奈米量測技術 (I)_部分

連興隆

內容

- BET Analyzer
- Particle size distribution analyzer
- SEM
- TEM
- XRD
- XPS

Zeta potential →Chemisorption
Ion-pair formation (outer-sphere model)
Ligand exchange reaction (inner-sphere model)

Types of Adsorption

- Physical Adsorption
  - result of intermolecular forces causing preferential binding of certain substances to certain adsorbents
  - reversible by addition of heat (via steam, hot inert gas, oven)
  - Attachment to the outer layer of adsorbent material
- Chemisorption
  - result of chemical interaction
  - large amount heat released
  - irreversible
  - mainly found in catalysis

Physisoption and Chemisoption

PHYSISORPTION	CHEMISORPTION
WEAK, LONG RANGE BONDING Van der Waals interactions (e.g. London dispersion, dipole-dipole)..	STRONG, SHORT RANGE BONDING Chemical bonding involving orbital overlap and charge transfer.
NOT SURFACE SPECIFIC Physisorption takes place between all molecules on any surface providing the temperature is low enough.	SURFACE SPECIFIC E.g. Chemisorption of hydrogen takes place on transition metals but not on gold or mercury.
$-\Delta H_{ads}$ = 5 ….. 35 kJ mol^{-1}	**$-\Delta H_{ads}$ = 35 ….. 500 kJ mol^{-1}**
Non activated with equilibrium achieved relatively quickly. Increasing temperature always reduces surface coverage.	Can be activated, in which case equilibrium can be slow and increasing temperature can favour adsorption.
No surface reactions.	Surface reactions may take place:- Dissociation, reconstruction, catalysis.
MULTILAYER ADSORPTION	MONOLAYER ADSORPTION
BET Isotherm used to model adsorption equilibrium.	Langmuir Isotherm used to model adsorption equilibrium..

BET Isotherm

$$\frac{1}{V\left[(P_o/P)-1\right]} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left(\frac{P}{P_o}\right)$$

where:

V = volume of gas adsorbed at pressure P

V_m = volume of gas required to form monolayer

C = B.E.T. constant

P/P_o = *relative* pressure of adsorbate

equation shown in form Y=aX+b, plot Y *v* X

V= the amount adsorbed at pressure P (mg/g)

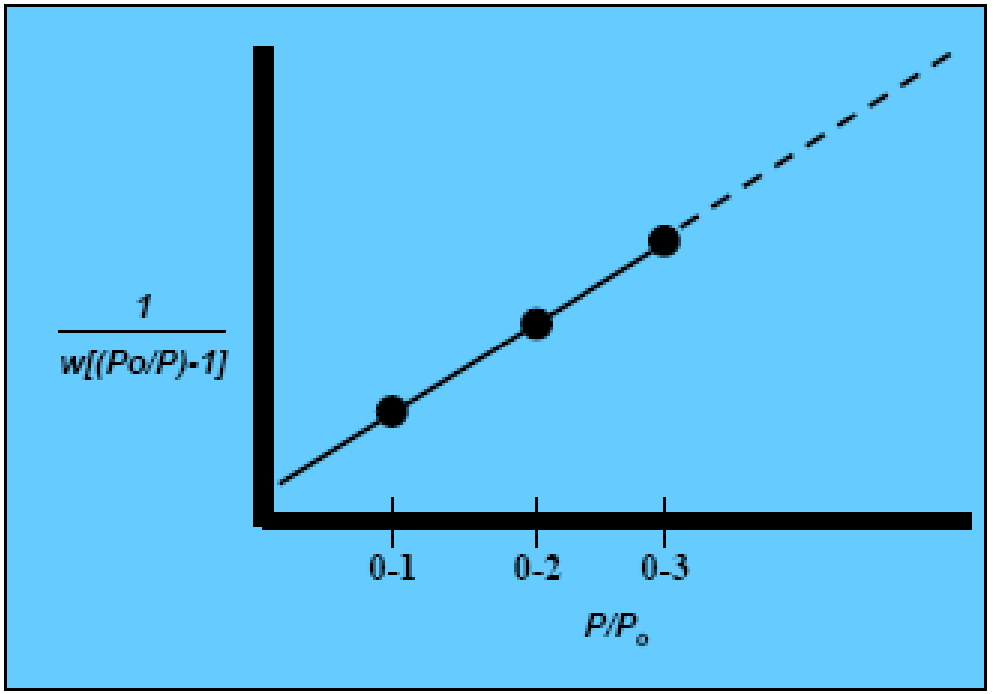
BET 比表面積的計算

$$\text{slope (s)} = \frac{C-1}{V_m C}$$

$$\text{intercept (i)} = \frac{1}{V_m C}$$

$$V_m = \frac{1}{s + i}$$

$$S_{total} = \frac{V_m N}{22{,}414} A_{xs}$$



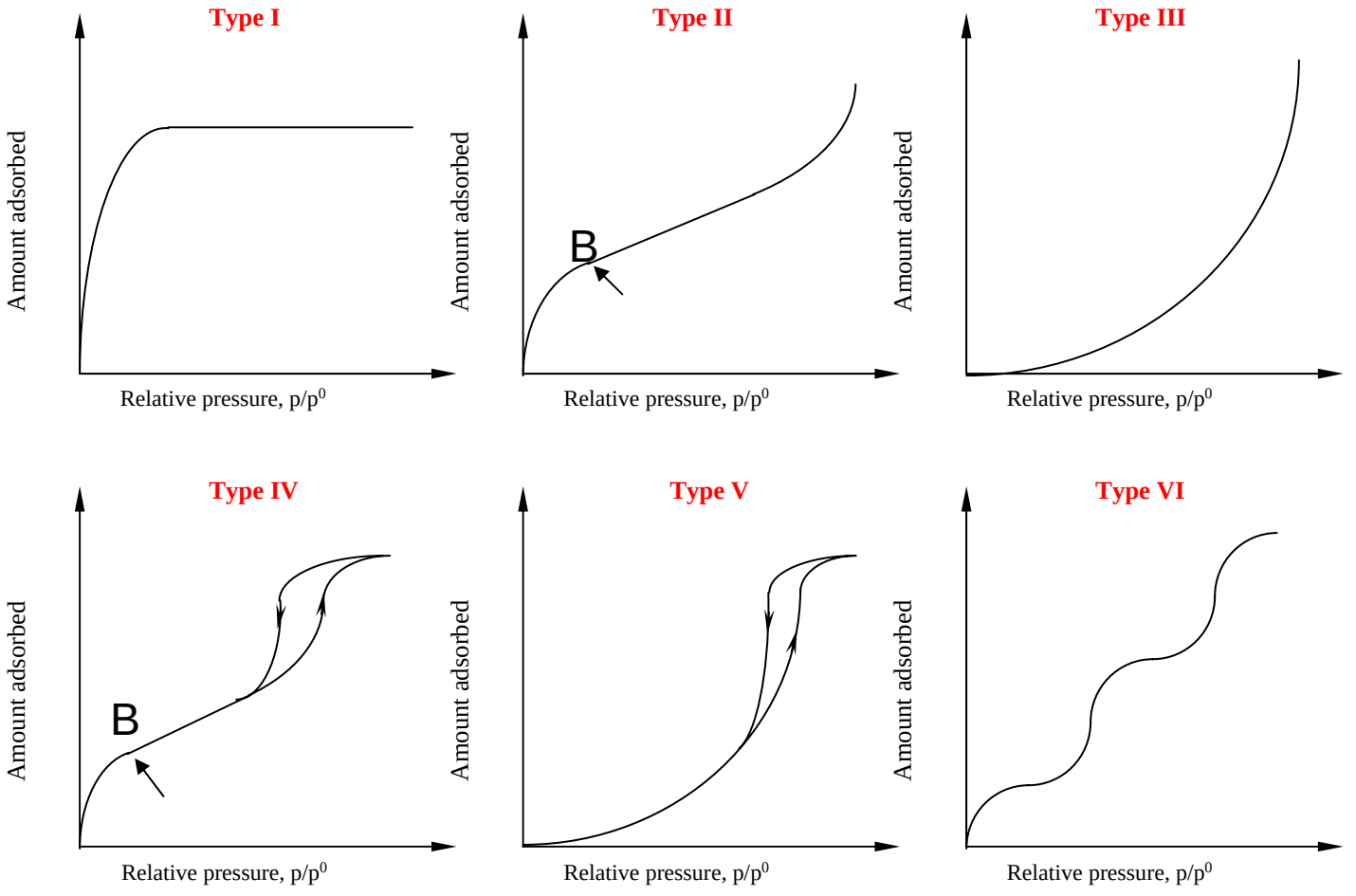
Where, N = Avogadro's number

A_{xs}= cross-sectional area of adsorbate molecule

A_{xs} = N_2的 分子截面積 0.162 nm^2

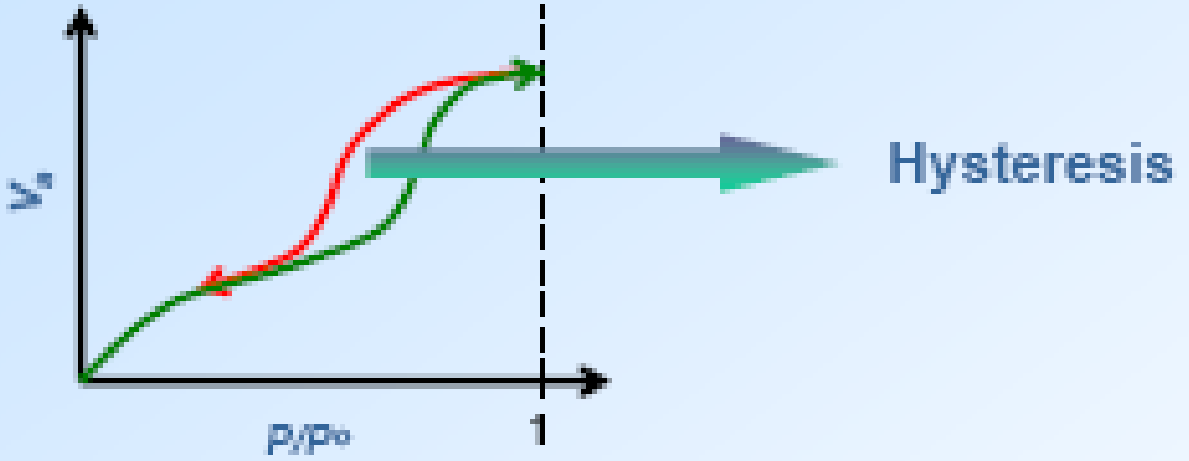
N = 6.02×10^{23}

IUPAC classification of gas adsorption isotherms

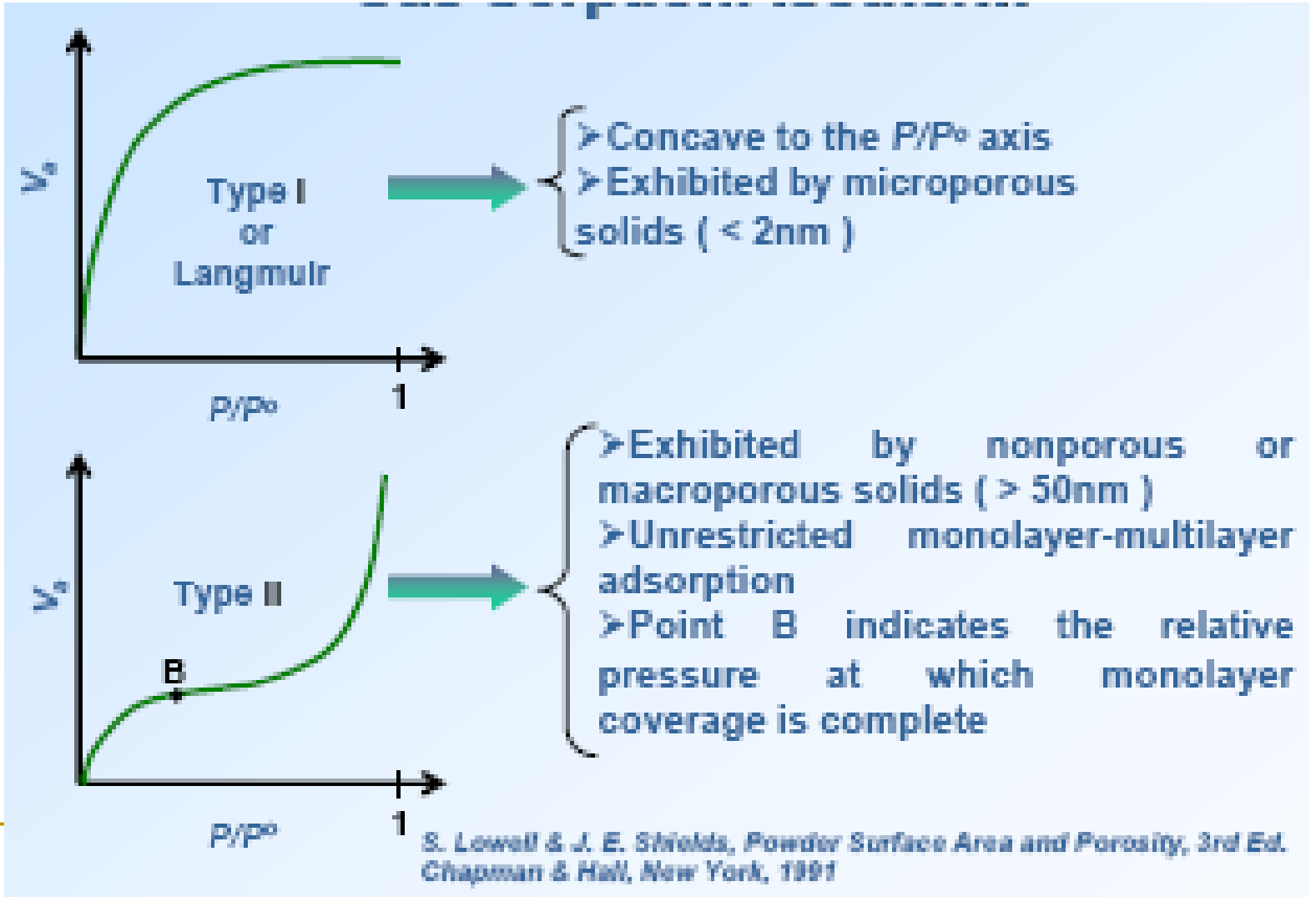


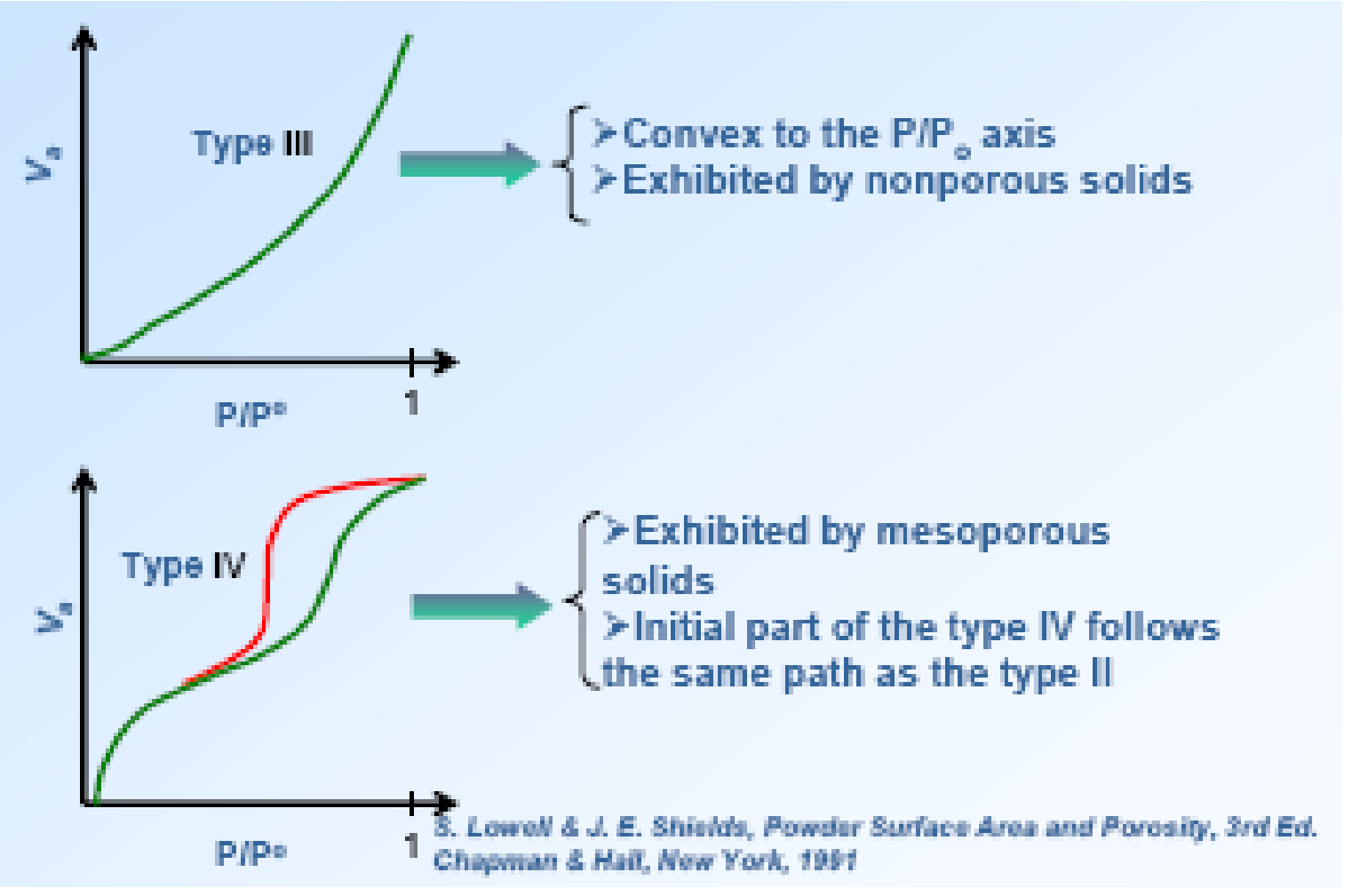
Pore size regions

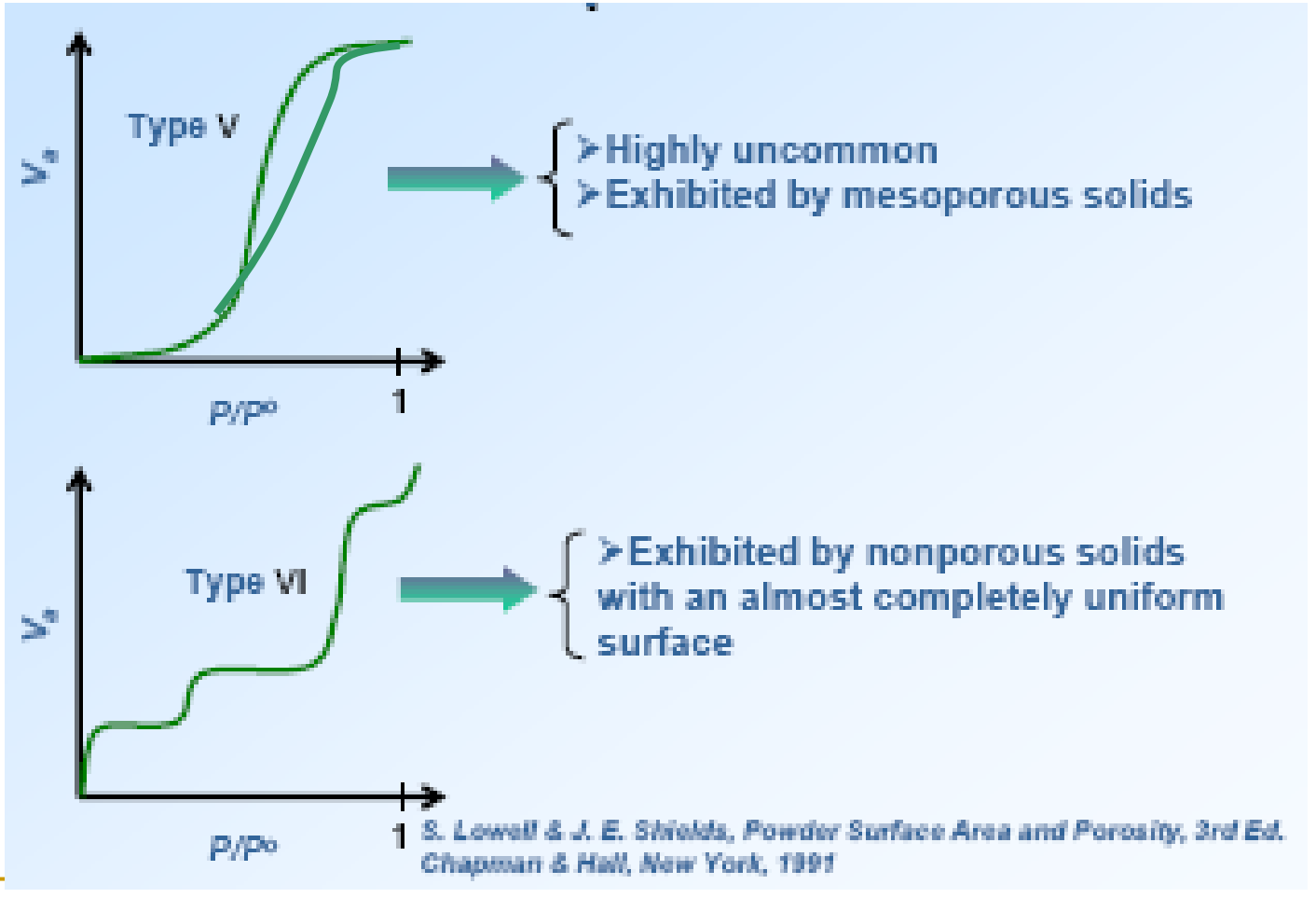
- Micropores: < 2 nm
- Mesopores: 2- 50 nm
- Macropores: > 50 nm



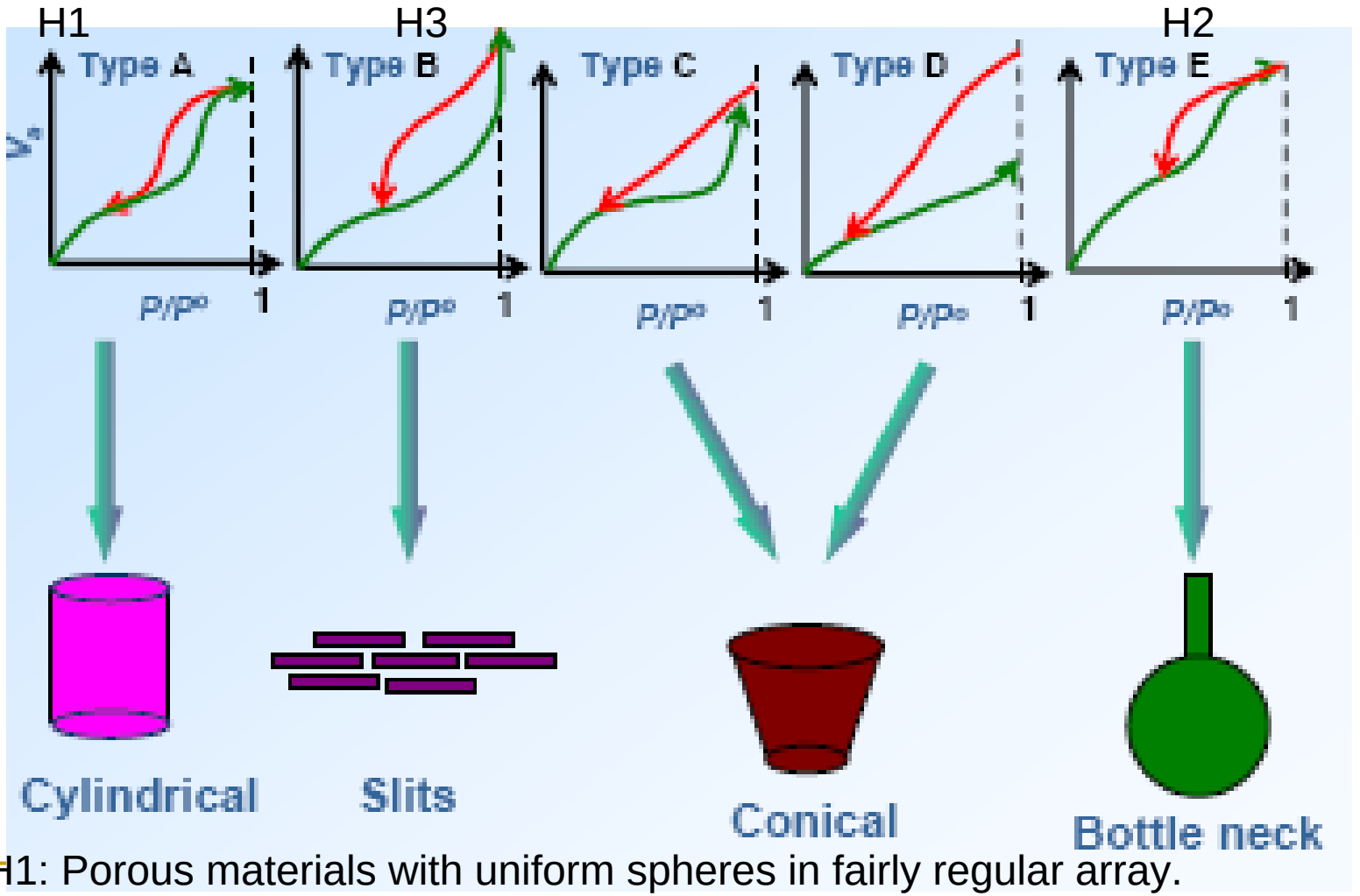
- Hysteresis indicates the presence of mesopores.
- Hysteresis gives information regarding pore shapes .
- Types I, II and III isotherms are generally reversible but type I can have a hysteresis. Types IV and V exhibit hysteresis.


Vₐ
Type I
or
Langmuir
P/P°
1
➢Concave to the P/P° axis
➢Exhibited by microporous solids (< 2nm)
Vₐ
Type II
B
P/P°
1
➢Exhibited by nonporous or macroporous solids (> 50nm)
➢Unrestricted monolayer-multilayer adsorption
➢Point B indicates the relative pressure at which monolayer coverage is complete
S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991


Type III
V_a
P/P°
1
➢Convex to the P/P$_o$ axis
➢Exhibited by nonporous solids
Type IV
V_a
P/P°
1
➢Exhibited by mesoporous solids
➢Initial part of the type IV follows the same path as the type II
S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991


Type V
V_a
P/P°
1
➢Highly uncommon
➢Exhibited by mesoporous solids
Type VI
V_a
P/P°
1
➢Exhibited by nonporous solids with an almost completely uniform surface
S. Lowell & J. E. Shields, Powder Surface Area and Porosity, 3rd Ed. Chapman & Hall, New York, 1991

吸脫附曲線的特徵與意涵



H1: Porous materials with uniform spheres in fairly regular array.
H2 Porous materials, inorganic oxide gels, porous glasses

Pore size calculation

Kelvin equation

$$\ln \frac{P}{P_0} = \frac{2\gamma V}{rRT} \cos\theta$$

r (Å) = 4.14 log P_0/P

$\bar{V}$ = liquid molar volume

θ (wetting) = 0

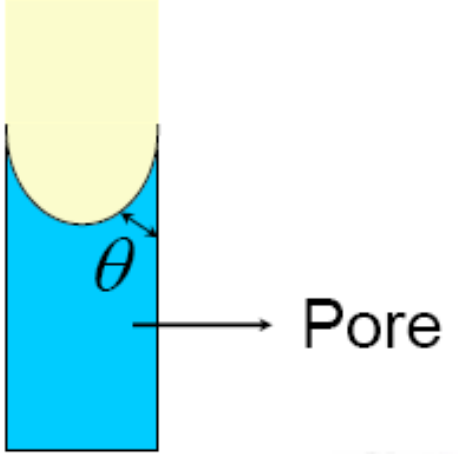
r = pore radius (Kelvin radius)

P = equilibrium pressure

P_0 = saturated equilibrium pressure

γ = surface tension liquid nitrogen

R = universal gas constant



γ = 液態氮的表面張力 8.855 mN/m

T =液態氮的沸點 77.3 K

V =液態氮的莫爾體積 34.6 cm^3 /mol

Why not 22.4 L?

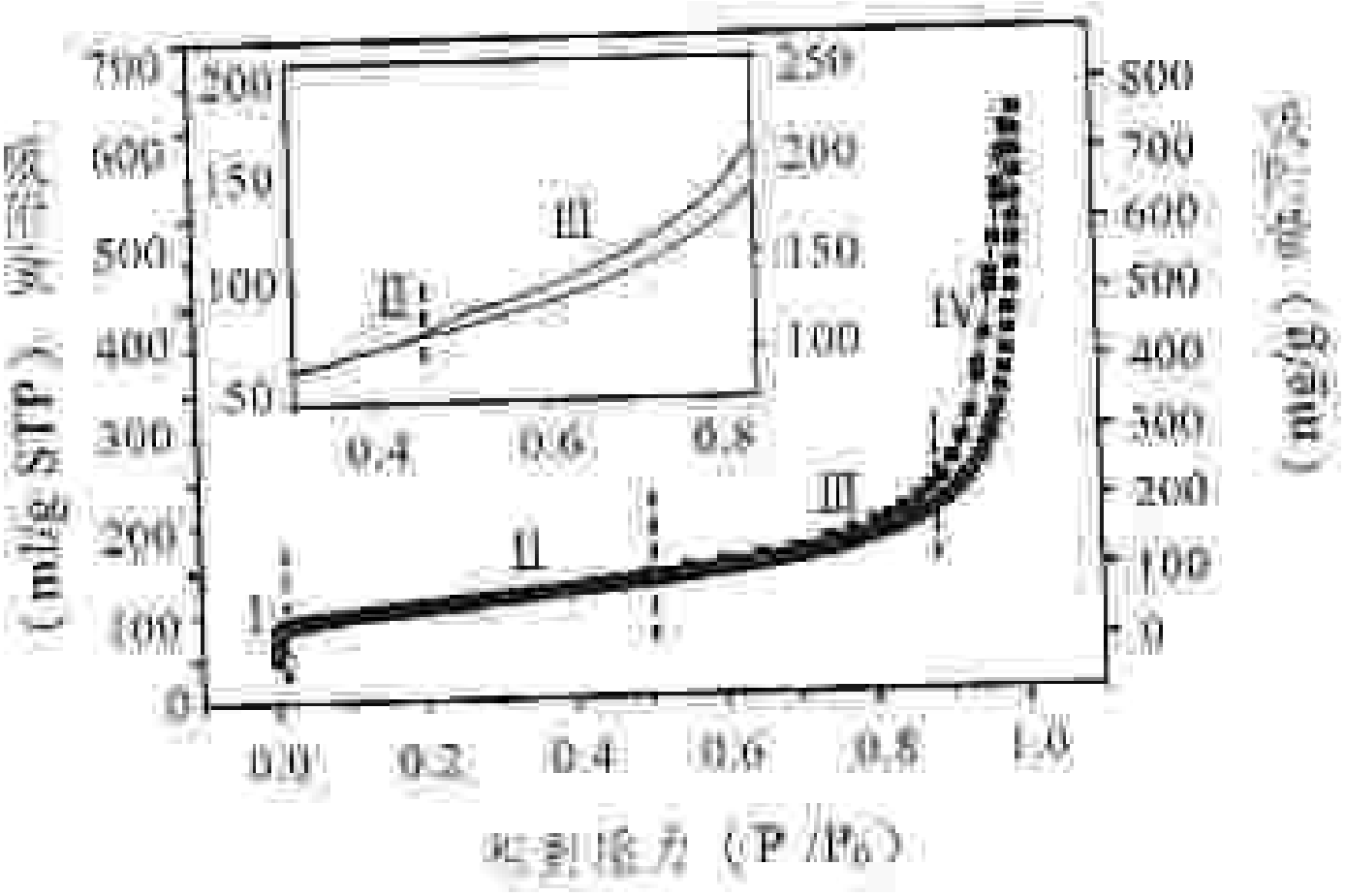
問題

- 有一材料為Type I 的等溫吸附行為, 請問可否利用BET分析其比表面積?
- BET分析比表面積適用之吸脫附型態為何者?
- Kelvin equation僅適用於哪一型的等溫吸脫附曲線?

回家作業一

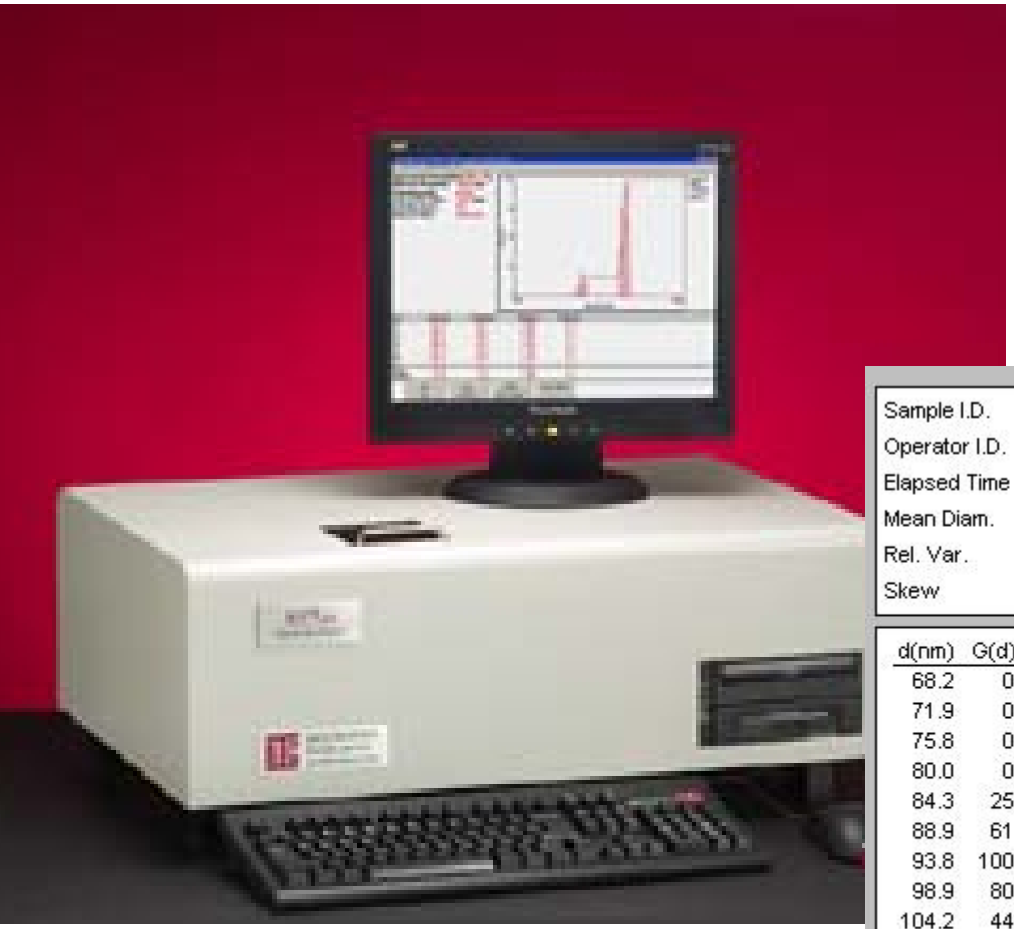
一奈米碳管的吸脫附曲線,請說明:

1. 屬哪一類型的吸脫附曲線
2. 判斷奈米碳管的孔隙組成
3. 計算BET比表面積值
4. 計算在P/P_o為 0.2, 0.5, 0.8 與0.9 時之孔隙半徑

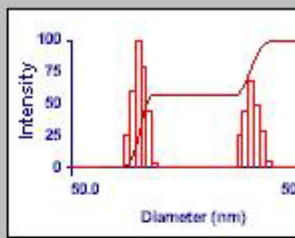


90Plus
Particle Size Analyzer

Range <1 nm to 6 µm



Sample I.D.	Mixed Nom 98/270 (Combined)
Operator I.D.	Peter Debye
Elapsed Time	00:30:00
Mean Diam.	168.6 nm
Rel. Var.	0.275
Skew	0.394



d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)	d(nm)	G(d)	C(d)
68.2	0	0	122.2	0	59	218.9	0	59
71.9	0	0	128.9	0	59	230.9	0	59
75.8	0	0	135.9	0	59	243.4	26	63
80.0	0	0	143.3	0	59	256.7	44	72
84.3	25	5	151.1	0	59	270.6	69	85
88.9	61	16	159.3	0	59	285.4	49	94
93.8	100	35	168.0	0	59	300.9	28	99
98.9	80	50	177.1	0	59	317.3	4	100
104.2	44	58	186.7	0	59	334.6	0	100
109.9	2	59	196.9	0	59	352.8	0	100
115.9	0	59	207.6	0	59	372.0	0	100

Theory: Particle Size Analyzer

光—diffraction; random movement

Brownian motion

$$P(r,t|0,0)=(4\pi Dt)^{-3/2}\ \exp\left(-r^2/4Dt\right)$$

Viscosity of air :1.78E-5 kg/ms at 15 oC
Water E-3 kg/ms at 20 oC

Stoke-Einstein relation

$$D=k_B T/6\pi\eta a$$

where a is the radius of the particles, k_B is the Boltzmann constant, T is the temperature in Kelvin degrees (in this experiment it will be considered as if it is taking place at room temperature) and η is the viscosity of the solvent.

回家作業二

- 請計算下列分子的大小 (T = 298K)
- Benzene: D (cm^2/s) 1.02 x 10^{-5} in water
- Benzene: D (cm^2/s) 0.096 in air
- Oxygen: D (cm^2/s) 2.6 x 10^{-5} in water
- Oxygen: D (cm^2/s) 0.071 in air

- 顯微鏡其解析力之公式

α＝0.61λ／NA，α為解析力，λ為波長，NA為光口角，NA以油鏡最佳直約 1.4,

故光學顯微鏡解像力之極限以自然光時為0.25μ，(2500A°)

以單色4,000A°之光源時為0.17μ。

- 920年代de Broglie 氏首先發表之電子波動說，電磁波之特性與光波極為類似，但波長很短，電磁波波長之公式為

$\lambda = 12.2 / \sqrt{V}$，$\lambda$ 為波長A°，V為加速電壓，

- 當加速電壓為 50,000 V 時波長約為 0.535A°。