

## 14.9: The Dependence of Chemical Potential on Other Variables

The chemical potential of a substance in a particular system is a function of all of the variables that affect the Gibbs free energy of the system. For component  $A$ , we can express this by writing

$$\mu_A = \mu_A(P, T, n_1, n_2, \dots, n_A, \dots, n_\omega)$$

for which the total differential is

$$d\mu_A = \left(\frac{\partial \mu_A}{\partial T}\right)_P dT + \left(\frac{\partial \mu_A}{\partial P}\right)_T dP + \sum_{j=1}^{\omega} \left(\frac{\partial \mu_A}{\partial n_j}\right)_{PT} dn_j$$

Recalling the definition of the chemical potential and the fact that the mixed second-partial derivatives of a state function are equal, we have

$$\left(\frac{\partial \mu_A}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\right)_P \left(\frac{\partial G}{\partial n_A}\right)_{TP} = \left(\frac{\partial}{\partial n_A}\right)_{TP} \left(\frac{\partial G}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial n_A}\right)_{TP} = -\bar{S}_A$$

Similarly,

$$\left(\frac{\partial \mu_A}{\partial P}\right)_T = \left(\frac{\partial}{\partial P}\right)_T \left(\frac{\partial G}{\partial n_A}\right)_{TP} = \left(\frac{\partial}{\partial n_A}\right)_{TP} \left(\frac{\partial G}{\partial P}\right)_T = \left(\frac{\partial V}{\partial n_A}\right)_{TP} = \bar{V}_A$$

Thus, the total differential of the chemical potential for species  $A$  can be written as

$$d\mu_A = -\bar{S}_A dT + \bar{V}_A dP + \sum_{j=1}^{\omega} \left(\frac{\partial \mu_A}{\partial n_j}\right)_{PT} dn_j$$

To illustrate the utility of this result, we can use it to derive the Clapeyron equation for equilibrium between two phases of a pure substance. In [Chapter 12](#), we derived the [Clapeyron equation](#) using a thermochemical cycle. We can now use the total differential of the chemical potential to present essentially the same derivation using a simpler argument. Letting the two phases be  $\alpha$  and  $\beta$ , the total differentials for a system that contains both phases becomes

$$d\mu_\alpha = -\bar{S}_\alpha dT + \bar{V}_\alpha dP + \left(\frac{\partial \mu_\alpha}{\partial n_\alpha}\right)_{PT} dn_\alpha + \left(\frac{\partial \mu_\alpha}{\partial n_\beta}\right)_{PT} dn_\beta$$

and

$$d\mu_\beta = -\bar{S}_\beta dT + \bar{V}_\beta dP + \left(\frac{\partial \mu_\beta}{\partial n_\alpha}\right)_{PT} dn_\alpha + \left(\frac{\partial \mu_\beta}{\partial n_\beta}\right)_{PT} dn_\beta$$

Since equilibrium between phases  $\alpha$  and  $\beta$  means that  $\mu_\alpha = \mu_\beta$ , we have also that  $d\mu_\alpha = d\mu_\beta$  for any process in which the phase equilibrium is maintained. Moreover,  $\alpha$  and  $\beta$  are pure phases, so that  $\mu_\alpha$  and  $\mu_\beta$  are independent of  $n_\alpha$  and  $n_\beta$ . Then

$$\left(\frac{\partial \mu_\alpha}{\partial n_\alpha}\right)_{PT} = \left(\frac{\partial \mu_\beta}{\partial n_\alpha}\right)_{PT} = \left(\frac{\partial \mu_\alpha}{\partial n_\beta}\right)_{PT} = \left(\frac{\partial \mu_\beta}{\partial n_\beta}\right)_{PT} = 0$$

Hence,

$$-\bar{S}_\alpha dT + \bar{V}_\alpha dP = -\bar{S}_\beta dT + \bar{V}_\beta dP$$

and the rest of the derivation follows as before.

---

This page titled [14.9: The Dependence of Chemical Potential on Other Variables](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Paul Ellgen](#) via [source content](#) that was edited to the style and standards of the LibreTexts platform.