III. Hydrolysis and Condensation of Silicates

♦ ***General***

silicon: atomic number 14

electrons: $3s^2\ 3p^2$

ionic radius: 0.41 Å

oxidation state: z = +4

coordination number: N = 4

Partial positive charge
δ(Si)=+0.32
δ(Ti)=+0.63
δ(Zr)=+0.65

⇒ Less electropositive (compared to transition or IIIA metals)

⇒ Less susceptible to nucleophilic attack

⇒ Hydrolysis and condensation are slower (compared to transition or IIIA metals)

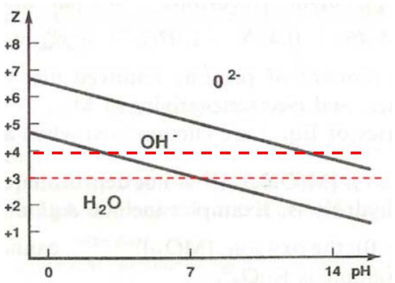
♦ *Aqueous silicates*

Hydrolysis

$$SiCl_4 + 4H_2O \xrightarrow{\text{intermediate pH}} Si(OH)_4 + 4HCl$$

(hydroxo)

"Si-OH" – silanol group



$$Si(OH)_4 + xOH^- \xrightarrow{\text{pH >> 7}} [SiO_x(OH)_{4-x}]^{x-} + xH_2O$$

Condensation

$$\equiv Si\text{-}OH + OH^- \longrightarrow \equiv Si\text{-}O^- + H_2O \quad \text{fast}$$

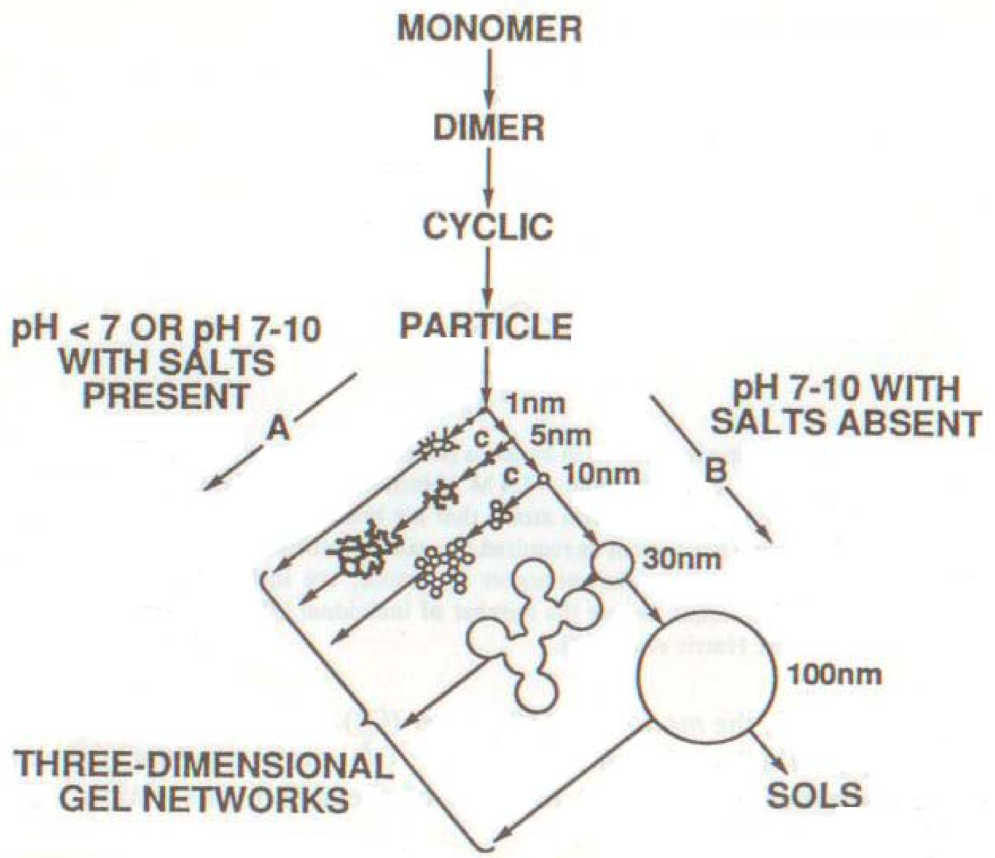
$$\equiv Si\text{-}O^- + HO\text{-}Si\equiv \longrightarrow \equiv Si\text{-}O\text{-}Si\equiv + OH^- \quad \text{slow}$$

Iler's View:

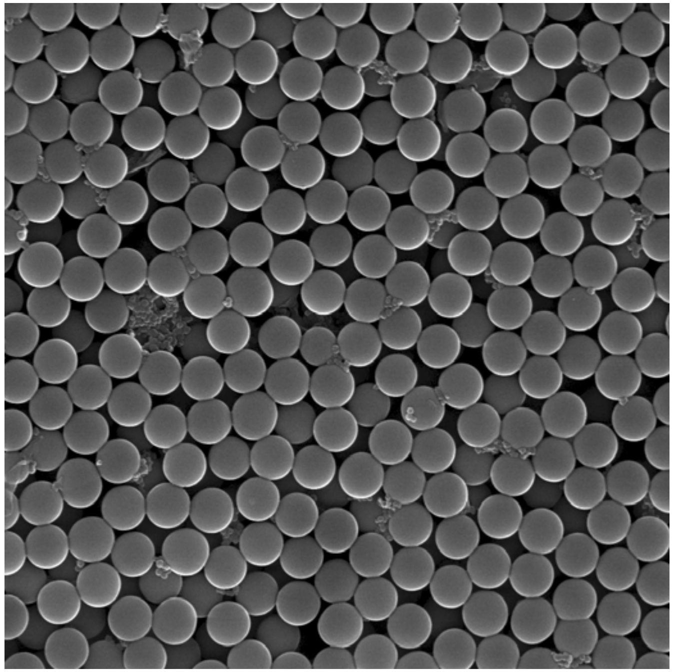
Condensation takes place in such a fashion as to maximize the number of "Si-O-Si" bonds and minimize the number of terminal hydroxyl groups through internal condensation.

Three Stages of Condensation of Silicates

1. Polymerization of monomers to form ultrasmall (< 1nm) particles;
2. Growth of particles;
3. Linking of particles into chain and networks

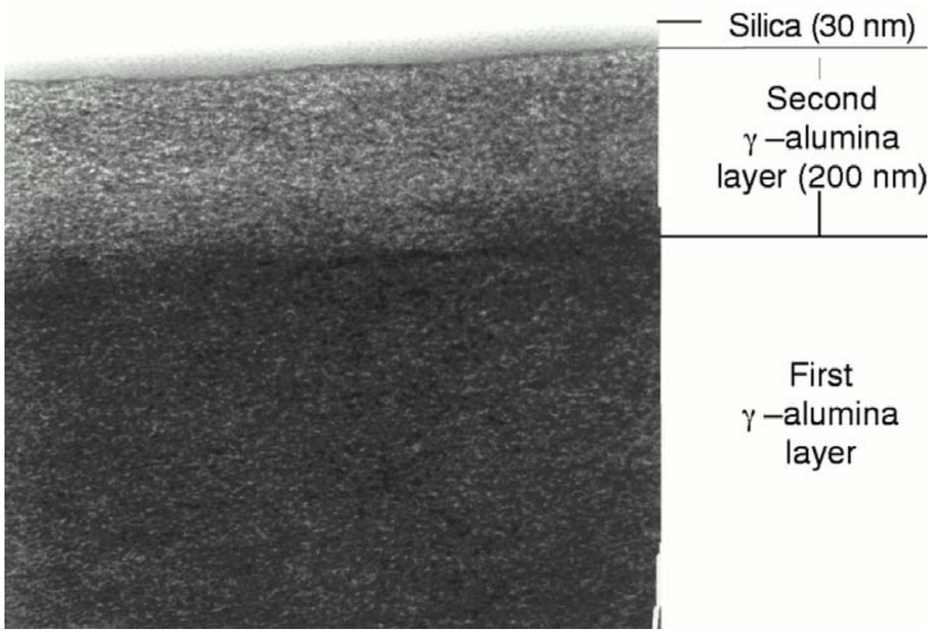


Silica particles
by Stoeber method



(in basic solution)

Silica membrane
for gas separation



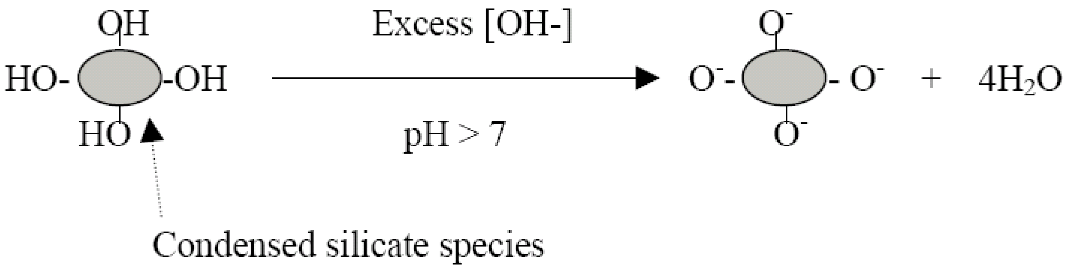
(in acidic solution)

R.M. de Vos and H. Verweij, Science, 1998.

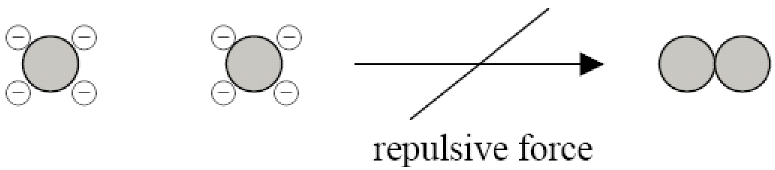
◆ *Condensation after formation of ultrasmall particles (< 1 nm)*

Condensation at pH > 7

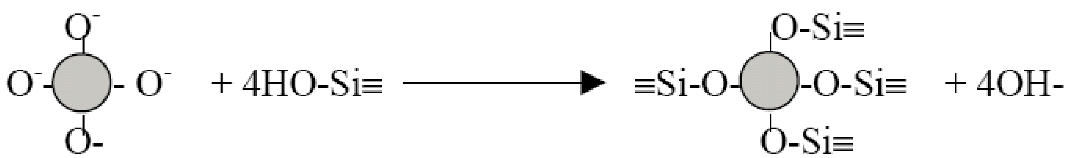
At pH > 7, all condensed species (particles) are more likely to be ionized:



Condensation in following fashion is unlikely:

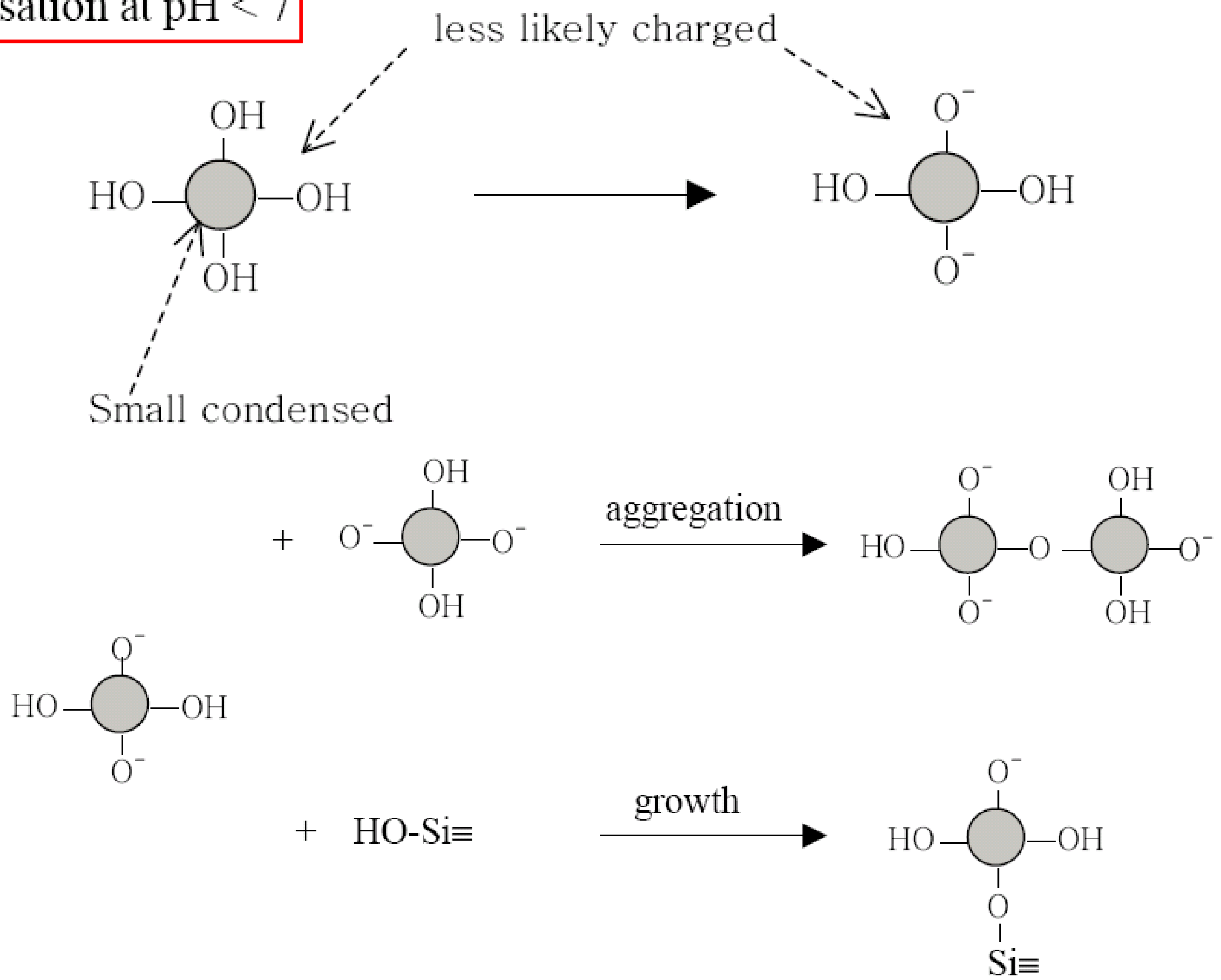


Instead, the particles grow in the following fashion:



Highly condensed large particles are formed (particulate sols)

Condensation at pH < 7



The particles grow and aggregate into three-dimensional networks and form gels.

HYDROLYSIS AND CONDENSATION OF SILICON ALKOXIDES

- ***Most common silicon alkoxide precursors***

Tetraethyl Othosilicate (TEOS)	$Si(OC_2H_5)_4$
Tetramethyl Othosilicate (TMOS)	$Si(OCH_3)_4$

- ***Hydrolysis and Condensation of silicon alkoxides***

Hydrolysis (⇒)

(A) $\equiv Si\text{-}OR + H_2O \Leftrightarrow \equiv Si\text{-}OH + ROH$

Esterification (⇐)

Alcoxolation (⇒)

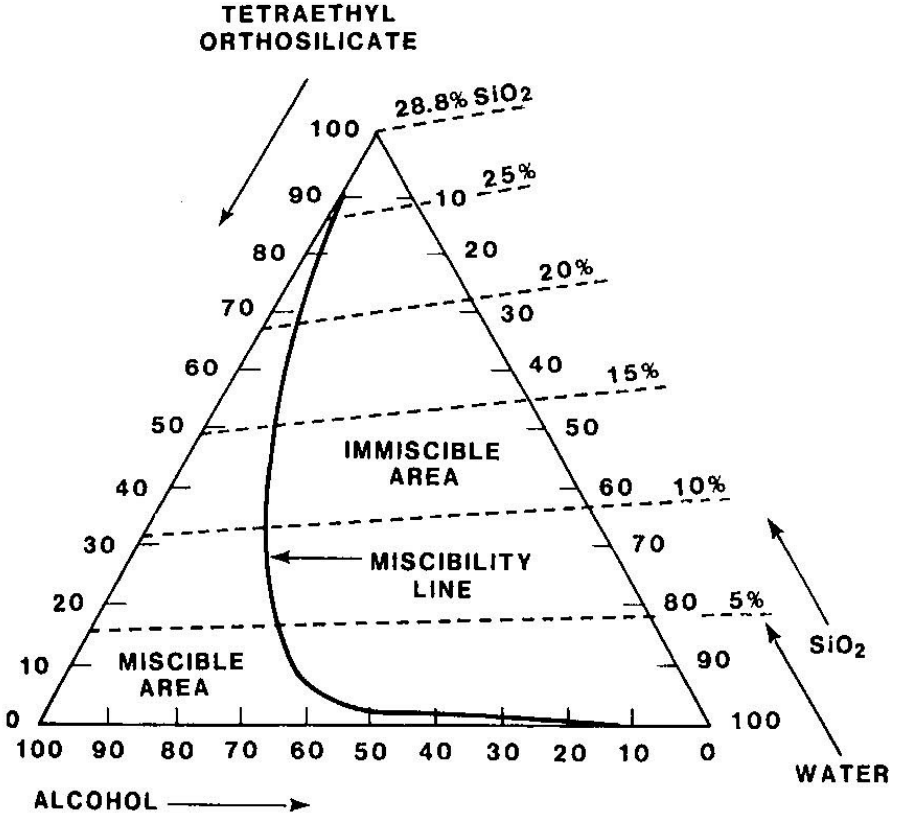
(B) $\equiv Si\text{-}OR + HO\text{-}Si\equiv \Leftrightarrow \equiv Si\text{-}O\text{-}Si\equiv + ROH$

Alcoholysis (⇐)

Water condensation (⇒)

(C) $\equiv Si\text{-}OH + HO\text{-}Si\equiv \Leftrightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$

Hydrolysis (⇐)



Because water and alkoxysilanes are immiscible,
a mutual solvent such as alcohol is used as a homogenizing agent.

However, gels can be prepared from silicon alkoxide-water mixtures without added solvent.
Why?

Effects of Relative Rate of Hydrolysis to Condensation on Sol Structure

Hydrolysis rate	*Condensation rate*	*Particulate Sol*	*Polymeric Sol*
↑	↓	↑	↓

Effects of Water and Alcohol Concentration

		$[H_2O]$ ↑	[ROH] ↑
Hydrolysis	[Reaction (A)]	↑	↓
Condensation	[Reaction (B)]	-	↓
	[Reaction (C)]	↓	-

Effects of Acid Catalyst

Hydrolysis

$$\equiv \mathrm{Si\text{-}OR} \quad + \quad \mathrm{H^+} \xrightarrow[\text{fast}]{\text{Electrophilic attack}} \equiv \mathrm{Si\text{-}}\underset{\substack{| \\ \mathrm{R}}}{\mathrm{O}}\mathrm{\text{-}H^+}$$

$$\equiv \mathrm{Si\text{-}}\underset{\substack{| \\ \mathrm{R}}}{\mathrm{O}}\mathrm{\text{-}\ H^+} \quad + \quad \mathrm{H_2O} \xrightarrow[\text{slow}]{} \equiv \mathrm{Si\text{-}OH} \quad + \quad \mathrm{ROH} \quad + \mathrm{H^+}$$

Condensation

$$\equiv \mathrm{Si\text{-}OR} \quad + \quad \mathrm{H^+} \xrightarrow[\text{fast}]{\text{Electrophilic attack}} \equiv \mathrm{Si\text{-}}\underset{\substack{| \\ \mathrm{R}}}{\mathrm{O}}\mathrm{\text{-}H^+}$$

$$\equiv \mathrm{Si\text{-}}\underset{\substack{| \\ \mathrm{R}}}{\mathrm{O}}\mathrm{\text{-}\ H^+} \quad + \quad \mathrm{HO\text{-}Si}\equiv \xrightarrow[\text{slow}]{} \equiv \mathrm{Si\text{-}O\text{-}Si}\equiv \quad + \quad \mathrm{ROH} \quad + \mathrm{H^+}$$

The hydrolysis is due to the electrophilic attack of on the alkoxy group.

As the hydrolysis progresses:

Number of OR groups	Reactivity	Hydrolysis rate	Rel. Condensation rate
↓	↓	↓	↑

Therefore the acid catalyst will result in more likely a polymeric sol.

Effects of Base Catalyst

Hydrolysis

$$\equiv Si\text{-}OR + OH^- \xrightarrow[\text{slow}]{\text{nucleophilic attack}} \equiv Si\text{-}O\text{-}H + OR^-$$

$$OR^- + H_2O \longrightarrow ROH + OH^-$$

Condensation

$$\equiv Si\text{-}OH + OH^- \xrightarrow[\text{fast}]{} \equiv Si\text{-}O^- + H_2O$$

$$\equiv Si\text{-}O^- + HO\text{-}Si\equiv \xrightarrow[\text{slow}]{} \equiv Si\text{-}O\text{-}Si\equiv + OH^-$$

Base catalyzed hydrolysis proceeds through the nucleophilic substitution of [OH-] ions.
As the hydrolysis progreses:

Number of OR groups	Reactivity	Hydrolysis rate	Rel. Condensation rate
↓	↑	↑	↓

≡Si-OH
Partial Charge of Si
Is more positive

Therefore the base catalyst will result in more likely a particulate sol.

Sol-Gel Kinetics

Hydrolysis

$$\equiv\text{Si-OR} \;+\; \text{H2O} \xrightarrow{k_h} \equiv\text{Si-OH} \;+\; \text{ROH} \qquad \text{(A)}$$

Water Condensation

$$\equiv\text{Si-OH} \;+\; \text{HO-Si}\equiv \xrightarrow{k_{cw}} \equiv\text{Si-O-Si}\equiv \;+\; H_2O \qquad \text{(B)}$$

Alcohol condensation

$$\equiv\text{Si-OR} \;+\; \text{HO-Si}\equiv \xrightarrow{k_{ca}} \equiv\text{Si-O-Si}\equiv \;+\; \text{ROH} \qquad \text{(C)}$$

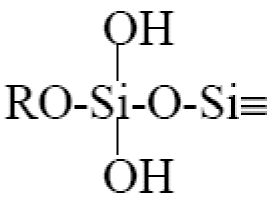
General formula for the species involved in the hydrolysis and condensation process:

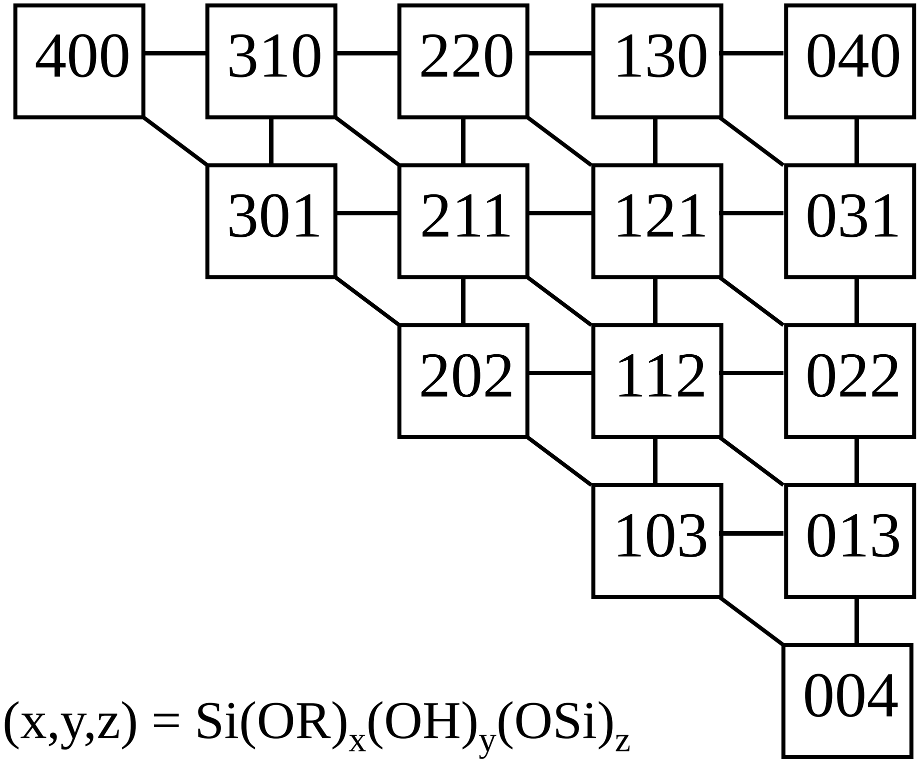
(x, y, z)

$\equiv Si(OR)_x(OH)_y(OSi\equiv)_z$

$x+y+z=4$

e.g., (1,2,1)





$(x,y,z) = Si(OR)_x(OH)_y(OSi)_z$

$x+y+z=4$

For reaction (A) (Hydrolysis)

$\equiv$Si-OR $\longrightarrow$ $\equiv$Si-OH

[x, y, z] $\Rightarrow$ [x-1, y+1, z]

10 possible reactions, 10 k_h for the hydrolysis steps

For reaction (C) (Alcohol condensation):

$\equiv$Si-OH + $\equiv$Si-OR $\longrightarrow$ $\equiv$Si-O-Si$\equiv$

For the first Si:

[x, y, z] $\Rightarrow$ [x, y-1, z+1]

Total 10 reactions

For the second Si:

[x, y, z] $\Rightarrow$ [x-1, y, z+1]

Total 10 reactions

So in total, there are 10$\times$10 = 100 possible reactions (C), 100 k_{ca}.

For reactions (B) (Water Condensation) there are 55 possible reactions.

For the hydrolysis and condensation of silicon alkoxide there are 165 forward reactions steps.