Simple mixtures

- towards dealing with reactions, consideration of substances that do not react is necessary

- Binary mixtures: components A + B

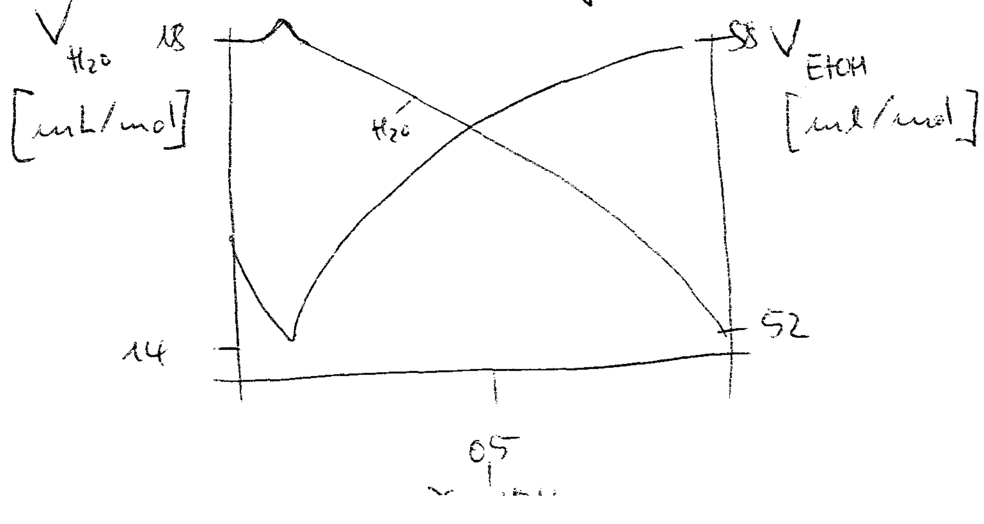
$$x_A + x_B = 1$$

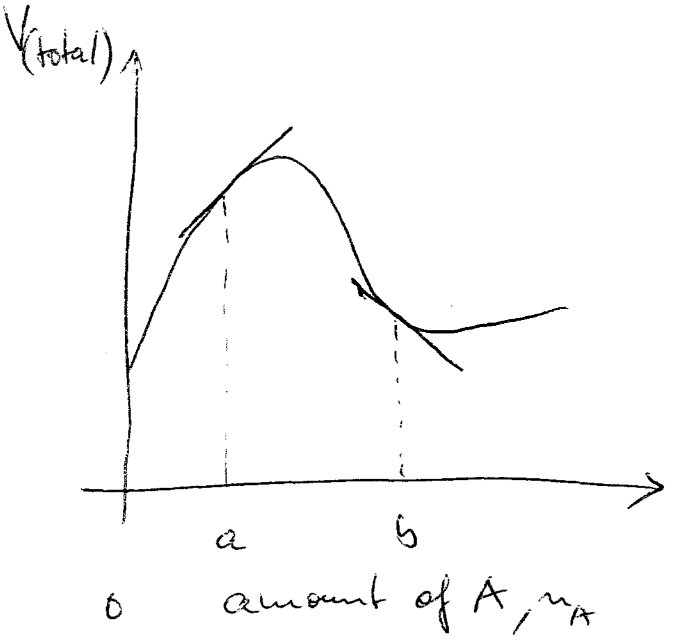
Partial molar quantities

- easiest to visualize: partial molar volume
- example water + ethanol
- observation sum of each component's volume different from mixture volume of the same composition

Def. partial molar volume $\left(\frac{\partial V}{\partial n_j}\right)_{p,T,n'}$

n': amounts of all other components





As amount of J changes, the partial molar volume is the slope of the plot of the total volume

<u>Total volume change</u>

$$dV = dn_A \left(\frac{\partial V}{\partial n_A}\right)_{T,P,n_B} + dn_B \left(\frac{\partial V}{\partial n_B}\right)_{T,P,n_A}$$

with the knowledge of the partial volume, the total volume of a mixture can be derived

$$V = n_A V_A + n_B V_B$$

Example: total volume of ethanol at 25°C containing 1000 kg water follows

$$V/ml = 1002.93 + 54.66 b + 0.363 b^2 + 0.028256$$

b = molality of ethanol

$$V_{Ethanol} = \left(\frac{\partial V}{\partial b}\right) = 54.66 + 2 \cdot 0.363 b + 3 \cdot 0.028256 b^2$$

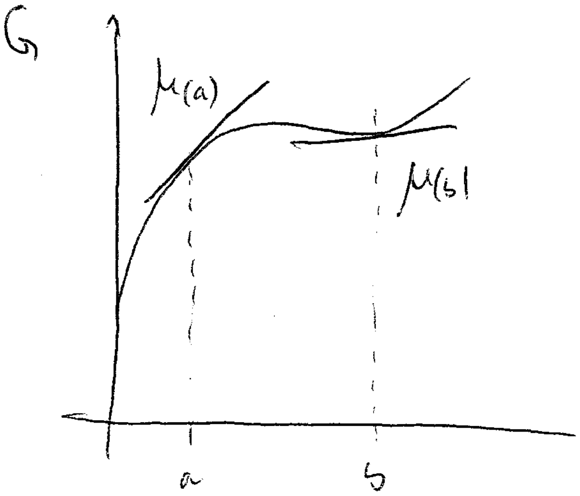
Molar volume : always positive

partial molar quantities : can also be negative

Partial molar Gibbs energies

pure substance: chemical potential = molar Gibbs ene

substance in a mixture: chemical potential <u>defined</u> as partial molar Gibbs



$$\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$$

analog to volume:

$$G = n_A \mu_A + n_B \mu_B$$

- wider significance of ten chemical potential

$G = U + pV - TS$

<u>infinitesimal change in U</u>, internal energy, for a system of variable composition

$$\to dU = -pdV - Vdp + TdS + SdT + dG$$

$$= -pdV - \cancel{Vdp} + TdS + \cancel{SdT} + \overbrace{\left(\cancel{Vdp} - \cancel{SdT} + \mu_A dn_A + \mu_B dn_B\right)}$$

$$= -pdV + TdS + \mu_A dn_A + \mu_B dn_B + \ldots$$

at $V, S = \text{const.}$ $\Rightarrow$ $dU = \mu_A dn_A + \mu_B dn_B + \ldots$

and, hence $\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{n', V, S}$

chemical potential shows G changes but also internal energy changes

Further relations: $\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{n', p, S}$ $\mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{n', V, T}$

μ_J shows how all central thermodynamic properties H, U, A, depend on composition

The Gibbs - Duhem equation

Total Gibbs energy of a mixture (binary):

$G = n_A \mu_A + n_B \mu_B$

infinitesimal changes:

$dG = \mu_A dn_A + \mu_B dn_B + n_A d\mu_A + n_B d\mu_B$

at constant p, T: $dG = \mu_A dn_A + \mu_B dn_B$ (see above)

$\Rightarrow$ implies that $n_A d\mu_A + n_B d\mu_B = 0$

more general:

$$\sum_J n_J d\mu_J = 0$$ Gibbs - Duhem equation

$\rightsquigarrow$ binary mixture: $d\mu_B = -\frac{n_A}{n_B} d\mu_A$

No independent change of the chemical potential of 1 mixture component!

Thermodynamics of mixing

- mixing of gase occurs spontaneously: decrease in G
- two perfect gases in a container; p, T = const

pure values: $\mu = G_m$

$$\mu = \mu^\ominus + RT \ln \frac{p}{p^\ominus}$$

$\ominus$ standard conditions (p=1 bar)

Initial G before mixing

$$G_i = \mu_A n_A + \mu_B n_B$$

$$= n_A \left(\mu_A^\ominus + RT \ln \frac{p}{p^\ominus} \right) + n_B \left(\mu_B + RT \ln \frac{p}{p^\ominus} \right)$$

After mixing: $p = p_A + p_B$

$$G_f = n_A \left(\mu_A^\ominus + RT \ln \frac{p_A}{p^\ominus} \right) + n_B \left(\mu_B + RT \ln \frac{p_B}{p^\ominus} \right)$$

$$\Delta_{mix} G = G_f - G_i = n_A RT \ln \frac{p_A}{p} + n_B RT \ln \frac{p_B}{p}$$

and with Dalton's law $x_J = \frac{p_J}{p}$, $n_J = x_J n$

$$\Delta_{mix} G = (nRT)(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta_{mix} S = \left(\frac{-\partial \Delta_{mix} G}{\partial T} \right)_{p, n_A, n_B} = -nR(x_A \ln x_A + x_B \ln x_B)$$

but: $\Delta H = \Delta G - T\Delta S$

$= 0$ (