The "Gibbs-Duhem test”

Since 1998, theriak includes a so-called “Gibbs-Duhem” test for each solution model. Here is a short explanation what it means:

For constant temperature and pressure the Gibbs-Duhem equation is usually written as:

$$\sum_{i=1}^{nc} n_i \cdot \mu_i = 0.$$

Because $\left(\frac{\partial G}{\partial n_i}\right) = \mu_i$, it can be shown, that

$$RT \ln(a_m) = G + \left(\frac{\partial G}{\partial x_m}\right)_{x_j \neq m} - \sum_{j=1}^{nc} x_j \left(\frac{\partial G}{\partial x_i}\right)_{x_j \neq i} \qquad (1)$$

e.g. Redlich and Kister (1948), de Capitani and Kirschen (1999)

Equivalent expressions given in the literature sometimes require differentiation with constant $(x_m + x_n)$ (Berman and Brown,1984) or constant (x_m / x_n) (Darken and Gurry, 1953; Ghiorso, 1990). In general, the advantage of formula (1) is that even for more complex solution models all required derivatives can be looked up in mathematical tables or computed using mathematical software libraries like Maxima, Mathematica or Maple, where $\left(\frac{\partial G}{\partial x_i}\right)$ is the partial derivative (with all other variables fixed).

G is either given by the equation $G^{mix} + G^{conf} + G^{ex}$ or is calculated using the activities from a subroutine $G = G^{mix} + \sum_{i=1}^{nc} RT \ln(a_i)$

The "Gibbs-Duhem" test in theriak consists of calculating the activities by finite differences with equation (1) and to compare the results with the activities from a given equation $a_i = f(\vec{x})$. It is usually a good test to find typing errors. It also should be noted, that solutions that use forced equipartitioning fail this test.