Chemical Potentials; Solutions; 1:1 Salts

There is an important point to consider in the context of salt solutions. For a dilute aqueous solution containing sodium chloride, osmotic and colligative properties confirm that for each mole of sodium chloride the aqueous solution contains (almost exactly) two moles of solutes. These observations result in an added complexity in that chemists describe the solute, sodium chloride in two ways. In one description there is one solute - 'sodium chloride'. In another description there are two solutes sodium ions and chloride ions. The latter description is certainly attractive because we can ring the changes through a series of solutes; NaCl → NaBr → KBr → KCl → ......... etc. Here we change in stepwise fashion one chemical substance in the salt to produce a new solute. There is, however, one crucial condition. Aqueous solutions are electrically neutral although the solutions contain ions. Therefore, the total charge on all cations equals in magnitude the total charge on all anions in the same solution. There is, therefore, a major problem. We cannot examine the properties of aqueous solutions containing, for example, just cations. We can only examine the properties of electrically neutral solutions. How can we obtain the properties of ionic substance (e.g. Na+) in aqueous solutions at defined temperature and pressure? The frustrating answer is that we cannot measure the thermodynamic properties of single ions in solution. This realisation does not stop us speculating about such properties. In fact, a common procedure involves estimating the properties of single ions but then in the last stage of the analysis we pull the derived single ion properties together to describe the properties of a given salt solution.

The chemical potential of each ionic substance i in solution is related to its molality $m_i$ using equation (a) for a solution at fixed temperature and fixed pressure. We assume that the latter is ambient pressure and therefore close to the standard pressure $P^0$.

$$\mu_i(aq) = \mu_i^0(aq) + R \cdot T \cdot \ln\left( \frac{m_i}{m_i^0} \right)$$  \hspace{1cm} (a)
Here \( \mu_i^0(aq) \) is the standard chemical potential of ion \( i \) in an aqueous solution where both the molality \( m_i \) and single ion activity coefficient \( \gamma_i \) are unity (at the same \( T \) and \( p \)). However, the terms \( \mu_i(aq), \mu_i^0(aq) \) and \( \gamma_i \) have no practical significance because, we cannot prepare a solution containing just one ionic chemical substance. The way forward involves using equation (a) for all ionic substances in the solution. In order to show how the argument develops we consider an aqueous solution containing a 1:1 salt (e.g. NaCl) which we assert is fully dissociated into ions. We make two (extrathermodynamic) assumptions.

(i) The chemical potential of the 1:1 salt in solution is given by the sum of the single ion chemical potentials for cations and anions.

For salt \( j \) (at fixed \( T \) and \( p \)),

\[
\mu_j(aq) = \mu_+(aq) + \mu_-(aq)
\]

(ii) The chemical potential of salt \( j \) in an ideal solution at unit salt molality \( (m_j = 1.0 \text{ mol kg}^{-1}) \) is given by the sum of the corresponding reference chemical potentials of cations and anions (at the same temperature and pressure).

\[
\mu_j(aq;id;m_j = 1 \text{ mol kg}^{-1}) = \mu_+(aq;id;m_+ = 1 \text{ mol kg}^{-1}) + \mu_-(aq;id;m_- = 1 \text{ mol kg}^{-1})
\]

As demanded by the analysis, such an ideal solution would be electrically neutral. But we have no information concerning the contributions which the ions make to the overall chemical potential, \( \mu_j(aq;id;m_j = 1 \text{ mol kg}^{-1}) \). We anticipate that such contributions are characteristic of the ions. For a 1:1 salt combination of the three previous equations yields for a solution at fixed \( T \) and \( p \), equation (d).

\[
\mu_j(aq) = \mu_j^0(aq;id;m_j = 1 \text{ mol kg}^{-1}) + R \cdot T \cdot \ln(m_+ \cdot m_- \cdot \gamma_+ \cdot \gamma_- / m_0 \cdot m_0^0)
\]

A (geometric) mean ionic activity coefficient \( \gamma_z^2 \) is defined by equation (e).

\[
\gamma_z^2 = \gamma_+ \cdot \gamma_-
\]

Also for a 1:1 salt \( m_j^2 = m_+ \cdot m_- \). Therefore (at fixed temperature and
pressure), \[ \mu_j(aq) = \mu_j^0(aq) + 2 \cdot R \cdot T \cdot \ln(m_j \cdot \gamma_\pm / m^0) \] (f)

where \[ \mu_j^0(aq) = \mu_j^0(aq; id; m_j = 1 \text{ mol kg}^{-1}; p \equiv p^0) \]

By definition limit \[ (m_j \to 0)\gamma_\pm = 1.0 \text{ at all T and p} \] (g)

The origin of the integer '2' in equation (f) is the stoichiometry of the salt; each mole of salt forms two moles of ions assuming complete dissociation. Hence \[ \mu_j^0(aq) \] is the chemical potential of salt j in an ideal solution at the same T and p (\( \equiv p^0 \)) where the molality of the salt is 1 mol kg\(^{-1}\). If the properties of the salt are ideal the chemical potential of the salt is given by equation (h).

\[ \mu_j(aq; id) = \mu_j^0(aq) + 2 \cdot R \cdot T \cdot \ln(m_j / m^0) \] (h)

When \( m_j > m^0 \), the chemical potential of the salt in the ideal solution \( \mu_j(aq; id) > \mu_j^0(aq) \); the salt is at a higher chemical potential than in the reference state. When \( m_j < 1.0 \text{ mol kg}^{-1} \), the chemical potential of the salt in the ideal solution is lower than in the reference solution where \( m_j = 1.0 \text{ mol kg}^{-1} \).

Returning to the equation (f), there is merit in writing the equation in the following form.

\[ \mu_j(aq) = \mu_j^0(aq) + 2 \cdot R \cdot T \cdot \ln(m_j / m^0) + 2 \cdot R \cdot T \cdot \ln(\gamma_\pm) \] (i)

Or, \[ \mu_j(aq) = \mu_j(aq; id) + 2 \cdot R \cdot T \cdot \ln(\gamma_\pm) \] (j)

The difference \[ [\mu_j(aq) - \mu_j(aq; id)] \] is a measure of the extent to which the chemical potential of a salt in a real salt solution differs from the chemical potential of the same salt in an ideal solution. For KCl(aq; 298.2 K; 0.1 mol kg\(^{-1}\)) the mean ionic activity coefficient \( \gamma_\pm \) equals 0.769; \( 2 \cdot R \cdot T \cdot \ln(0.769) \)

\[ = -1.30 \text{ kJ mol}^{-1}. \] In other words, KCl in this solution is at a lower chemical potential than in the corresponding ideal solution. In fact, \( \gamma_\pm \) for most dilute aqueous salt solution is < 1.0 at ambient T and p, and so this pattern in chemical potentials is quite common. However, even though we know \( \gamma_\pm \) for these systems we are not in a position to
comment on the single ion activity coefficients for the reasons discussed above [1].

The difference described by equation (j) prompts the definition of an excess chemical potential, $\mu_j^{E}(aq)$.

Thus $\mu_j^{E}(aq) = 2 \cdot R \cdot T \cdot \ln(\gamma_\pm)$  \hspace{1cm} (k)

A key contribution to $\mu_j^0(aq)$ emerges from cation-water and anion-water interactions, namely ionic hydration. In contrast $\gamma_\pm$ is determined by ion-ion interactions in real solutions.

For a solution at pressure $p$, equation (f) takes the following form.

$$
\mu_j(aq; p) = \mu_j^0(aq; p^0) + 2 \cdot R \cdot T \cdot \ln(m_j \cdot \gamma_\pm / m^0) + \int_{p^0}^{p} V_j^\infty(aq) \cdot dp \hspace{1cm} (l)
$$

**Footnotes**