Algorithm for Species Distribution

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1 Ideal Solutions

We stipulate that there are basis species and non-basis species in a solution phase. The basis species assume the role of thermodynamic components. They span the composition space and are linearly independent vectors in that space. The non-basis species, or dependent species, may be formed by a linear stoichiometric transformation of the basis species. They are compositionally dependent but energetically independent. Their existence contributes to the configuration entropy and to the non-coplanarity of the mechanical mixing terms in the Gibbs energy of solution. By assumption of solution ideality, the excess Gibbs free energy of mixing is zero.

1.1 Homogeneous equilibrium

Assume that we have n_b-basis species and n_s dependent species. Let $\mathbf{e}$ be a concentration vector of components in the system; generally this is a vector of elemental concentrations. The vector $\mathbf{e}$ may be partitioned between basis ($\mathbf{e_b}$) and non-basis (dependent) species ($\mathbf{e_s}$), as

$$\mathbf{e} = \mathbf{e_b} + \mathbf{e_s} \tag{1}$$

Then there exists a stoichiometric matrix, $\mathbf{C_b}$, that relates a vector of moles of basis species, $\mathbf{b}$, to the mole vector, $\mathbf{e_b}$:

$$\mathbf{C_b e_b} = \mathbf{b} \tag{2}$$

There also exists a stoichiometric matrix, $\mathbf{C_s}$, that relates a vector of non-basis species, $\mathbf{s}$, to the mole vector, $\mathbf{e_s}$:

$$\mathbf{C_s e_s} = \mathbf{s} \tag{3}$$

The inverse transformations are simply given by:

$$\mathbf{e_b} = \mathbf{C_b^T b} \tag{4}$$

and

$$\mathbf{e_s} = \mathbf{C_s^T s} \tag{5}$$

The length of the vector $\mathbf{b}$, n_b, is identical to the length of the vector $\mathbf{e}$, n_e. Accordingly, $\mathbf{C_b}$ is a square matrix of full rank and, consequently, $\mathbf{C_b}$ is invertible.

We can construct balanced reactions between non-basis and basis species by inserting elemental abundances given by Eq(4) into Eq(5):

$$\mathbf{C_s C_b^T b} = \mathbf{s} \tag{6}$$

The matrix product, $\mathbf{C_s C_b^T}$ is a reaction stoichiometry matrix, more conveniently written as $\mathbf{R}$.

The law of mass action for the i^{th} species is given by

$$0 = \Delta G_i = \Delta G_i^o + RT \ln Q_i \tag{7}$$

where

$$\Delta G_i^o = \mu_i^o - \sum_j^{n_b} R_{ij} \mu_j^o \tag{8}$$

and

$$Q_i = \frac{X_{s_i}}{\prod_j^{n_b} X_{b_j}^{R_{ij}}} \tag{9}$$

Mass balance constraints on the basis and non-basis species may be written

$$\mathbf{e} = \mathbf{C_b^T b} + \mathbf{C_s^T s} \tag{10}$$

If n_T is the totalnumber of moles of combined basis and non-basis species, then Eq(10) may be rewritten as

$$\mathbf{e} = n_T \left(\mathbf{C_b^T X_b} + \mathbf{C_s^T X_s} \right) \tag{11}$$

where $\mathbf{X_b}$ and $\mathbf{X_s}$ are vectors of mole fraction concentrations equivalent to $\mathbf{b}$ and $\mathbf{s}$, respectively. Remember that n_T need not be the total number of moles of elements in the system.

From Eqs(7 and 9) it follows that

$$Q_i = \exp\left(-\frac{\Delta G_i^o}{RT} \right) \tag{12}$$

and

$$Q_i \prod_j^{n_b} X_{b_j}^{R_{ij}} = X_{s_i} \tag{13}$$

Assimbling the Q_i into a vector $\mathbf{Q}$ transforms Eq(13) into

$$\mathbf{Q}^T \begin{bmatrix} \prod_j^{n_b} X_{b_j}^{R_{1,j}} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \prod_j^{n_b} X_{b_j}^{R_{n_s,j}} \end{bmatrix} = \mathbf{X_s} \tag{14}$$

Substituting Eq(14) into Eq(11) gives

$$\mathbf{e} = n_T \mathbf{C_b^T X_b} + n_T \mathbf{C_s^T Q}^T \begin{bmatrix} \prod_j^{n_b} X_{b_j}^{R_{1,j}} & 0 & 0 \\ 0 & \ddots & 0 \\ 0 & 0 & \prod_j^{n_b} X_{b_j}^{R_{n_s,j}} \end{bmatrix} \tag{15}$$

which is a non-linear system of equations in n_b unknowns (n_T and any $n-1$ terms of $\mathbf{X_b}$).

1.2 Gibbs free energy of solution

The Gibbs free energy of solution is given by:

$$G = n_T \sum_i^{n_b} \mu_i^o X_{b_i} + n_T \sum_i^{n_s} \mu_i^o X_{s_i} + n_T RT \sum_i^{n_b} X_{b_i} \ln X_{b_i} + n_T RT \sum_i^{n_s} X_{s_i} \ln X_{s_i} \tag{16}$$

In practical applications, the quantity computed from Eq(16) may be a scalar multiple of the quantity required. Say, for example, that the composition of the system is expressed as a vector of moles of elements, $\mathbf{e}$, then if e_T is the total number of moles of elements, except by rare coincidence e_T is unlikely to be numerically equivalent to n_T. Hence, the Gibbs free energy of interest need be scaled as:

$$G^{elem} = \frac{n_e}{n_T} G \tag{17}$$

Sunstitution of Eqs (13) and (16) in Eq (17) gives

$$\begin{aligned} G^{elem} &= n_e \sum_i^{n_b} \mu_i^o X_{b_i} + n_e \sum_i^{n_s} \mu_i^o Q_i \prod_j^{n_b} X_{b_j}^{R_{ij}} \\ +n_e RT \sum_i^{n_b} X_{b_i} \ln X_{b_i} &+ n_e RT \sum_i^{n_s} \left(Q_i \prod_j^{n_b} X_{b_j}^{R_{ij}} \right) \ln \left(Q_i \prod_j^{n_b} X_{b_j}^{R_{ij}} \right) \end{aligned} \tag{18}$$

which demonstrates that G^{elem} is solely a function of T, P, and $\mathbf{X_b}$.

Eq (18) can be simplified for faster consumption by Sympy (and faster compilation). Expanding the logarithmic terms, substituting

$$\ln \left(\prod_j^{n_b} X_{b_j}^{R_{ij}} \right) = \sum_j^{n_b} R_{ij} \ln X_{b_j} \tag{19}$$

and collecting common terms gives:

$$\begin{aligned} G^{elem} &= n_e \sum_i^{n_b} \mu_i^o X_{b_i} + n_e RT \sum_i^{n_b} X_{b_i} \ln X_{b_i} \\ +n_e \sum_i^{n_s} Q_i &\left(\mu_i^o + RT \ln Q_i + RT \sum_j^{n_b} R_{ij} \ln X_{b_j} \right) \prod_j^{n_b} X_{b_j}^{R_{ij}} \end{aligned} \tag{20}$$

Inserting Eqs(7) gives:

$$\begin{aligned} G^{elem} &= n_e \sum_i^{n_b} \mu_i^o X_{b_i} + n_e RT \sum_i^{n_b} X_{b_i} \ln X_{b_i} \\ +n_e \sum_i^{n_s} Q_i &\left(\mu_i^o - \Delta G_i^o + RT \sum_j^{n_b} R_{ij} \ln X_{b_j} \right) \prod_j^{n_b} X_{b_j}^{R_{ij}} \end{aligned} \tag{21}$$

And, inserting Eq(8) gives

$$G^{elem} = n_e \sum_i^{n_b} \mu_i^o X_{b_i} + n_e RT \sum_i^{n_b} X_{b_i} \ln X_{b_i} + n_e \sum_i^{n_s} Q_i \left(\prod_j^{n_b} X_{b_j}^{R_{ij}} \right) \sum_j^{n_b} R_{ij} \left(\mu_j^o + RT \ln X_{b_j} \right) \tag{22}$$