

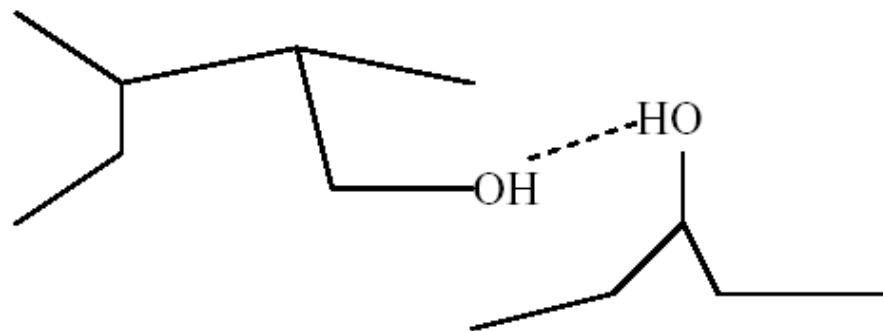
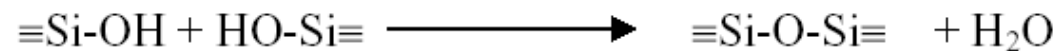
VI. Aging of Gel

The chemical reactions that cause gelation continue long after the gelation point, producing strengthening, stiffening and shrinkage of the network.

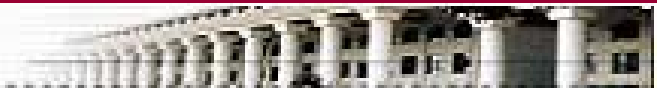
For different mechanisms:

(A) Polymerization

Increase in connectivity of the gel network produced by condensation reactions



Producing new bridging bonds \Rightarrow stiffening and strengthening the network

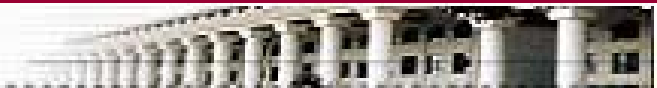
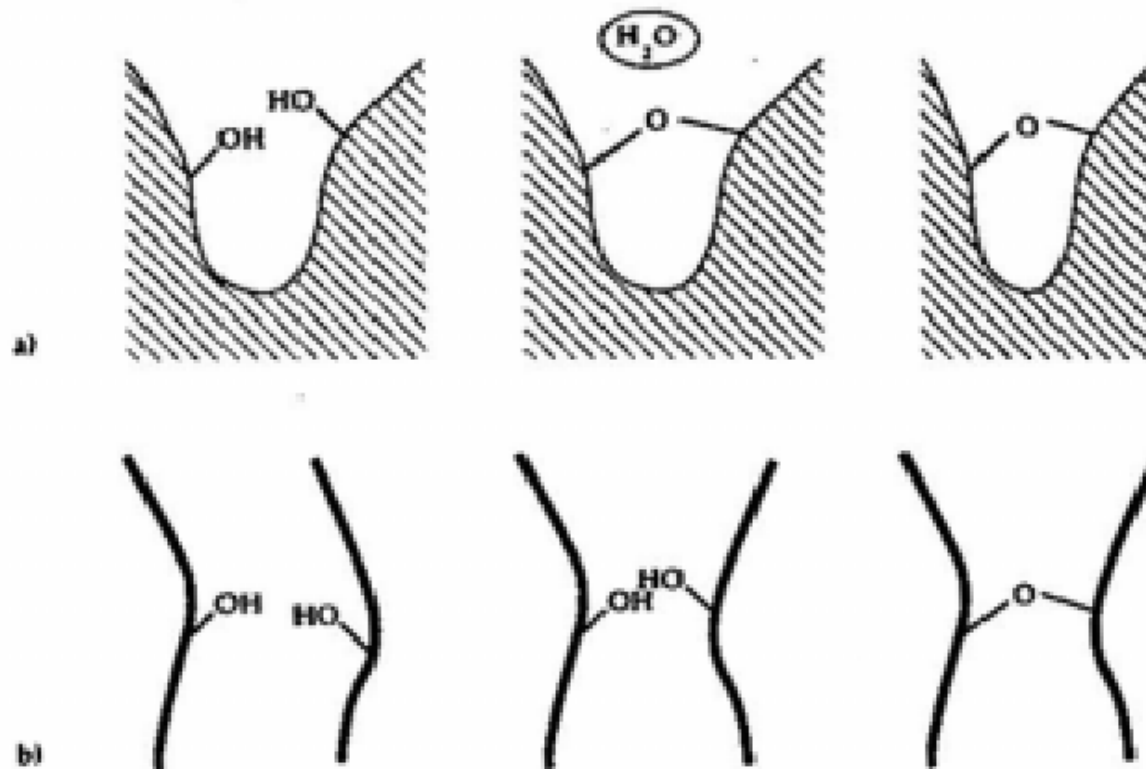


(B) Syneresis

Shrinkage of the gel network resulting in expulsion of liquid from pores

-Macroscopic Syneresis (Macrosyneresis)

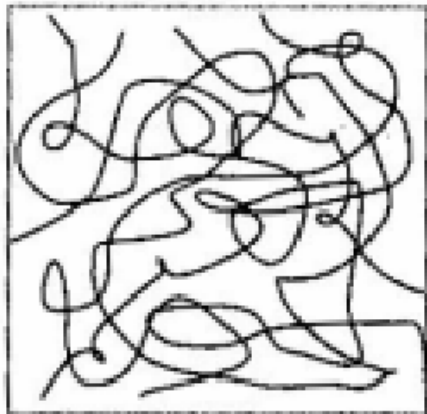
The whole gel network shrinks as a result of the continuous condensation.



-Microsyneresis

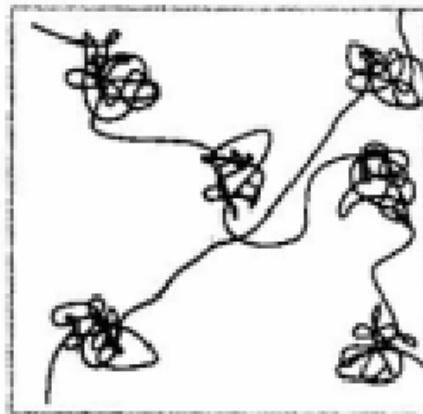
Phase separation in which the polymers cluster together, creating regions of free liquid.

Driving force: greater affinity of the polymer for itself than for the pore liquid.



A

Uniform network

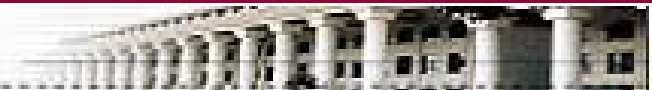
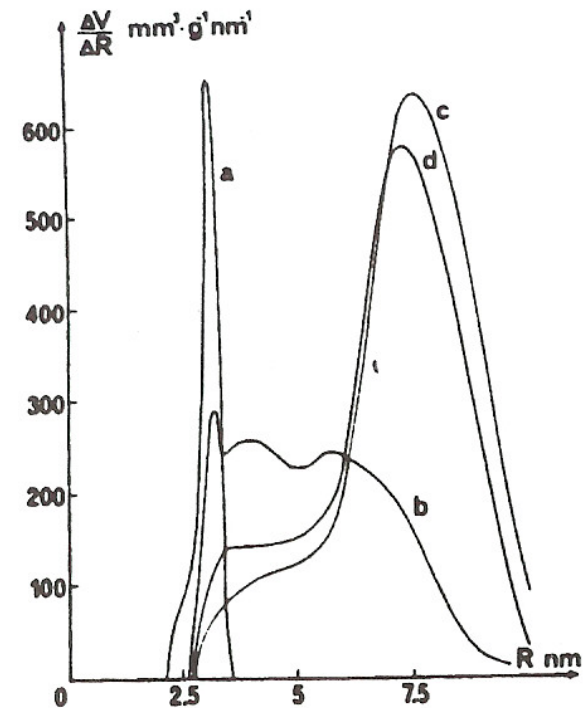


B

Phase separated

Effects of microsyneresis on the pore size distribution of a titania gel:

- a – 0 day
- b – 1 day
- c- 9 days
- d – 45 days

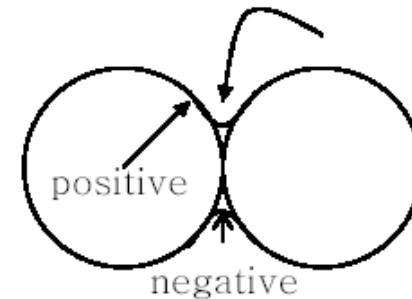


(C) Coarsening or Ripening

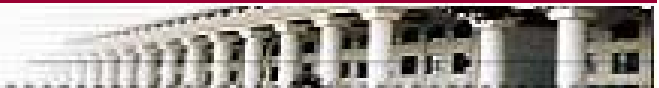
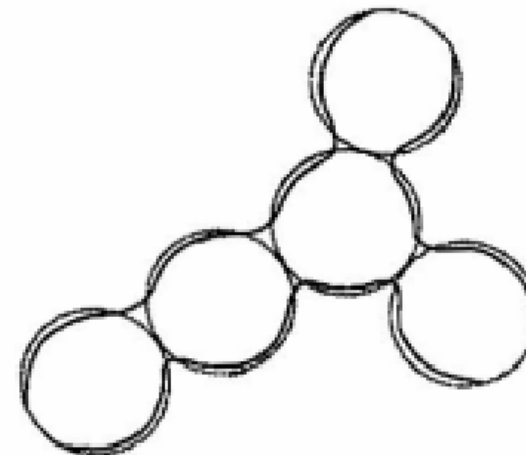
Dissolution and reprecipitation driven by differences in solubility (referred to Ostwald mechanism)

$$S(\text{positive curvature}) \geq S(\text{negative curvature})$$

Materials dissolves from the surface of particle with positive curvature and depositive in regions with negative curvature.



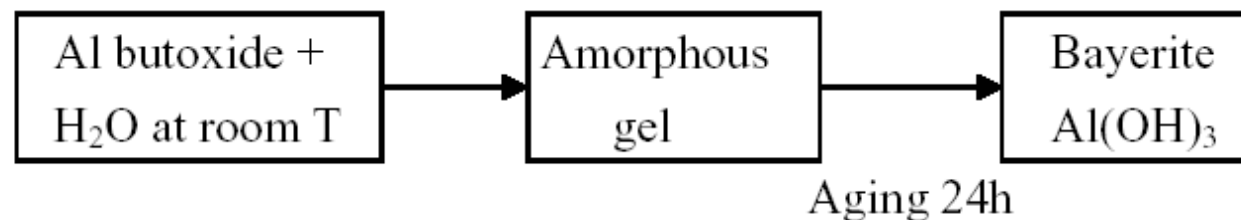
Dissolution and reprecipitation
Causes growth of necks between
Particles, increasing the strength
and stiffness of the gel.



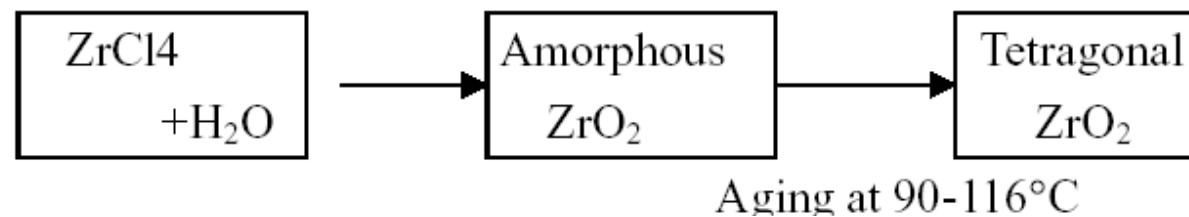
(D) Phase Transformation

Many gels or precipitates of hydrous oxides are amorphous as formed, but aging of the solution allows reorganization of the structure, resulting in a crystalline product.

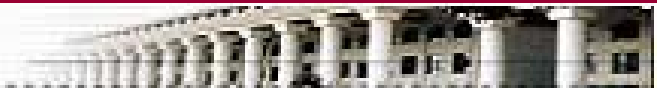
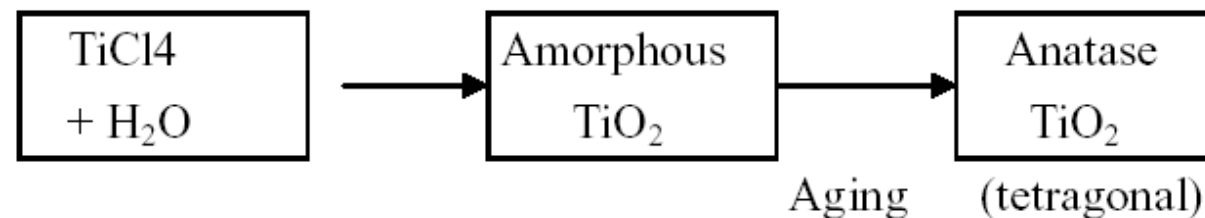
Alumina Gel



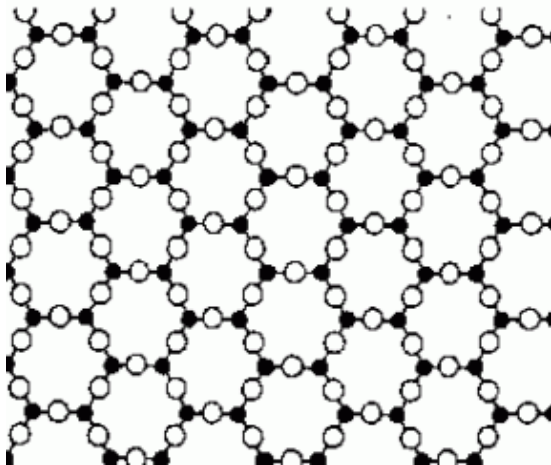
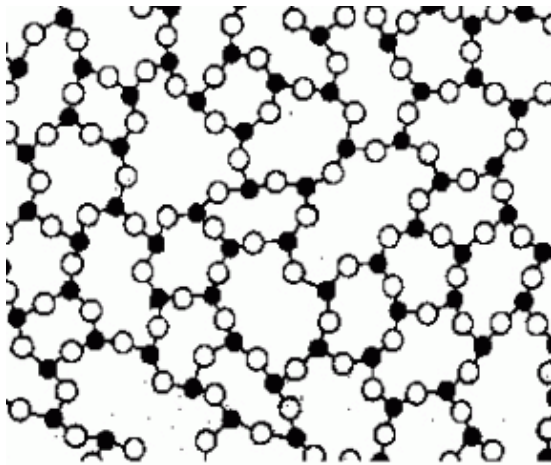
Zirconia Gel



Titania Gel



amorphous



crystalline

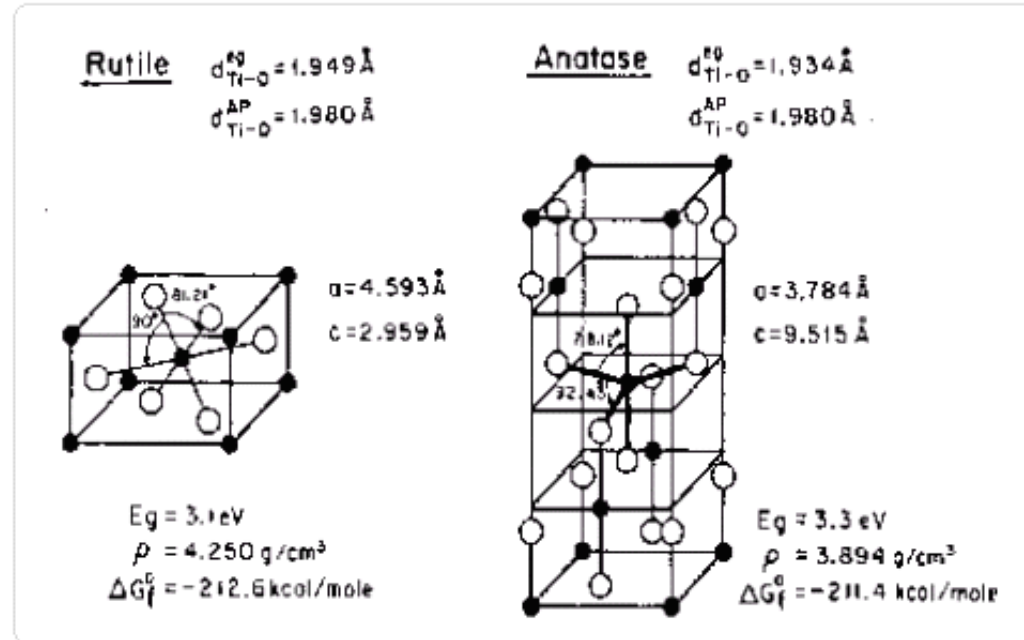
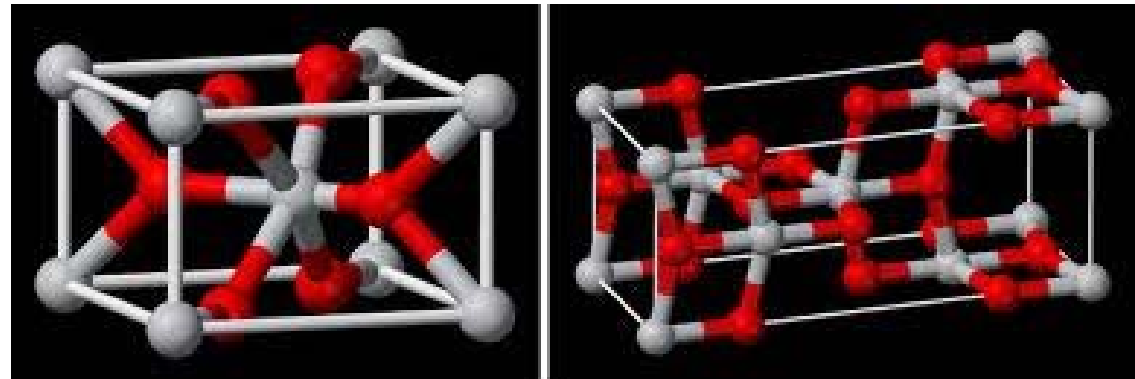


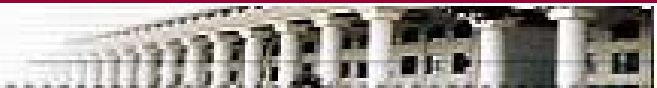
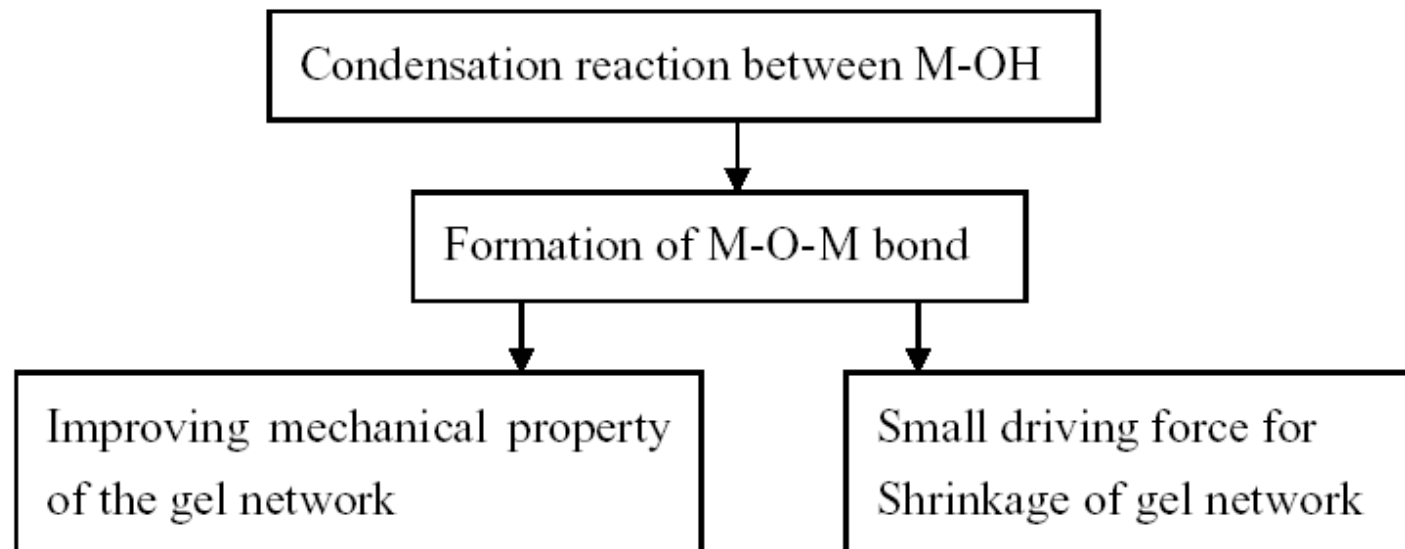
그림 1-5 TiO₂의 rutile과 anatase 의 구조비교



Driving Force For Shrinkage

◆ Chemical Reactions (Attraction Force)

The attraction force for the solid network results from condensation reactions between M-OH groups, i.e. formation of M-O-M bonds between solids. The chemical reactions are less important for their contribution to the driving force for shrinkage than for their impact on the mechanical properties of the gel.



◆ Disjoining Force (Repulsive Force)

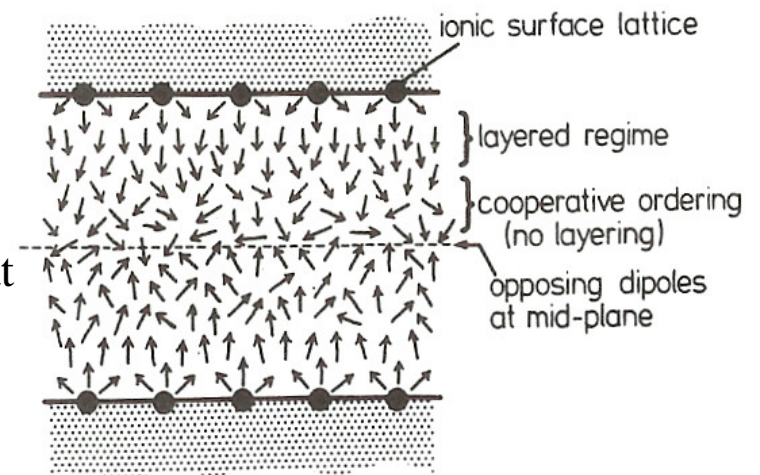
Double-Layer Repulsion



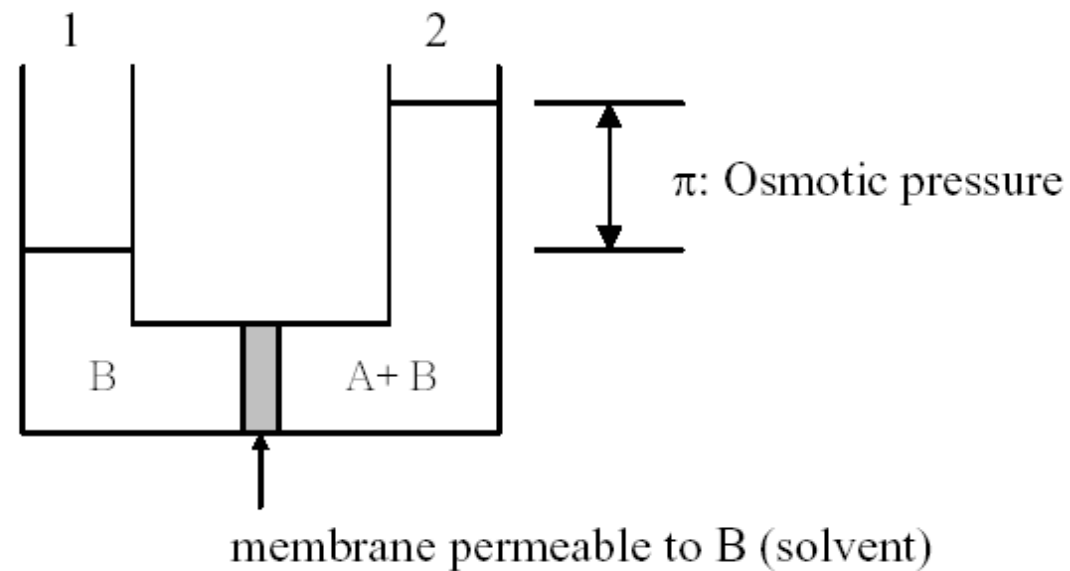
Structural-Layer Repulsion

Liquid molecules adopt a special structure in the vicinity of a solid surface, inhibiting close approach of surface, as they resist overlapping.

Orientation of water molecules around a charged hydrophilic surface. The molecules closest to each surface exhibit a diffuse layered structure; beyond that there may be some cooperative ordering.



◆ Osmosis Forces

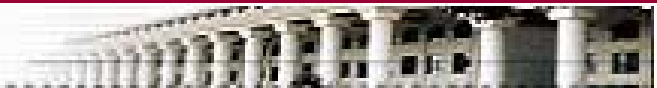


Osmosis is a process of diffusion driven by a chemical potential gradient.

$$\text{Side 1: } \mu_B^1 = RT \ln P_0 + \mu_0$$

$$\text{Side 2: } \mu_B^2 = RT \ln P_V + \mu_0$$

$$\frac{P_V}{P_0} = x_B < 1 \Rightarrow \mu_B^2 < \mu_B^1$$



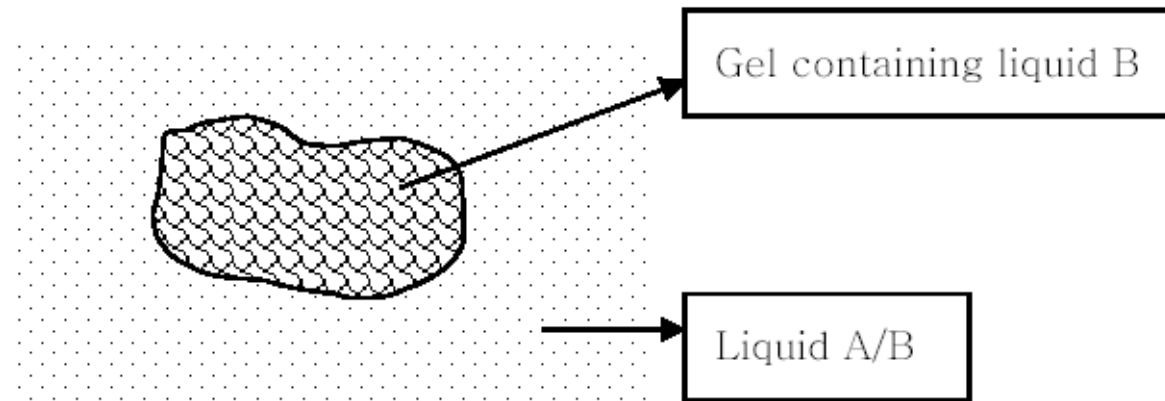
To increase μ_B^2 , one has to raise P at side 2. The increase in P in side 2: $\Delta P = \pi$

$$V_m \Delta P = \pi V_m = \mu_B^1 - \mu_B^2$$

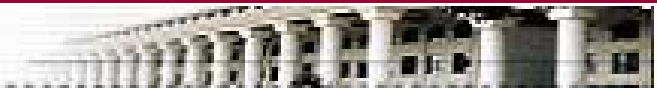
$$\pi = -\left(\frac{RT}{V_m}\right) \ln(x_B)$$

V_m : molar volume of the solvent B

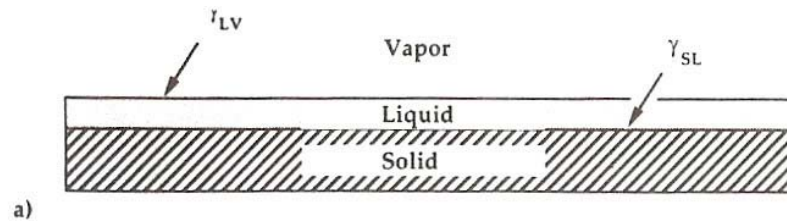
For gel



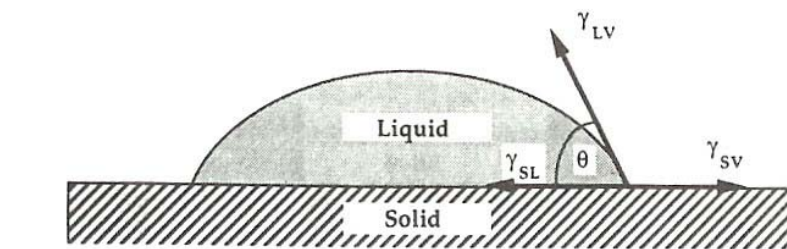
If only liquid B can permeate out of the gel, but liquid A can not permeate into the gel,
Will the gel swell?



◆ Capillary Forces (Attraction Forces)



(a) Liquid film on solid surface has two interfaces with energies γ_{SL} and γ_{LV}



(b) Contact angle θ is determined by balance of forces at intersection of solid-vapor and liquid-vapor interfaces

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$

The change in energy, ΔE , produced by spreading of a liquid film on a solid surface is

$$\Delta E = (\gamma_{SL} - \gamma_{LV}) - \gamma_{SV}$$

γ : specific energy of an interface (surface tension)

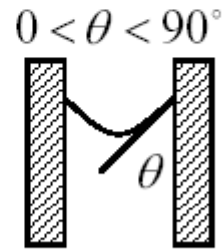


If $\Delta E \leq 0$, liquid spreads spontaneously (Fig. (a))

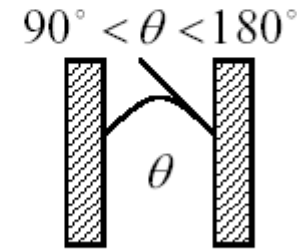
If $\Delta E > 0$, result is shown in Fig. (b).

Balance of tension in Fig.(b) gives:

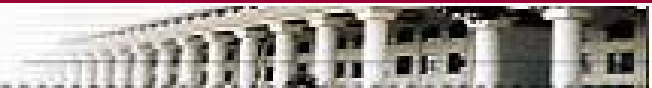
$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta$$



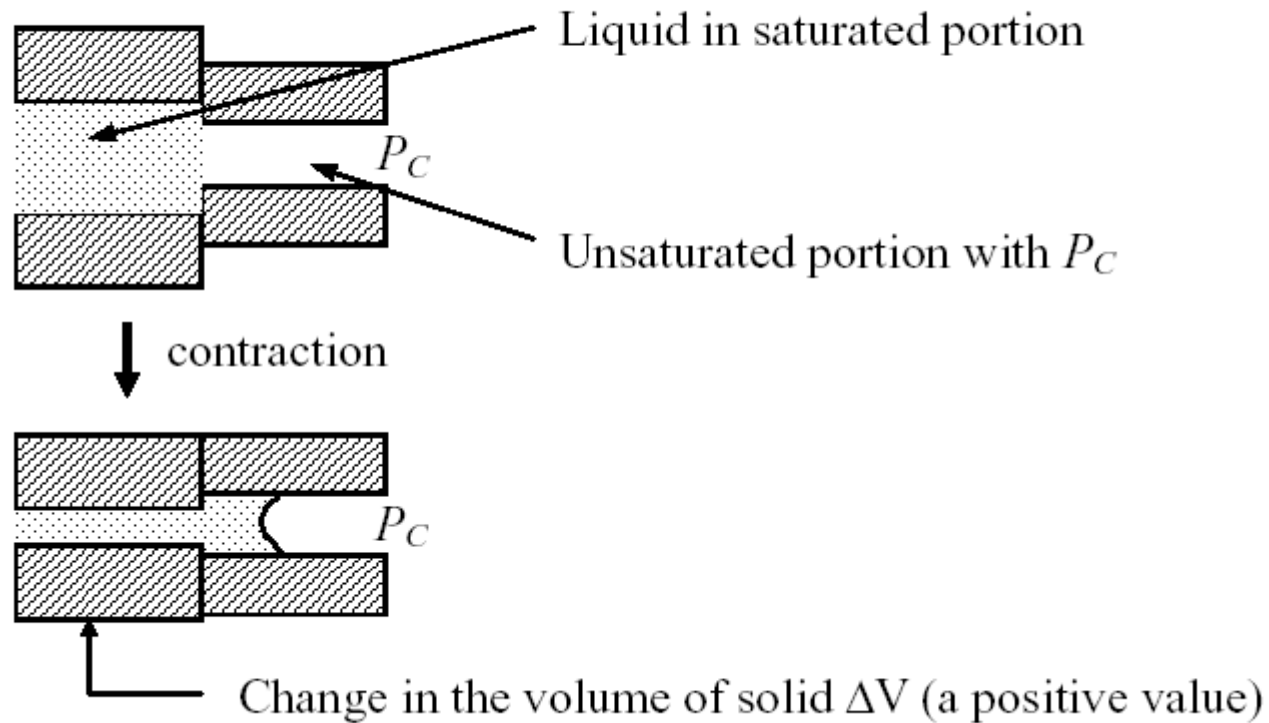
water intrusion



Hg intrusion

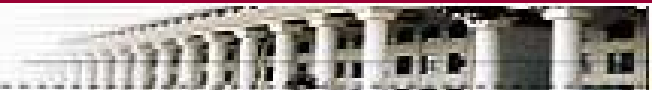


Capillary Pressure (P_C)



Work done by liquid in the contraction process:

$$W = - P_C \Delta V \quad (\text{sign “-” means work done by solid on liquid})$$



The energy increase of liquid due to the covering of more solid surface:

$$\Delta U = (\gamma_{SL} - \gamma_{SV}) \Delta V (S_p / v_p)$$

S_p : specific surface area

v_p : pore volume

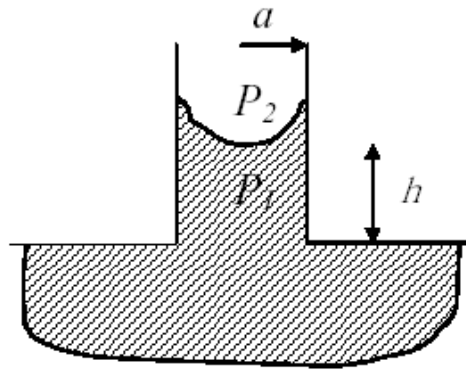
Since $\Delta U = -W$,

$$P_C = -(\gamma_{SV} - \gamma_{SL})(S_p / v_p) = -\gamma_{LV} \cos \theta (S_p / v_p)$$

For $0 < \theta < 90^\circ$, $P_C < 0$



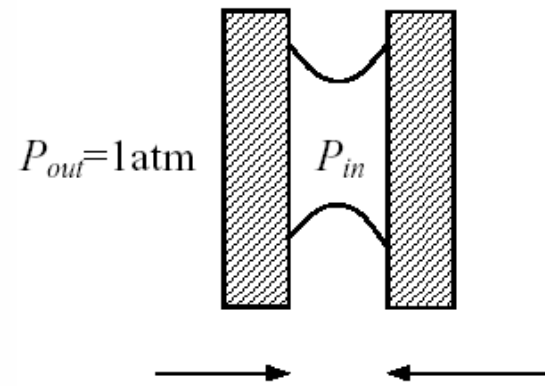
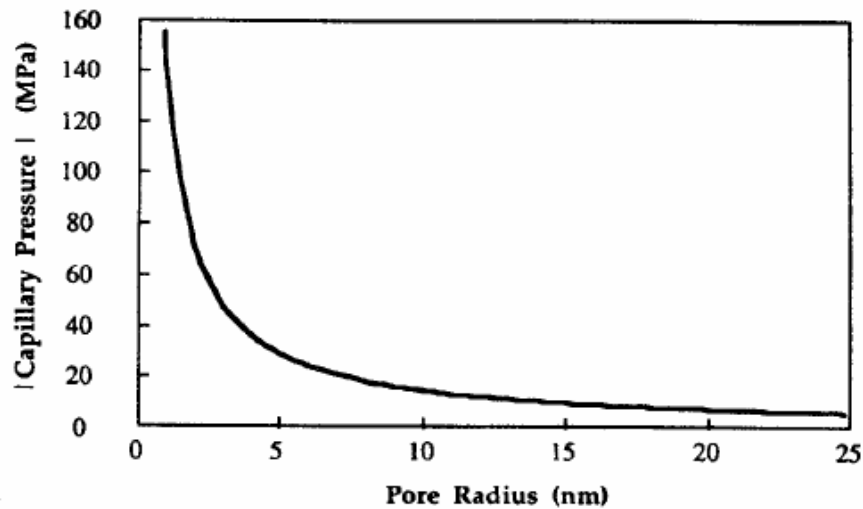
Capillary Tube



$$P_1 - P_2 = \Delta P = P_C < 0$$

$$P_1 < P_2$$

$$S_p = 2\pi ah, \quad v_p = \pi a^2 h \quad \Rightarrow \quad P_C = -\frac{2\gamma_{LV} \cos\theta}{a}$$



$$P_{in} - P_{out} = P_C < 0$$

$$\Rightarrow P_{in} < P_{out}$$

