2.2 Chemical potential and activity of ionic solutions/salts

In the following we will discuss ionic solutions

$$\mathrm{B} \equiv \mathrm{M}_{\nu+}^{z+}\mathrm{X}_{\nu-}^{z-} \quad . \tag{2.7}$$

Here $z+$ and $z-$ are the charges and $\nu+$ and $\nu-$ are the number of cations and anions for each formula unit. Such solutions differ strongly from regular solutions as discussed in the section before because even at very small concentration no ideal behavior is found. Again deviation from the ideal case as described by Eq. (1.30) are incorporated by

$$\mu_B = \mu_B^0 + RT\ln\frac{m_B}{m^0} + RT\ln\gamma_B \equiv \nu_+\mu_+ + \nu_-\mu_- \quad . \tag{2.8}$$

Here γ is the activity coefficient and m^0 the standard molarity (= 1 mol/kg). Thus $\gamma = 1$ means the ideal case. Using the activity

$$a = m/m^0\gamma \tag{2.9}$$

the chemical potentials for both components are

$$\mu_+ = \mu_+^0 + RT\ln\frac{m_+}{m^0} + RT\ln\gamma_+ \quad \text{and} \quad \mu_- = \mu_-^0 + RT\ln\frac{m_-}{m^0} + RT\ln\gamma_- \quad . \tag{2.10}$$

leading to

$$\mu_B = \nu_+\mu_+ + \nu_-\mu_- = \nu_+\mu_+^0 + \nu_-\mu_-^0 + RT\ln\left[\left(\frac{m_+}{m^0}\right)^{\nu+}\left(\frac{m_-}{m^0}\right)^{\nu-}\right] + RT\ln\left(\gamma_+^{\nu+}\gamma_-^{\nu-}\right) \quad . \tag{2.11}$$

We will see later that all parameters but γ_+ and γ_- can be extracted from experiments.
Defining the geometric mean for the molarity $m_\pm = \left(m_+^{\nu+}m_-^{\nu-}\right)^{1/\nu}$ and the geometric mean for the activity coefficient $\gamma_\pm = \left(\gamma_+^{\nu+}\gamma_-^{\nu-}\right)^{1/\nu}$ with $\nu = \nu^+ + \nu^-$ we finally get

$$\mu_B = \nu_+\mu_+^0 + \nu_-\mu_-^0 + RT\ln\left[\gamma_\pm\frac{m_\pm}{m^0}\right]^\nu = \mu_B^0 + \nu RT\ln\left[\gamma_\pm\frac{m_\pm}{m^0}\right] \quad . \tag{2.12}$$

Only $\gamma_\pm$ can be extracted from experiments. According to the definition 2.9 we find for the activity

$$a_B = a_+^{\nu+}a_-^{\nu-} = \left(\gamma_\pm\left(\frac{m_\pm}{m^0}\right)\right)^\nu = \gamma_\pm^\nu\frac{m_+^{\nu+}m_-^{\nu-}}{(m^0)^\nu} \quad . \tag{2.13}$$