II. Hydrolysis and Condensation of Non-silicates

(Transition Metals and IIIA Metals)

◆ Hydrolysis: a process in which inorganic salt or metal organic precursor is dissolved in a liquid solvent (mainly water or water/alcohol mixture) to form ligands which are capable of forming polymer or crystalline particles

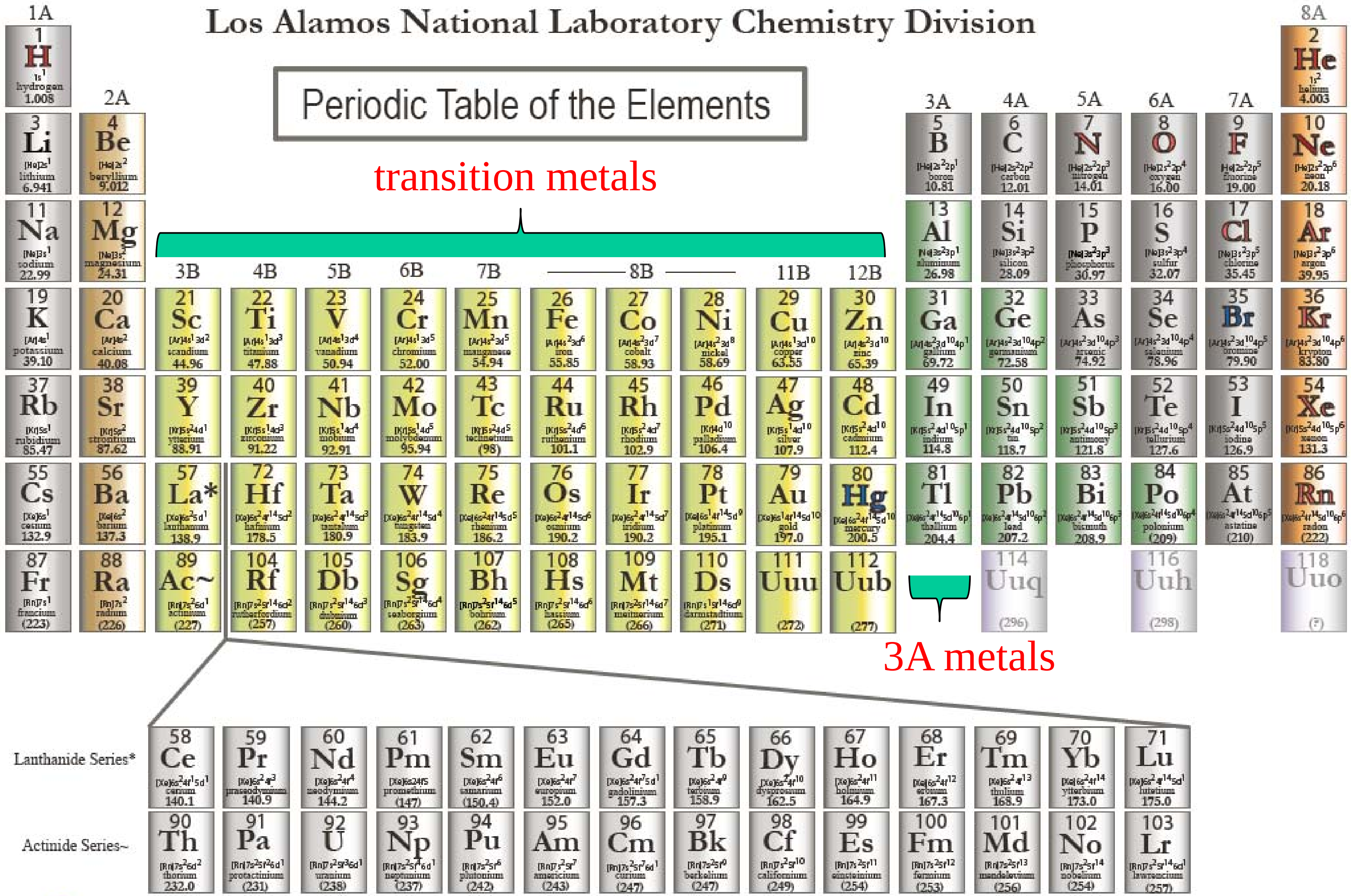
◆ Condensation: a process in which the ligands formed in the hydrolysis are linked to form larger molecules (or crystalline particles)

◆ Transition metals: metals with partially or completely filled “d” electron orbital

◆ IIIA Metals:

metals with 1 electron in “p” orbital

in comparison with silicon, these metals have: lower electronegativity, several coordination states → Greater chemical reactivity



element names in blue are liquids at room temperature
element names in red are gases at room temperature
element names in black are solids at room temperature

- Hydrolysis of Inorganic Precursors

Metal Salt $\xrightarrow{\textit{dissolved in water}}$ M^{z+}

z: number of positive charge of the metal ion

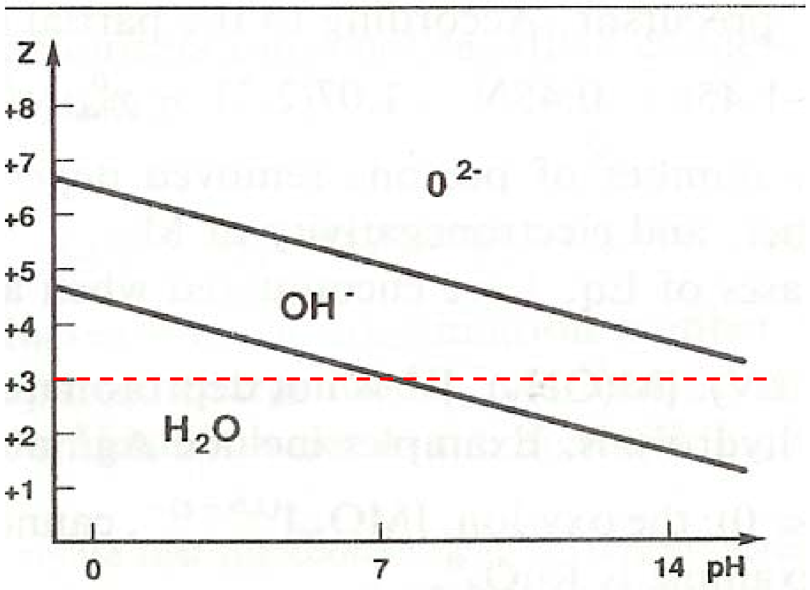
$M^{z+} + :OH_2 \xrightarrow{\textit{Solvated by water molecules}} [M \leftarrow OH_2]^{z+}$

The following equilibriums are established:

$$[M(OH_2)]^{z+} \Leftrightarrow [M\text{-}OH]^{(z-1)+} + H^+ \Leftrightarrow [M\text{-}O]^{(z-2)+} + 2H^+$$

The equilibrium depends on acidity (or pH) of water as well as z of the metal ion

$M\text{-}(OH_2)$	"Aquo"
M-OH	"Hydroxo"
M=O	"Oxo"



(e.g.) Hydrolysis of $AlCl_3$

Al^{3+} r = 0.5 Å

N = 6 (coordination number)

z = 3

At pH=3

$AlCl_3$ ⟶ $[Al(OH_2)_6]^{3+}$

Dissolved in H_2O (aquo)

Increasing pH (> 3)

$[Al(OH_2)_6]^{3+} + hH_2O \longrightarrow [Al(OH)_h(OH_2)_{6-h}]^{(3-h)+} + hH_3O^+$

Aquo-hydroxo complex

General Formula for the Ligands

$[MO_NH_{2N-h}]^{z-h}$

N: coordination number of water molecules

h: molar ratio (water:metal) of hydrolysis

Table 1

h	Ligand	Charge Distrib. δ (on H_{2N-h})	Nucleo-philicity	Conden. Mechanism S_N	A_N
h = 0	Aquo $[M(OH_2)_N]^{+Z}$	↑ +	Leaving group ↓	No	No
0 < h < N	Complex Aquo-Hydroxo			Yes	Yes
h = N	Hydroxo $[M(OH)_N]^{+Z-N}$			Yes	Yes
N < h < 2N	Complex Hydro-oxo			Yes	Yes
h = 2N	Oxo $[MO_N]^{+Z-2N}$	-	Nucleophile	No	Yes*

* at least one of the reactant species is coordinatively unsaturated (N < Z)

Ligand with large nucleophilicity ⇒ nucleophile

Ligand with small nucleophilicity ⇒ leaving groups

CONDENSATION AFTER HYDROLYSIS OF INORGANIC PRECURSOR

- Nucleophilic Substitution (S_N)

$$M_1\text{-}OX + M_2\text{-}\underline{OY} \longrightarrow M_1\text{-}\overset{\overset{X}{\uparrow}}{O}\text{-}M_2 + \underline{OY}$$

separated

Charge distribution (more positive, leaving group)

Preferred coordination number is satisfied

(e.g.) Formation of Dimer

$$(H_2O)_5Al(OH)^{2+} + (HO)Al(OH_2)_5^{2+}$$

$$\longrightarrow (H_2O)_4Al\langle{}^{OH}_{OH}\rangle Al(H_2O)_2^{4+} + 2H_2O$$

- Nucleophilic Addition (A_N)

$$M_1\text{-}OX + M_2\text{-}OY \longrightarrow M_1\text{-}\overset{\overset{X}{\uparrow}}{O}\text{-}M_2\text{-}OY$$

Less positive nucleophile

Preferred coordination number not satisfied

Table 2

Condensation Process	Mechanism (see Table 1)	Conditions	Kinetics
Olation "-OH-" bridge formed	S_N	Preferred coordination satisfied	Rate ↑ As z ↓ & size ↑
Oxolation "-O-" bridge formed	A_N	Coordination unsatisfied	Rapid
Two-step M-OH + M-OH → M-O-M-OH (with H on the bridging O) → M-O-M + H2O	A_N/S_N	Oxohydroxy ligands	slower

In the hydrolysis/condensation process, whether precipitation or gelation occurs, or whether polymeric sol or particulate sol is formed depends on:

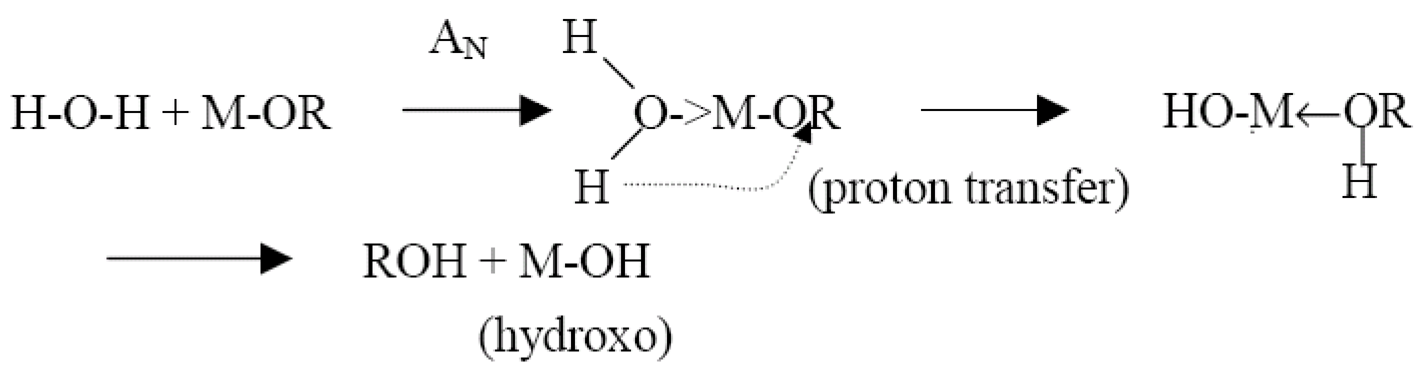
- √ precursor properties
- √ temperature
- √ condensation kinetics
- √ pH
- √ speed of mixing
- √ solvent: water/alcohol ratio

HYDROLYSIS AND CONDENSATION OF METAL ALKOXIDE PRECURSORS

$M(OR)_Z$: Very reactive due to the presence of highly electronegative "OR" group

Stabilizing M in its highest oxidation state, susceptible to nucleophilic attack

Hydrolysis



Condensation

(a) Alcoxolation:

$$M\text{-}OH + M\text{-}OR \longrightarrow M\text{-}O(H)\text{-}M\text{-}OR$$

$$\longrightarrow M\text{-}O\text{-}M\text{-}OR(H) \longrightarrow M\text{-}O\text{-}M + ROH$$

(b) Oxolation:

$$M\text{-}OH + M\text{-}OH \longrightarrow M\text{-}O(H)\text{-}M\text{-}OH$$

$$\longrightarrow M\text{-}O\text{-}M\text{-}OH_2$$

$$\longrightarrow M\text{-}O\text{-}M + H_2O$$