محاسبهٔ سطح بیرونی و سطح درونی یک جسم جاذب از روی برجذبی گازها به کمک ماشین حساب برنامه‌ای

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چکیده :

دراین مقاله روش محاسبهٔ سطح بیرونی و سطح درونی یک جسم جاذب را از روی ایزوترم برجذبی گازهای مختلف شرح داده‌ایم . نخست بایک آزمایش دقیق ایزوترم برجذبی جسم را رسم کرده ، سپس با استفاده از معادلهٔ BET ومعادلهٔ Pickett چهار پارامتر مهم جسم جاذب را باچند مرحله محاسبهٔ پی‌درپی بدست می‌آوریم . برای داشتن مقادیر دقیق‌تر می‌توان مراحل محاسبه را ادامه داد . بابهره مندی ازیک ماشین حساب برنامه‌ای که برنامه‌ها را بصورت کارت‌های سوراخ شده می‌پذیرد، محاسبات باسرعت کافی وبدون اینکه نیازی به‌ماشین حسابگر بزرگ احساس شود انجام می‌گیرد .

میدانیم که ایزوترم برجذبی یک جسم جاذب ازاندازه گیری حجم گاز جذب شده در واحد وزن آن درفشارهای تعادلی مختلف و دمای ثابت بدست می‌آید . طرز ترسیم این منحنی وساختن دستگاه‌های مربوط را درگفتارهای گذشته شرح داده‌ایم (٣،٢،١) . از روی شکل عمومی این ایزوترم‌ها که باتخلخل ،ساختمان منفذی pore structure جسم جامد و شمارهٔ لایه‌های جذب شده بستگی دارد آنها را برپنج دستهٔ مهم تقسیم می‌کنند .

ازبررسی ریاضی ایزوترم‌ها ومحاسبات گوناگون،اطلاعات ارزنده‌ای دربارهٔ n عدهٔ لایه‌های ملکولهای جذب شده برسطح آزاد ، Σ وسعت سطح آزاد جسم جاذب برحسب مترمربع بر گرم ، v_m پوشش یک لایه‌ای

برحسب سانتیمترمکعب گاز جذب شده برگرم (پس از تبدیل به شرایط متعارفی) بدست می‌آید . ونیز از روی تعداد لایه‌های ملکولهای جذب شده بویژه درفشار اشباعی، چون ابعاد این ملکولها معلوم است ، می‌توان بزرگی منافذ یا قطر لوله‌های موئین موجود درساختمان داخلی جسم متخلخل را پیش‌بینی کرد .

اگر باخارج کردن تدریجی گاز جذب شده ایزوترم واجذبی یا شاخهٔ بازگشت Desorption branch را دردمای ثابت فوق رسم کنیم منحنی حاصل گاهی اوقات برشاخهٔ اصلی منطبق نخواهد بود ویک مدار پسماندی Hysteresis loop درست خواهد شد که با پدیدهٔ تراکم موئین Capillary condensation ارتباطی نزدیک دارد . از روی شکل مدارهای پسماندی de Boer دانشمند هلندی نیز ایزوترم‌ها را بر پنج گونه مهم تقسیم کرده وهرکدام را باساختمان منفذی معین وشکل ویژه‌ای ازمنافذ ولوله‌های موئین مربوط دانسته است . به شاخهٔ بازگشتی ایزوترم برجذبی می‌توان معادلهٔ Kelvin را اطلاق کرده وقطر منافذ را ازاین راه نیز بدست آورد .

پیش‌بینی‌هایی که دربارهٔ ساختمان داخلی جسم متخلخل از روی ایزوترم‌های جذب سطحی بعمل می‌آید باید بانتیجه‌های حاصل از روشهای دیگر توافق داشته باشد که مهمترین آنها بقرار زیر است :

۱ ـ برجذبی مواد قابل جذب ازفاز مایع (محلولها) Adsorption from solution

۲ ـ اندازه‌گیری گرمای حاصل از ترشدن جسم جامد Wetting heat

۳ ـ مشاهدات میکرسکوپی

۴ ـ روشهای مربوط به تداخل پرتوهای ایکس

۵ ـ قابلیت نفوذ دربرابر جریان گازها Permeablity to gas flow

۶ ـ اندازه‌گیری چگالی درون جیوه تحت فشار Mercury porosimeter

۷ ـ بهره‌مندی ازمعادلهٔ Kelvin روی شاخه واجذبی وبدست آوردن منحنی توزیع درشتی منافذ Pore size distribution وچند روش دیگر .

برتری روش جذب گازها وترسیم ایزوترم‌ها دراینست که با کشیدن یک منحنی آزمایشی اطلاعات گوناگونی درخصوص وسعت سطح آزاد ، نوع منافذ ، قطر آنها وگرمای برجذبی بدست می‌آید . اما این نتایج ازبررسی وتحلیل ریاضی منحنی تجربی حاصل می‌شود ونیازمند محاسبه‌های طولانی و دقیق می‌باشد . به همین دلیل فقط عدهٔ کمی از ایزوترم‌های منتشرشده که شمارهٔ آنها به چندهزار می‌رسد تا کنون ازنظر ریاضی بخوبی تحلیل وبررسی شده است .

ما دراین گفتار روش محاسبهٔ سطح بیرونی وسطح درونی جسم جاذب و مراحل مختلف محاسبه را از روی ایزوترم برجذبی آن ونیز بدست آوردن تعداد لایه‌های جذبی و مقدار گرمای جذب را با بهره‌مندی

۱۱۳

ازیک‌ماشین حساب برنامه‌ای Programmable calculator که درسالهای اخیر به‌بهای ارزانی به‌بازار آمده است شرح داده‌ایم . مرحله‌های پی‌درپی محاسبه طوری تنظیم‌شده که باداشتن‌نقاط منحنی ایزوترم وبا استفاده ازبرنامه‌های آماده بصورت کارت‌های سوراخ شده بدست‌آوردن پارامترهای مهم جسم‌جاذب درزمان اندکی میسر است .

جسم جاذب انتخاب شده پنبهٔ کوهی یا آسبست می‌باشد که درسالهای اخیر اهمیت صنعتی‌کسب کرده است وگازهای بکار رفتهٔ اکسیژن ، ازت وکریپتین می‌باشد .

مشروح مقالـه ونیز جدول‌ها و مراحل محاسبه ومنابع خارجی مقالـه دربخش انگلیسی این گفتار آمده است .

منابع

۱ —ف. فرحان ، نشریهٔ دانشکدهٔ فنی ، شمارهٔ ۲ ، ۱۳٤٤ ، صفحهٔ ۳۱ تا ۳۸

۲ — ف. فرحان ، نشریهٔ دانشکدهٔ فنی ، شمارهٔ ۸ ، ۱۳٤٦ ، صفحهٔ ۱ تا ۱٦

۳ —ف. فرحان ، نشریهٔ دانشکدهٔ فنی ، شمارهٔ ۲۱ ، ۱۳۵۰ ، صفحهٔ ۲۷ تا ۳۸

Calculation of External and Internal Surface Areas by Gas Adsorption With Programmable Calculator Application

by :

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INTRODUCTION

One of the most important applications of physical adsorption is the use ef adsorption isotherms to determine the surface areas of finely divided and porous solids. Surface area is a highly significant paremeter in nearly all physical and chemical processes involving powdered solids.

The specific surface area, Σ, of a solid is defined as the surface area per unit mass, usually in square meters per gram. The monolayer capacity, v_m, is defined as the quantity of adsorbate which would be required to cover the adsorbent with a monolayer only. v_m is commonly expressed as cubic centimeters at S.T.P. per gram of adsorbent. Σ and v_m are related by:

$$\Sigma = 0.269 \; \sigma_m \; v_m \tag{1}$$

8

where σ_m is the area in square ångströms which 'one adsorbed molecule would occupy in the completed monolayer.

The famous BET equation, derived by Brunauer, Emmet and Teller (1) reads:

$$\frac{v}{v_m} = \frac{Cx}{(1-x)(1-x+Cx)} \tag{2}$$

where v is the volume of gas adsorbed at relative pressure $p/p^\circ = x$, and C is a constant characteristic of the solid-gas system. According to the BET theory, this equation is applicable only to adsorbents capable of receiving an unlimited number of adsorbate layers on their surface. Therefore, it is sometimes called ∞ — layer BET equation. Written in the linearized form:

$$\frac{x}{v(1-x)} = \frac{1}{v_m C} + \frac{C-1}{v_m C} x \tag{3}$$

it is universally used for the calculation of v_m and C. $\dfrac{x}{v(1-x)}$ being a linear function of x, the two parameters may be easily obtained by using the least squares method, (L. Sq. M.), preferably with a computer or a programmable calculator:

$$\text{slope} + \text{intercept} = \frac{1}{v_m}$$

$$\tag{4}$$

$$\text{slope}/\text{intercept} = C - 1$$

Strictly speaking, Equation 2 is capable of describing type II or type III isotherms (2, 3). However its use is permissable even for limited adsorption in micropores at low coverages (0.03 to 0.3).

For the case where the solid adsorbent can only receive a restricted number of adsorbate layers, n, the authors of BET theory have proposed the following equation:

$$\frac{v}{v_m} = \frac{Cx}{1-x} \times \frac{1-(n+1)x^n + nx^{n+1}}{1+(C-1)x - Cx^{n+1}} \tag{5}$$

known as the n-layer BET Equation (4)

9

In both cases the ratio $\frac{v}{v_m}$ is the mean value of the number of adsorbate layers. At saturation, that means for $p=p°$ or $x=1$, the number of layers should become infinity in equation 2 (∞ — form), whereas in Equation 5 (n — layer form) it should tend to n. Unfortunately, the limit of the quantity $\frac{v}{v_m}$ in Equation 5 is different from n at saturation. For $x=1$, this limit is $\frac{Cn(n+1)}{2(Cn+1)}$, which may be proved by derivating twice. This limit is a function of C, its value cannot exceed $\frac{n}{2} + \frac{1}{2}$. This discrepancy is a major drawback of the n—layer BET equation. The theoretical curve agrees with experimental isotherm only within the range $0 < x < 0.4$, in a few favorable cases up to $x=0.8$ (5).

Pickett (6) has modified the n — layer BET treatment by taking into account the decrease in probability of escape of the n th layer molecules, as the capillaries become completely full of adsorbate.

Pickett's equation :

$$\frac{v}{v_m} = \frac{Cx\,(1-x^n)}{(1-x)\,(1-x+Cx)} \tag{6}$$

gives a better agreement with experimental results, and its simplicity is remarkable.

Dellyes (7) derived the same equation with a more logical assumption. Moreover, by dividing the adsorption surface into external and internal areas, and introducing a fourth parameter, v_{mi}, (monolayer capacity for internel surface) he attained a satisfactory fit up to the saturation point $(x=1)$.

On the external surface of an adsorbent, the number of adsorbed layers, is by definition unlimited. The ∞ — form BET equation is applicable to this surface. On the contrary, in internal areas only a restricted number of layers can be inserted. The n—layer Pickett's equation should be valid for internal sites.

The relative value of internal and external surfaces is in relation with the granulation and porosity of solid adsorbent. For example a pile of micro- spheres exhibits a large external surface, the internal area consisting only of contact points between particles. Conversely, in a microporous and compact adsorbent, the adsorption surface is mostly internal. Obviously, internal and

external areas measured by gas adsorption should be consistent with the geometrical structure of the adsorbent.

The external monolayer capacity, v_{me}, may be calculated independently. We assume that the adsorption of gases at saturation is exclusively ∞ — layer, and hence external. Using Equation 2, v_{me} should be the limit of $\dfrac{v(1-x)(1-x+Cx)}{Cx}$ for $x=1$. The numerical values of this expression may be fitted into a cubic function of the form $Y=a+bX+CX^2+dX^3$ and the parameters a, b, c, and d determined by L, Sq. method. v_{me} is equal to $a+b+c+d$.

This result is rather insensitive to the value of C constant. For each x, volume of the gas adsorbed externally, v_e, is obtained from Equation 2. Using v_i values from $v_i = v - v_e$, a better agreement of equation 6 with experimental points may be expected.

In this paper, we are describing a simple procedure for the calculation of Σ_e, Σ_i and n, by successive approximations. It is sufficient to use the punched program cards of linear function $Y=a+bX$, cubic function

$$Y=a+bX+CX^2+dX^3$$

and power curve $Y=aX^b$, applying the L. Sq. method in each case.

CALCULATION OF v_{me}, v_{mi} and n

This computation is performed according to the following steps.

1) v_m and C for both surfaces (First approximation) — $L=\dfrac{x}{1-x}$ and $Q=\dfrac{L}{v}=\dfrac{x}{v(1-x)}$ are calulated for each value of x. According to Equation 3, Q is a linear function of x, specifically up to $x=0.3$ (BET Method). Using L. Sq. method for $Q=a+bX$ we find

$$b+a=\frac{1}{v_m}$$

$$b/a=C-1$$

11

2) v_{me} and $v_e - v_{me}$ is the limit of $\dfrac{v(1-x)(1-x+Cx)}{Cx}$ for $x=1$. First

$R = \dfrac{1-x+Cx}{C}$ is calculated, using the value of C obtained in step 1). Then,

the function $Y = \dfrac{R}{Q}$ for seven largest values of x, up to $x=0.95$, is fitted

into $Y = a + bx + cx^2 + dx^3$. After obtaining a, b, c and d by L. Sq. M., v_{me} is

equal to $a+b+c+d$. The quantities $v_e = \dfrac{v_{me}L}{R}$, and $v_i = v - v_e$ are tabulated

next for each value of x.

3) n, number of layers adsorbed internally — volume of gas adsorbed externally, v_e,

$$v_e = \frac{v_{me}Cx}{(1-x)(1-x+Cx)}$$

volume of gas adsorbed internally, v_i,

$$v_i = \frac{v_{mi}Cx(1-x^n)}{(1-x)(1-x+Cx)}$$

total adsorption $v = v_e + v_i$

$$v = \frac{Cx}{(1-x)(1-x+Cx)}(v_m - v_{mi}x^n)$$

This equation is converted to a power function of the form $Y' = ax^b$

$$\frac{v_{mi}}{v_m}x^n = 1 - \frac{v(1-x)(1-x+Cx)}{v_m Cx}$$

$$Y' = \frac{v_{mi}}{v_m}x^n = 1 - \frac{R}{v_m Q}$$

Y' is calculated for seven largest values of x, and $n=b$ is computed from the power curve by L. Sq. M. As for v_{mi}, it is obtained in step (4) with a better precision.

4) v_{mi} and C_i — For internal adsorption Pickett's equation is applied using a better value of C,

$$\frac{v_i}{v_{mi}} = \frac{C_i x(1-x^n)}{(1-x)(1-x+C_i x)}$$

12

Put in the linear form, it reads

$$S = \frac{x(1-x^n)}{v_i(1-x)} = \frac{1-x+C_ix}{v_{mi}C_i} \doteq \frac{1}{v_{mi}C_i} + \frac{C_i-1}{v_{mi}C_i}x$$

After calculation of $(1-x^n)$, we obtain $S = \frac{L(1-x^n)}{v_i}$ for every x. S is a linear function of x in a wider range than Q. For the linear portion we have

$$\text{slope} + \text{intercept} = \frac{1}{v_{mi}}$$

$$\text{slope}/\text{intercept} = C_i - 1$$

The calculated value of v_{mi} should be smaller than v_m, because $v_m = v_{me} + v_{mi}$. If the difference is less than 3% (the usual precision of experimental points in drawing adsorption isotherm) any distinction between v_i and v_e is impossible. Similarly, C_i should be larger than C.

It is well known that the constant C is proportional to $e^{\frac{E_1-E_L}{RT}}$, $E_1 - E_L$ being the difference between the heat of adsorption in the first layer and the heat of liquefaction, it is known as the net heat of adsorption. R and T are gas constant and Kelvin temperature. In the inner adsorption sites E_1 is larger because of the potential overlap between walls, and hence $C_i > C$.

5) New n—If $v_{mi} < v_m$ and $C_i > C$, the calculation may be continued to obtain a bettwer value for n.

$$\frac{v_i}{v_{mi}} = \frac{C_ix(1-x^n)}{(1-x)(1-x+C_ix)}$$

$$x^n = 1 - \frac{v_i(1-x)(1-x+C_ix)}{v_{mi}C_ix} = Y''$$

The largest values of Y'' are fitted into $Y'' = aX^b$, similarly to step 3). The new value of n should be different from the previous one.

6) Using the new n, the function $\frac{x(1-x^n)}{v_i(1-x)}$ is recalculated for every x. The plot against x should have a wider linear range, Using this portion we obtain new values for v_{mi} and C_i.

The computation steps may be continued in the same manner. However, as soon as the new results become indistinguishable form previous ones, further continuation would have no significance.

NUMERICAL ILLUSTRATION

As an example, application of this calculation method to an adsorbent of low surface area is outlined briefly. The adsorption isotherm of oxygen on chrysotile asbestos (in pellet form) at 88.8°K, described in a previous paper (8), is chosen for this purpose. The surface area of asbestos was 9.67 m²/g. This isotherm is illustratively type II, and scattering of experimental points is less than 3%. The values of v, volume of oxygen adsorbed per gram of adsorbent, at S. T. P., are obtained from plotted isotherm in 0.05 intervals of x. The sequence of calculation steps is shown in the following Table. Consecutive results are compiled in columns from left to right.

The calculator system employed was the Seiko Desk Top Computor S—301, with a Card Puncher. Unfortunately, little attention has been given to the potential uses of such programmable calculators in Chemical Engineering. Their low costs, simplicity and large problem solving capabilities make them attractive (9).

RESULTS AND DISCUSSION

After obtaining v_m and C in the usual way (step 1), we find $v_{me} = 0.10$ cc/g in step 2. Thus, $\dfrac{v_{me}}{v_m} = \dfrac{\Sigma_e}{\Sigma} = 4.23\%$. That means, 95.77% of the total surface is internal. This result is in compliance with the tubular structure of the adsorbent. Asbestos crystallite aggregates form hollow fibers having an inner diameter of several hundred angstöms (10).

In step 3, we find $n = 8.52$. The mean value of the number of layers formed on each wall is 8.52. This is consistent with the diameter of capillaries.

In step 4, the function $\dfrac{x(1 - x^{8.52})}{v_i(1 - x)}$ is linear up to $x = 0.65$. From this linear portion we calculate $v_{mi} = 2.359 > v_m$ and $c_i = 23.7 < c$. The conditions

14

STEP 1

STEP 2

Table of
STEP 2

x	$v_{cc/g}$	$L=\dfrac{x}{1-x}$	$Q=\dfrac{x}{v(1-x)}=\dfrac{L}{v}$	$R=\dfrac{1-x+Cx}{C}=\dfrac{1+27.6\,x}{28.6}$	$\dfrac{v(1-x)(1-x+Cx)}{Cx}=\dfrac{R}{Q}=Y$
0.05	1.60	1/19	0.0329*	0.08322	2.5295
0.10	1.93	1/9	0.0576*	0.13147	2.2825
0.15	2.25	3/17	0.0784*	0.17972	2.2923
0.20	2.55	1/4	0.0980*	0.22797	2.3262
0.25	2.85	1/3	0.1169*	0.27622	2.3629
0.30	3.12	3/7	0.1373*	0.324475	2.36325
0.35	3.52	7/13	0.1530	0.37273	2.4361
0.40	3.92	2/3	0.170	0.42098	2.47635
0.45	4.40	9/11	0.186	0.46923	2.5227
0.50	4.90	1	0.204	0.51748	2.53667
0.55	5.35	11/9	0.228	0.56573	2.48127
0.60	5.90	3/2	0.254	0.61399	2.51728
0.65	6.42	13/7	0.289	0.66224	2.2951*
0.70	7.00	7/3	0.333	0.71049	2.1336*
0.75	7.60	3	0.395	0.75874	1.92086*
0.80	8.30	4	0.482	0.80699	1.67425*
0.85	9.15	17/3	0.619	0.85524	1.38165*
0.90	10.25	9	0.878	0.90350	1.029*
0.95	11.70	19	1.624	0.95175	0.58605*

Q values marked with *, $Q=a+bx$, $\dfrac{1}{a+b}=v_m=2.347$, $\dfrac{b}{a}+1 = C=28.6$

15

Calculations

STEP 3   STEP 4

$$x<0.65,\quad S=a-bx,\quad \frac{1}{a+b}=v_{mi}=2.3587,\quad \frac{b}{a}+1=C_i=23.7$$

$$Y'=ax^b,\quad b=n=8.52$$

$1-\dfrac{v(1-x)(1-x+Cx)}{v_mCx}=1-\dfrac{R}{v_mQ}=Y'$	$v_e=\dfrac{v_{me}L}{R}$	$v_i=v-v_e$	$1-x^n=1-x^{8.52}$	$\dfrac{x(1-x^{8.52})}{v_i(1-x)}=\dfrac{L(1-x^n)}{v_i}=S$
	0.063	1.537		0.03424
	0.084	1.846		0.06019
	0.0976	2.152		0.08200
	0.109	2.441		0.10242
	0.120	2.730		0.12210
	0.1313	2.989		0.14338
	0.1436	3.376		0.15950
	0.1574	3.763		0.17716
	0.1733	4.227		0.19356
	0.1921	4.708		0.21240
	0.2148	5.135	0.9939	0.23655
	0.2429	5.657	0.9871	0.26175
0.02365	0.2788	6.141	0.9745	0.29471
0.0910	0.3265	6.673	0.9521	0.33292
0.1816	0.393	7.207	0.9118	0.37954
0.2866	0.4927	7.807	0.8506	0.43581
0.4113	0.6587	8.491	0.7696	0.50026
0.5616	0.990	9.260	0.5925	0.57586
0.7503	1.985	9.7155	0.3541	0.69249

$$=0.09941\ cc/g$$

Y values marked*, $Y=a+bx+cx^2+dx^3$, $v_{me}=a+b+c+d+$

mentioned previously in step 4 are not satisfied. Therefore, calculation can not be continued any further. Such a result is predictable with an adsorbent of low surface area.

NOTATION

x = relative pressure, $p/p°$

v = volume of gas adsorbed, in cc/g, at S. T. P.

v_e = volume of gas adsorbed externally

v_i = volume of gas adsorbed internally, $v = v_e + v_i$

Σ = specific surface area in m^2/g

Σ_e and Σ_i = as before, $\Sigma_e + \Sigma_i = \Sigma$

v_m = monolayer capacity in cc/g

v_{me} and v_{mi} = as before, $v_m = v_{me} + v_{mi}$

L. Sq. M. = least squares method

Greek Letters

σ_m = area occupied by a molecule, in square augströms

Subscripts

e = external

i = internal

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