Chemical Potentials; Solute; Concentration and Molality Scales

For a given solution we can express the chemical potential of solute $j$, $\mu_j^{\text{(aq)}}$ in an aqueous solution at temperature $T$ and pressure $p$ ($=p^0$) using two equations. Therefore, at fixed $T$ and $p$,

$$\mu_j^{0}(\text{aq}) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) =$$

$$\mu_j^{0}(\text{aq}; \text{c-scale}) + R \cdot T \cdot \ln(c_j \cdot y_j / c_i)$$  \hspace{1cm} (a)

Therefore,

$$\ln(y_j) = \ln(\gamma_j) + \ln(m_j \cdot c_i / m^0 \cdot c_j)$$

$$+ \left(1 / R \cdot T \right) \left[\mu_j^{0}(\text{aq}) - \mu_j^{0}(\text{aq}; \text{c-scale})\right]$$  \hspace{1cm} (b)

In the latter two equations the composition variables $m_j$ and $c_j$ are expressed in the units ‘mol kg$^{-1}$’ and ‘mol dm$^{-3}$’, respectively [1]. The ratio ‘$c_j/m_j$’ equals the density expressed in the unit ‘kg dm$^{-3}$’. For dilute solutions, $c_j / m_j = \rho_j^{\ast}(\ell)$, the density of the pure solvent.

Also, $c_j / m^0 = [\text{mol dm}^{-3}] / [\text{mol kg}^{-1}] = [\text{kg dm}^{-3}]$ \hspace{1cm} (c)

For dilute aqueous solutions at ambient pressure and 298.2 K [2,3],

$$\ln(m_j \cdot c_i / m^0 \cdot c_j) = -\ln(0.997)$$  \hspace{1cm} (d)

With reference to equation (b), with increasing dilution,

$$y_j \rightarrow 1, \quad \gamma_j \rightarrow 1, \quad (m_j \cdot c_i / m^0 \cdot c_j) \rightarrow c_i / m^0 \cdot \rho_j^{\ast}(\ell).$$

Hence, $\mu_j^{0}(\text{aq}; \text{c-scale}) - \mu_j^{0}(\text{aq}) = R \cdot T \cdot \ln[c_i / m^0 \cdot \rho_j^{\ast}(\ell)]$ \hspace{1cm} (e)

We combine equations (b) and (e).

$$\ln(y_j) = \ln(\gamma_j) + \ln(m_j \cdot c_i / m^0 \cdot c_j) - \ln[c_i / m^0 \cdot \rho_j^{\ast}(\ell)]$$

$$\ln(y_j / \gamma_j) = m_j \cdot \rho_j^{\ast}(\ell) / c_j$$ \hspace{1cm} (f)

Hence, $(y_j / \gamma_j) = m_j \cdot \rho_j^{\ast}(\ell) / c_j$ \hspace{1cm} (g)
Footnotes

[1] A given solution is prepared by adding $n_j$ moles of solute $j$ to $w_1$ kg of solvent.

\[
\text{Molality of solute } j /\text{mol kg}^{-1} = \frac{n_j}{w_1}
\]

Total mass of solution/kg = $w_1 + n_jM_j$

where molar mass of solute/kg mol$^{-1}$ = $M_j$

Volume of solution/m$^3$ = $V$

Density of solution $\rho /\text{kg m}^{-3} = \left[ \frac{w_1 + n_jM_j}{V} \right]$

By convention chemists express the composition of solutions in terms of (i) concentration using the unit ‘mol dm$^{-3}$’ and (ii) molality using the unit, ‘mol kg$^{-1}$’. These composition scales stem from the fact that at 298.15 K, 1 dm$^3$ of water has a mass of approx. 1 kg. So as we swap composition scales a conversion factor is often required.

For dilute solutions $w_1 > n_jM_j$ and density of solution $\rho$ equals the density of the pure solvent (at same temperature and pressure), i.e. density $\rho = \rho_1^*(\ell)$ kg m$^{-3}$.

[2] A typical conversion takes the following form for water at 298.2 K and ambient pressure.

Density = 0.997 g cm$^{-3}$ = 0.997 (10$^{-3}$ kg) (10$^{-2}$ m)$^3$

= 0.997 X 10$^3$ kg m$^{-3}$

= 997 kg m$^{-3}$ = 0.997 kg dm$^{-3}$

Then $\frac{c_j}{\text{mol dm}^{-3}} = \frac{n_j}{\text{mol}} \cdot \frac{w_1}{\text{kg}} = \frac{w_1}{\text{kg}} \cdot \frac{V}{\text{dm}^3} = \frac{\rho}{\text{kg dm}^{-3}}$

\[
\ln(m_j \cdot c_j / m^0 \cdot c_j) = \ln[(c_j / m^0) / (c_j / m_j)] = \ln[(kg \text{ dm}^{-3}) / \rho] = -\ln(\rho / kg \text{ dm}^{-3})
\]

[3]