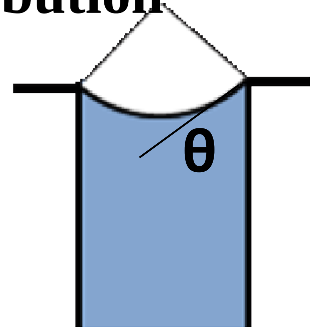
8. Pore analysis by adsorption

8.1. Kelvin equation

Adsorption data → pore size or pore size distribution



$$\ln\left(\frac{P}{P_0}\right) = -\frac{2}{r}\frac{\gamma\bar{V}}{RT}\cos\theta$$

$$\Rightarrow \ln\left(\frac{P}{P_0}\right) = -\frac{2}{r}\frac{\gamma\bar{V}}{RT} \quad if\ \theta = 0$$

r : pore radius

γ : surface tension

$\bar{V}$: molar volume of liquid

P : equilibrium P in pores with a radius r.

P_0 : equilibrium P_0 on planar surface.

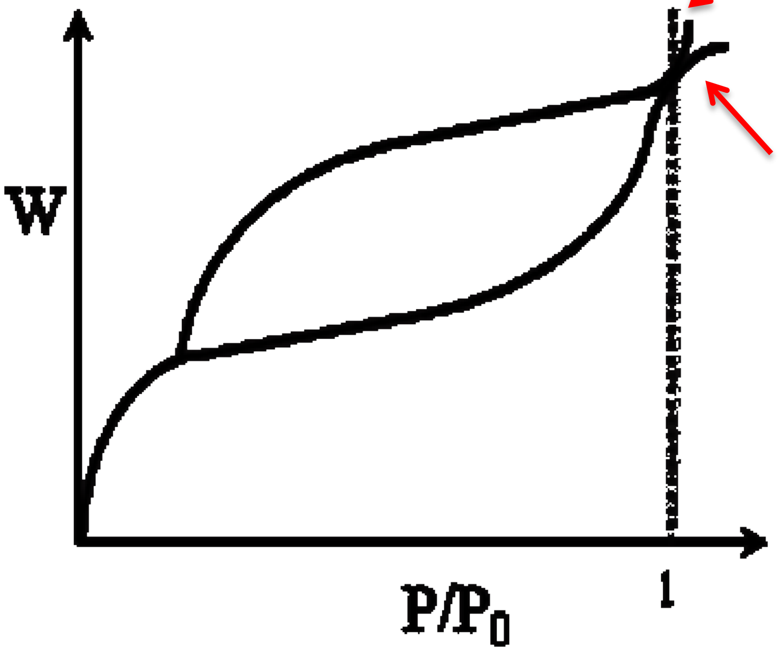
In a pore, the overlapping potential of the wall can overcome the translational energy of an adsorbate molecule. So that condensation will occur at a lower pressure. Thus, as the relative pressure is increased, condensation will occur first in pores of smaller radii and will progress into larger pores.

In five isotherms, Types I, IV, V are related to porosity.

Type I → microporosity

Type IV → r = 15-1000Å

Type V → rarely observed

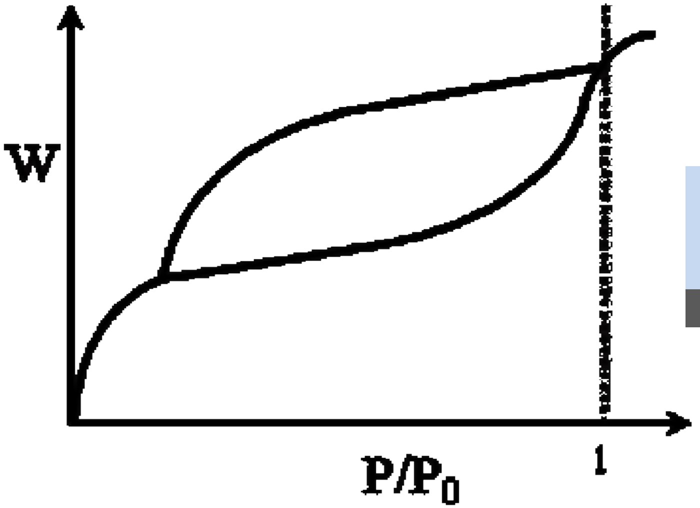


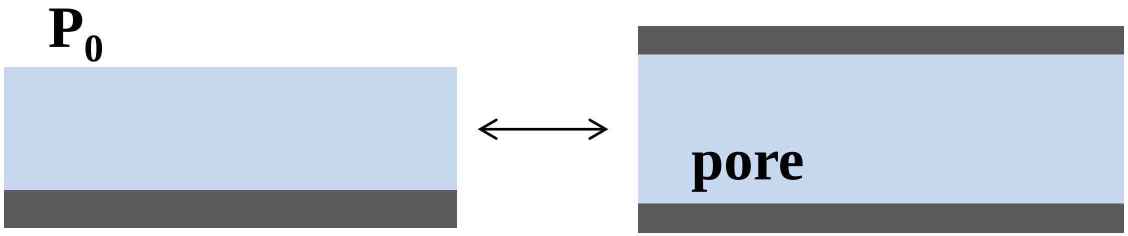
Complete wetting, θ=0˚, cosθ=1

Incomplete wetting, θ=20˚, cosθ=0.94

8.2. Adsorption hysteresis

Hysteresis:
two relative pressures corresponding to a given quantity:
$(P/P_0)_{ads} > (P/P_0)_{des}$





$$\Delta G_{ads} = RT\left(\ln P_{ads} - \ln P_0\right)$$

$$\Delta G_{des} = RT(\ln P_{des} - \ln P_0)$$

$$\because P_{des} < P_{ads} \quad \Rightarrow \quad \Delta G_{des} < \Delta G_{ads}$$

∴desorption value corresponds to the more stable condition

→desorption isotherm should be used for pore analysis.

Theories for hysteresis:

Zsigmondy : different contact angles during adsorption and desorption.

McBain : bottle neck

Cohan : adsorption on a cylindrical meniscus
desorption from a hemispherical meniscus.

8.3. Total Pore Volume

Gurvitsh rule:

At saturation ($P/P_0 \approx 1$) the liquid volume of different adsorbates, when measured on porous adsorbents, is essentially constant and is independent of adsorbate.

This constancy of adsorbed liquid at saturation provides direct evidence that the pores are filled.

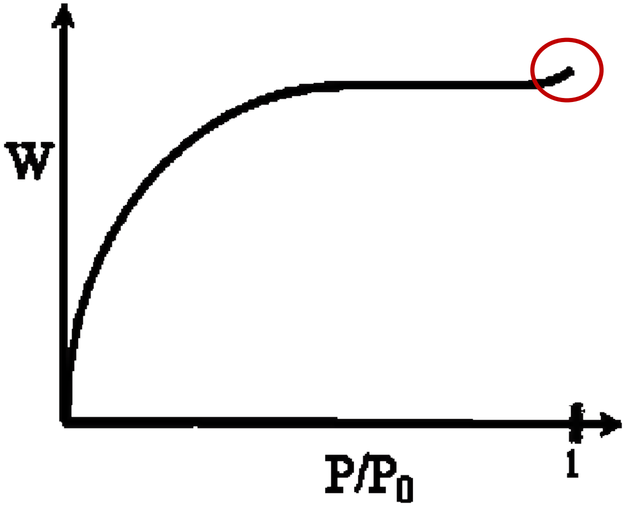
$\therefore$ at $P/P_0 \approx 1$

The amount of adsorption can be used to calculate total pore volume.

For example

At $P/P_0 = 0.99$ W_a gram of N_2 are adsorbed

$V_p = \dfrac{W_a}{\rho}$ **, ρ = liquid density**

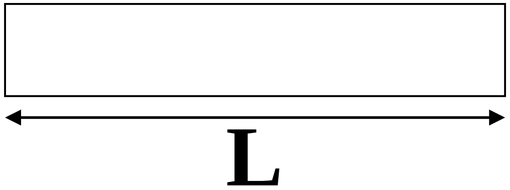


Based on Kelvin eq., the largest pore radii are given by

$$r_\kappa = \frac{-2\gamma\bar{V}}{RT\ln(\frac{P}{P_0})} = \frac{-2\left(8.85\frac{erg}{cm^2}\right)\left(34.6\frac{cm^2}{mol}\right)}{\left(8.314\times10^7\frac{erg}{K\cdot mol}\right)(77K)(\ln 0.99)} = 950\times10^{-8}\ cm = 950\ \text{Å}$$

$\therefore V_p$ represents the pore volume of all the pores up to 950Å.

An implicit assumption: no surface other than the inner walls of the pores exists.



$$V_p = \pi\bar{r}_p^2 \cdot L$$

$$S_{BET} = 2\pi\bar{r}_p \cdot L$$

Average pore size = $2\cdot\bar{r}_p$

$$\bar{r}_p = \frac{2V_p}{S_{BET}}$$

Porous materials: most of the surface area is contributed by the pore wall

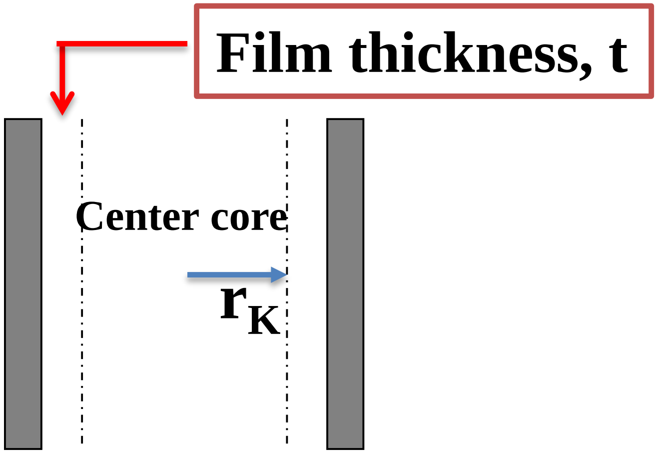
8.4. Pore Size Distribution (PSD)

PSD is usually measured using the desorption isotherm.

N_2 as the adsorbate

$$r_k = \frac{4.15}{\log\left(P_0/P\right)} \quad [\text{Å}]$$

r_k : Kevin radius or critical radius



Film thickness, t

Center core

r_K

Pore radius, $r_p = r_K + t$

It is difficult to estimate film thickness over the inner walls.

Assumptions for adsorption in pores.

1. **A planar surface**
2. **Adsorbate evenly distributed over surface.**

$$t = \left(\frac{W_a}{W_m}\right)\tau$$

W_a : weight adsorbed
W_m : weight for monolayer coverage.
τ : thickness of one layer

For liquid N_2

One mole of molecules spread on surface

$S = (16.2\ Å^2)(6.02 \cdot 10^{23}) = 97.5 \cdot 10^{23}\ Å^2/\text{gmol}$

$\bar{V} = 34.6 \cdot 10^{24}\ Å^3/\text{gmol}$

$$\tau = \frac{\bar{V}}{S} = 3.54\,Å \qquad t = \left(\frac{W_a}{W_m}\right) \cdot 3.54\,Å$$

On nonporous surface, it has been shown that when W_a/W_m is plotted vs. P/P_0, the data all approximately fit a common Type II curve as $P/P_0 > 0.3$ regardless of the adsorbent used.

This is an implication of even distribution of the adsorbate.

ie. When $W_a/W_m = 3 \Rightarrow t = (3 \times 3.54) = 10.62\ Å$

Halsey equation for N_2 adsorption on planar surface to predict t.

Halsey equation for N_2 adsorption on planar surface to predict t.

$$t = 3.54\left(\frac{5}{2.303\cdot\log\left(P_0/P\right)}\right)^{\frac{1}{3}}$$

Table 8.1 (Next page)

consider both the layering and condensation.

◆ **Similar to the BJH method (Barrett, Joyner and Halenda), only for mesopores**

Table 8.1

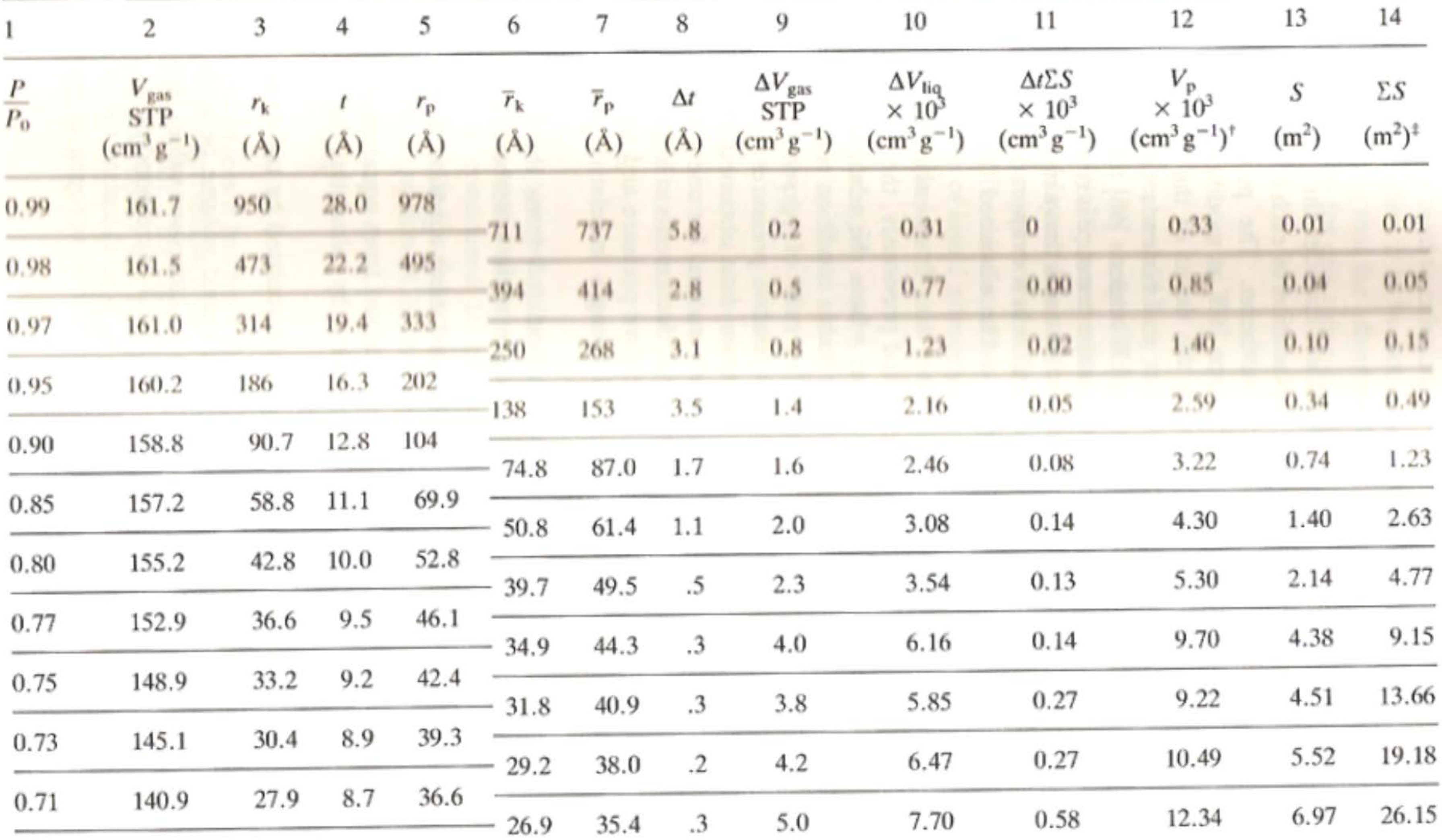
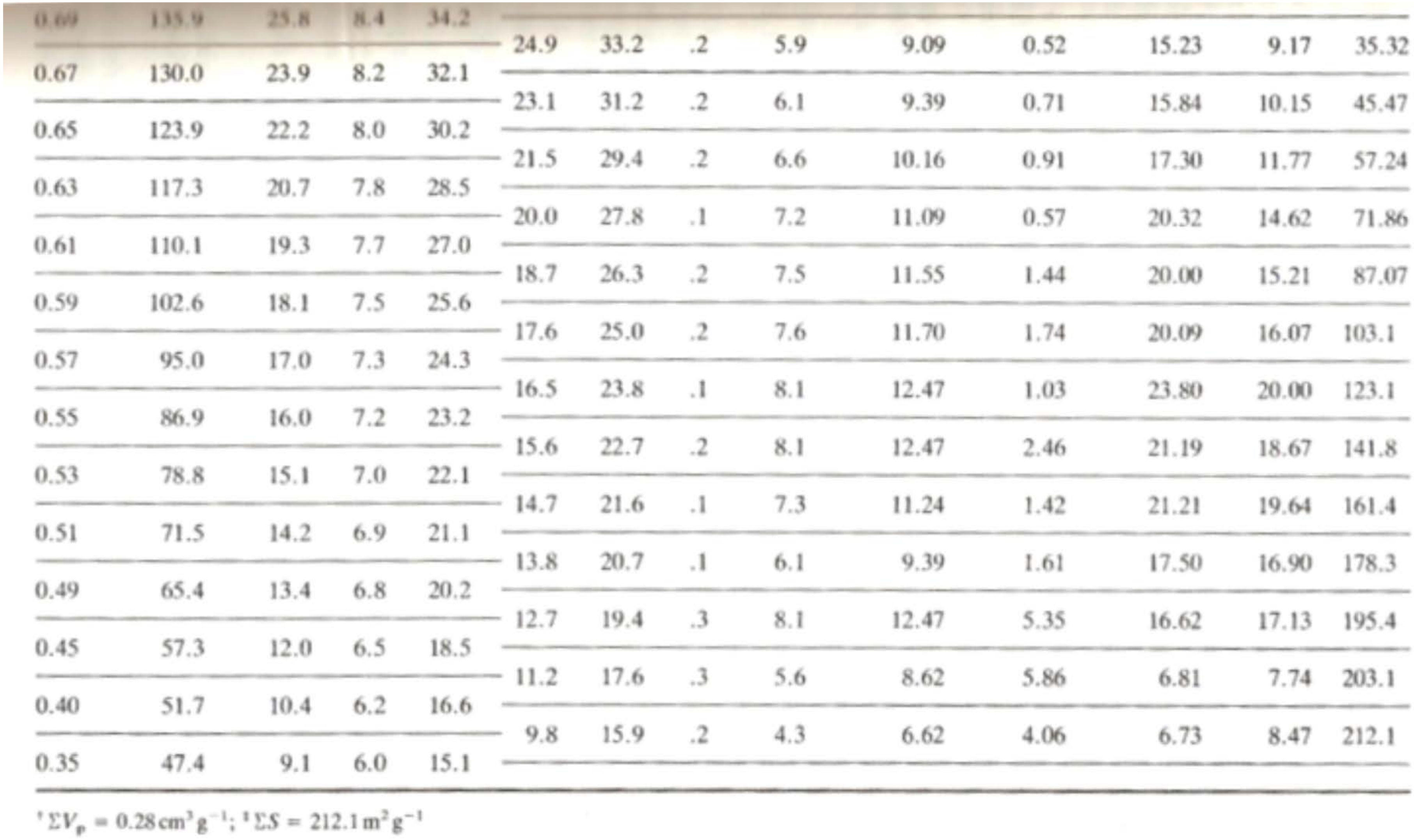


Table 8.1 Pore size distribution work table

1	2	3	4	5	6	7	8	9	10	11	12	13	14
$\frac{P}{P_0}$	V_{gas} STP ($cm^3 g^{-1}$)	r_k (Å)	t (Å)	r_p (Å)	$\bar{r}_k$ (Å)	$\bar{r}_p$ (Å)	Δt (Å)	ΔV_{gas} STP ($cm^3 g^{-1}$)	ΔV_{liq} $\times 10^3$ ($cm^3 g^{-1}$)	$\Delta t \Sigma S$ $\times 10^3$ ($cm^3 g^{-1}$)	V_p $\times 10^3$ ($cm^3 g^{-1}$)†	S (m^2)	ΣS (m^2)‡
0.99	161.7	950	28.0	978									
					711	737	5.8	0.2	0.31	0	0.33	0.01	0.01
0.98	161.5	473	22.2	495									
					394	414	2.8	0.5	0.77	0.00	0.85	0.04	0.05
0.97	161.0	314	19.4	333									
					250	268	3.1	0.8	1.23	0.02	1.40	0.10	0.15
0.95	160.2	186	16.3	202									
					138	153	3.5	1.4	2.16	0.05	2.59	0.34	0.49
0.90	158.8	90.7	12.8	104									
					74.8	87.0	1.7	1.6	2.46	0.08	3.22	0.74	1.23
0.85	157.2	58.8	11.1	69.9									
					50.8	61.4	1.1	2.0	3.08	0.14	4.30	1.40	2.63
0.80	155.2	42.8	10.0	52.8									
					39.7	49.5	.5	2.3	3.54	0.13	5.30	2.14	4.77
0.77	152.9	36.6	9.5	46.1									
					34.9	44.3	.3	4.0	6.16	0.14	9.70	4.38	9.15
0.75	148.9	33.2	9.2	42.4									
					31.8	40.9	.3	3.8	5.85	0.27	9.22	4.51	13.66
0.73	145.1	30.4	8.9	39.3									
					29.2	38.0	.2	4.2	6.47	0.27	10.49	5.52	19.18
0.71	140.9	27.9	8.7	36.6									
					26.9	35.4	.3	5.0	7.70	0.58	12.34	6.97	26.15



0.69	135.9	25.8	8.4	34.2									
					24.9	33.2	.2	5.9	9.09	0.52	15.23	9.17	35.32
0.67	130.0	23.9	8.2	32.1									
					23.1	31.2	.2	6.1	9.39	0.71	15.84	10.15	45.47
0.65	123.9	22.2	8.0	30.2									
					21.5	29.4	.2	6.6	10.16	0.91	17.30	11.77	57.24
0.63	117.3	20.7	7.8	28.5									
					20.0	27.8	.1	7.2	11.09	0.57	20.32	14.62	71.86
0.61	110.1	19.3	7.7	27.0									
					18.7	26.3	.2	7.5	11.55	1.44	20.00	15.21	87.07
0.59	102.6	18.1	7.5	25.6									
					17.6	25.0	.2	7.6	11.70	1.74	20.09	16.07	103.1
0.57	95.0	17.0	7.3	24.3									
					16.5	23.8	.1	8.1	12.47	1.03	23.80	20.00	123.1
0.55	86.9	16.0	7.2	23.2									
					15.6	22.7	.2	8.1	12.47	2.46	21.19	18.67	141.8
0.53	78.8	15.1	7.0	22.1									
					14.7	21.6	.1	7.3	11.24	1.42	21.21	19.64	161.4
0.51	71.5	14.2	6.9	21.1									
					13.8	20.7	.1	6.1	9.39	1.61	17.50	16.90	178.3
0.49	65.4	13.4	6.8	20.2									
					12.7	19.4	.3	8.1	12.47	5.35	16.62	17.13	195.4
0.45	57.3	12.0	6.5	18.5									
					11.2	17.6	.3	5.6	8.62	5.86	6.81	7.74	203.1
0.40	51.7	10.4	6.2	16.6									
					9.8	15.9	.2	4.3	6.62	4.06	6.73	8.47	212.1
0.35	47.4	9.1	6.0	15.1									

$^{\dagger}\Sigma V_p = 0.28\,\mathrm{cm}^3\,\mathrm{g}^{-1}$; $^{\ddagger}\Sigma S = 212.1\,\mathrm{m}^2\,\mathrm{g}^{-1}$

Table 8.1 shows that : the pore volume = 0.28 $\mathrm{cm}^3\mathrm{g}^{-1}$ for $r_p > 15.1$ Å

◆ **BJH takes into account the film thickness change after each decrement of P/Po.**

Three conditions Kelvin eq. analysis should be terminated

1. $P/P_0 < 0.3$, adsorption in micropore range
The validity of Kelvin eq. becomes questionable, because the uncertain -ty regarding molar volume and surface tension when only one or two molecular diameters are involved.

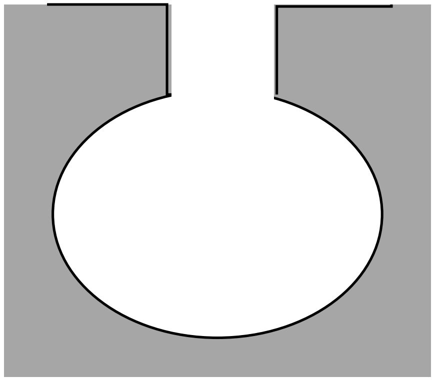
2. When $\Delta t \sum S \approx \Delta V_{liq}$, represents the absence of evaporation from center cores

3. Hysteresis loop closes,
Micropore vol. = total pore vol. – $\sum V_p$ (BJH, column 12)

$$\frac{{}^{Wa}\!/_{{}^{P}\!/_{P0}} = 0.99}{\rho_l}$$

$\sum S$ = 212.1 m^2g^{-1} (in Table 8.1) ←does not include micropore S.A.

($\therefore$ $\sum S$ should be smaller than BET area)

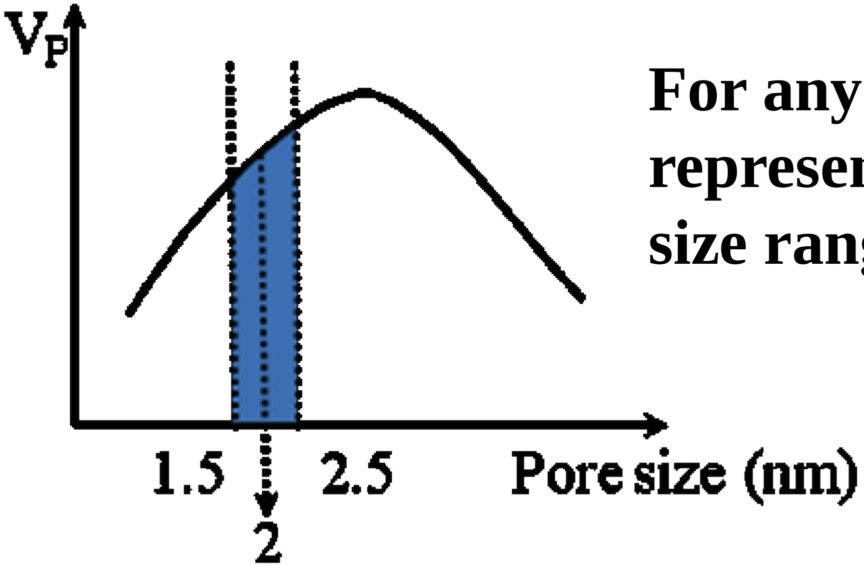


But in some cases, you obtain $\sum S$ > BET S.A , indicating the presence of ink-bottle pores.

You use a small r and a correct ΔV_{liq} to estimate the surface area,

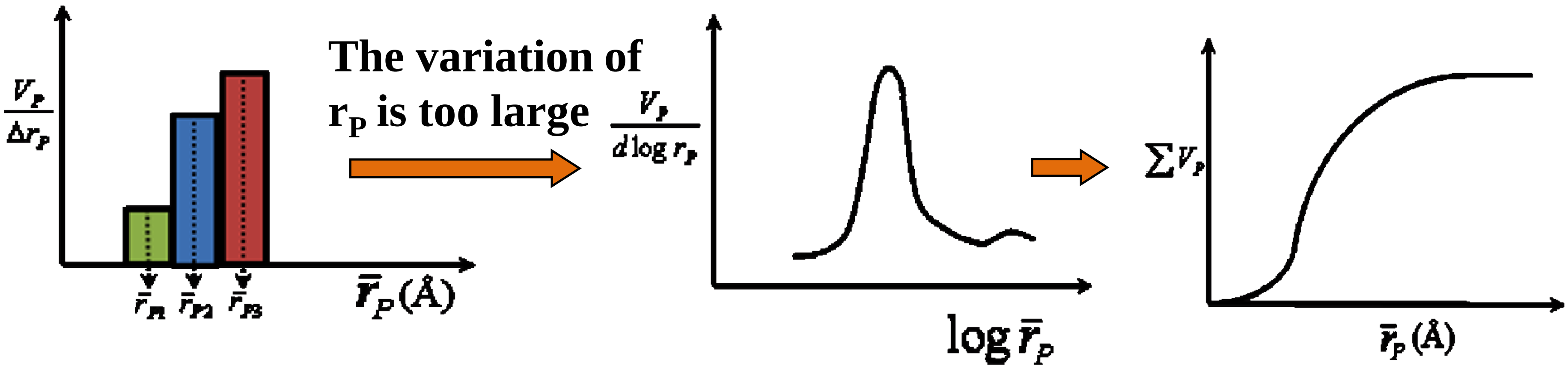
$$S = \frac{2 \cdot \Delta V}{r}$$

(you should use the adsorption isotherm to calculate pore size distribution)



For any distribution, the integrated area represents the volume within the pore size range.

BJH pore size distribution



The variation of r_P is too large

8.7. V-t curves

Adsorption on nonporous materials

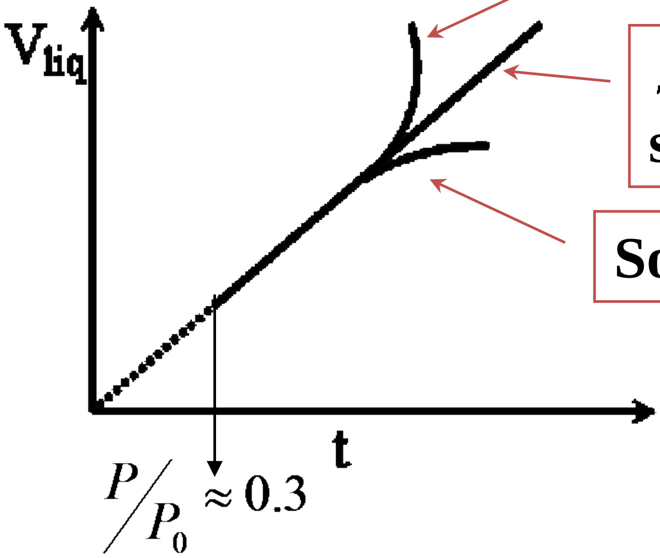
If plot W_a/W_m vs. P/P_0

The data fit a common Type II curves, especially for $P/P_0 > 0.3$ and

$t = (W_a/W_m)\cdot 3.54$Å is used (t : statistical depth)

∴ t vs. P/P_0 should show Type II curves.

$$t = \frac{V_{liq}}{S} \times 10^4 (\text{Å}) , V_{liq} = [\text{cm}^3], S = [\text{m}^2]$$



Condensation into pores

$slope = S \times 10^{-4}$, **the SA value is very similar to BET SA.**

Some pores are filled up.

9. Microporosity

9.1. Introduction

Pore diameter analyzed by Kelvin eq. 15-1000 Å

Dubinin's definition:

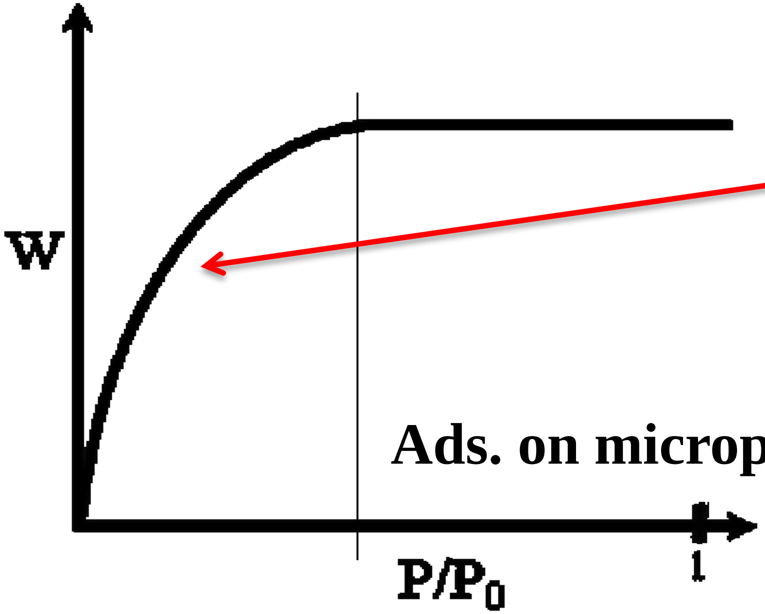
Pore diameter	**> 1000 Å**	**macropores**
	15–1000 Å	**transitional (Kelvin)**
	< 15 Å	**micropores**

IUPAC :

← 20 Å —— 500 Å →

micropore **mesopore** **macropore**

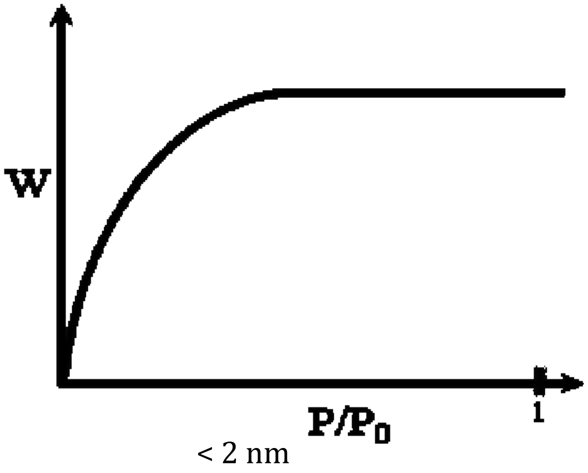
Langmuir eq. (Type I isotherm) can describe the adsorption on microporous materials, but may be only a correct mathematical description.



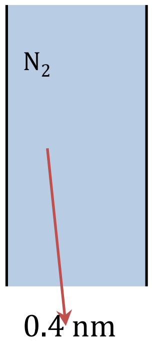
Micropores have high overlapping potential, so they can be filled at low P

Ads. on microporous materials

Microporosity



∴ in micropore regime, pore filling starts from the pores with larger over potentials (or adsorption energy).



Because the pore size is so small, once a molecule is attached to the pore wall, the pore size reduction will initiate the filling of the pore. (no layering behavior in micropores.)

9.2. Langmuir Plots for Microporous Surface Area

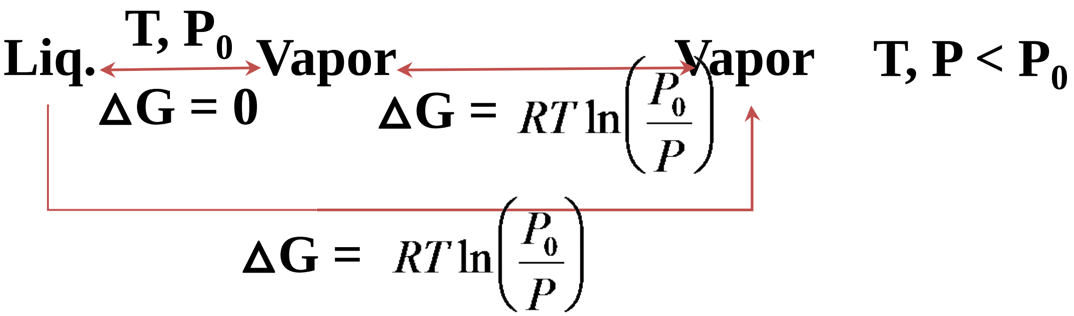
∵ adsorption in micropores belongs to Type I, Langmuir equation can describe the isotherm.

$$\frac{P}{W} = \frac{1}{K W_m} + \frac{P}{W_m}$$

$\frac{P}{W}$ vs. P → $\frac{1}{W_m}$ => $St = \frac{W_m \bar{N} A}{\bar{M}}$

In reality, adsorption in micropores is not monolayer, and Langmuir usually over estimates the S.A.

9.3. Polanyi's Theory for Micropore Volume and Area



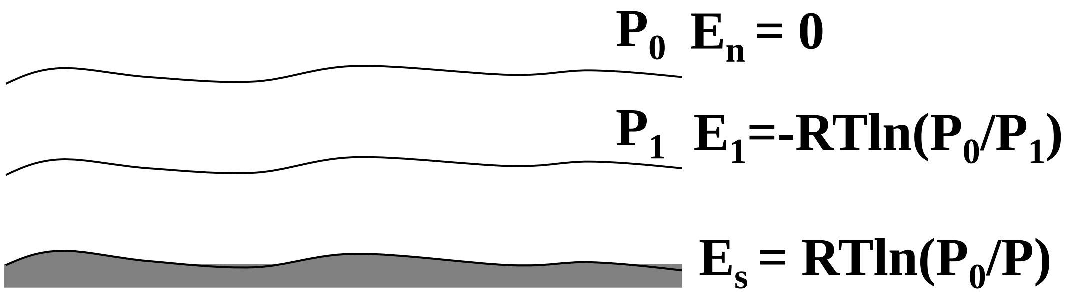
Liq. $\xleftrightarrow{T,\ P_0}$ **Vapor** $\longleftrightarrow$ **Vapor** **T, P < P_0**

$\Delta G = 0$

$\Delta G = RT\ln\left(\dfrac{P_0}{P}\right)$

$\Delta G = RT\ln\left(\dfrac{P_0}{P}\right)$

Polanyi's potential theory of adsorption



P_0 $E_n = 0$

P_1 $E_1 = -RT\ln(P_0/P_1)$

$E_s = RT\ln(P_0/P)$

Adsorption represents that adsorbates can be trapped on surfaces with energies between E_n and E_s

P↑ ⇒ adsorption potential required ↓

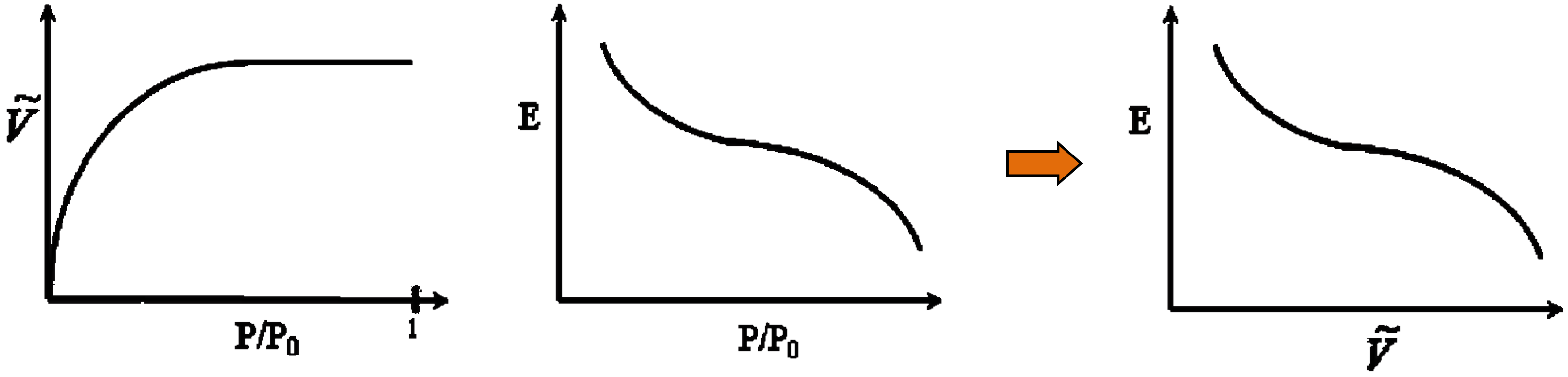
$P = P_0$ ⇒ adsorption potential required = 0

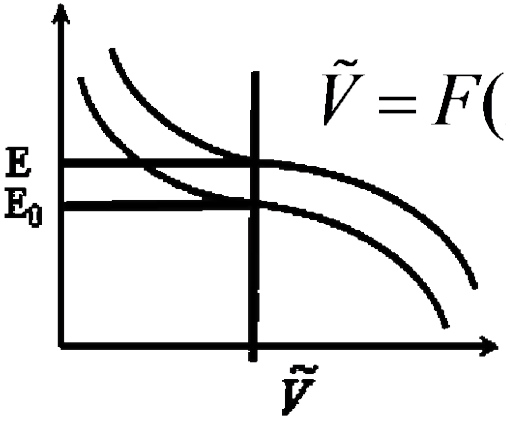
P is very small ⇒ required potential is large

Let adsorption vol. $\tilde{V} = \dfrac{W}{\rho}$

W= f(P/P$_0$)

E = f(P/P$_0$)





$$\tilde{V} = F(E)$$

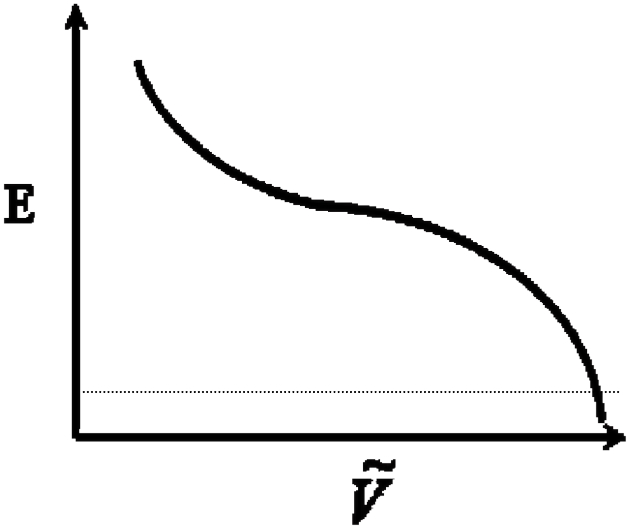
Characteristic curve for different adsorbates.

At the same $\tilde{V}$ **value,** $\dfrac{E}{E_0}$ **represents the relative affinity**

Dubinin assumed that E/E$_0$ are constant at different $\tilde{V}$ **values,**

$$\frac{E}{E_0} = \beta = affinity\ coefficient$$

∴.for the reference, $\tilde{V} = F\left(\frac{E}{\beta}\right)$ **=F (E$_0$)**



Normally, benzene is used as the reference.

Dubinin and Radushkevich assume

$$\tilde{V} = \tilde{V}_0 \cdot e^{-KE_0^2} \Rightarrow \tilde{V} = \tilde{V}_0 \cdot e^{-K\left(\frac{E}{\beta}\right)^2}$$

Can only be used for microporous materials.

$\tilde{V}_0$ **= total adsorption volume**

$$\because E = RT\ln\left(\frac{P_0}{P}\right)$$

$$\tilde{V} = \tilde{V}_0 \cdot \exp\left[-\frac{K}{\beta}(RT)^2 \cdot \left(\ln\frac{P_0}{P}\right)^2\right]$$

$$\log W = \log(W_0) - 2.303K\left(\frac{RT}{\beta}\right)^2\left[\log\frac{P_0}{P}\right]^2$$

or

$$\log W = \log(W_0) - k\left[\log\frac{P_0}{P}\right]^2 \ldots D\text{–}R\ equation$$

log(W) vs. [log(P_0/P)]^2 $\xrightarrow{\text{intercept}}$ log(W_0) → $\tilde{V}_0 = \frac{W_0}{\rho}$

at P/P_0 = 10^{-5} ~ 10^{-1}, give good linear fit for DR eq.

$$\tilde{V} = \tilde{V}_0 \cdot e^{-KE_0^2}$$

Let $K = \left(\frac{1}{\varepsilon_0}\right)^2$

When E_0 = ε_0 => $\tilde{V} = \tilde{V}_0 \cdot e^{-1} = 0.368 \cdot \tilde{V}_0$

ε_0 is called the characteristic adsorption energy.

For slit-like micropores

Stoeckli:

$$L(nm) = \frac{10.8}{\varepsilon_0(kJ \cdot mol^{-1}) - 11.4}, \quad S_{mi}(m^2g^{-1}) = \frac{2000 \cdot \tilde{V}_0(cm^3g^{-1})}{L(nm)}$$

9.4 The t-method

de Boer et al. used microporous material isotherm and standard type II isotherm

t-method to determine micropore vol. and surface area

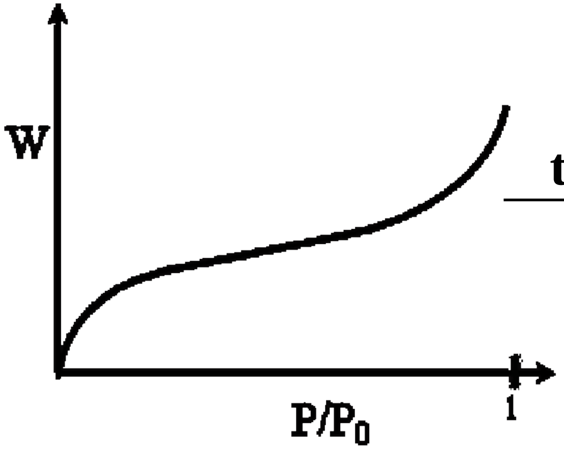
de Boer equation

$$t(\dot{A}) = \left(\frac{13.99}{\log {}^{P_0}\!/_{P} + 0.034} \right)^{\frac{1}{2}}$$

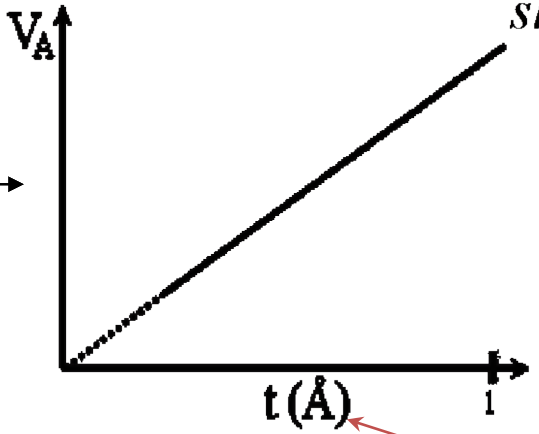
, standard t curve for N_2 adsorption

t: statistical thickness on nonporous materials, but with C value close to that of microporous materials

for the standard sample



t-plot

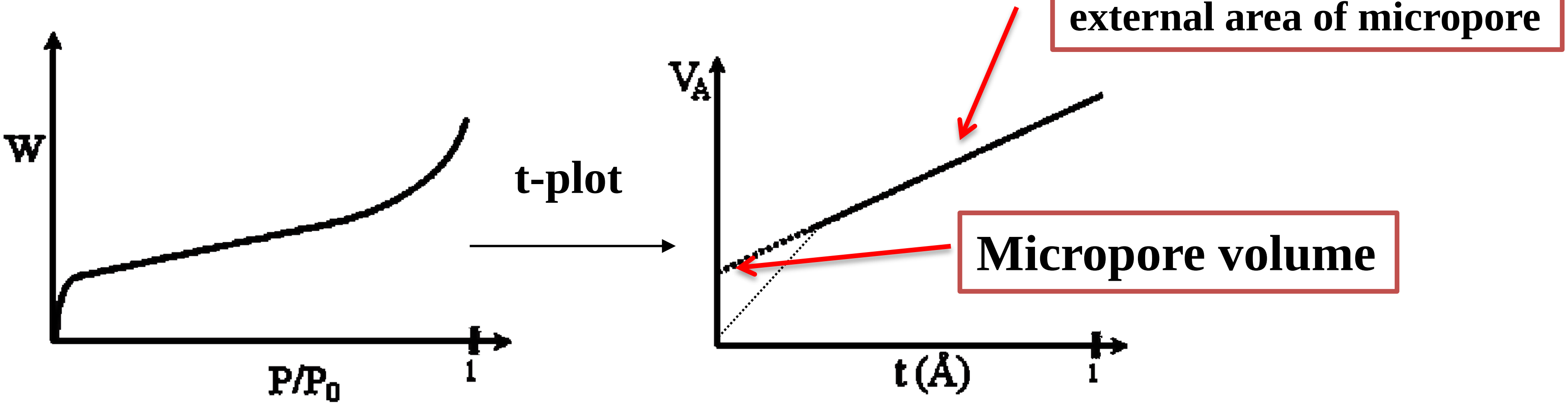


$$slope = \frac{S_t(m^2)}{10^4}$$

$$S_t(m^2) = \frac{V_{liq}(cm^3)}{t(\dot{A})} \times 10^4$$

de Boer

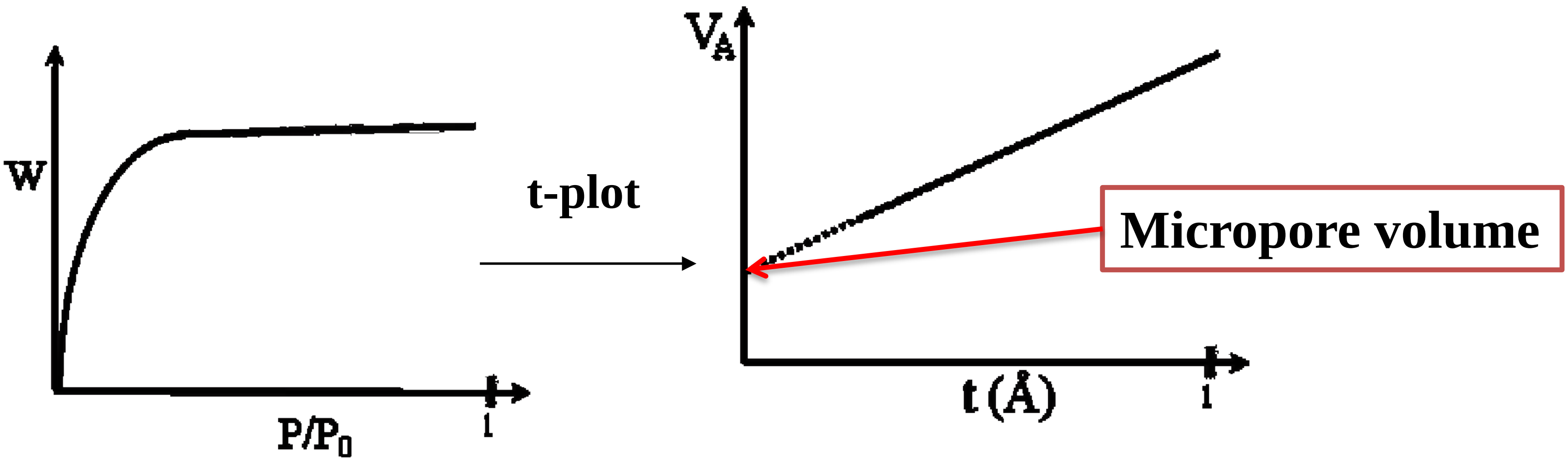
Microporous + standard



Slope = area of standard + external area of micropore

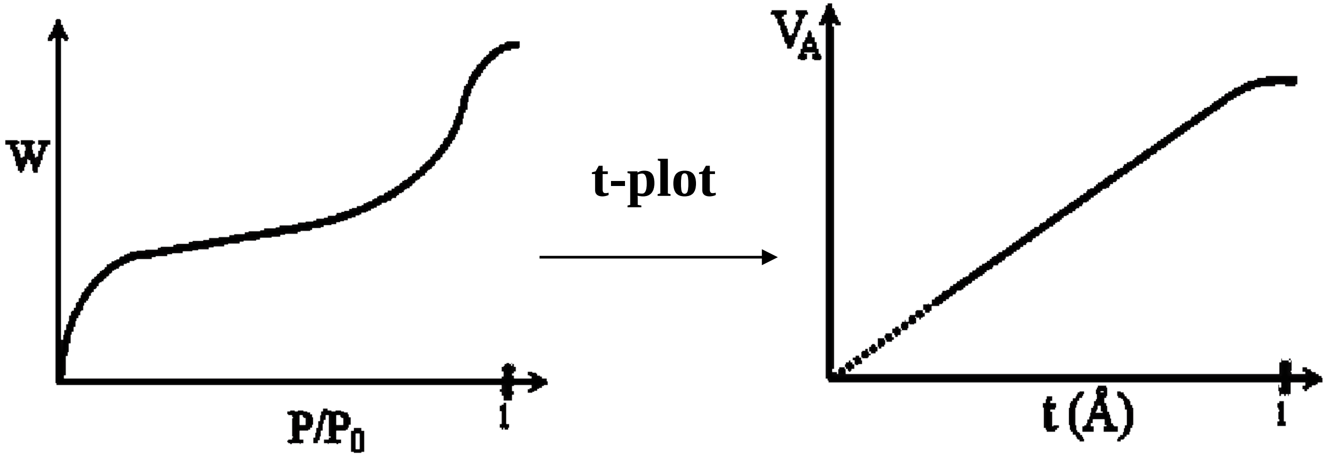
Micropore volume

Microporous



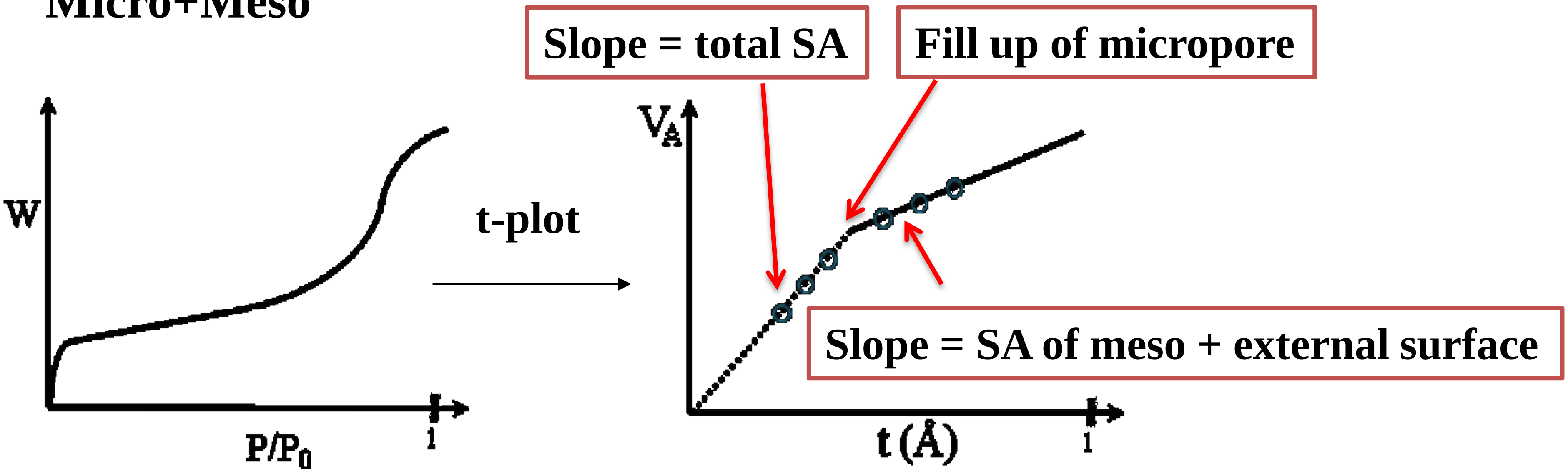
Micropore volume

Mesoporous + standard



t-plot

Micro+Meso



t-plot

Slope = total SA

Fill up of micropore

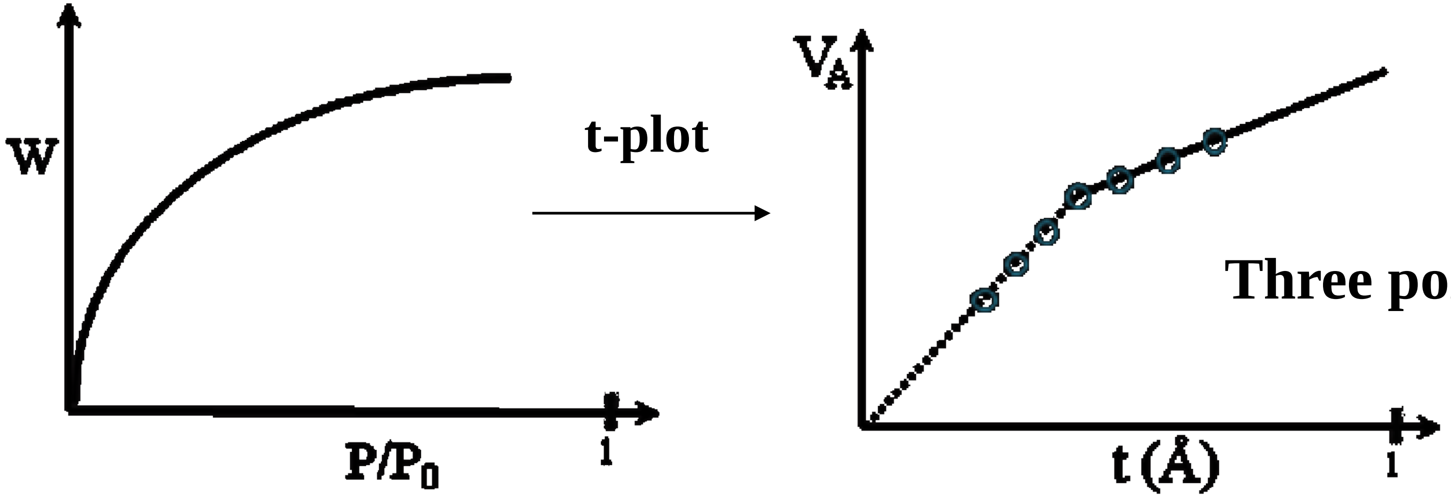
Slope = SA of meso + external surface

$$S_{micro} = \left[\left(\frac{V_{liq}}{t}\right)_{lower} - \left(\frac{V_{liq}}{t}\right)_{upper}\right] \times 10^4$$

or

$$S_{micro} = S_{BET} - \left(\frac{V_{liq}}{t}\right)_{upper} \times 10^4$$

9.6 The micropore analysis method (MP method)



Three point for 1 line.

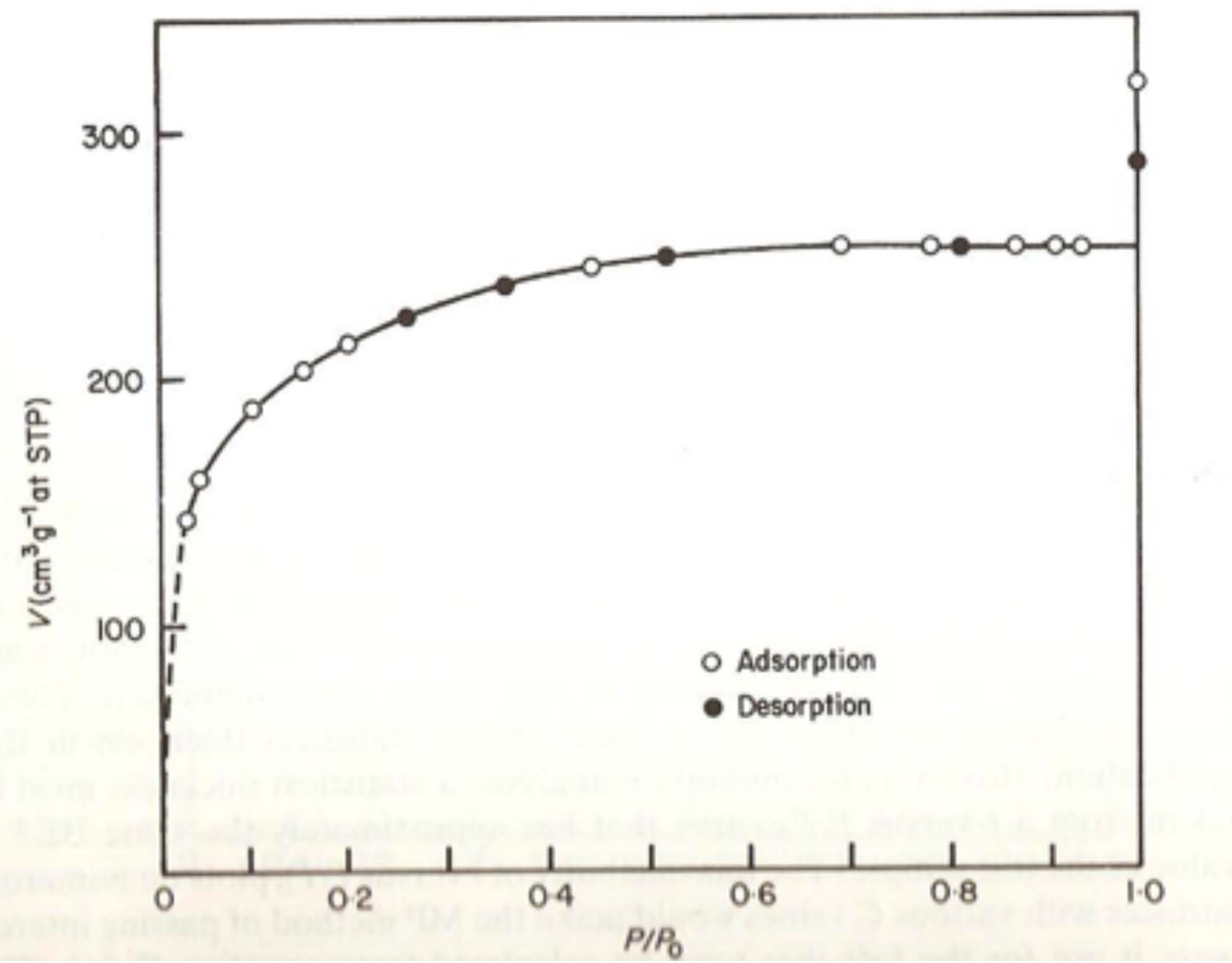


Fig. 9.5 Isotherm of N2 silica gel, Davidson 03 at 77.3°K

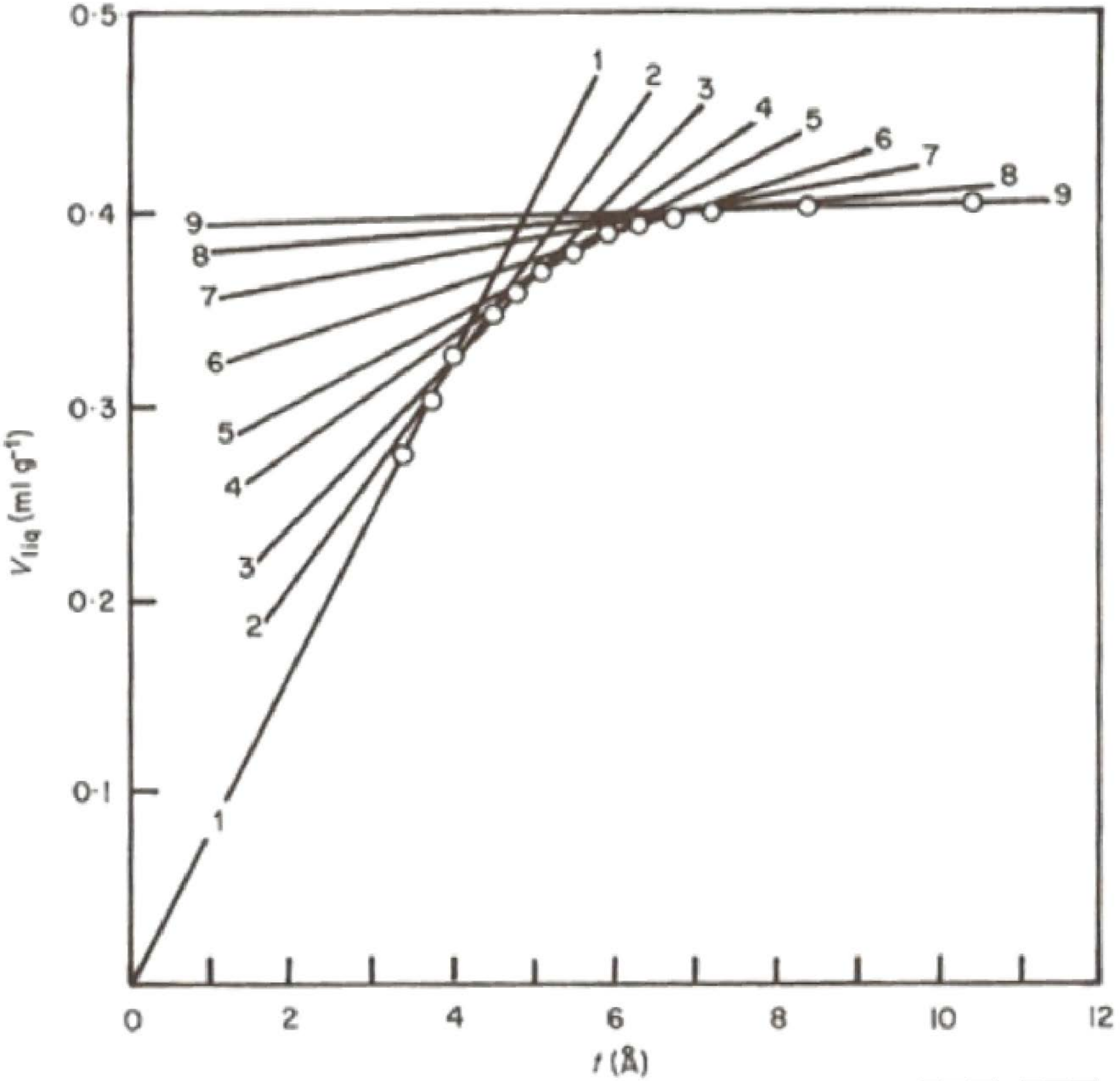


Fig. 9.6 V-t curve from Fig. 9.5

Slope of line 1 → S=792 m^2/g

0.0792 (>4Å)

Slope of line 2 → S=520 m^2/g

0.0520 (>4.5Å)

Slope of line 3 → S=360 m^2/g

0.0360 (>5Å)

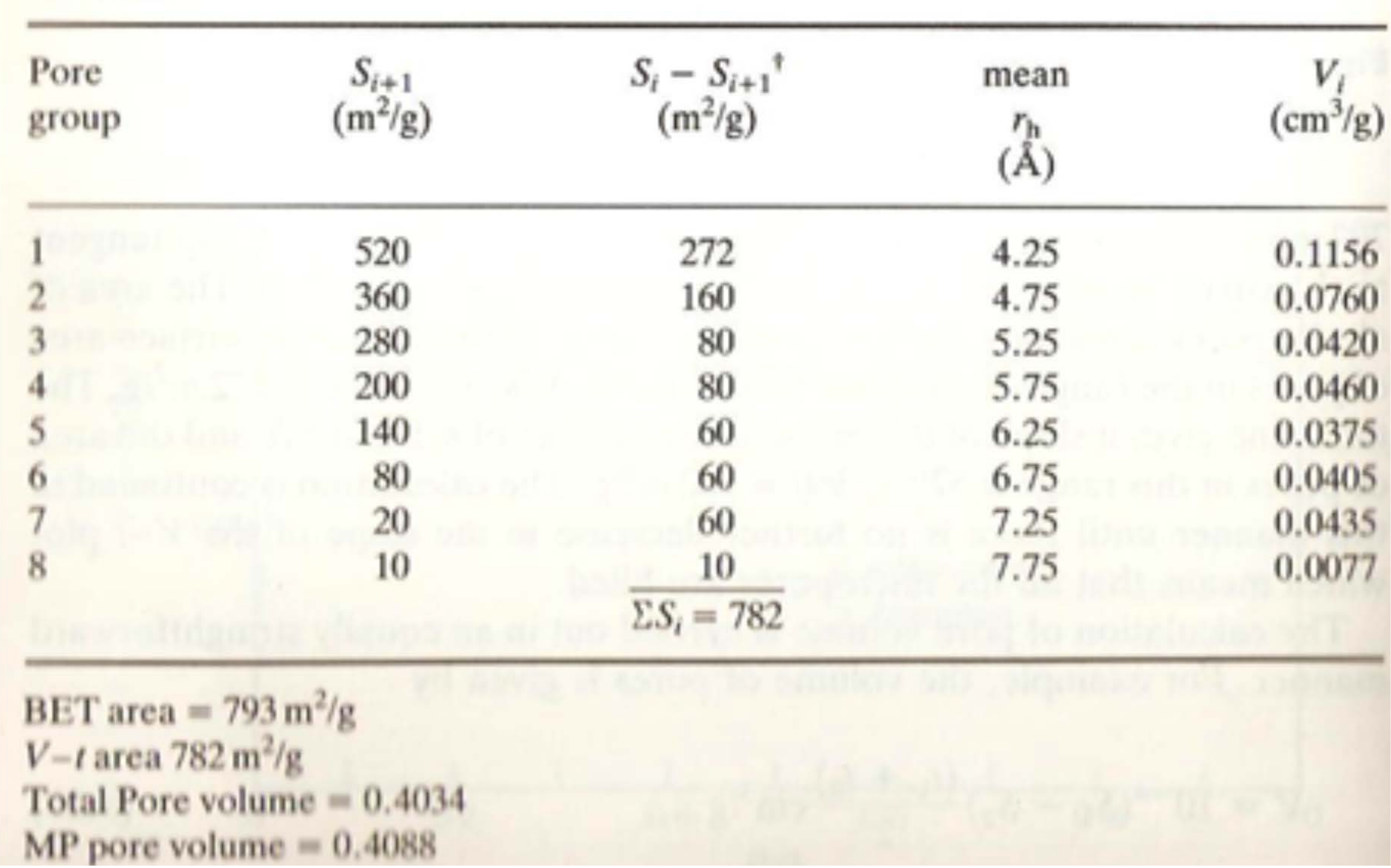
$\Delta S = 160$, pores of 4.5~5Å are filled up

$$\bar{r} = 4.75\text{Å}, \quad V = \Delta S \cdot \bar{r} \times 10^4 \ cm^3/g = 0.076 \ cm^3/g$$

The calculation is continued in this manner until there is no further decrease in the slope. $S_{min} = S_{ext}$

$\sum \Delta S$ = micropore SA $\sum V$ = micropore vol.

Table 9.1



Pore group	S_{i+1} (m^2/g)	$S_i - S_{i+1}$[†] (m^2/g)	mean r_h (Å)	V_i (cm^3/g)
1	520	272	4.25	0.1156
2	360	160	4.75	0.0760
3	280	80	5.25	0.0420
4	200	80	5.75	0.0460
5	140	60	6.25	0.0375
6	80	60	6.75	0.0405
7	20	60	7.25	0.0435
8	10	10	7.75	0.0077
		$\Sigma S_i = 782$		

BET area = 793 m^2/g

V–t area 782 m^2/g

Total Pore volume = 0.4034

MP pore volume = 0.4088

The authors attributed the difference between the V-t and BET areas to surfaces that did not lie within pores.