5.12 Activities 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 electrons 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 for the ideal case in Eq. (5.6) for free particles (the ideal gas), i.e.

$$\begin{aligned} \Delta_{mix}G_m &= \Delta_{mix}G_m^{id} + G_m^{ex} = RT\,(x_A \ln a_A + x_B RT\, \ln a_B) \\ &= RT\,\,(x_A \ln x_A + x_B \ln x_B + x_A \ln \gamma_A + x_B \ln \gamma_B) \quad . \end{aligned} \tag{5.37}$$

Thus for the excess Gibbs molar energy we find

$$G_m^{ex} = RT\,\,(x_A \ln \gamma_A + x_B \ln \gamma_B) \quad . \tag{5.38}$$

Particle interaction in regular solutions can e.g. be described by

$$\ln \gamma_A = \beta x_B^2 \quad \text{and} \quad \ln \gamma_B = \beta x_A^2 \quad , \tag{5.39}$$

$$\text{so} \qquad G_m^{ex} = RT\,\left(x_A \beta x_B^2 + x_B \beta x_A^2\right) = RT\,\beta x_A x_B\,(x_B + x_A) = RT\,\beta x_A x_B = \Omega\, x_A x_B = H_m^{ex} \quad . \tag{5.40}$$

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. $$a_A = \gamma_A x_A = x_A e^{\beta(1-x_A)^2} \quad , \tag{5.41}$$
   i.e. a typical dependence of the activity on x_A
2. $$p_A = p_A^* a_A = p_A^* x_A e^{\beta(1-x_A)^2} \quad . \tag{5.42}$$

Fig. 5.10 shows results of Eq. (5.42) for several values of β. For $x_A \approx 1$ 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). For $x_A \to 0$ we find Henry's law where K_A depends strongly on β.
Typical mixing effects for the partial pressures are shown in Fig. 5.11:

- In Fig. 5.11 a) no deviation from average values are found for highly related components, i.e. A-A ≈ B-B ≈ A-B. Thus ideal behavior is found.
- In Fig. 5.11 b) shows an example for a positive deviation from Raoult's law: $p(mix)$ is larger than for an ideal solution, i.e. the intermolecular forces A-B are weaker than A-A and B-B; in this example the CS_2 disturbs the H-bonding in acetone (keto-enol-tautomerism).
- Strong deviations can also occur when dissociation (increases number of particles) or association (decreases number of particles) of the solute occurs, leading to an entropy contribution to mixing.

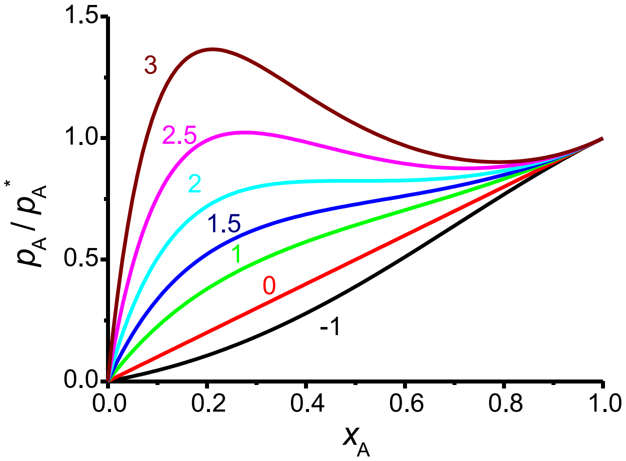

Figure 5.10: Partial pressures for several β.

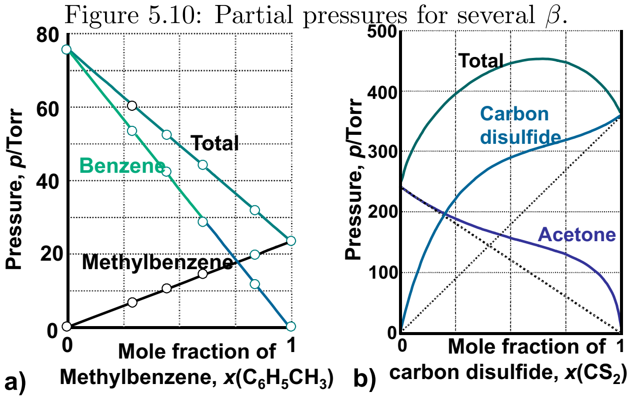

Figure 5.11: Examples for partial pressures of mixtures: a) mixing of similar components; b) mixing of dissimilar liquids.