PROPERTIES OF SOLUTIONS

Activities

Solvent Activity

The general form of the chemical potential for a solvent, whether real or ideal it given by:

$$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*} \tag{1}$$

Ideal solvents obey Raoult's law no matter what the concentration is, which can be expressed as:

$$\mu_A = \mu_A^* + RTx_A. \tag{2}$$

Deviations from ideal behaviour can be represented by an equation of the form given in Equation (2) above by replacing the mole-fraction by something called the activity of A, a_A. That is,

$$\mu_A = \mu_A^* + RTa_A. \tag{3}$$

As Eq (1) is general, $$a_A = \frac{p_A}{p_A^*}. \tag{4}$$

The activity of a solvent can be readily determined experimentally by measuring the vapour pressure of the substance A in the solution and dividing that by the vapour pressure of pure A.

Example, the vapour pressure of a 0.500 molar water-solution of KNO2 is 749.7 Torr (mmHg). Therefore the activity of the water in the solution is 749.7/760.0 = 0.9864.

Earlier we noted that Raoult's law is a good approximation of the behaviour of a solution at very low concentrations. That is, as $x_A \rightarrow 1$; and it becomes exact for pure A (when $x_A = 1$). We can state this relationship mathematically by expressing the activity in terms of the mole-fraction x_A and the activity coefficient γ_A.

$$a_A = x_A \gamma_A; \text{ where } \gamma_A \rightarrow 1 \quad \text{as} \quad x_A \rightarrow 1.$$

Thus,

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A. \tag{5}$$

Solute Activities

Note that in a binary mixture, for example a mixture of solvent A and solute B, the above relationship approaches ideal-dilute behaviour (Henry's Law) as $x_B \to 0$ (no B), rather than as $x_B \to 1$ (pure B).

Ideal-dilute solutions

The vapour pressure of a solute (B) obeying Henry's law is given by $p_B = K_B x_B$ (where K_B is an empirically determined constant). Here, the chemical potential of B is

$$\mu_B = \mu_B^* + RT \ln \frac{p_B}{p_B^*} \tag{6}$$

Hence,

$$\mu_B = \mu_B^* + RT \ln \frac{K_B}{p_B^*} + RT \ln x_B \tag{7}$$

As both K_B and p_B^* are properties of the solute, we can define a new standard chemical potential as:

$$\mu_B^{\ominus} = \mu_B^* + RT \ln \frac{K_B}{p_B^*} \tag{8}$$

Thus the chemical potential of B is,

$$\mu_B = \mu_B^{\ominus} + RT \ln x_B . \tag{9}$$

Real Solutes

We now modify the above to account for deviation from ideal behaviour. By analogy with real solvents, we introduce an activity a_B.

$$\mu_B = \mu_B^{\ominus} + RT \ln a_B \tag{10}$$

$$a_B = \frac{p_B}{K_B} \tag{11}$$

Further, as before, we introduce an activity coefficient γ_B.

$$a_B = \gamma_B x_B \tag{12}$$

where $a_B \to x_B$ and $\gamma_B \to 1$ as $x_B \to 0$.

This makes sense, as the deviation from ideal behaviour decreases as the solution becomes more dilute, and the solution becomes ideal when the concentration of B in the solution becomes zero.

Activities expressed in terms of molalities

> *Note on concentration definitions of binary solutions:*
> Mole-fraction, x_B, is the number moles of solute n_B per total moles in the solution $(m_A + n_B)$. That is, $x_B = n_B/(m_A+n_B)$.
> Molarity, M_B, is the number of moles of solute n_B per litre of solution in solvent A.
> Molality, b_B, is number of moles of solute n_B per kg of solution in solvent A.

The standard state is arbitrary. Therefore, we are free to choose whichever one that best suits our purposes. In chemistry, compositions are often expressed in terms of molalities, b, rather then mole-fractions, x.

Hence,

$$\mu_B = \mu_B^{\ominus} + RT \ln b_B. \tag{13}$$

The only difference is that the standard chemical potential is numerically different when expressed in terms of b_B rather than x_B.

Note that as $b_B \to 0$, $\mu_B \to \infty$. This explains why it is difficult to fully purify a solvent.

As in both examples above, we can accommodate deviations from ideal behaviour by introducing an activity coefficient and writing:

$$a_B = \gamma_B \frac{b_B}{b_B^{\ominus}}, \quad \text{where,} \quad \gamma_B \to 1 \text{ as } b_B \to 0 \tag{14}$$

Activities of Regular Solutions

Activities of Ion Solutions

In ion solutions, *e.g.*, a salt solution, the interactions between the solvent and the solute are very high. This means that the deviation from ideal behaviour is also very high. Therefore, our approximations made above are only accurate for very dilute solutions.

The molar Gibbs energy for an ideal solution of M+ and X- is the sum of the chemical potentials:

$$G_m^{ideal} = \mu_+^{ideal} + \mu_-^{ideal}$$

Therefore for a real solution we have:

$$G_m = \mu_+ + \mu_- = \mu_+^{ideal} + \mu_-^{ideal} + RT\gamma_+ + RT\gamma_- = G_M^{ideal} + RT\gamma_+\gamma_-$$

Thus, all deviations from ideal behaviour are contained in the last term.