



Glass Processing

Advanced Fabrication: Sol-Gel Processing

Part I: February 12, 2015

Processing Steps and Chemistry

Part II: February 17, 2015

Applications, Monoliths and Thin Films

Lisa C. Klein

Materials Science & Engineering Department

Rutgers University

Piscataway, NJ

(848) 445-2096/ licklein@rci.rutgers.edu



Sol-Gel Processed Glasses Come in Many Shapes and Sizes

Monoliths
Xerogels
Aerogels
Hosts for Dyes
Thin Films
Composites
Hybrids
etc.



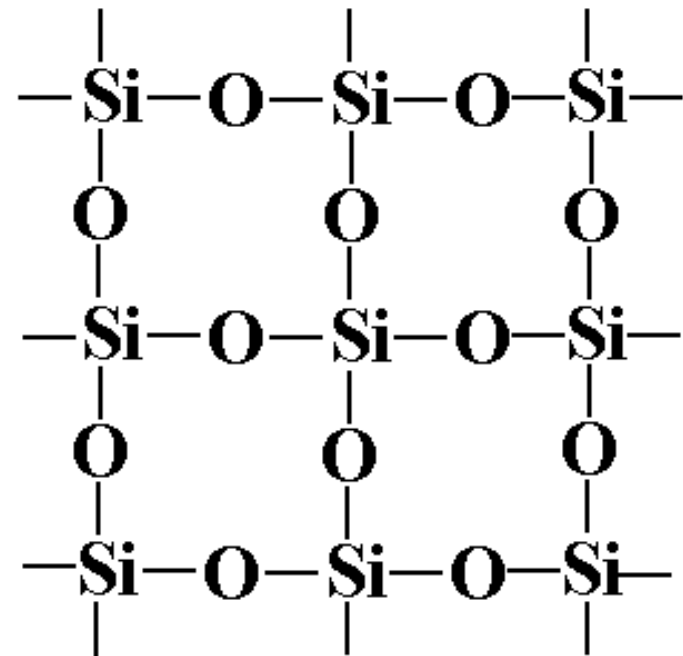
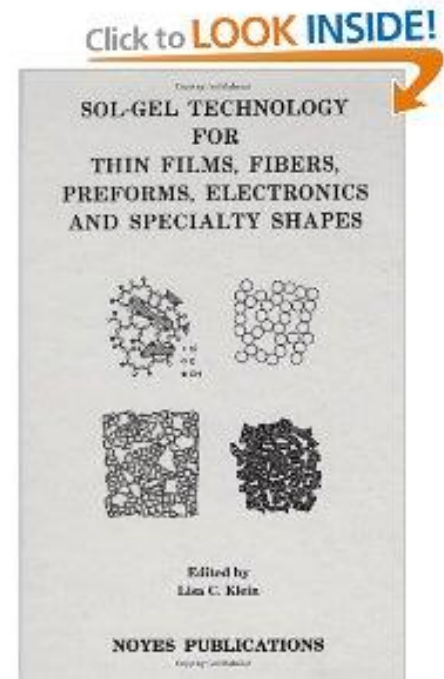
Overview of Sol-Gel Processing: “Bottom-up” in Liquids

- What is Sol-Gel Processing?
 - Chemical route to oxides, using alkoxides, oxychlorides and soluble salts (precursors)
- What are Precursors?
 - Molecules that contain the elements of the future network, and that allow its formation by chemical reactions in liquid medium, silicas, aluminas, zirconias, etc.

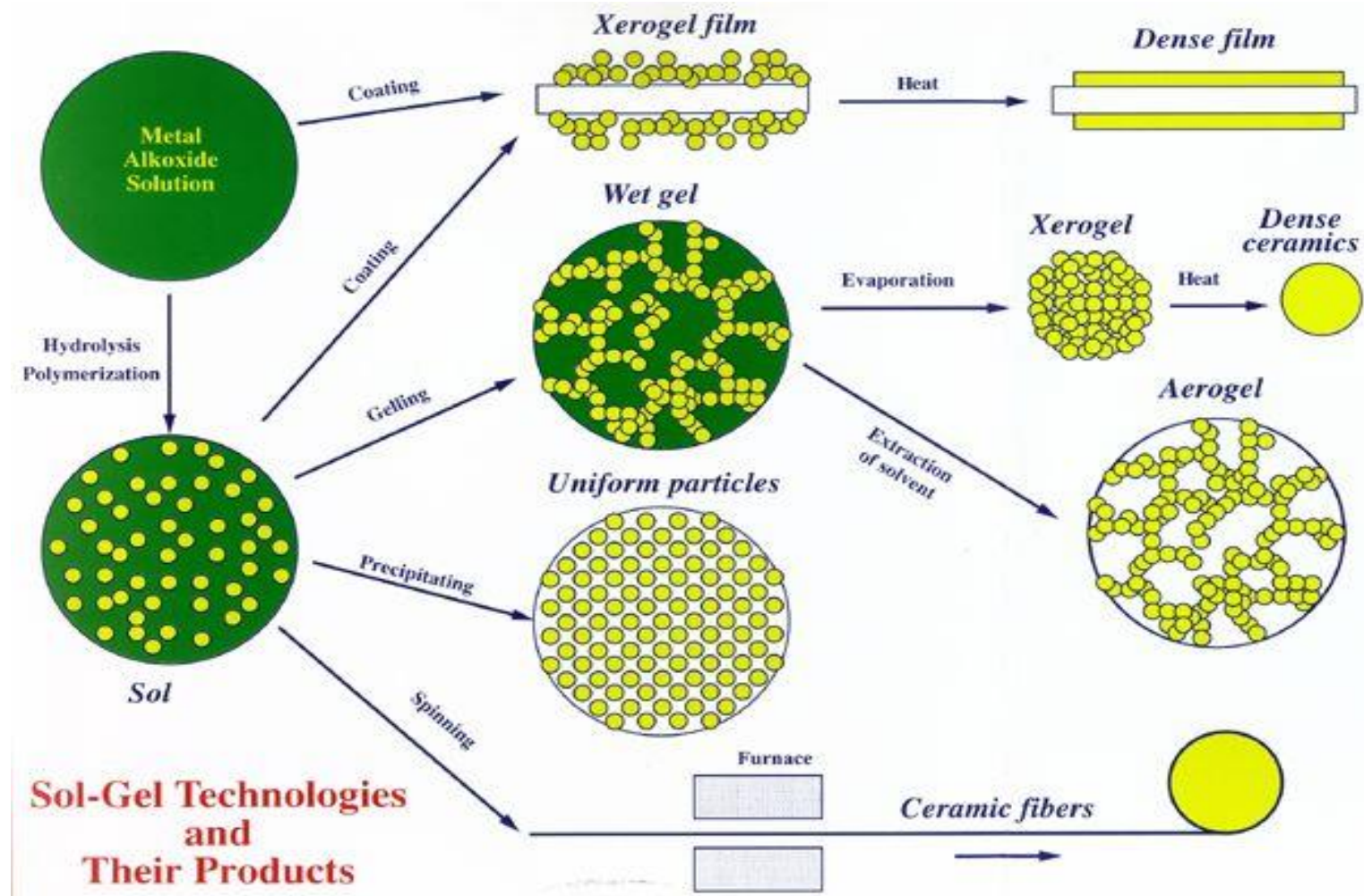
Working Definition:

The Sol-Gel Process refers to preparation of an inorganic network in solution.

Typically, inorganic **oxides** are formed. → Sol-gel processing has been a “nanomaterial” process from the start.



Global View of Sol-Gel Processing (www.chemat.com)



What is the sol-gel process?

- The sol-gel process can be used to produce polymers or particles.
- A sol is a colloidal suspension of nanoparticles dispersed in a liquid, usually water.
- A sol exhibits **Brownian motion** (random walk driven by momentum of collisions) and short-range forces (such as van der Waals), while gravitational forces are negligible.

What is Sol-Gel Processing?

- Based on acid–base reactions
- Metal alkoxide salts are generally soluble in alcohols
- Alcohols are very weak acids
 - Essentially no tendency to lose H^+
- Alkoxide ions are very strong bases
 - React with water to form alcohol and OH^-

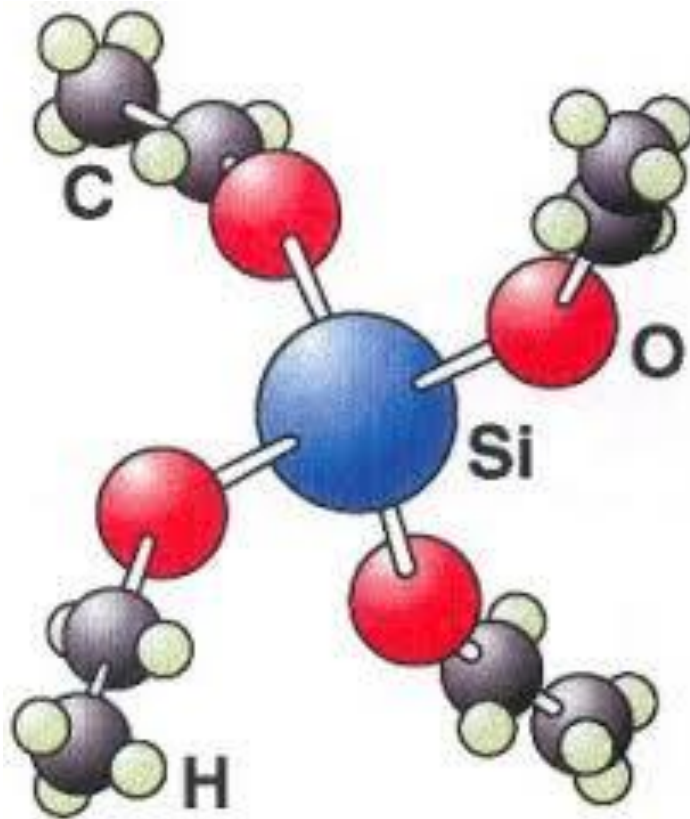
Chemistry of the Sol-Gel Process

- Alkane – molecule containing only carbon and hydrogen linked by a single bond, such as **methane**, CH_4
- Alkyl – ligand created by removing one hydrogen from the alkane, such as **methyl**, $-\text{CH}_3$
- Alcohol – adding one hydroxyl (OH) to an alkyl, such as **methanol**, CH_3OH
- Alkoxy – removing a proton (H^+) from an alcohol, such as **methoxy**, $-\text{OCH}_3$
- Alkoxide – metalorganic compound, in which an organic ligand attaches to a metal atom, M-OCH_3
- Organometallic – a compound with a direct metal-carbon bond.

Metal Alkoxide Precursors

- Metal alkoxides are popular precursors because they react with water.
- The hydrolysis reaction goes to **completion** when there is **excess** water and catalyst.
- Alkoxy groups are replaced with OH
$$\text{Si(OR)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{ROH}$$
- If there is **deficit** water, the system is **partially** hydrolyzed
- Two partially hydrolyzed molecules can link together in a condensation reaction, which liberates water.
- Linking monomers connect and extend to form a polymer skeleton.

Most Common Precursor: Tetraethylorthosilicate (TEOS)



Ligands –functional group attached to central metal atom

Ligands present in the complex will direct the reactions

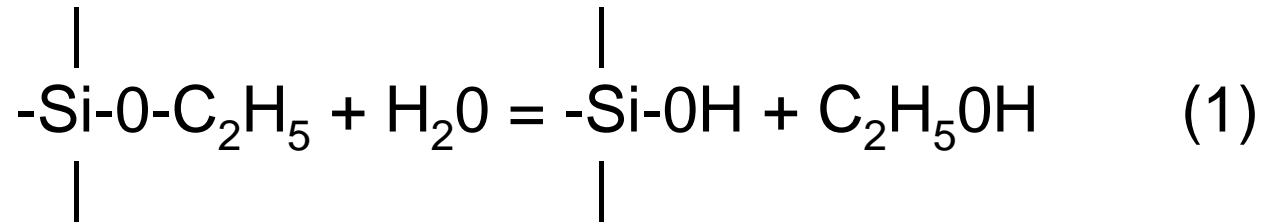
- Can **slow down** the reaction due to steric (size and geometry) reasons
- Can **stop** the reaction with blocking (not able to hydrolyze) groups
- Can yield different morphologies of products with different ligands

Functionality

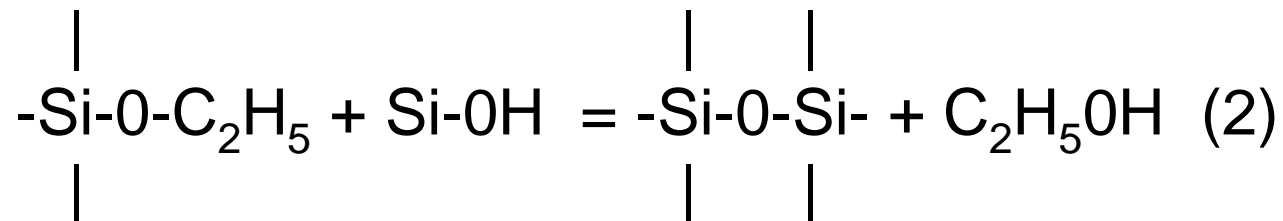
- The **number** of bonds a monomer can form is called its functionality.
- The formation of a 3-D cross-linked network (polycondensation).
- Dimer \rightarrow Chain \rightarrow Ring is the progression in the polymerization process.
- Polyfunctional monomers tend to form **fractal** surfaces, polymeric clusters resulting from branching and random bonding.
- If a monomer can make 2 or more bonds, it can increase its molecular size without limit.

Simplified Chemical Reactions of the Sol-Gel Process

Hydrolyzation

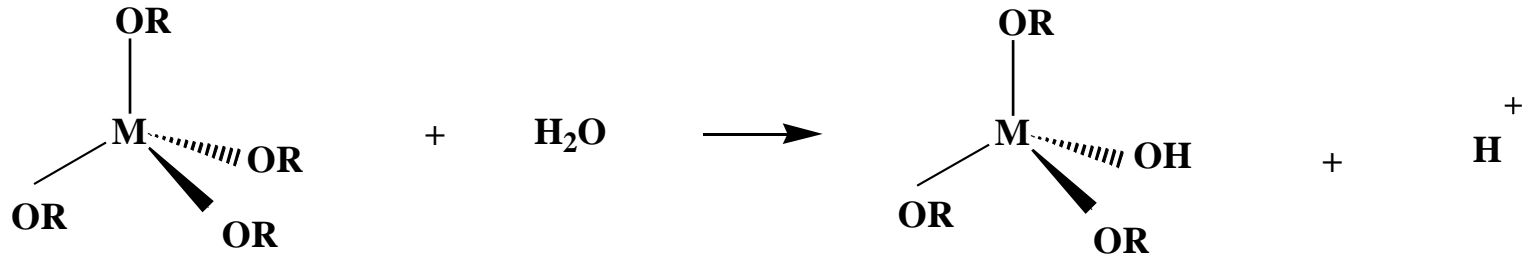


Polymerization

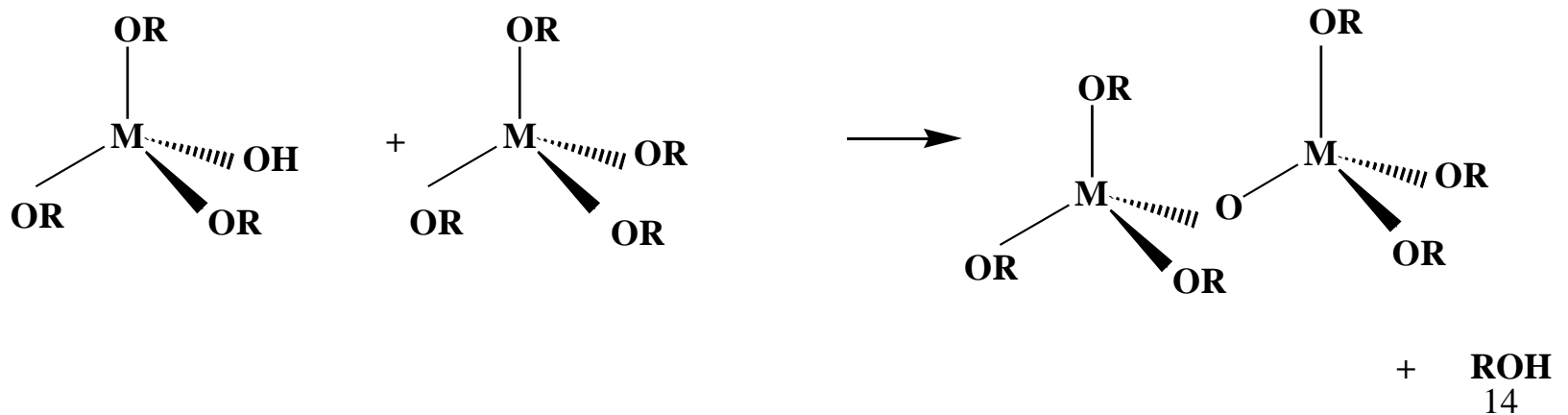


Chemical Reactions

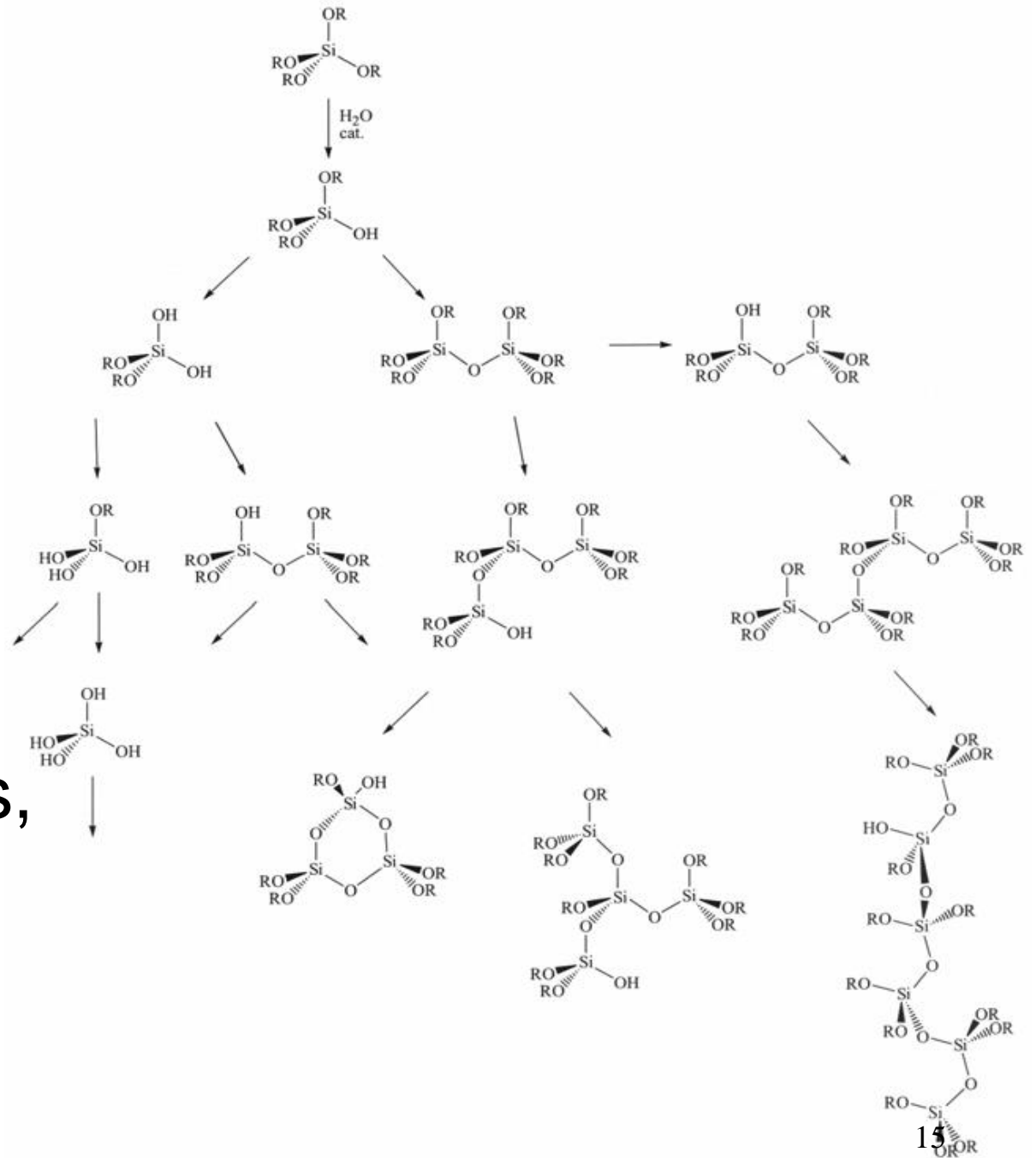
Hydrolysis



Condensation



Possible Hydrolysis and Condensation Reactions



Producing Various Dimers, Trimers and Oligomers

Partial Charge Model (Livage)

- Transformations depend upon partial charge of atoms within a complex.
 - Negative partial charge - nucleophilic species.
 - Positive partial charge - electrophilic species.
- Equilibrium is achieved when all electrons of a molecule or complex transfer from atom to atom until they all reach the same equilibrium chemical potential.
 - This is in turn related to **electronegativity**.
 - In principle, one can predict which complex of precursor M will exist by calculating the electronegativity of all possible combinations of metal-ligand interactions.

Partial Charge

- Partial Charge on atom i in complex relates to difference in electronegativity in the complex from some reference electronegativity.

$$\delta_i = \frac{\chi - \chi_i^0}{1.36 \sqrt{\chi_i^0}}$$

The electronegativity of the complex X(C) is calculated according to:

$$X(C) = \frac{\sqrt{X_{Si}^\circ} + N\sqrt{X_O^\circ} + (2N-h)\sqrt{X_H^\circ} + 1.36(z-h)}{\frac{1}{\sqrt{X_{Si}^\circ}} + \frac{N}{\sqrt{X_O^\circ}} + \frac{2N-h}{\sqrt{X_H^\circ}}}$$

based on electronegativities (given in Homework) and definition of partial charge.

N (coordination number = 4)

z (valence/formal charge of Si = 4)

h (number of hydroxo ligands)

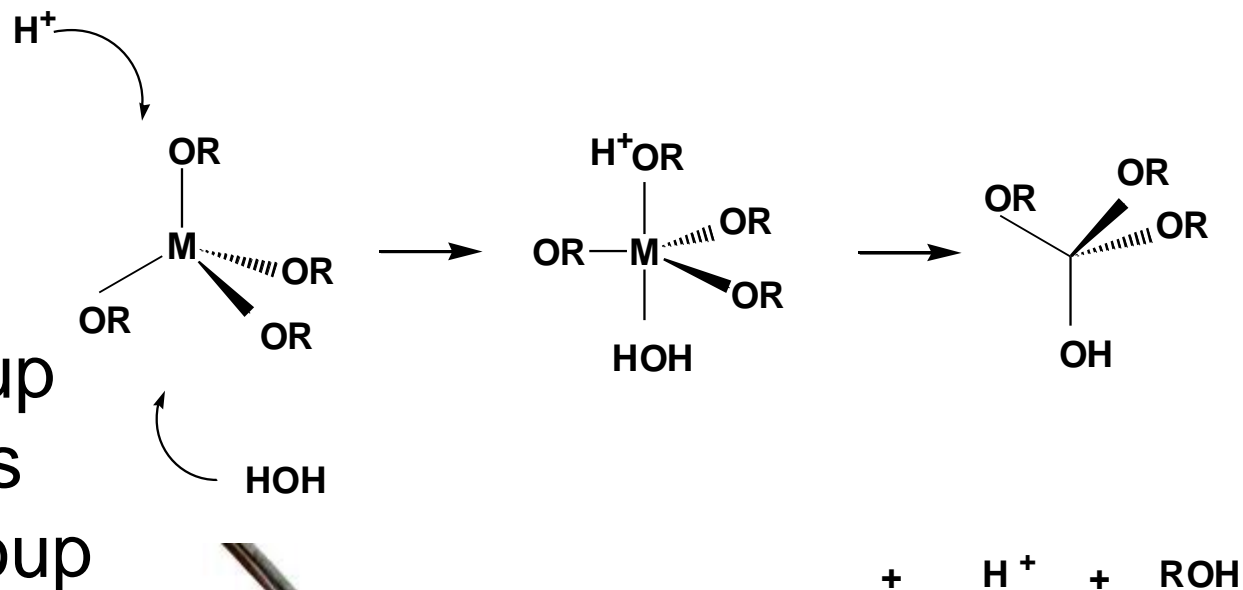
Electronegativity of Water

$$\chi_{H_2O} = \frac{2\sqrt{\chi_H^0} + \sqrt{\chi_O^0}}{2 + 1} = 2.49$$

- $\chi(\text{SiO}_2) = 2.6$
- $\chi(\text{CH}_4) = 2.1$
- $\chi(\text{NaCl}) = 1.6$

Acid Catalyzed Hydrolysis

- S_N2 type of reaction
- Electrophilic substitution
- Leaving group **same** side as attacking group
- Leads to **polymer** formation



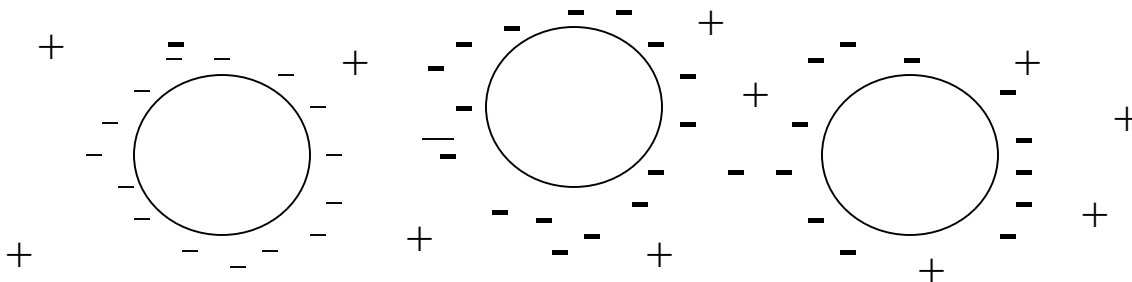
“Tangled Spaghetti”



Base Catalyzed

- Fast hydrolysis (above pH = 7)
- Condensation mechanism (above pH=2):

$$\begin{aligned} \equiv\text{SiOH} + \text{OH}^- &\rightarrow \equiv\text{SiO}^- + \text{H}_2\text{O} \\ \equiv\text{SiO}^- + \equiv\text{SiOH} &\rightarrow \equiv\text{SiOSi}\equiv + \text{OH}^- \end{aligned}$$
- Nucleophilic attack: Reaction between most acidic silanols is favored.
- Form highly condensed species
- Large particles grow at the expense of small particles (ripen)

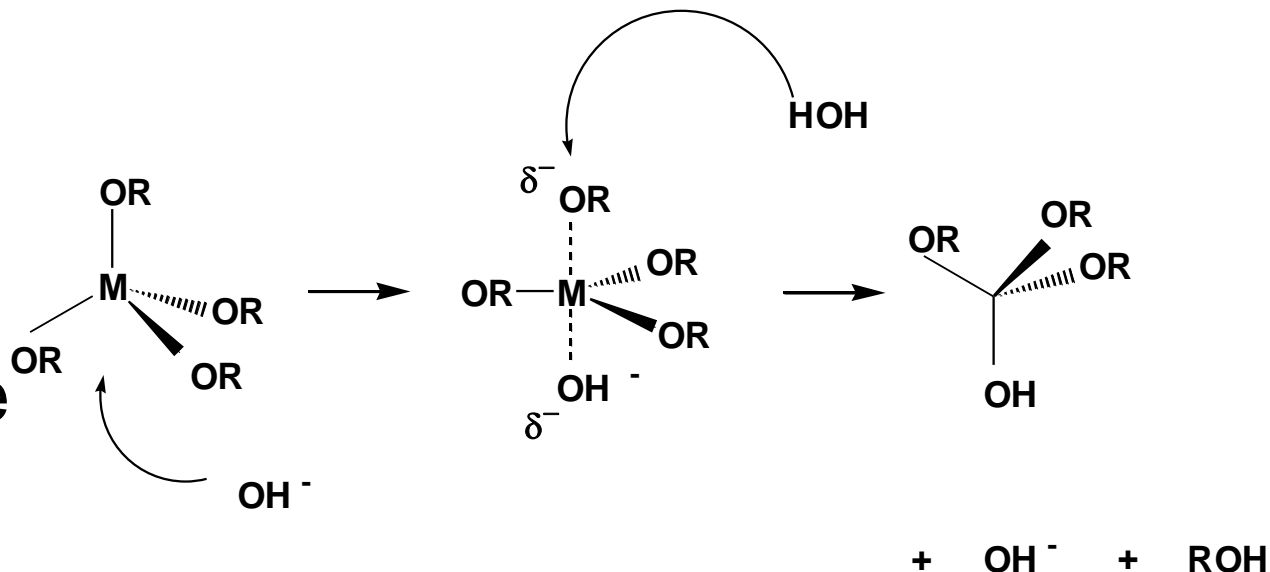


Base Catalyzed Hydrolysis

Sn2 type of reaction

Leaving group on **opposite** side of attacking group

Leads to **particle** formation



“Tumbleweeds”

Acid vs. Base

Catalyst	Acid	Base
Mechanism	Electrophilic	Nucleophilic
Side of Attack	Front	Back
Rate w.r.t. condensation	Slower	Faster
Crosslinking	Weak	Strong
Effect of polymerization	Small	Large
Hydrolysis	Complete	Incomplete
Reversibility	Good	Poor

Role of Water

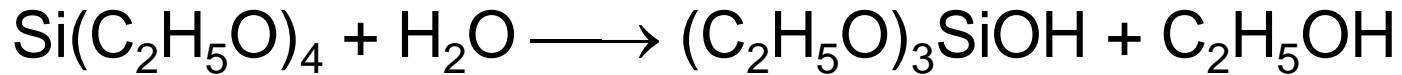
- Water is often the **solvent**
 - Precursors must be dissolved
 - Other solvents are typically alcohols
- Water is also a **reactant**
- Because of its reactivity, sometimes we need to employ sub-stoichiometric quantities
 - e.g., $\text{Ti(OR)}_4 + 2\text{H}_2\text{O}$ (not $4\text{H}_2\text{O}$)
- Water is also a **product**

Getting Started...

- Measure components by volume
- Set molar ratios of alkoxide:alcohol:water
- Adjust pH of water
- Gradually add water to alcohol solution of alkoxide
- For multicomponent oxides, add alkoxides in order of increasing reactivity (e.g., Si < Al < Ti)
- Alkoxide ions gradually replaced by OH⁻ ions
- When two (C₂H₅O)₃SiOH encounter each other, they undergo an acid-base reaction and condense H₂O

Clear Solution Stirring with Heat

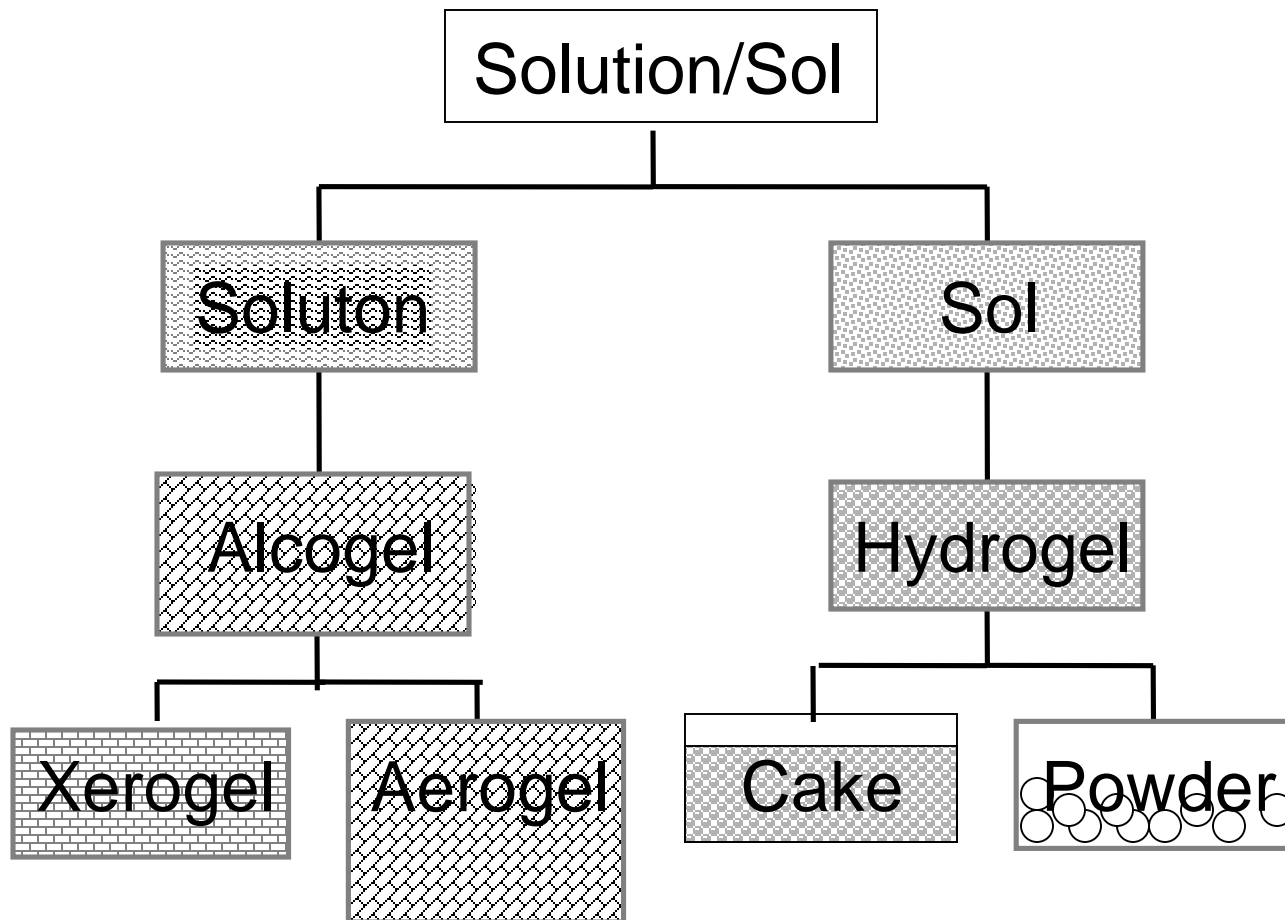
- Hydrolysis reaction



- As more H_2O is added:
 - More alkoxide ions converted to alcohols
 - More oxide linkages bridging ions
 - May stay clear or become cloudy when very fine particles of metal oxides with residual OH ions become suspended in alcohol (gel-like)



Sol-Gel Process: Alkoxide vs Colloidal Route

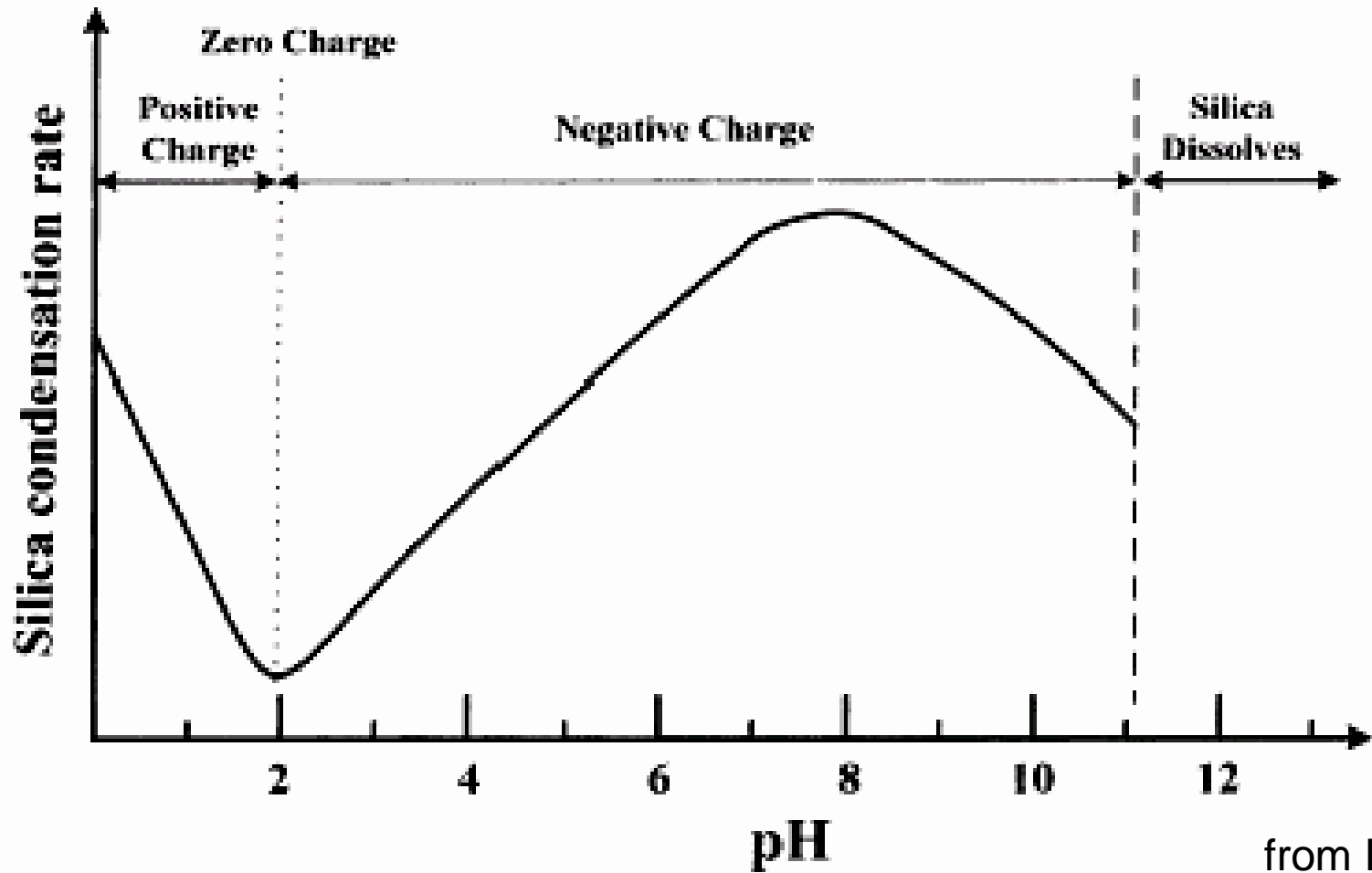


Gelation

- The gel point is a transition, sol-to-gel transition
- Empirical “time-to-gel” when solution no longer flows
- $t < t_{\text{gel}}$ behavior is that of a fluid, described by viscosity η
- $t > t_{\text{gel}}$ behavior is that of a solid, described by shear modulus G
- At t_{gel} , viscoelastic behavior,
- reflecting structure



Role of pH



from Iler

Time-to-gel and Aging

- Time-to-gel – by examination, it is the time when no flow is observed when the sample is tilted
- **Isoelectric point** ~pH 2 gives the **maximum** gelation time
 - because of increased mutual repulsion from electrostatic charge
- Aging – time when gel is surrounded by liquid before drying
- Effect of aging on porosity
 - pH<2 gives microporosity that is little effected by aging
 - pH>2 gives mesoposity that can be altered by aging

Sol-to-Gel Transition

- Hydrolysis occurs in single phase solution
- Polymerization occurs in single phase and in 2-phase gel
- Gellation leads to 2 phases, oxide skeleton plus solvent (water and alcohol in “alcogel”) where Si is surrounded by mostly bridging oxygens
- 1 phase → 2 phases means creation of interface
- Solvent phase is replaced by vapor phase by natural evaporation (xerogel) or hypercritical evacuation (aerogel)

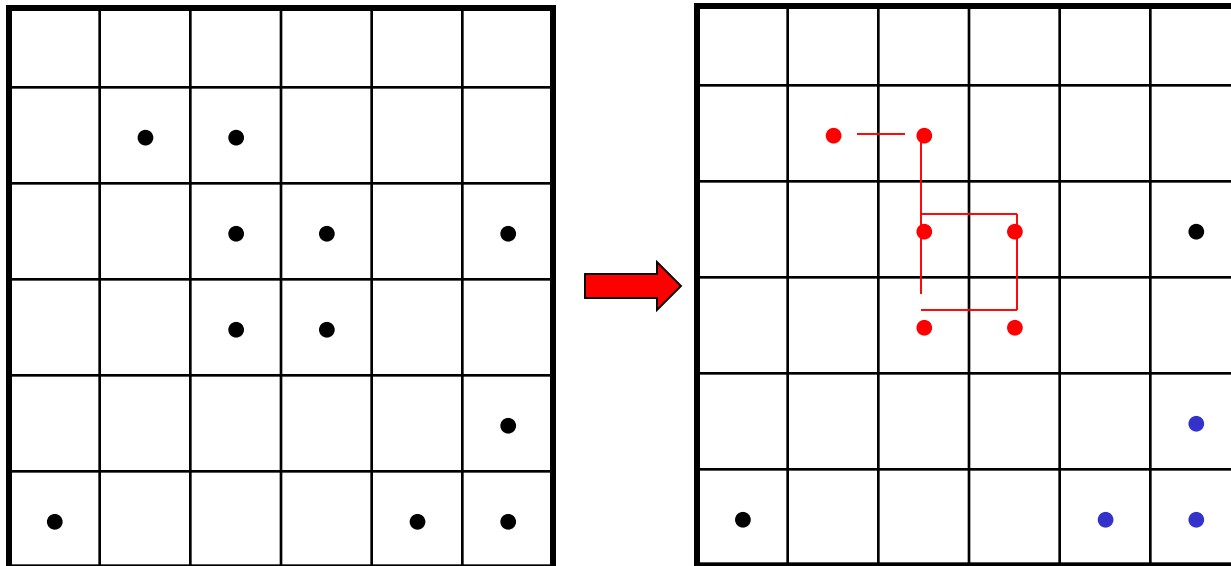
What is a “gel”?

- A gel is a continuous solid **skeleton** encapsulating a liquid phase, formed from the entanglement of polymer chains or van der Waals forces between particles.
- Gelation occurs when clusters impinge and link to one another constructing a **network**.
- Initially, the gel is soft, until portions of the gel network move close enough together for additional condensation reactions.
- **Aging** results in changes in structure and properties after gelation, generally leading to shrinkage.

Percolation

- *Percolation* is the study of **how systems of discrete objects are connected** to each other.
- More specifically, percolation is the analysis of clusters - their statistics and their properties.
- The applications of percolation are numerous: phase transitions (physics), forest fires, epidemics, fracture, etc.
- For *site percolation* there is a critical concentration (of occupied sites), above which a cluster exists that spans the domain, i.e. connects the left hand edge to the right hand edge.

Generating Bond Percolation on the Way to Percolation Threshold



“Connect the Dots”

Drying

Xerogel

- Natural evaporation
- High capillary stresses
- Shrinkage, as much as 70% reduction in volume
- Problems with cracking

Aerogel

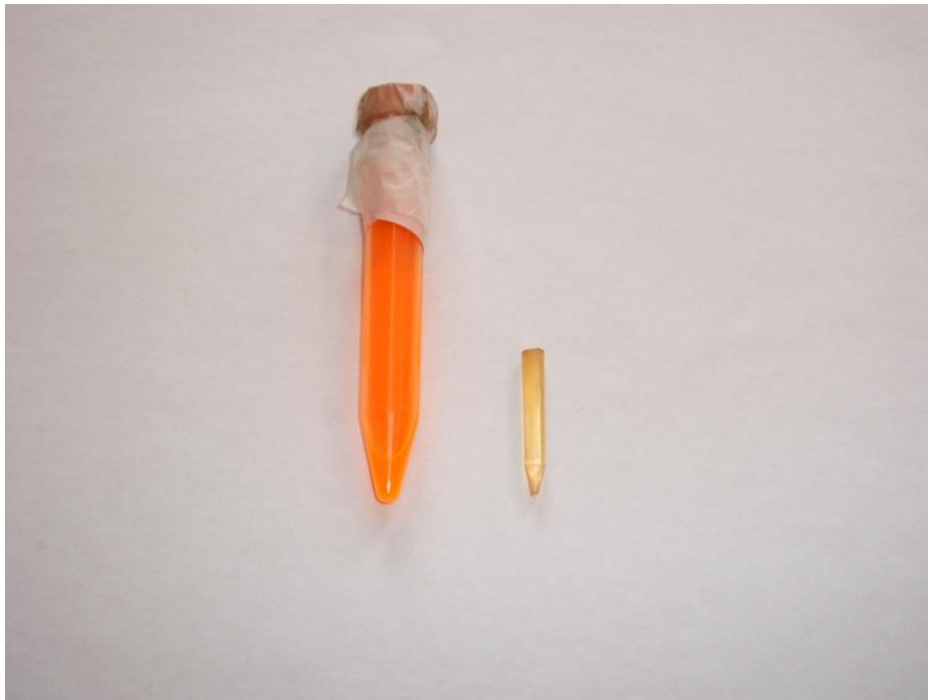
- Supercritical drying/CO₂ exchange
- No shrinkage
- Densities less than 0.1 g/cm³
- Surface areas > 1,000 m²/g

Drying leads to shrinkage

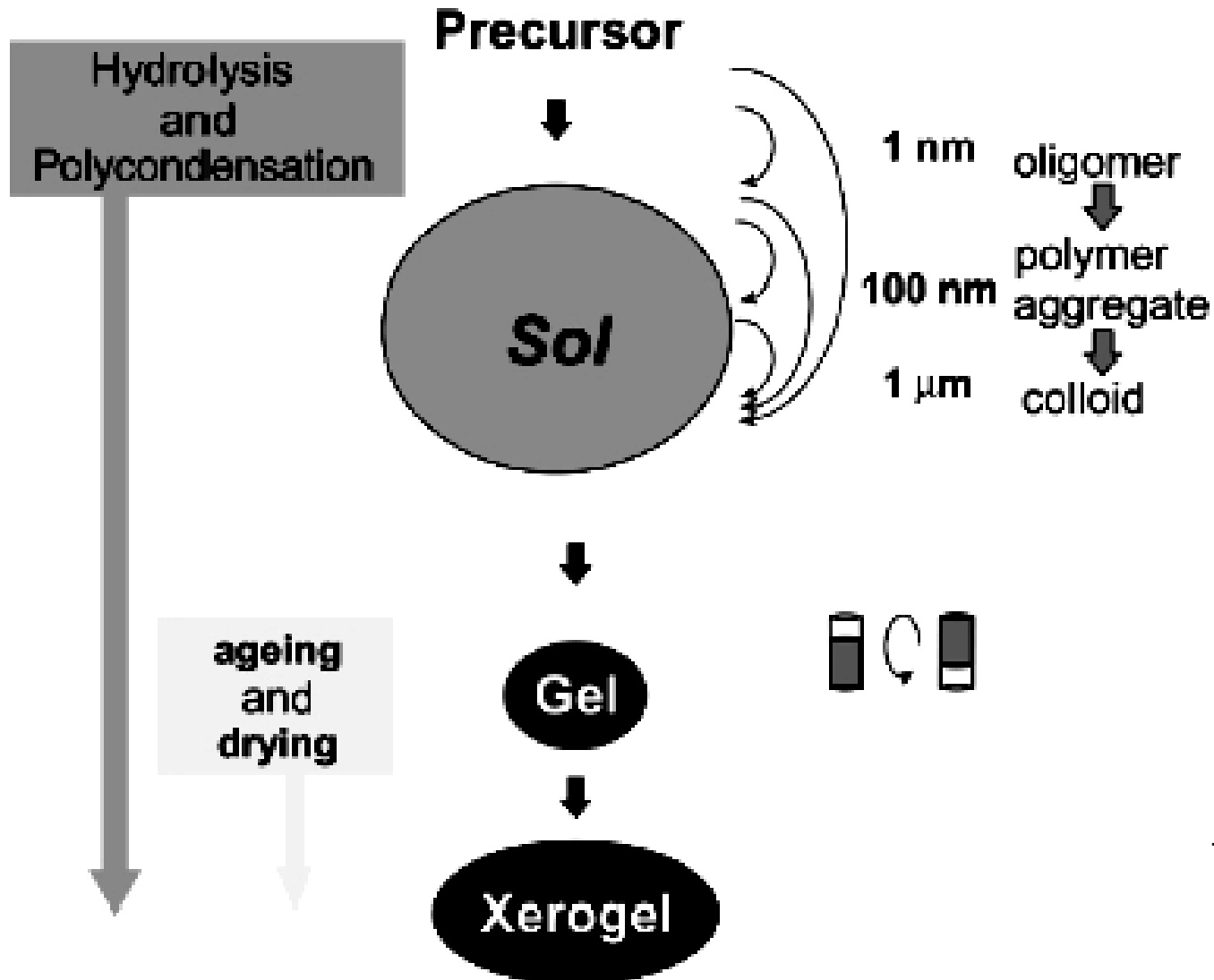
Sometimes the reduction in size is close to 70%

The sample on the left (which contains Rhodamine 6B dye) has gelled, synerized, and is beginning to shrink. The shrinkage has been arrested by sealing the container.

If the container is opened and the sample is allowed to shrink and dry, the sample on the right is achieved in about 1 month.



Size Scale: Is it Nano?

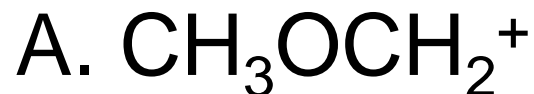


Is it Glass?

- X-ray amorphous
- Random network
- Same as conventional glass? **Not yet**
- Can be multicomponent
- Most glass components available in alkoxide form
- No stoichiometric limits

Are you paying attention?

Which of the following is an example of an alkoxide ion ?



Sol-Gel Process: Processing Steps

- Formulation
 - Acid-addition
 - Base-addition
 - Dilution
- Reaction
 - Hydrolysis
 - Polymerization
- Gellation – polymerization to “no-flow” condition
- Syneresis-spontaneous expulsion of solvent
- Drying – removal of pore fluid
- Shrinkage
- Consolidation
- Sintering