

## Topic590

### Chemical Potentials; Solute; Molality Scale

A given aqueous solution comprises  $n_1$  moles of solvent (e.g. water) and  $n_j$  moles of solute (e.g. urea) at equilibrium, temperature  $T$  and pressure  $p$ . Thus the molality of solute  $j$  is given by equation (a).

$$m_j = n_j / w_1 = n_j / n_1 \cdot M_1 \quad (a)$$

$$\mu_j(\text{aq}; T; p) = \mu_j^0(\text{aq}; T; p^0) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) + \int_{p^0}^p V_j^\infty(\text{aq}) \cdot dp \quad (b)$$

- (i)  $\mu_j(\text{aq}; T; p)$  = chemical potential of solute  $j$  in solution.
- (ii)  $\mu_j^0(\text{aq}; T; p)$  = chemical potential of solute  $j$  in the corresponding ideal solution (where  $\gamma_j = 1.0$ ) at temperature  $T$  where  $m_j = 1 \text{ mol kg}^{-1}$  and where the pressure is the standard pressure  $p^0$ .
- (iii)  $m^0 = 1 \text{ mol kg}^{-1}$
- (iv)  $V_j^\infty(\text{aq})$  is the limiting partial molar volume of solute  $j$  at temperature  $T$ .
- (v) By definition,  $\lim(m_j \rightarrow 0) \gamma_j = 1$  at all  $T$  and  $p$ .

Activity coefficient  $\gamma_j$  takes account of the fact that the thermodynamic properties of real solutions are not ideal [1]. An important consideration in understanding the factors which affect  $\gamma_j$  is the distance between solute molecules in solution. As we dilute the solution such that  $m_j$  approaches zero so inter solute distances approach infinity; i.e. in the limit of infinite dilution or zero molality.

If pressure is ambient and hence close to the standard pressure the integral term in equation (b) is negligibly small.

$$\text{Hence, } \mu_j(\text{aq}; T; p) = \mu_j^0(\text{aq}; T) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) \quad (c)$$

At this stage we focus attention on the activity coefficient  $\gamma_j$ . We start with equation (c) and by split the logarithm term. For solutions where the pressure  $p$  is close to the standard pressure  $p^0$

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

If the properties of the solution are ideal, equation (c) takes the following form.

$$\mu_j(\text{aq}; \text{id}; T; p) = \mu_j^0(\text{aq}; T) + R \cdot T \cdot \ln(m_j / m^0) \quad (\text{e})$$

If  $m_j < 1.0 \text{ mol kg}^{-1}$ ,  $R \cdot T \cdot \ln(m_j / m^0)$  is  $< 0$ .

$\mu_j(\text{aq}; \text{id}; T; p) < \mu_j^0(\text{aq}; T)$ . Solute-j is stabilised relative to solute j in the solution reference state, an ideal solution having unit molality. If  $m_j > 1.0 \text{ mol kg}^{-1}$ ,  $R \cdot T \cdot \ln(m_j / m^0)$  is  $> \text{zero}$ . Hence,  $\mu_j(\text{aq}; \text{id}; T; p) > \mu_j^0(\text{aq}; T)$ ; solute-j is destabilised relative to solute j in the (ideal) solution reference state.

We also compare the chemical potentials of solute j in real and ideal solutions at the same molality leading to the definition of an excess chemical potential for solute j,  $\mu_j^E(\text{aq})$ .

$$\mu_j^E(\text{aq}) = \mu_j(\text{aq}) - \mu_j(\text{aq}; \text{id}) \quad (\text{f})$$

$$\text{Hence, } \mu_j^E(\text{aq}) = R \cdot T \cdot \ln(\gamma_j) \quad (\text{g})$$

where  $\lim_{m_j \rightarrow 0} \gamma_j = 1$  and  $\ln(\gamma_j) = 0$  at all T and p. (h)

Equation (g) highlights the role played by activity coefficient  $\gamma_j$ ;  $\gamma_j$  can be neither zero nor negative; the range for  $\gamma_j$  is from below to above unity. In contrast  $\ln(\gamma_j)$  can be zero (as in an ideal solution) and be either greater or less than zero.

Activity coefficients are interesting quantities. For a given solute j at molality  $m_j$  in an aqueous solution (at fixed temperature and pressure)  $\gamma_j$  describes the impact on the chemical potential  $\mu_j(\text{aq})$  of solute - solute interactions. The basis of this conclusion follows from the definition given in equation (h) [3]. As a solution is diluted, so the mean distance of separation of solute molecules increases. In these terms a model for an ideal solution, molality  $m_j$  is one in which each solute molecule contributes to the properties of a given solution independently of all other solutes in the system. In an operational sense, each solute molecule is unaware of the presence of other solute molecules in solution and in these terms the solute molecules are infinitely far apart.

We emphasise the point that activity coefficient  $\gamma_j$  is an interesting and important quantity;  $\gamma_j$  describes the impact on chemical potential

$\mu_j(\text{aq}; T; p)$  of solute - solute interactions. These interactions can be cohesive (i.e. attractive) such that  $\gamma_j < 1$ ,  $\ln(\gamma_j) < 0$  and  $\mu_j(\text{aq}; \text{real}; T; p) < \mu_j(\text{aq}; \text{ideal}; T; p)$ , a stabilising influence. On the other hand, solute - solute interactions may be repulsive. In view of the fact that molecules have a real size, this contribution is always present. Consequently the latter (together with other forms of solute - solute repulsions) contribute to cases where  $\gamma_j > 1.0$ ,  $\ln(\gamma_j) > 0$  and  $\mu_j(\text{aq}; \text{real}; T; p) > \mu_j(\text{aq}; \text{ideal}; T; p)$ . In principle, activity coefficient  $\gamma_j$  contains an enormous amount of information [4]. Many of the interesting properties of aqueous solutions are packed in the parameter  $\gamma_j$ . Unfortunately only in rare instances is it possible to dissect a given  $\gamma_j$  into the several contributing interactions. A common though obviously dangerous procedure sets  $\gamma_j$  equal to unity, assuming that the properties of a given solute  $j$  are ideal. However in many cases we have no alternative but to make this assumption at least in initial stages of an analysis of experimental results.

Equation (e) is satisfactory for very dilute solutions of neutral solutes. Indeed this equation has enormous technological significance. The task of producing a very pure liquid requires lowering the molalities of solutes in a solution. With decreasing molality of a given solute, the chemical potential of a solute decreases; i.e. the solute is stabilised. So as more solute, an impurity, is removed, the trace remaining is increasingly stabilised [5].

We cannot put a number value to either  $\mu_j(\text{aq}; T; p)$  or  $\mu_j^0(\text{aq}; T)$ . These quantities measure the contribution made by a solute  $j$  to the total energy of a solution. One contribution to, for example,  $\mu_j^0(\text{aq}; T)$  emerges from solvent-solute interactions. Interestingly, we can in general put a number value to the corresponding limiting partial molar volume,  $V_j^\infty(\text{aq})$  [6]. The concept of infinite dilution is extremely important in a practical sense. Nevertheless, we enter a word of caution. Returning to equation

(b) for the chemical potential, we note that  $\lim(m_j \rightarrow 0) \ln(m_j)$  tends to minus  $\infty$ .

Hence (at all T and p)  $\lim(m_j \rightarrow 0) \mu_j(\text{aq}) = -\infty$  (i)

The practical significance of equation (i) is that with increasing dilution so the chemical potential of a solute decreases - the solute is increasingly stabilised. That is why the challenge of removing the last traces of unwanted solute presents such a formidable task, particularly to those industries where very high solvent purity is essential; *e.g.* the pharmaceutical industry [5].

### Footnotes

[1] Activity coefficients have a 'bad press'. They are not 'loved' except by a minority of chemists. Nevertheless these coefficients contain information concerning the way in which solute molecules 'communicate' to each other in solution.

[2] M. Spiro, *Educ. Chem.*, 1966, **3**, 139.

[3] The concept of an activity coefficient for a solute tending to unity at infinite dilution was proposed by A.A. Noyes and W.C. Bray:

*J. Am. Chem. Soc.*, 1911, **33**, 1643.

[4] E. Wilhelm, *Thermochim. Acta*, 1987, **119**, 17; *Interactions in Ionic and Non-Ionic Hydrates*, ed. H. Kleenber, Springer-Verlag, Berlin, 1987, p. 118.

[5] S. F. Sciamanna and J. M. Prausnitz, *AIChE J.*, 1987, **33**, 1315.

[6] Throughout this subject, it is good practice to examine equations describing the dependence of partial molar properties of solvent and solute in the limit that the composition of the solution tends to increasingly dilute solutions; see J. E. Garrod and T. M. Herringon, *J. Chem. Educ.*, 1969, **46**, 165.