

Redlich-Kister Expansion

This equation can be used to fit activities in two component mixtures over the entire concentration range, and to calculate the activities of both components. It is used *E-A/M* for aqueous solutions of single organic compounds, and is an alternative to UNIFAC for those compounds for which the necessary activity data exist.

The expansion is described by Prausnitz et al. (1986), and is also covered in other chemical engineering textbooks. McGlashan (1963) gives examples of the use of the equation to illustrate the types of activity curves that are observed for different two component mixtures.

In *E-A/M* the Redlich-Kister expansion can be used with up to 10 fitted parameters. Examples of the use of the equation, to represent the properties of aqueous solutions of dicarboxylic acids at 298.15 K, are given by Clegg and Seinfeld (2006). These acids are present in the public database of compounds, on the Available Compounds selection page, and can be included in model calculations.

Expressions for solute (S) and water (W) mole fraction activity coefficients are given below, for terms including the first 5 fitted parameters (C_1 to C_5).

$$\ln(f_S) = g^e/RT + [(1 - x_S) \times d(g^e/RT)/d(x_S)]$$

$$\ln(f_W) = g^e/RT - [x_S \times d(g^e/RT)/d(x_S)]$$

where the excess Gibbs energy per mol of substance, g^e , is given by:

$$g^e/RT = x_S(1 - x_S)[C_1 + C_2(1 - 2x_S) + C_3(1 - 2x_S)^2 + C_4(1 - 2x_S)^3 + C_5(1 - 2x_S)^4 \dots]$$

and its differential with respect to x_S , $d(g^e/RT)/d(x_S)$, is given by:

$$\begin{aligned} d(g^e/RT)/d(x_S) = & C_1(1 - 2x_S) + C_2[-2x_S(1 - x_S) + (1 - 2x_S)^2] \\ & + C_3[-4x_S(1 - x_S) + (1 - 2x_S)^2](1 - 2x_S) + C_4[-6x_S(1 - x_S) + (1 - 2x_S)^2](1 - 2x_S)^2 \\ & + C_5[-8x_S(1 - x_S) + (1 - 2x_S)^2](1 - 2x_S)^3 \dots \end{aligned}$$

where C_i are the fitted parameters. Both activity coefficients are relative to a reference state of the pure liquid. The logarithm of the activity coefficient of the solute can be adjusted to a reference state of infinite dilution in water (f_S^*) by subtracting the value obtained with the equation above for $x_S = 0$, yielding:

$$\ln(f_S^*) = \ln(f_S) - (g^e/RT + d(g^e/RT)/d(x_S))$$

This expression is valid for any concentration but, as stated above, the final term in g^e/RT and its differential is calculated for $x_S = 0$.

References

S. L. Clegg and J. H. Seinfeld (2006) Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. 1. The acids as nondissociating components. *J. Phys. Chem. A* **110**, 5692-5717.

M. L. McGlashan (1963) Deviations from Raoult's law. *J. Chem. Educ.* **40**, 516-518.

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