Precipitation
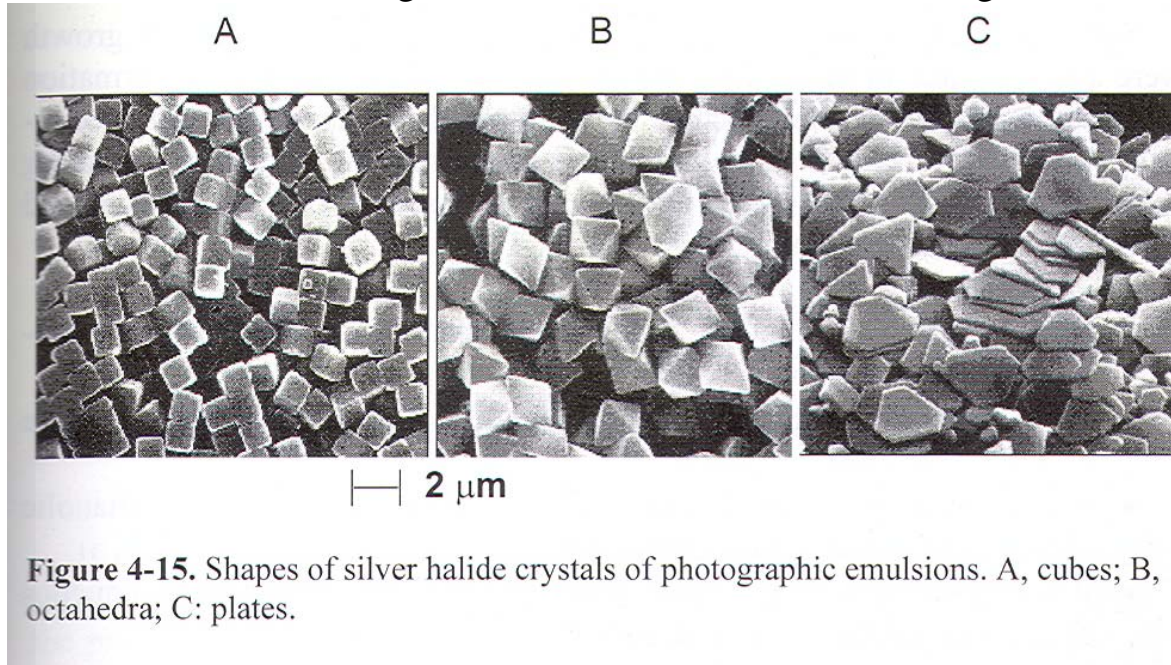
Precipitation is easy
Control over crystallite size, size distribution, morphology… is hard

Example: Silver halides for photographic emulsions
Strong dependence on size, shape and composition

Silver nitrate is added to a gelatin solution at 30-80°C under vigorous stirring

Figure 4-15. Shapes of silver halide crystals of photographic emulsions. A, cubes; B, octahedra; C: plates.

Precipitation

Processes which may be involved in precipitation:
- **Nucleation**
- **Crystal growth**
- **Ostwald ripening**
- **Recrystallization**
- **Coagulation**
- **Agglomeration**

It is necessary to control each of these steps in order to e.g. form monodisperse particles with a well-defined and reproducible morphology

Monodisperse materials are interesting e.g. for formation of stable dispersions, uniform ceramics powders, pigments with reproducible colour, catalysts and nano-objects.

The solvent is usually water, but may be other solvents or molten salts.

Nucleation and growth

In melts, temperature was the decisive factor.
In solutions, concentration must be increased

- Direct reaction of ions (e.g. adding bromine ions to a solution containing silver cations)
- Redox reactions (e.g. reduction of HAuCl4 with formaldehyde to give colloidal gold)
- Precipitation by poor solvents (e.g. adding water to an ethanolic solution of sulphur)
- Decomposition of compounds (e.g. adding acid to an aqueous solution of thiosulphate to precipitate sulphur)
- Hydrolysis

Decomposition or removal of complexing agents:
Precipitation and growth of large crystals of Ag_2CO_3 from $NH_{3(aq)}$
Precipitation of α-TiHPO$_4$ H$_2$O using complexing by HF

Temperature control

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LaMer model

- The concentration of the solute is increased up to the minimum concentration for nucleation, c_0. No precipitation
- Nucleation starts at c_0. The concentration of the solute is still rising until the maximum concentration for nucleation, c_N, where it starts to decrease due to nucleation and precipitation. The range between c_S and c_N is the supersaturation range.
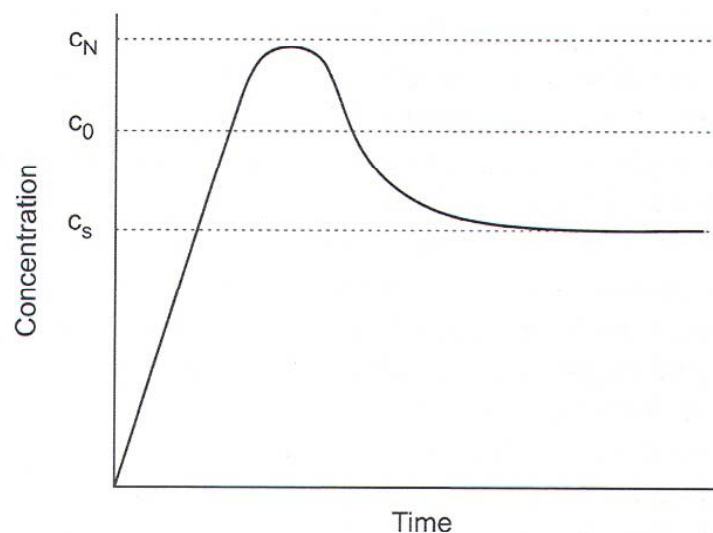- Below c_0, nucleation ceases, and crystallization proceeds until c_S.

Figure 4-16. Concentration of the solute before and after nucleation.

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Growth

If new nuclei form during growth, a range of particle sizes is obtained.
In order to obtain monodisperse crystals, nucleation and growth must be separated.

The rate of growth may be controlled by diffusion of dissolved species to the particles or by the rate of condensation.

Another source of particle forming species is dissolution of smaller particles (more soluble due to surface curvature.)

Ostwald ripening effects usually work up to 5nm particles.

Forced hydrolysis

Precipitation of metal oxides or hydroxides by deprotonating the hydrated metal ions resulting in polycondensation reactions.

$$\left[M-O\begin{matrix} H \\ \\ H \end{matrix} \right]^{n+} \xrightleftharpoons{-H^+} \left[M-OH \right]^{(n-1)+} \xrightleftharpoons{-H^+} \left[M=O \right]^{(n-2)+}$$

(4-10)

Formation of oxides is favoured by high charge on the metal ions and/or high pH
Hydrolysis of low-valent (<4) cations yield aquo, hydroxy or aquo-hydroxy complexes. Higher valent cations form oxo or oxo-hydroxy compounds.
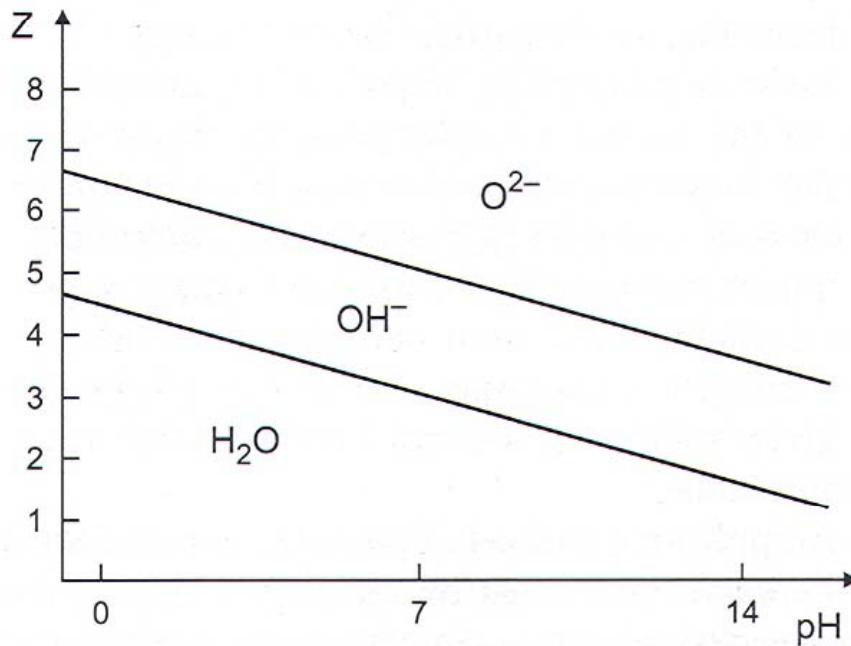
Figure 4-17. Charge (Z) versus pH diagram indicating the domains of aquo, hydroxo, and oxo species.

The reaction may be shifted towards oxides from metal salts. Formamide may be used to raise the pH gradually (decomposes to yield ammonia)

Aging at higher temperatures promotes dissociation of protons.

Iron oxides

Precipitation of iron oxide/hydroxide by aging acidic solutions of Fe(III)-salts.
Obtained either FeOOH or Fe_2O_3 depending on conditions
Cubic, ellipsoidal, pyramidal, rod-like or spherical particles may be formed.
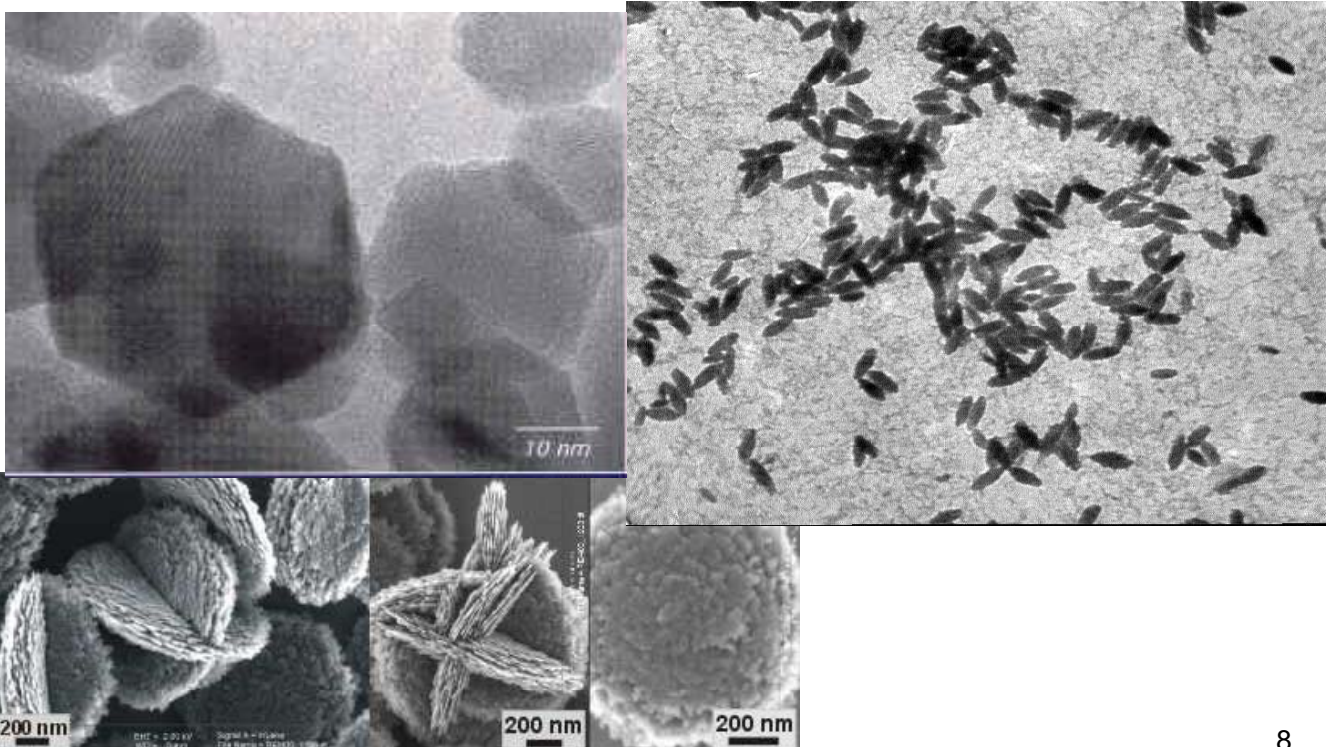
Double jet precipitation

Introduction of solutions forming sparingly soluble salt into a stirred reactor.
Fast nucleation in the injection zone, followed by growth in the outer zone.
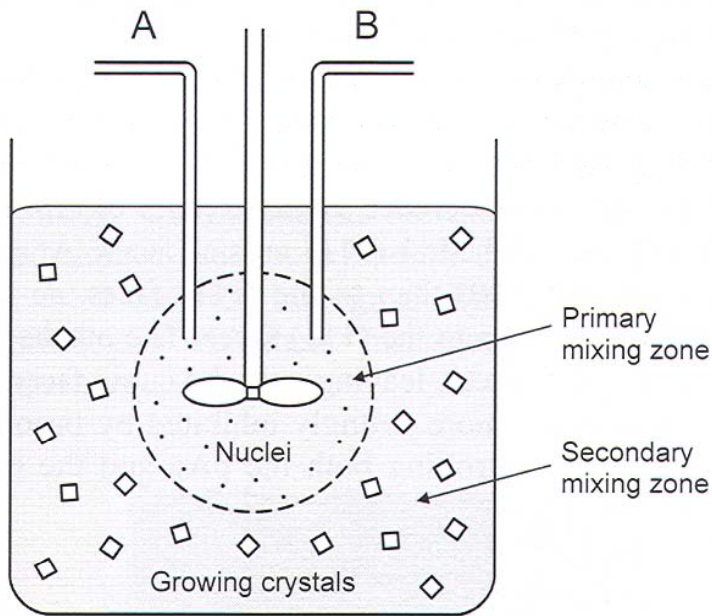High supersaturation in the mixing zone (10^5-10^8 times)

Figure 4-18. Model of a crystallizer for the controlled double jet precipitation (CDJP) process.

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