2.1 Activity of regular solutions

Completely analogous to the concept of effective mass which allows to incorporate non idealities like lattice periodic potentials into the model of free particles non ideal mixtures are described by replacing molar fractions x_A and x_B by activities a_A and a_B (respectively activity coefficients $a_A = \gamma_A x_A$ and $a_B = \gamma_B x_B$) but choosing the same functionality as described in Eq. (1.37) for free particles (the ideal gas), i.e.

$$\begin{aligned}\Delta_{mix}G_m &= \Delta_{mix}G_m^{id} + \Delta_{mix}G_m^{ex} = RT\left(x_A \ln a_A + x_B RT \ln a_B\right) \\ &= RT\left(x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B\right) \quad .\end{aligned} \tag{2.1}$$

Thus for the excess Gibbs molar energy we find

$$\Delta_{mix}G_m^{ex} = RT\left(x_A \ln \gamma_A + x_B \ln \gamma_B\right) \quad . \tag{2.2}$$

Particle interaction in regular solutions are often described by

$$\ln \gamma_A = \beta x_B^2 \quad \text{and} \quad \ln \gamma_B = \beta x_A^2 \quad , \tag{2.3}$$

$$\text{so} \qquad \Delta_{mix}G_m^{ex} = RT\left(x_A \beta x_B^2 + x_B \beta x_A^2\right) = RT\beta x_A x_B\left(x_B + x_A\right) = RT\beta x_A x_B = \Omega\, x_A x_B = H_m^{ex} \quad . \tag{2.4}$$

Quite obviously $\Omega\, x_A x_B$ is the most simple energy functionality for an interaction A-B.
As very important consequences we find

1. $$a_A = \gamma_A x_A = x_A e^{\beta(1-x_A)^2} \quad , \tag{2.5}$$

   i.e. a typical dependence of the activity on x_A

2. $$p_A = p_A^* a_A = p_A^* x_A e^{\beta(1-x_A)^2} \quad . \tag{2.6}$$

Fig. 2.1a) shows results of Eq. (2.6) for several values of β. It demonstrates the typical deviation from Raoult's law and shows that Raoult's law is valid for $\beta = 0$ and for all curves when $x_A \to 1$ (pure state). At least the activity coefficients behave correctly for dilute solutions: $\gamma_A \to 1$ as $x_B \to 0$ and $\gamma_B \to 1$ as $x_A \to 0$. For $\beta > 0$ we have an unfavorable interaction between $A - B$ and thus an increase of p. Thus a competition between entropy maximization favoring mixing and repelling interaction favoring decomposition exists which can lead to $\Delta_{mix}G(x_A)$ curves as shown in Fig. 2.1b). For large β a non convex shape of the $\Delta_{mix}G(x_A)$ is found which translates into a phase separation (by adding a common tangent between the two minima).

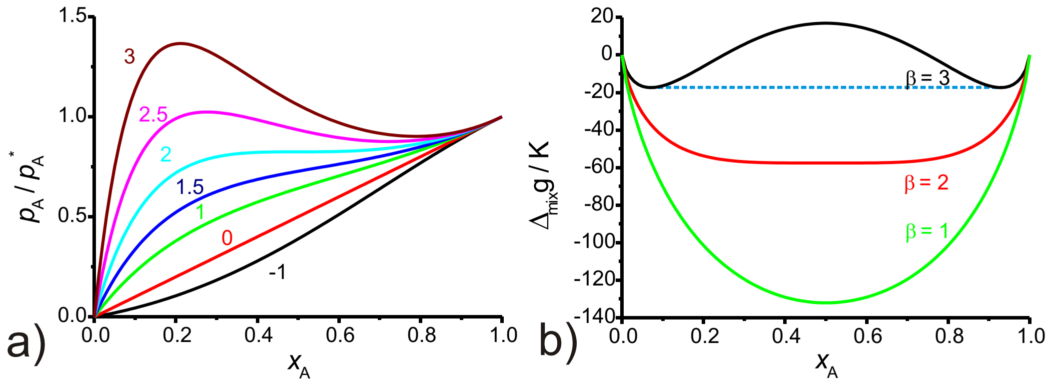

Figure 2.1: a) Partial pressures for several β; b) chemical potential and Maxwell construction for phase separation.