

Immiscibility/Phase Separation: Glass Microstructure

Different liquids have different properties and so, when combined, some will:

- Form a single, homogeneous mixture → **miscible**
 - Alcohol and water- alcohol is hydrophilic- -OH terminated
- Not mix, heterogeneous → **immiscible** or **phase separated**
 - Oil and water- oil is hydrophobic

Similar processes occur in oxide melts: some oxide combinations are miscible, some are immiscible.

Example

Droplet of glassy component 'A' dispersed in glassy matrix 'B'.

Shelby Fig. 4-3
(Droplet-in-matrix morphology)

Phase separation occurs in highly viscous samples, 'frozen in' on cooling below T_g . (Initial viscosity has to be low enough for material to re-arrange into separate regions).

Why do certain compositions exhibit phase separation?

- *Thermodynamic Explanation*

Slide 1:

Phase 1 and Phase 2 each have their own 'internal' or free energy (G_1 , G_2 , respectively).

Case A

Case B

Component 1
 X_1

Component 2
 X_2

$G_A = X_1 G_1 + X_2 G_2$

$G_B = G_A + \Delta G_{mix}$

$\Delta G_{mix} = \Delta H_m - T\Delta S_m$ (Shelby 4.1)

$\Delta S_m = -R[X_1 \ln X_1 + X_2 \ln X_2]$ (4.2)

$\Delta H_m = \alpha X_1 X_2$ (4.3)

$\alpha = -ZN_A[E_{1,2} - (E_1 + E_2)/2]$

where E represents bond energies

Total free energy for case A (two separate phases) is summation of those internal energies times respective concentrations: $G_A = X_1 G_1 + X_2 G_2$.

When mixed (case B), total free energy is changed by free energy of mixing (ΔG_m), which depends on the *enthalpy* of mixing (ΔH_m , could be exothermic or endothermic) and the *entropy* of mixing (ΔS_m).

For *Regular Solutions*: $\Delta S_m = -R[X_1 \ln X_1 + X_2 \ln X_2]$

Entropy is related to system disorder. Upon mixing, systems become more disordered, ΔS_m always increases, causing ΔG_m to become more negative.

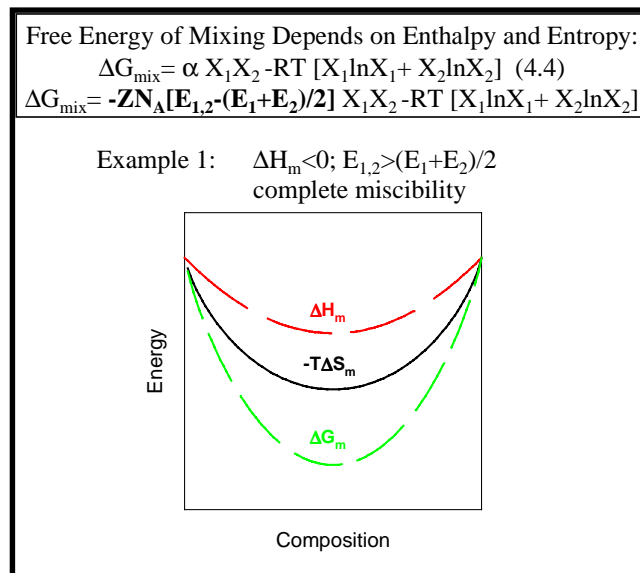
- Entropy promotes mixing.
- $\Delta H_m \approx \Delta E_m$: change in bond energies
 - to make a mixture, must break 1-1 (E_1) and 2-2 (E_2) bonds to create 1-2 ($E_{1,2}$) bonds. Is the net energy change positive or negative?
- $\Delta H_m \approx \alpha X_1 X_2$ where $\alpha \approx -ZN_{Avog}[E_{1,2} - (E_1 + E_2)/2]$ (Z = coordination number)
 - when $E_{1,2} > (E_1 + E_2)/2$, $\Delta H_m < 0$, 1-2 bonds are stronger than 1-1 and 2-2 bonds, so the system will prefer to mix.
 - when $E_{1,2} < (E_1 + E_2)/2$, $\Delta H_m < 0$, 1-2 bonds are weaker than 1-1 and 2-2 bonds, so the system will avoid mixing- more stable as separate phases.

Competition between entropy and enthalpy determines if $\Delta G_m < 0$ (system will be miscible); eq. 4-1. **(Slide 2)**

- Entropy of mixing always decreases ΔG_m .
- Enthalpy can either increase or decrease ΔG_m .

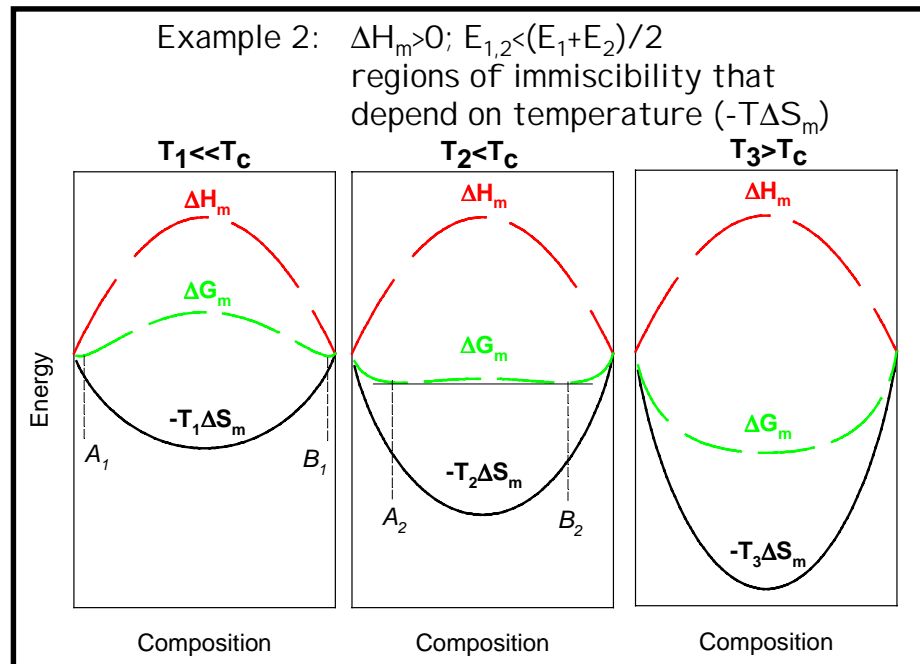
Example 1: $\Delta H_m < 0$, $E_{1,2}$ more stable than $E_1 + E_2$.

- Complete miscibility (alcohol and water); any combination of components leads to a reduction in ΔG_m



Example 2: $\Delta H_m > 0$, $E_{1,2}$ less stable than E_1+E_2 .

- Enthalpy (positive) and entropy (negative) are competing (**Slide 3**)
- At low temperature:
 - small entropy contribution; enthalpy change is most important
 - mixing causes ΔG_m to increase- barrier; phases prefer to be separate, for *most* combinations
- Note that there are certain compositions for which $\Delta G_m < 0$
 - at T_1 , the minima are at compositions A_1 and B_1
 - at T_2 , the minima are at compositions A_2 and B_{2a}
 - at T_3 , $-T\Delta S_m$ dominates the free energy and $\Delta G_m < 0$ for all combinations (100% miscible).

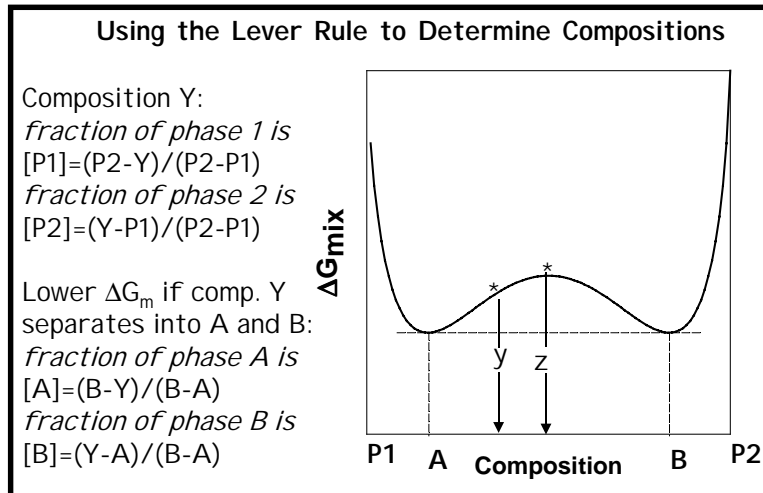


Consolute Temperature (T_c): upper temperature at which separate phases are thermodynamically stable. (Or, lowest temperature at which a single phase liquid is thermodynamically stable.)

What are the consequences of these free energy minima?

- Free energy of the system will be reduced if the liquid separates into two phases: with compositions A and B.
 - *Common Tangent (tie-line)*: identifies the lowest energy combinations
 - How much of each phase forms? *Lever Rule*

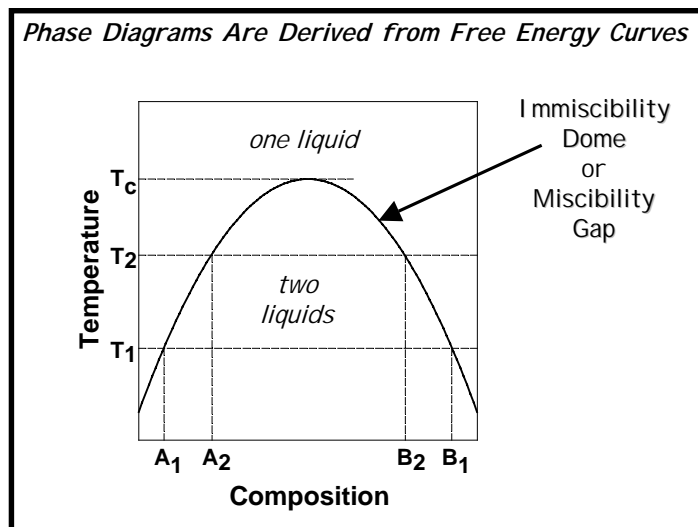
Slide 4: combinations between compositions A and B have lower ΔG_{mix} if they separate into A and B rather than staying as a single phase mixture.



Note: compositions *not* between A and B are miscible: viz., ΔG_{mix} is lower as a single phase mixture than if different phases separated from the mixture

Move to composition 'z'; end up with mixture that has more B-phase.

- From **slide 3**, increasing temperature decreases the distance between A' and B' (shorter tie-line)→smaller range of immiscible combinations until at $T \approx T_c$ above which no mixtures are immiscible.
 - These free energy curves 'map out' *immiscibility domes* in a phase diagram (**slide 5**).



Free energy/composition analysis indicates the thermodynamic underpinnings of phase separation, but provide no information about *kinetics*.

- Similar temperature-dependence on viscosity.
 - If viscosity is low in an immiscibility dome: rapid phase separation
 - If viscosity is high in an immiscibility dome: slow phase separation (can be avoided if melt is quenched fast enough).

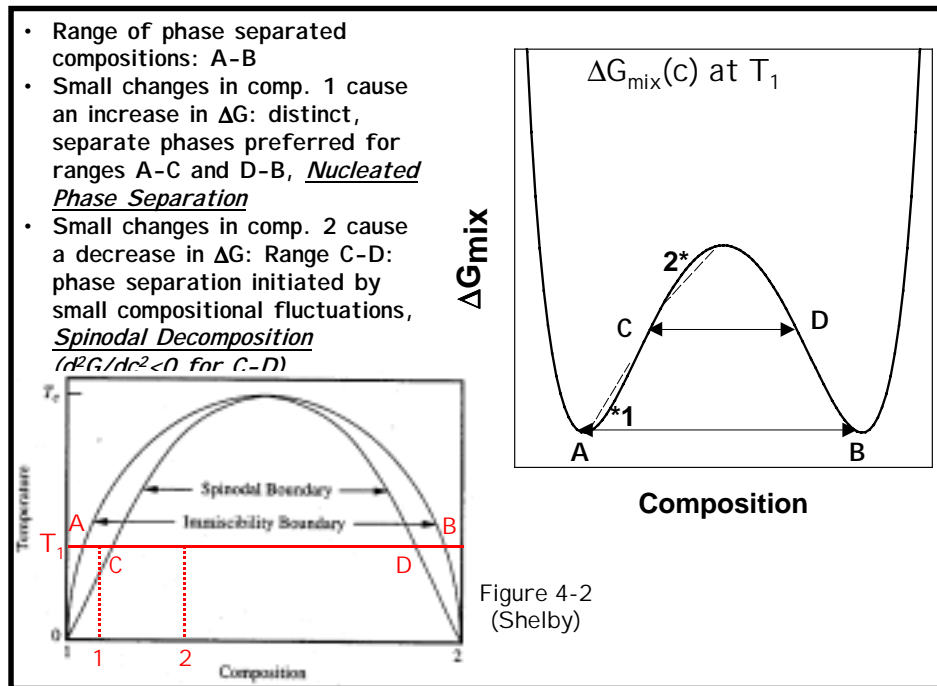
Mechanisms for Phase Separation:

1. *Nucleation and Growth*

- Analogous to nucleation/crystallization
 - distinctly different liquid-in-liquid compositions
 - overcome surface energy barrier
 - must reach critical size to remain stable
 - undercooling provides thermodynamic driving force: $(T_c - T)^2$
 - material diffusion to interface to form separate droplets
 - high viscosity → slow diffusion → slow particle growth

2. *Spinodal Decomposition*

- Compositional fluctuations (Δc) reduce ΔG_{mix} , promote gradual phase separation (**slide 6**).
 - This occurs when $d^2G/dc^2 < 0$ (between inflection points C and D)
 - The compositions of the inflection points also vary with temperature and so map out a second dome where $d^2G/dc^2(T) < 0$: *Spinodal Dome*



(See Varshneya (Fig. 4-5, next page) for a diagram that shows shapes of the first and second derivatives of the free energy curves).

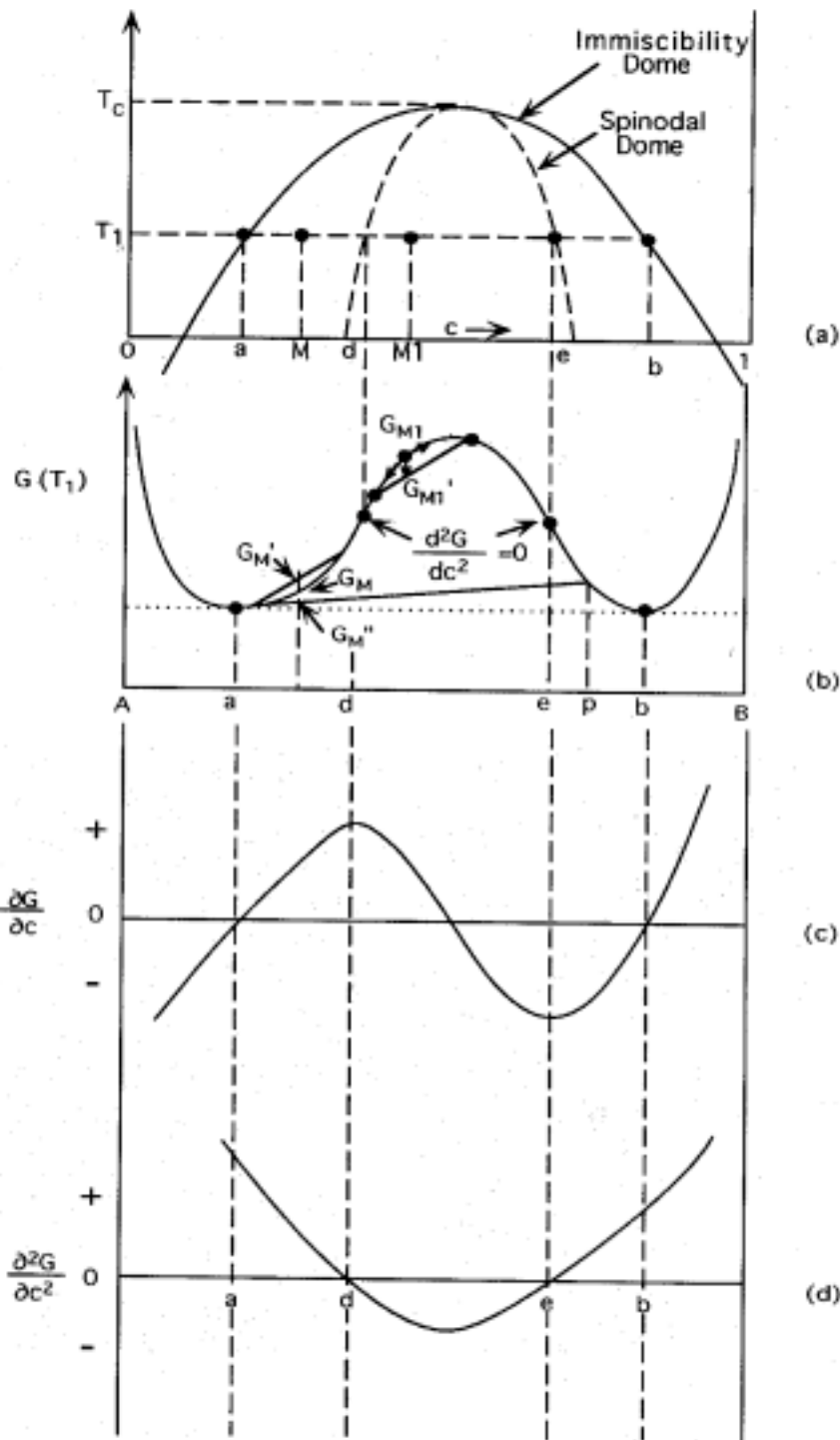


Figure 4-5. Details of the (a) phase diagram, (b) free energy of mixing at T_1 , (c) the first derivative of the free energy at T_1 , and (d) the second derivative of the free energy at T_1 when immiscibility occurs.

Different mechanisms lead to different topologies for phase separated systems:

- Nucleated: sharp interfaces, invariant (distinct) compositions
- Spinodal: diffuse interfaces, compositions vary with time.

Table 4-1. Distinction between Phase Separation Mechanisms^a

Nucleation and growth	Spinodal decomposition
Invariance of second-phase composition with time at constant temperature	Continuous variation of both extremes in composition with time until equilibrium compositions are reached
Interface between phases is always same degree of sharpness during growth	Interface between phases initially is very diffuse, eventually sharpens
Tendency for random distributions of particle sizes and positions in matrix	Regularity of second-phase distribution in size and position characterized by a geometric spacing
Tendency for separation of second-phase spherical particles with low connectivity	Tendency for separation of second-phase, nonspherical particles with high connectivity

^a After J. W. Cahn and R. J. Charles, *Phys. Chem. Glasses*, 6(5), 181–191 (1965).

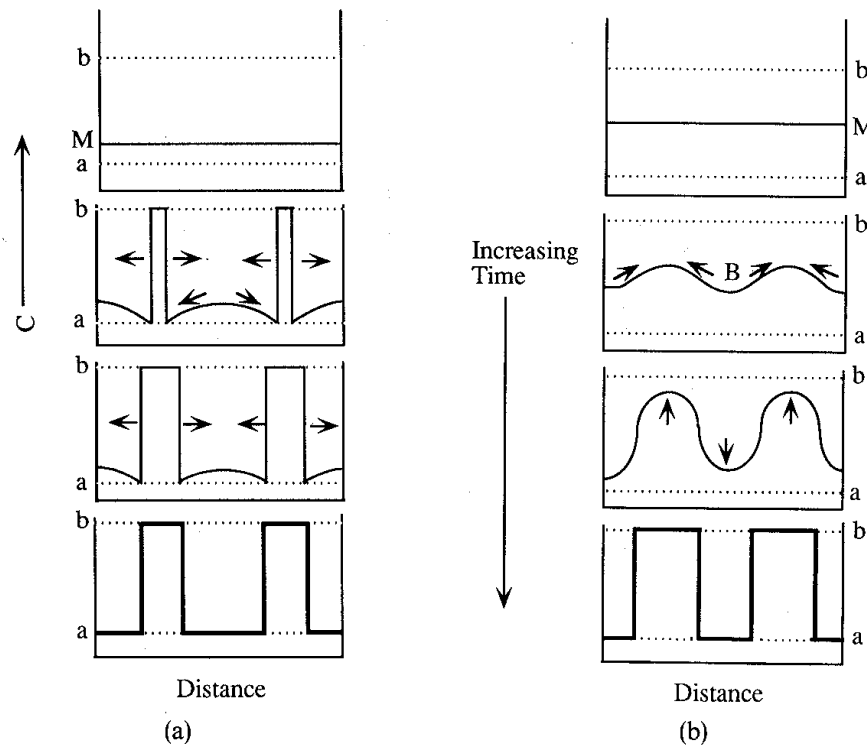


Figure 4-7. Growth of the phase separation for (a) nucleated-type and (b) spinodal-type mechanisms with time at a given temperature. Note that in the nucleated-type mechanism, the droplets have a fixed composition “b” with an interfacial composition “a.” The growth is in the physical size of the droplet. In the spinodal-type mechanism, a small fluctuation in composition gradually grows over a period of time via “uphill” diffusion. The terminal compositions in each case are “a” and “b.” The ratio of the two phases depends upon the starting composition.

Shelby 4.3 or Varshneya 4-13:

"Droplet in Matrix"
Morphology

Shelby 4.4 or Varshneya 4-13:

"Interpenetrating Phases"
Morphology

Immiscibility in Glass Forming Systems:

- common- most systems will phase separate (with proper thermal history)
- size of phase separated regions depends on quench rate- analogous to the critical cooling rate for nucleation/crystallization.
 - Quench to below T_g to avoid phase separation
 - No phase separation when $T > T_c$ or $T < T_g$
 - Viscous melts are less prone to phase separation than fluid melts ($D \sim \eta^{-1}$)

Stable Immiscibility: $T_c > T_{liquidus}$ ($T_{liq.}$ is maximum temperature at which crystals are stable in a melt).

- very common (binary $RO \bullet SiO_2$, $\bullet GeO_2$, $\bullet B_2O_3$ systems)
- fast kinetics (low viscosity)

Metastable Immiscibility: $T_c < T_{liquidus}$: '**S-shaped liquidus**'

- crystals are stable, but in general, phase separation kinetics are faster than crystallization kinetics (atomic re-arrangements necessary for crystallization slow that process down).
- slower kinetics (high viscosity)
- binary $Li_2O \bullet SiO_2$, $Na_2O \bullet SiO_2$, Na-borosilicates

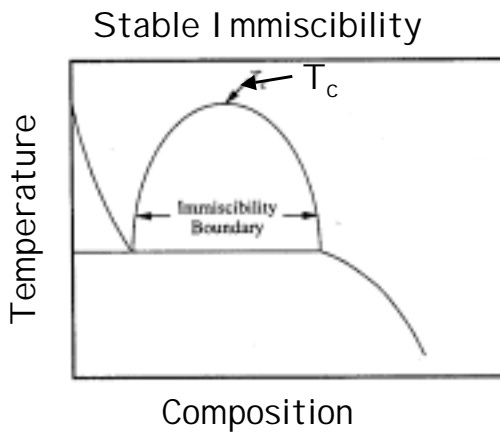


Figure 4-5 (Shelby)

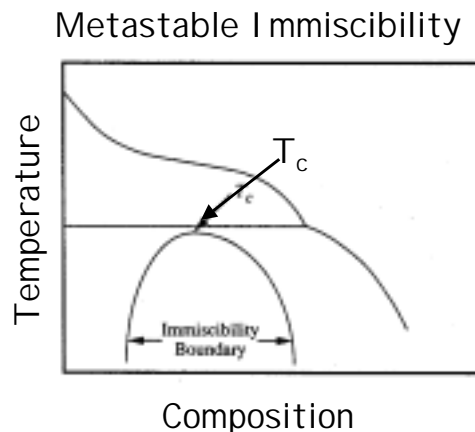


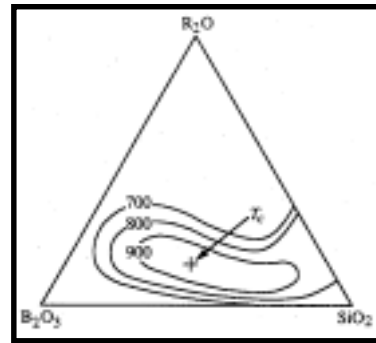
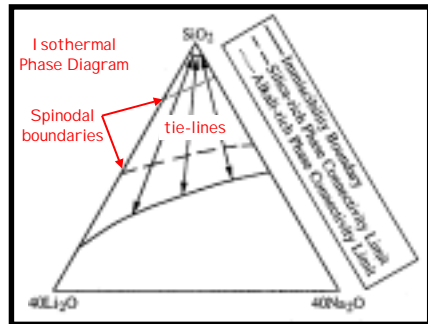
Figure 4-6 (Shelby)

Observations:

- electron microscopy
- 'clearing' studies (see demo from gradient furnace)
 - visible scattering; phase separated glasses turn white
 - confirm by x-ray diffraction
- x-ray scattering (Shelby figure 4-7).

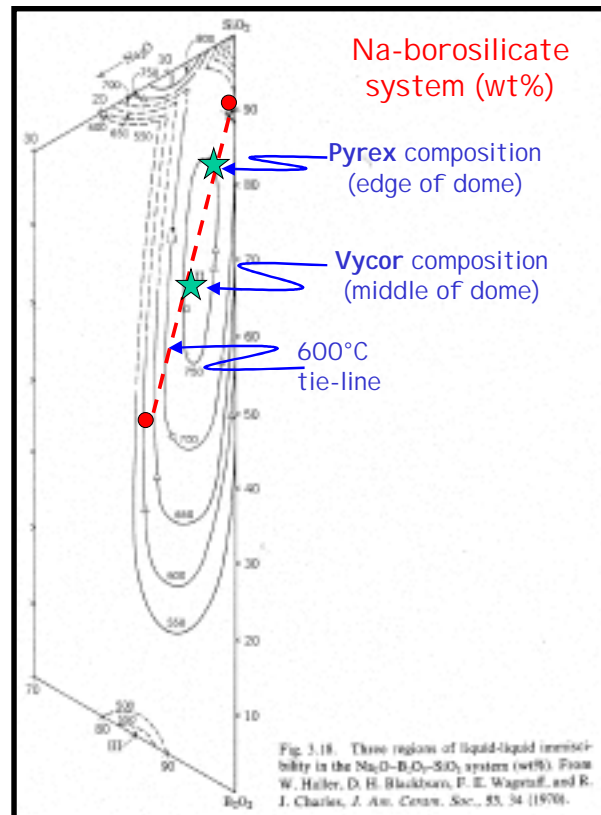
In ternary systems, immiscibility domes are represented by contour lines which show outer boundaries of the phase separated regions; note broader regions at lower temperatures.

- Tie-lines indicate where the 'stable' separate compositions are.



Vycor (96% SiO₂)

- Choose composition near center of immiscibility dome to create spinodal microstructure.
- Melt at 1500°C, then process (press, blow, draw, etc.) at $T > T_c$.
- Heat treat at ~600°C to develop interpenetrating microstructures of phases with boundary compositions
 - one phase is ~96% SiO₂
 - other phase is acid-soluble Na-borosilicate glass
- Leach out the soluble phase in 90°C H₂SO₄ to leave porous, high-silica skeleton (see micrograph from Vogel, 6-27)
- 'Thirsty Glass' can be used as porous substrate (filters, catalyst supports, time-release substrate, etc.) or can be sintered to dense glass at 1100°C- inexpensive substitute for pure silica.
- Key is the development of spinodal microstructure.



Pyrex glass: another phase separated Na-borosilicate composition

- Lower B_2O_3 , lower Na_2O than Vycor; closer to edge of immiscibility dome
 - Nucleated 'drop-in-matrix' morphology
- Cooled rapidly through T_g to produce 20-50Å *Na-borate droplets* in a chemically inert *high-silica matrix*.
- Na-borate reduces process melt/temperature but the droplet microstructure ensures outstanding chemical durability (and low thermal expansion coef.)

Finally, 'step-wise' immiscibility can lead to interesting microstructures

- Multiple heat treatments: Ba-borosilicate glass
 - Phase-within a Phase-within a Phase
- Further heat-treatments yield crystallized phases.

From Vogel, *Chemistry of Glass*, 1985