

3.32 Fundamental equations for open systems ($dn_i \neq 0$)

For systems containing only one component we already introduced the chemical potential μ (cf. e.g. Eq (3.33)). To later on allow for the description of chemical reactions we now will generalize this concept to systems with many components i ; the fundamental equations now are

$$\begin{aligned}
 dH &= \left(\frac{\partial H}{\partial S}\right)_{p,n_i} dS + \left(\frac{\partial H}{\partial p}\right)_{S,n_i} dp + \sum_i \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{i \neq j}} dn_i \\
 dU &= \left(\frac{\partial U}{\partial S}\right)_{V,n_i} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n_i} dV + \sum_i \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{i \neq j}} dn_i \\
 dG &= \left(\frac{\partial G}{\partial T}\right)_{p,n_i} dT + \left(\frac{\partial G}{\partial p}\right)_{T,n_i} dp + \sum_i \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{i \neq j}} dn_i \\
 dF &= \left(\frac{\partial F}{\partial T}\right)_{V,n_i} dT + \left(\frac{\partial F}{\partial V}\right)_{T,n_i} dV + \sum_i \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{i \neq j}} dn_i
 \end{aligned} \tag{3.83}$$

so one finds

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{i \neq j}} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{i \neq j}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{i \neq j}} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{i \neq j}} \tag{3.84}$$

So as an example μ_i gives the change of G when component i is added to the system at constant T , p , and constant number of moles of all of the other species, thus μ represents the chemical non-expansion work. Thus for a pure phase we find $\mu = G/n$.