

The algorithm used in VCLab.

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Version November 12, 2015

This is part of the documentation of the Virtual CALPHAD Laboratory software.

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1 Introduction

The algorithm to calculate thermodynamic equilibria for multi-component systems was widely introduced in various papers and books. In this document, the algorithm is explained in the way that directly relate to programming.

In thermodynamics, phases equilibrium is a state when the chemical potential in all phases are equal for every component at given conditions. In mathematics, phases equilibrium is the global minimum point of the overall Gibbs energy function, with given constraints.

The Gibbs energy function can be written as:

$$G = \sum_{\alpha} n^{\alpha} G^{\alpha}(T, P, y_{ks}^{\alpha}) \quad (1)$$

where n^{α} is the moles amount of the phase α and G^{α} is the Gibbs energy per mole formula of phase α . T and P is the temperature and pressure, y_{ks}^{α} is the site fractions in the s lattices of phase α .

The equality constraint are:

(1) sum of the site fractions on sublattice s of phase α should be unity:

$$\sum_k y_{ks}^{\alpha} - 1 = 0 \quad (2)$$

(2) sum of the components amount should equal to overall components amount:

$$\sum_{\alpha} n^{\alpha} N_A^{\alpha} - \tilde{N}_A = 0 \quad (3)$$

where \tilde{N}_A is the overall amount of component A.

The inequality constraint are:

$$y_{ks}^{\alpha} > 0 \quad (4)$$

$$n^{\alpha} > 0 \quad (5)$$

charge balance is not consider at the moment.

2 Lagrangian method

A strategy for finding the minima of a function subject to equality constraints is lagrangian methods. Lagrange multipliers can be used to convert it into an unconstrained problem whose number of variables is the original number of variables plus the original number of equality constraints.

$$L = G + \sum_{\alpha} \lambda_s^{\alpha} (\sum_k y_k^{s,\alpha} - 1) + \sum_A \mu_A (\sum_{\alpha} n^{\alpha} N_A^{\alpha} - \tilde{N}_A) \quad (6)$$

where λ^{α}, μ_A are multipliers.

The minimum can be reach, when the derivative of the Lagrangian with respect to all the variables are zeros.

$$G_M^{\alpha} + \sum_A \mu_A N_A^{\alpha} = 0 \quad (7)$$

$$\sum_k y_k^{s,\alpha} - 1 = 0 \quad (8)$$

$$n^{\alpha} \frac{\partial G^{\alpha}}{\partial y_k^{s,\alpha}} - n^{\alpha} \mu_A \frac{\partial N_A^{\alpha}}{\partial y_k^{s,\alpha}} - \lambda_s^{\alpha} = 0 \quad (9)$$

$$\sum_{\alpha} n^{\alpha} N_A^{\alpha} - \tilde{N}_A = 0 \quad (10)$$

In order to solve this nonlinear equations, Newton's method can be used. We then get:

$$\begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & \frac{\partial^2 G^{\alpha}}{\partial y_k^{s,\alpha} \partial y_k^{s,\alpha}} & 0 & \frac{\partial N_A^{\alpha}}{\partial y_k^{s,\alpha}} & \frac{\partial^2 G^{\alpha}}{\partial y_k^{s,\alpha} \partial T} & \frac{\partial^2 G^{\alpha}}{\partial y_k^{s,\alpha} \partial P} \\ 0 & \frac{\partial G^{\alpha}}{\partial y_k^{s,\alpha}} + \mu_A \frac{\partial N_A^{\alpha}}{\partial y_k^{s,\alpha}} & 0 & N_A^{\alpha} & \frac{\partial G^{\alpha}}{\partial T} & \frac{\partial G^{\alpha}}{\partial P} \\ 0 & n^{\alpha} \frac{\partial N_A^{\alpha}}{\partial y_k^{s,\alpha}} & N_A^{\alpha} & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} \Delta \lambda_s^{\alpha} \\ \Delta y_k^{s,\alpha} \\ \Delta n^{\alpha} \\ \Delta \mu_A \\ \Delta T \\ \Delta P \end{pmatrix} = \begin{pmatrix} \sum_k y_k^{s,\alpha} - 1 \\ \frac{\partial G^{\alpha}}{\partial y_k^{s,\alpha}} - \mu_A \frac{\partial N_A^{\alpha}}{\partial y_k^{s,\alpha}} - \lambda_s^{\alpha} \\ G_M^{\alpha} + \sum_A \mu_A N_A^{\alpha} \\ \sum_{\alpha} n^{\alpha} N_A^{\alpha} - \tilde{N}_A \end{pmatrix} \quad (11)$$

We called left coefficient matrix the equilibrium matrix. We begin with a first guess of the variables X_0 , then solve this equations to get new values of the variables X_1 as:

$$X_1 = X_0 + \Delta X \quad (12)$$

The process is repeated, until the changes are sufficiently small.

3 External conditions

There are more variables than equations in eq. 11. Therefore, in order to solve the equations, some of the variables must be fixed. That exactly external conditions means.

When some variables are fixed, the corresponding columns and rows in the euqilibrium matrix should be removed. For example, when T and P fixed.

$$\begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & \frac{\partial^2 G^\alpha}{\partial y_k^{s,\alpha} \partial y_{k'}^{s,\alpha}} & 0 & \frac{\partial N_A^\alpha}{\partial y_k^{s,\alpha}} \\ 0 & \frac{\partial G^\alpha}{\partial y_k^{s,\alpha}} + \mu_A \frac{\partial N_A^\alpha}{\partial y_k^{s,\alpha}} & 0 & N_A^\alpha \\ 0 & n^\alpha \frac{\partial N_A^\alpha}{\partial y_k^{s,\alpha}} & N_A^\alpha & 0 \end{pmatrix} \begin{pmatrix} \Delta \lambda_s^\alpha \\ \Delta y_k^{s,\alpha} \\ \Delta n^\alpha \\ \Delta \mu_A \end{pmatrix} = \begin{pmatrix} \sum_k y_k^{s,\alpha} - 1 \\ \frac{\partial G^\alpha}{\partial y_k^{s,\alpha}} - \mu_A \frac{\partial N_A^\alpha}{\partial y_k^{s,\alpha}} - \lambda_s^\alpha \\ G_M^\alpha + \sum_A \mu_A N_A^\alpha \\ \sum_\alpha n^\alpha N_A^\alpha - \tilde{N}_A \end{pmatrix} \quad (13)$$

4 Global minimum

Four kinds of results we may get from eq. 11 when different initial values are given:

- (1) divergency
- (2) local minimum
- (3) global minimum
- (4) wrong minimum out of bounds (inequality constraint)

That's the reasons why we should use a global minimum technology to get a reasonable initial value.

In most papers and book, local minimum is believed to be related with miscibility gap. Because the Gibbs energy of phase with miscibility gap is not a convex function. Actually, local minimum is exist for all case. In eq. 1, the Gibbs energy of all phases are convex function can not guaranteed their sum is a convex function. Because new variables n^α are add.

5 Summary

Not finished yet. More detail should be added.