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II - Low temperature methods

The so called low temperature reactions or preparations are said to proceed below the temperatures at which the thermodynamically stable phases are prepared. This crude definition mainly concerns metastable phase preparation or crystallisation from solutions or fluxes.

1. "Chimie douce"

Metastable phase preparation has lead to the development of a full area of chemistry : the "chimie douce". After the preparation of proton exchanged $HMM'O_6$ pyrochlores (M=Ti, Sb, M'=Nb, W), of hexagonal WO_3 by M. Figlarz and co-workers, numerous examples have been found (TiO_2-B, FeF_3 pyrochlore). An illustration, from the author's experience of this "chimie douce" process, concerns the synthesis of an amorphous form of iron trifluoride FeF_3,xHF. It is prepared from $FeCl_3$ under HF gas flow at 60-80 °C.

$$(3+x)HF + FeCl_3 \xrightarrow{60-80°C,12h} FeF_3, xHF + 3HCl \qquad 0.4 \le x \le 1.0$$

On heating above 100 °C, the loss of gaseous HF gradually increases. The amorphous green powder crystallises at $T = 315\ °C$ (heating rate 10 °C/h), to give the stable ReO_3 type phase α-FeF_3 :

$$FeF_3, xHF \rightarrow FeF_3 + xHF$$

2. Growth in solutions

Salts with an endothermic dissolution enthalpy, present a solubility which increases with the temperature. Exothermic dissolution corresponds to the opposite effect. These features are qualitatively demonstrated by considering a saturated solution (B solute in a solvent) in equilibrium with the solid at two different temperatures :

$$B_{solid} \rightleftarrows B_{solv} \qquad K_c = x_B^1$$

The solubility variation is related to the dissolution Gibbs energy ΔG_d^0 :

$$\frac{(\mathrm{Log}\ x_B^1)_{T_2} - (\mathrm{Log}\ x_B^1)_{T_1}}{T_2 - T_1} \approx \frac{d(\mathrm{Log}\ K_c)}{dT} = -\frac{d(\Delta G_d^0/RT)}{dT} = \frac{\Delta H_d^0}{RT^2} \qquad \{9\}$$

A positive dissolution enthalpy ΔH_d^0 gives a solubility which increases with the temperature.

Crystallisation of B from the solvent can be achieved either by a variation of T, from T_1 to T_2 (horizontal paths in figure 8), by solvent evaporation (vertical paths in figure 8) or by the addition of a salt which decreases the solubility of B.

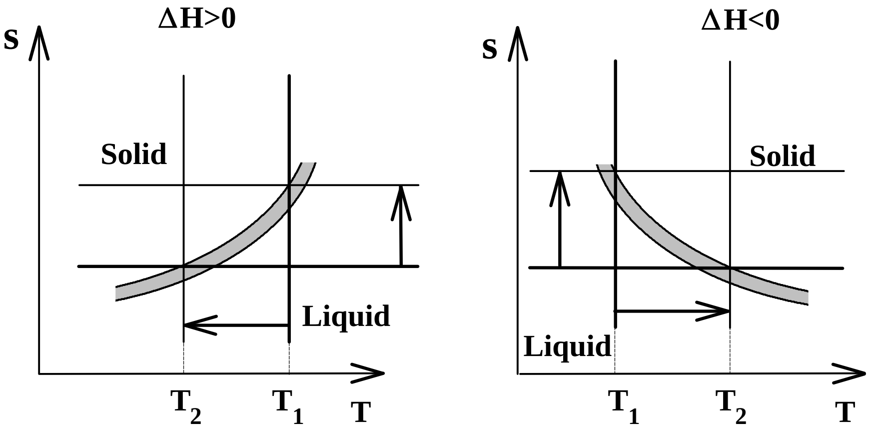

Figure 8. - Crystallisation paths for solutes with positive or negative ΔH_d *dissolution enthalpy*

The metastable saturation zone (hatched domains in figure 8) must be crossed when crystallisation takes place in the absence of crystal seeds (see Box 3).

In a steady state hypothesis, (very slow continuous growth of a crystal face), the diffusion equation of Box 3 is oversimplified to give the boundary layer model (figure 9) :

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial y^2} = 0 \qquad \text{with } J = -D\frac{\partial C}{\partial y} = v$$

The growth speed v is proportional to supersaturation (C_1-C_0) at the liquid-solid interface level $v = k(C_1 - C_0)$; the concentration of the supersaturated solution is C_2 and the reference frame is taken at the interface.

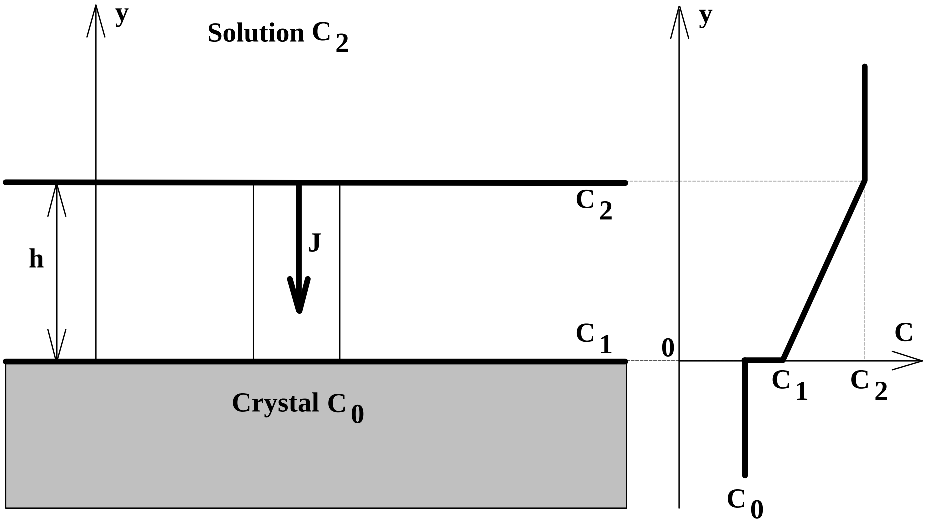

Figure 9. - Crystallisation of a solid from a sursaturated solution.

If the concentration in the boundary layer (height h) is supposed to vary linearly with y, $C = \left(\frac{C_2 - C_1}{h}\right)y + C_1$, the growth speed v is : $$v=\left(\frac{1}{k}+\frac{h}{D}\right)^{-1}(C_2-C_0) \qquad \{10\}$$

This model is not physically realistic ; however, it shows that growth speed is proportional to supersaturation (C_2-C_0) and increases with stirring (h decreases). Diffusion at the interface slowers the growth speed : the h/D factor adds to 1/k, which depends only on the growth mechanism.

Numerous salts, which present medium or large solubility can be grown from solutions (water is evidently the most commonly used solvent) : alkaline halides or "ate" salts (borates, phosphates, sulfates, chromates, iodates ....). As an example, the synthesis conditions of $KB_5O_8,4H_2O$ are :

H_3BO_3/KOH = (3-3.5)/1, pH = (6.9-6.6)

Temperature variation	70 °C - 50 °C	rate	0.1 - 0.2 °C/day
	50 °C - 40 °C		0.2 - 0.4 °C/day
	40 °C - RT		0.5 - 0.7 °C/day

Mean growth rate along [001]=0.2 mm/day

3. Growth in gels

Low solubility $A_x^{n+}B_y^{m-}$ salts are easily prepared by mixing two solutions which contain the required amounts of A^{n+} and B^{m-} ions. For example, PbI_2 crystallites precipitate by mixing $Pb(NO_3)_2$ and KI solutions. The growth of large crystals needs a slow countermove diffusion of both A^{n+} and B^{m-} species. Gels are very efficient restrainers of diffusion and crystals can be obtained in a vertical test tube (figure 10). Large solubility salts of the A^{n+} and B^{m-} ions are dissolved separately in a solvent (upper zone) and in the gel (lower zone) where $A_x^{n+}B_y^{m-}$ crystals form. The size can reach 5-10 mm. However, optical quality is frequently hampered by gel inclusion. Microcrystallisation also occurs in horizontal strates, separated by increasing spacing, giving rise to beautiful Liesegang rings. Simple test tubes or U-tubes can be used.

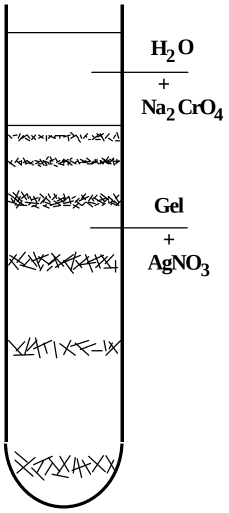

Figure 10.
Crystal growth of Ag_2CrO_4 from a gel.

Gels can be stable in a large range of pH and temperature (pH=0 to pH=10 for tetramethoxysilane gel) which can monitor the nature of the crystallised salts. For example, PbI_2 and PbI(OH) crystallise respectively in acidic conditions and at pH=8. Natural (gelatin, cellulose, pectin, agar-agar alginate) or synthetic gels are used. However, silica hydrogels are generally preferred. Such gels , free of alkaline cations, can be prepared from a solution of Na_2SiO_3 ; Na^+ cations are exchanged over an acidic resine (amberlite) and the resulting solution of H_2SiO_3 is left for gelling.

Numerous phases (halides, "ate" salts) were grown : CuCl (laser modulator), calcium tartrate, AgI, AgCl, Ag_5IO_6 or Ag_3IO_5 (ionic conduction), calcite or aragonite $CaCO_3$, hydroxyapatite $Ca_5(PO_4)_3$ (OH), NH_4MnF_3, $Ca(WO_4)$, Cu, Au, PbS, triglycine sulfate (ferroelectric).

More and more gel grown materials, prepared at higher temperature (120-200 °C), are reported : the microporous compounds, which associate an organic reagent (template) and a mineral open subnetwork. Other examples include cement or plaster : their setting involves crystallisation from an intermediate amorphous gel. Natural TiO_2 rutile needles in quartz crystals are also said to have grown from a gel.