Gibbs Energies; Salt Solutions; Aqueous Mixtures

The solubilities of chemical substance \( j \) in two liquids \( \ell_1 \) and \( \ell_2 \) (at the same \( T \) and \( p \)) offers a method for comparing the reference chemical potentials, using the transfer parameter \( \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 \). A similar argument is advanced in the context of salt solutions in which comparison of the solubility of salt \( j \) in two liquids leads to the transfer parameter for the salt. However the argument does not stop there. In the case of, for example a 1:1 salt \( M^+X^- \), the derived transfer for the salt is re-expressed as the sum of transfer parameters for the separate ions \( M^+ \) and \( X^- \).

Thus \( \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 (M^+X^-) = \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 (M^+) + \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 (X^-) \) (a)

However granted that we can obtain an estimate of the transfer parameter for the salt, \( \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 (M^+X^-) \), thermodynamics does not offer a method for calculating the corresponding ionic transfer parameters. Several extra-thermodynamic procedures yield estimated single ion thermodynamic transfer parameters. The simplest approach adopts a reference ion (e.g. \( H^+ \)) and reports relative transfer ionic chemical potentials.

\[ \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 (H^+) = 0 \] (b)

For example; \( \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 (C\ell^-) = \Delta(\ell_1 \rightarrow \ell_2)\mu_j^0 (HC\ell) \) (c)

Solubilities and Transfer Parameters

A closed system (at fixed \( T \) and ambient pressure) contains a solid salt \( j \) in equilibrium with salt \( j \) in aqueous solution. At equilibrium,

\[ \mu_j^*(s) = \mu_j^0 (aq) + \nu \cdot R \cdot T \cdot \ln(Q \cdot m_j^eq (aq) \cdot \gamma_{eq}^\pm (aq) \cdot m^0) \] (d)

Similarly for an equilibrium system where the solvent is a binary aqueous mixture, mole fraction \( x_2 \),

\[ \mu_j^*(s) = \mu_j^0 (s \ln; x_2) + \nu \cdot R \cdot T \cdot \ln(Q \cdot m_j^eq (s \ln; x_2) \cdot \gamma_{eq}^\pm (s \ln; x_2) \cdot m^0) \] (e)

Then,

\[ \Delta(aq \rightarrow x_2)\mu_j^0 (s \ln) = \mu_j^0 (s \ln; x_2) - \mu_j^0 (aq) \]

\[ = -\nu \cdot R \cdot T \cdot \ln[m_j^eq (s \ln; x_2) \cdot \gamma_{eq}^\pm (s \ln; x_2) / m_j^eq (aq) \cdot \gamma_{eq}^\pm (aq)] \] (f)

A key assumption sets the ratio of mean ionic activity coefficients to unity. In effect we assume that the solubilities do not change dramatically as \( x_2 \) is changed.

Therefore, \( \Delta(aq \rightarrow x_2)\mu_j^0 (s \ln) = -\nu \cdot R \cdot T \cdot \ln[m_j^eq (s \ln; x_2) / m_j^eq (aq)] \) (g)
Thus the ratio \( \frac{m_j^{\text{aq}}(s \ln x_2)}{m_j^{\text{aq}}(\text{aq})} \) is effectively the ratio of solubilities of salt \( j \) in the mixed aqueous solutions and aqueous solution. If the solubility of the salt increases with increase in \( x_2 \), \( \Delta(\text{aq} \rightarrow x_2)\mu_j^0(\text{s ln}) \) is negative. In other words, the salt in aqueous solutions is stabilised by adding the co-solvent.

Granted that solubility data lead to an estimate for \( \Delta(\text{aq} \rightarrow x_2)\mu_j^0(\text{s ln}) \), this quantity involves contributions from both cations and anions. For a salt containing two ionic substances
\[ \Delta(\text{aq} \rightarrow x_2)\mu_j^0(\text{s ln}) = \Delta(\text{aq} \rightarrow x_2)\mu_j^0(\text{s ln}) + \Delta(\text{aq} \rightarrow x_2)\mu_j^0(\text{s ln}) \] (h)

The background to this type of analysis centres on classic studies into the electrical conductivities of salt solutions. For a given salt in a solvent (at fixed \( T \) and \( p \)), the molar conductivity approaches a limiting value with decrease in concentration;
\[ \lim(c_j \to 0)\Lambda_j = \Lambda_j^0. \] The limiting molar conductivity of a salt solution \( \Lambda_j^0 \) containing a 1:1 salt can be written as the sum of limiting ionic conductivities \( \lambda_i^0 \) of anions and cations.
\[ \Lambda_j^0 = \lambda_+^0 + \lambda_-^0 \] (i)

The transport number of an ion \( t_j \) measures the ratio \( \lambda_j^0 / \Lambda \). Both \( t_j \) and \( \Lambda \) can be measured and hence \( \lambda_j^0 \) calculated in the limit of infinite dilution characterises ion \( j \) in a given solvent at defined \( T \) and \( p \). Discrimination between anions and cations arises from their electrical charges and hence the direction of migration of ions in an electric field. Nevertheless the task of measuring both \( t_j \) and \( \Lambda \) is not trivial and some simple working hypothesis is often sought. The argument is advanced that the molar conductivities are equal in magnitude for two ions having similar size and solvation characteristics. This ‘extrathermodynamic’ assumption has been applied [1-8] to a range of ‘onium salts including (1) \( \text{Bu}_4\text{N}^+ \text{Ph}_3\text{FB}^- \), (2) \( \text{iso-Bu}_3\text{N}^+ \text{H}_4\text{B}^- \), (3) \( \text{Bu}_4\text{N}^+ \text{Ph}_4\text{B}^- \), (4) \( \text{iso-Am}_3\text{BuN}^+ \text{H}_4\text{B}^- \) (5) \( \text{iso-Am}_4\text{N}^+ \text{iso-Am}_4\text{B}^- \); so
\[ \lambda_j^0 \text{ (big cation)} = \lambda_j^0 \text{ (big anion)} \]. This ‘big ion – big ion’ assumption is carried over to the analysis of thermodynamic properties where we lack the discrimination between cations and anions based on their mobilities in an applied electric potential. gradient. Then for example the change in solubility of one such salt in aqueous solution on
adding a cosolvent (e.g. ethanol) can be understood in terms of equal transfer thermodynamic potentials.

\[
\frac{1}{2} \Delta (aq \rightarrow x_2) \mu^0 (\text{big cation } \text{big anion}; s \ln) = \\
\Delta (aq \rightarrow x_2) \mu^0 (\text{big cation}; s \ln) = \Delta (aq \rightarrow x_2) \mu^0 (\text{big anion}; s \ln) \quad (j)
\]

For example having obtained \( \Delta (aq \rightarrow x_2) \mu^0 (\text{big cation}; s \ln) \), the difference in solubilities of the corresponding salt iodide is used to obtain the transfer parameter for iodide ions in the two solvents.

\[
\Delta (aq \rightarrow x_2) \mu^0 (I^-; s \ln) = \\
\Delta (aq \rightarrow x_2) \mu^0 (\text{big cation }; \text{iodide}; s \ln) - \Delta (aq \rightarrow x_2) \mu^0 (\text{big cation } s \ln) \quad (k)
\]

Considerable information is available in the chemical literature concerning ionic transfer parameters, particularly for solutes in binary aqueous mixtures at 298.2 K and ambient pressure. There is no agreed composition scale for transfer parameters. Information includes transfer parameters based on concentration, molality and mole fractions scales for the solutes. The situation is further complicated by the fact that different scales are used to express composition of liquid mixtures. Common scales include mass\%, mole fraction and vol\%. Conversion between these scales is a tedious. Some examples of the required equations are presented in an Appendix to this Topic.

**Footnotes**


Appendix

Conversion between Composition Scales: Aqueous Solutions.

Solute j in Aqueous Solution

We write down two equations for the same quantity, the chemical potential of solute j. For the chemical potential of solute j in an ideal aqueous solution at ambient pressure (i.e. close to the standard pressure, \( p^0 \)),

\[
\mu_j^{\text{aq}} = \mu_j^{\text{aq}; m^0} + R \cdot T \cdot \ln[m_j / m^0]
\]

(i)

Here \( m_j \) is the molality of solute j; \( m^0 = 1 \) mol kg\(^{-1} \), the reference molality.

However we may decide to express the composition of the solution in terms of the mole fraction of solute. If the properties of the solute are ideal, the chemical potential of solute j, \( \mu_j^{\text{aq}} \) is related to the mole fraction of solute \( x_j \).

\[
\mu_j^{\text{aq}} = \mu_j^{\text{aq}; x_j = 1} + R \cdot T \cdot \ln[x_j]
\]

(ii)

Equations (i) and (ii) describe the same property, \( \mu_j^{\text{aq}} \). The property \( \mu_j^{\text{aq}; x_j = 1} \) is interesting because it describes the chemical potential of solute j in aqueous solution where the mole fraction of solute is unity; it is clearly an ‘extrapolated’ property of the solute.
If \( n_j \) is the amount of solute in a solution prepared using 102 kg of water, we can combine equations (i) and (ii); \( x_j = n_j /([(10^2 / M_1) + n_j] \) where for a dilute solution \( (10^2 / M_1) >> n_j \); \( M_1 \) is the molar mass of water.

\[
\mu_j^0(\text{aq}; m^0) + R \cdot T \cdot \ln[n_j / 10^2 \cdot m^0] = \mu_j^0(\text{aq}; x_j = 1) + R \cdot T \cdot \ln[n_j \cdot M_1 / 10^2] \quad (iii)
\]

Or,

\[
\mu_j^0(\text{aq}; m^0) - \mu_j^0(\text{aq}; x_j = 1) = R \cdot T \cdot \ln[m^0 \cdot M_1] \quad (iv)
\]

We note that \([m^0 \cdot M_1] = [\text{mol kg}^{-1}] \cdot [\text{kg mol}^{-1}] = [1]\)

**Solute \( j \) in a Solvent prepared as a Binary Aqueous Mixture**

If \( n_j \) is the amount of solute \( j \) in 102 kg of a solvent mixture, the chemical potential of solute \( j \) is given by equation (iv)

\[
\mu_j(\text{mix}) = \mu_j^0(\text{mix}; m^0) + R \cdot T \cdot \ln[n_j / 10^2 \cdot m^0] \quad (v)
\]

We note that \([n_j / 10^2 \cdot m^0] = [\text{mol/kg} \cdot \text{mol} \cdot \text{kg}^{-1}] = [1].\]

If the binary solvent mixture comprises \( w_2\% \) of the non-aqueous component, for a dilute solution of solute \( j \), the mole fraction of solute \( x_j \) is given by equation (vi) where \( M_2 \) is the molar mass of the cosolvent.

\[
x_j = \frac{n_j}{[(10^2 - w_2\%) / M_1] + \{w_2\% / M_2\}} \quad (vi)
\]

Using the mole fraction scale for solute \( j \), the chemical potential of solute \( j \) in the mixture, composition \( w_2\% \) is given by equation (vii).

\[
\mu_j(\text{mix}) = \mu_j^0(\text{mix}; x_j = 1) + R \cdot T \cdot \ln\left[\frac{n_j}{[(10^2 - w_2\%) / M_1] + \{w_2\% / M_2\}}\right] \quad (vii)
\]

Equations (v) and (vii) describe the same property, the chemical potential of solute \( j \) in a mixed solvent system. Hence,

\[
\mu_j^0(\text{mix}; m^0) + R \cdot T \cdot \ln[n_j / 10^2 \cdot m^0] = \mu_j(\text{mix}; x_j = 1) + R \cdot T \cdot \ln\left[\frac{n_j}{[(10^2 - w_2\%) / M_1] + \{w_2\% / M_2\}}\right] \quad (viii)
\]

Or,

\[
\mu_j^0(\text{mix}; m^0) = \mu_j^0(\text{mix}; x_j = 1) + R \cdot T \cdot \ln\left[\frac{10^2 \cdot m^0}{[(10^2 - w_2\%) / M_1] + \{w_2\% / M_2\}}\right] \quad (ix)
\]
We note that
\[ \frac{10^2 \cdot m^0}{\{(10^2 - w_2 \%) / M_1 \} + \{w_2 \% / M_2 \}} = \frac{[1]}{[mol \ kg^{-1}]} = [1] \]

**Conversion of Scales.**

It is convenient at this point to comment on the difference in reference chemical potentials of solute j in aqueous solutions and a solvent mixture.

Thus from equation (iv).
\[ \mu_j^0(aq; m^0) - \mu_j^0(aq; x_j = 1) = R \cdot T \cdot \ln[m^0 \cdot M_j] \quad (x) \]

And from equation (ix)
\[ \mu_j^0(mix; m^0) - \mu_j^0(mix; x_j = 1) = R \cdot T \cdot \ln\left[\frac{10^2 \cdot m^0}{\{(10^2 - w_2 \%) / M_1 \} + \{w_2 \% / M_2 \}}\right] \quad (xi) \]

The difference between equations (x) and (xi) yields an equation relating transfer parameters for solute j on the two composition scales.
\[ \mu_j^0(mix; m^0) - \mu_j^0(aq; m^0) = \mu_j^0(mix; x_j = 1) - \mu_j^0(aq; x_j = 1) \]
\[ = R \cdot T \cdot \ln\left[\frac{10^2 \cdot \{10^2 - w_2 \% \} + \{w_2 \% \cdot M_1 / M_2 \}}{10^2}ight] \quad (xii) \]

Hence
\[ \Delta(aq \rightarrow mix)\mu_j^0(m - scale) = \Delta(aq \rightarrow mix)\mu_j^0(x - scale) \]
\[ = R \cdot T \cdot \ln\left[\frac{10^2 \cdot \{10^2 - w_2 \% \} + \{w_2 \% \cdot M_1 / M_2 \}}{10^2}\right] \quad (xiii) \]

\[ \Delta(aq \rightarrow mix)\mu_j^0(m - scale) = \Delta(aq \rightarrow mix)\mu_j^0(x - scale) \]
\[ = -R \cdot T \cdot \ln\left[1 - \{w_2 \% / 10^2\} + (w_2 \% / 10^2) \cdot (M_1 / M_2)\right] \quad (xiv) \]

\[ \Delta(aq \rightarrow mix)\mu_j^0(m - scale) = \Delta(aq \rightarrow mix)\mu_j^0(x - scale) \]
\[ = -R \cdot T \cdot \ln\left[1 - \{(M_1 / M_2) \cdot (w_2 \% / 10^2)\}\right] \quad (xv) \]

If solute j is a salt which is completely dissociated into v ions in both aqueous solution and in the mixed solvent system,
\[ \Delta(aq \rightarrow mix)\mu_j^0(m - scale) = \Delta(aq \rightarrow mix)\mu_j^0(x - scale) \]
\[ = -v \cdot R \cdot T \cdot \ln\left[1 - \{(M_1 / M_2) \cdot (w_2 \% / 10^2)\}\right] \quad (xvi) \]

Thus for each ionic substance contributing to the transfer property for the salt,
\[ \Delta(aq \rightarrow mix)\mu_j^0(s \ln) = \]
\[ = v_+ \cdot \Delta(aq \rightarrow mix)\mu_j^0(s \ln) + v_- \cdot \Delta(aq \rightarrow mix)\mu_j^0(s \ln) \quad (xvii) \]
Equations (xv) and (xvi) show that the difference between the transfer chemical potentials on the x- and m- scales is independent of temperature. The difference is based on the mass of the solvent components in the mixture. Consequently the transfer enthalpies on the two scales are equal.

\[ \Delta(aq \rightarrow mix)H_j^0(m - scale) = \Delta(aq \rightarrow mix)H_j^0(x - scale) \]  

(xviii)

Therefore the difference in the transfer chemical potentials can be traced to differences in the transfer entropies. At constant pressure,

\[ -\Delta(aq \rightarrow mix)S_j^0(m - scale) = d\Delta(aq \rightarrow mix)\mu_j^0 / dT \]

\[ = -\Delta(aq \rightarrow mix)S_j^0(x - scale) + \nu \cdot R \cdot \ln \{[1 - 1 - (M_1 / M_2)] \cdot (w_2 \%/ 10^2) \} \]

(xix)

A similar argument notes that the masses of the solvents forming the mixed solvents are independent of pressure (at fixed temperature) Therefore the volumes of transfer on molality and mole fraction scales are equal. In summary (at fixed T an p),

\[ \Delta(aq \rightarrow mix)H_j^n(s ln) = H_j^n(mix) - H_j^n(aq) \]

\[ = -T^2 \cdot \left[ \partial \{\Delta(aq \rightarrow mix)\mu_j^0(sln; T)/dT\} / dT \right] \]

(xx)

Further, for the isobaric partial molar heat capacities,

\[ \Delta(aq \rightarrow mix)C_{pj}^n(s ln) = C_{pj}^n(mix) - C_{pj}^n(aq) \]

\[ = \left[ \partial \{\Delta(aq \rightarrow mix)H_j^n(sln; T)/\partial T\} / \partial p \right] \]

(xxii)

Also \( \Delta(aq \rightarrow mix)V_j^n(s ln) = V_j^n(mix) - V_j^n(aq) \)  

(xxii)

**Transfer Parameters: Molality and Concentration Scales.**

The procedures described above are repeated but now in a comparison of the molality and concentration scales.

For a solute \( j \) (at fixed \( T \) and \( p \)) in a solution having ideal thermodynamic properties, the chemical potential of solute \( j \) is related to concentration of solute \( j \), \( c_j \) which by convention is expressed in terms of amount of solute in 1 dm\(^3\) of solution at defined \( T \) and \( p \); i.e. \( c_j = [mol \ dm^{-3}] \). A reference concentration \( c_r \) describes a solution where one dm\(^3\) of solution contains one mole of solute. Because the volume of a liquid depends on both temperature and pressure, these variables must be specified.

Thus \( \mu_j(aq) = \mu_j^0(c - scale; aq) + R \cdot T \cdot \ln[ c_j(aq) / c_r ] \)  

(xxiii)

The units of both \( c_j(aq) \) and \( c_r \) are [mol dm\(^{-3}\)]. Hence using equations (i) and (xxiii),
\[ \mu_j(aq) = \mu_j^0(m;aq) + R \cdot T \cdot \ln [m_j(aq)/m^0] \]
\[ = \mu_j^0(c - \text{scale};aq) + R \cdot T \cdot \ln [c_j(aq)/c_j] \quad (\text{xxiv}) \]

For a solution in \(10^2\) kg of solvent, \(m_j(aq) = n_j / 10^2\) mol kg\(^{-1}\) \(\quad (\text{xxv})\)

For a dilute solution, density \(\rho(aq) = \rho_j^*(\ell)\) \(\quad (\text{xxvi})\)

Volume of a dilute solution with mass \(10^2\) kg = \(10^2 / \rho_j^*(\ell)\) \(\quad (\text{xxvii})\)

Concentration, \(c_j = n_j \cdot \rho_j^*(\ell) / 10^2\) \(\quad (\text{xxviii})\)

Therefore equation (xxiv) can be written in the following form
\[ \mu_j^0(m;aq) + R \cdot T \cdot \ln [n_j / 10^2 \cdot m^0] \]
\[ = \mu_j^0(c - \text{scale};aq) + R \cdot T \cdot \ln [n_j \cdot \rho_j^*(\ell)/c_j] \quad (\text{xxix}) \]

For the solution in a binary aqueous mixture,
\[ \mu_j^0(m;\text{mix}) + R \cdot T \cdot \ln [n_j / 10^2 \cdot m^0] \]
\[ = \mu_j^0(c - \text{scale};\text{mix}) + R \cdot T \cdot \ln [n_j \cdot \rho(\text{mix})/c_j] \quad (\text{xxx}) \]

Then,
\[ \Delta(aq \rightarrow \text{mix})\mu_j^0(m) \]
\[ = \Delta(aq \rightarrow \text{mix})\mu_j^0(c - \text{scale}) + R \cdot T \cdot \ln [\rho(\text{mix})/\rho_j^*(\ell)] \quad (\text{xxxi}) \]

In the event that solute is a salt which produces \(v\) moles of ions for each mole of salt,
\[ \Delta(aq \rightarrow \text{mix})\mu_j^0(m) \]
\[ = \Delta(aq \rightarrow \text{mix})\mu_j^0(c - \text{scale}) + v \cdot R \cdot T \cdot \ln [\rho(\text{mix})/\rho_j^*(\ell)] \quad (\text{xxxii}) \]

For each ionic substances, e.g. a cation
\[ \Delta(aq \rightarrow \text{mix})\mu_+^0(m) \]
\[ = \Delta(aq \rightarrow \text{mix})\mu_+^0(c - \text{scale}) + v \cdot R \cdot T \cdot \ln [\rho(\text{mix})/\rho_j^*(\ell)] \quad (\text{xxxiii}) \]

Because the densities of water and each mixture depends on temperature at fixed pressure, the transfer enthalpies on molality and concentration scales differ.

Thus
\[ \Delta(aq \rightarrow \text{mix})H_+^0(m) \]
\[ = \Delta(aq \rightarrow \text{mix})H_+^0(c - \text{scale}) - v \cdot R \cdot T^2 \cdot [\partial \ln [\rho(\text{mix})/\rho_j^*(\ell)]/\partial T]_p \quad (\text{xxxiv}) \]