Linear least-squares optimization - Theory

$$y = b_1 x_1 + b_2 x_2 + b_3 x_3 + \cdots\cdots + b_m x_m$$

y = dependent variable
x_j = independent variables
b_j = coefficients to be calculated

Experimental data points: $y_i, x_{i1}, x_{i2}, x_{i3}, \cdots x_{im}$ $[i = 1, N]$

Find coefficients b_j by minimizing $S = \sum_{i=1}^{N}\left(y_i - \sum_{j=1}^{m} b_j x_{ij}\right)^2$

Example: $y = b_1 + b_2 x + b_3 x^2 + b_4 x^3 + b_5 \ln x$

N experimental points y_i, x_i $[i = 1, N]$

Let: $x_{i1} = 1$ $x_{i2} = x_i$ $x_{i3} = x_i^2$ $x_{i4} = x_i^3$ $x_{i5} = \ln x_i$

Example: Gibbs energies: $g^E = \sum \phi_j [X_A X_B^{j+1}]$ N_1 data points

$g_A^E = \sum \phi_j [(X_B - jX_A) X_B^{j+1}]$ N_2 data points

$g_B^E = \sum \phi_j [(j+1) X_A^2 X_B^j]$ N_3 data points

Let: $i = 1, N_1$ $y_i = g_i^E$ $x_{ij} = X_{A_i} X_{B_i}^{j+1}$

$i = (N_1+1), (N_1+N_2)$ $y_i = g_{A_i}^E$ $x_{ij} = (X_{B_i} - jX_{A_i}) X_{B_i}^{j+1}$

$i = (N_1+N_2+1), (N_1+N_2+N_3)$: $y_i = g_{B_i}^E$ $x_{ij} = (j+1) X_{A_i}^2 X_{B_i}^j$

SUGGESTIONS FOR OPTIMIZATION

(1) Generally $|G^{E(LIQ)}| < |G^{E(SOL)}|$

(2) Generally $|\Delta h| > |TS^E|$ $G^E = \Delta H - TS^E$

(3) $\Delta S^o_{fusion} \approx 2$ cal/°K-atom (Richard's Rule)

(4) Solidus data (especially when measured by DTA) are not usually as accurate as liquidus data.

(5) $\Delta S^{ideal} = -R(X_1 \ln X_1 + X_2 \ln X_2) = 1.38$ cal/mol°K at $X_1 = X_2 = ½$

Generally $|S^E|_{x=0.5} < 1.38$