5.7 Gibbs-Duhem equation

We will now discuss an astonishingly general relation which holds for all extensive properties $\Phi(p, T, n_i)$ of a mixture which can be written as

$$\Phi = \sum_i n_i \varphi_i \quad \text{with} \quad \varphi_i = \left(\frac{\partial \Phi}{\partial n_i}\right)_{p,T,n_{j\neq i}} \tag{5.17}$$

As for any function with the same coordinates as the Gibbs potential for constant p and T the total derivative is

$$d\Phi = \sum_i \left(\frac{\partial \Phi}{\partial n_i}\right)_{p,T,n_{j\neq i}} dn_i = \sum_i \varphi_i dn_i \tag{5.18}$$

On the other hand for a special function defined by Eq. (5.17) the total derivative can be written as

$$d\Phi = \sum_i \varphi_i dn_i + \sum_i n_i d\varphi_i \tag{5.19}$$

Comparing Eq. (5.18) and Eq. (5.19) we find

$$0 = \sum_i n_i d\varphi_i \tag{5.20}$$

which is the Gibbs-Duhem equation. So in a system with N components, only $N - 1$ partial molar quantities are independent, e.g. the chemical potential of one component in a solution cannot be varied independently of the chemical potentials of the other components. Integration of Eq. (5.20) allows to calculate $\Delta\phi_i$ relations:

$$\int d\varphi_1 = -\frac{n_2}{n_1} \int d\varphi_2 \tag{5.21}$$