VII. Drying of Gel

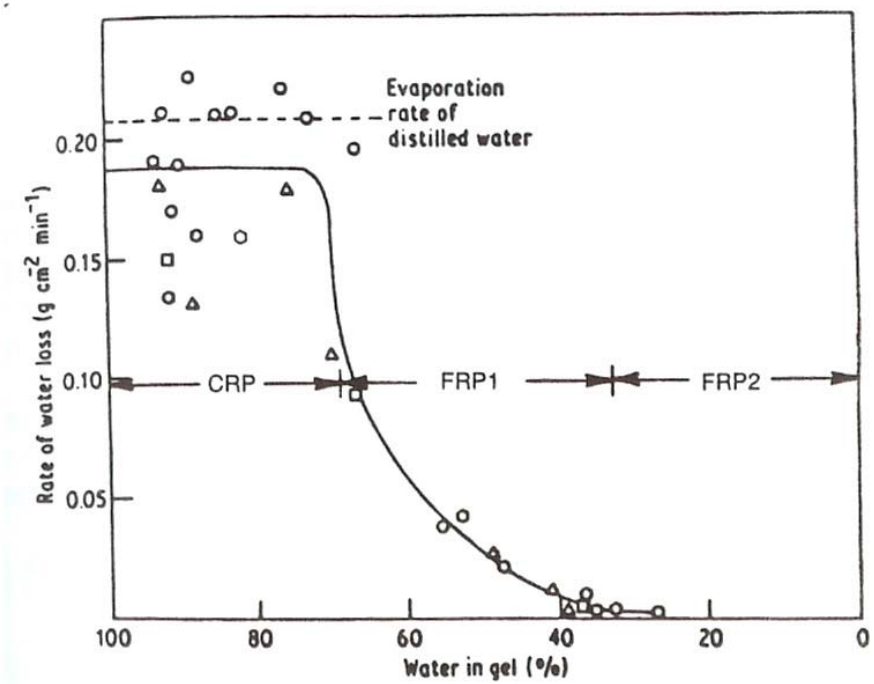
General

Three stages (periods) of the gel drying process

Constant rate period (CRP)

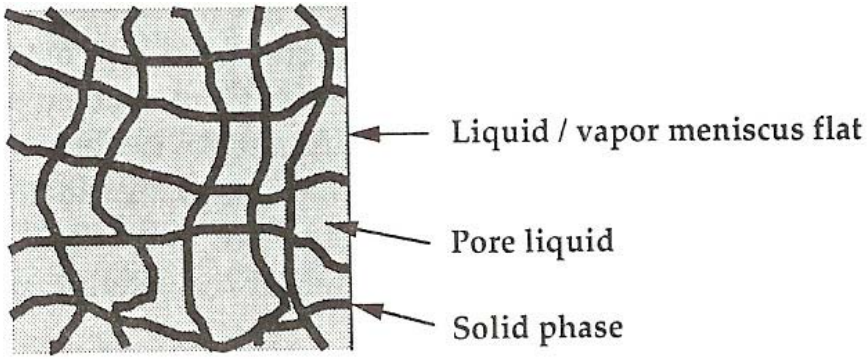
First falling rate period (FRP1)

Second falling rate period (FRP2)



- Constant Rate Period

Mass Transfer Rate (Evaporation Rate)



$$q = k\,(P_V - P_A) \qquad (1)$$

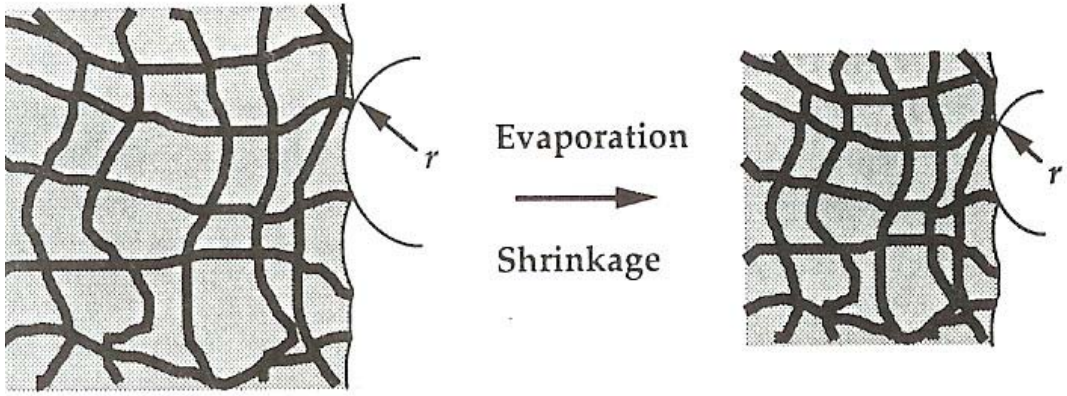
q: Evaporation rate

k: evaporation mass transfer constant

P_V : saturated vapor pressure on surface

P_A : ambient vapor pressure of solvent (constant)

In CRP



Vapor pressure in concave surface

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

$$k = -1/r$$

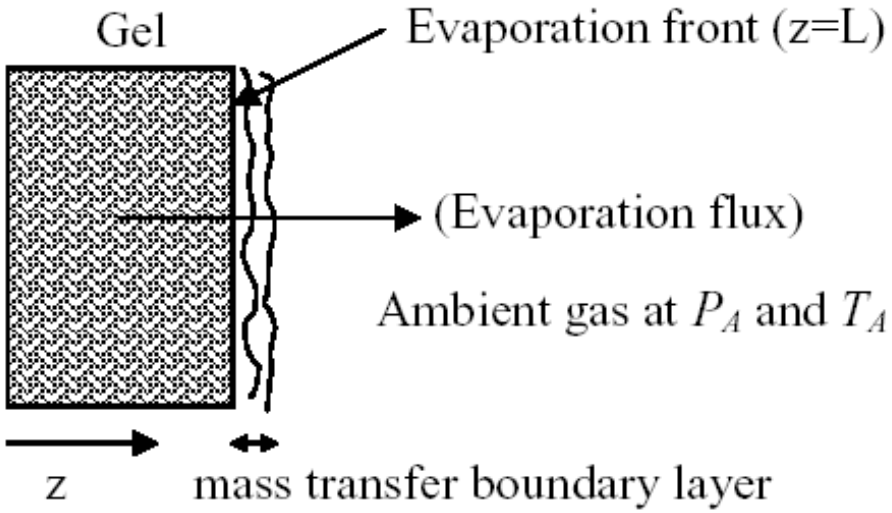
Capillary Pressure

$$P_C = -2\gamma_{LV} / r$$

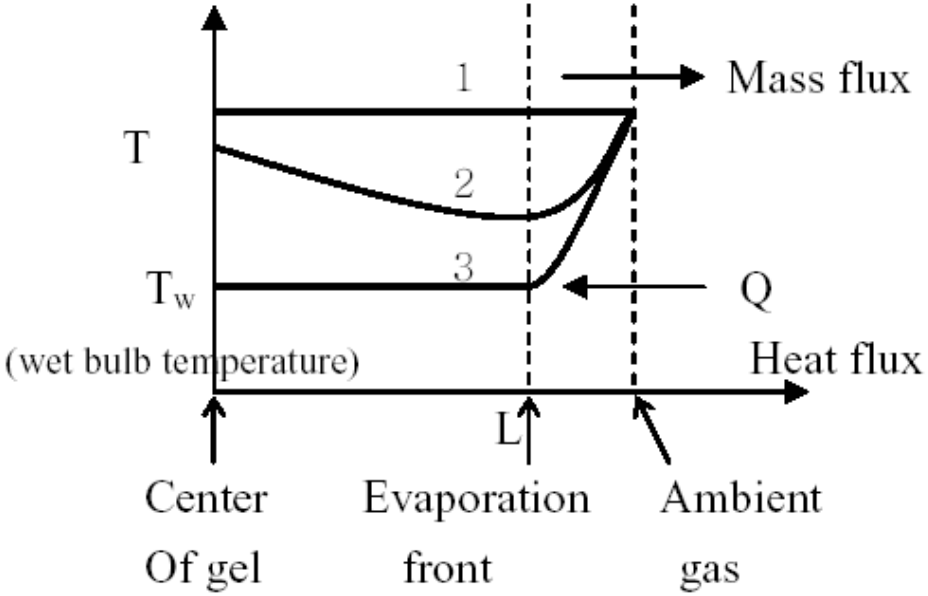
Small capillary force ⇒ shrinkage of gel (5-10 times in volume) ⇒ pore size decreases

⇒curvature of solvent surface unchanged ⇒ P_V constant

Heat Transfer



At z=L liquid-vapor phase transformation ⇒ heat consumed ⇒ temperature decreases in z around L ⇒ eventually steady state reaches



1. before drying
2. drying starts
3. Equilibrium (steady state)

Heat flux at steady state:

$$Q = k_h (T_A - T_W) \qquad (2)$$

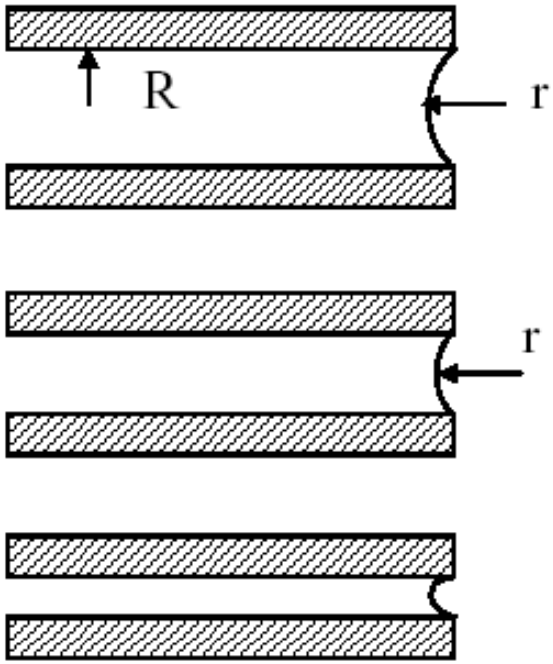
Also $Q = q \Delta H$

Heat of evaporation

Combination of eq.(1) and (2) gives:

$$P_A \downarrow \Rightarrow q \uparrow \Rightarrow Q \uparrow \Rightarrow T_W \downarrow$$

- Critical Point



(a) CRP, Initially

r : radius of meniscus

R: radius of Pore

(b) CRP, Network shrinks

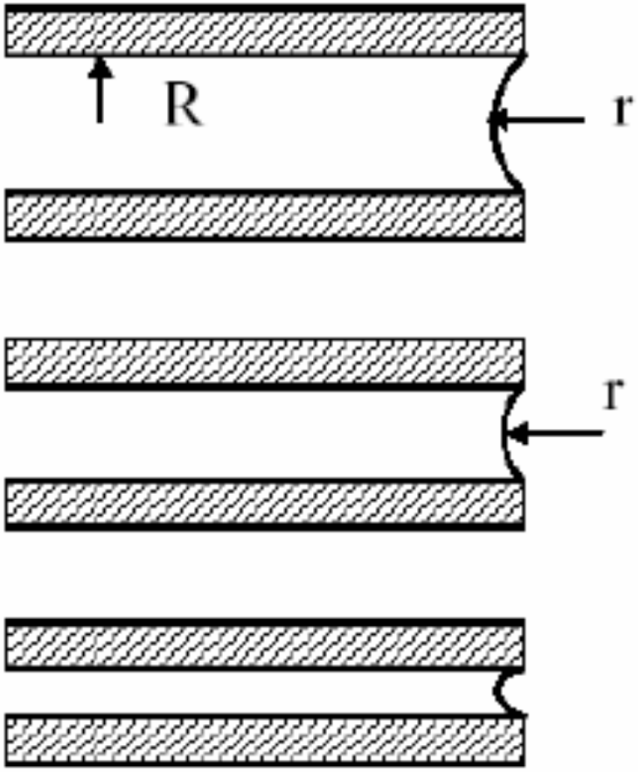
r is the same as in (a)

(c) Critical point

The network stiffens, shrinkage becomes negligible, r=R

↓

Critical volume fraction of solid



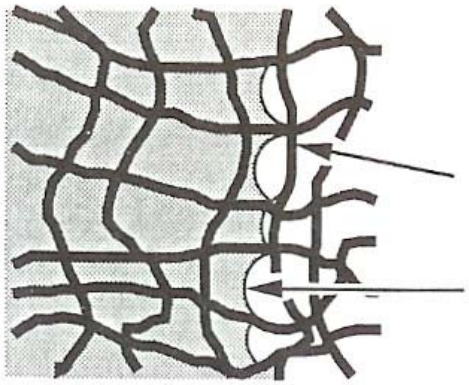
(a) The capillary pressure is low, and r>>R

(b) As drying proceeds, the network becomes increasingly stiff, because new bonds are forming and the porosity is decreasing, and the tension in the liquid rises correspondingly.

(c) Once the radius of the meniscus becomes equal to The radius of the pores in the gel, the liquid exerts The maximum possible force. ⇒ the end of CRP

Beyond that point, the tension in the liquid cannot overcome further stiffening of the gel network, so the meniscus recedes into the pores, leaving air-filled pores near the outside of the gel

- First Falling Rate Period



Maximum capillary pressure:

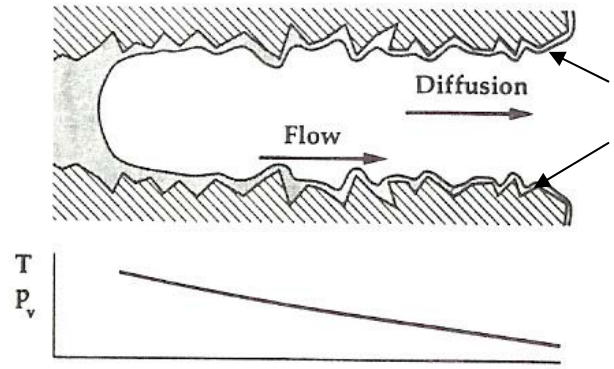
$$P_R = \frac{(\gamma_{SV} - \gamma_{SL})\, S_p}{V_p}$$

. Evaporation front is located at the exterior surface

. Liquid has continuous path to the outside

. Liquid flow is driven by capillary pressure

Flow in liquid phase (dominant)



Evaporation (large Pv)

Capillary pressure gradient is the driving force

$$J = -\left(\frac{F}{\mu}\right)\left(\frac{dP_L}{dz}\right)$$

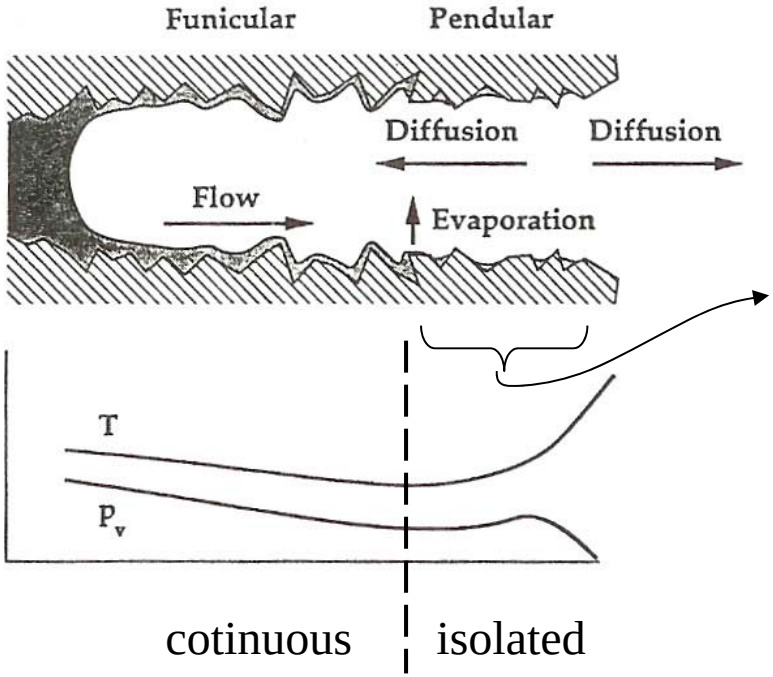
F: permeability in Darcy's equation

Temperature gradient is due to the consumption of heat by the evaporations at the exterior surface.

$$Lower\ T \rightarrow \begin{pmatrix} higher\ \gamma_{LV} \\ lower\ P_0 \end{pmatrix} \rightarrow lower\ \ P_V$$

Therefore the vapor pressure gradient provides the driven force for diffusion of the vapor molecules.

- Second Falling Rate Period



Liquid in outer region is isolated in pockets so no liquid flows in the direction to the outside

. Evaporation front is inside the solid network

. Minimum temperature is at the region where the evaporation takes place (inside the network)

. Mass transfer takes place via liquid flow and vapor diffusion

- Drying Rate

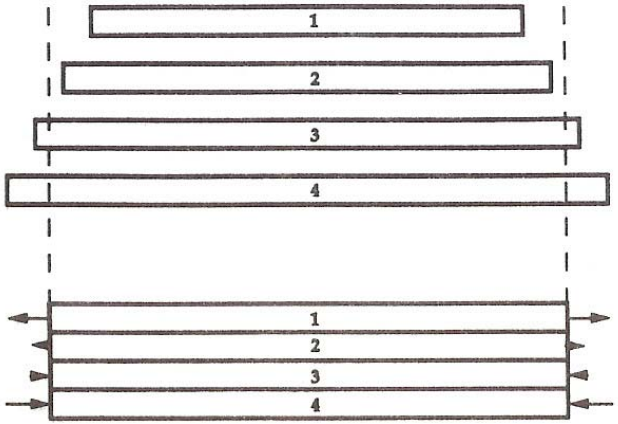
q =	(Rate constant)	×	(Driving force)
CRP	Mass transfer coefficient k		$(P_V - P_A)$
FRP (liquid)	Permeability F in Darcy's eqn.		Capillary pressure Gradient
FRP (vapor)	Knudsen diffusivity		Vapor pressure gradient

Stress and Crack

– Crack Formation

Free strain

True strain



At the exterior

↓

Higher tension

↓

Greater contraction

↓

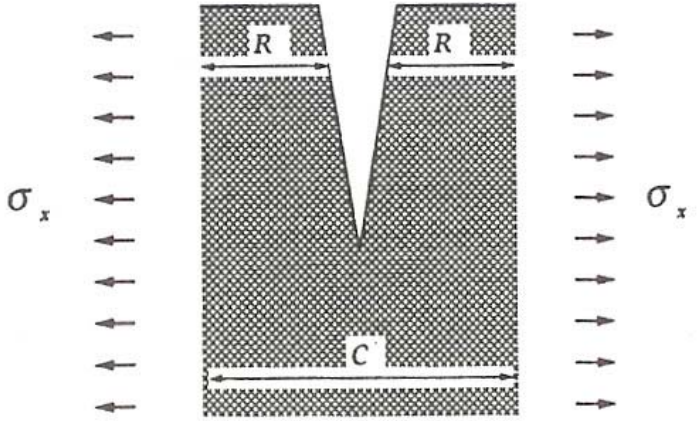
Inhibited by slower contraction interior,

which “stretch” the exterior

↓

“CRACK”

Exterior



The greatest tension (stress) is P at z=L (exterior surface of gel)

$$\sigma_x \approx P - \langle P \rangle$$

at z=L

$$\sigma_x = \frac{\dot{H}_G \dot{V}_E}{L}\left[\frac{\alpha \cosh(\alpha z / L)}{\sinh(\alpha)} - 1\right]$$

where $\alpha = \sqrt{L^2 \eta_L / D H_G}$

When $\alpha \le 1$,

$$\sigma_x(L) = L \eta_L \dot{V}_E / 3D$$

So, $L\uparrow,\ \dot{V}_E\uparrow,\ \eta_L\uparrow, D\downarrow \Rightarrow \sigma_x(L)\uparrow$

Note: Capillary pressure does not appear in the above equation. The crack (or stress) is caused by the difference in the pressure through the thickness of the drying body, not the capillary itself.

However, the larger the capillary pressure, the more a drying gel shrinks, and the smaller the permeability D. Thus, $D\downarrow \Rightarrow \sigma_x(L)\uparrow$, so a larger capillary pressure will cause a higher tension at the drying surface.

For a gel with a pore size distribution,

Smaller pores → larger capillary pressure

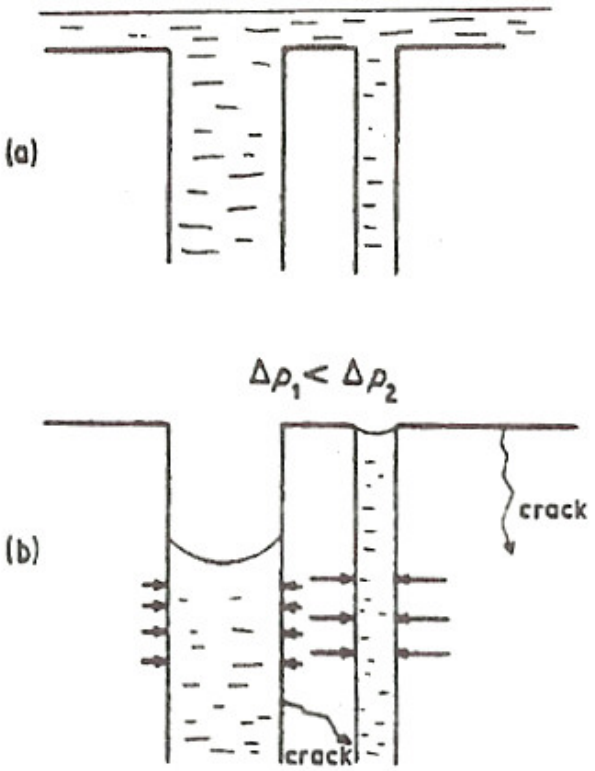
Larger pores → smaller capillary pressure

⇓

Nonuniform stress along the gel surface

⇓

Crack formation



- Methods to Avoid Cracking

Preparing gels with uniform and large pores

Large pores → Smaller capillary pressure ⇒ smaller pressure (stress) gradient
Large permeability

However, the pore size of a gel is limited (or determined) by the preparation method and material, as well as the requirement of final product. Furthermore, to get a dense body by sintering, a dried gel with a larger pore size will require a higher sintering temperature.

Aging of Gel

Aging a gel before drying → Strengthen the network → Reduce the risks of fracture

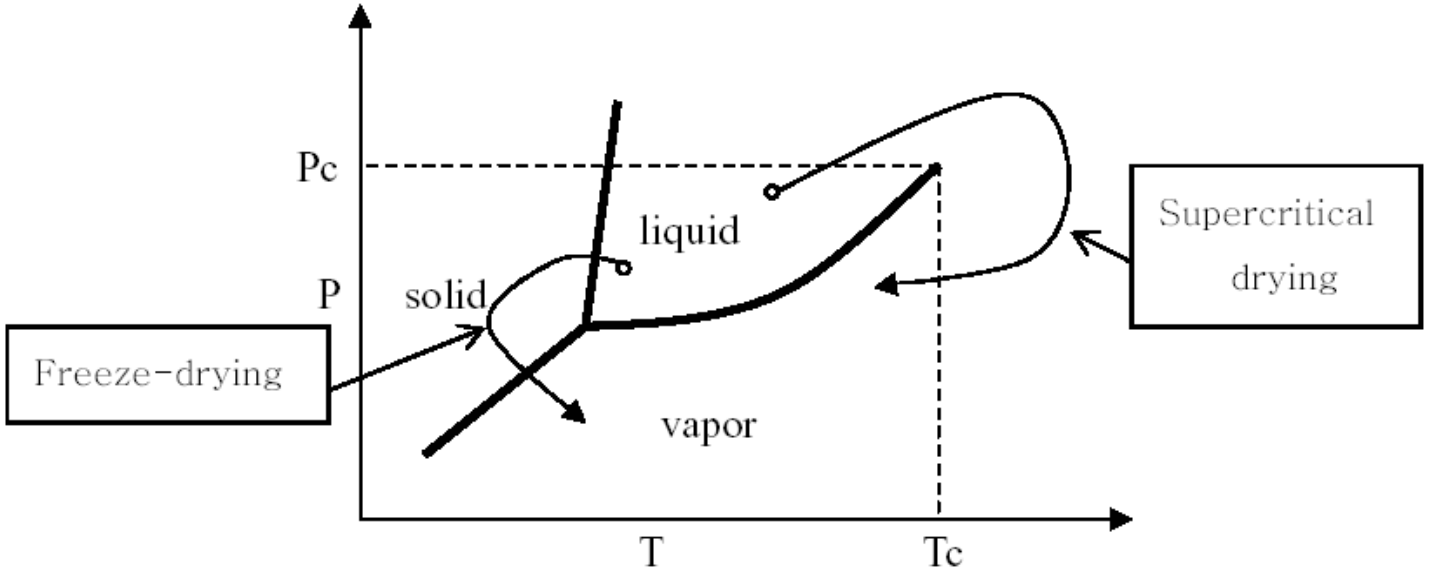
Chemical Additives

By doping a group of chemicals, known as drying controlled chemical additives (DCCA) (e.g. PVA) in the sol (or gel), the additives strongly adsorb on the gel surface and are likely to reduce the capillary pressure in two ways;

(1) by forming a film on the surface of gel (properties), it reduces the contacting angles,

(2) because of its low vapor pressure it will not evaporate, but will be retained in the smallest pores.

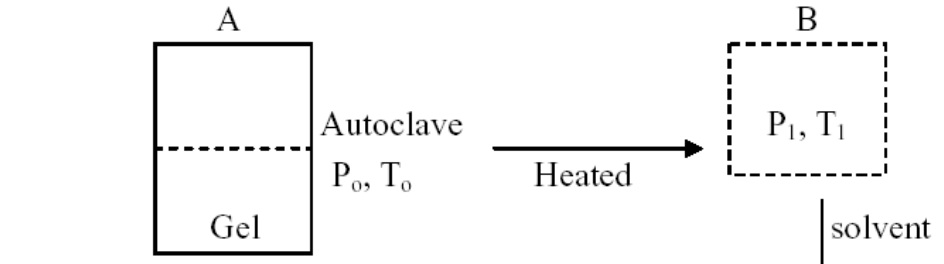
Supercritical Drying and Freeze

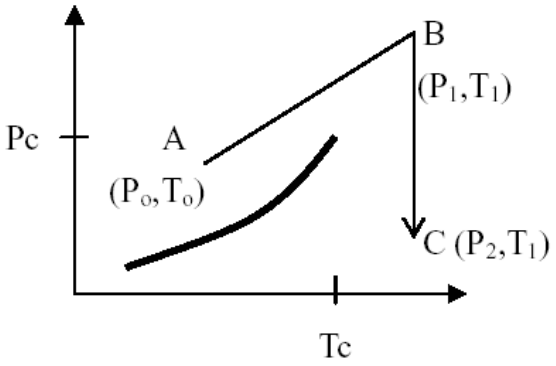


Supercritical Drying (formation of aerogel)

Removing the liquid from the pores above the critical temperature (Tc) and pressure (Pc) of the solvent.

Above the critical point, there is not any distinction between the liquid and vapor phases, no capillary pressure occurs during the drying process.





Freeze Drying

Cool the gel to solidify the solvent, then reduce pressure to sublime the solid solvent.