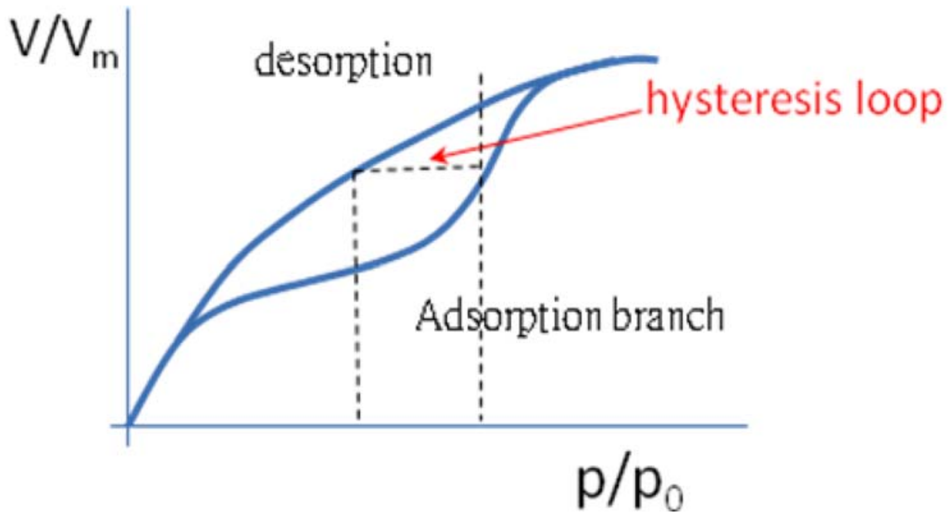
3.10. Capillary Condensation and Adsorption Hysteresis

We shall restrict our attention to the adsorption behavior of porous solids.



- **Hysteresis: two quantities of adsorbed material for each equilibrium pressure.**
- **Less adsorption for the adsorption branch relative to that for the desorption branch.**
- **In the hysteresis region, the process is irrev.,**
- **Adsorption hysteresis is often associated with porous solids. Laplace equation can provide the explanation.**

As a first approximation, we may imagine a pore to be a cylindrical capillary of radius r.

∵ r is very small, the surface of any liquid condensed in this capillary will be described by a radius of curvature relative to r.

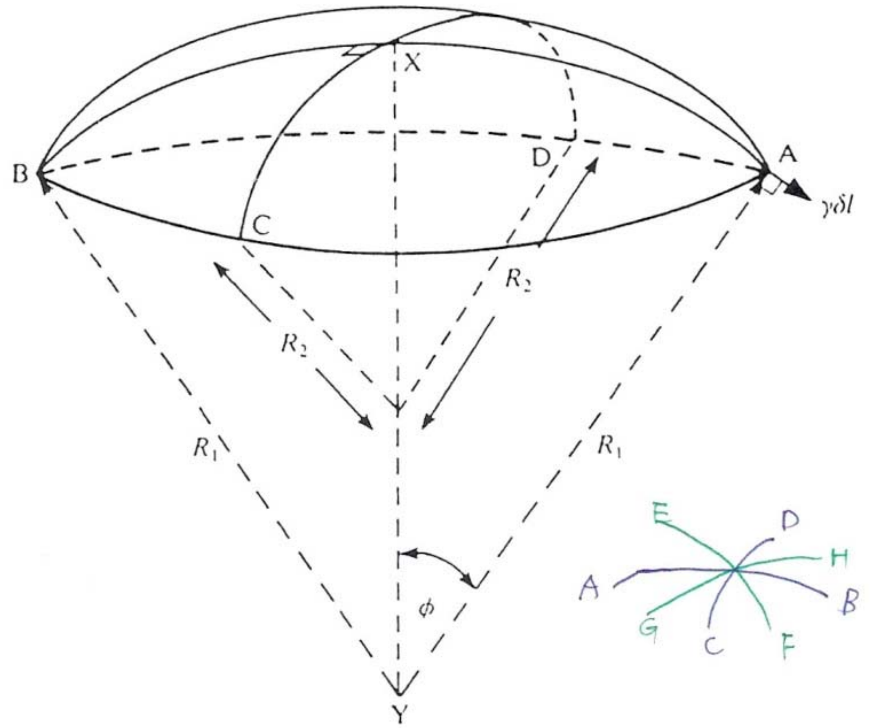


Fig. 5.3. Defining the meaning of the curvature of a surface at the point X. (See text.)

◆ **The curvature of any surface can be defined by two radii of two arcs.**
e.g. AXB: r_1 CXD: r_2

These two curves are perpendicular

and $$\frac{1}{r_1}+\frac{1}{r_2}= J = \text{const}$$

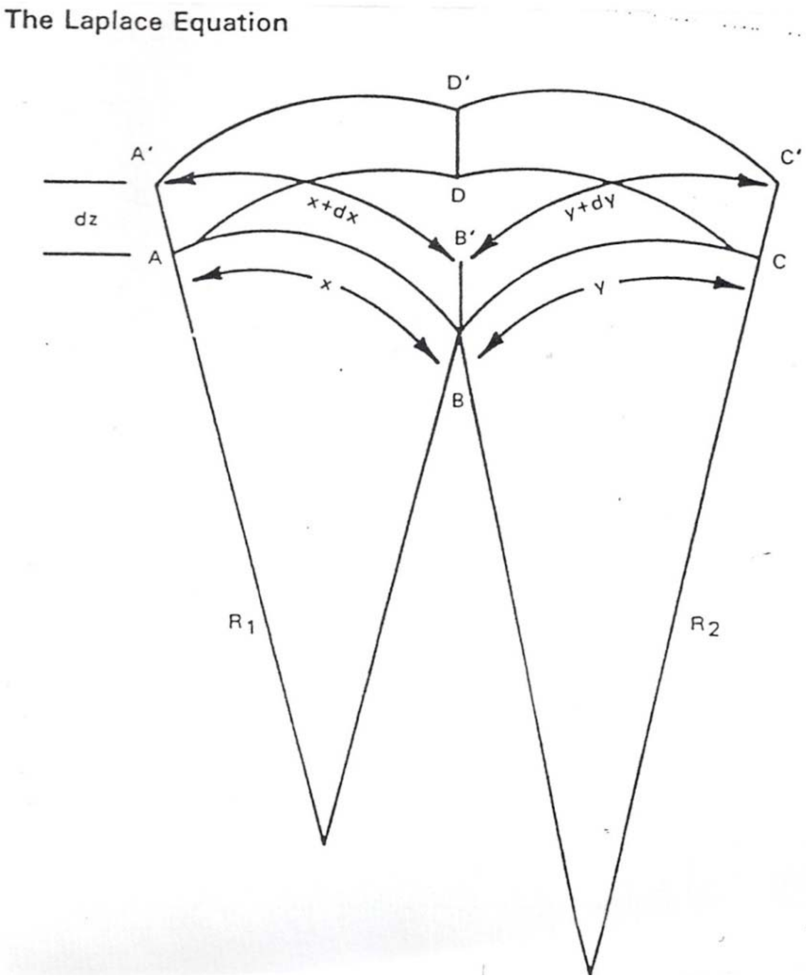
for any sets of radius pair AXB and CXD

J= "mean curvature" for any sets of the radii

The choice of radii
If $r_1 = R_1 = \max \rightarrow r_2 = R_2 = \min$

Then R_1 and R_2 are the principal radii of the curvature of the surface.

The Laplace equation can explain hysteresis



The Laplace Equation

- Suppose that a spot (ABCD) on a curved surface has been cut by two planes which are perpendicular to each other, and have radii of R_1 and R_2.
- x and y are the lengths of the curved surfaces.
- Now the surface is moved outward by a small amount (e.g. perturbation) to a new position A'B'C'D'.
- Obviously the area of the surface must increase. The work required to accomp -lish this must be supplied by a pressure difference ∆p across the surface area.

$dA = (x+dx)(y+dy) - xy = xdy + ydx + dxdy$

Surface energy increase = work expanding the surface

$\gamma(xdy+ydx) = \Delta p \cdot xy \cdot dz$ ……(1)

similar triangles $\frac{x+dx}{R_1+dz} = \frac{x}{R_1} (\rightarrow \frac{dx}{dz} = \frac{x}{R_1})$ $\quad \frac{y+dy}{R_2+dz} = \frac{y}{R_2} (\rightarrow \frac{dy}{dz} = \frac{y}{R_2})$

→ $\frac{dx}{xdz} = \frac{1}{R_1}$ **and** $\frac{dy}{ydz} = \frac{1}{R_2}$

Substituting into (1) $\Delta p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ **Laplace equation**

1. for a sphere surface $R_1 = R = R_2$ → $\Delta p = \frac{2\gamma}{R}$

$\gamma[4\pi(R+\Delta z)^2 - 4\pi R^2] = \Delta p(4\pi R^2)\Delta z$

2. for a cylindrical surface $R_1 = \infty$ R_2 = radius of the cylinder

$\Delta p = \gamma\left(\frac{1}{\infty} + \frac{1}{R}\right) = \frac{\gamma}{R}$ **$\gamma[2\pi(R+\Delta z)L - 2\pi RL] = \Delta p(2\pi RL)\Delta z$**

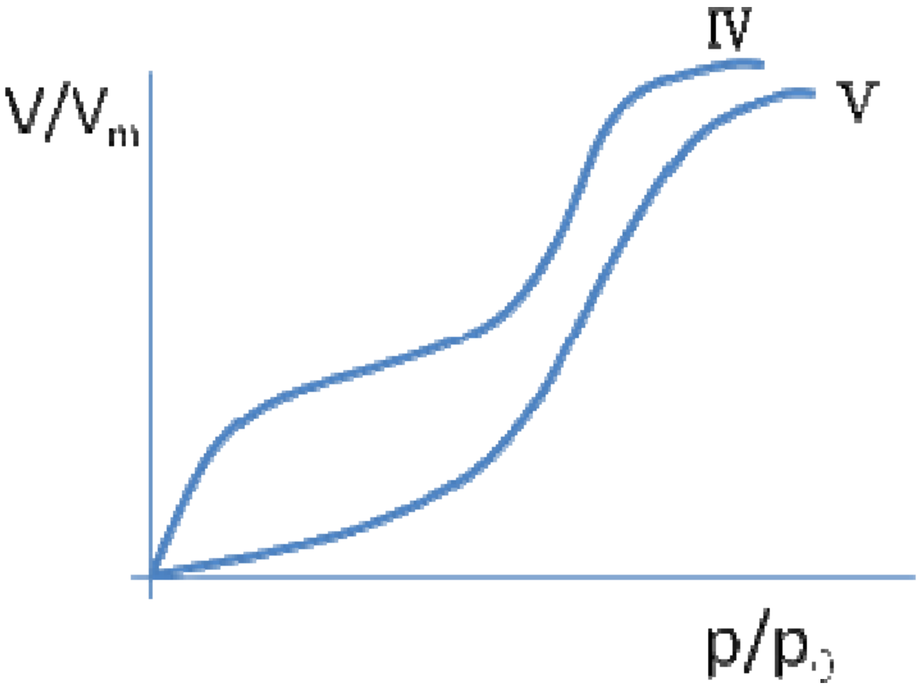
3. for a planar surface $R_1 = \infty$ $R_2 = \infty$ → $\Delta p = 0$

◆ **Implication from the Laplace equation**

For porous solids, we can imagine a pore to be cylindrical capillary of radius r,

when r ↓ → $\Delta p \uparrow$

∴ vapor will condense in small capillaries at pressures less than the normal pressure P_0 (defined for planar surface)



for Type IV and V isotherms, condensation occurs at $P < P_0$

because there are small pores inside the porous solids.

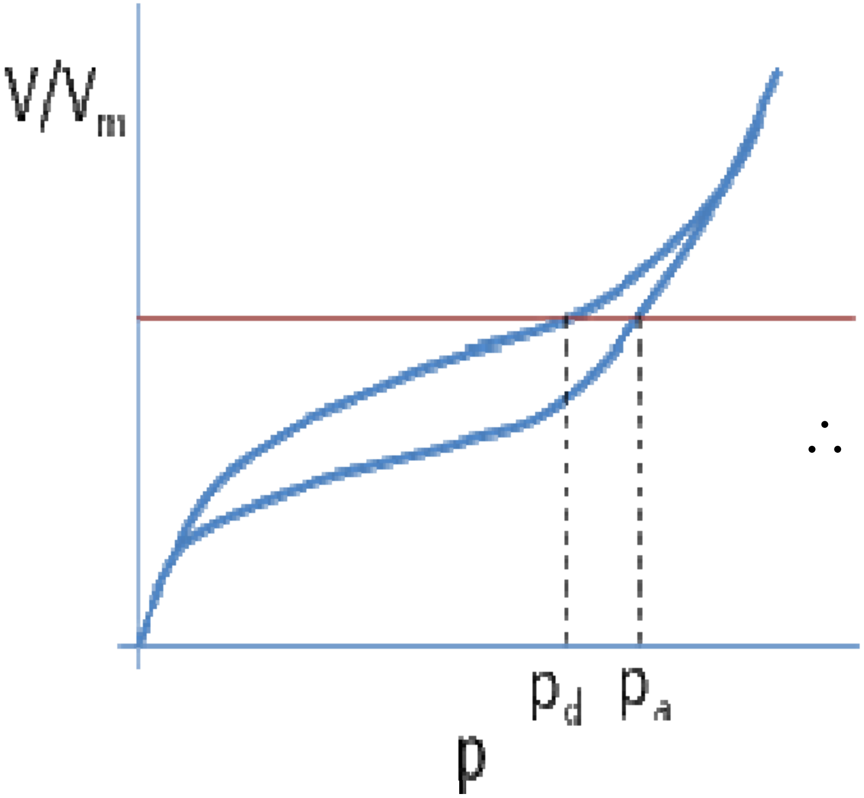
Laplace eq. describes ΔP across the interface.

<u>Kelvin</u> eq. describes the actual P for phase equilibrium on a curved plane.

$$N_A kT\ln\left(\frac{P}{P_0}\right) = -\frac{2M\gamma}{\rho R}$$

where M: molecular wt.
γ: surface tension
R: pore radius
ρ: Liquid phase density

∴R ↓ → p ↓ for condensation

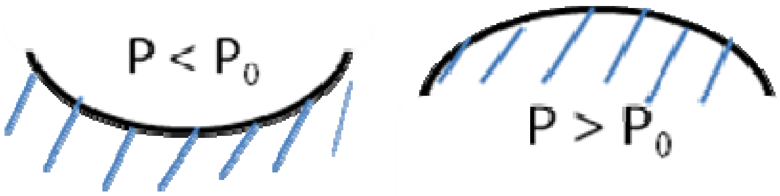


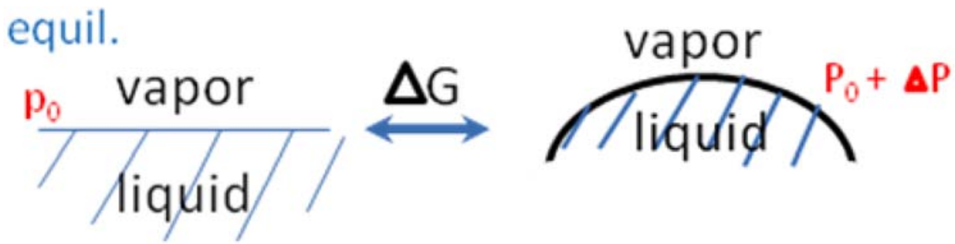
◆ **In hysteresis, adsorption occurs at relative pressures that are large than those for desorption.**

∴ **according Kelvin eq. it is as if adsorption took place in larger pores than did desorption.**

Derivation for Kelvin equation

- **It is generally observed for condensation pressure P that:**

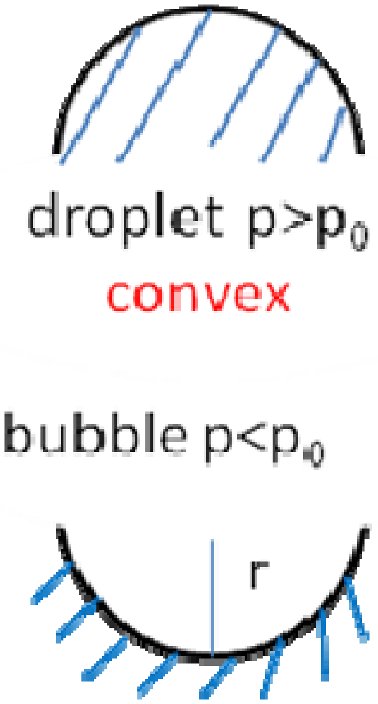




- **for liquid: dG = VdP – SdT**

$$\Delta G = \int_{p_0}^{p_0+\Delta p} \underset{\substack{\uparrow \\ \text{mol. vol of liq}}}{V_L}\, dP = \mathbf{V_L}\, \underset{\text{Laplace eq.}}{\mathbf{\Delta p} = \frac{2V_L\gamma}{r}}$$

- **for vapor:** $dG = VdP = \frac{RT}{p} dP$

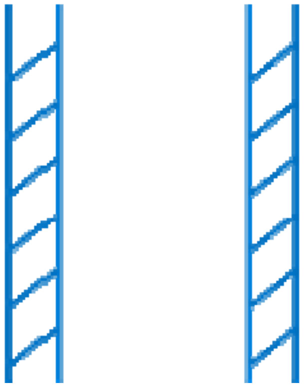


$$\Delta G = RT \ln\left(\frac{P_0 + \Delta P}{P_0}\right) = RT \ln\left(\frac{P}{P_0}\right)$$

$$\Delta G_{liq} = \Delta G_{vap}$$

$$\rightarrow + \frac{2V_L\gamma}{r} = RT \ln\left(\frac{P}{P_0}\right) > 0$$

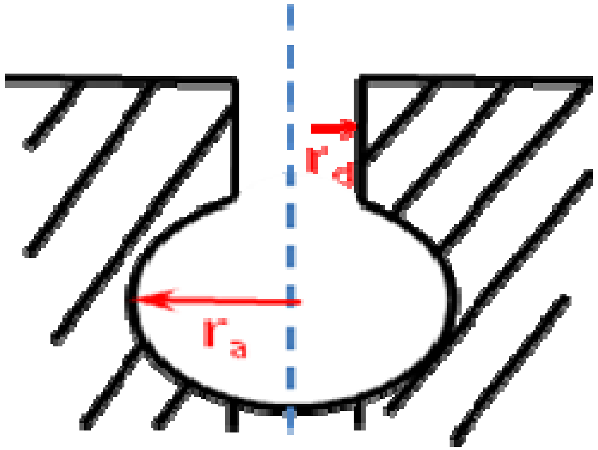
$$\rightarrow RT \ln\left(\frac{P}{P_0}\right) = -\frac{2V_L\gamma}{r} = -\frac{2M\gamma}{\rho r}$$



$$\text{cylindrical} \rightarrow RT \ln\left(\frac{P}{P_0}\right) = -\frac{M\gamma}{\rho r}$$

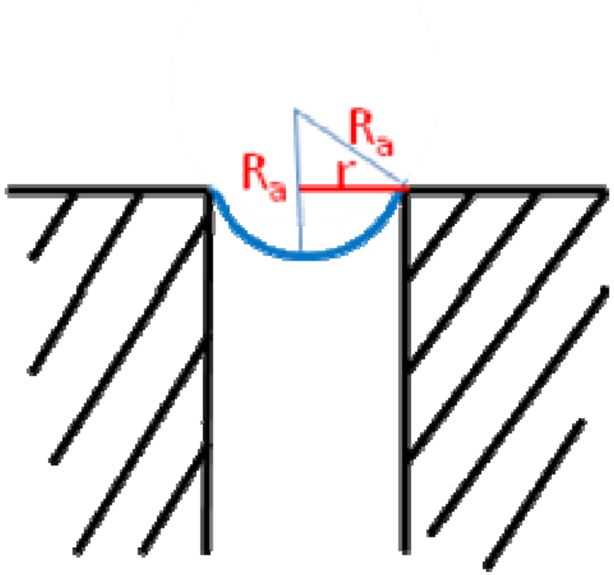
◆ Models for hysteresis (capillary condensation)

1.



ink-bottle

2.



$\because$ when liquid begins to condense, we should consider r_a, which is larger.

$\therefore$ P_a is larger.

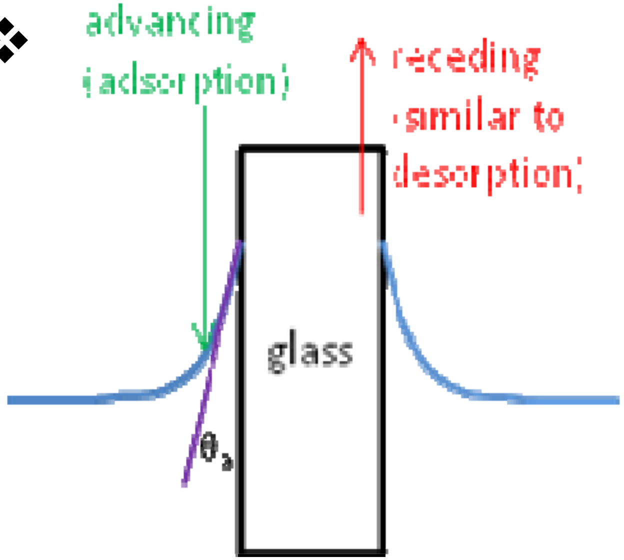
Once the pore has been filled, r_d, which is smaller, should be considered for desorption and a lower pressure is required for desorption.

$\therefore$ P_d is smaller (than P_a).

$$r = R\sin\phi = R\cos\theta$$

$$N_A kT\ln\left(\frac{P}{P_0}\right) = -\frac{2M\gamma\cos\theta}{\rho r}$$

❖



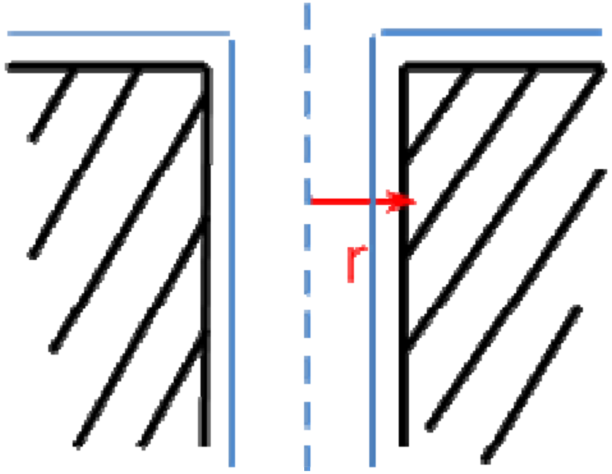
$\theta_{adv} > \theta_{rec}$

$\therefore$ **in capillary condensation ($\theta_a > \theta_d$)**

P smaller as cosθ larger (or θ smaller)

$\theta_a > \theta_d$ (it requires a smaller P to empty the capillary)

3.

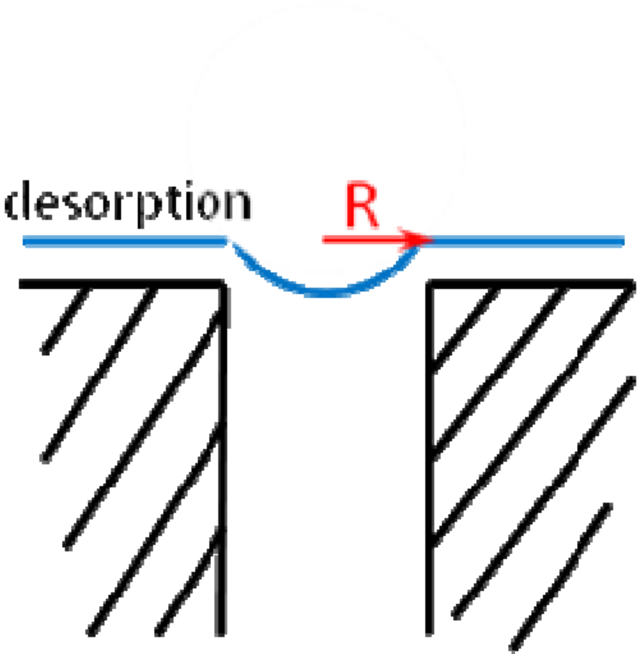


$$N_A kT\ln\left(\frac{P}{P_0}\right)_a = -\frac{M\gamma}{\rho(r-t)}$$

If t << r and R = r

t = the thickness of the adsorbed layer

(multilayer adsorption before condensation)



$$N_A kT\ln\left(\frac{P}{P_0}\right)_d = -\frac{2M\gamma}{\rho R}$$

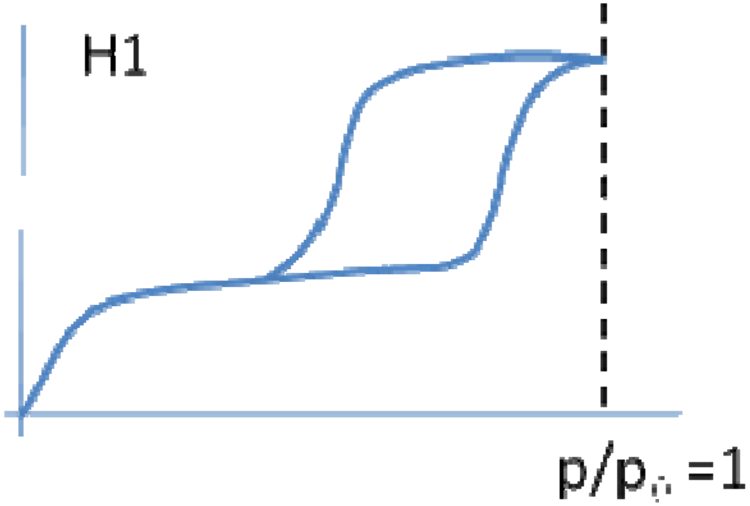
consider the same pore

$$\rightarrow \left(\frac{P}{P_0}\right)_d^{1/2} = \left(\frac{P}{P_0}\right)_a < 1$$

$\therefore P_a > P_d$ → **hysteresis behavior**

◆ Different hysteresis shapes

1.

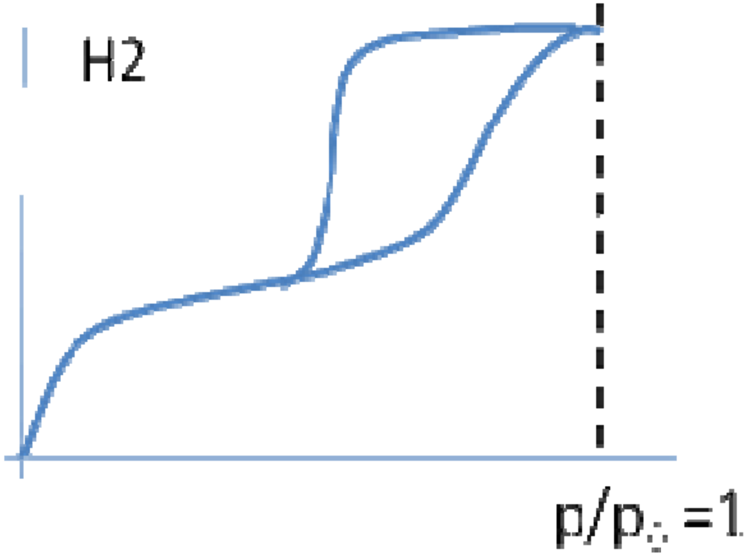


Hysteresis loop is vertical, adsorption and desorption branches are parallel.

(1) uniform size cylindrical pores (mesoporous materials)

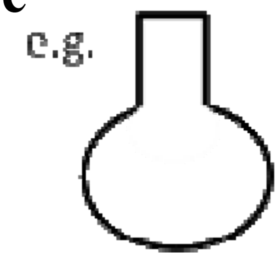
(2) agglomerates or compacts of spheroidal particles of uniform size

2.



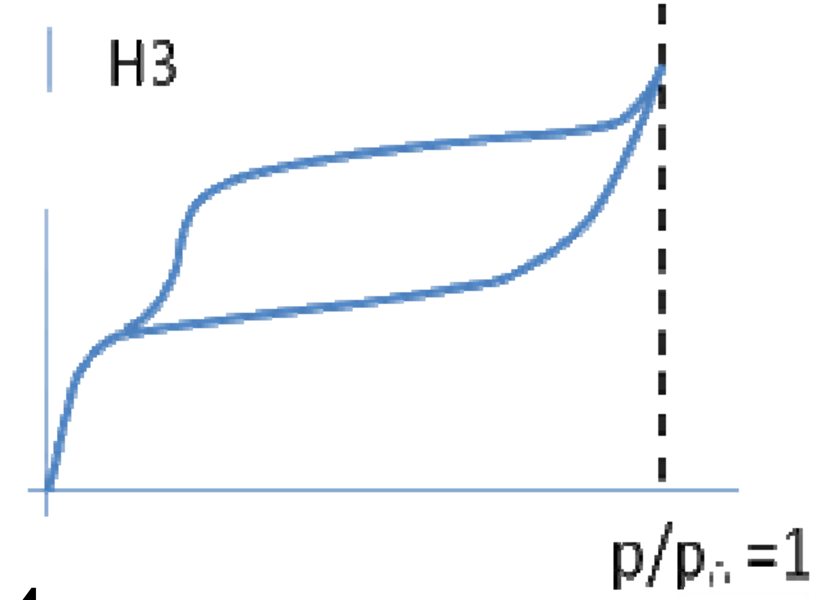
Corpuscular system (e.g. silica gels)

- ◆ **same opening size**
- ◆ **different void size**



sizes

3.

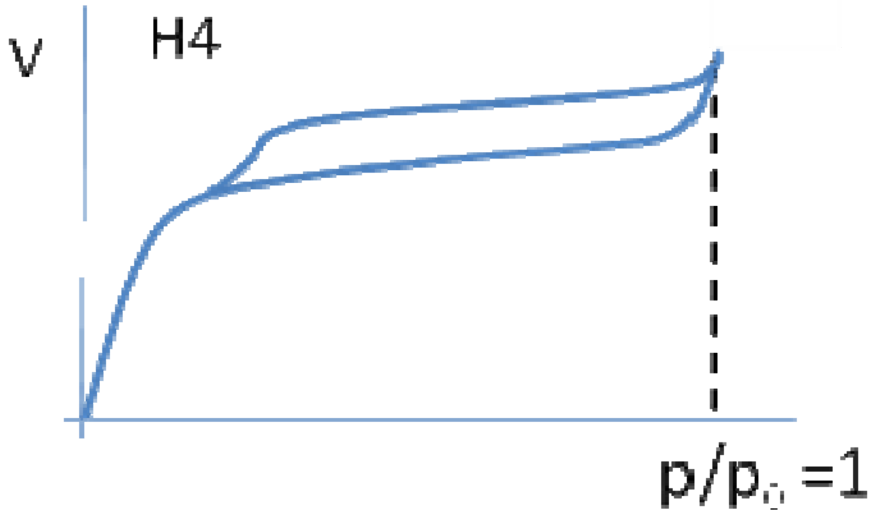


flat and parallel hysteresis

◆ **uniform size slit pores**

Slits with planar walls, adsorption branch similar to that for nonporous materials; desorption from cylindrical pores.

4.



slit-like micropores + mesopores