JOURNAL OF MATERIALS SCIENCE 20 (1985) 2071–2086

Characterization of structural parameters of porous materials by a new adsorption isotherm

P. T. JOHN*, D. K. SURI, K. C. NAGPAL‡
Materials Characterisation Division, National Physical Laboratory, New Delhi 110012, India

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A new adsorption isotherm equation, log log $P = C + n \log v$, has been developed which characterizes many properties of the structure of porous materials, such as monolayer capacity of isotherms of Types I, II and IV, limiting micropore volume at extremely low pressure, degree and dispersion of micropores, mesopore surface area, mean pore size, etc. The equation has been successfully extended to binary and ternary mixtures, data for which have been obtained from the individual isotherms. It is also shown that a linear plot of the new isotherm implies that the distribution of adsorption volume with adsorption potential is Gaussian. Various other well know isotherm equations have been deduced from this new equation. The equation is direct and involves fewer mathematical calculations for solving the structural parameters of porous materials.

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1. Introduction

Adsorption, in particular gas–solid adsorption, is of great practical value in many industrial applications. Adsorption is related to pressure or relative pressure by means of the adsorption isotherm. Fundamentally, the adsorption isotherm should be derived from a molecular-statistical analysis, but almost all the working isotherms are analytical in origin. A number of adsorption isotherms have been developed in recent years [1–3]. The isotherm developed by Polanyi [4] based on potential theory is one of the earliest isotherms. Dubinin [5] also based his isotherm on potential theory. According to this theory, the field of attractive forces of the adsorbent surface is characterized by the adsorption potential. This is thermodynamic, is determined by the spatial positions of gas or vapour molecules and is independent of other molecules in the potential field. It implies that the adsorption potential in this respect is similar to the gravitational potential. Adsorption potential A is the work done by adsorption forces in transferring one mole of normal liquid in equilibrium with the saturation vapour pressure p_s to the adsorbed liquid state at a given point in equilibrium with vapour pressure p. It is given by

$$A = \int_p^{p_s} (RT/p)\,\mathrm{d}p = 2.303RT \log (p_s/p) \tag{1}$$

There are a number of other methods for the analysis of isotherm data, such as the t-method of Lippens and de Boer [6], the α_s-method of Sing [7, 8], comparison plots [9, 10] and the f-method [11, 12], etc., which make use of standard isotherms obtained with selected non-porous reference materials to derive surface and porous properties.

In this paper, we have reviewed the various structural properties of porous materials by the application of the new isotherm developed by John and co-workers [13–16]. Various other well known adsorption equations have also been derived from the new isotherm equation.

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*Present address: 749 JNU Quarters, New Campus, New Delhi 110067, India.
‡To whom correspondence may be addressed.

0022–2461/85 $03.00 + .12

2. Adsorption model

According to the model based on potential theory, the change in free energy is equivalent to the potential energy of attraction of adsorbent on adsorbate. The model considers the van der Waals attraction based on a power law $(v/v_s)^n$ and the change in free energy is taken as a function of $\log(v/v_s)^n$. Because of the simplicity of the model, the isotherm equation of a pure gas has a simple mathematical form. The isotherm equation of a mixture can be formed using the constants of the pure gas isotherms. This makes the mixture isotherm as simple as a pure gas isotherm.

3. Deduction of the isotherm

For a non-adsorbing gas, the work done in terms of volumes is given by the relation

$$w = 2.303RT\log(v^\circ/v_s^\circ) \qquad (2)$$

where v° and v_s° are respectively the volumes at pressures p and p_s. The amounts of gas in v° and v_s° are the same. When v and v_s are the volumes adsorbed respectively at pressures p and p_s, the amounts in v and v_s are not the same. In this case the potential in terms of volumes adsorbed is given semiempirically by the relation

$$\begin{aligned} A &= 2.303B_0RT\log(v_s/v) \\ &= 2.303BRT\log(v_s/v)^n \qquad (3) \end{aligned}$$

Note that $B_0 = Bn$. Since $-\log(v/v_s)^n \approx b(1-x)$, where $x = (v/v_s)^n$, the above equation can be written as [13–16]

$$A = G(v_s^n - v^n) \qquad (4)$$

where $G = 2.303BRTb/v_s^n$. Equating Equations 1 and 4 one gets

$$A = 2.303RT\log(p_s/p) = G(v_s^n - v^n) \quad (5)$$

Considering v_0 to be the amount adsorbed at a very low pressure p_0, an equation similar to Equation 5 can be written (when $p_s > p \gg p_0$) as

$$A_0 = 2.303RT\log(p_s/p_0) = G(v_s^n - v_0^n) \ (6)$$

Subtracting Equation 5 from Equation 6 and dividing the resultant by Equation 6, and assuming that $v_s > v \gg v_0$, the following equation can be obtained

$$\log p = \log p_0 + \log(p_s/p_0)\,(v/v_s)^n \qquad (7)$$

Taking p_0 as 1, such that v_0 (the amount adsorbed at p_0) will be negligible compared to v or v_s and $\log p_s = N_0$, the above equation becomes

$$\log p = N_0(v/v_s)^n$$

Taking logarithms one gets

$$\log\log p = C_0 + n\log v \qquad (8)$$

where $C_0 = \log N_0 - n\log v_s$. Equation 8 is an adsorption isotherm equation and it can be used when adsorption is given as a function of pressure and not as a function of relative pressure.

Again from Equation 7, we have

$$\log(p/p_s)\,(p_s/p_0) = \log(p_s/p_0)\,(v/v_s)^n$$

or

$$\log(p/p_s)\,10^N = \log(10^N)\,(v/v_s)^n$$

$$\log P = N(v/v_s)^n \qquad (9)$$

where $P = (p/p_s)10^N$ and $\log(p_s/p_0) = \log(10^N) = N$. Taking logarithms of Equation 9 one gets

$$\log\log P = C + n\log v \qquad (10)$$

where $C = \log N - n\log v_s$. Equation 10 is designated as John's adsorption isotherm equation. Here N is an integer between 2 and 6. It may be stated that v (the amount adsorbed) is given as a function of relative pressure p/p_s. Here $\log\log(p/p_s)$ cannot be evaluated since $\log(p/p_s)$ is negative. Hence p/p_s is multiplied by 10^N so that $\log P$ is posititive and $\log\log P$ can be evaluated. It may be pointed out that the isotherm Equation 10 is semiempirical and is similar to the Halsey equation (Section 24).

4. Deduction of the equation as a solution of the differential equation of diffusion

John's adsorption isotherm equation can be deduced from the differential equation of diffusion of vapour from an isothermal adsorbing column of finely divided material kept at a vapour pressure gradient [17, 18]. Let v_0, v and v_s respectively be the amounts adsorbed at relative pressures p_0/p_s, p/p_s and 1. It is observed from experiments [19] that diffusion depends on vapour pressure p, second differential of vapour pressure, porosity ϵ and diffusion constant D. Hence the equation is

$$D(\mathrm{d}^2p/\mathrm{d}m^2) = \partial p/\partial t + A\epsilon p \qquad (11)$$

where $m = (1-x)$ and $x = (v/v_s)^n$. At steady state the first term on the right-hand side becomes zero. The diffusion constant $D = D_0\epsilon b$ where D_0 is the diffusion constant in free atmosphere and b is the tortuosity function of pores. Hence the above equation can be written as

$$(\mathrm{d}^2p/\mathrm{d}m^2) - K^2p = 0 \qquad (12)$$

where $K^2 = A/D_0b$. Equation 12 is a second-order homogeneous differential equation whose solution is given by

$$p = B\exp(-Km) \qquad (13)$$

At the lower boundary where the vapour pressure is p_s (or relative pressure is 1), the amount adsorbed is v_s and so $m = 0$. Hence $p = B = p_s$. At the upper boundary where the vapour pressure is p_0 (or relative pressure is p_0/p_s), the amount adsorbed is v_0 and hence $m = 1$. Therefore $K = \log(p_s/p_0) = N$. Hence Equation 13, after putting in the above boundary conditions, becomes

$$p = p_s\exp(-Nm) \qquad (14)$$

Since $m = 1 - (v/v_s)^n$ and $P = (p/p_s)(p_s/p_0)$ one could rewrite the above equation as

$$\log P = N(v/v_s)^n$$

Taking logarithms one gets

$$\log\log P = C + n\log v \qquad (15)$$

where $C = \log N - n\log v_s$. Equation 15 is the same as Equation 10, which is John's adsorption isotherm equation. According to Hobson [20] an equation applicable at very low pressure should have logarithmic dependence both on pressure and adsorption. Equations 8 and 10 applicable at all ranges of pressure are such equations.

5. Distribution function

It can be shown from Equation 14 that

$$\log(p_s/p) = N(1-x) \qquad (16)$$

Multiplying both sides by $2.303RT$ and squaring the above equation one gets with the help of Equations 5 and 6

$$A^2 = (2.303RT)^2N^2n[-\log(v/v_s)]/b$$

or

$$A^2 = A_0^2n[-\log(v/v_s)]/b$$

or

$$\ln(v/v_s) = -A^2/(A_0^2n/2.303b)$$

or

$$v = v_s\exp(-A^2s_0) \qquad (17)$$

where $s_0 = (2.303b/A_0^2n)$. The equation shows that the distribution of adsorbed volume with potential is Gaussian [15, 16].

6. Meaning of *n*

Multiplying both sides of Equation 16 by $2.303RT$ one gets

$$A = 2.303RT\log(p_s/p) = 2.303RTN(1-x) \qquad (18)$$

Since $(1-x) = (-\log x)/b = -(n/b)\log(v/v_s)$, the above equation becomes

$$A = 2.303RT\log(p_s/p)$$
$$= (2.303RTNn/b)\log(v_s/v) \qquad (19)$$

An equation similar to Equation 19 can be written for a standard gas using subscript 1. The equation is

$$A_1 = 2.303RT\log(p_{s1}/p_1)$$
$$= (2.303RTNn_1/b)\log(v_{s1}/v_1) \qquad (20)$$

Dividing Equation 19 by Equation 20 one gets [16, 21]

$$A/A_1 = n/n_1 = \beta$$

β may be designated as relative adsorbability. Thus n is a measure of adsorbability. It is interesting to note that in general the adsorbate (adsorbent being the same) which gives the greater slope n for John's isotherm is the one which has a higher van der Waals constant [22]. This is specially true in the case of elemental adsorbates. But there is no simple relation between n and the van der Waals constant, probably due to other forces involved in adsorption [22]. It may also be stated that the van der Waals constant is a measure of adsorbability. The magnitude of n characterizes the type of interaction between a vapour and solid. It is also observed that the higher the Brunauer, Emmett and Teller (BET) constant C, the higher is the slope n of John's isotherm.

7. Phases of adsorption

When John's isotherm is plotted, the plot gives straight lines with kinks or sudden changes in slope at the point where the phase changes. Each of the straight lines indicates a phase. These phases may represent pore filling, submonolayer, multilayer, capillary condensation and free liquid. It is found that in general micropore filling gives one phase. Type I gives mainly one phase with a very short phase (in a few cases) near saturation. Type II gives three phases and Type IV gives mainly three phases with a short phase near saturation [16, 23]. It is interesting to note that "point B" (endpoint of submonolayer) is interpreted as the point where the monolayer is completed and the BET method determines it analytically.

Physical adsorption theory demands that a phase transition be characterized by a distinct discontinuity in the isotherm. The transitions take place due to changes in the physical properties of the adsorbate as a result of changes in adsorbent–adsorbate interaction as more and more adsorption takes place. According to Brunauer [1] each phase has roughly the same heat of adsorption. A break in the isotherm was explained in terms of the adsorbed phase [24, 25]. Such a change was observed by Madan *et al.* [26] at monolayer capacity in the case of the graph relating moisture adsorbed and period of drying for cotton. A sudden change in the properties of the adsorbed layer at the kink can be expected. The point where the affinity of the surface for vapour changes marks a sudden change in slope. Thus it is reasonable to identify the first kink in John's isotherms of Types II and IV as the point where the monolayer is completed. This change at monolayer can be observed by other methods also. It was observed by Dubinin *et al.* [27] that dielectric properties showed clearcut variation with monolayer completion, capillary condensation and adsorption hysteresis. Fig. 1 shows the different phases of adsorption by means of John's isotherms.

8. Monolayer capacity from Types II and IV

It was observed by John and Bohra [28] that the first kink in John's isotherms of Types II and IV invariably occurs at monolayer capacity v_m. One could also identify this kink as the point at which the experimental observations deviate from the extrapolated straight line joining the points in the lower pressure range [29]. The last experimental point on the straight line is taken as $\log v_m$, the logarithm of monolayer capacity. In this case points should be taken at short intervals near where the deviation starts. Fitzer and Laudenklos [30] used the method to determine the monolayer capacity v_m. The method was also applied to determine the monolayer capacity from solute and dye adsorption [31]. Adamson [32] stated that fitting an isotherm equation to the data is an insufficient test for the validity of the isotherm. He stated that a seemingly more stringent test would be to determine the ratios of areas for various solids, as obtained by a given isotherm equation, which are independent of the nature of the adsorbate. Table I shows the monolayer capacity values for Type I, II and IV isotherms.

9. Mean pore size and surface area from Type IV isotherm

When adsorption data are plotted according to John's isotherm, it is observed that the second kink occurs at a pressure which when substituted in Kelvin's equation gives r_m, the mean capillary radius of the adsorbent pores. Then using the well known equation [33]

$$S_w = 2V_s/(r_m + t) \tag{21}$$

one can find the surface area. Here S_w, V_s and t respectively stand for surface area per gram, saturation volume and adsorbed thickness at the above pressure at the second kink. Results obtained using the method are given in Table II, from which it is evident that areas of a particular adsorbent determined by John's isotherm using

TABLE I Monolayer capacity for Type I, II and IV isotherms [16]

No.	Adsorbent	Adsorbate	Temp. (K)	Monolayer capacity ($cm^3 g^{-1}$)	
				John's method	Literature value
1	Coconut charcoal	N_2	77.2	324	325
2	Carbon 1	N_2	90.2	405	393
3	Carbon 17	N_2	90.2	306	300
4	Carbon 1	N_2	77.2	436	431
5	Carbon 17	N_2	77.2	327	311
6	Carbon 1	N_2	77.4	290	280
7	Carbon 4	N_2	77.4	442	426
8	Carbon 19	N_2	77	319.5	308.2
9	Carbon 20	N_2	77	117.9	116.4
10	PVC separator	CCl_4	306	13.5	13.1
11	H.G. catalyst	CO	78	63.0	60.4
12	Porous glass	N_2	79.4	27.2	27.8
13	Ferric oxide gel	C_2H_5OH	333	27.4	28.1

Numbers 1–5 are of Type I, 6–10 are of Type II and 11–13 are of Type IV.

TABLE II Surface area determined by means of mean pore size

Number	Adsorbent	Adsorbate	Temperature (K)	Surface area ($m^2 g^{-1}$)		Reference
				Present method	Literature data	
1	Ferric oxide gel	C_2H_5OH	333	296	299	[23]
2	Ferric oxide gel	C_6H_6	273	315	299	[23]
3	Silica gel	$C_2H_5NHC_2H_5$	298	356	320(N_2)	[23]
4	Silica gel	$C_4H_9NH_2$	298	320	320(N_2)	[23]
5	Silica gel	$C_4H_9NHC_4H_9$	298	340	320(N_2)	[23]
6	Porous glass	C_4H_{10}	333	114	118	[23]
7	Porous glass	Ar	77	143	112	[33]
8	Porous glass	N_2	79.2	136	120	[33]

different adsorbates are independent of the nature of the adsorbates.

10. Limiting micropore volume

According to the present idea, the Type I isotherm is also due to pore filling as in the case of extremely low-pressure isotherms. When data of Type I and extremely low-pressure isotherms are plotted according to John's isotherm, one obtains mainly a straight line plot. In some cases for Type I, a kink and a very short second phase are obtained near saturation. The logarithm of the limiting micropore volume, $\log v_s$, is obtained by extrapolating the straight line connecting the lower points to $\log\log P$ (where $p/p_s = 1$) [34, 35]. The corresponding value of $\log v$ at $\log\log P_s$ is taken as $\log v_s$ (Fig. 1). It is observed that the value of $\log v$ at the kink of Type I (when it exists) is almost identical to the extrapolated $\log v_s$ value. Results obtained by this method are given in Table III.

11. Micropore and mesopore volumes and mesopore area in the presence of micropores

When adsorption takes place in porous materials containing all types of pores, v_t (the total adsorption at any relative pressure) can be expressed by the relation [36, 37]

$$v_t = v_{ma} + v_{me} + v_{mi}$$

where subscripts t, ma, me and mi respectively stand for total, macro-, meso- and micropores. Since v_{ma} contributes little towards area, the above equation can be written as

$$v_t = v_{mi} + S_{me}t \qquad (22)$$

Note that $S_{me}t = v_{me}$. When v_{mi} is not a function of pressure, the micropores will be filled at low pressure and the surface area and micropore volume could be determined by plotting a curve of v_t against t according to Equation 22. The slope will give S_{me} and the intercept will give the micro-

TABLE III Limiting micropore volume [16]

No.	Adsorbent	Adsorbate	Temp. (K)	Micropore volume	
				v_0 (Dubinin)	v_s (John)
				($mmol\,g^{-1}$)	
1	Active carbon 1	C_6H_6	293.2	0.82	0.86
2	Active carbon 2	C_6H_6	293.2	1.07	1.07
3	Active carbon 3	C_6H_6	293.2	2.43	2.46
4	Active carbon 5	C_6H_6	293.2	5.75	5.75
5	Active carbon D2	C_6H_6	293.2	0.254	0.279
6	Active carbon E2	C_6H_6	293.2	0.200	0.200
				($cm^3 g^{-1}$)	
7	Coconut charcoal	N_2	77.2	325	324
8	Carbon 1	N_2	90.2	393	405
9	Carbon 17	N_2	90.2	300	306
10	Carbon 1	N_2	77.2	431	436
11	Carbon 17	N_2	77.2	311	327

Numbers 1–7 are extremely low-pressure adsorption cases and the rest are of Type I.

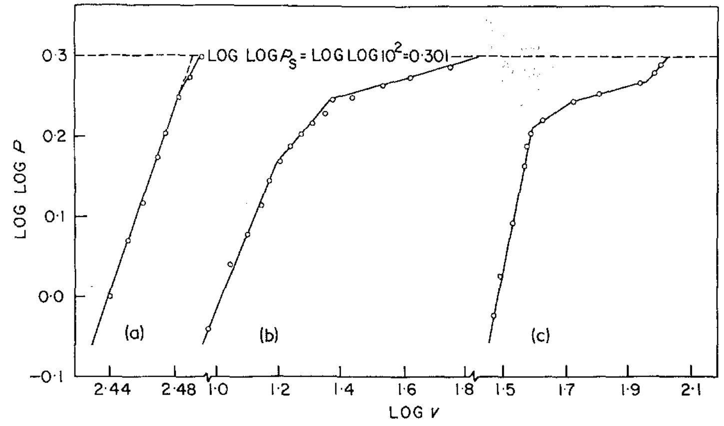

Figure 1 (a) Adsorption isotherm of N_2 on carbon 1 at − 195.8° C (Type I). (b) Adsorption isotherm of CCl_4 on PVC separator at 32.8° C (Type II). (c) Adsorption isotherm of C_2H_5OH on ferric oxide gel at 60° C (Type IV) [23].

pore volume v_{mi}. When v_{mi} is a function of pressure, the t-method described above is not applicable to determine S_{me} and v_{mi}. In that case, v_{mi} could be expressed in terms of John's isotherm [36, 37] as

$$v_{mi} = v_s[(\log P)/N]^{1/n} = v_s J \qquad (23)$$

where $J = [(\log P)/N]^{1/n}$. Substituting Equation 23 in Equation 22 and dividing by J one obtains

$$v_t/J = v_s + S_{me}t/J \qquad (24)$$

The mesopore area and the micropore volume are obtained from the slope and intercept respectively of the plot of Equation 24 as shown in Fig. 2. The results are shown in Table IV. It is important to choose the correct $1/n$ value for Equations 23 and 24. At the start of the linear portion of the curve, after the knee between v and p/p_s, adsorption is mainly in micropores. The coordinates of this point (the start of the linear portion after the knee) on John's isotherm are $\log\log P_1$ and $\log v_1$. It was shown by Kadlec and Danes [38] that v at the start of hysteresis (on the curve between v and p/p_s) is almost equal to v_s (the limiting micropore volume). The coordinates of that point according to John's isotherm are $\log\log P_s$ and $\log v_s$. Hence

$$1/n = (\log v_s - \log v_1)/(\log\log P_s - \log\log P_1) \qquad (25)$$

John *et al.* [14] have also shown that

$$1/n = 0.434BT^2N^2/1.1\beta^2 \qquad (26)$$

It may be stated that in the region between the start of the knee and the start of hysteresis (of the curve between v and p/p_s) the contributions of micropore filling and adsorption on mesopores cannot be separated from v_t (the total adsorption). But as stated by Dubinin and Kadlec [39] adsorption on mesopores is negligibly small and hence v_{mi} is almost equal to v_t. Hence, mesopore volume is obtained by subtracting v_s (the limiting micropore volume) from total adsorption V_s at saturation.

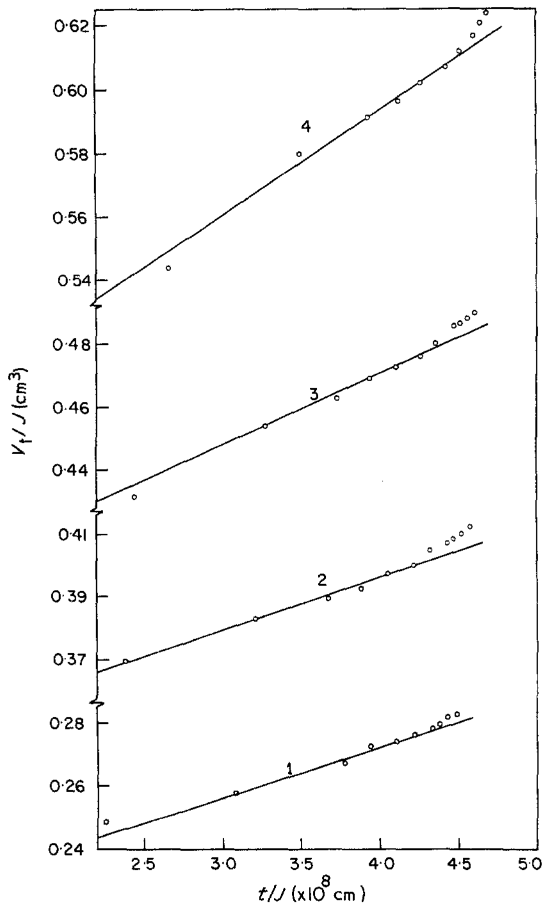

Figure 2 Plots of v_t/J against t/J for benzene adsorbed on different active carbons 1 to 4 at 293 K [37].

TABLE IV Micropore volume and comparison of mesopore surface area and $1/n$ values determined by present and Kadlec methods [37]

No.	Adsorbent	Adsorbate	Temp. (K)	Micropore volume ($cm^3 g^{-1}$)		Mesopore surface area ($m^2 g^{-1}$)		$1/n$ value	
				Present	Kadlec	Present	Kadlec	Present (Eqn. 25)	Calculated (Eqn. 26)
1	Active carbon 1	C_6H_6	293	0.21	0.22	157	90	0.07	0.07
2	Active carbon 2	C_6H_6	293	0.33	0.33	168	153	0.13	0.12
3	Active carbon 3	C_6H_6	293	0.38	0.38	227	223	0.16	0.17
4	Active carbon 4	C_6H_6	293	0.46	0.44	321	310	0.25	0.21

12. Dispersion of micropores

When John's isotherm is drawn using various data, broadly one can obtain four types of isotherms [31, 40, 41].

1. In this case all the experimental points lie on a straight line. It indicates that the material has monodisperse micropore structure (Fig. 3a).

2. In this case points in the lower-pressure region lie on a straight line but as the pressure rises above a certain value the experimental points deviate more and more from the extrapolated straight line joining the points in the low-pressure region. This indicates that there are mesopores which are being filled at higher pressure (Fig. 3b).

3. In this type two straight lines connect the experimental points. The lower line is due to finer pores and the upper line is due to coarser pores. The limiting micropore volumes can be found by extrapolating the lines to $\log \log P$ (where $p/p_s = 1$) and taking the corresponding value of $\log v_s$. The two lines are expressed by [42]

$$\log \log P = C_f + n_f \log v \qquad (27)$$

and

$$\log \log P = C_c + n_c \log v \qquad (28)$$

The subscripts f and c stand for fine and coarse pores (Fig. 3c).

4. Progressive activation increases but progressive impregnation reduces both porosity and pore size. From their adsorption isotherms one could see when the structural change occurs. Parallel isotherms of the progressively activated or impregnated material indicate that there are no structural changes since there is no change in the dispersion of pores. Fig. 2 shows that the isotherms of progressively activated carbons 1 and 2 are similar in structure but activated carbons 3 and 4 have undergone structural change. Since isotherms of activated carbons 3 and 4 are not parallel to activated carbons 1 and 2, structural change is indicated. All these cases are illustrated in Fig. 2.

13. Size, range and degree of microporosity

It is clear from Equation 25 that

$$n = (\log \log P_s - \log \log P_1)/(\log v_s - \log v_1) \qquad (29)$$

P_1 refers to a very low pressure. If the amount adsorbed corresponding to pressure P_1 is very small, then n will not be high. This indicates that pores are distributed over a large range. But when the value of v_1 is very near to v_s, the n value will be high, indicating that the pores are in a narrow

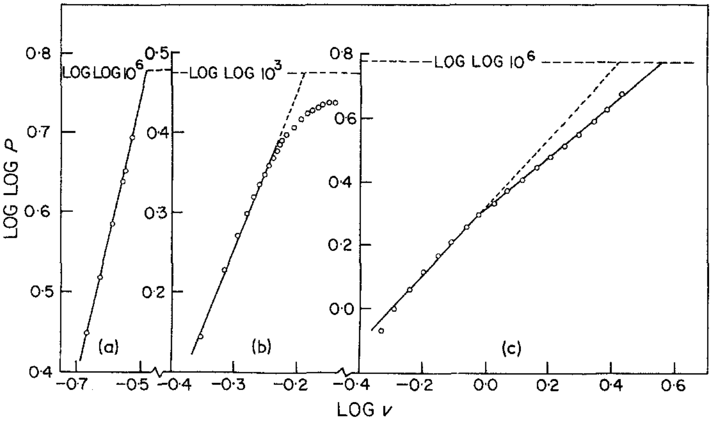

Figure 3 (a) Adsorption isotherm of benzene on active carbon 27 at 20° C (monodisperse). (b) Adsorption isotherm of benzene on active carbon AU8 at 20° C. (c) Adsorption isotherm of benzene on active carbon D2 at 20° C (bidisperse) [16].

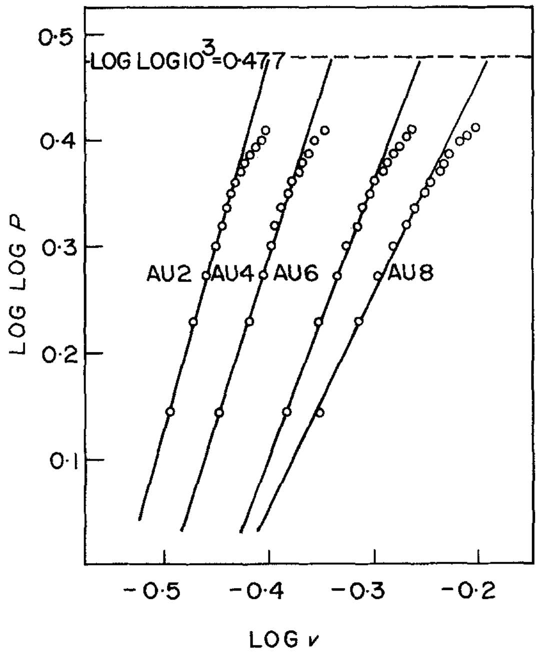

Figure 4 John's isotherm plots for the system AU2, AU4, AU6 and AU8 [41].

range and are finer. Thus n is an indication of size, range and degree of microporosity of micropores [41].

Kadlec and Danes [38] prepared charcoal of relatively uniform grain size by aereal separation from common granulated gas charcoal activated by water vapour at 900° C. This material was separated into eight fractions of different specific weights. In this manner they obtained a series of samples with gradually varying degree of activation. The least activated and hence the most dense was designated AU1. The most activated and hence the least dense was designated AU8. The others were designated AU2, AU3, etc., depending on the degree of activation. Using the adsorption data collected as stated above, John's isotherm plots for the systems AU2, AU4, AU6 and AU8 were drawn and are shown in Fig. 4. The results obtained along with the published data are given in Table V. It is clear from Fig. 4 and Table V that n decreases with activation. Earlier [14, 35] n was shown to depend on the adsorption potential. The high value of n of the less activated materials implies that their potential is high. Potentials will be higher in finer pores since the whole space in micropores is under the influence of adsorption forces emanating from all the side of the walls, thereby increasing adsorption fields in a substantial way. Hence one could conclude that higher n implies finer pores. In Fig. 4, AU2 has the finest pores, as shown by the n value. As n decreases with the series, the pores become wider, in agreement with the fact that the more activated ones have wider pores. Thus the n value of the isotherms decreases from the least to the most dense activated charcoals. Any point in the finer pores is affected by the proximity of the walls of the pores. This is the reason why narrow pores are filled at very low pressure.

14. Reason for extrapolation

The purpose of any isotherm is to obtain a linear plot in the whole range or at least in part of the range of adsorption. It is assumed that the isotherm is valid in the linear range. The linear plot of John's isotherm implies a Gaussian distribution of adsorption volume with potential. Thus since the law of distribution is known, extrapolation can be made with a degree of certainty that is rather high. Extrapolation of the straight line portion of the isotherm means that the particular law of variation is also valid in the extrapolated range. This explains why extrapolation is made to log log P_s and the value of log v corresponding to log log P_s is taken as log v_s, the logarithm of limiting micropore volume.

15. Effect of linearity range on extrapolation

It is found that monolayer capacity or limiting micropore volume depend on the range of linearity of the isotherms. For the same data the linear portions obtained by two different isotherms may

TABLE V Comparison of micropore volumes and the values of n in the adsorbents [41]

Adsorbent	Adsorbate	Temp. (K)	Micropore volume (cm^3 g^{-1})		n
			v_0 (Dubinin)	v_s (John)	
AU2	C_6C_6	293	0.379	0.400	3.46
AU4	C_6C_6	293	0.440	0.458	3.14
AU6	C_6H_6	293	0.532	0.556	2.59
AU8	C_6H_6	293	0.610	0.646	2.00

be in different pressure ranges. It will be observed that the limiting micropore volume obtained by extrapolation or the monolayer capacity will be greater for the isotherm that gives a linear portion in the lower pressure range [42, 43]. In the lower pressure range, since the number of molecules adsorbed per unit area is less, they do not react with one another. This is because the distance between adsorbed molecules is much larger than the diameter of the molecules. Reaction between molecules depends also on atomic number, shape, size and polarizability of the molecules. At higher pressure there will be more molecules per unit area, the distance between molecules will be less hence there will be a reaction between molecules causing the molecules to move away from each other. This will cause a decrease in the number of molecules per unit area. Both adsorption and repulsion take place not one after the other but simultaneously. Hence when this portion is used to extrapolate to determine limiting micropore volume or monolayer capacity, the result will be lower than that obtained from the lower pressure region [42, 43]. Thus it will be seen that the number of molecules adsorbed per unit area in the upper pressure region is lower than it would have been if there was no reaction between molecules and vice versa. Hence when the portion having fewer molecules than normally expected is used to determine v_m or v_s, the value determined will be lower. This effect will be more with more polar molecules and molecules having higher molecular weight. It may be stated that the linear range of BET isotherms is higher than the linear range of John's isotherms for the same data. Hence v_m values determined by the BET method will be lower than those obtained by John's method.

16. John's isotherm for total adsorption from binary and ternary mixtures

A basic understanding of mixture adsorption is of great value in problem like separation and purification of gases, recovery of industrial solvents, production of gas masks, etc. Binary mixture adsorption data are scarce and ternary data are still scarcer. Considering binary mixture adsorption of gases 1 and 2, one can write the pure gas adsorption equations similar to Equation 8 as follows [44–46]

$$\log \log p_1^\circ = C_1 + n_1 \log v_1^\circ \qquad (30)$$

and

$$\log \log p_2^\circ = C_2 + n_2 \log v_2^\circ \qquad (31)$$

The binary mixture equation is given by

$$\log \log p_{12} = C_{12} + n_{12} \log v_{12} \qquad (32)$$

where subscripts 1, 2 and 12 respectively stand for gas 1, gas 2 and the binary mixture. The superscript $^\circ$ stands for pure component. Here

$$n_{12} = y_1 n_1 + y_2 n_2 \qquad (33)$$

and

$$C_{12} = y_1 C_1 + y_2 C_2 \qquad (34)$$

where y_1 and y_2 are mole fractions of gas 1 and gas 2. Note that $y_1 + y_2 = 1$. When ternary mixture adsorption is considered, the ternary mixture adsorption is given by [46]

$$\log \log p_{123} = C_{123} + n_{123} \log v_{123} \qquad (35)$$

where the isotherm of the third component is (using subscript 3)

$$\log \log p_3^\circ = C_3 + n_3 \log v_3^\circ \qquad (36)$$

Subscript 123 stands for the ternary mixture. Here

$$n_{123} = y_1 n_1 + y_2 n_2 + y_3 n_3 \qquad (37)$$

and

$$C_{123} = y_1 C_1 + y_2 C_2 + y_3 C_3 \qquad (38)$$

17. Determination of partial adsorption from binary and ternary mixtures when gases have similar adsorbabilities

Two gases have similar adsorbabilites when their van der Waals forces are nearly equal. It was shown earlier that n is a measure of adsorbability. Hence it is reasonable to assume that the ratio of partial adsorption to total adsorption (i.e. v_i/v_{12}) at any total is $y_i n_i : n_{12}$ the ratio of n value contribution of component i to the total n value of the mixture [22] or

$$x_i = y_i n_i / n_{12} = v_i / v_{12} \qquad (39)$$

where x_i is the mole fraction of component i adsorbed. Hence

$$v_i = x_i v_{12} \qquad (40)$$

Note that for binary mixtures $x_1 + x_2 = 1$. Similarly it can be shown that for ternary mixtures the partial adsorption is given by [22]

$$v_i = x_i v_{123} \qquad (41)$$

where $x_1 + x_2 + x_3 = 1$ for ternary adsorption.

Table VI shows the total and partial values calculated by Equations 32 and 40 respectively. The data have been taken for adsorption of a mixture of N_2O and CO_2 on carbon at 0°C from Courty [47]. The gas phase composition is 73.9%

TABLE VI Experimental data to show the validity of Equations 32 and 40 to determine total and partial adsorption in the binary mixture [22]

No.	Total pressure (mmHg)	Total amount adsorbed (cm^3)		Partial adsorption of CO_2 (cm^3)	
		Published [47]	Calculated (Eqn 32)	Published [47]	Calculated (Eqn 40)
1	113.9	31.1	29.3	19.3	20.6
2	286.5	50.2	49.2	33.4	34.6
3	567.6	68.8	68.6	47.8	48.2
4	984.2	86.4	87.1	61.8	61.3
5	1556.2	101.4	105.4	73.7	74.2

$n_1(N_2O) = 0.3908$; $C_1(N_2O) = -0.2957$.
$n_2(CO_2) = 0.3273$; $C_2(CO_2) = -0.1546$.
$n_{12} = 0.3438$; $C_{12} = -0.1914$.

CO_2 and 26.1% N_2O. It could be shown to be true by drawing the adsorbed phase diagram, as was shown by John [22].

18. Limiting micropore volume using binary and ternary mixtures

Total mixture adsorption at various total pressures are calculated using Equations 32 and 35 respectively depending on whether the mixture is binary or ternary. These equations are used when the amounts adsorbed are expressed in terms of pressure p. When the amounts adsorbed are expressed as a function of relative pressure, total adsorption for various relative pressures are calculated using an equation similar to Equation 10. Such an equation for a binary mixture is [44, 46, 48, 49]

$$\log\log P_{12} = C_{12} + n_{12} \log v_{12} \qquad (42)$$

and that for a ternary mixture is [48, 49]

$$\log\log P_{123} = C_{123} + n_{123} \log v_{123} \qquad (43)$$

Then John's isotherm is drawn according to the above equations. The plot is extrapolated to the saturation line (where $p/p_s = 1$) and the corresponding $\log v$ is taken as $\log v_s$ (the logarithm of limiting micropore volume). Fig. 5 shows the graph used to calculate the limiting micropore volume v_s for the case of a ternary mixture and Table VII shows the values of v_s for binary and ternary mixtures.

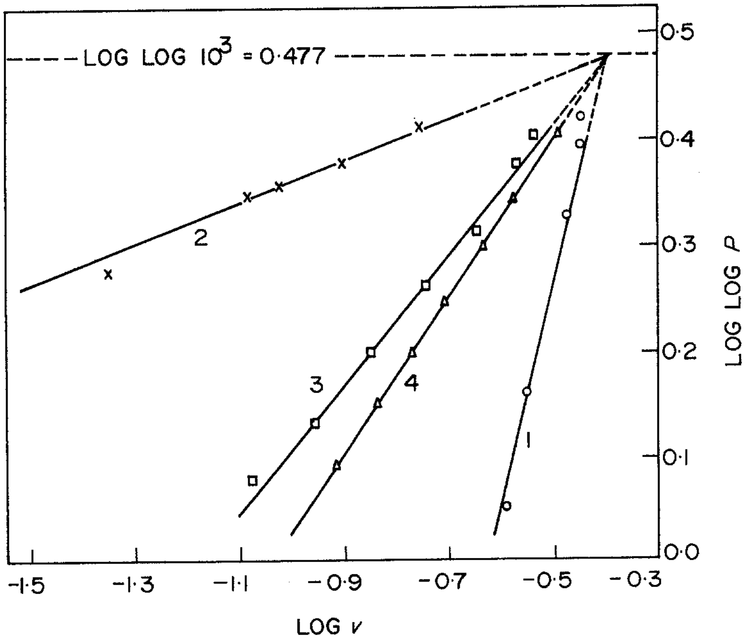

Figure 5 Adsorption isotherms for (1) benzene, (2) methanol, (3) ethanol and (4) a mixture (20% benzene, 40% methanol and 40% ethanol) on AC29 at 20° C according to Equations 30, 31, 36 and 43 respectively [49].

TABLE VII Limiting micropore volumes [49]

No.	Adsorbent	Adsorbate	Temp. (°C)	Limiting micropore volume, v_s(cm^3 g^{-1}) Calculated	Published
1	Active carbon	C_2H_5Cl	50	0.477	0.465
2	Active carbon	$C_2H_5OC_2H_5$	50	0.477	0.466
3	Active carbon	Binary mixture of 1 & 2 (50:50)	50	0.477	0.459
4	AC29	C_6H_6	20	0.400	–
5	AC29	CH_3OH	20	0.400	–
6	AC29	C_2H_5OH	20	0.400	–
7	AC29	Ternary mixture of 4, 5 & 6 (20:40:40)	20	0.400	–

19. Application of the Langmuir equation to determine the monolayer capacity and surface area from mixture adsorption

Type I is attributed to microporosity in the adsorbent. Now it is generally accepted that the Langmuir model of localized monolayer adsorption is applicable only to certain special cases. Adsorption v_{12} (or v_{123}) corresponding to p_{12} (or p_{123}) can be determined by means of Equation 32 (or Equation 35). The Langmuir equation for a binary mixture is [48, 49]

$$p_{12}/v_{12} = 1/(v_{m12}b) + p_{12}/v_{m12} \qquad (44)$$

The Langmuir equation of ternary mixture adsorption is obtained by replacing subscript 12 by 123 in Equation 44. A graph is drawn of p_{12}/v_{12} against p_{12} in the case of binary (p_{123}/v_{123} against p_{123} in the case of ternary) mixture adsorption. From the Langmuir plot, monolayer capacity v_{m12} (or v_{m123}) is determined by taking the reciprocal of the slope. Once the monolayer is obtained, the contribution of each component is obtained by application of the equation of Lewis *et al.*, which for a binary mixture is [45, 49, 50]

$$(v_1/v_1^\circ) + (v_2/v_2^\circ) = 1 \qquad (45)$$

where v_1°, v_2° and v_{12} ($= v_1 + v_2$) are the amounts adsorbed at $p_1^\circ = p_2^\circ = p_{12}$ ($= p_1 + p_2$). At monolayer capacity one has to replace v_1 and v_2 in Equation 45 by v_{m1} and v_{m2}. Note that $v_{m12} = v_{m1} + v_{m2}$. Solving Equation 45 one can find v_{m1} and v_{m2} since v_{m12} is known from the Langmuir equation as stated earlier. Since v_{m1} and v_{m2} are known, the area can be found by the usual method. In the case of ternary mixtures, one can write an equation similar to Equation 45 and determine v_{m1}, v_{m2} and v_{m3} provided one of them is known. The value of v_{m123} can be easily determined by plotting the Langmuir graph as stated earlier.

20. Application of the BETmethod to determine monolayer capacity and surface area from mixture adsorption

Total adsorption v_{12} (or v_{123}) is determined corresponding to various total pressures by means of Equation 30 (or Equation 33). The BET equation for binary adsorption is [45, 48, 49]

$$x_{12}/v_{12}(1 - x_{12}) = (1/C^* v_{m12}) + (C^* - 1)x_{12}/C^* v_{m12} \qquad (46)$$

where $x_{12} = p_{12}/p_{s12}$ and C^* is a constant. The BET equation for ternary mixture adsorption is obtained by replacing the subscript 12 by 123. Using the relative pressure and the corresponding amount adsorbed, a graph is drawn of x_{12} against x_{12}/v_{12} $(1 - x_{12})$. Then the slope and intercept of the graph are evaluated. The monolayer capacity of the mixture is found from the reciprocal of the sum of slope and intercept, and v_{m123} for a ternary mixture can be found by the same method. The contribution from each component is found by the method of Lewis *et al.* as was described in the last section. The area S_w (in m^2 g^{-1}) for a binary mixture can be evaluated by the following equation

$$S_w = S_{w1} + S_{w2} = (v_{m1}/V_1)Ns_1 \times 10^{-20} + (v_{m2}/V_2)Ns_2 \times 10^{-20} \qquad (47)$$

where V_1 and V_2 are molar volumes and s_1 and s_2 are molecular areas of gases 1 and 2 respectively.

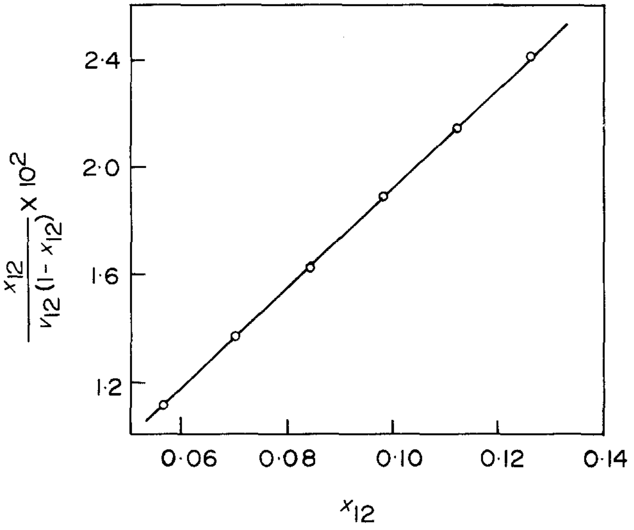

Figure 6 BET graph of a binary mixture of N_2 and O_2 on iron catalyst at −183° C [45].

Fig. 6 shows the BET graph of the binary mixture of N_2 and O_2 on an iron catalyst at −183° C. Individual adsorption data have been taken from Fig. 100 of Brunauer [1]. The n values are 1.4 and 0.729 and C values are −0.599 and −0.072 for N_2 and O_2 respectively, and $n_{12} = 1.064$ and $C_{12} = -0.335$. The area calculated by means of Equation 47 comes out to be 22.355 $m^2 g^{-1}$ and monolayer capacity $v_{m12} = 5.366$ $cm^3 g^{-1}$ ($v_{m1} = 3.587$ $cm^3 g^{-1}$, $v_{m2} = 1.779$ $cm^3 g^{-1}$).

Monolayer capacity and surface area values in the case of a binary mixture and monolayer capacity of a ternary mixture of O_2, N_2 and Ar absorbed on activated charcoal at −183° C are given in Table VIII. Fig. 7 shows adsorption isotherms of individual gases and their ternary mixture for the calculation of monolayer capacity values.

21. Equation of state for adsorbed gas on non-microporous adsorbents

The equation of state for the adsorbate involves three thermodynamic quantities, p, v and T. The isostere equation is also an equation of state involving p and T, when v is kept constant. According to Zemansky [51] the equation of state is not a theoretical deduction from thermodynamics but is usually an experimental addition to it. It expresses the results as accurately as the experiments in the range of values measured. Based on Equation 9 John and Datta showed that [52]

$$(\log P)/Tv^n = \text{constant} \qquad (48)$$

This implies that when the amount adsorbed is kept constant (isostere), Equation 48 becomes

TABLE VIII Monolayer capacity and surface area values at −183° C [49]

No.	Adsorbent	Adsorbate	Monolayer capacity, v_m(cm^3)		Surface area (m^2)
			Calculated	Published	
1	Activated charcoal	O_2	43.4	45.2	165.8
2	Activated charcoal	N_2	30.9	32.4	134.5
3	Activated charcoal	Binary mixture of 1 & 2 (40 : 60)	37.0	–	149.7 (71.0 of N_2 and 78.7 of O_2)
4	Activated charcoal	O_2	43.4	45.2	–
5	Activated charcoal	N_2	30.9	32.4	–
6	Activated charcoal	Ar	40.5	41.4	–
7	Activated charcoal	Ternary mixture of 4, 5 & 6 (20 : 30 : 50)	34.4	–	–

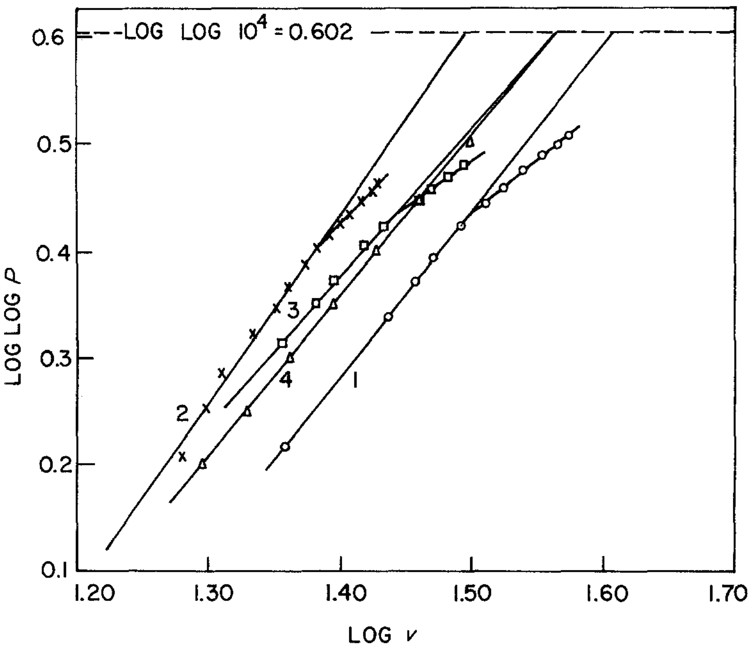

Figure 7 Adsorption isotherms of (1) oxygen, (2) nitrogen, (3) argon and (4) a mixture (20% nitrogen, 30% oxygen and 50% argon) on activated charcoal at $-183°$ C according to Equations 30, 31, 36 and 43 respectively [49].

$$(\log P)/T = \text{constant} \qquad (49)$$

and when temperature is kept constant, Equation 48 becomes

$$(\log P)/v^n = \text{constant} \qquad (50)$$

When P is constant, Equation 48 reduces to

$$Tv^n = \text{constant} \qquad (51)$$

Nagpal and John [53] compared the well known isostere equation of Bikerman [54]

$$T\log(p_s/p) = \text{constant} \qquad (52)$$

with the isostere $(\log P)/T$ based on John's isotherm Equation 49. They found that both the isosteres are satisfactory at low relative pressures but for higher relative pressures the latter equation seems to have greater applicability. Examples to prove the fact are given in Table IX.

22. Identity of the equations of John and Dubinin

It was shown earlier (Equation 16) that

$$\log(p_s/p) = N(1-x)$$

TABLE IX Comparison of isostere Equations 49 and 52 [53]

No.	Adsorbate/ Adsorbent	Temperature (K)	Volume	Relative pressure	Calculated values		Mean error (%) in calculated values	
					Eqn 49 ($\times 10^{-3}$)	Eqn 52 ($\times 10^{2}$)	Eqn 49	Eqn 52
			($cm^3\ g^{-1}$)					
1	SO_2 / Silica gel	193.0	100	0.0672	4.29	2.26	1.0	1.0
		219.0	100	0.0894	4.34	2.30		
		232.6	100	0.1047	4.38	2.28		
		193.0	130	0.2059	6.81	1.32	5.6	6.0
		219.0	130	0.2269	6.19	1.41		
		232.6	130	0.2660	6.13	1.34		
			(g/100 g)					
2	H_2O/ Carbon	302.0	0.225	0.25	4.63	1.82	0.08	5.2
		313.2	0.225	0.30	4.72	1.64		
		302.0	1.0	0.65	6.00	5.65	0.0	15.4
		313.2	1.0	0.75	6.00	3.91		

22.1. Case I

Since $(1-x)$ is nearly equal to $-[\log(v/v_s)^n]/b$, the Equation 16 can be written as [14, 35]

$$\log(p_s/p) = -(N/b)\log(v/v_s)^n$$

$$= -(Nn/b)\log(v/v_s)$$

or

$$\log v = \log v_s - D_1 \log(p_s/p) \qquad (53)$$

where $D_1 = b/Nn$ and $b = 0.55$ for the range $0.5 \leqslant x \leqslant 0.95$. Equation 53 is known as Dubinin's second structural type equation. It is also known as a Freundlich type equation.

22.2 Case II

Squaring Equation 16 one gets

$$[\log(p_s/p)]^2 = N^2(1-x)^2$$

Since $(1-x)^2 = -[\log(v/v_s)^n]/b$, the above equation becomes

$$[\log(p_s/p)]^2 = -(N^2/b)\log(v/v_s)^n$$

or

$$[\log(p_s/p)]^2 = -(N^2n/b)\log(v/v_s)$$

Hence

$$\log v = \log v_s - D_2[\log(p_s/p)]^2 \qquad (54)$$

where $D_2 = b/N^2n$ and $b = 1.1$ for the range $0.15 \leqslant x \leqslant 0.5$. Equation 54 is known as Dubinin's first structural type equation. It is also known as the equation of the theory of volume filling of micropores.

22.3. Case III

Cubing Equation 16 one gets

$$[\log(p_s/p)]^3 = N^3(1-x)^3$$

It can be shown that $(1-x)^3$ is nearly equal to $-(\log x)/b$. Hence

$$[\log(p_s/p)]^3 = -(N^3n/b)\log(v/v_s)$$

or

$$\log v = \log v_s - D_3[\log(p_s/p)]^3 \qquad (55)$$

where $D_3 = b/N^3n$ and $b = 1.5$ in the range $0.05 \leqslant x \leqslant 0.35$. Equation 55 is a variation of Dubinin's equation corresponding to very fine micropores [55]. It has been shown that Equation 16 can also be raised to non-integer values between 2 and 3. Thus it is clear that all the equations of Dubinin's isotherms can be represented by John's isotherm.

23. Deduction of a few other well known isotherms from John's isotherm [56]

23.1. Henry's equation

Equation 7 can be written as

$$\log(p/p_o) = N(v/v_s)^n$$

where $N = \log(p_s/p_0)$. Hence

$$p = p_0 \exp[N(v/v_s)^n] \qquad (56)$$

Considering the very low-pressure region, where v will be very small compared to v_s, and expanding Equation 56 when $n = 1$, one gets

$$p = p_0 + p_0 N(v/v_s) + \ldots$$

where higher power of $N(v/v_s)$ are neglected. Hence one could write the above equation as

$$v = A + Bp \text{ (Henry's equation)} \qquad (57)$$

where $A = -(v_s/N)$ and $B = v_s/p_0N$.

23.2. Temkin's equation

Taking logarithms of Equation 56 when $n = 1$, one gets

$$\log p = \log p_0 + N(v/v_s)$$

or

$$\log p = A + Bv \text{ (Temkin's equation)} \qquad (58)$$

where $A = \log p_0$ and $B = N/v_s$.

23.3. Freundlich's equation

Consider Equation 56 in the low-pressure region. Expanding, one gets

$$p = p_0[1 + N(v/v_s)^n + \ldots]$$

Higher powers of $N(v/v_s)^n$ have been neglected. Hence

$$p - p_0 = Cv^n$$

where $C = p_0N/v_s^n$. Since p_0 is very small compared to p, one could write the above equation as

$$p = Cv^n$$

or

$$v = C_0 p^{1/n} \qquad \text{(Freundlich's equation)} \; (59)$$

where $C_0 = (1/C)^{1/n}$.

23.4. de Boer and Zwikker's equation

When $n = 1$, Equation 16 becomes

$$\log(p_s/\text{p}) = N(1 - v/v_s)$$

It can be shown that $(1 - v/v_s)$ is nearly equal to $\exp[-(v/v_s)]$. Hence

$$\log(p_s/p) = N\exp[-(v/v_s)]$$

Since v_s (the saturation value) is a multiple of monolayer capacity v_m, one may write $v_s = mv_m$. Hence the above equation can be written as

$$\log(p_s/p) = N\exp[-(v/v_m m)] = NK_0^{v/v_m}$$

where $K_0 = \exp[-(1/m)]$. Taking logarithms of the above equation, one gets,

$$\log\log(p_s/p) = \log N + (v/v_m)\log K_0$$

$$\text{(de Boer and Zwikker's equation)} \qquad (60)$$

24. Deduction of John's isotherm from the Frenkel–Halsey–Hill equation

The Frankel–Halsey–Hill (FHH) equation obtained by equating the expression for potential energy of atrraction with change in free energy of a mole of an ideal gas is [57]

$$(v/v_m)^3 = K/\log(p_s/p) \qquad (61)$$

where K is a constant which can be calculated in principle from the properties of the adsorbent and adsorptive. The index 3 arises form integration of the atomic separation term in the inverse power law which describes the dependence of attraction on atomic separation. Halsey [58] formulated a more general equation as

$$(v/v_m)^n = K/\log(p_s/p) \qquad (62)$$

where the index n is no longer necessarily an integral, and may be expected to be between 2 and 3. The value of n may be taken as a rough guide to the strength of interaction between the adsorbate and the solid.

John's adsorption isotherm can be deduced from Equation 62 when exponent is 3 or n. It can be shown that $\log(p_s/p)$ is inversely proportional to $\log p$, i.e. $\log(p_s/p) = A/\log p$ where A is a constant. Hence Equation 62 becomes

$$\log p = K_1(v/v_m)^n \qquad (63)$$

where $K_1 = A/K$. Taking logarithms of Equation 63, one gets

$$\log\log p = C_0 + n\log v$$

which is John's isotherm equation where $C_0 = \log K_1 - n\log v_m$. Thus when the exponent as determined by Equation 62 is 3, the isotherms have a theoretical basis. On the other hand when the exponent is other than 3, the isotherms have a semitheoretical basis. It may be stated that the higher the exponent in a power law, the shorter the range of interaction. Thus John's isotherms have a theoretical/semitheoretical basis depending on the exponent in Equation 62 and an algebraic modification of the Halsey equation.

25. Summary

A new equation has been derived in a semiempirical way from potential thoery as well as via solution of a differential equation of diffusion. The equation can be applied to determine monolayer capacity from Types I, II and IV and the limiting micropore volume from an extremely low-pressure isotherm. The isotherm enables the identification of different phases of adsorption and determines mean pore size of adsorbents giving Type IV isotherm. The isotherm can be applied to determine mesopore area of adsorbents having micropores which will be a function of pressure and along with that it can determine the micropore and mesopore volumes. The isotherm can identify mono- and bidisperse pores and can detect structural change in progressively activated or impregnated carbon or other porous materials. Total mixture adsorption from binary and ternary mixtures can be calculated using the constants of pure components. Partial adsorption in the case of a binary mixture can be determined provided the components have similar adsorbabilities. John's isotherm implies that the distribution of adsorption volume with potential is Gaussian and it can be used for gas, dye and solute adsorption. Some of the well known isotherms including that of Dubinin can be derived from John's isotherm.

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Received 26 March
and accepted 31 July 1984