

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

For systems containing only one component we already introduced the chemical potential  $\mu$  (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  $\mu_i$  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  $\mu$  represents the chemical non-expansion work. Thus for a pure phase we find  $\mu = G/n$ .