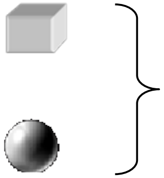
Powder Surface Area and Porosity, by Lowell and Shields, 3rd edition

I. Introduction

1.1. Real Surfaces

$S = 6\,l^2$

$S = 4\pi r^2$



Theoretical (geometric) area

Surface imperfections will create real SA
Imperfections: voids, steps, pores
Real SA > theoretical SA

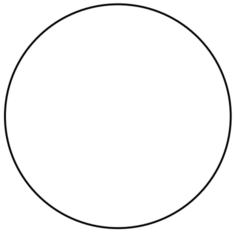
1.2 Factors affecting surface area

a. **Particle size: whenever matter is divided into smaller particles, new surfaces must be produced**

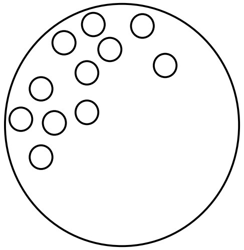
b. Particle shape:

for a fixed mass.

sphere



Minimum area-to-volume ratio



maximum area-to-volume ratio
(microscopic)

Specific surface area = area per-gram of powder
= function (size, shape, porosity, …)

e.g. powder consisting of spherical particles of various sizes

$$S_t = 4\pi \times (r_1^2 N_1 + r_2^2 N_2 + \cdots\cdots + r_i^2 N_i)$$

$$= 4\pi \times \sum_{i=1} r_i^2 N_i$$

$$V_t = \frac{4}{3}\pi \times (r_1^3 N_1 + \cdots\cdots) = \frac{4}{3}\pi \sum r_i^3 N_i$$

$$V_t = \frac{m}{\rho}$$

$$Specific\ area = S = \frac{St}{m} = \frac{3}{\rho}\frac{\sum N_i r_i^2}{\sum N_i r_i^3}$$

If the spheres are of the same radius

$$S = \frac{3}{\rho r}$$

For density = 3 g cm^{-3}

r = 1 μm => S = 1 m^{2}g^{-1}
r = 0.1μm => S = 10 m^{2}g^{-1}
r = 10 nm => S = 100 m^{2}g^{-1}

activated carbon usually has an area of >1000 m^{2}g^{-1}

contribution from porosity is significant.

1.3 Surface area from particle size distribution

A number of methods can be used to determine “equivalent spherical diameter”, such as

Coulter counter (microchannel)
Stoke’s law (settling of particles in fluid)
Light scattering
Permeametric methods
Sieving
SEM
TEM

Surface areas calculated from particle size will establish the lower limit by the assumptions of regular geometric shape and by ignoring the imperfections on the surface.

2. Gas adsorption

2.1. Introduction

- surface imperfections and pores can generally be disclosed with an electron microscope, but they remain hidden because of being small or inner.
- gas adsorption can probe the surface irregularity and pore interiors even at the atomic level.

a powerful method to generate detailed information about the morphology of surface.

- W = *f* (P, T, E)

W: weight of gas adsorbed

E : interaction potential between vapor and solid

E varies with the properties of vapor and solid and coverage.

At constant temperature

W = *f* (P, E) sorption isotherm

Were it not for the presence of E, all adsorption isotherms would be identical.

2.2. Chemical and Physical Adsorption

2.3. Physical Adsorption Forces

ΔS: negative ∵ **condensed state is more ordered due to the loss of at least one degree of translation freedom.**

ΔG: negative ∵ **adsorption is spontaneous.**

$\Delta H = \Delta G + T\Delta S < 0$, exothermic process; higher amounts of adsorption at lower temperatures.

Forces

a. Dispersion forces (Van der Waals)

instantaneous dipole moment (asymmetric electron moving), leading to a net attracting potential between neighboring molecules.

b. Ion-dipole: ionic solid + polar adsorbate.

c. Dipole-dipole: polar solid + polar adsorbate.

d. Ion-induced dipole: ionic solid + polarizable adsorbate.

e. Quadrapole interactions: symmetric molecules.

e.g. $^{-}O{-}^{+}C^{+}{-}O^{-}$ No dipole moment, but atoms with different electronegativities

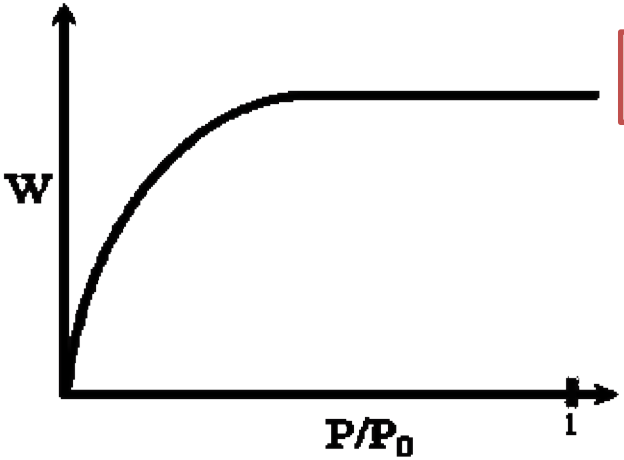
Adsorption forces are similar to those for liquefaction of vapors.

III. Adsorption Isotherms

Type I a. Monolayer (seldom observed for physisorption)

b. Microporous powder

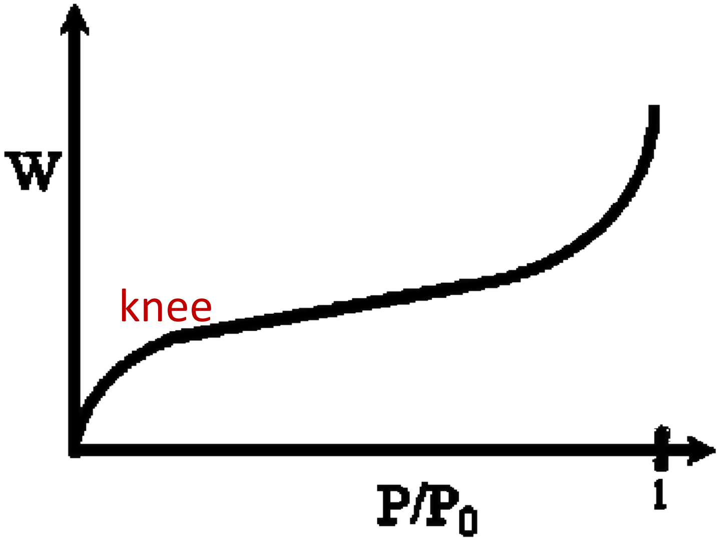
Almost all the surface of the solid is contained in micropores. On the basis of Kelvin eq., condensation in micropores occurs at low P/P_0.



plateau

(The external area is negligible.)

Type II



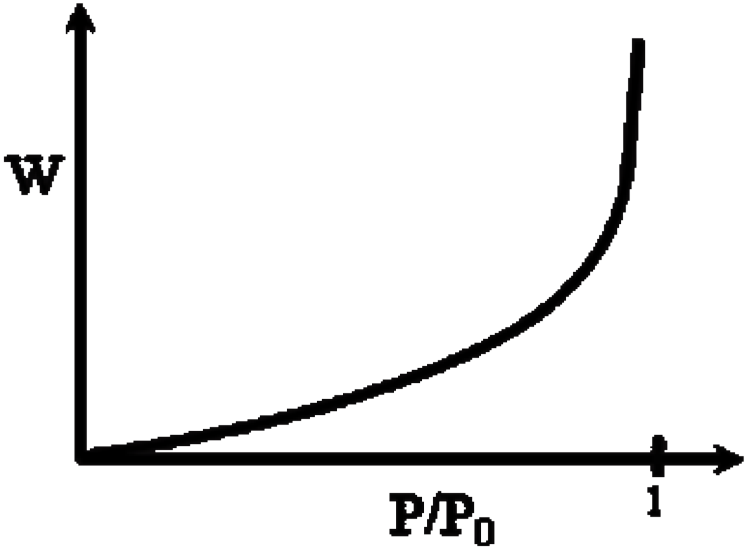
a. **Nonporous powder**
(layer-by-layer adsorption)

knee ─ near the completion of 1st layer.

As P/P_0↑ → multilayer → infinite layers

b. Powders with meso-macropores.

Type III

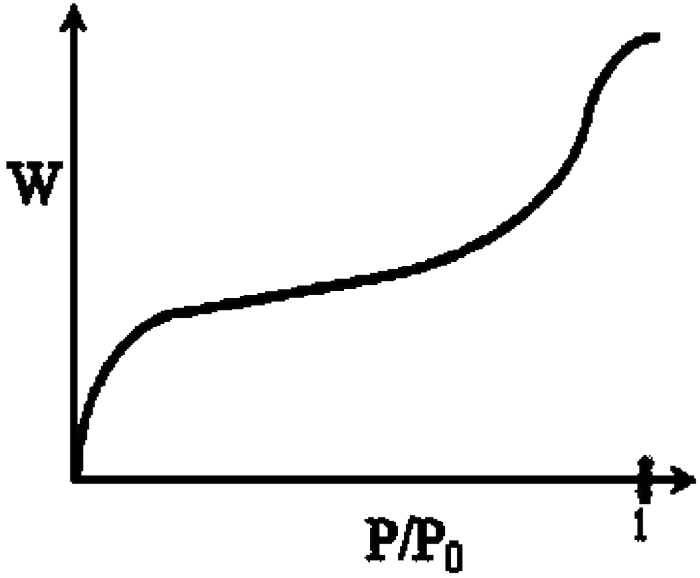


Adsorbate-adsorbed layer interaction

greater than

adsorbate- absorbent interaction

Type IV



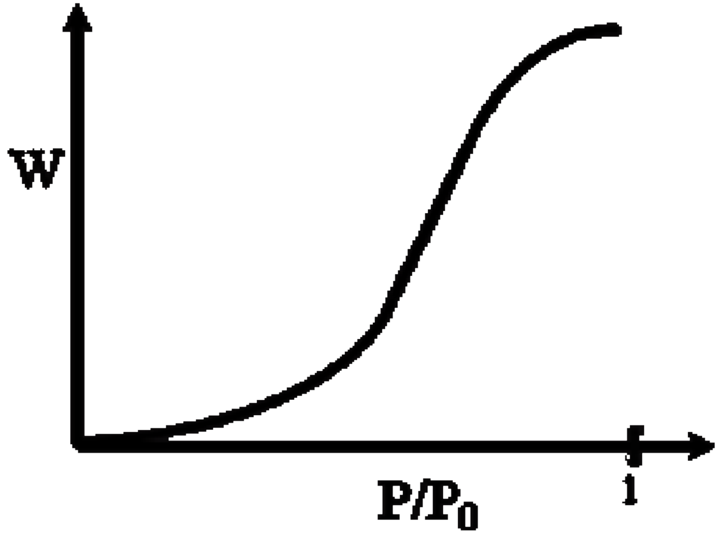
Similar to Type II
But the powders contain pores in a range of 15-1000Å

1st knee: near monolayer completion

2nd knee: (15-1000 Å) pores are filled up

P/P_0↑ → infinite layers (condensation on the external)

Type V



Strong interaction between adsorbate and powders containing 15-1000Å pores.

4. Langmuir and BET theories (kinetic isotherms)

4.1. The Langmuir Isotherm Assumption: monolayer

Avogadros’s No.

$$N = \frac{\bar{N}\cdot P}{(2\pi \bar{M}RT)^{\frac{1}{2}}} = no.\ of\ striking / cm^{2}s$$

$$N' = N\cdot\theta_0 = kP\theta_0 = collision\ on\ unoccupied surface / cm^{2}s$$

$$N_{ads} = kP\theta_0 A_1$$

A_1: condensation coefficient

$$N_{des} = N_m \theta_1 \nu_1 \times e^{\frac{-E}{RT}}$$

$$\theta_1 + \theta_0 = 1$$

$$N_m = number\ of\ completed\ monolayer / cm^{2}$$

At equilibrium

$$N_{ads} = N_{des}$$

$$\Rightarrow \theta_1 = \frac{kPA_1}{N_m \upsilon_1 e^{\frac{-E}{RT}} + kPA_1}$$

Let $K = \dfrac{kA_1}{N_m \upsilon_1 e^{\frac{-E}{RT}}}$

$$S_t = \frac{W_m \bar{N} A}{\bar{M}}$$

A = cross-sectional area of a molecule

$$\begin{tikzcd}
\therefore \theta_1 = \dfrac{KP}{1+KP} \\
\dfrac{N}{N_m} = \dfrac{W}{W_m} \arrow[u]
\end{tikzcd}$$

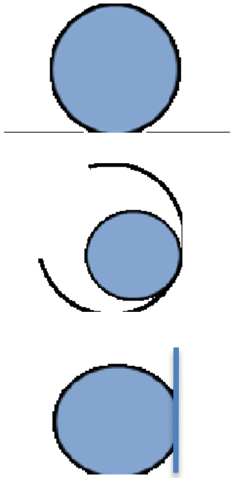
$$\therefore \frac{W}{W_m} = \frac{KP}{1+KP}$$

$$\Rightarrow \frac{P}{W} = \frac{1}{KW_m} + \frac{P}{W_m}$$

4.2. The BET Theory

Understanding the adsorption situation before discussing the BET

a. At low P/P_0, the first sites to be covered are the more energetic ones.



High energy sites:

- **1. Within narrow pores**
- **2. Between horizontal and vertical edges**

need more energy for separation

- ❖ **In principle, the sites with <u>overlapping potential</u> are the high energetic sites.**
- ❖ **Surface heteroatoms (eq. organic solids, impure materials, or functional groups) will affect the adsorption potentials.**

b. More energetic sites covered first does not imply no adsorption on less energetic ones.

Rather, it implies that the residence time of adsorbates is longer on more energetic sites (Kinetic theory)

c. As P/P_0 is allowed to increase and the surface becomes progressively covered, prior to monolayer coverage multilayer adsorption will commence.

BET theory enables an experimental determination of the number for monolayer coverage.

In reality, there exists no pressure for monolayer coverage to occur.

BET theory

Limiting no. of layers = n

$$\frac{W}{W_m}=\frac{c}{\left[\left(\frac{P}{P_0}\right)-1\right]}\frac{\left[1-(n+1)\left(\frac{P}{P_0}\right)^{n}+n\left(\frac{P}{P_0}\right)^{n+1}\right]}{\left[1+(c-1)\left(\frac{P}{P_0}\right)^{n}+c\left(\frac{P}{P_0}\right)^{n+1}\right]}$$

$$c=const.\times e^{\frac{(E-L)}{RT}}$$

E: ads. energy
L: heat of liquefaction

Classical BET equation

$$n = \infty$$

$$\frac{W}{W_m} = \frac{c\frac{P}{P_0}}{\left(1-\frac{P}{P_0}\right)\left[1-\left(\frac{P}{P_0}\right)+c\left(\frac{P}{P_0}\right)\right]}$$

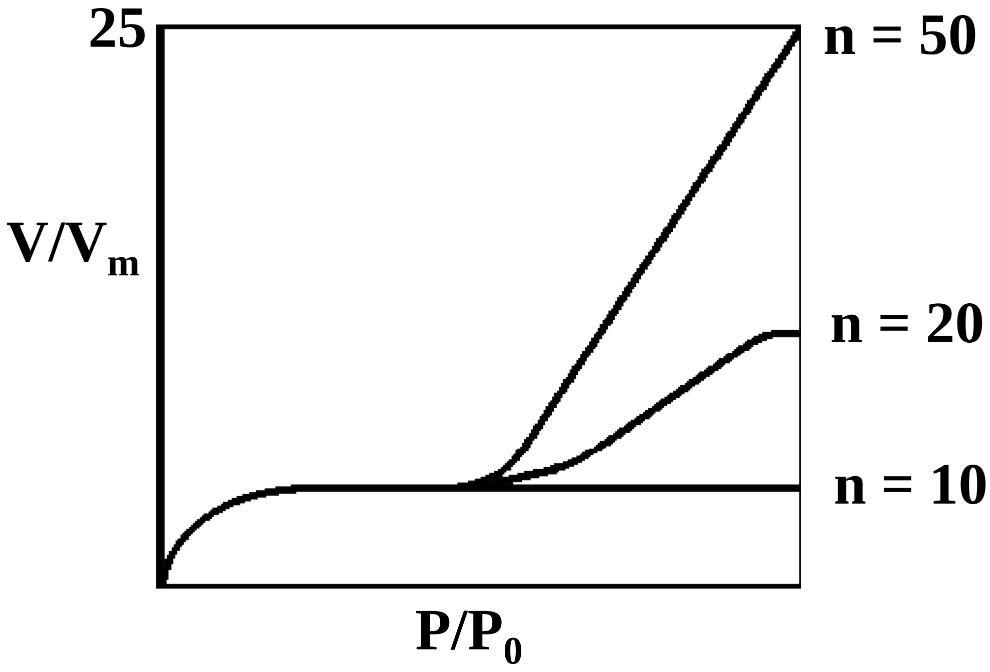
$$n = 1$$

$$\Rightarrow Langmuir$$

Modification:
Using specific n values for BET to simulate the whole isotherm.

- **n → ∞ => classical BET (poor for high P/P_0)**
- **n = 1 =>** $\frac{V}{V_m} = \frac{cx}{1+cx}$ **(not applicable for multilayer)**

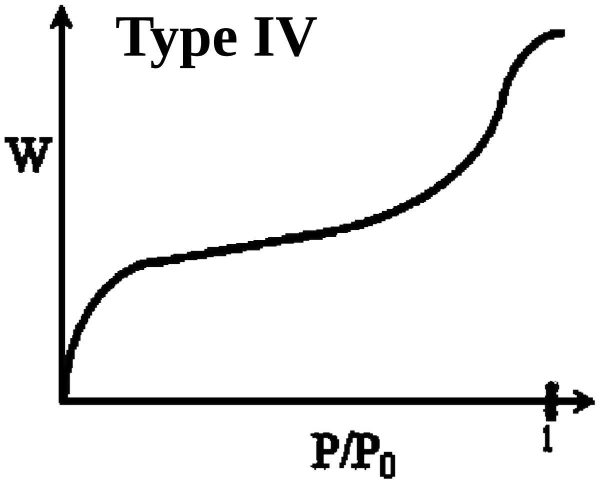
- **$P \to P_0$ or $x \to 1$,** $\lim_{x \to 1} \frac{V}{V_m} = \frac{n(n+1)c}{2(nc+1)}$

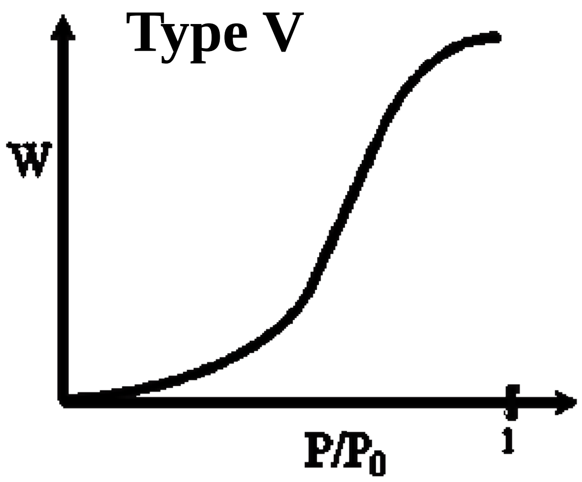


For c = 100

The fit is good for Type I, II, III.

BET eq. can deal with types I, II and III, but it does not explain the plateau observed IV and V.


Type IV


Type V

Brunauer et al. proposed a modification.
In pores, the last adsorbed layer in a capillary is attached to both sides.

∴the adsorption energy is greater than the heat of adsorption.

We denote the extra energy as Q.

$$k_a P S_0 = k_{d1} S_1 \qquad k_{d1} = \upsilon \exp\left(\frac{-E}{RT}\right)$$

$$k_a P S_{i-1} = k_{di} S_i \qquad k_{di} = \upsilon \exp\left(\frac{-E_L}{RT}\right)$$

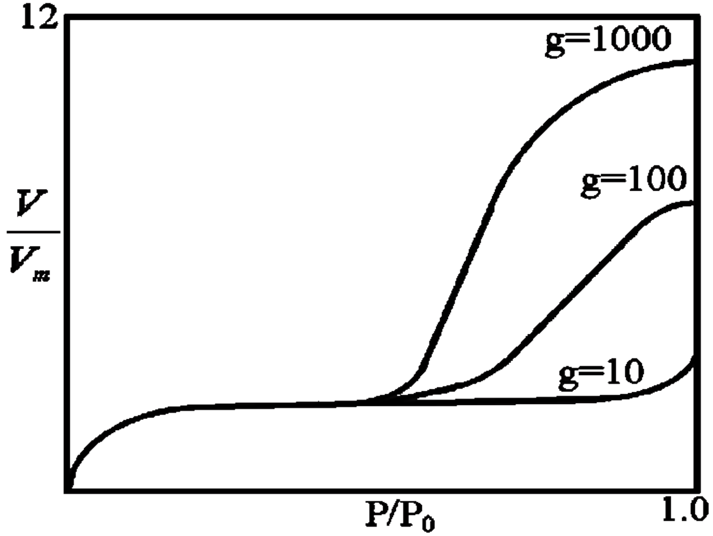
$$\vdots$$

$$k_a P S_{n-1} = k_{dn} S_n \qquad k_{dn} = \upsilon \exp\left(\frac{-(E_L + Q)}{RT}\right)$$

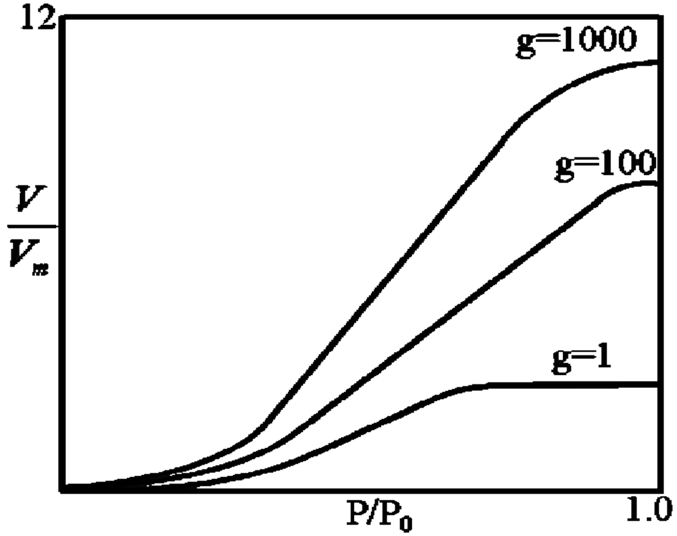
$$\frac{V}{V_m} = \frac{cx}{1-x} \frac{1 + (\frac{ng}{2} - n)x^{n-1} - (ng - n + 1)x^n + (\frac{ng}{2})x^{n+1}}{1 + (c-1)x + (\frac{cg}{2} - 2)x^n - (\frac{ng}{2})x^{n+1}}$$

$$g = \exp(\frac{Q}{RT})$$

Because of extra Q introduced, the last layer finds it harder to desorb.



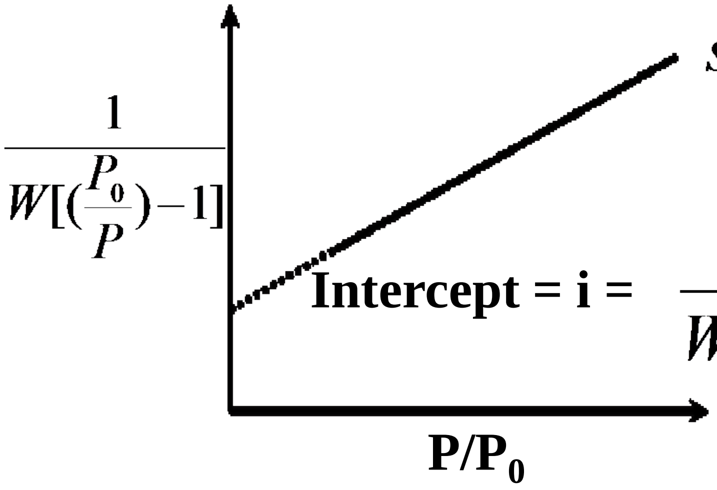
n = 10, c = 100, type IV



n = 10, c = 0.05, type V

Reference Book:
Adsorption Analysis: Equilibria and Kinetics. D.D. Do, Imperial College press.1998

4.3 Surface Areas from BET



$$slope = S = \frac{c-1}{W_m c}$$

Intercept = i = $\frac{1}{W_m c}$

$$W_m = \frac{1}{S+i} \quad , \quad c = \frac{S}{i} + 1 \quad , \quad S_t = \frac{W_m \cdot \bar{N} \cdot A}{\bar{M}}$$

4.4 The meaning of monolayer coverage

Hill has shown : $(\theta_0)_m = \dfrac{c^{\frac{1}{2}} - 1}{c - 1}$ **,**

where $(\theta_0)_m$ = the fraction of surface not covered by any molecules at $W = W_m$

$c \propto e^{\frac{(E-L)}{RT}}$ **, c↑as E↑⇒ $(\theta_0)_m$↓**

∵with large c, it is easier to achieve a single monolayer.

E.g. for c = 100 => $(\theta_0)_m = \dfrac{c^{\frac{1}{2}} - 1}{c - 1}$ **= 0.091 = 9.1%**

∴ average number of layers on each occupied sites = $\dfrac{N_m}{(1-0.091)N_m}$

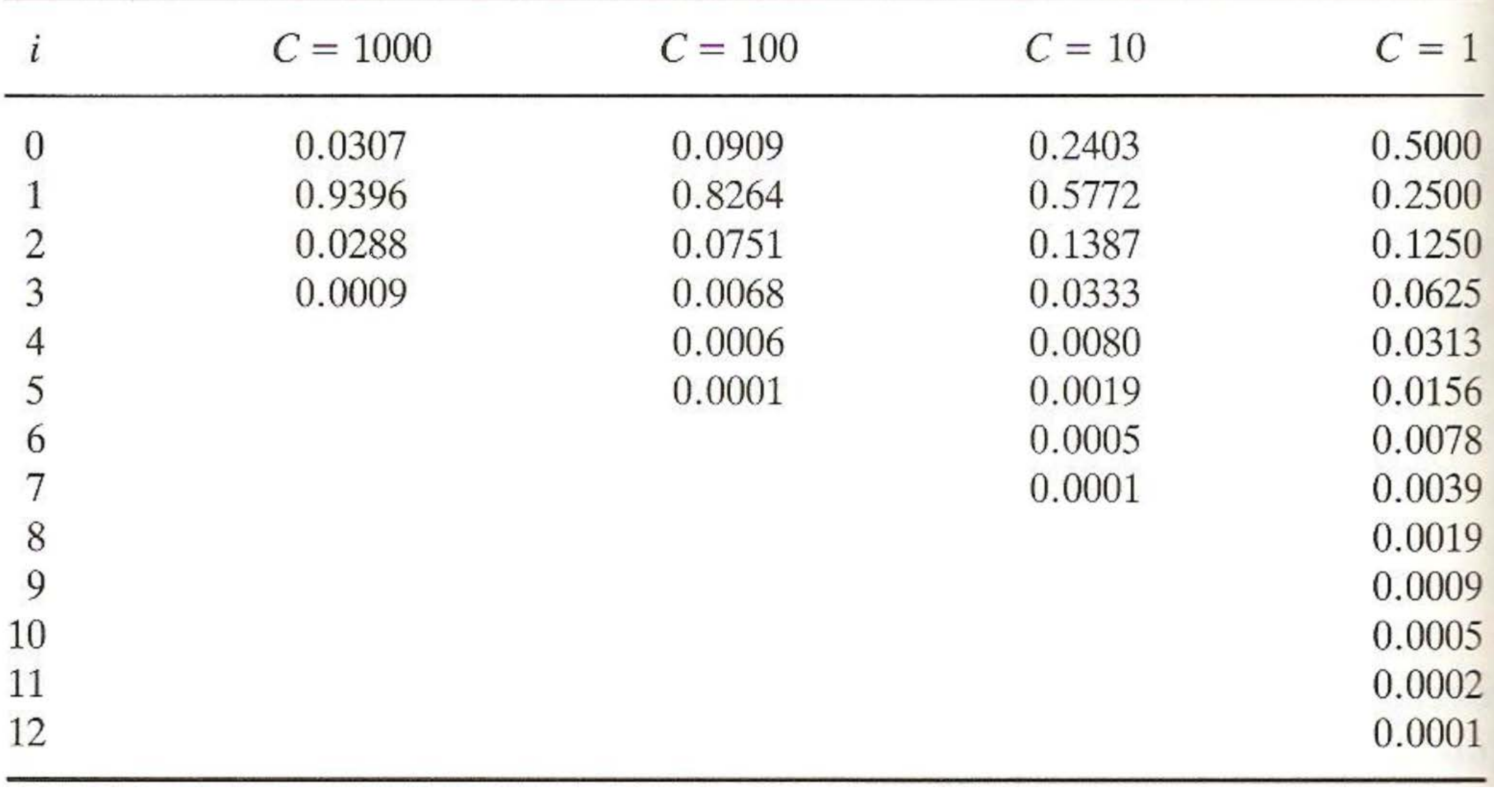
= 1.1 layer

4.5 The BET constant and site occupancy

Lowell has shown $(\theta_i)_m = c\left(\frac{c^{\frac{1}{2}}-1}{c-1}\right)^{i+1}$

$(\theta_i)_m$: the fraction of surface covered by layer i molecules deep at $W=W_m$

Table 4.1 Value for $(\theta_i)_m$ from equations (4.44)and(4.45)



i	$C = 1000$	$C = 100$	$C = 10$	$C = 1$
0	0.0307	0.0909	0.2403	0.5000
1	0.9396	0.8264	0.5772	0.2500
2	0.0288	0.0751	0.1387	0.1250
3	0.0009	0.0068	0.0333	0.0625
4		0.0006	0.0080	0.0313
5		0.0001	0.0019	0.0156
6			0.0005	0.0078
7			0.0001	0.0039
8				0.0019
9				0.0009
10				0.0005
11				0.0002
12				0.0001

4.6. Applicability of the BET theory

Ability of BET theory

a. For n=1 gives Type I isotherms (Langmuir)

b. For n=∞ (classical BET eq.) **c > 2 gives Type II isotherms**

c < 2 gives Type III isotherms

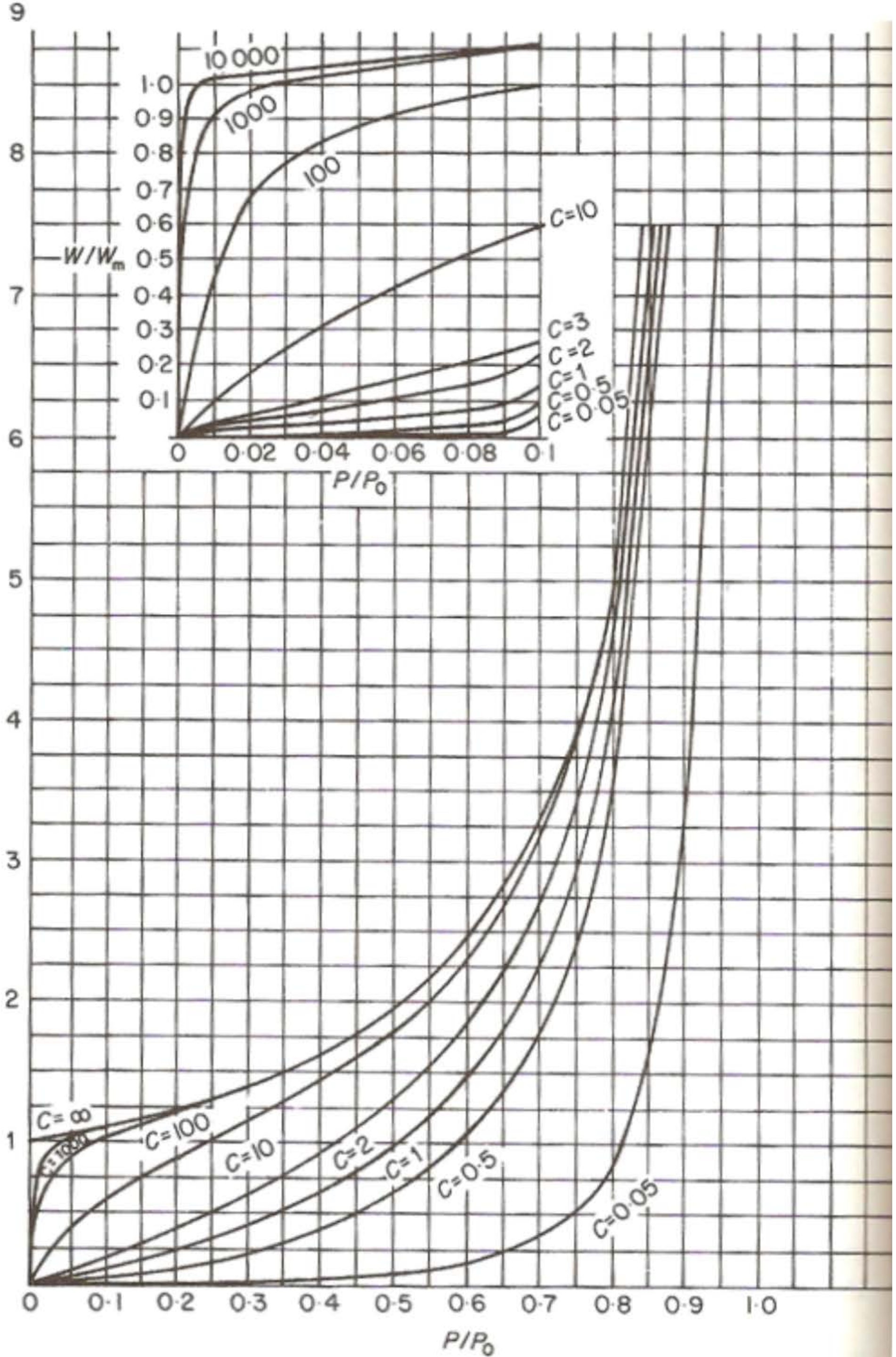
c. Types IV and V are modifications of Type II and III isotherms due to the presence of pores.

BET theory cannot exactly match an experimental isotherm over its entire range of pressures. In the region near completed monolayer ($W = W_m$, i.e. $0.05 \le P/P_0 \le 0.35$), the BET and experimental isotherms do agree well.

c value≡[3 , 1000] (the great majority of isoterms)
reflects P/P_0≡[0.05 , 0.35] for $W = W_m$

For Type III ($c \le 2$), applicability of BET theory is in question.

Changing the adsorbate to one with a higher c value may be the solution.



<u>Fig. 4.2</u> Isotherm shapes as a function of BET C values.

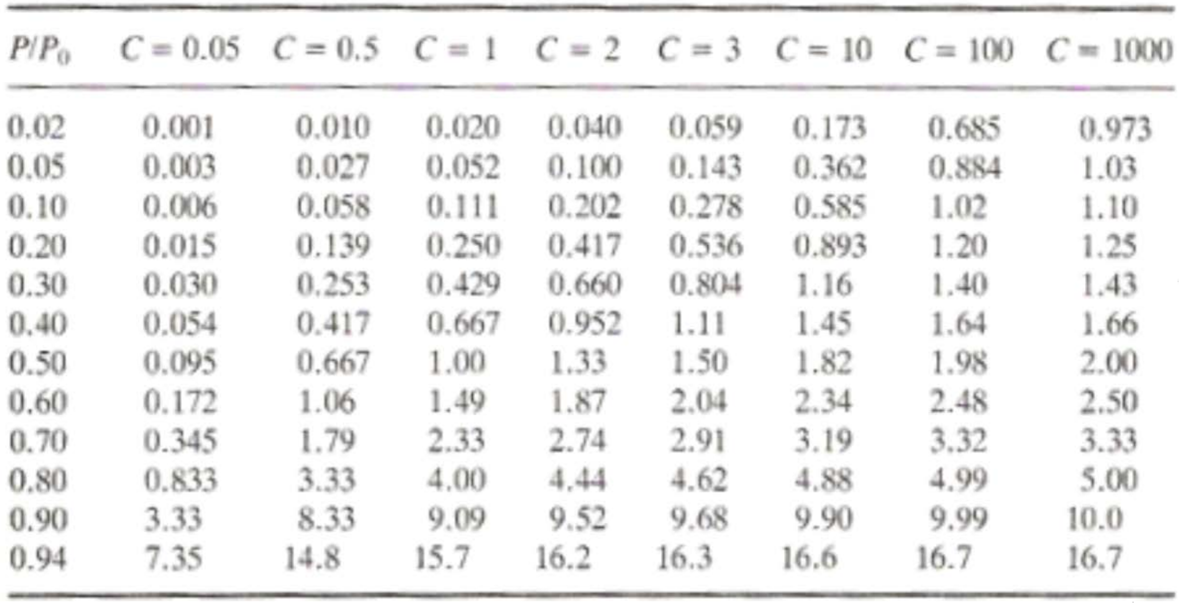
4.7 Some criticism of the BET theory

a. Surface is not energetically homogeneous. High energy sites are occupied at low pressures.

b. Lateral interaction between adsorbates is important at high coverage because of the increase in overlapping potential.

However, the above two effects counteract each other in the region of P/P_0 [0.05 , 0.35], and the constant c assumption in BET is generally valid.

Table 4.2 Value of W/W_m and relative pressures for various value of C



P/P_0	$C = 0.05$	$C = 0.5$	$C = 1$	$C = 2$	$C = 3$	$C = 10$	$C = 100$	$C = 1000$
0.02	0.001	0.010	0.020	0.040	0.059	0.173	0.685	0.973
0.05	0.003	0.027	0.052	0.100	0.143	0.362	0.884	1.03
0.10	0.006	0.058	0.111	0.202	0.278	0.585	1.02	1.10
0.20	0.015	0.139	0.250	0.417	0.536	0.893	1.20	1.25
0.30	0.030	0.253	0.429	0.660	0.804	1.16	1.40	1.43
0.40	0.054	0.417	0.667	0.952	1.11	1.45	1.64	1.66
0.50	0.095	0.667	1.00	1.33	1.50	1.82	1.98	2.00
0.60	0.172	1.06	1.49	1.87	2.04	2.34	2.48	2.50
0.70	0.345	1.79	2.33	2.74	2.91	3.19	3.32	3.33
0.80	0.833	3.33	4.00	4.44	4.62	4.88	4.99	5.00
0.90	3.33	8.33	9.09	9.52	9.68	9.90	9.99	10.0
0.94	7.35	14.8	15.7	16.2	16.3	16.6	16.7	16.7

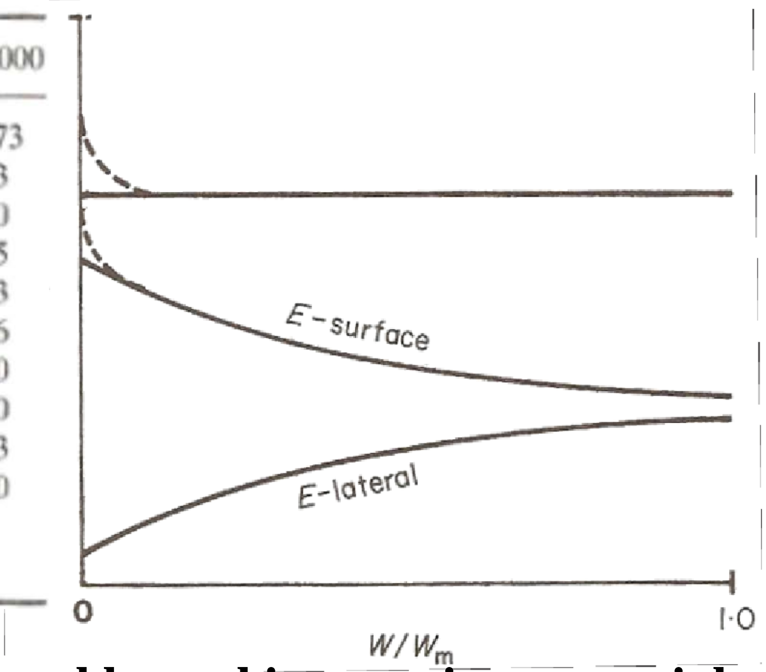
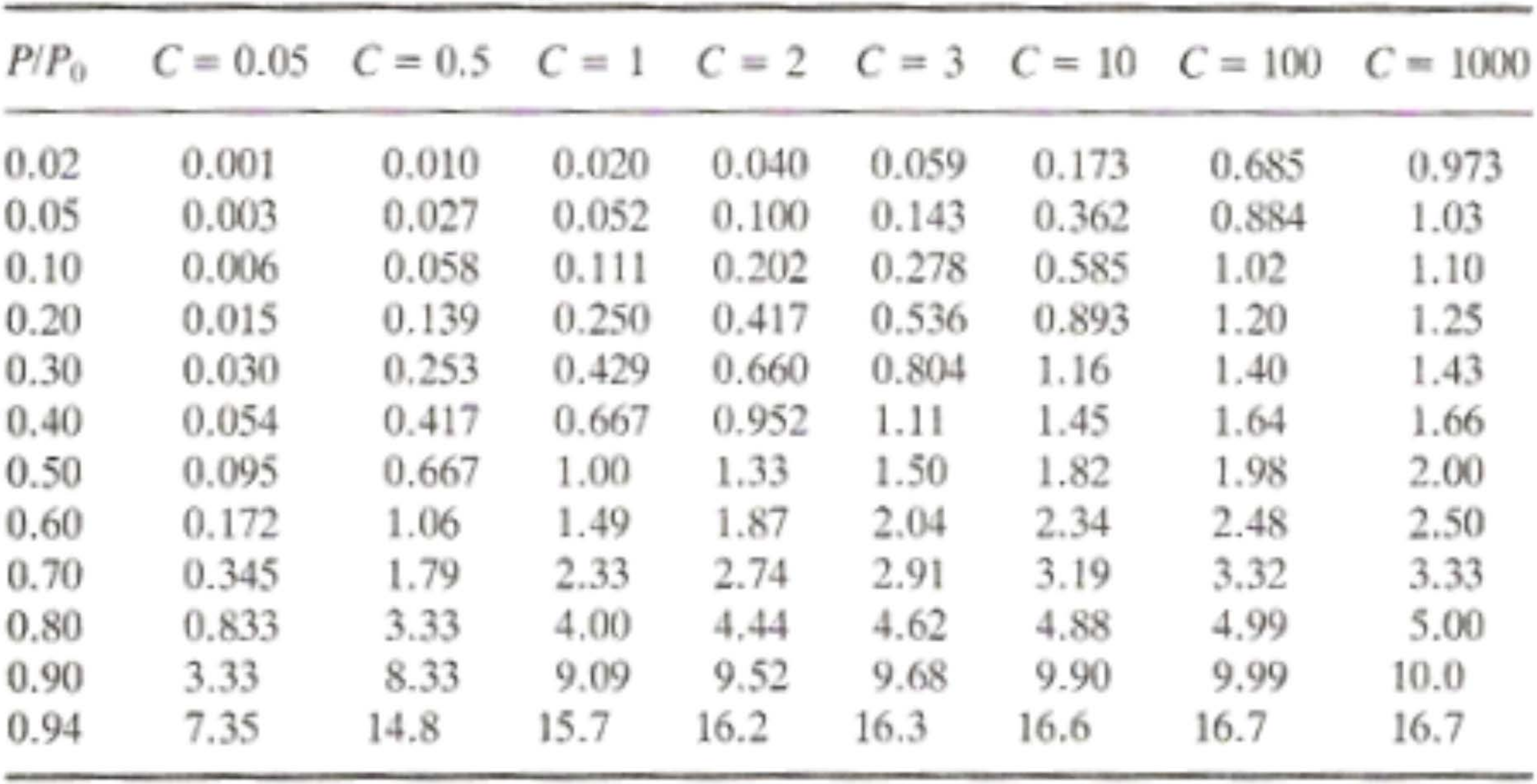


Fig. 4.3 Variation in adsorption and lateral interaction potential

Table 4.2 Value of W/W_m and relative pressures for various value of C



P/P_0	$C = 0.05$	$C = 0.5$	$C = 1$	$C = 2$	$C = 3$	$C = 10$	$C = 100$	$C = 1000$
0.02	0.001	0.010	0.020	0.040	0.059	0.173	0.685	0.973
0.05	0.003	0.027	0.052	0.100	0.143	0.362	0.884	1.03
0.10	0.006	0.058	0.111	0.202	0.278	0.585	1.02	1.10
0.20	0.015	0.139	0.250	0.417	0.536	0.893	1.20	1.25
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0.40	0.054	0.417	0.667	0.952	1.11	1.45	1.64	1.66
0.50	0.095	0.667	1.00	1.33	1.50	1.82	1.98	2.00
0.60	0.172	1.06	1.49	1.87	2.04	2.34	2.48	2.50
0.70	0.345	1.79	2.33	2.74	2.91	3.19	3.32	3.33
0.80	0.833	3.33	4.00	4.44	4.62	4.88	4.99	5.00
0.90	3.33	8.33	9.09	9.52	9.68	9.90	9.99	10.0
0.94	7.35	14.8	15.7	16.2	16.3	16.6	16.7	16.7

Above 0.35(P/P_0), extensive multilayer adsorption would provide complexity that cannot be resolved by a constant C. (BET would fail)

For microporous materials, linear BET plots are found at even lower P/P_0 (micropores exhibit high adsorption potentials due to the overlapping potential from the pore walls).

5. The single point BET method (simple and speedy)

5.1 Derivation of the single point method

BET equation: $\frac{1}{W[(P_0/P)-1]} = \frac{1}{W_m c} + \frac{c-1}{W_m c}\left(\frac{P}{P_0}\right)$ $\qquad \frac{S}{i} = c-1$

If c value is large, i is negligible, then

$$\frac{1}{W[(P_0/P)-1]} = \frac{c-1}{W_m c}\left(\frac{P}{P_0}\right) = \left(\frac{1}{W_m} - \frac{1}{W_m c}\right)\left(\frac{P}{P_0}\right) \Rightarrow W_m = W\left(1 - P/P_0\right)$$

$S_t = W\left(1 - P/P_0\right)\frac{\bar{N}}{\bar{M}} \cdot A$, **W: the amount of adsorption at P/P$_0$**

5.2 Comparison of the single point and multipoint methods

$$(W_m)_{mp} = W\left(\frac{P_0}{p} - 1\right)\left[\frac{1}{c} + \frac{c-1}{c}\left(\frac{P}{P_0}\right)\right] \qquad (W_m)_{sp} = W\left(1 - \frac{P}{P_0}\right)$$

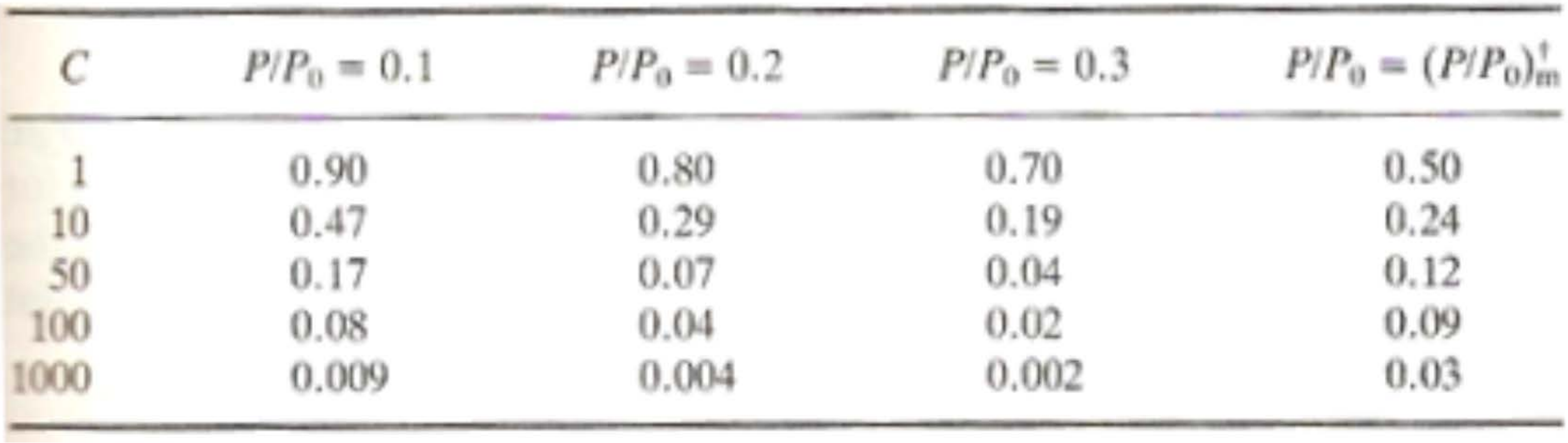
The relative error from the single point method

$$=\frac{(W_m)_{mp}-(W_m)_{sp}}{(W_m)_{mp}}=\frac{1-\frac{P}{P_0}}{1+(c-1)\frac{P}{P_0}}$$

Table 5.1 shows that relative error decreases as c↑and P/P_0↑

In most cases, $P/P_0 = 0.3$ is suitable for single point BET.
A smaller P/P_0 should be.used for porous materials.
$P/P_0 > 0.3$ is not applicable for BET.

Table 5.1 Relative error using the single point method at various relative pressures.



C	$P/P_0 = 0.1$	$P/P_0 = 0.2$	$P/P_0 = 0.3$	$P/P_0 = (P/P_0)^{\dagger}_{m}$
1	0.90	0.80	0.70	0.50
10	0.47	0.29	0.19	0.24
50	0.17	0.07	0.04	0.12
100	0.08	0.04	0.02	0.09
1000	0.009	0.004	0.002	0.03

6. Adsorbate cross-sectional areas

A= adsorbate cross-sectional area, in Å²

$$S_t = \frac{W_m \bar{N} A}{\bar{M}} \times 10^{-20} \ \ m^2$$

6.1 Cross-sectional areas from the liquid molar volume

Assume adsorbate on surface in close-packed hexagonal arrangement of spheres.

Fig. 6.1 Sectional view of a close-packed hexagonal arrangement of spheres.

$$\Rightarrow A = 1.091\left(\frac{\bar{V}}{\bar{N}}\right)^{\frac{2}{3}} \times 10^{16}\left[A^{\circ 2}\right] \quad \text{.................(1)}$$

Factors limit the applicability of the above eq.

1. **Lateral motion will be highly disruptive.**
2. **Complex molecules exhibit different cross-section areas.**
3. **Orientation of polar molecules depends on the polarity of the Adsorbents.**
4. **Strong interactions with surface lead to localized adsorption.**
5. **Fine pores may not be accessible to adsorbate**

6.2 Nitrogen as the standard adsorbate

Requirements for appropriate adsorbates

a. **Should exhibit BET c value sufficiently low to preclude localized adsorption.**

b. **BET c value should not be too small, otherwise lateral motion will disrupt the tendency toward organized structure.**

N_2 is a suitable adsorbate for almost all surfaces.
(with c ranging within 50-300)

Other species as the adsorbate, e.g. n-pentane adsorption on different solids (with known surface areas).

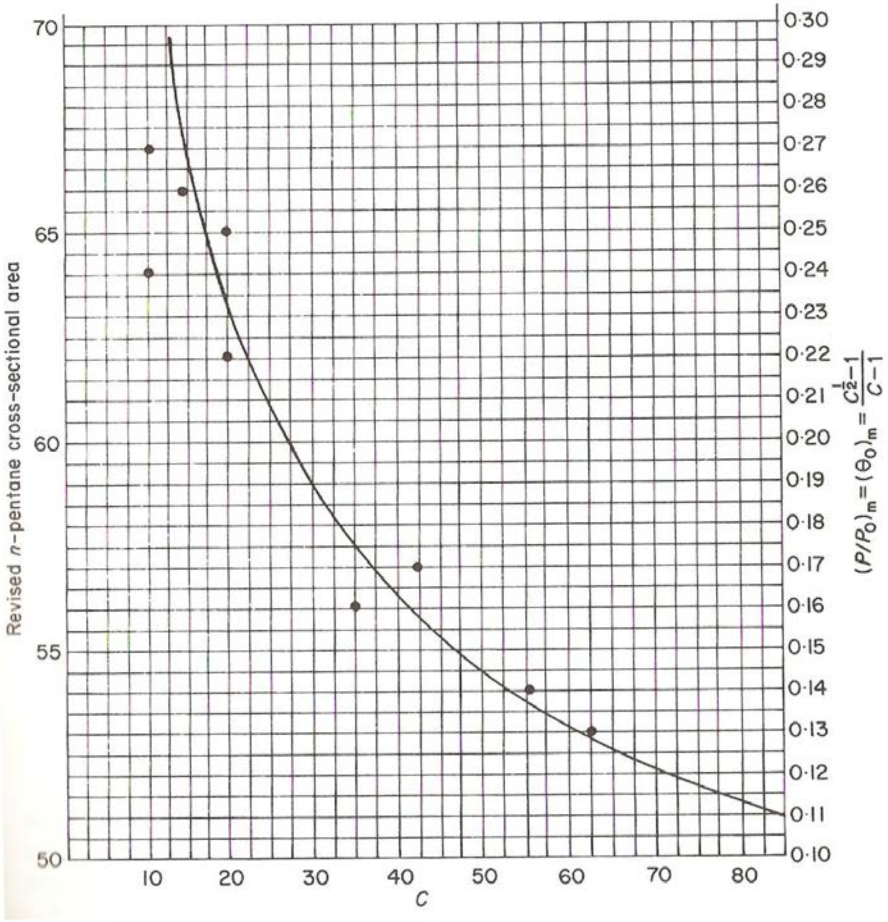
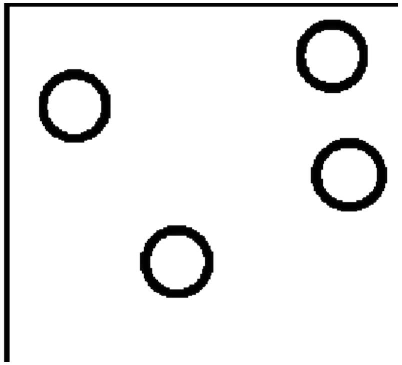


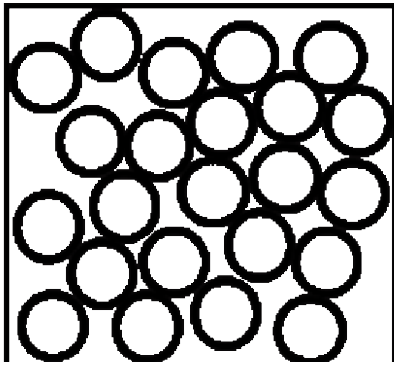
Fig. 6.2 Variation of n-pentane cross-section area with BET C constant (point) and $(\theta_0)_m$ (solid line)

The figure shows that the "effective area" or "occupied area" of a molecule decreased with increasing c.

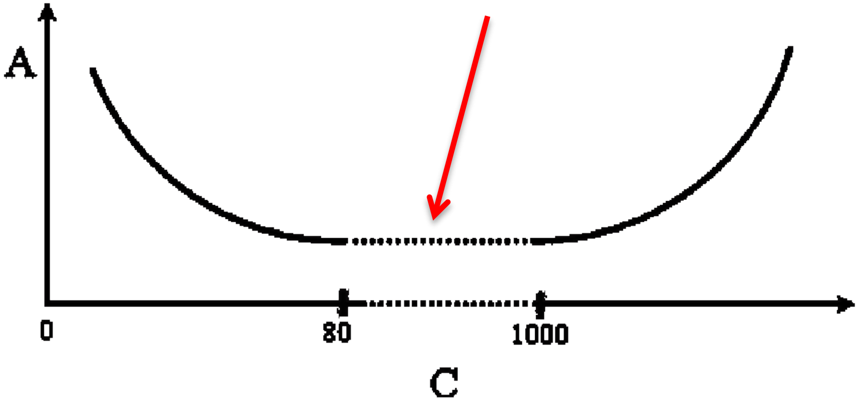
Because of the small c value, n-pentane behaves like a 2-D gas (tightly packed structure cannot be formed).



C small



C large

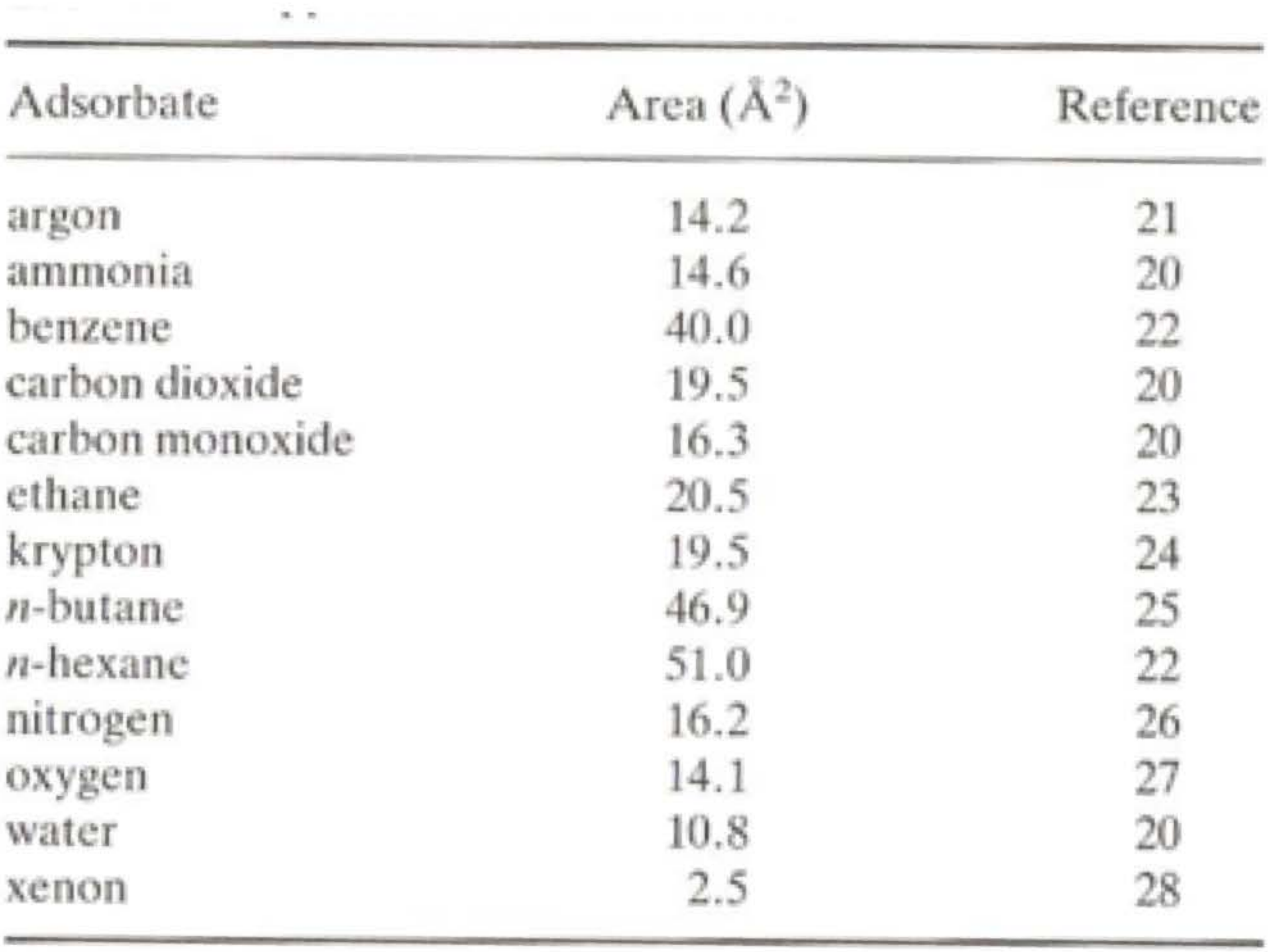


Constant c value

If C was further increased, A increases with increasing c value. The reason is that site-specific adsorption is not easy for hexagonal arrangement.

6.3 Some Adsorbate Cross-Sectional Area

Table 6.1 Approximate cross-sectional areas



Adsorbate	Area (Å^2)	Reference
argon	14.2	21
ammonia	14.6	20
benzene	40.0	22
carbon dioxide	19.5	20
carbon monoxide	16.3	20
ethane	20.5	23
krypton	19.5	24
n-butane	46.9	25
n-hexane	51.0	22
nitrogen	16.2	26
oxygen	14.1	27
water	10.8	20
xenon	2.5	28