For binary liquid mixtures at fixed $T$ and $p$, an important task is to fit the dependence of $G^E_m$ on $x_2$ to an equation in order to calculate the derivative $dG^E_m / dx_2$ at required mole fractions. The Guggenheim - Scatchard [1,2] (commonly called the Redlich - Kister [3] ) equation is one such equation. This equation has the following general form.

$$X^E_m = x_2 \cdot (1 - x_2) \cdot \sum_{i=1}^{i=k} A_i \cdot (1 - 2 \cdot x_2)^{i-1}$$  \hspace{1cm} (a)

$A_i$ are coefficients obtained from a least squares analysis of the dependence of $G^E_m$ on $x_2$. The equation clearly satisfies the condition that $G^E_m$ is zero at $x_2 = 0$ and at $x_2 = 1$.

In fact the first term in the G - S equation has the following form.

$$X^E_m = x_2 \cdot (1 - x_2) \cdot A_1$$  \hspace{1cm} (b)

According to equation (b) $X^E_m$ is an extremum at $x_2 = 0.5$, the plot being symmetric about the line from $X^E_m$ to ‘$x_2 = 0.5$’. In fact for most systems the $A_1$ term is dominant. For the derivative $dG^E_m / dx_2$, we write equation (a) in the following general form.

$$X^E_m = (x_2 - x_2^2) \cdot Q$$  \hspace{1cm} (c)

Then $dX^E_m / dx_2 = x_2 \cdot (1 - x_2) \cdot dQ / dx_2 + (1 - 2 \cdot x_2) \cdot Q$  \hspace{1cm} (d)

where $dQ / dx_2 = -2 \cdot \sum_{i=2}^{i=k} (i-1) \cdot A_i \cdot (1 - 2 \cdot x_2)^{i-2}$ \hspace{1cm} (e)

Equation (a) fits the dependence with a set of contributing curves which all pass through points, $X^E_m = 0$ at $x_1 = 0$ and $x_1 = 1$. The usual procedure involves fitting the recorded dependence using increasing number of terms in the series, testing the statistical significance of including a further term.

Although equation (a) has been applied to many systems and although the equation is easy to incorporate into computer programs using packaged least square and graphical routines, the equation suffers from the following disadvantage. As one incorporates a further term in the series, (e.g. $A_j$) estimates of all the previously calculated parameters (i.e. $A_2$, $A_3$...$A_{j-1}$ ) change.

For this reason orthogonal polynomials have been increasingly favoured especially where the appropriate computer software is available. The only
slight reservation is that derivation of explicit equations for the required
derivative \( dX_m^E \) is not straightforward. The problem becomes rather more
formidable when the second and higher derivatives are required. The derivative
\( d^2X_m^E \) is sometimes required by calculations concerning the properties of
binary liquid mixtures.

The derivative \( dG_m^E / dx_1 \) and \( G_m^E \) are combined to yield an equation for
\( \ln(f_1) \).

\[
\ln(f_1) = \frac{G_m^E}{R \cdot T} + \frac{(1-x_1)}{R \cdot T} \cdot \frac{dG_m^E}{dx_1} \quad (f)
\]

A similar equation leads to estimates of \( \ln(f_2) \). Hence the dependences are
obtained of both \( \ln(f_1) \) and \( \ln(f_2) \) on mixture composition.

It is of interest to explore the case where the coefficients \( A_2, A_3 \ldots \) in equation (a)
are zero.

Then \( X_m^E = x_2 \cdot (1 - x_2) \cdot A_1 \quad (g) \)

and \( dX_m^E / dx_2 = (1 - 2 \cdot x_2) \cdot A_1 \quad (h) \)

With reference to the Gibbs energies,

\[
\ln(f_2) = (1 / R \cdot T) \cdot [x_2 \cdot (1 - x_2) + (1 - x_2) \cdot (1 - 2 \cdot x_2)] \cdot A_1^G \quad (i)
\]

\[
\ln(f_2) = (A_1^G / R \cdot T) \cdot [1 - 2 \cdot x_2 + x_2^2] \quad (j)
\]

or, \( \ln(f_2) = (A_1^G / R \cdot T) \cdot [1 - x_2]^2 \quad (k) \)

In fact the equation reported by Jost et al. [4] has this form.

Rather than using the Redlich-Kister equation, recently attention has been
directed to the Wilson equation [5] written in equation (\( \ell \)) for a two-
component liquid [6].

\[
G_m^E / R \cdot T = -x_1 \cdot \ln(x_1 + A_{12} \cdot x_2) - x_2 \cdot \ln(x_2 + A_{21} \cdot x_1) \quad (\ell)
\]

Then, for example [7],

\[
\ln(f_1) = -\ln(x_1 + A_{12} \cdot x_2) + x_2 \cdot \left( \frac{A_{12}}{x_1 + A_{12} \cdot x_2} - \frac{A_{21}}{A_{21} \cdot x_1 + x_2} \right) \quad (m)
\]

The Wilson equation forms the basis for two further developments, described
as the NRTL (non-random, two-liquid) equation [8-10] and the UNIQUAC
equation [9-10]. Nevertheless Douheret et al. [11] show how an excess
property must be carefully defined. Davis et al. have explored how excess
molar properties for liquid mixtures can be analysed in terms of different mole fraction domains [12].

Footnotes

    (c) C. W. Bale and A. D. Pelton, Metallurg. Trans., 1974, **5**, 2323.
[7] From equation (c),

\[
\frac{1}{R \cdot T} \cdot \frac{dG_m^E}{dx_1} = -\ln(x_1 + \Lambda_{12} \cdot x_2) - \frac{x_1 \cdot (1 - \Lambda_{12})}{x_1 + \Lambda_{12} \cdot x_2} + \ln(\Lambda_{21} \cdot x_1 + x_2) - \frac{x_2 \cdot (\Lambda_{21} - 1)}{\Lambda_{21} \cdot x_1 + x_2}
\]

Then using equation (f) with \(1 - x_1 = x_2\),

\[
\ln(f_i) = -x_1 \cdot \ln(x_1 + \Lambda_{12} \cdot x_2) - x_2 \cdot \ln(\Lambda_{21} \cdot x_1 + x_2) - x_2 \cdot \ln(x_1 + \Lambda_{12} \cdot x_2) - \frac{x_1 \cdot x_2 \cdot (1 - \Lambda_{12})}{x_1 + \Lambda_{12} \cdot x_2} + x_2 \cdot \ln(\Lambda_{21} \cdot x_1 + x_2) + \frac{(x_2)^2 \cdot (1 - \Lambda_{21})}{\Lambda_{21} \cdot x_1 + x_2}
\]

Or,

\[
\ln(f_i) = -(x_1 + x_2) \cdot \ln(x_1 + \Lambda_{12} \cdot x_2) + x_2 \cdot \left[ \frac{\Lambda_{12} \cdot x_1 - x_1 - \Lambda_{21} \cdot x_2 - x_2}{x_1 + \Lambda_{12} \cdot x_2 - \Lambda_{21} \cdot x_1 + x_2} \right]
\]

But \(\Lambda_{12} \cdot x_1 - x_1 = \Lambda_{12} \cdot (1 - x_2) - x_1 = \Lambda_{12} - (x_1 + \Lambda_{12} \cdot x_2)\)
Hence,
\[
\ln(f_i) = -\ln(x_1 + \Lambda_{12} \cdot x_2) + x_2 \cdot \left[ \frac{\Lambda_{12} - (x_1 + \Lambda_{12} \cdot x_2)}{x_1 + \Lambda_{12} \cdot x_2} - \frac{\Lambda_{21} - (\Lambda_{21} \cdot x_1 + x_2)}{\Lambda_{21} \cdot x_1 + x_2} \right]
\]
Or, \(\ln(f_i) = -\ln(x_1 + \Lambda_{12} \cdot x_2) + x_2 \cdot \left[ \frac{\Lambda_{12}}{x_1 + \Lambda_{12} \cdot x_2} - \frac{\Lambda_{21}}{\Lambda_{21} \cdot x_1 + x_2} \right]\)

[13] Finally we note that the Redlich-Kister equation can be expressed in the following form.

\[
X^E_m = x_1 \cdot (1 - x_1) \cdot \sum_{i=1}^{\infty} B_i \cdot (1 - 2 \cdot x_1)^{i-1}
\]

Then \(A_i = B_i \cdot (-1)^i\)