# SYNTHESIS OF INORGANIC MATERIALS AND NANOMATERIALS

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# Outline

**IV - FORMATION OF SOLIDS FROM SOLUTIONS**

**1) Glass**

**2) Precipitation**

**3) Biomaterials**

**a) Biogenic materials and biomineralization**

**b) Synthetic biomaterials**

**c) Biomimetic materials chemistry**

**4) Solvothermal synthesis**

**5) Sol-gel processes**

# 2) Precipitation

It is easy to obtain a precipitate

Ex.: $NO_3^-(aq) + Ag^+(aq) + Na^+(aq) + Br^-(aq) \rightarrow AgBr(s) + NO_3^-(aq) + Na^+(aq)$

But it is not easy to control

- the size and size distribution of the crystallites
- the shape of the crystallites
- the agglomeration of the crystallites into grains

→ video: $HgI_2$, $PbI_2$

Generally, we observe the formation of complex mixtures.

Precipitation is a complex phenomena comprising:

- nucleation
- particle growth
- aging (Ostwald ripening): small particles ↓, large particles become larger
- recrystallization
- coagulation
- agglomeration

What happen when we increase the concentration through a chemical reaction?

→ see figure concentration vs time

→ $C_s$ to $C_M$: range of supersaturation

→ video: supersaturated solution of $NaCH_3CO_2 \cdot 3H_2O$

# 2) Precipitation

**How can we obtain uniform crystallites?**

**➔ separation between nucleation step and growth step**

**Ex.: formation of hydroxides by pH variation**

**➔ see equation**

**➔ acid-base equilibrium**

**➔ stability domains**

**Ex.: $Fe^{3+}(aq) + HO^{-}(aq)$ ➔ $Fe_2O_3(s)$, $Fe_2O_3 \cdot nH_2O$, $Fe(OH)_3$, $FeO(OH)$**

**How to control nature, shape, size and agglomeration of crystallites?**

**➔ concentration**

**➔ nature of reactant: NaOH, $Na_2CO_3$, $NH_3(aq)$…**

**➔ key parameter: rate of pH variation**

**- difficult to control by adding the second reactant: large local increase of pH**

**- use of a neutral reactant which will transform slowly into a basic species**

**➔ urea $NH_2CONH_2$**

$$NH_2CONH_2(aq) + 2\ H_2O(l) \rightarrow 2\ NH_4^+(aq) + CO_3^{2-}(aq)$$

**Slow hydrolysis controlled by temperature and concentration**

**Then** $$NH_4^+(aq) + CO_3^{2-}(aq) = NH_3(aq) + HCO_3^-(aq)$$

**Final pH controlled by $NH_4^+(aq)/NH_3(aq)$ acid-base couple: ➔ pH ~ 9.3**

# 2) Precipitation

Ex.: AgBr $NO_3^-(aq) + Ag^+(aq) + Na^+(aq) + Br^-(aq) \rightarrow AgBr(s) + NO_3^-(aq) + Na^+(aq)$

We can control $[Ag^+]$ or $[Br^-]$

$K_s = [Ag^+]\,[Br^-] = 5 \times 10^{-13}$ solubility product

$[Ag^+] > 3 \times 10^{-8}$ (or $[Br^-] < 1.7 \times 10^{-5}$) → cubic particles with faces (1 0 0)

$[Ag^+] < 3 \times 10^{-9}$ (or $[Br^-] > 1.7 \times 10^{-4}$) → octahedron particles with faces (1 1 1)

→ difference due to adsorption of $Br^-$ on different faces of AgBr particles

When $[Ag^+] > 3 \times 10^{-8}$ mol $L^{-1}$

→ adsorption of $Br^-$ mainly on faces (1 0 0)

→ growth rate is larger for faces (1 1 1)

See figure

→ the growing faces (1 1 1) disappear → remaining faces (1 0 0)

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# 3) Biomaterials a) Biogenic materials and biomineralization

**Biomineralization → living cells and organisms are able to produce solids at room temperature and pressure**

**Ex.: $CaCO_3$ (calcite or aragonite)**

- **egg shell, seashells**
- **coral, ivory**
- **see-urchin spines**

**Ex.: hydroxyapatite ($Ca_5(PO_4)_3(OH)$)**

- **bones**

**Ex.: fluoroapatite ($Ca_5(PO_4)_3F$)**

- **enamel (teeth)**

**Ex.: calcium oxalate monohydrate ($CaC_2O_4 \cdot H_2O$)**

- **kidney stone**

**Ex.: amorphous silica $SiO_n(OH)_{4-2n}$**

- **diatom valves, sponge spicules**

**→ complex processes inside the cells**

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# 3) Biomaterials b) Synthetic biomaterials

**Non-ability to command living cells to tailor dedicated materials**
**Biomaterials used in prostheses or medical devices in contact with living body**

**Polymers → ophtalmology, skin wound treatments**

**Metals → fracture fixation, dental amalgams, dental implant**

**Glass, ceramics → bioactive components for a better adhesion of implants**

**bone substitutes → carbonate-containing hydroxyapatite similar to bone mineral**
**→ $Ca_{8.8}(HPO_4)_{0.7}(PO_4)_{4.5}(CO_3)_{0.7}(OH)_{1.3}$ size about 20 nm**

**Joint prostheses → metal + porous coating - bone (artificial hip prostheses)**

**Polymer or ceramic → false teeth**

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# 3) Biomaterials c) Biomimetic materials chemistry

**Ex. 1: oxide or hydroxide growth**
**See figure: membrane-mediated precipitation of metal oxides or hydroxides in vesicles**

**Ex. 2: layered sulfide formation on surfactant monolayers (model for surface of biological membranes)**
**See figure**

**➔ formation of a porous sulfide semiconductor film**

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  - **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**

# 4) Solvothermal synthesis  a) Hydrothermal synthesis of single crystals

**Solvent: $H_2O$, $NH_3$**

**Parameters:**

- **Temperature: T > boiling temperature (up to 300 °C)**
- **Pressure: increase with temperature**
- **Volume**

| **Ex.: water** | **T /°C** | **P /bar** | |
|---|---|---|---|
| | **120** | **1.9** | **(kitchen pressure cooker)** |
| | **150** | **4.5** | |
| | **200** | **14** | |
| | **250** | **33** | |

**➔ use of autoclaves**

**1845, Papin's pot ➔ formation of quartz crystals  size > 10 µm**

**➔ piezoelectric quartz for electronics industry, oscillator (watches)**

**➔ Possibility to obtain large crystals, gemstones (amethyst, citrine…)**

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# 4) Solvothermal synthesis b) Hydrothermal synthesis of nano-materials

**Size < 1 µm**

**Ex.:** $Ba(OH)_2(aq) + TiO_2 \rightarrow BaTiO_3(s) + H_2O(l)$
temperature 150 – 250 °C

**Ex.:** synthesis of zeolites
$MI_x[Al_xSi_yO_{2(x+y)}]\cdot zH_2O$

$Na_2SiO_3 + NaOH + Al_2(SO_4)_3 + C_3H_7\text{-}NH_2 + (C_3H_7)_4N^+Br^- + H_2O$
160 °C, several days $\rightarrow$ zeolites ZMS-5

**See figures**

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# 5) Sol-gel processes  a) The physics of sols

**Sol gel process ➔ creation of a network by condensation reactions**

**Definitions:**

**Sol:** stable suspension of colloidal solid particles (or polymers) in a liquid
particles amorphous or crystalline, size 1 to 1000 nm

**Gel:** porous 3-D solid network supporting a continuous liquid phase (wet gel)

**Colloidal gels: network made by agglomeration of dense colloidal particles**

**➔ See figure: sol-gel processing**

**Type of bonds:**

- **covalent bonds ➔ sol-gel process irreversible**
- **van der Waals bonds, H-bonds ➔ sol-gel process reversible**

**➔ See figure: PZT films $PbZr_{1-x}Ti_xO_3$ perovskite type (x = 0.47)**
**➔ crystallite size: 6 to 10 nm**
**➔ ferroelectric properties**

# 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**

| | $SiO_2$ | $SnO_2$ | $TiO_2$ | $Al_2O_3$ | 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 $\Phi_H$**
**- slip plane: between diffuse layer and bulk; potential $\Phi_\zeta$**

# 5) Sol-gel processes a) The physics of sols

**In an electric field, the particle 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 $\Phi_\zeta$ 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**