2.8 *G*-plot and chemical potentials

As already discussed in the last chapter (cf. Eq. (1.32) and Eq. (1.33)) for any mixture holds

$$dG = \mu_A dn_A + \mu_B dn_B \tag{2.58}$$

and

$$G(n_A, n_B, T, p) = \mu_A n_A + \mu_B n_B \quad , \tag{2.59}$$

where $\mu_A(n_A, n_B)$ and $\mu_B(n_A, n_B)$ may depend on the composition (n_A/n_B).
Here we briefly repeat the proof of the Gibbs-Duhem equation starting with the general implication of Eq. (2.59)

$$dG = \mu_A dn_A + n_A d\mu_A + \mu_B dn_B + n_B d\mu_B \tag{2.60}$$

which gives the Gibbs-Duhem equation

$$0 = n_A d\mu_A + n_B d\mu_B \quad . \tag{2.61}$$

So according to

$$\frac{d\mu_A}{d\mu_B} = -\frac{n_B}{n_A} \tag{2.62}$$

of chemical potentials must change with the composition of the mixture.
To prove the geometric relations shown in Fig. 2.10 a) for the tangent we calculate

$$x_A \frac{dG_m}{dx_B} = x_A \mu_A \frac{dx_A}{dx_B} + x_A \mu_B \frac{dx_B}{dx_B} = -x_A \mu_A + x_A \mu_B \quad . \tag{2.63}$$

Combining Eq. (2.59) and Eq. (2.63) we get

$$G_m + x_A \frac{dG_m}{dx_B} = x_A \mu_A + x_B \mu_B - x_A \mu_A + x_A \mu_B = \mu_B (x_A + x_B) = \mu_B \quad , \tag{2.64}$$

or

$$\mu_B = G_m + (1 - x_B) \frac{dG_m}{dx_B} \quad . \tag{2.65}$$

So by extrapolating the tangent at any point along the $G(x_B)$ to the axis $x_A = 0$ and $x_B = 0$ we find the chemical potentials μ_B and μ_A.
Fig. 2.10 b) shows the Gibbs energy curves for the liquid and solid solution in the binary system Si–Ge at 1500 K. The common tangent construction shows the compositions of the two phases in equilibrium.

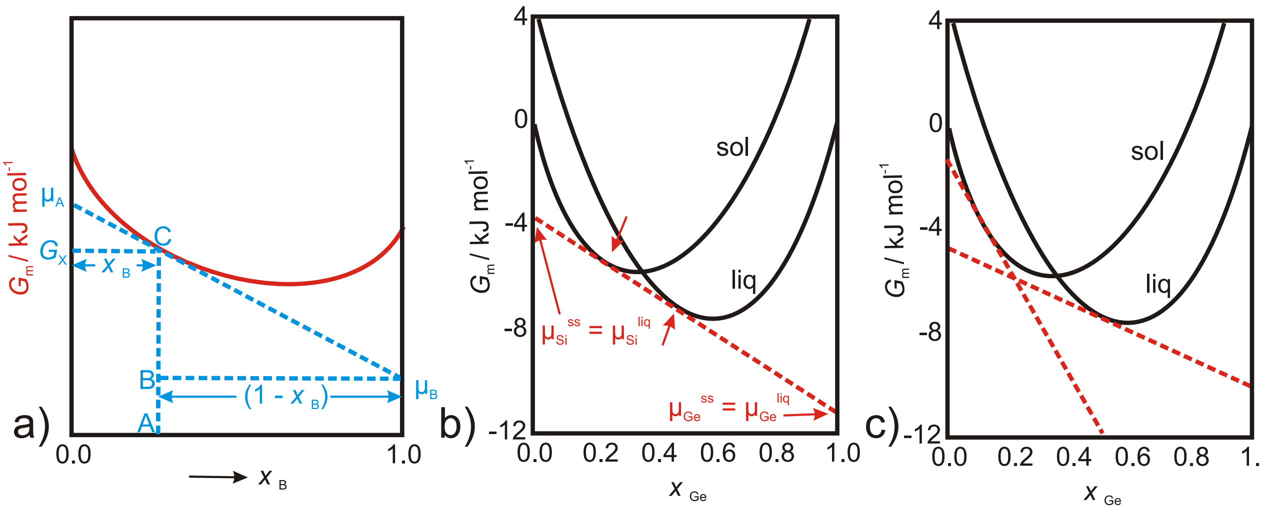

Figure 2.10: *G*-plots: a) dependence of *G* on composition and chemical potentials μ_A and μ_B; b) common tangent and phase separation in equilibrium; c) non equilibrium case.

The extrapolation to the two axis emphasizes that for both components, Si and Ge, liquid and solid solution (ss) phase are in equilibrium. Fig. 2.10 c) shows the Gibbs energy curves in a non equilibrium case giving rise to

overheating and undercooling effects like the composition in this case. Fig. 2.11 illustrates the relation between G-plots and the phase diagram for the binary system Si-Ge for several characteristic temperatures. Since the liquid has higher entropy than the solid generally the G-value difference between liquid and solid solution is reduced when cooling down.
For the five temperatures marked by the numbers we find:

- 1: Liquid is stable over the whole x_{Ge}-range
- 2: Common tangent at $x_{Si} = 1$, i.e. melting of point of pure Si
- 3, 4: Common tangent: phase separation into l- and ss-phase
- 5: Solid solution stable for all compositions

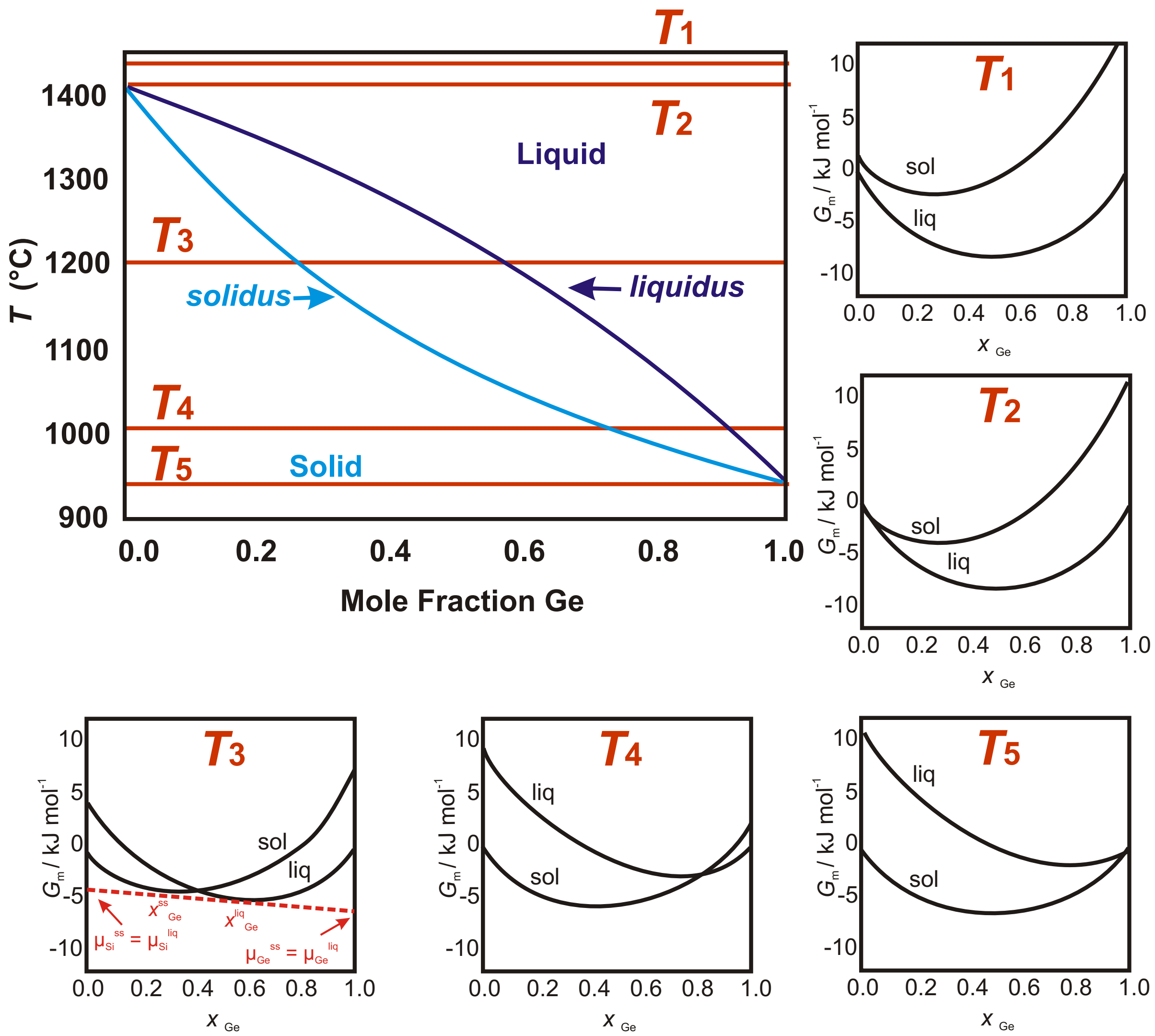

Figure 2.11: Phase diagram for mixing of Si and Ge. For the 5 temperatures the corresponding Gibbs potentials of the liquid and solid phase are shown.