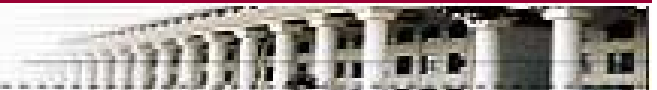


II. Hydrolysis and Condensation of Non-silicates

(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



Los Alamos National Laboratory Chemistry Division

Periodic Table of the Elements

transition metals

1A 1 H hydrogen 1.008	2A 4 Be beryllium 9.012											3A 5 B boron 10.81	4A 6 C carbon 12.01	5A 7 N nitrogen 14.01	6A 8 O oxygen 16.00	7A 9 F fluorine 19.00	8A 2 He helium 4.003	
3 Li lithium 6.941	11 Na sodium 22.99	12 Mg magnesium 24.31	3B 21 Sc scandium 44.96	4B 22 Ti titanium 47.88	5B 23 V vanadium 50.94	6B 24 Cr chromium 52.00	7B 25 Mn manganese 54.94	8B 26 Fe iron 55.85	27 Co cobalt 58.93	28 Ni nickel 58.69	11B 29 Cu copper 63.55	12B 30 Zn zinc 65.39	31 Ga gallium 69.72	32 Ge germanium 72.58	33 As arsenic 74.92	34 Se selenium 78.96	35 Br bromine 79.90	36 Kr krypton 83.80
37 Rb rubidium 85.47	38 Sr strontium 87.62	39 Y yttrium 88.91	40 Zr zirconium 91.22	41 Nb niobium 92.91	42 Mo molybdenum 95.94	43 Tc technetium (98)	44 Ru ruthenium 101.1	45 Rh rhodium 102.9	46 Pd palladium 106.4	47 Ag silver 107.9	48 Cd cadmium 112.4	49 In indium 114.8	50 Sn tin 118.7	51 Sb antimony 121.8	52 Te tellurium 127.6	53 I iodine 126.9	54 Xe xenon 131.3	
55 Cs cesium 132.9	56 Ba barium 137.3	57 La* lanthanum 138.9	72 Hf hafnium 178.5	73 Ta tantalum 180.9	74 W tungsten 183.9	75 Re rhenium 186.2	76 Os osmium 190.2	77 Ir iridium 192.2	78 Pt platinum 195.1	79 Au gold 197.0	80 Hg mercury 200.5	81 Tl thallium 204.4	82 Pb lead 207.2	83 Bi bismuth 208.9	84 Po polonium (209)	85 At astatine (210)	86 Rn radon (222)	
87 Fr francium (223)	88 Ra radium (226)	89 Ac~ actinium (227)	104 Rf rutherfordium (261)	105 Db dubnium (262)	106 Sg seaborgium (263)	107 Bh bohrium (264)	108 Hs hassium (265)	109 Mt meitnerium (266)	110 Ds darmstadtium (271)	111 Uuu (272)	112 Uub (277)	114 Uuq (296)	116 Uuh (298)	118 Uuo (?)				
Lanthanide Series*		58 Ce cerium 140.1	59 Pr praseodymium 140.9	60 Nd neodymium 144.2	61 Pm promethium (147)	62 Sm samarium (150.4)	63 Eu europium 152.0	64 Gd gadolinium 157.3	65 Tb terbium 158.9	66 Dy dysprosium 162.5	67 Ho holmium 164.9	68 Er erbium 167.3	69 Tm thulium 168.9	70 Yb ytterbium 173.0	71 Lu lutetium 175.0			
Actinide Series~		90 Th thorium 232.0	91 Pa protactinium (231)	92 U uranium (238)	93 Np neptunium (237)	94 Pu plutonium (242)	95 Am americium (243)	96 Cm curium (247)	97 Bk berkelium (247)	98 Cf californium (249)	99 Es einsteinium (254)	100 Fm fermium (253)	101 Md mendelevium (256)	102 No nobelium (254)	103 Lr lawrencium (257)			

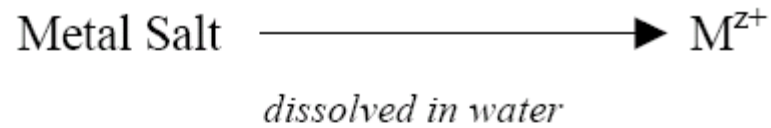
3A metals



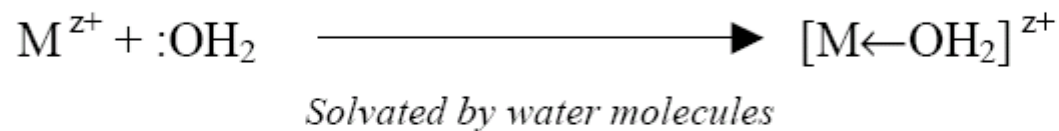
element names in blue are liquids at room temperature
 element names in red are gases at room temperature
 element names in black are solids at room temperature



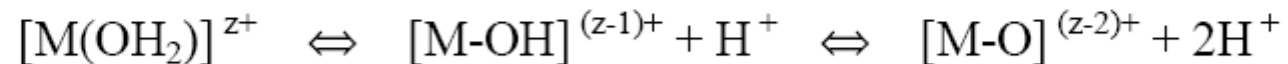
◆ Hydrolysis of Inorganic Precursors



z: number of positive charge of the metal ion



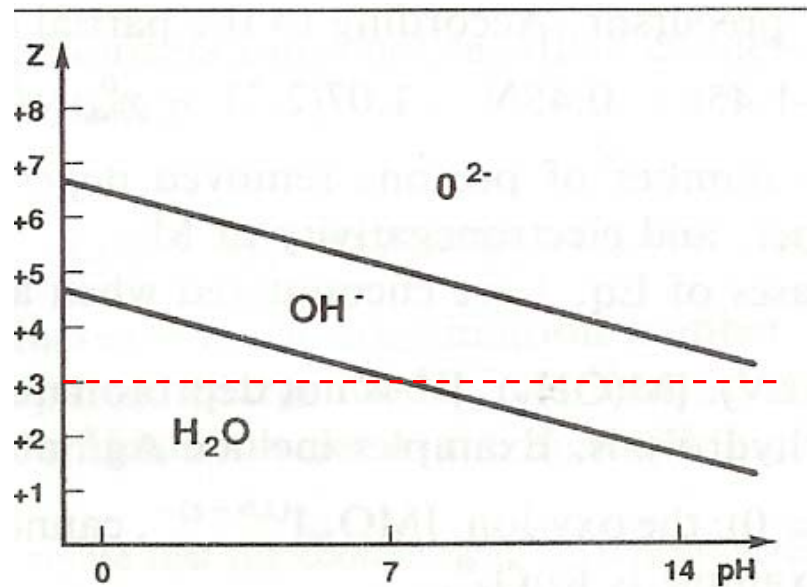
The following equilibriums are established:



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

M-(OH ₂)	“Aquo”
M-OH	“Hydroxo”
M=O	“Oxo”





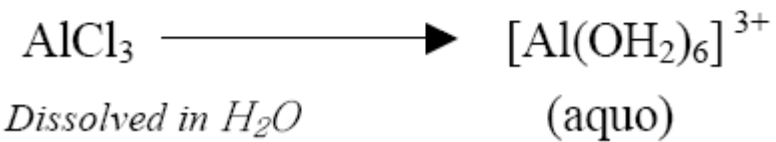
(e.g.) Hydrolysis of AlCl_3

Al^{3+} $r = 0.5 \text{ \AA}$

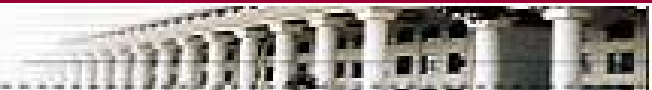
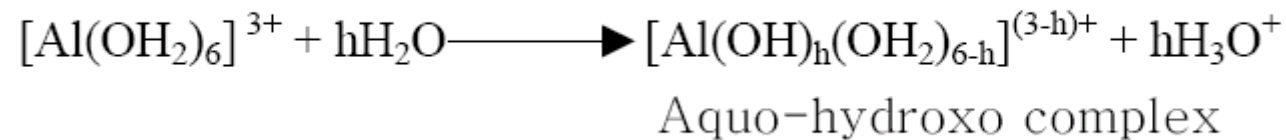
$N = 6$ (coordination number)

$Z = 3$

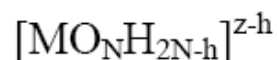
At $\text{pH} = 3$



Increasing $\text{pH} (> 3)$



General Formula for the Ligands



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

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

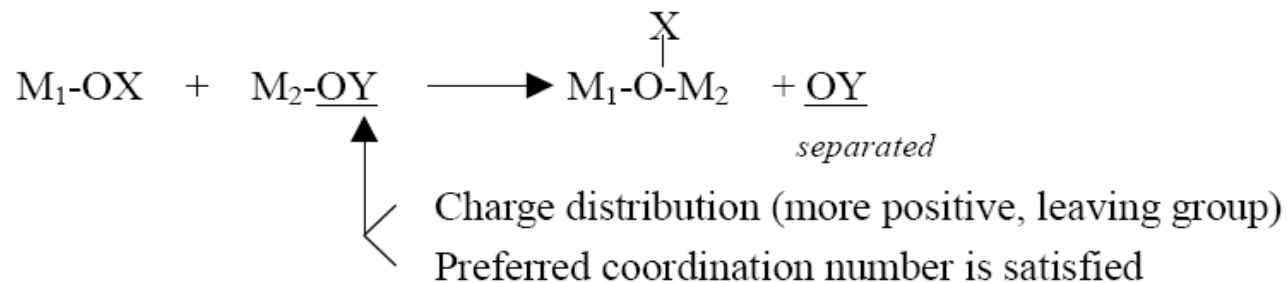
Ligand with large nucleophilicity \Rightarrow nucleophile

Ligand with small nucleophilicity \Rightarrow leaving groups

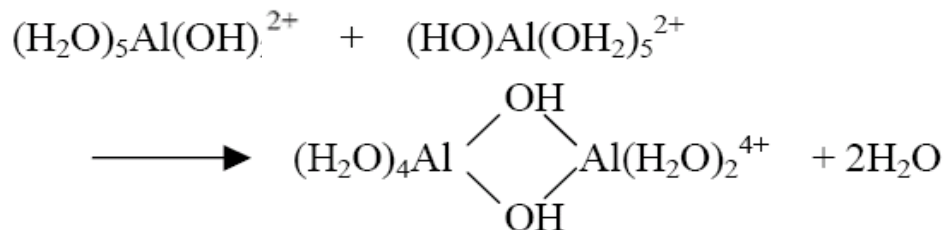


CONDENSATION AFTER HYDROLYSIS OF INORGANIC PRECURSOR

◆ Nucleophilic Substitution (S_N)



(e.g.) Formation of Dimer



◆ Nucleophilic Addition (A_N)

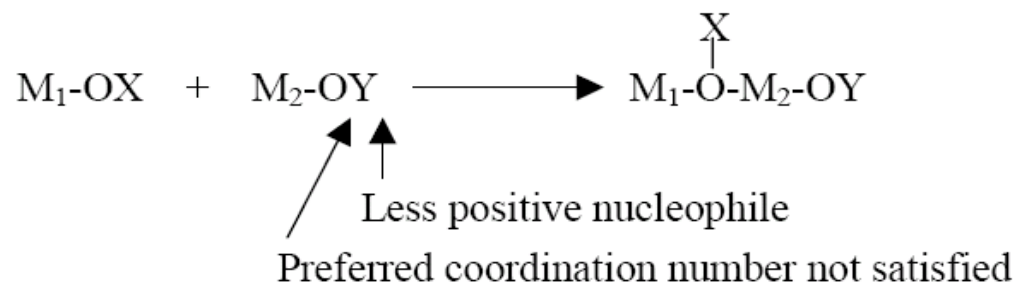


Table 2

Condensation Process	Mechanism (see Table 1)	Conditions	Kinetics
Olation “-OH-“ bridge formed	S_N	Preferred coordination satisfied	Rate \uparrow As $z \downarrow$ & size \uparrow
Oxolation “-O-“ bridge formed	A_N	Coordination unsatisfied	Rapid
Two-step $M-OH + M-OH$ \swarrow $M-O-M-OH$ \downarrow H \searrow $M-O-M + H_2O$	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

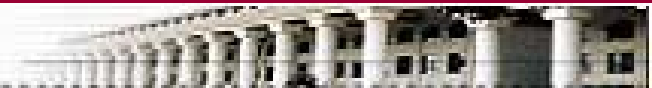
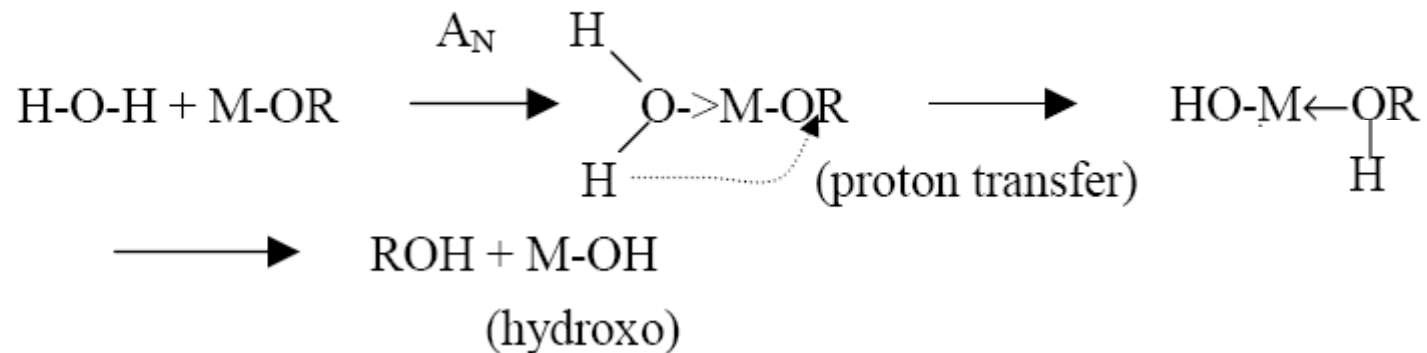


HYDROLYSIS AND CONDENSATION OF METAL ALKOXIDE PRECURSORS

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

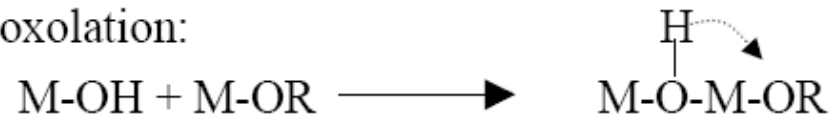
Stabilizing M in its highest oxidation state, susceptible to nucleophilic attack

Hydrolysis



Condensation

(a) Alcoxolation:



(b) Oxolation:

