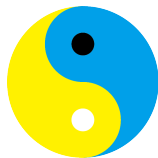


# Virtual Calphad Laboratory

An open-source software for CALPHAD Calculations



written by Xing Wang

Central South University, China

Version 0.1

# Contents

<b>1</b>	<b>Preface</b>	<b>3</b>
<b>2</b>	<b>Introduction</b>	<b>3</b>
<b>3</b>	<b>Installation</b>	<b>3</b>
<b>4</b>	<b>Input files</b>	<b>3</b>
4.1	Dimension . . . . .	4
4.2	Mode . . . . .	4
4.3	Database File . . . . .	4
4.4	Variables . . . . .	5
4.5	Global Grid Interval . . . . .	5
<b>5</b>	<b>Gibbs energy surface</b>	<b>5</b>
5.1	1D . . . . .	5
5.2	2D . . . . .	5
<b>6</b>	<b>Equilibrium Calculations</b>	<b>7</b>
6.1	Single point . . . . .	7
6.1.1	Fixed x and T . . . . .	7
6.1.2	Fixed x and Phase . . . . .	8
6.2	Step . . . . .	8
6.3	Map . . . . .	8
6.4	High dimensions calculations . . . . .	8
<b>7</b>	<b>Algorithm</b>	<b>9</b>
7.1	Gibbs energy function . . . . .	9
7.2	Lagrangian method . . . . .	10
7.3	External conditions . . . . .	11
7.4	Global minimum . . . . .	11
<b>8</b>	<b>Summary</b>	<b>12</b>

# 1 Preface

I start to wrote VCLab in September. Two month passed, VCLab-0.1 was born, with about 6000 lines code. I don't know if I will continue my work in the field of CALPHAD. So I guess it is time to write a documentation and end this stage of work.

Apart from software, one other thing I wish to do is establish a platform for open source database. Everyone could submit their own database to this platform, and everyone can edit, improve and use it, like Wikipedia. This is a big project need great efforts of CALPHAD community.

Today is my father's 50th birthday, To father's love.

Xing Wang

November 14, 2015

# 2 Introduction

VCLab (Virtual Calphad Laboratory) is a open source software for CALPHAD calculations, written in C++.

# 3 Installation

To be added.

# 4 Input files

The VCLInput.txt is the central input file of VCLab. It determines what to do and how to do it. One example for this file list below:

Each line consists of a keyword (i.e. a string) the equation sign "=" and one or several values. Values are separated by a colon ":". One parameter one single line ended by !. Comments are normally preceded by the number sign #. Defaults are supplied for some parameters. For example, a default for the "Global Grid Interval" is 0.5.

The following sections will describe the parameters given in the VCLInput file.

## 4.1 Dimension

This tag determines the number of variables.  $nD$  means  $n$  variables. 0D corresponding single point calculation in Thermo-Calc, 1D is step, 2D is map. VCLab can handel any number of variables.

## 4.2 Mode

This flag determines what property to calculate.

(1) Equilibrium

Calculate the thermodynamic equilibrium

(2) Gibbs energy surface

Calculate the Gibbs energy surface of specific phase.

Properties not implemented yet:

(1) Elastic

Calculate the single crystal elastic constants and poly-crystal elastic modules of specific phase.

To be added.

## 4.3 Database File

Database has the same format used in commercial software like Thermo-Calc and Pandat. One could put the Database file in the same folder with VCLab, or give the relative path of it, for instance `..\ TDB \ AlZn.TDB`

Mode	=	Equilibrium
Dimension	=	1 !
Database File	=	AlZn.TDB!
Elements	=	Al, Zn!
Compositions	=	0.6, 0.4!
Pressure	=	101325!
Variables	=	Temperature !
V Start	=	300 !
V End	=	2000 !
V Interval	=	10 !
Result Output File	=	Result.txt !
Global Grid Interval	=	0.05 !

## 4.4 Variables

Number of variables must equal to dimension value. The start, end and interval values also should be given.

## 4.5 Global Grid Interval

This flag determines mesh size for creating the global grid point.

# 5 Gibbs energy surface

## 5.1 1D

Example file of VCLInput:

```
Mode           = Energy Surface  !
Database_File  = AlZn.TDB       !
Elements       = Al, Zn         !
Phases_Selected = Liquid, HCP_A3, FCC_A1  !
Phases_Rejected = none         !
Pressure       = 101325         !
Temperature    = 550            !
Global_Grid_Interval = 0.02     !
```

Running times: 0.009 s.

## 5.2 2D

Example file of VCLInput:

```
Mode           = Energy Surface  !
Database_File  = cusnti.TDB     !
Elements       = cu, sn, ti     !
Phases_Selected = BCC_A2        !
Phases_Rejected = none          !
Pressure       = 101325         !
Temperature    = 800            !
Global_Grid_Interval = 0.02     !
```

Running times: 0.137 s.

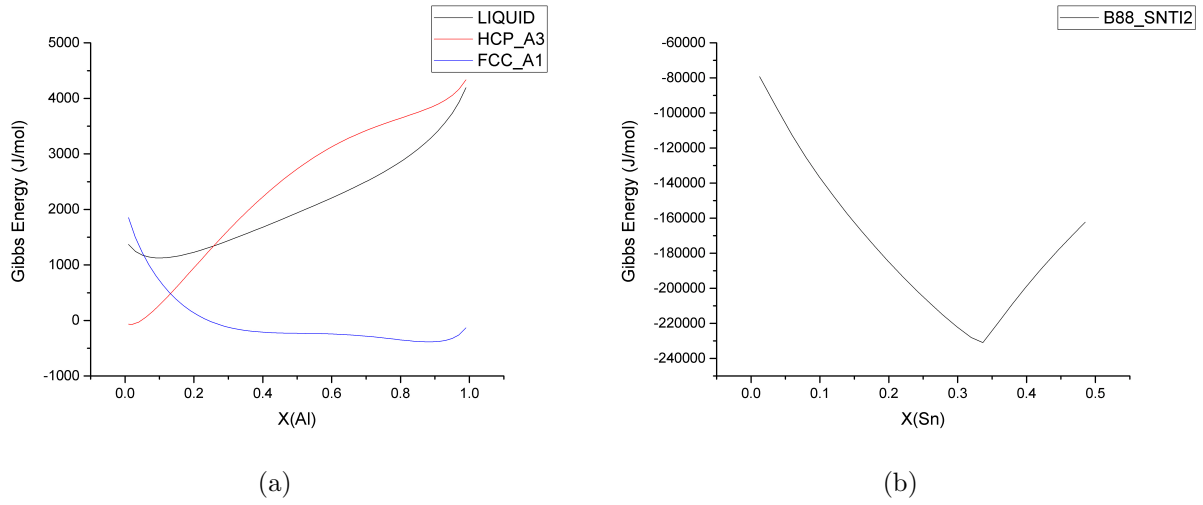


Figure 1: The Gibbs energy curves. (a) Al-Zn binary with one sublattices; (b) B88\_STi2 phase with two sublattices.

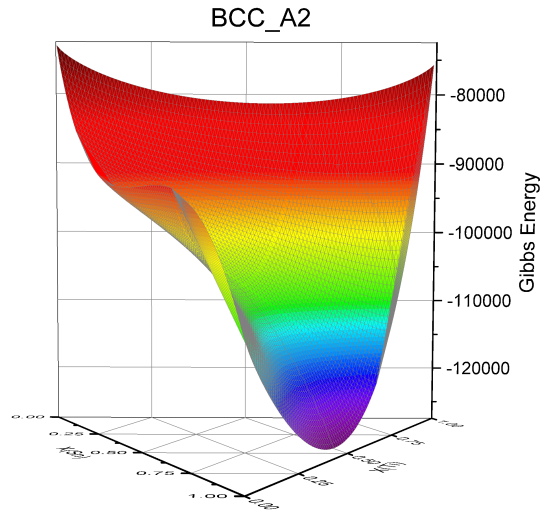


Figure 2: The Gibbs energy surface of BCC\_A2 Phases in Cu-Sn-Ti ternary system.

## 6 Equilibrium Calculations

### 6.1 Single point

#### 6.1.1 Fixed x and T

Example file of VCLInput:

```
Mode           = Equilibrium  !
Dimension      = 0           !
Database_File  = AlZn.TDB    !
Elements       = Al, Zn     !
Phases_Selected = all       !
Phases_Rejected = none      !
Pressure       = 101325     !
Temperature    = 600        !
Compositions   = 0.6, 0.4   !
Global_Grid_Interval = 0.02 !
```

Equilibrium can be found in the VCLOutput.txt file. A example is list below:

```
=====
Conditions: T = 600 P = 10500 N = 1
X(AL) = 0.7
X(ZN) = 0.3
=====
```

Equilibrium:

Chemical potential:

AL 580.969  
ZN 495.04

Phase:

FCC\_A1#2  
Moles: 0.702168  
X(AL) = 0.777535  
X(ZN) = 0.222465

FCC\_A1

Moles: 0.297832  
X(AL) = 0.517203  
X(ZN) = 0.482797

Running times: 0.027 s.

### 6.1.2 Fixed x and Phase

To be added.

## 6.2 Step

```
Example file of VCLInput: Mode           = Equilibrium  !
Dimension           = 1  !
Database_File       = cusnti.TDB  !
Elements            = cu, sn, ti  !
Compositions        = 0.1, 0.6, 0.3  !
Phases_Selected     = all  !
Phases_Rejected     = none  !
Pressure            = 101325  !
Variables           = Temperature  !
V_start             = 300  !
V_end               = 2000  !
V_Interval          = 5  !
Global_Grid.Interval = 0.02  !
```

Running times: 2.137 s.

Results of phase fractions are stored in phase fractions.txt file. One examples in Cu-Sn-Ti ternary system is show in Fig. 3

## 6.3 Map

To be added.

## 6.4 High dimensions calculations

To be added.



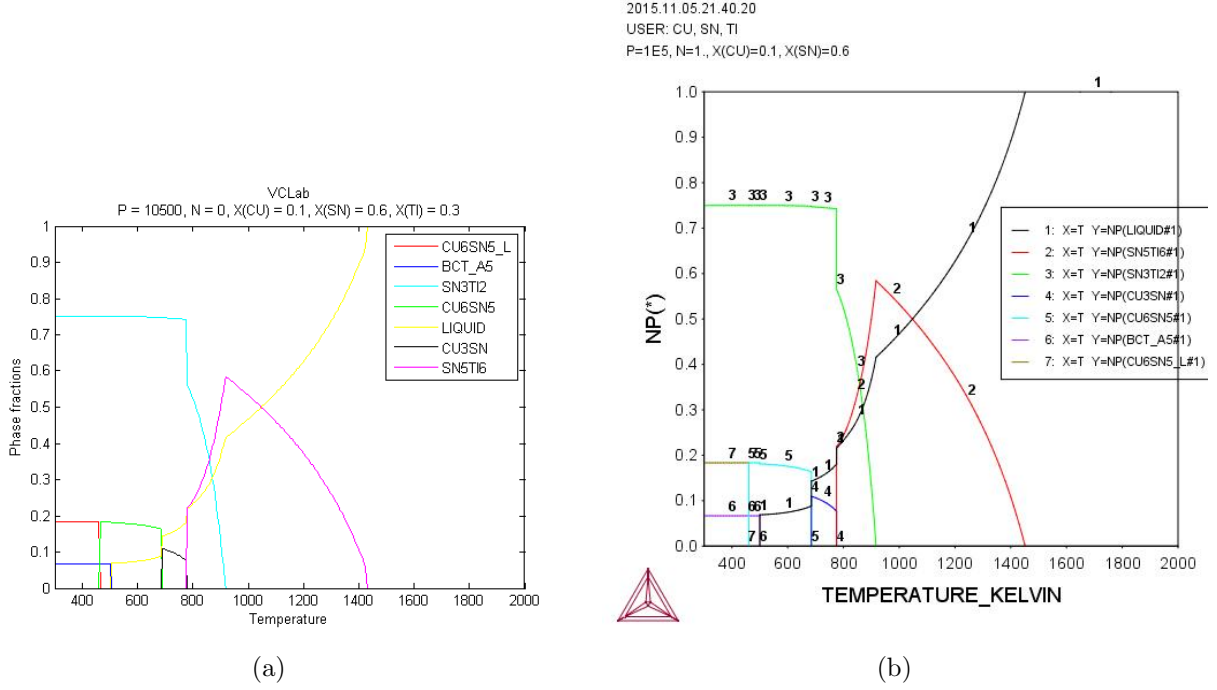


Figure 3: Equilibrium solidification process of a Cu-Sn-Ti alloys. (a) VCLab; (b) Thermo-Calc 2015 demo version.

## 7 Algorithm

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.

### 7.1 Gibbs energy function

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

The equality constraint are:

(1) sum of the site fractions on sublattice s of phase  $\alpha$  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.

## 7.2 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  $\lambda^\alpha, \mu_A$  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.

### 7.3 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 euilibrium matrix should be removed. For example, when T and P fixed.

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

### 7.4 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  $n^\alpha$  are add.

## 8 Summary

Not finished yet. More detail will be added.