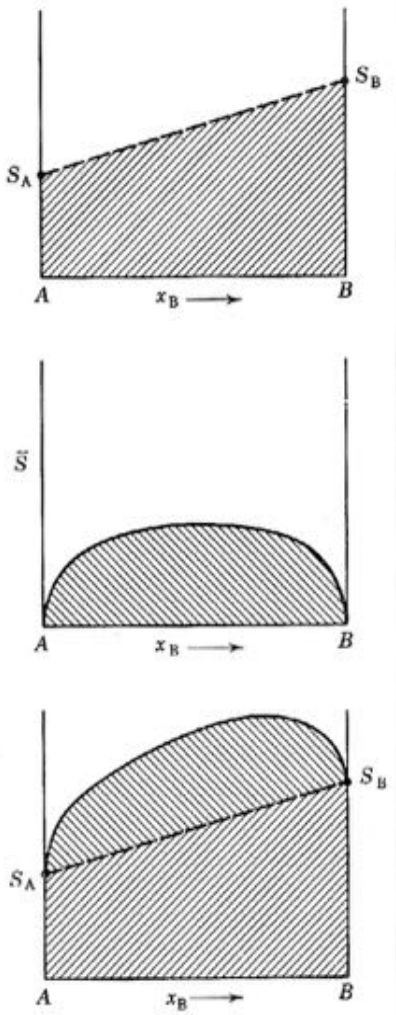
Phase separation in glass

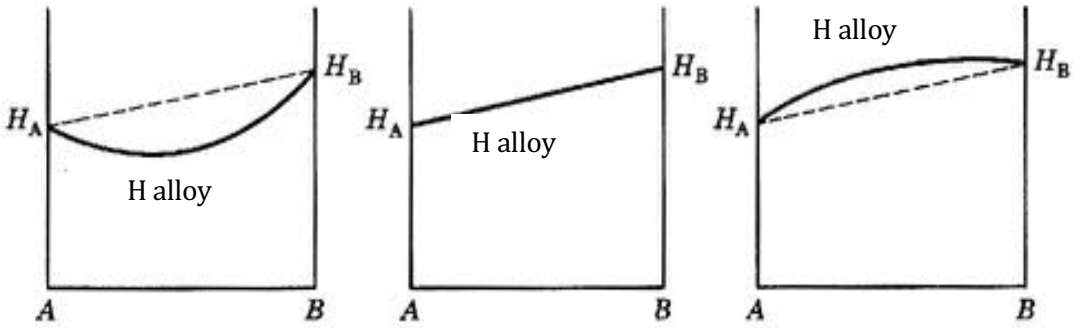
Introduction to glass science and technology, 2° ed., J. E. Shelby, The Royal Society of Chemistry, 2005 – Ch. 4

Free energy of mixture: $\Delta G_m = \Delta H_m - T\,\Delta S_m$

entropy - ΔS_m



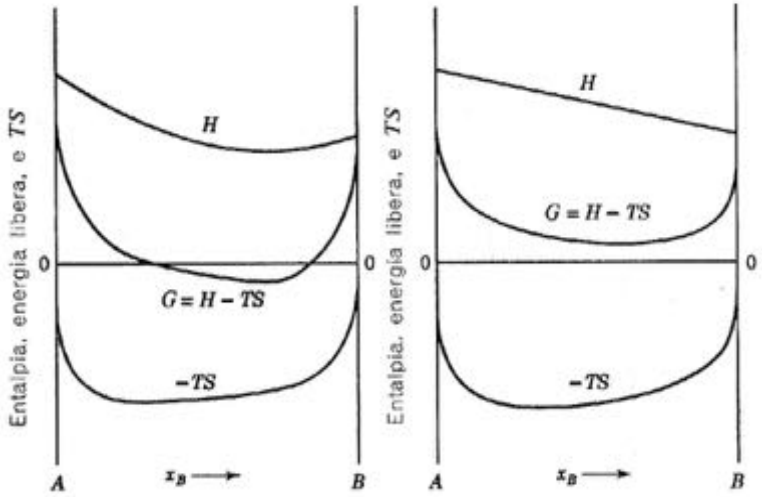
entalpy - ΔH_m



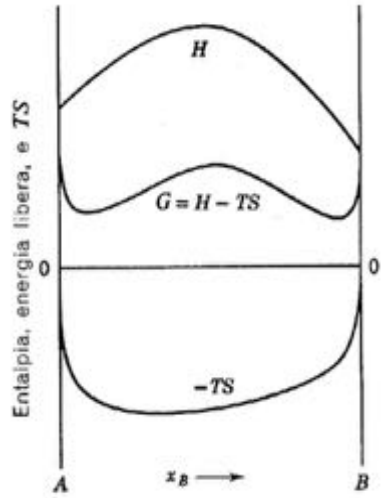
A,B affine *ideal situation* *A,B not affine*

Termodinamica strutturale, J.H. Brophy, R.M. Rose, J. Wulff, Ambrosiana Ed., 1975

free energy - ΔG_m



complete miscibility in one single phase



incomplete miscibility two phases

Termodinamica strutturale, J.H. Brophy, R.M. Rose, J. Wulff, Ambrosiana Ed., 1975

Free energy variation associated to composition fluctuations

(possible in a liquid)

$$G(c) = G(c_0) + \left.\frac{\partial G}{\partial c}\right|_{c_0} (c - c_0) + \left.\frac{1}{2}\frac{\partial^2 G}{\partial c^2}\right|_{c_0} (c - c_0)^2 + ...$$

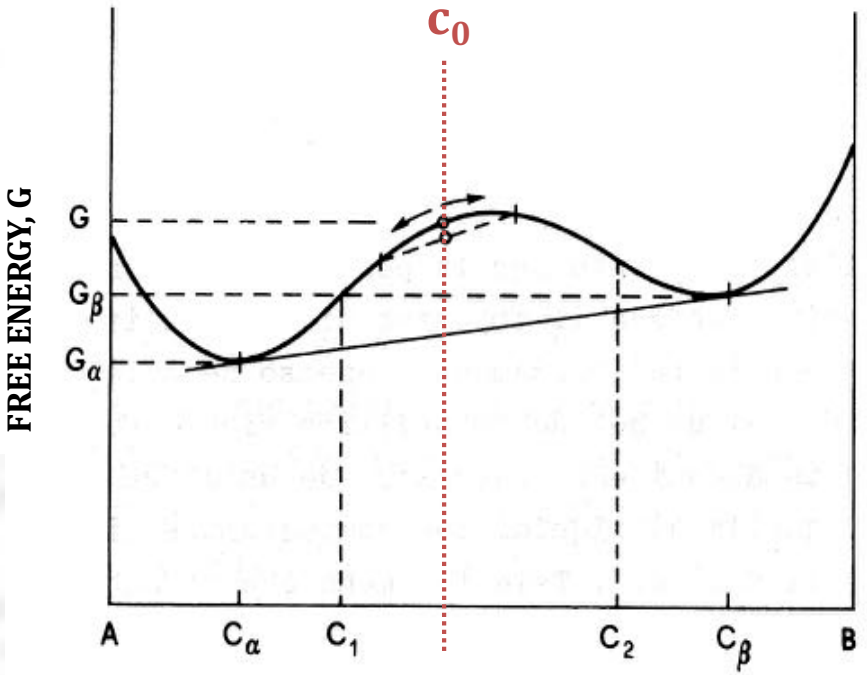
If $c' = c_0 - \Delta c < c_0 < c'' = c_0 + \Delta c$

$$\overline{G} = G(c_0) + \left.\frac{1}{2}\frac{\partial^2 G}{\partial c^2}\right|_{c_0} \Delta c^2$$

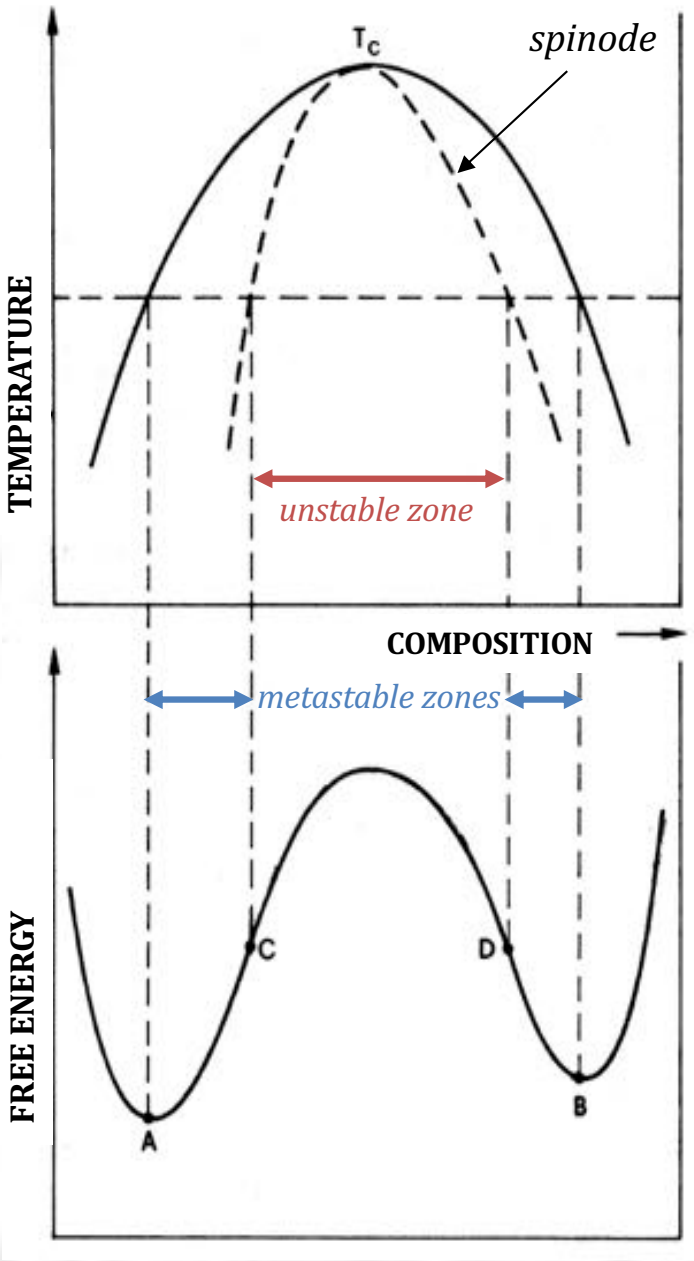
$$\Delta G = \overline{G} - G(c_0) = \left.\frac{1}{2}\frac{\partial^2 G}{\partial c^2}\right|_{c_0} \Delta c^2$$

$$\left.\frac{\partial^2 G}{\partial c^2}\right|_{c_0} > 0 \quad \rightarrow \Delta G > 0$$

$$\left.\frac{\partial^2 G}{\partial c^2}\right|_{c_0} < 0 \quad \rightarrow \Delta G < 0$$



Struttura e genesi dello stato vetroso, A. Maddalena, Cleup, 1983



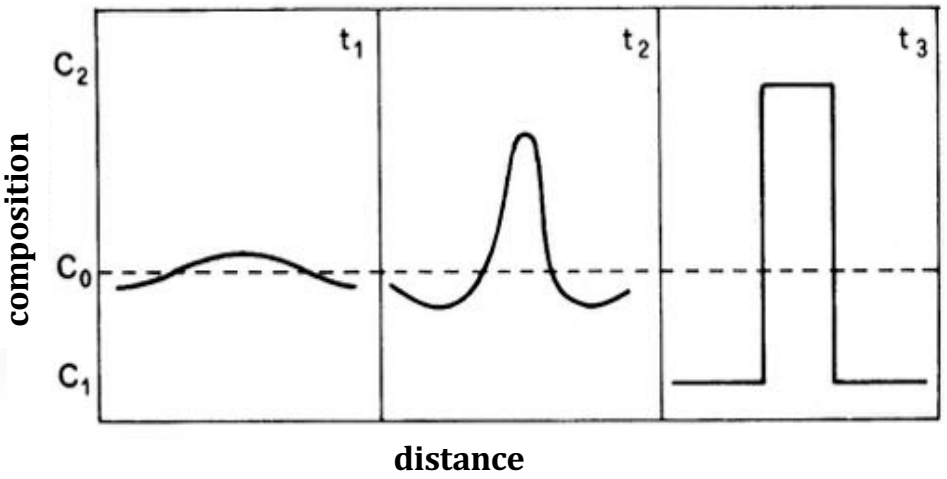
$T > T_C$: complete miscibility

$T < T_C$: immiscibility

Separation mechanisms:

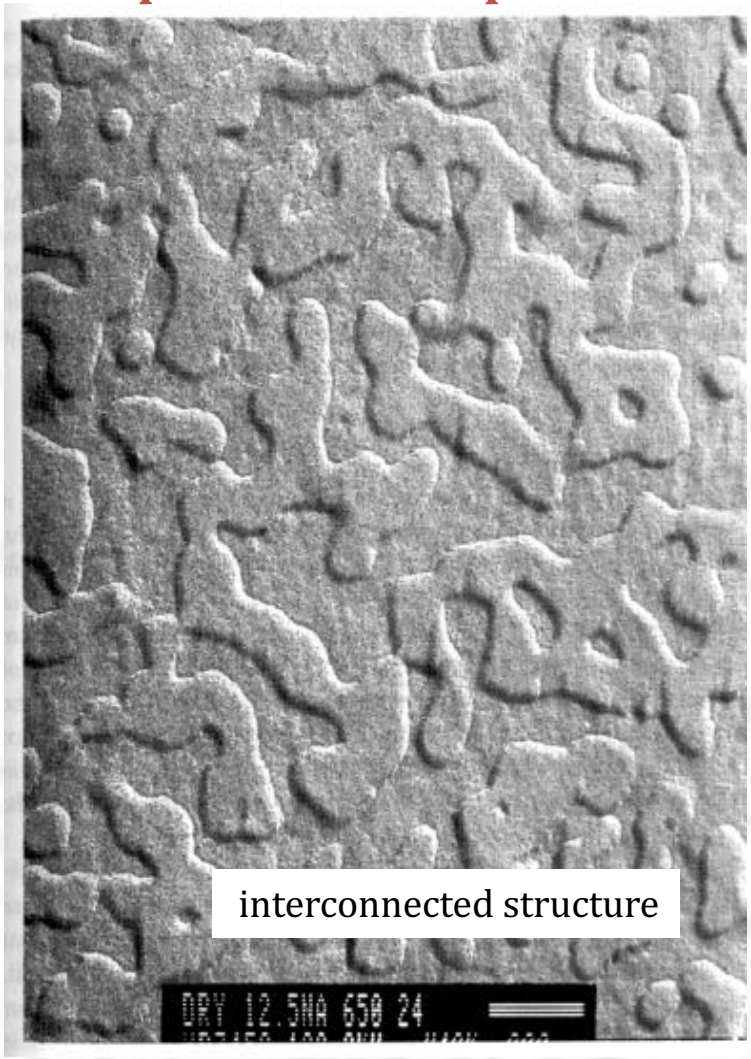
- **nucleation and growth**
  (metastable zone)
  large variation of G

- **spinodal decomposition**
  (unstable zone)
  gradual variation of composition (spontaneous)

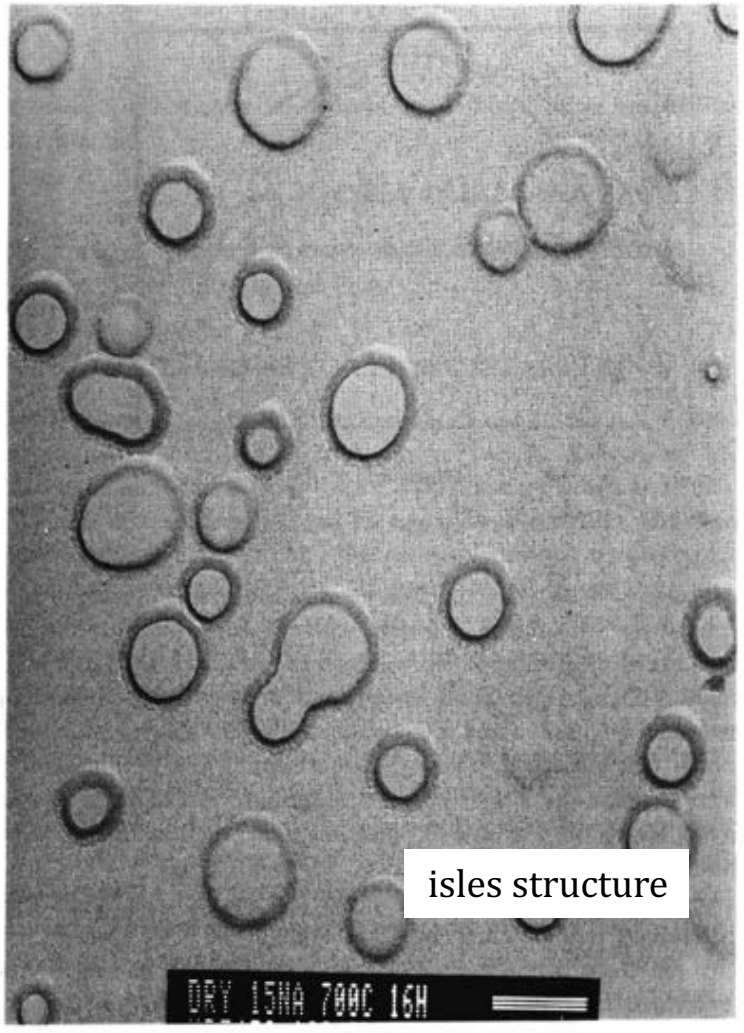


Struttura e genesi dello stato vetroso, A. Maddalena, Cleup, 1983

spinodal decomposition



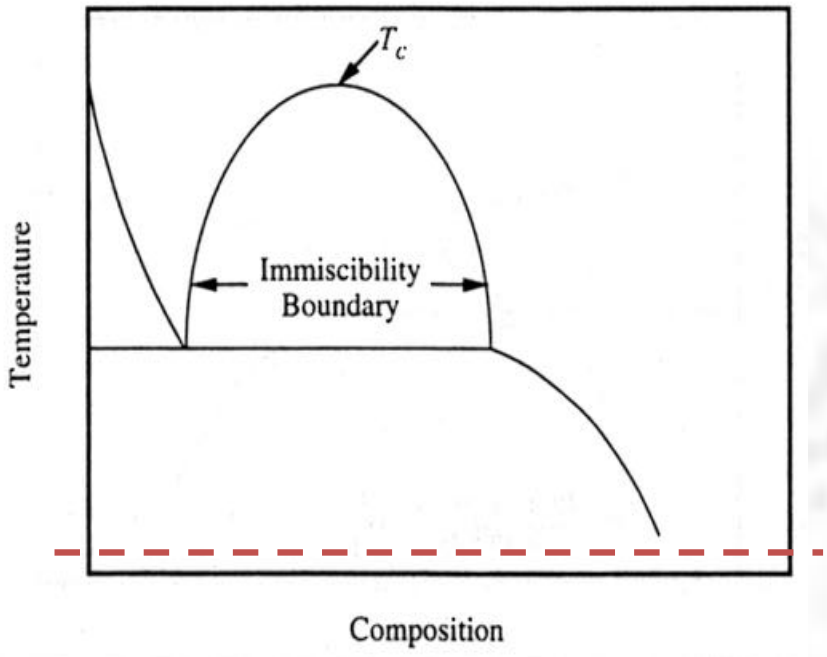
nucleation and growth



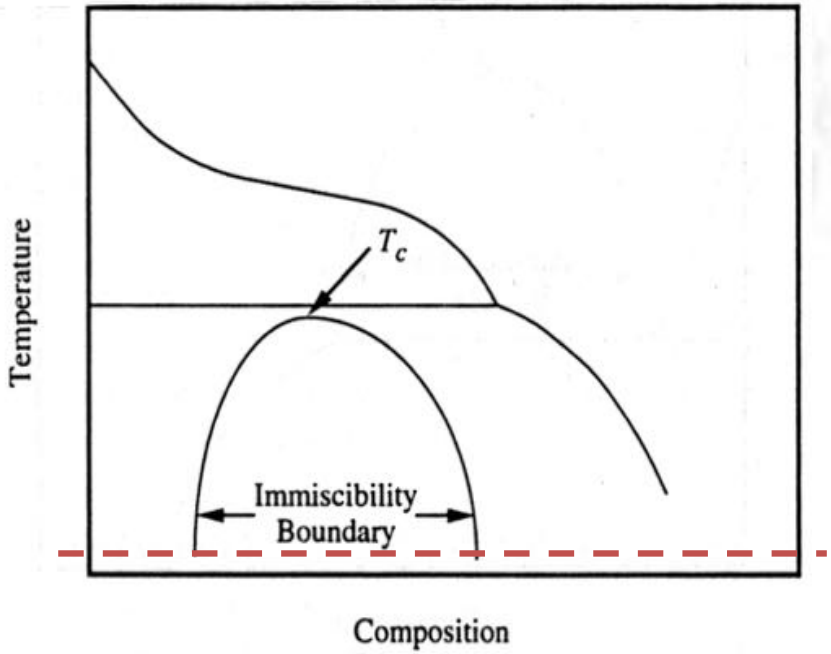
Introduction to glass science and technology, J. E. Shelby, The Royal Society of Chemistry, 1997

Immiscibility diagrams

stable immiscibility



metastable immiscibility



T_g

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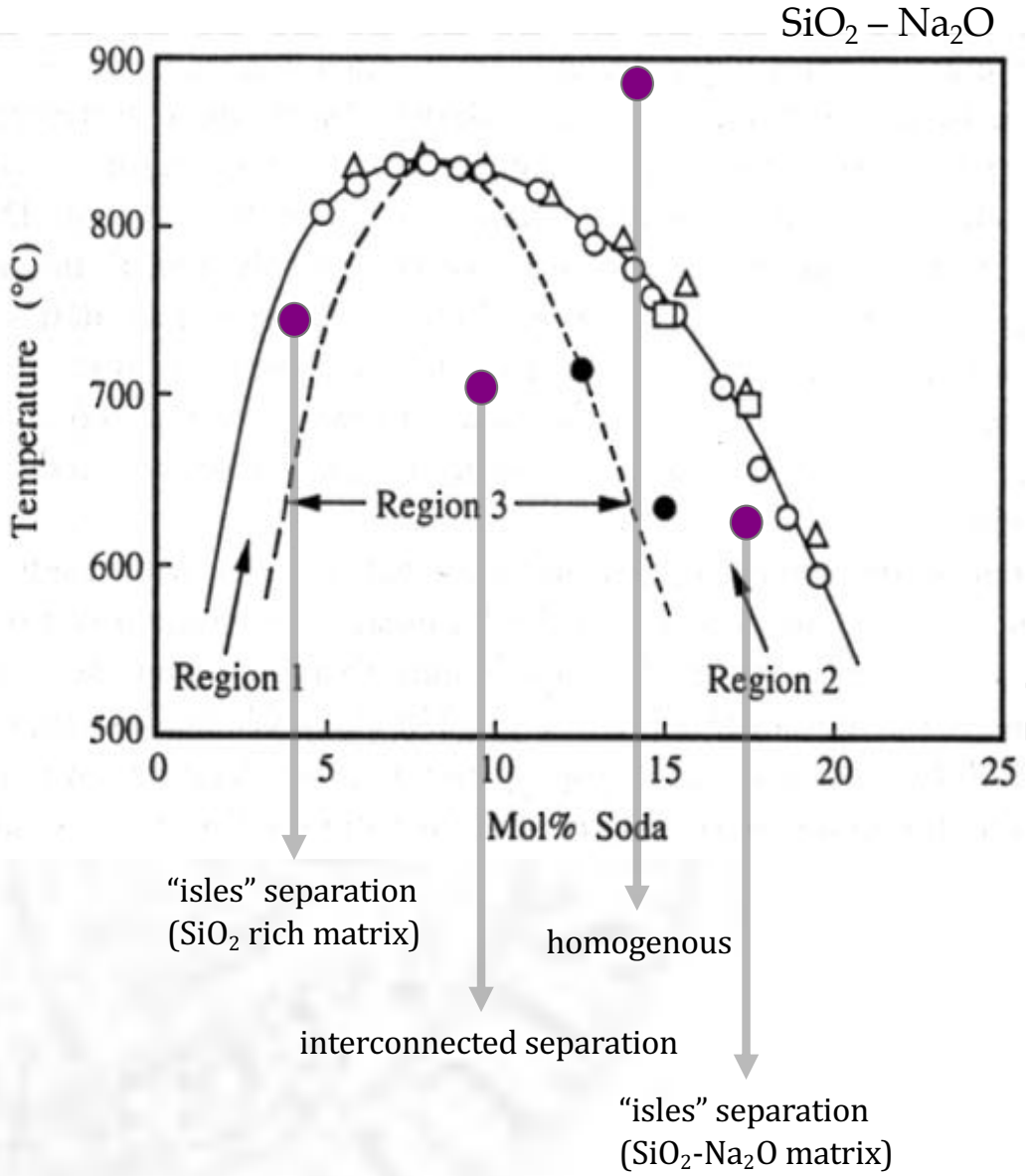
Homogenous and biphasic glass



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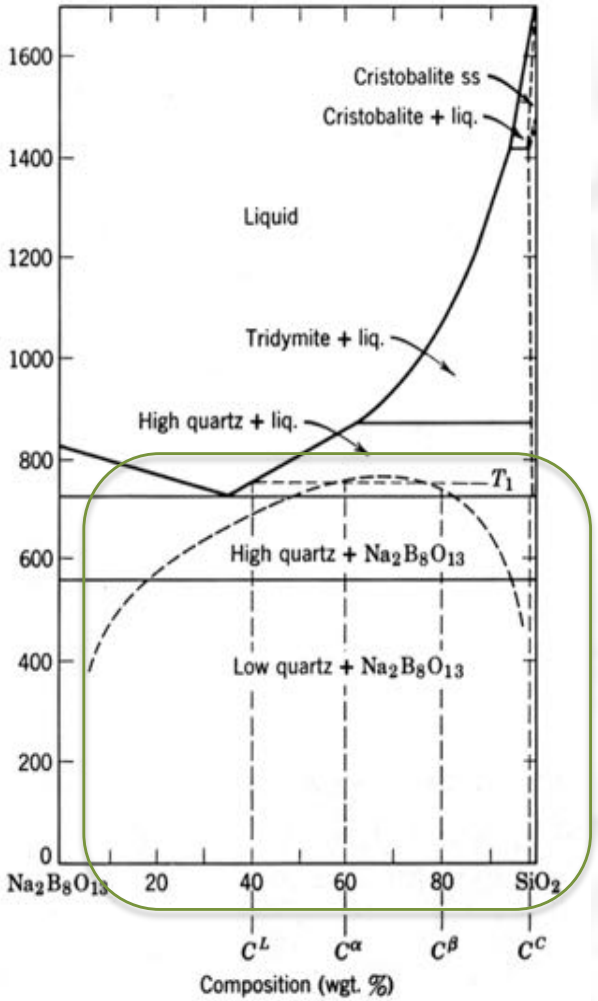
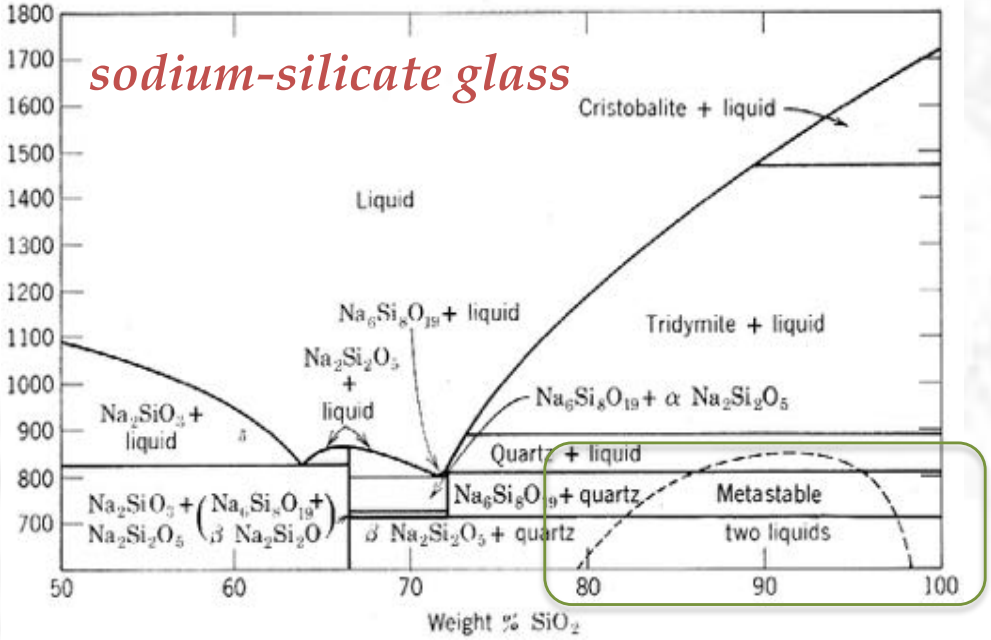
Examples:

sodium-borosilicate glass

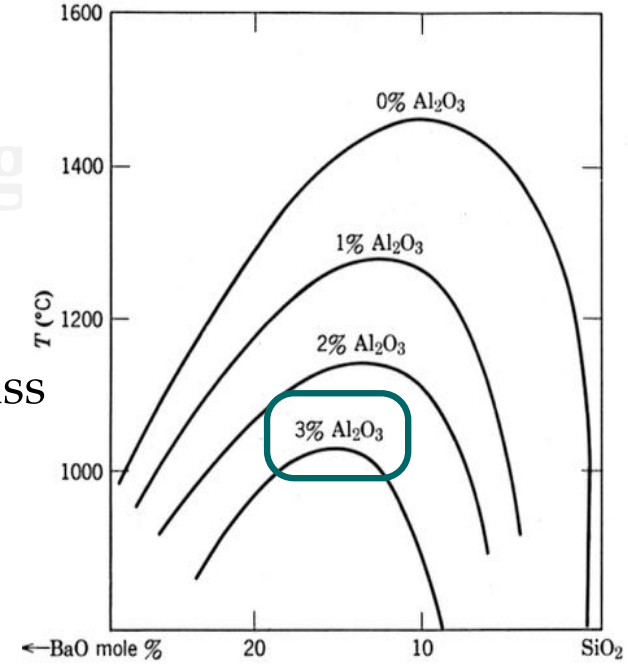


sodium-silicate glass



barium-silicate glass

(effect of Al_2O_3 additions)



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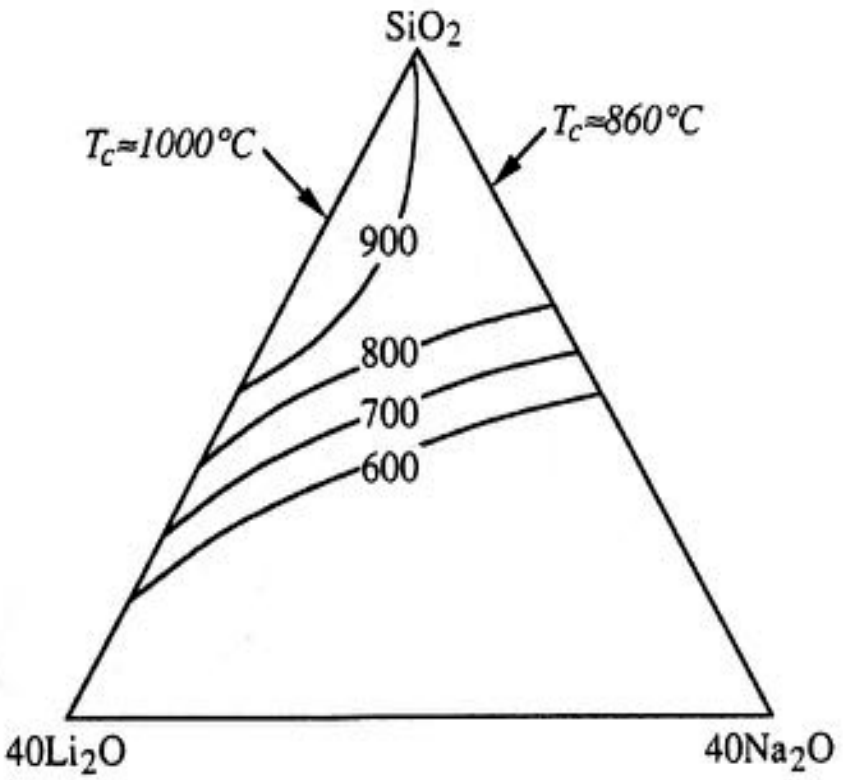
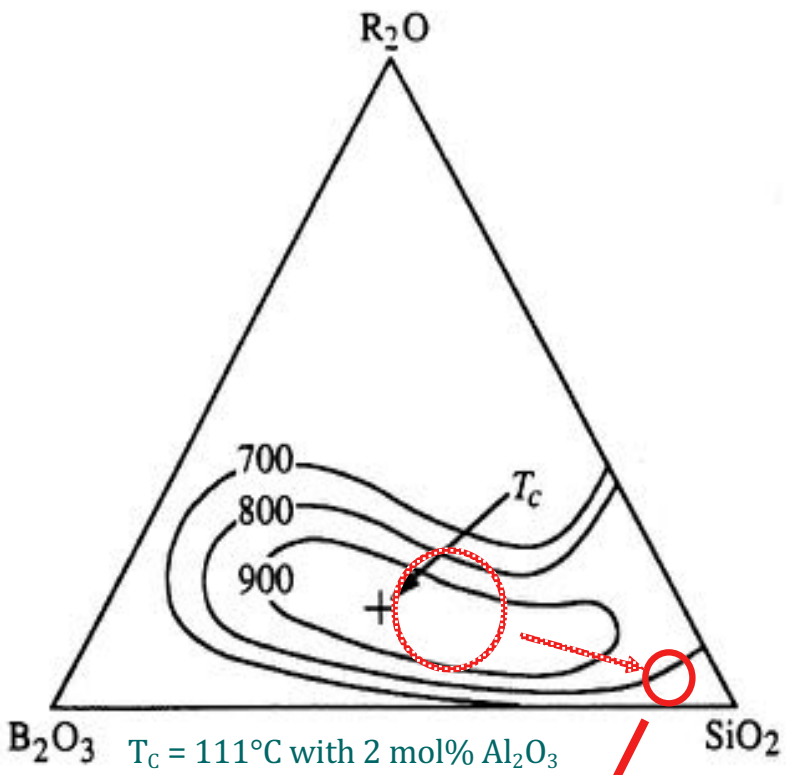
lithium-sodium-silicate glass



alkali-borosilicate glass



T_C = 111°C with 2 mol% Al_2O_3

microporous and/or Vycor® glass

Introduction to glass science and technology, J. E. Shelby, The Royal Society of Chemistry, 1997

Technological implications

- trasparence - opacity (d ≈ visible wavelength = 450-700 nm)

- heterogeneous nucleation → crystallization

- production of high silica glass (Vycor®)