We consider a salt $j$ having the following general formula:

$$\nu_+ M^{z+} \nu_- X^{z-}. \quad (a)$$

Here $\nu_+$ and $\nu_-$ are the (integer) stoichiometric coefficients; $z$, and $z$ - are the (integer) charge numbers. We assume the salt $j$ is completely dissociated in aqueous solution. Hence the solution contains (apart from solvent) two chemical substances. With complete dissociation each mole of salt produces $\nu$ moles of ions. The condition of electric neutrality is expressed by equation (b).

$$|\nu_+ \cdot z_+| = |\nu_- \cdot z_-| \quad (b)$$

For a solution molality $m_j$, the molalities of cations and anions are $\nu_+ \cdot m_j$ and $\nu_- \cdot m_j$ respectively. If the chemical potentials of cations and anions are $\mu_+^{(aq)}$ and $\mu_-^{(aq)}$ respectively, the chemical potential of salt $j$ in aqueous solution (at molality, $m_j$ temperature $T$ and ambient pressure) is given by equation (c).

$$\mu_j^{(aq)} = \nu_+ \cdot \mu_+^{(aq)} + \nu_- \cdot \mu_-^{(aq)} \quad (c)$$

In an ideal solution (at the same $T$ and ambient pressure) where the molality of the salt $j$ is $1 \text{ mol kg}^{-1}$.

$$\mu_j^0^{(aq)} = \nu_+ \cdot \mu_+^0^{(aq)} + \nu_- \cdot \mu_-^0^{(aq)} \quad (d)$$

For each ionic substance $i$, the chemical potential (at the same $T$ and $p$) is given by equation (e) where $\gamma_i$ is the single ionic activity coefficient.

$$\mu_i^{(aq)} = \mu_i^0^{(aq)} + R \cdot T \cdot \ln(m_i \cdot \gamma_i / m^0) \quad (e)$$

Hence for the salt with $m_+ = \nu_+ \cdot m_j$ and $m_- = \nu_- \cdot m_j$.

$$\mu_j^{(aq)} = [\nu_+ \cdot \mu_+^0^{(aq)} + \nu_- \cdot \mu_-^0^{(aq)}]$$

$$+ \nu_+ \cdot R \cdot T \cdot \ln(\nu_+ \cdot m_j \cdot \gamma_+ / m^0)$$

$$+ \nu_- \cdot R \cdot T \cdot \ln(\nu_- \cdot m_j \cdot \gamma_- / m^0) \quad (f)$$

We draw together the logarithm terms.

$$\mu_j^{(aq)} = [\nu_+ \cdot \mu_+^0^{(aq)} + \nu_- \cdot \mu_-^0^{(aq)}]$$

$$+ R \cdot T \cdot \ln[(\nu_+ \cdot m_j \cdot \gamma_+ / m^0)^{\nu_+} \cdot (\nu_- \cdot m_j \cdot \gamma_- / m^0)^{\nu_-}] \quad (g)$$
The latter far from elegant equation contains all the parameters we expect to be present. Here it is convenient to introduce a parameter $Q^{[1,3]}$.

$$Q^\nu = \nu_+^\nu_+ \cdot \nu_-^\nu_- \quad (h)$$

The (geometric) mean activity coefficient is defined by equation (i).

$$\gamma_\pm^\nu = \gamma_+^\nu_+ \cdot \gamma_-^\nu_- \quad (i)$$

Hence equation (g) can be rewritten in the following form.

$$\mu_j(aq) = \mu_j^0(aq) + \nu \cdot R \cdot T \cdot \ln[Q \cdot m_j \cdot \gamma_\pm / m^0] \quad (j)$$

The quantity $Q$ takes account of the stoichiometric composition of the salt. In preparing the salt solution we target the molality but this does not take account of how many moles of each ionic substance are produced by one mole of salt; the quantity $\nu$ only records how many moles of ionic substances are produced by each mole of salt. For the salt $M^{2+}2X^- \text{[e.g. Mg Br}_2^2 \text{]} \nu_+ = 1, \nu_- = 2$ where $Q^3 = 1^2 \cdot 2^2 = 4$. For this salt,

$$\mu_j(aq) = \mu_j^0(aq) + 3 \cdot R \cdot T \cdot \ln[4^{1/3} \cdot m_j \cdot \gamma_\pm / m^0] \quad (k)$$

The complex algebra associated with a thermodynamic description of salt solutions stems from a conflict of interests and practical chemistry. The ground rules in this subject are quite simple—measurements are made on electrically neutral solutions; e.g. NaCl(aq). In the latter case chemists often favour a description of this system in terms of an aqueous solution of two solutes, sodium ions and chloride ions. Rather than using an activity coefficient for the solute [e.g; $\gamma(\text{NaCl})$], we define a mean activity coefficient $\gamma_\pm$ which recognises the presence of two ionic substances. An indication of the presence of two solutes (i.e. $Na^+$ and $Cl^-$) rather than one solute (e.g. NaCl) is the stoichiometric parameter $\nu$ in the equation for the chemical potential of the solvent. This parameter is readily determined from the depression of solvent freezing points (i.e. cryoscopy) and osmotic pressures. Both properties are directed at the properties of solvents. The cryoscopic technique is based on measurement of the temperature at which solvent in a solution is in equilibrium (at fixed pressure) with pure solid solvent. The osmotic pressure $\pi$ characterises the equilibrium (a fixed temperature) between the solution at pressure $p + \pi$ and pure solvent at pressure $p$. Both techniques determine $\nu$ or, in
colloquial terms, count solute particles. The molar mass of NaCl and urea are roughly equal; the number of solute particles in NaCl(aq) is twice that in urea(aq) for the same mass of solute in 1 kg of water. We confirm this observation by measuring the depressions of freezing points or the osmotic pressures of two solutions.

Equation (j) signals an important challenge. If we could separate out ionic contributions to $\mu_j^0(aq)$ for salt $j$, we could probe the contributions made by ion-water interactions, the hydration properties for a given ion $i$ at defined $T$ and $p$ to $\mu_i^0(aq)$. In this exercise we might then extend the analysis to single ion enthalpies $H_i^0(aq)$, volumes $V_i^0(aq)$, and entropies $S_i^0(aq)$. Unfortunately the story is not simple. Indeed we cannot measure these chemical potentials and then obtain absolute estimates for the above derived properties.

Footnotes