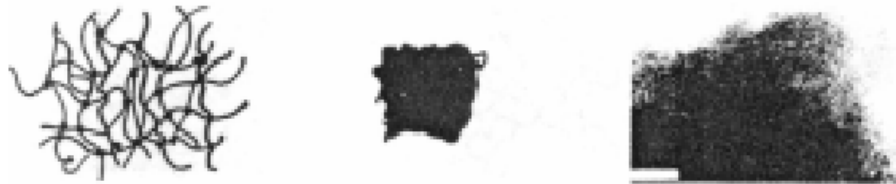


VIII. Structure of Porous Gel

- Classification

A. Acid-catalyzed gel (from polymeric sol)



Before drying

After drying (xerogel)

C. Base-catalyzed gel (from particulate sol)



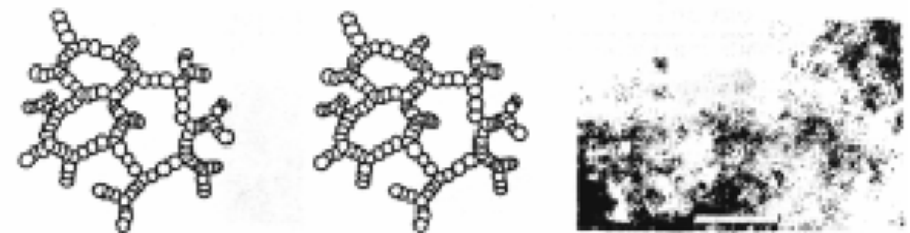
D. Aerogel

B. Two-step acid-base catalyzed gel



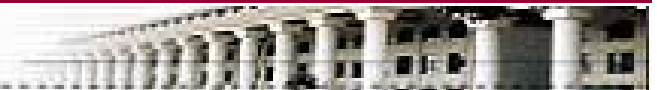
Before drying

After drying (xerogel)

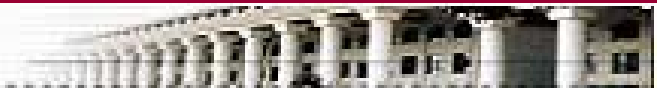
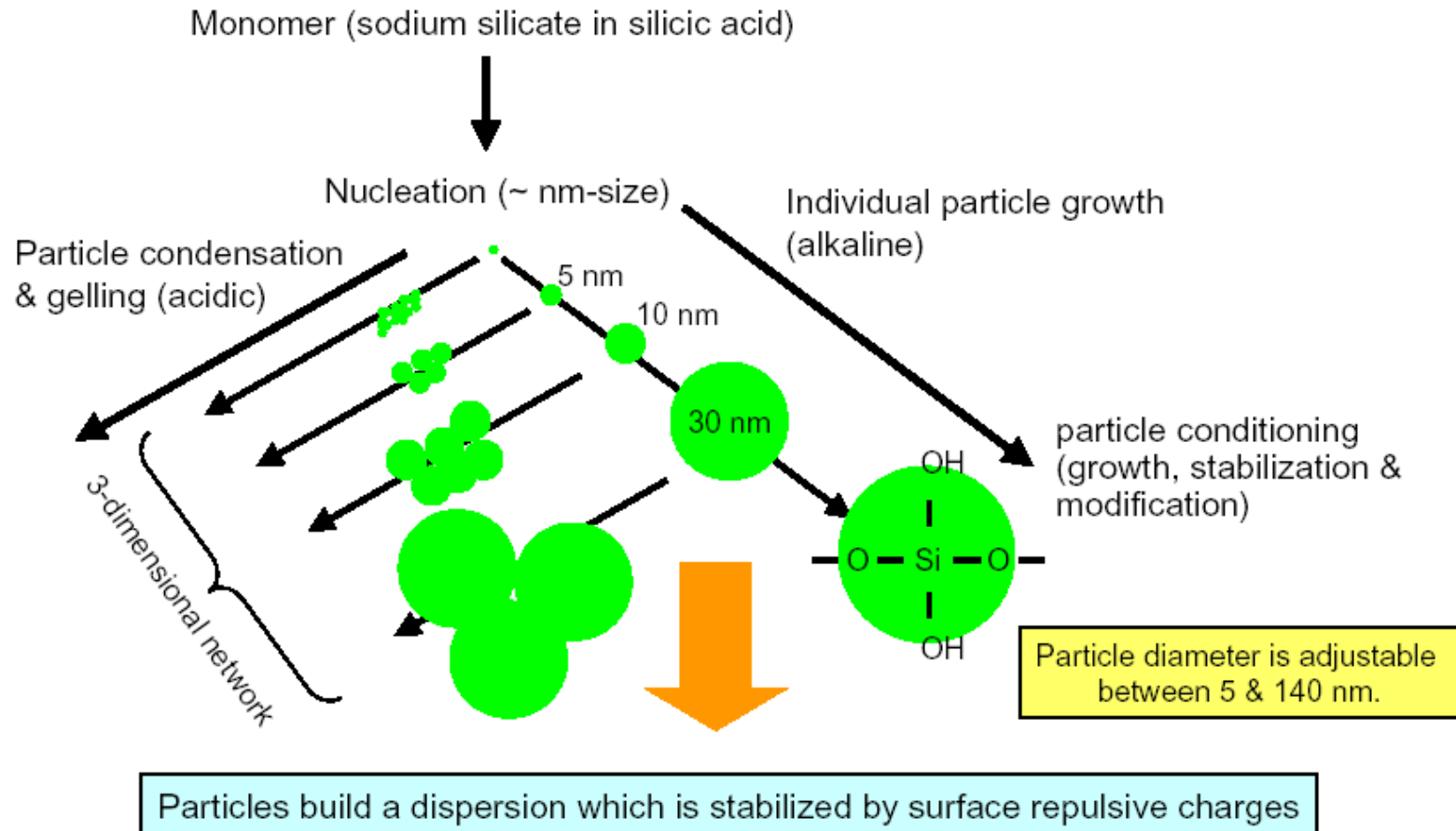


Before drying

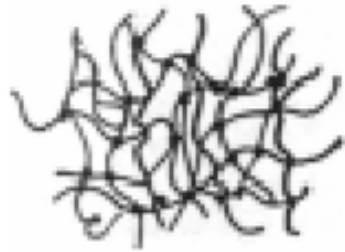
After drying (aerogel)



Colloidal Silica Synthesis



A. Acid-catalyzed gel (from polymeric sol)



Before drying



After drying (xerogel)

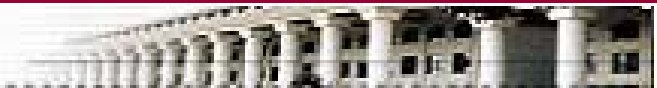


Extremely fine “texture”
(TEM image)

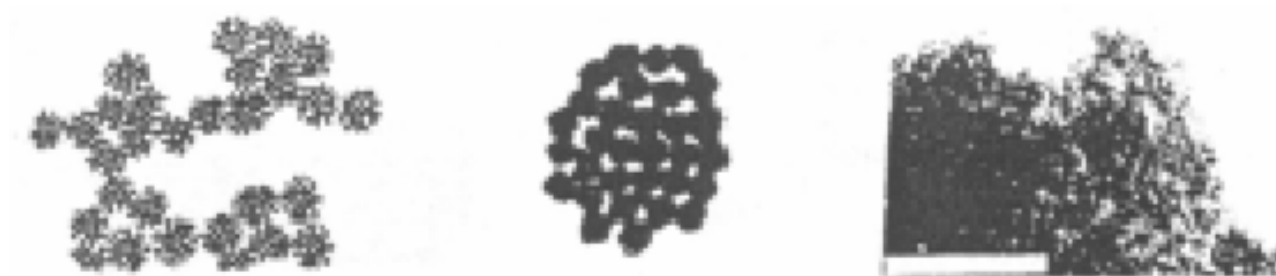
Two-step acid catalyzed
silica gel
Weakly branched system

Desiccated xerogel

- √ Condensation rate is low, overlapped (interwoven) at the gel point
- √ Structure can rather freely shrink in response to solvent removal
- √ The enormous capillary pressure (up to 200 Mpa) attained at the final stage of drying causes a further compaction of the structure



B. Two-step acid-base catalyzed gel



Before drying

Two-step acid-base
catalyzed gel

After drying (xerogel)

Desiccated xerogel

- √ More highly branched structures are prevented from interpenetrating due to strong intercluster, steric screening effects
- √ With solvent evaporation, individual clusters undergo shrinkage and rearrangement to achieve higher coordination of the impinging clusters
- √ Shrinkage stops at an early stage of drying due to the stiffness of the impinging clusters
→ larger pores
- √ Two types of pores: microporosity within clusters, mesoporosity between clusters



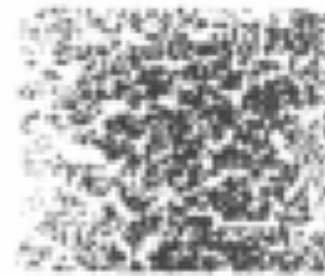
C. Base-catalyzed gel (from particulate sol)



Hierarchical packing of
Colloid particles



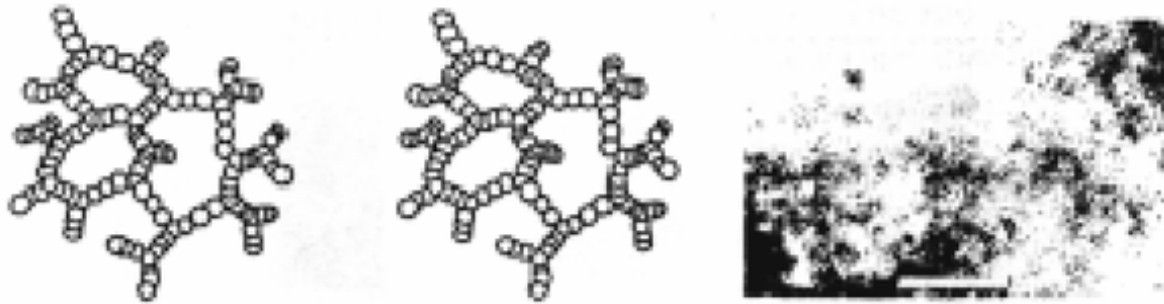
Random packing of
colloid particles
(coordination # = 3)



- √ Particulate xerogels are composed of uniform particles
- √ Drying can serve only to rearrange the particle assemblage to achieve higher coordination #
- √ Capillary pressure is much lower for particulate systems than the previous A and B
- √ The pore volume of the xerogels depends only on the particle-packing geometry



D. Aerogel



Before drying

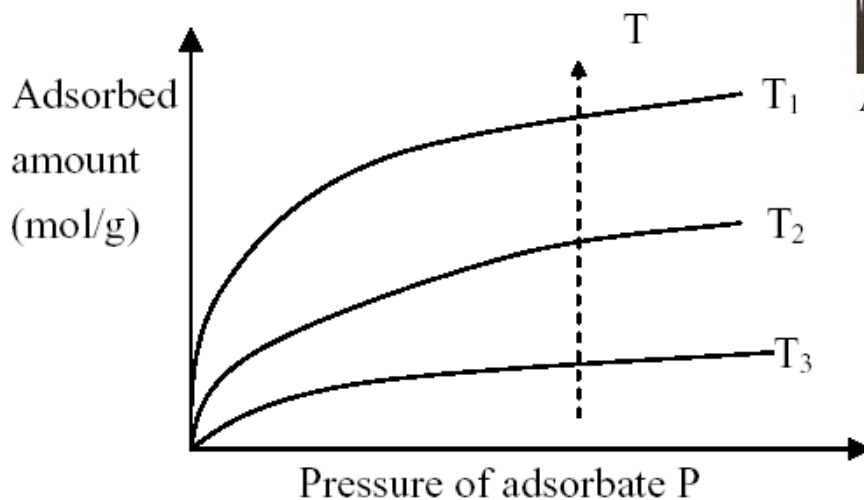
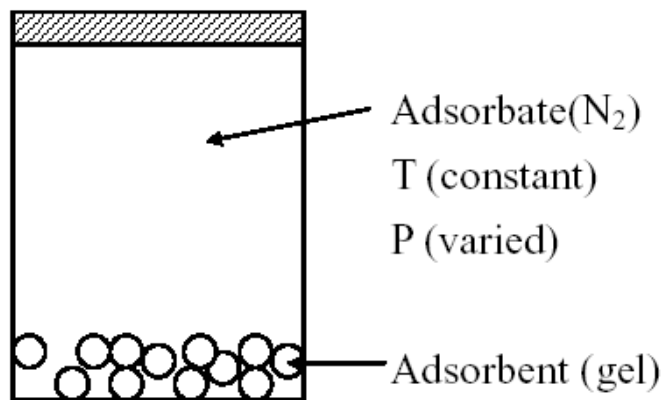
After drying (aerogel)

- √ Removal of solvent above its critical point (no capillary pressure, no liquid-vapor interface)
- √ Greatly reduced driving force for shrinkage in aerogel process
- √ Compared to xerogels, aerogels are expanded structures that are often more closely related to the structure of the gel that existed at the gel point



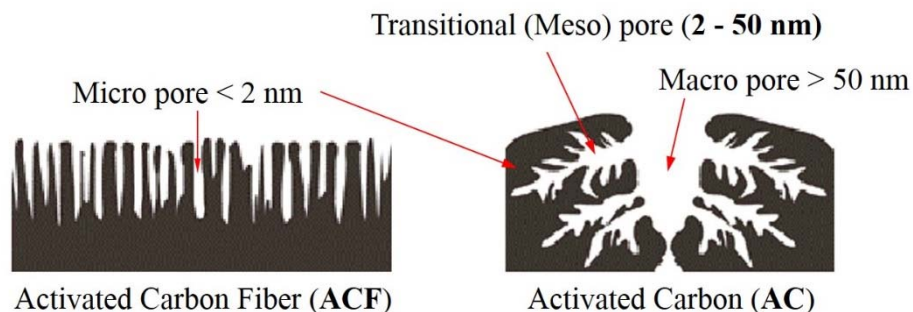
- Pore Structure Characterization by Adsorption

Adsorption Isotherm



Experimental Methods

- Gravimetric
- Volumetric
- G.C.

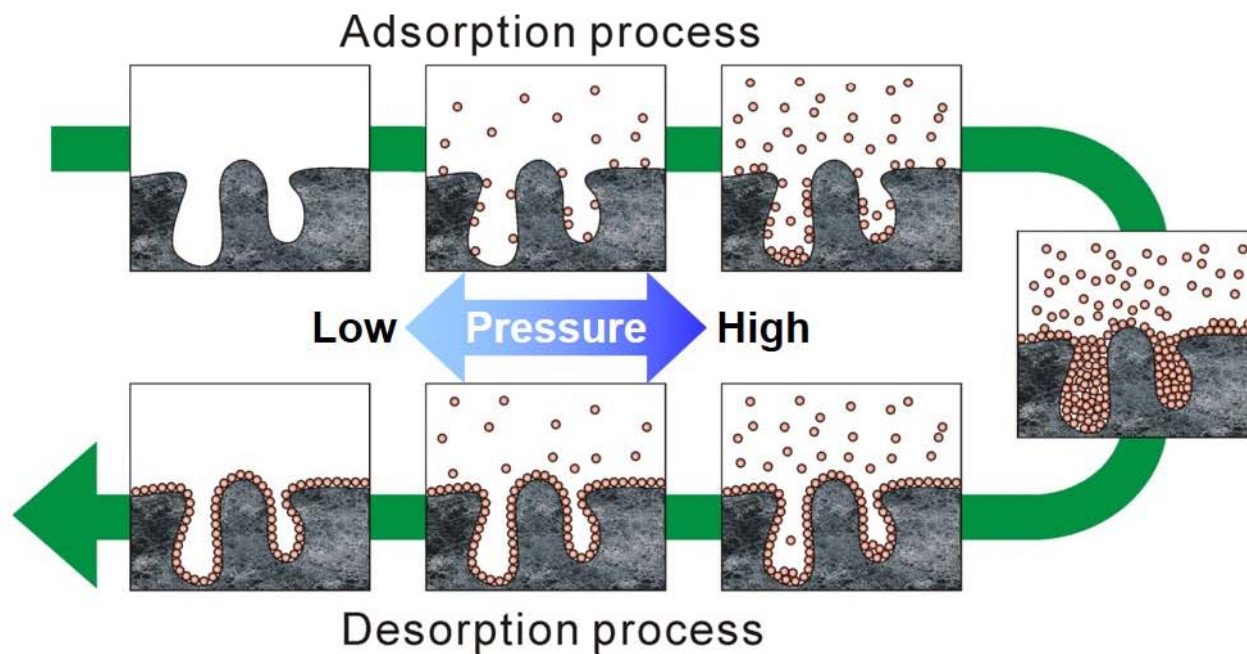


Physisorption

- Weak adsorption
- Reversible
- Surface area/pore analysis

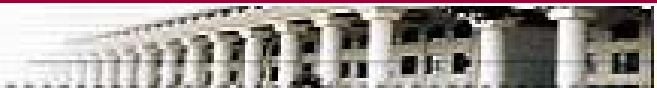
Chemisorption

- Strong adsorption
- Irreversible
- Surface chemical property

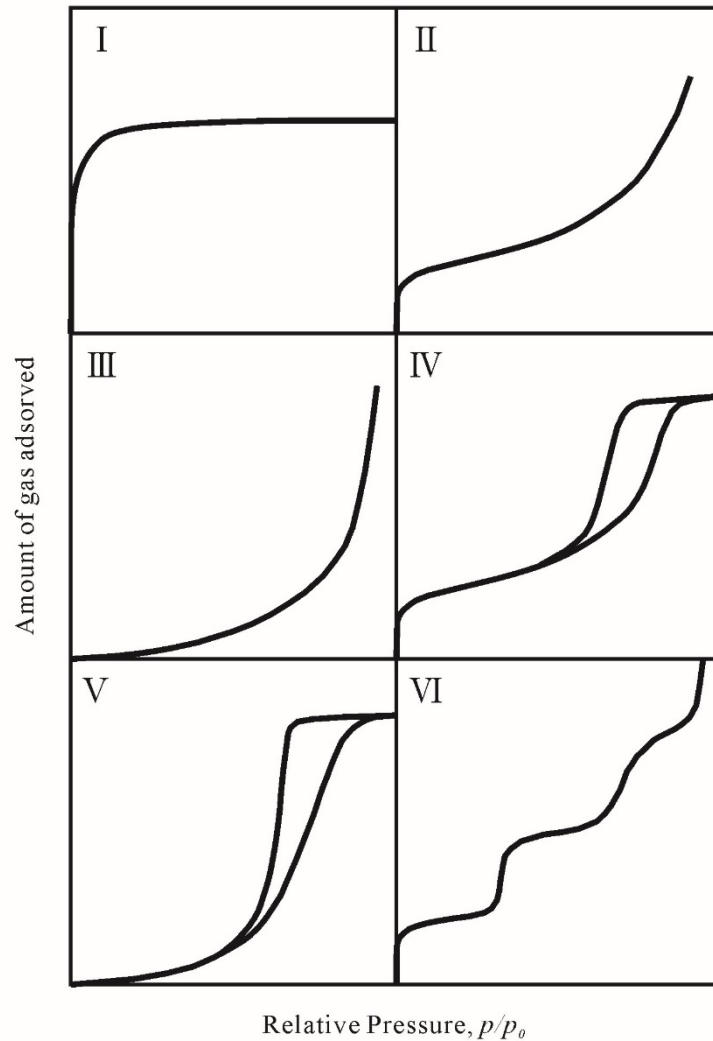


– Physical adsorption vs. Chemisorption

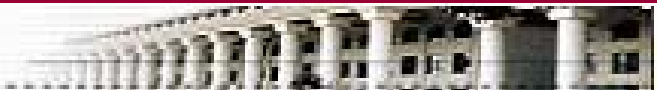
Criterion	Physical adsorption	Chemisorption
Force	Van der Waals force	Chemical bonding
Coverage	Multilayer	Monolayer
Adsorbent	All solids	Some solid
Adsorbate	All gases below critical temp.	Chemically reactive vapor
Reversibility	Completely reversible	May be reversible or irreversible
Rate	Rapid	May be fast or slow
Temp. dependence	Decreases with increasing temp.	May be complex
Activation energy	Zero	Usually small
Heat effect*	Always exothermic; similar to heat of condensation	Usually exothermic; similar to heat of reaction
Heat of adsorption	2-10 kcal/mol	15-100 kcal/mol



– Classification of isotherms



I	Microporous (Active carbon, Zeolite)
II	Non-porous (Metal powder, Quarts sand)
III	Non porous and weak adsorption interaction
IV	Mesoporous (Silicagel)
V	Porous and weak adsorption interaction
VI	Energetically uniform surface

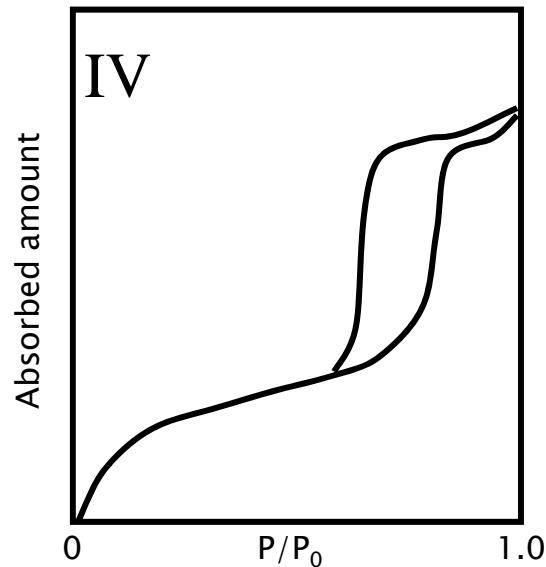


– Hysteresis loop in adsorption/desorption

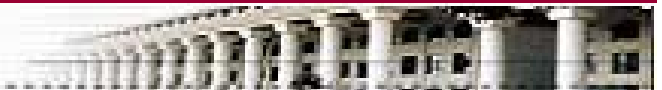
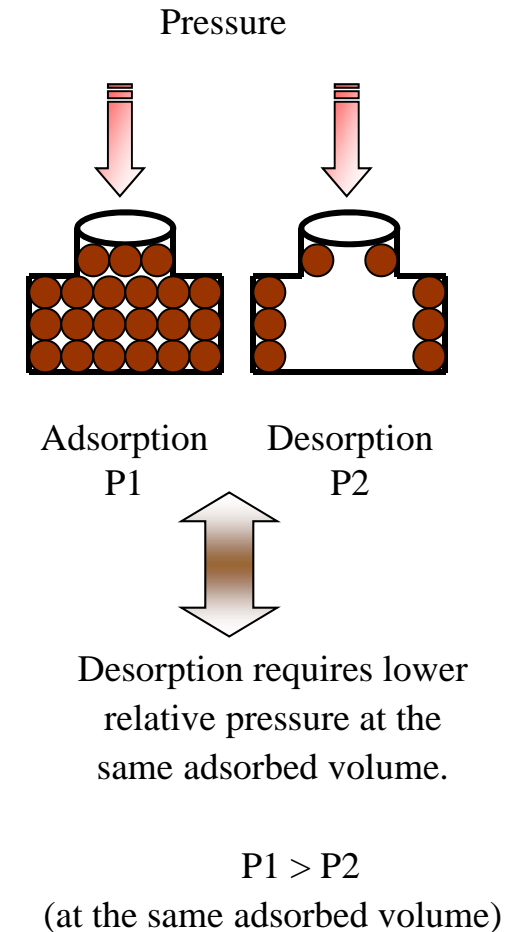
IV, V types

❖ link-bottle theory

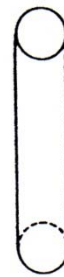
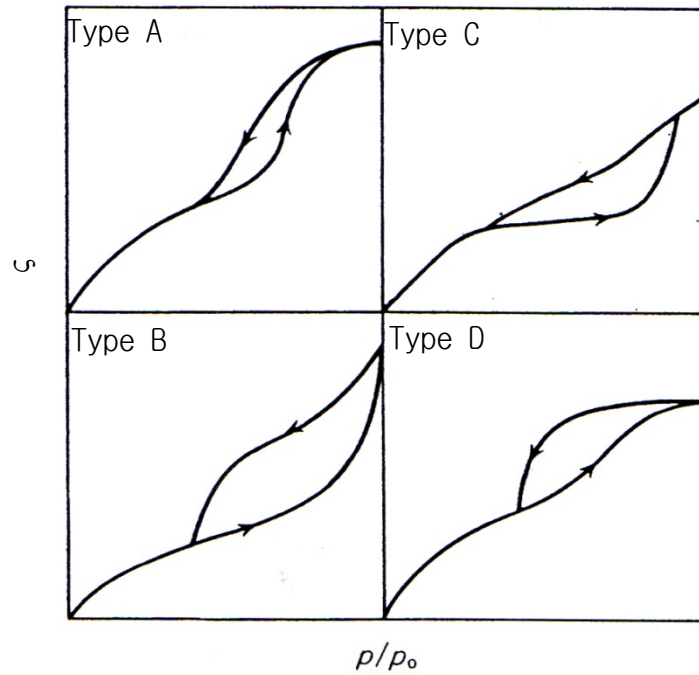
Based on the different sizes of cavity
And throat.



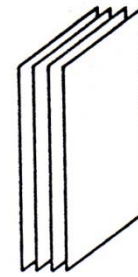
During adsorption, molecules are adsorbed on the broad cavities. In contrast, desorption takes place through narrow throat. Hysteresis loop is observed on the samples having mesopores due to Capillary condensation.



– Types of Hysteresis loop



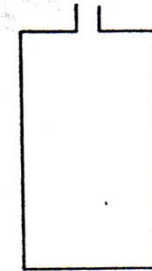
(a) cylinder



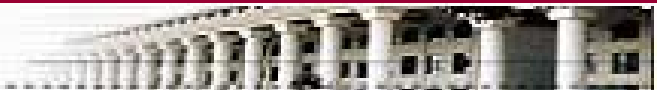
(b) slit



(c) wedge



(d) ink-bottle



– Information from Isotherm

Information	Analysis	Note
Specific surface area	BET method	Commonly used to calculate specific surface area.
	Langmuir method	Once used for specific surface area calculation but not now.
	t-plot	Especially effective for microporous material.
	α_s -plot	Similar to t-plot
Pore size distribution	BJH	For mesopore analysis. Based on Kelvin equation and cylindrical pore model.
	CI	
	DH	
	MP	For micropore analysis. Derived from t-plot.
	HK,SF	(Basically) for micropore analysis.
	NLDFT/GCMC	From micropore to mesopore.
	Molecular probe	For micropore analysis. Plural isotherms are required.
Pore volume	DA method	Pore volume and adsorption energy can be obtained.
Chemical property	Metal dispersion rate	To evaluate metal supported catalysts. Surface acidity, basicity, hydrophobicity and hydrophilicity.

It is important to understand the features, applicable limit of each analysis method, and use appropriate analysis.

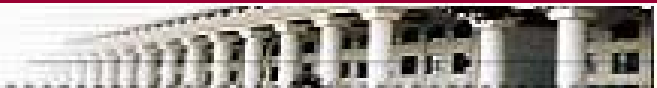


- Analysis of Porous materials by Adsorption

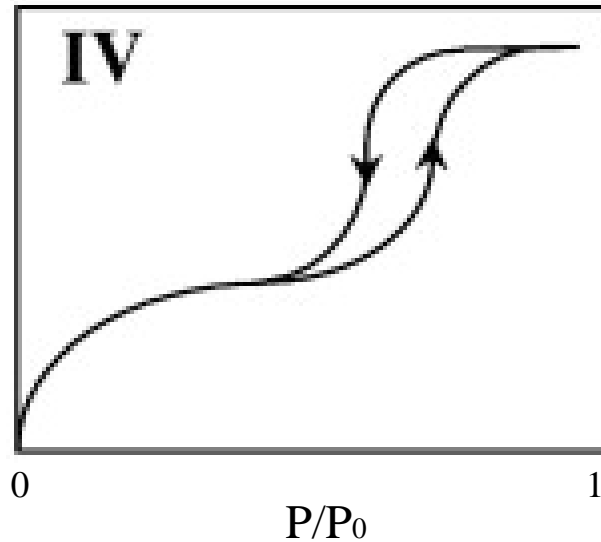
- Specific surface area
- Pore shape
- Total pore volume
- Pore size distribution

< Gas Characteristics used for Adsorption >

Gas	Typical adsorption temp. (K)	Saturated Vapor Pressure at adsorption temp. (Pa)	Adsorbed area (nm ² /molecule)
Nitrogen	77	1.013×10^5 at 77.4 K (liquid)	0.162
Argon	77	2.78×10^4 at 77.4 K (solid)	0.15
	87	1.013×10^5 at 87.34 K (liquid)	
Krypton	77	239 at 77.4 K (solid)	0.20
	77	338 at 77.4 K (solid)	0.20
	90	2.74×10^3 at 90.2 K (solid)	0.20
Xenon	90	8.25 at 90.2 K (solid)	0.23
Methane	90	1.08×10^4 at 90.2 K (solid)	0.16
N-butane	273	1.013×10^5 at 272.7 K (liquid)	0.44
CO ₂	195	1.013×10^5 at 194.7 K (solid)	0.20



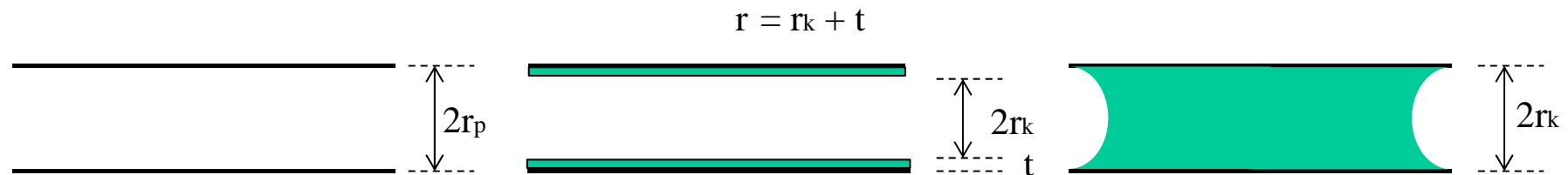
Type IV isotherm, hysteresis, typical for most gels derived from sol-gel process



Surface area

Measured from the adsorption isotherm in relative pressure < 0.3 using the BET multilayer adsorption isotherm equation

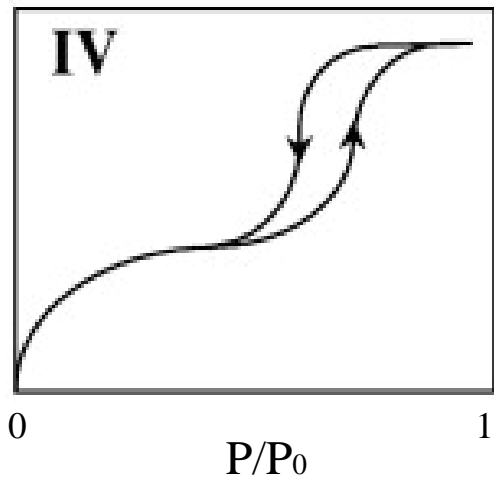
Adsorption in cylindrical pores



Pore Volume, V_p

Calculated from saturated amount of adsorbate adsorbed

Pore Size Distribution, $P(r)$



Calculated from ad- or desorption isotherm

P/P_0 gives V_d

By Kelvin equation

$$P_v = P_0 \exp(V_m \gamma_{LV} k / RT)$$

$$k = -(1/r_{k1} + 1/r_{k2}) \quad \begin{cases} -1/r_{k1} \text{ for adsorption} \\ -1/r_{k2} \text{ for desorption} \end{cases}$$

$$r_k = f(P_v/P_0)$$

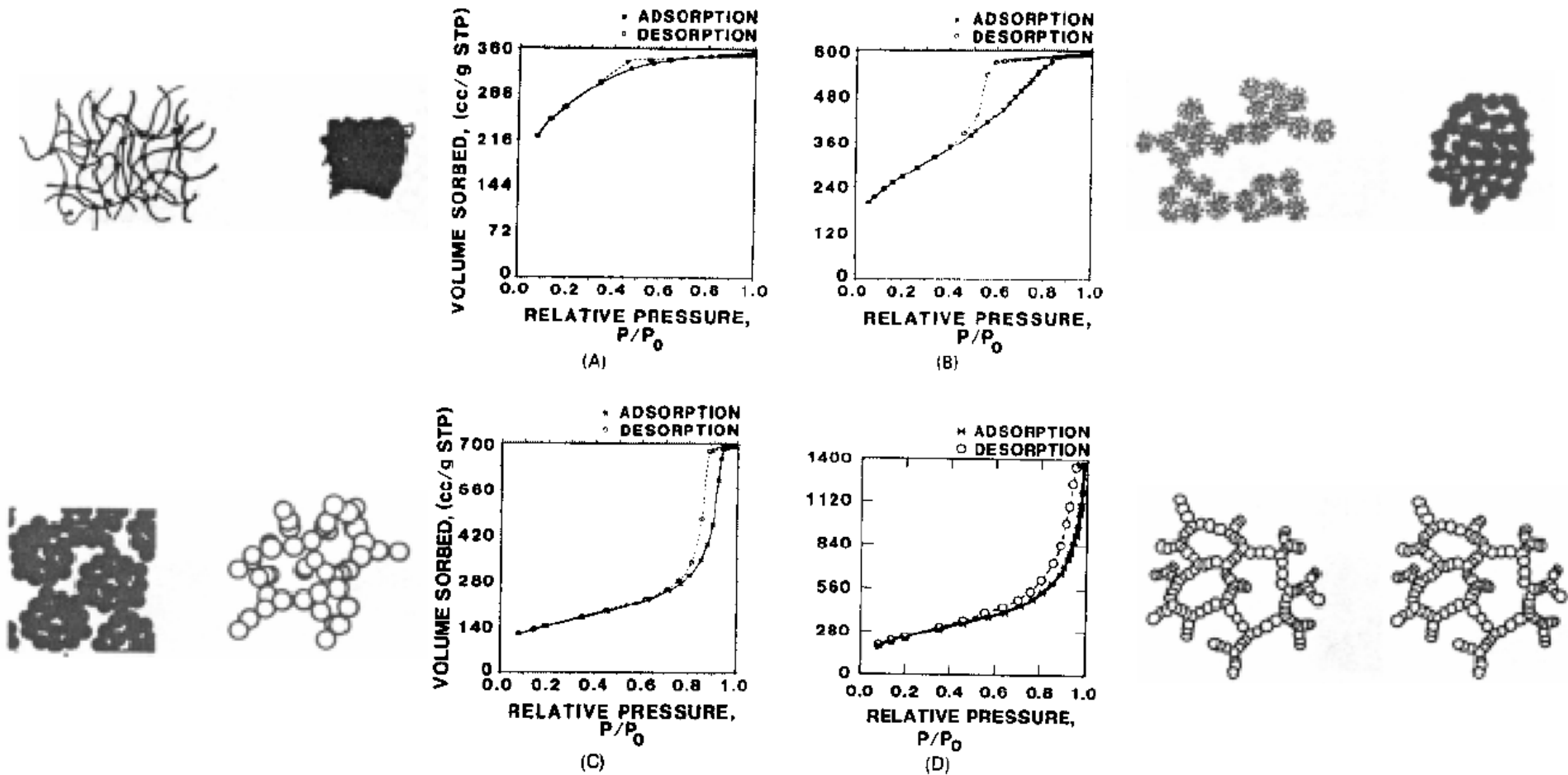
$$V_p - V_d(r) = \int_r^\infty P(r) dr \quad \Rightarrow \quad P(r) = -dV_d(r) / dr$$

V_p : total pore volume

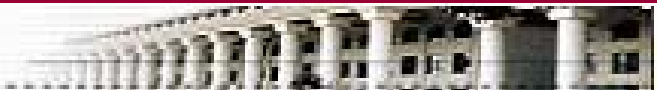
$V_d(r)$: volume of all pores having radii less than r



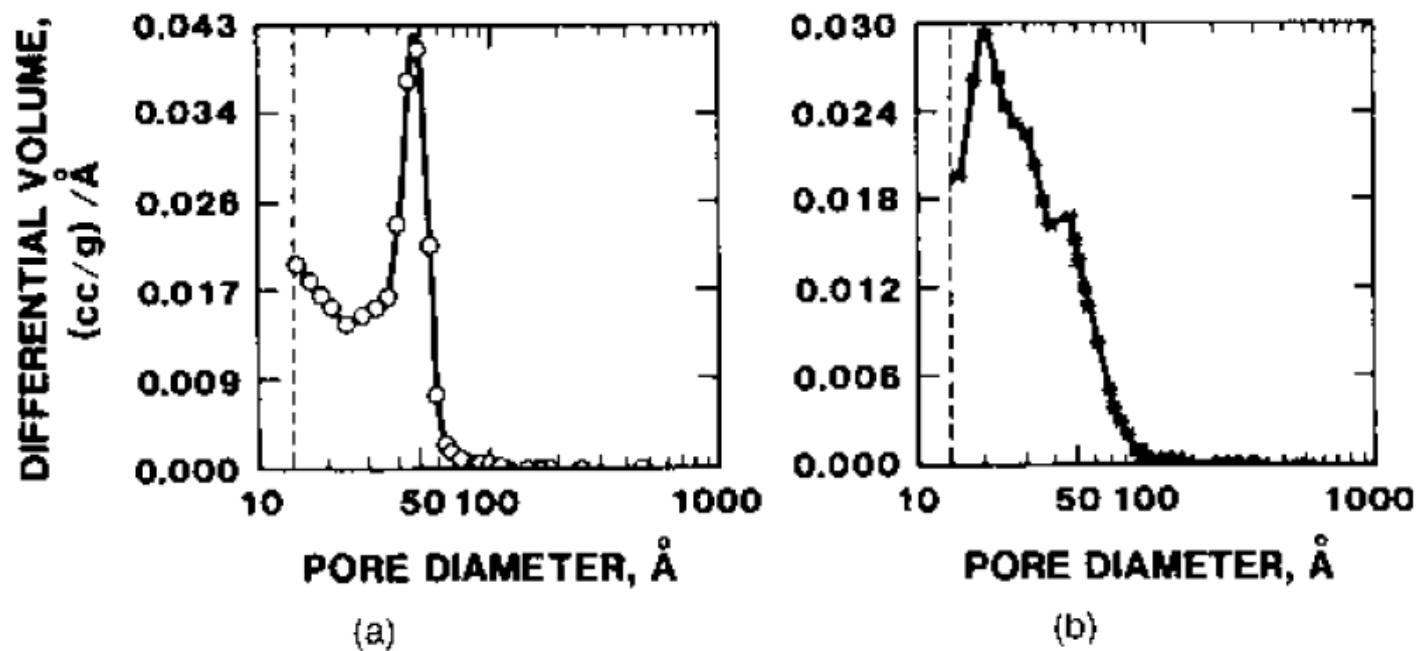
- Adsorption Isotherms of Nitrogen on Four Dried Silica Gels



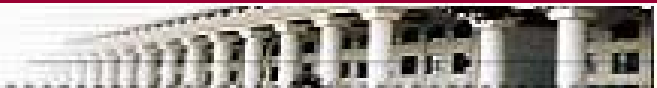
Nitrogen adsorption-desorption isotherms at 77 K for the desiccated silica gels examined by TEM in Fig. 3. (A) Two-step acid-catalyzed xerogel. (B) Two-step acid-base-catalyzed xerogel. (C) Particulate xerogel. (D) Two-step acid-base-catalyzed aerogel. *: adsorption; O: desorption [?].



- Pore size distribution of Gel B



Pore size distributions for the two-step acid-base-catalyzed xerogel determined from (a) the adsorption isotherm and (b) the desorption isotherm in Fig. 4b.



- Summary of Pore Structure of the Four Gels

Sample	Pore Volume (cm ³ /g N ₂ STP)	V_p^a	Surface Area (m ² /g)	Pore Diameter (Å) (adsorption)	Pore Diameter (Å) (desorption)	Bulk Density ^b (g/cm ³)
Two-step acid-catalyzed xerogel (A2 in Table 8)	345	0.54	740	10-50	18	1.54
Two-step acid-base-catalyzed xerogel (B2 in Table 8)	588	0.67	910	10-100	46	0.99
Particulate (one-step base-catalyzed xerogel)	686	0.70	515	10-200	125	~0.6
Two-step acid-base-catalyzed aerogel	1368	0.82 ^c	858	10-500 ^c	186 ^c	0.30

^a Volume fraction porosity based on the theoretical SiO₂ skeletal density of 2.2 g/cm³.

^b Measured at ~25% RH.

^c Because most of the adsorption occurs near P/P₀ near 1, pore volumes and pore size distributions may be inaccurate for aerogels.

