

IV. Particulate Sols and their Stability

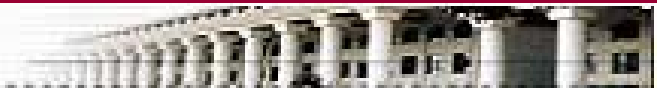
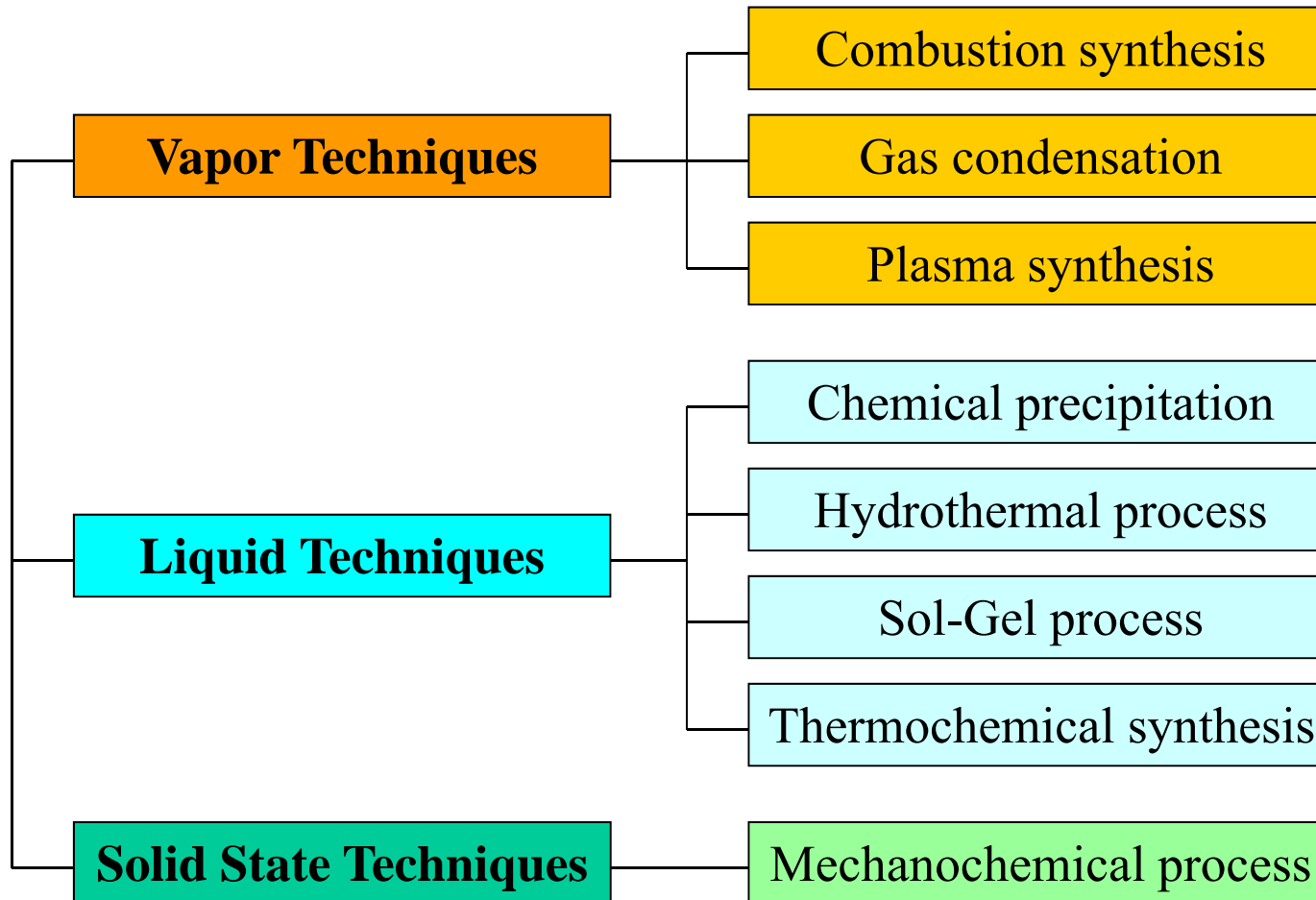
Particulate sols may be made in solution directly (hydrolysis and condensation), or by dispersing particles prepared by other method (e.g., vapor phase method) in aqueous solvent.

◆ Primary Particles

Primary particles are referred to ultrafine dense particles (1-5 nm in size) formed in the initial hydrolysis and condensation step. Within a primary particle, the chemical composition, crystalline structure, density etc. should be the same (uniform). The primary particles can be aggregated to form larger sol particles (5 nm – 500 nm)

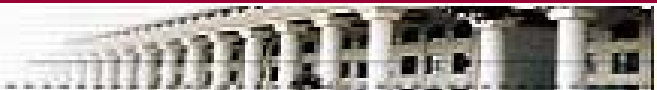
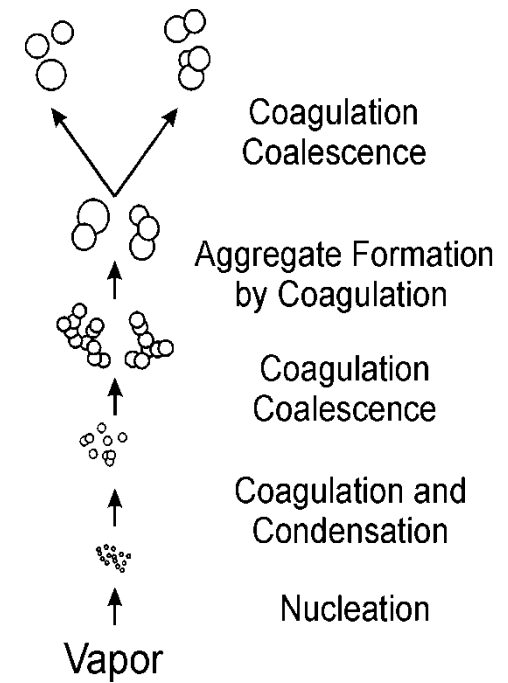
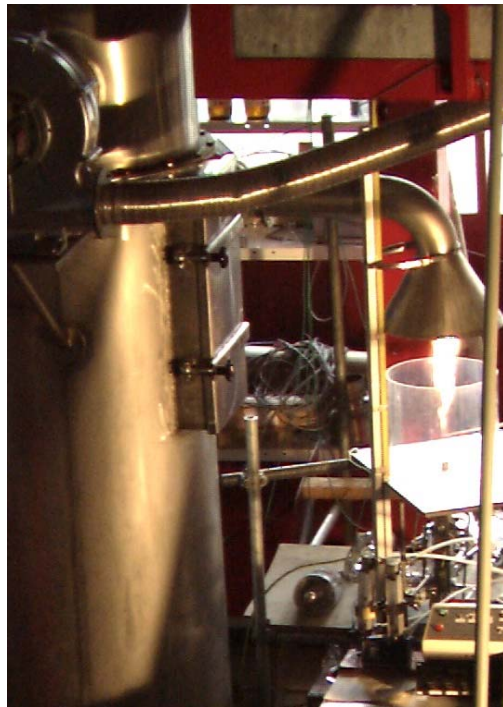


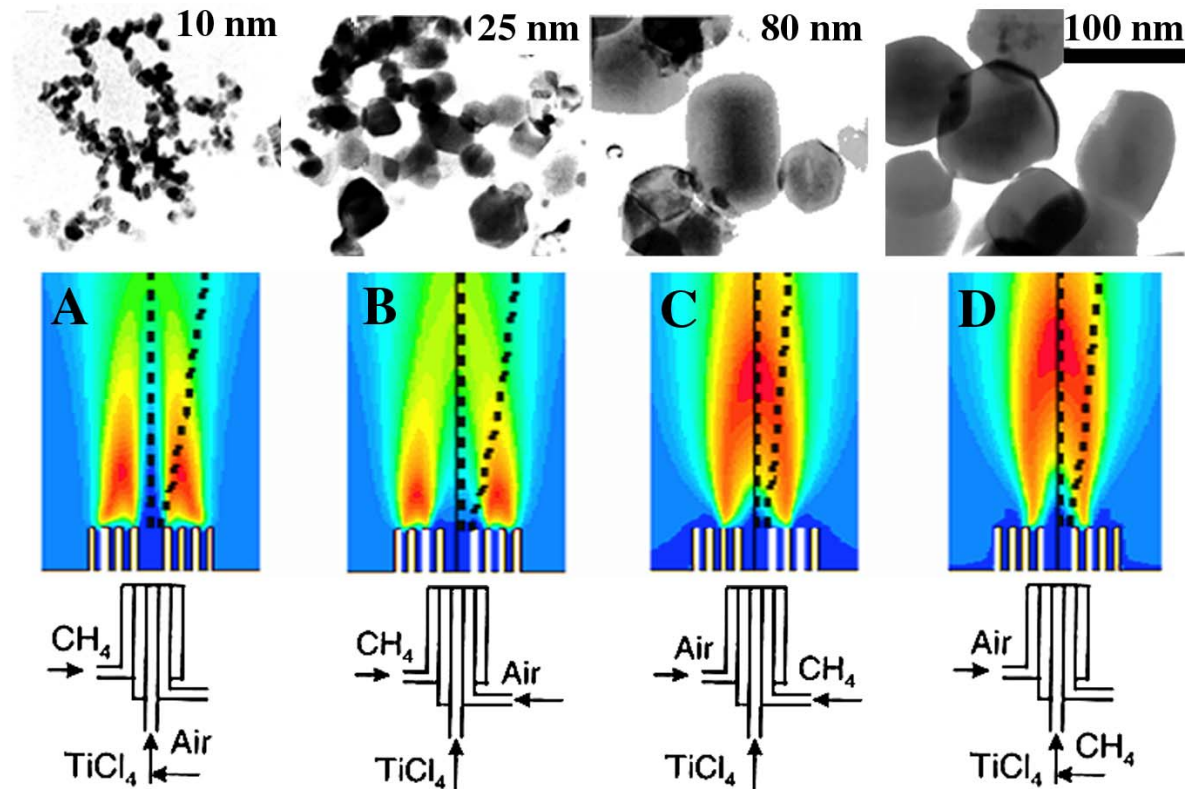
◆ Nanoparticle Preparation Techniques



◆ Flame synthesis (Combustion Process)

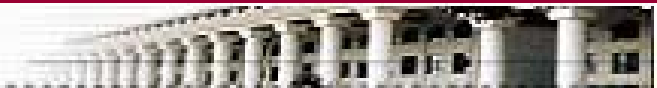
Synthesis of ceramic nanoparticles by flame synthesis



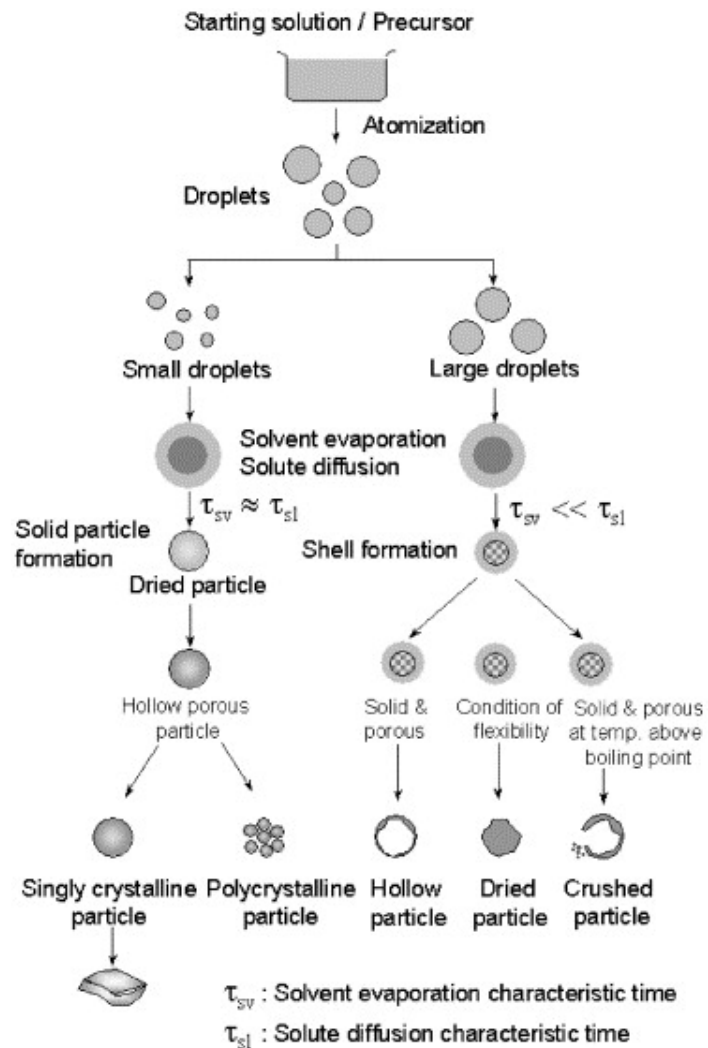
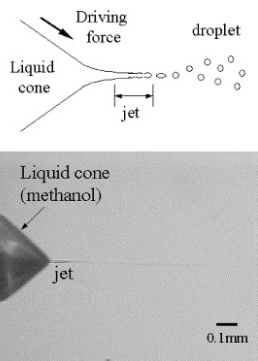
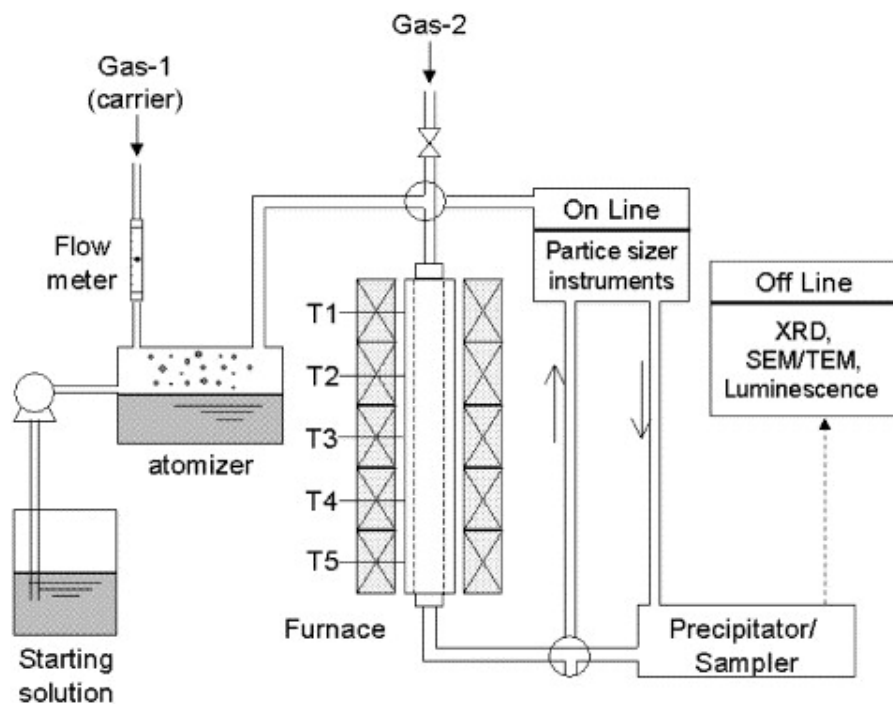


The particle size is controlled in the range from 10 to 100 nm only by reactant mixing. FLUENT simulations show the corresponding flame temperature profiles.

Pratsinis et al., 2002



◆ Spray Pyrolysis



Okuyama & Lenggoro, 2003



● Salt-assisted spray pyrolysis (SAD) vs. Conventional spray pyrolysis (CAD)

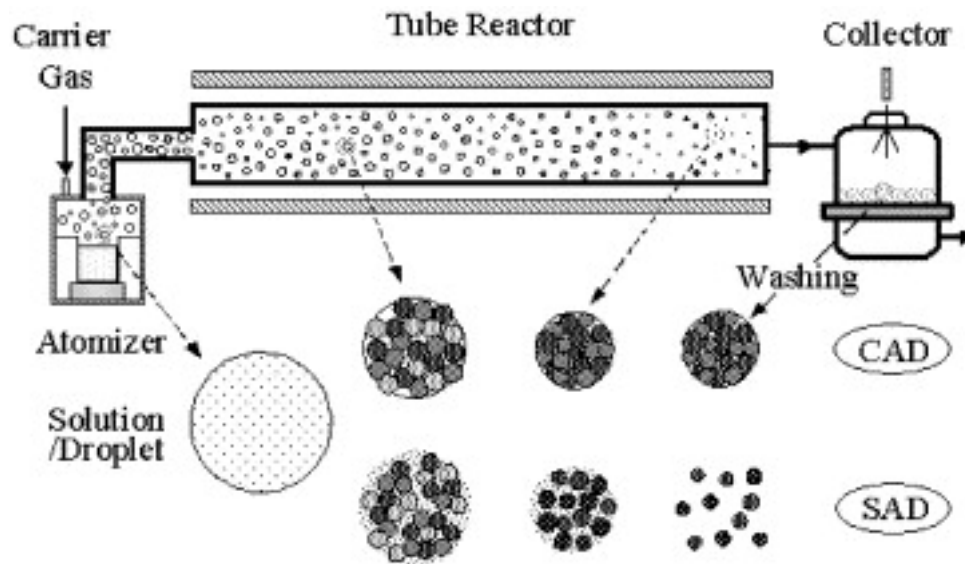


Fig. 5. Schematic illustration of the experimental apparatus and an illustration of particle formation both for the CAD and the SAD processes. Solution droplets were generated by an atomizer and were carried by a gas into a tube reactor typically operated betw...

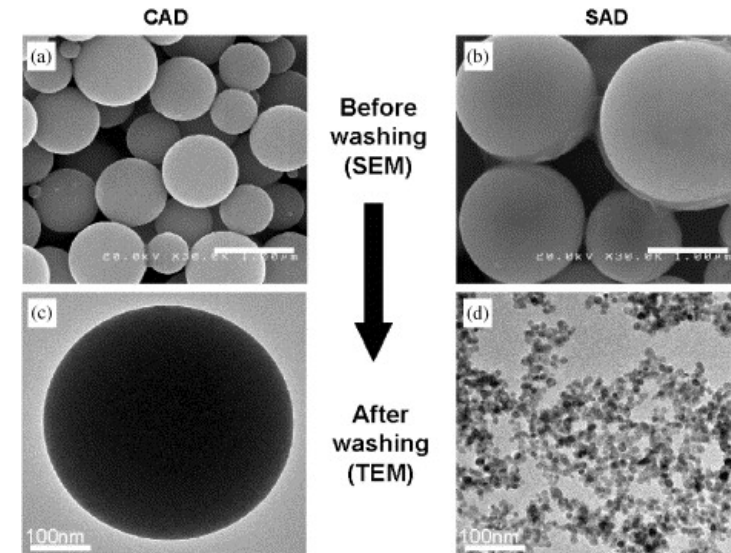
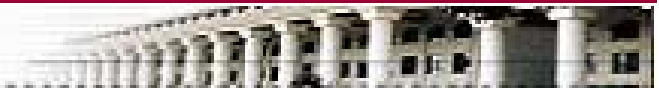


Fig. 6. $Y_2O_3-ZrO_2$ samples synthesized by the CAD process (a,b) and the SAD process (c,d). (a,c) SEM images of the samples before washing and (b,d) TEM images after washing. Note that the unwashed SAD particles (c) are larger than the unwashed CAD particles (a)...

Okuyama & Lenggoro, 2003



Morphology control using PS latex particles

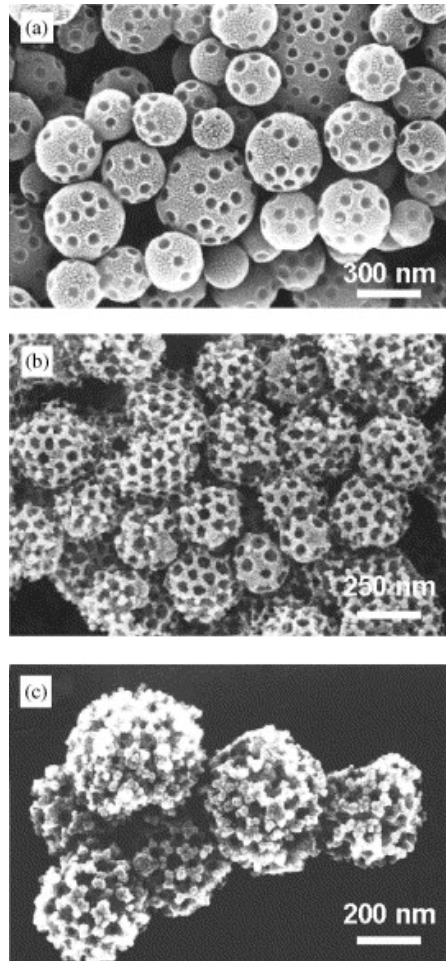


Fig. 10. SEM images of a spherical silica powder produced by varying the content ratio of PS latex and silica

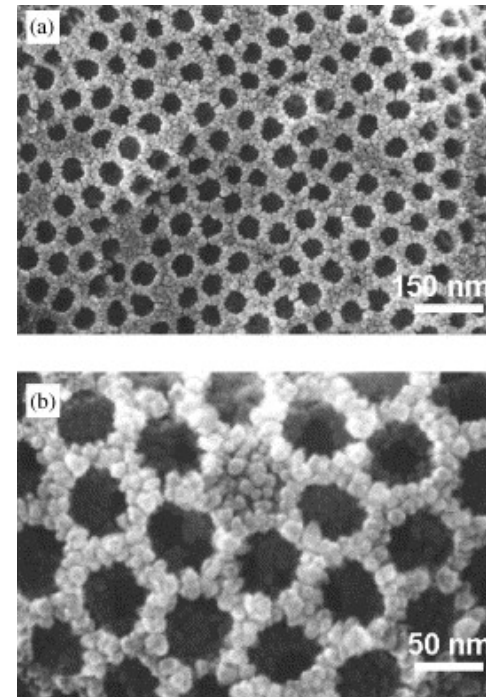
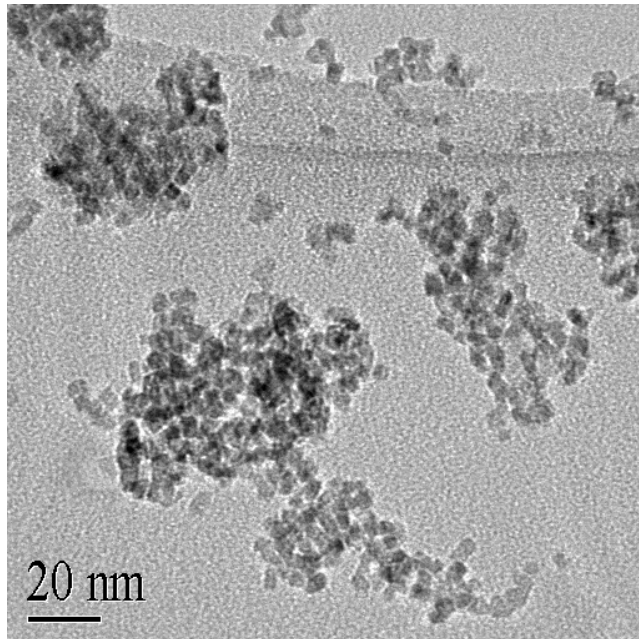


Fig. 9. SEM images of the surface morphology of silica powders using 79 nm PS latex particles

Okuyama & Lenggoro, 2003

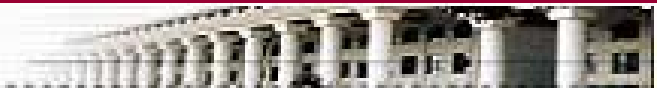




CeO₂ particles
from thermal hydrolysis



TEM of aggregate obtained by aging at 90°C for 12 h a solution of 0.015 M (NH₄)₂Ce(NO₃)₆, 0.064 M H₂SO₄, and 0.16 M Na₂SO₄, pH 1.1. From Hsu *et al.* [108].



◆ Ostwald Ripening for Primary Particles

The solubility of a particle:

$$S = S_0 \exp\left(\frac{2\gamma_{SL}V_M}{RT_r}\right)$$

S_0 : Solubility of a flat plate

γ_{SL} : Solid/liquid interfacial energy

V_M : Molar volume of the solid phase

r : Radius of particle

For positive curvature ($r > 0$)

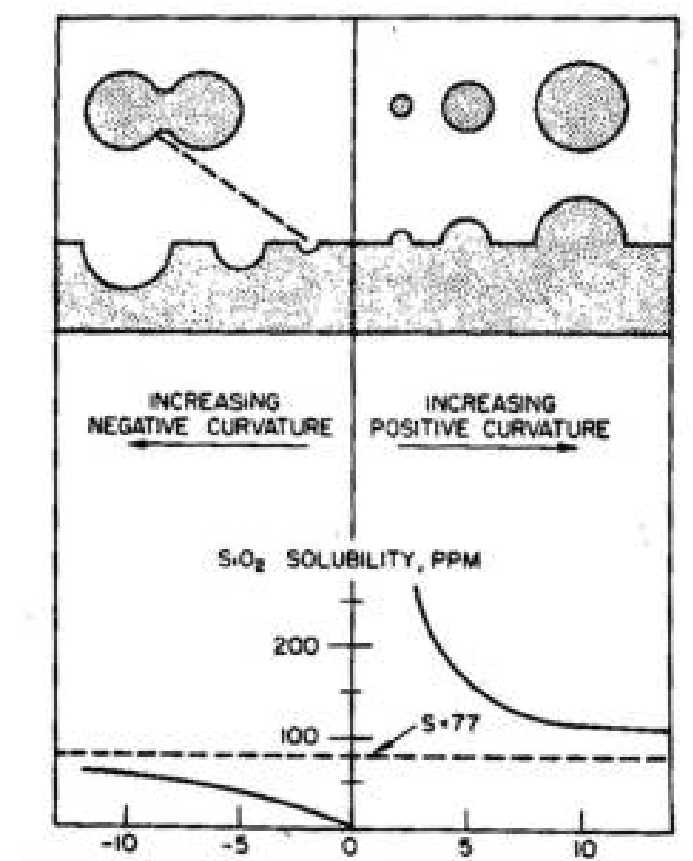
$S \uparrow$ with $r \downarrow$

For negative curvature ($r < 0$)

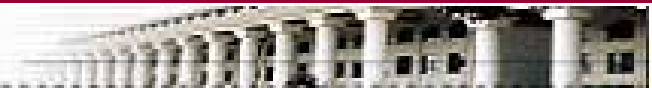
$S \uparrow$ with $|r| \uparrow$

Smaller particles \Rightarrow larger solubility

\Rightarrow easier to be dissolved and reprecipitate on larger particles



Thus, particles grow in size and decrease in number. Growth stops when the difference in solubility between the smallest and largest particles becomes only a few ppm. (Ostwald Ripening).



◆ **Stability of Sols**

DLVO theory (Derjaguin, Landau, Verwey, Overbeek)

The stability of a colloid suspension depends on van der Waals forces & Electrostatic repulsion.

van der Waals forces (attraction forces)

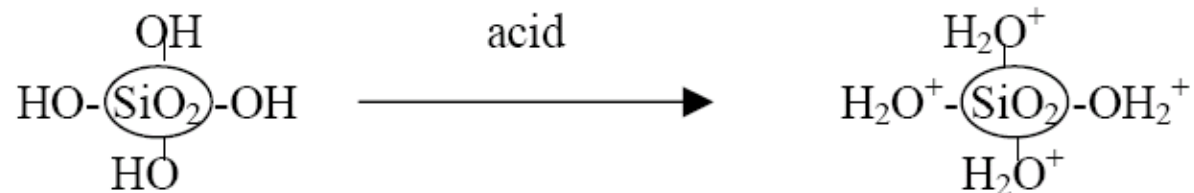
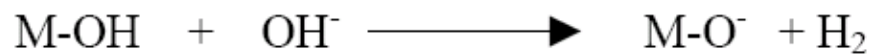
Attraction forces between atoms due to the fact that electrons surrounding a nucleus do not constitute a spatially and temporally uniform screen

- . Keesom forces: Permanent dipole-permanent dipole
- . Debye forces: Permanent dipole-induced dipole
- . London forces: Transitory dipole-transitory dipole



Electrostatic Repulsion

Surface of a hydrous oxide particles is charged by protonating or deprotonating the M-OH bonds on the surface as:



The ions that control the charge on the particle surface (M-OH_2^+ , M-O^-) are called charge-determining ions. Counterions are those in solution surrounding the particles and act to screen the charge of the particles. Since hydrous metal oxides are hydrophilic, water molecules are adsorbed at the particle surface (by hydrogen bonds or v.d. Waals forces). The counterions are also attracted by v.d. Waals forces and electrostatic potential of the charge determining ions.



ZETA POTENTIAL

: particle charge within
hydrodynamic radius

Double-layer
around a colloid particle

$$\phi_{\xi} = \phi_z$$

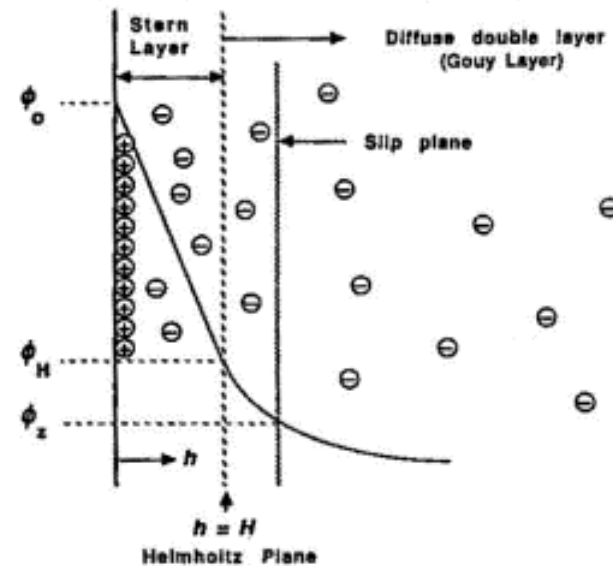
ξ (zeta) potential

Zeta-potential of a colloid system can be measured by an electrophoresis process in which the mobility of the colloid particles under an electric field is determined and used to calculate the zeta-potential.

Point of Zero Charge (PZC) is the pH value at which the particle is neutrally charged.

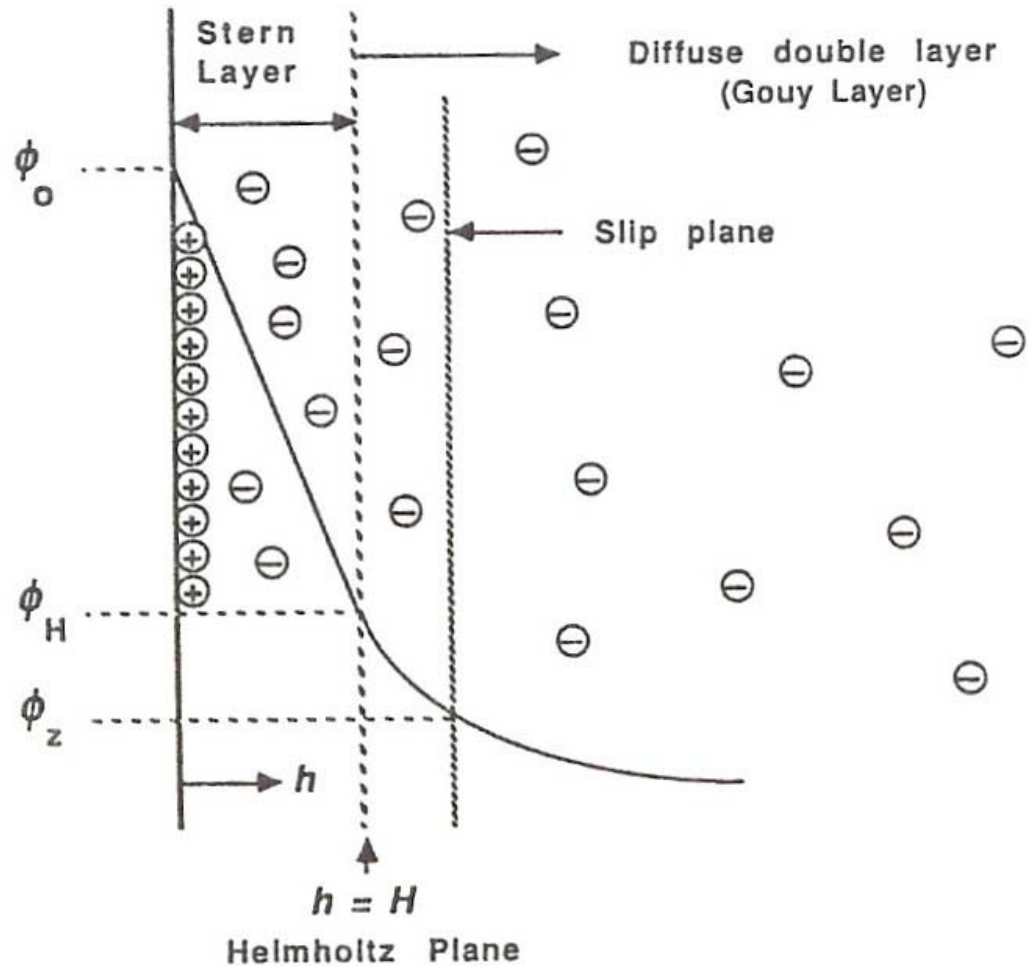
Isoelectric point (IEP) is the pH at which zeta-potential is zero.

IEP is not equal to PZC.



Schematic of Stern and Gouy layers. Surface charge on particle is assumed to be positive.





* Stern layer: the potential drops linearly through the tightly bound layer of water and counter ions.

* Gouy layer: the counterions diffuse freely.

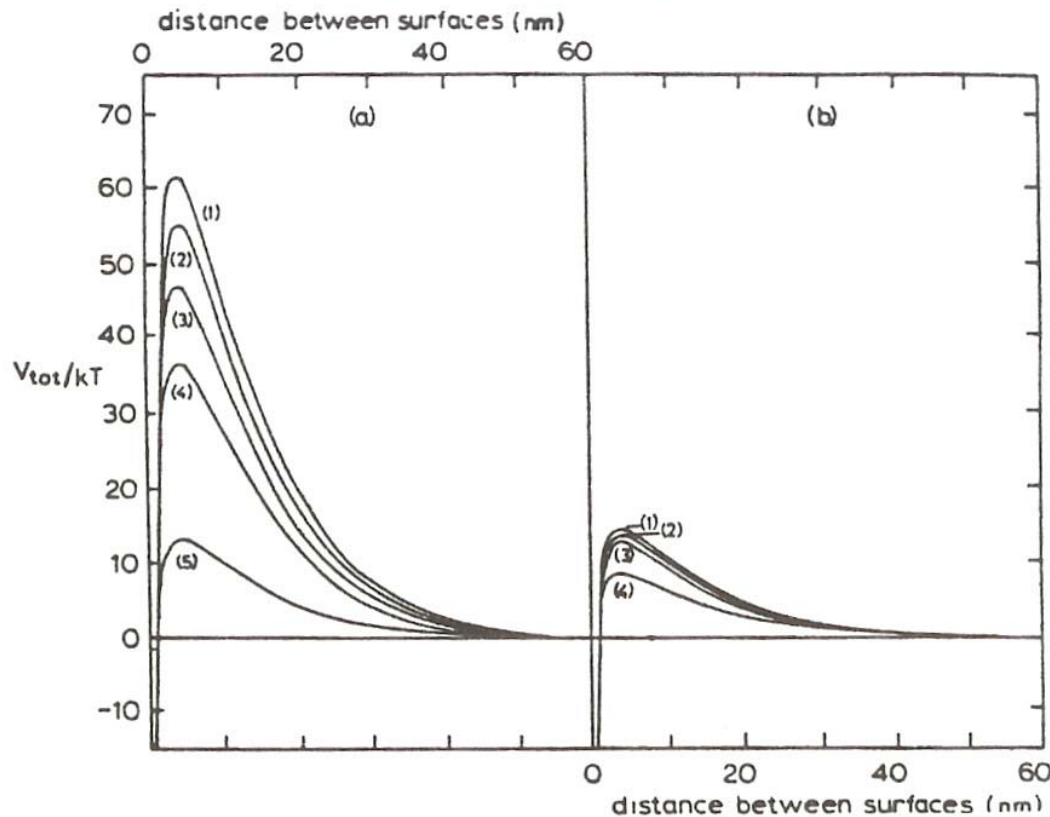
* Slip plane: the region of fluid that moves with the particle from the region that flows freely.

The stability of the colloid correlates closely with the magnitude of the ζ -potential; roughly speaking, stability requires a repulsive potential $\phi_\zeta > 30\text{-}50\text{mV}$.



Formation of Larger Colloid Particles from the Primary Particles

Fig. 5.



Theoretical curves of total potential energy against distance of separation of two spherical particles of radii a_1 and a_2 and equal surface potential (35.86 mV); $A = 5 \times 10^{-20}$ J, $1/\kappa = 10^{-6}$ cm $^{-1}$, $\epsilon = 78.5$.

(a): $a_1 = 125$ nm, $a_2 = 125$ nm (1), 100 nm (2), 75 nm (3), 50 nm (4), 12.5 nm (5).

(b): $a_1 = 12.5$ nm, $a_2 = 125$ nm (1), 100 nm (2), 75 nm (3), 12.5 nm (4). From Parfitt [24].

For the same distance:

Larger particles

⇒ larger repulsive barrier

The small(primary) particles turn to aggregate to form larger particles until the particles are in such a size that the repulsive barrier (electrostatic force) become so large that the particle will not approach each other. So eventually aggregates in relatively uniform size are formed in the sol.

