14.13: Relating the Differentials of Chemical Potential and Activity

Let us write $(d\mu_A)_{PT}$ to represent the differential of μ_A at constant pressure and temperature. From the general expression for $d\mu_A$ and the definition of activity, we can write the total differential of the chemical potential of substance A in a particular system in several equivalent ways

$$\begin{aligned} d\mu_A &= \left(\frac{\partial \mu_A}{\partial P}\right)_T dP + \left(\frac{\partial \mu_A}{\partial T}\right)_P dT + (d\mu_A)_{PT} \\ &= \left(\frac{\partial \mu_A}{\partial P}\right)_T dP + \left(\frac{\partial \mu_A}{\partial T}\right)_P dT + \sum_{j=1}^{\omega}\left(\frac{\partial \mu_A}{\partial n_j}\right)_{PT} dn_j \\ &= \overline{V}_A dP - \overline{S}_A dT + RT(d\ln \tilde{a}_A)_{PT} \\ &= RT\left(\frac{\partial \ln \tilde{a}_A}{\partial P}\right)_T dP + \left(\frac{\partial \mu_A}{\partial T}\right)_P dT + RT(d\ln \tilde{a}_A)_{PT} \end{aligned}$$

In short, we have developed several alternative notations for the same physical quantities. From the dependence of chemical potential on pressure, and because $\widetilde{\mu}_A^o$ is not a function of pressure, we have a very useful relationship:

$$\left(\frac{\partial \mu_A}{\partial P}\right)_T = RT\left(\frac{\partial \ln \tilde{a}_A}{\partial P}\right)_T = \overline{V}_A$$

From the definition of activity and the dependence of chemical potential on temperature, we have:

$$\left(\frac{\partial \mu_A}{\partial T}\right)_P = \left(\frac{\partial \widetilde{\mu}_A^o}{\partial T}\right)_P + R\ln \tilde{a}_A + RT\left(\frac{\partial \ln \tilde{a}_A}{\partial T}\right)_P = -\overline{S}_A$$

From the dependence of chemical potential on the composition of the system, we have

$$\sum_{j=1}^{\omega}\left(\frac{\partial \mu_A}{\partial n_j}\right)_{PT} dn_j = (d\mu_A)_{PT} = RT(d\ln \tilde{a}_A)_{PT}$$

This last equation shows explicitly that the activity of component A depends on all of the species present. The effects of interactions between A molecules and B molecules are represented in this sum by the term $(\partial \mu_A/\partial n_B)_{PT}$. When the effects of intermolecular interactions on the chemical potential are independent of the component concentrations, $(\partial \mu_A/\partial n_B)_{PT} = 0$, and the only surviving term is $(\partial \mu_A/\partial n_A)_{PT}$. If the interactions between A molecules and the rest of the system are constant over a range of concentrations of A, γ_A is constant over this range.