $t$ -curve, the portion of this curve ranging from  $\sim 0.9$  to  $\sim 0.4$  relative nitrogen pressure (desorption branch up to the beginning of hysteresis) being covered by an empirical equation of the form [13]

$$\lg(p_s/p) = 16.11t^{-2} - 0.1682 \exp[-0.1137t] \text{ for } t > 5 \text{ \AA} \quad (2)$$

Over this range of relative pressures, the cylindrical pore radius is given by

$$r = r_c + t \quad (3)$$

2. Broekhoff and de Boer have treated the effect of adsorption on capillary vaporization (desorption) from cylindrical pores. According to [3-5],  $\mu_a$ , the thermodynamic potential of the adsorbed phase, is determined by  $t$ , the distance of the adsorbate-vapor interface from the pore wall. Neglecting effects from the geometrical form of the pore, these authors derived the following expression for  $\mu_a$ :

$$\mu_a - \mu_L = F(t) \quad (4)$$

$\mu_L$  being the thermodynamic potential of the liquid in bulk, and  $F(t)$  a function of the form

$$F(t) = 2.303 RT [16.11 t^{-2} - 0.1682 \exp(-0.1137t)] \quad (5)$$

obtained from the  $t$ -curve equation of (2). For reversible transport of  $dN$  moles from the gaseous phase into the adsorption layer,  $\partial G_{p,T} = 0$  and [3]

$$RT \ln(p_s/p) - F(t) = \sigma v (r - t)^{-1} \text{ for } t = t_e \quad (6)$$

Equations (5) and (6) combined yield (7), an expression for  $t_e$ , the depth of the nitrogen layer adsorbed at  $77.3^\circ\text{K}$  and equilibrium  $p/p_s$  in cylindrical pores of radius  $r$

$$\lg \frac{p_s}{p} - \frac{16.11}{t_e^2} + 0.1682 \exp(-0.1137t_e) - \frac{2.025}{r - t_e} = 0 \text{ for } t_e > 5 \text{ \AA} \quad (7)$$

According to this equation,  $t_e$  is a function of both  $p/p_s$  and  $r$ .

By drawing on Eq. (4), Broekhoff and de Boer also derived the following expression for the thermodynamically reversible vaporization of nitrogen from cylindrical pores at  $77.3^\circ\text{K}$  [3];

$$r - t_e = \frac{4.05}{\lg(p_s/p)} + \frac{1}{(r - t_e) \lg(p_s/p)} \left\{ 32.22 \left[ \frac{r}{t_e} - 1 - \ln \frac{r}{t_e} \right] - \right. \\ \left. - 2.964 \exp(-0.1137 t_e) [r - t_e - 8.795] - 26.06 \exp(-0.1137 r) \right\} \quad (8)$$

for  $t_e > 5 \text{ \AA}$ .

The first term in the right-hand member of (8) is the classical Kelvin expression for the case of the hemispherical meniscus. The second term in this same member covers the effect of adsorption on the capillary vaporization process. Here consideration is no longer limited to the case of the hemispherical meniscus.

According to (7) and (8), capillary vaporization from cylindrical pores occurs in such manner that the reversible relative pressure above the liquid meniscus and the adsorption layer in the incompletely filled portion of the pore is a function of the pore radius  $r$  and the adsorption layer depth  $t_e$ . Methods of solving (7) and (8) will be discussed below.

3. The Broekhoff-de Boer treatment is based on the assumption that  $\sigma$ , the surface tension of the adsorbate, is constant. In actuality, however,  $\sigma$  must vary with the liquid meniscus curvature. Derivation of an expression relating  $\sigma$  with the meniscus curvature has been given in a recent paper dealing with the statistical theory of liquids [14]. Using the formulas and data for nitrogen at  $77.3^\circ\text{K}$  given in this latter work, it can be readily shown that  $\delta = 3.31 \text{ \AA}$ . For the spherical concave meniscus with absolute radius  $\rho$  ( $R_1 = \rho$  and  $R_2 = \rho$ ), one has

TABLE 1. Variation of the Surface Tension with the Curvature at 77.3°K

Method of calculation	$\sigma$ , dyne/cm, at the following values of $\rho$ , the absolute value of the radius of curvature, in Å				
	$\infty$	403.4	148.4	54.6	20.08
According to the data of Table 1 of [14]	9.09	9.25	9.52	10.37	13.55
Calculated by Eq. (9) with $\delta = 3.31$	9.09	9.24	9.51	10.34	13.56

$$\frac{\sigma}{\sigma_{\infty}} = \left(1 - \frac{2\sigma}{\rho}\right)^{-1} = \left(1 - \frac{6.62}{\rho}\right)^{-1} \quad (9)$$

while for the cylindrical convex meniscus ( $R_1 = \rho$ ,  $R_2 = \infty$ )

$$\frac{\sigma}{\sigma_{\infty}} = \left(1 - \frac{\delta}{\rho}\right)^{-1} = \left(1 - \frac{3.31}{\rho}\right)^{-1} \quad (10)$$

$\sigma_{\infty}$  being the surface tension for the planar liquid, and  $R_1$  and  $R_2$  the principal radii of curvature of the meniscus. Tolman has obtained similar expressions by quasi-thermodynamic methods.

A comparison of the results of [14] with values of  $\sigma$  for various values of  $\rho$  calculated from (9) with our values of  $\delta$ , 3.31 Å, and  $\sigma_{\infty}$ , 9.09 dyn/cm, is given in Table 1. It is obvious that (9) and, of course, (10) satisfactorily describe the variation of  $\sigma$  with  $\rho$  and can therefore be used in the solution of the present problem.

4. Let us now consider the effect of the meniscus curvature on the liquid surface tension, following the approximation methods of [3-5] and assuming the mean effective radius of curvature  $\rho$  of the meniscus in the cylindrical pore equal to the difference between the pore radius  $r$  and the adsorption layer depth  $t_e$  i.e.,

$$\rho = r - t_e \quad (11)$$

This same assumption has been used [15] in calculating specific surface charges in mesoporous adsorbents from data on the capillary condensation of nitrogen. With the introduction of certain correction terms it has been possible to attain almost perfect agreement between specific adsorbent surface areas calculated by the BET method and cumulative surface areas obtained from capillary condensation data.

The  $\sigma v/RT$  term of Eq. (7) for the cylindrical-type meniscus has the value 2.025, while the corresponding  $2\sigma v/RT$  term of Eq. (8) for the spherical meniscus is equal to 4.05. Since the terms in  $\sigma$  do not appear in the integral expressions involved in the derivation of (7) and (8), the  $\sigma/\sigma_{\infty}$  correction coefficient of (10) can be substituted into the last member of (7), and the corresponding coefficient of (9) substituted into the first term of the right-hand member of (8). As a result of elementary operations, one is finally led to

$$\lg \frac{p_s}{p} - \frac{16.11}{t_e^2} + 0.1682 \exp(-0.1137t_e) = \frac{2.025}{r - t_e - 3.31} \quad (12)$$

$$r - t_e = \frac{4.05(r - t_e)}{\lg \frac{p_s}{p}(r - t_e - 6.62)} + \frac{1}{(r - t_e) \lg \frac{p_s}{p}} \left\{ 32.22 \left[ \frac{r}{t_e} - 1 - \ln \frac{r}{t_e} \right] - 2.964 \exp(-0.1137t_e) [r - t_e - 8.795] - 26.06 \exp(-0.1137r) \right\} \quad (13)$$

Equations (12) and (13) are the analogs of (7) and (8).

5. Computer solution of (7) and (8) is entirely analogous to solution of (12) and (13), and discussion will therefore be limited to the second of these two systems. Substitution of the expression for  $\log(p_s/p)$  from Eq. (12) into (13) gives an equation of the form  $\varphi(r, t_e) = 0$ . From it one can obtain the value of  $t_e$  corresponding to any given value of  $r$ . Substitution back into (12) then gives the value of  $p/p_s$  corresponding to  $r$ .

By graphing it can be shown that there are three regions containing roots of the function  $\varphi$  for given values of  $r$ . Interest attaches to the  $t_e$  region ranging from 5 Å to  $r/2$ , roots in the neighborhood of the  $x = r$  asymptote having no physical significance. Having chosen a  $t_e$  region, search for the roots is carried out by dividing the interval into halves with the calculated value of the  $\varphi$  function in the middle [16]. This process is concluded when the  $\varphi$  value becomes less than some arbitrarily chosen small quantity, or when two successive root approximations differ by less than some such value. In the event that no roots appear, the interval is extended

TABLE 2. Basic Data for Calculating the Distribution of Mesopore Volumes over Pore Radii by Various Methods, for the Cylindrical Pore Model

$r, \text{\AA}$	Method I		Method II		Method III	
	$t, \text{\AA}$	$p/p_s$	$t_e, \text{\AA}$	$p/p_s$	$t_e, \text{\AA}$	$p/p_s$
500	38,44	0,980	51,89	0,977	51,30	0,977
450	35,61	0,978	48,18	0,974	47,59	0,974
400	32,61	0,975	44,23	0,971	43,56	0,970
350	29,49	0,971	39,95	0,966	39,20	0,966
300	26,35	0,966	35,23	0,960	34,42	0,959
250	23,24	0,960	30,19	0,952	29,37	0,950
200	20,21	0,949	25,18	0,939	24,44	0,937
180	19,03	0,944	23,28	0,932	22,56	0,929
160	17,84	0,936	21,45	0,923	20,76	0,920
140	16,64	0,972	19,69	0,911	19,01	0,907
120	15,40	0,915	17,96	0,895	17,30	0,890
110	14,76	0,907	17,11	0,885	16,44	0,879
100	14,10	0,897	16,24	0,874	15,57	0,865
90	13,42	0,885	15,37	0,859	14,67	0,849
80	12,70	0,871	14,47	0,841	13,74	0,827
70	11,94	0,852	13,53	0,817	12,76	0,800
65	11,54	0,840	13,04	0,802	12,24	0,782
60	11,12	0,826	12,53	0,785	11,69	0,761
55	10,68	0,810	11,99	0,765	11,12	0,737
50	10,21	0,791	11,43	0,741	10,51	0,706
45	9,72	0,768	10,84	0,712	9,85	0,669
40	9,19	0,739	10,20	0,676	9,14	0,621
39	9,08	0,732	10,07	0,668	8,99	0,610
38	8,97	0,725	9,93	0,659	8,84	0,598
37	8,86	0,718	9,79	0,650	8,68	0,586
36	8,74	0,710	9,65	0,640	8,52	0,573
35	8,62	0,702	9,51	0,630	8,36	0,559
34	8,50	0,794	9,36	0,619	8,19	0,544
33	8,38	0,685	9,21	0,608	8,02	0,529
32	8,26	0,675	9,06	0,596	7,84	0,513
31	8,13	0,665	8,90	0,584	7,66	0,495
30	8,00	0,654	8,74	0,570	7,48	0,477
29	7,86	0,643	8,58	0,556	7,29	0,457
28	7,73	0,631	8,41	0,541	7,09	0,436
27	7,59	0,618	8,24	0,527	6,89	0,414
26	7,45	0,605	8,06	0,509	6,68	0,390
25	7,30	0,630	7,88	0,491	6,47	0,365
24	7,15	0,575	7,70	0,472	6,25	0,339
23	7,00	0,558	7,51	0,452		
22	6,84	0,541	7,31	0,430		
21	6,68	0,521	7,11	0,408		
20	6,51	0,501	6,90	0,383		
19	6,33	0,479	6,68	0,358		
18	6,15	0,455	6,46	0,331		
17	5,97	0,429				
16	5,77	0,402				
15	5,57	0,372				

and the search continued as before. In the classical method, values of  $r_c$  and  $t$  corresponding to given  $r$  are calculated from Eq. (3).

This problem was solved on the M-222 computer, following an ALGOL program.

6. Table 2 summarizes the results of calculations by the three methods under consideration here: I, classical; II, Deryagin-Broekhoff-de Boer; and, III, the II approximation with  $\sigma = f(r-t_e)$ , for  $r$  values ranging from 500 to 15  $\text{\AA}$  in steps of varying magnitude. This table has been given in its entirety since the figures appearing in it can be used in developing distribution curves for mesopore volumes over pore radii for various adsorbents and catalysts.

Over the interval of relatively high cylindrical pore radii (500-150  $\text{\AA}$ ) the classical method I, and methods II and III with account taken of the effect of adsorption on capillary vaporization differ principally in the adsorbed layer depths to which they lead. In the interval of  $r$  values of 500-200  $\text{\AA}$ , the three methods lead to essentially the same values of the relative pressure  $p/p_s$ . Differences in the values of the relative pressure calculated by the various methods become more pronounced on passing to smaller  $r$  values. Over any one interval, values of  $t_e$  and  $p/p_s$  calculated by methods II and III are only slightly different, and vary in the same direction. Effects from variations in  $\sigma$  could be expected to be negligibly small in mesopores with radii in excess of 100  $\text{\AA}$ .

Significant differences in  $t_e$  and  $p/p_s$  values calculated by the various methods appear in the 100-50  $\text{\AA}$  range of mesopore radii. Here it is no longer possible to neglect the variation of the surface tension with the

mean meniscus curvature. Marked differences in calculated  $t_e$  and  $p/p_s$  values are found in mesopores of radii less than 50 Å, these differences being particularly pronounced in the case of the relative pressure. Comparison of results obtained by methods II and III indicates that the increase in  $\sigma$  accompanying reduction in  $(r - t_e)$ , the mean effective radius of curvature of the meniscus, leads to a pronounced reduction in the calculated value of  $t_e$ , this reduction being more pronounced at the lower radii.

It should be noted that Table 2 contains the raw data for calculating pore-volume distributions in adsorbents and catalysts. Methods II and III can be considered as refinements of the classical method I based on the Kelvin equation, correction for the depth of adsorption layer corresponding to a nonporous adsorbent of the same chemical type being obtained through experimental data. The effect of differences in these raw data on the pore volume distribution can be estimated by calculating sorption isotherms for certain characteristic adsorbents. The results of such calculations will be reported in a subsequent communication.

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## CONCLUSIONS

1. The attempt has been made to allow for the dependence of the surface tension on the radius of curvature of the liquid adsorbate meniscus in the Deryagin-Broekhoff-de Boer treatment of the capillary evaporation of nitrogen from cylindrical pores at 77.3°K.

2. Computer calculations have given comparable raw data for the development of mesopore distribution curves for adsorbents and catalysts based on the Kelvin equation and certain variants of the Deryagin-Broekhoff-de Boer method.

3. Estimates made of the range of pore radii over which the effects covered by these corrections to the Kelvin equation might be expected to predominate.

## LITERATURE CITED

1. M. M. Dubinin, *Zh. Fiz. Khim.*, **30**, 1652 (1956).
2. D. Dollimore and C. R. Heal, *J. Appl. Chem. Biotechnol.*, **14**, 109 (1964).
3. J. C. P. Broekhoff, *Adsorption and Capillarity*, Thesis at Delft University of Technology, Delft, Waltman, 1969.
4. J. C. Broekhoff and J. H. de Boer, *J. Catal.*, **9**, 8, 15 (1967); **10**, 153, 368, 377, 391 (1968).
5. V. G. Gilson (editor), *Structure and Properties of Adsorbents and Catalysts*, Mir (1973), Chap. 1, p. 23.
6. B. V. Deryagin, *Zh. Fiz. Khim.*, **14**, 137 (1940).
7. B. V. Derjagin (Deryagin), *Acta Phys.-Chem. USSR*, **12**, 139 (1940).
8. B. V. Derjaguin (Deryagin), *J. Colloid. Interface Sci.*, **24**, 357 (1967).
9. M. M. Dubinin and E. G. Zhukovskaya, *Zh. Fiz. Khim.*, **30**, 1840 (1956).
10. T. D. Oulton, *J. Phys. Colloid. Chem.*, **52**, 1296 (1948).
11. E. P. Barrett, L. G. Joyner, and P. P. Halenda, *J. Am. Chem. Soc.*, **73**, 373 (1951).
12. M. M. Dubinin, *Izv. Akad. Nauk SSSR. Ser. Khim.*, 996 (1974).
13. J. H. deBoer, B. C. Lippens, B. G. Linsen, and J. C. Broekhoff, *J. Colloid. Interface Sci.*, **21**, 405 (1966).
14. W. Ahn, M. Jhon, H. Pak, and S. Chang, *J. Colloid Interface Sci.* **38**, 605 (1972).
15. W. Ahn, K. Shin, and S. Chang, *J. Colloid. Interface Sci.*, **51**, 232 (1975).
16. M. I. Ageev, V. P. Alik, R. M. Galis, and Yu. I. Markov, *Library of Algorithms 1b-50b* [in Russian], Sovet-skoe Radio (1975).