

SYNTHESIS OF INORGANIC MATERIALS AND NANOMATERIALS

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Outline

IV - FORMATION OF SOLIDS FROM SOLUTIONS

1) Glass

2) Precipitation

3) Biomaterials

4) Solvothermal synthesis

a) Hydrothermal synthesis of single crystals

b) Hydrothermal synthesis of nano-materials

5) Sol-gel processes

 a) The physics of sols

b) Sol-gel processing of silicate materials

c) Sol-gel chemistry of metal oxides

d) Inorganic-organic hybrid materials

5) Sol-gel processes

a) The physics of sols

What are the forces in a colloidal suspension?

- electrostatic repulsion between charged particles
- van der Waals attraction

Influence of pH linked to surface hydroxyl groups M-OH (M = Al, Si, Zr, Ti, Fe...)

→ see equation

pH at which the particles are electrically neutral: PZC (Point of Zero Charge)

→ the particles do not move in an electrical field

	SiO ₂	SnO ₂	TiO ₂	Al ₂ O ₃	MgO
PZC	2.5	4.5	6.0	7.0-9.0	12

Formation of a double-layer on the surface → development of a surface potential

Ex.: positively charged surface → see figure

- rigid Stern layer containing water + counter ions → linear decrease of potential
- diffuse layer → exponential decrease of potential

- Helmholtz plane: between Stern layer and diffuse layer;

potential Φ_H

- slip plane: between diffuse layer and bulk;

potential Φ_ζ

5) Sol-gel processes

a) The physics of sols

In an electric field, the particles move with the counter ions

The slip plane separates the region of fluid that moves with the particles from the bulk

pH for $\Phi_\zeta = 0$ → isoelectric point IEP (different from ZPC)

For stable colloidal suspensions → $\Phi_\zeta > 30 - 50$ mV

If Φ_ζ decreases (pH change or ionic strength increases)

→ double layer is compressed

→ coagulation

Coagulated colloid can be redispersed → peptization

→ remove counter ions by washing

→ videos of gel formation

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Tetraethoxysilane



TEOS

Tetramethoxysilane



TMOS

→ The gelation can be initiated by pH change

Reactions occurring: → see scheme

→ competition between hydrolysis reactions and condensation reactions

→ See figure

How to explain these differences? → different relative rates

→ need of a simple model

Parameters:

- temperature

- pH

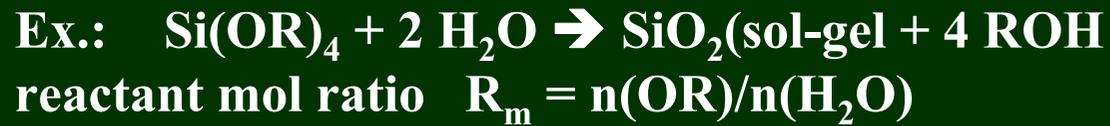
- catalyst

- nature of alkoxy group

- reactant mol ratio $R_m = n(\text{OR})/n(\text{H}_2\text{O})$

5) Sol-gel processes

b) Sol-gel processing of silicate materials



slow rate in water

Stoichiometry $R_m = 2$

$R_m < 2$ (excess water) \rightarrow hydrolysis

$R_m > 2$ (excess silane) \rightarrow condensation

See scheme

sol-gel transition

\rightarrow formation of a continuous network

\rightarrow viscosity increases strongly

\rightarrow gelification time:



5) Sol-gel processes

b) Sol-gel processing of silicate materials

Model: percolation theory

→ formation of clusters of particles

See figure

p: fraction of filled sites (sol particles)

2 neighboring filled sites can form a bond → cluster of size s

One important parameter

→ p_c = percolation threshold → gel point

At the gel point the network is formed, but unbounded clusters are still present

→ importance for aging process after reaching the gel point

This model → site percolation

Another model → bond percolation

Values of p_c

	site percolation	bond percolation
2-D square	0.5927	0.5000
3-D cubic	0.3116	0.2488
3-D fcc	0.1992	0.1202

Aging: gelification reactions continue due to the presence of isolated clusters

Drying step

- at 1 bar pressure → formation of xerogels,
 - shrinkage of the gel due to interface forces (liquid-vapor capillary forces)
 - network destroyed, formation of a powder
 - formation of films, coating layers after thermal treatments
- under supercritical conditions → formation of aerogels
 - volume of the gel is preserved
 - control of shrinkage

See part V

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Ex.: $[\text{Al}(\text{OH}_2)_6]^{3+}$

stable for $\text{pH} < 3$

Formation of alumina gel by increasing the pH

Acid-base equilibrium



Olation reaction



Oxolation reaction



Difference between Si^{4+} and M (Al^{3+} , Fe^{3+} , Zr^{4+} ...)?

Si coordination number 4, tetrahedral geometry (point group T_d)

M coordination number 6, octahedral geometry (point group O_h)

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Possibility of embedding organic molecules into an inorganic shell

→ Application for dyes, catalysts, sensor compounds, biomolecules, biosensors (enzymes, antibody...)



→ formation of cages: triangular prism, cube, pentagonal prism

See figures

→ formation of films and coatings: modification of surfaces properties

- mechanical protection against corrosion, abrasion, scratching
- optical application (mirrors for high power lasers)
- hydrophilic versus hydrophobic surfaces

Liquid on a solid → interfacial energy or surface tension

$$dE = \gamma d\sigma$$

γ = surface tension in N m^{-1} or J m^{-2}

See figure

$$\Delta E \text{ (per m}^2\text{)} = \gamma_{SL} + \gamma_{LG} \cos\theta - \gamma_{SG}$$

- $\Delta E < 0$ \rightarrow liquid will spread spontaneously onto the whole surface
 \rightarrow wetting behavior

- $\Delta E = 0$ \rightarrow equilibrium $\rightarrow \gamma_{SL} + \gamma_{LG} \cos\theta = \gamma_{SG}$
 \rightarrow Young's relation
 \rightarrow determination of contact angle

$0 < \theta < 90^\circ$ \rightarrow hydrophilic surface

$90 < \theta < 140^\circ$ \rightarrow hydrophobic surface

$140^\circ < \theta$ \rightarrow superhydrophobic surface

\rightarrow video magic sand.

\rightarrow video interfacial forces