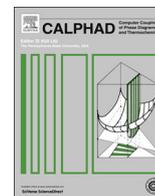




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# CALPHAD: Computer Coupling of Phase Diagrams and Thermochemistry

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## Calculation of property diagram as a Zero-Phase Fraction line of auxiliary phase<sup>☆</sup>

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## ABSTRACT

An approach to calculate various properties of solution is presented using CALPHAD phase diagram software. The properties include iso-bar, iso-activity, iso-activity coefficient, iso-sulfide capacity, iso-surface tension of various types of solutions such as liquid oxide or liquid alloy. Auxiliary phase(s) is introduced in order to set an equilibrium between a real solution and an auxiliary phase, where the property of the real solution is interesting. Gibbs energy of the auxiliary phase is set to yield a phase boundary between the real solution and the auxiliary phase, and the phase boundary becomes the iso-property line. The iso-property line is a phase boundary, therefore, it can be calculated as a Zero-Phase Fraction (ZPF) line of the auxiliary phase. This approach shows an easy way for calculating of the property diagram. The approach may be programmed into existing commercial CALPHAD software for the phase diagram calculation.

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## 1. Introduction

Various thermodynamic and physicochemical properties of solutions are valuable in design of materials processing. Those properties encompass not only activity, activity coefficient, enthalpy, etc. (thermodynamic properties) but also viscosity, surface and interfacial tension, thermal and electrical conductivity, etc. (physicochemical properties). Capacity of a solution (liquid metal or liquid slag) representing an ability to absorb impurities such as sulfide capacity of slag, phosphate capacity of slag, etc. is also practically useful property.

Large amounts of experimental data have been reported in the literature. CALPHAD type thermodynamic modeling has been performed during many years utilizing those experimental information. In the CALPHAD method, Gibbs energies of various phases are mathematically formulated. By minimizing Gibbs energy of the whole system, equilibrium information is obtained including some of the above-mentioned properties. In addition to this, phase diagram of multicomponent system is also easily obtained.

Conventionally, the phase diagram software has provided "phase diagram", which plots regions of stable phases using

various axis variables. Most typical type of such phase diagram is temperature–composition or composition–composition phase diagram. However, many different thermodynamic variables can be used to plot various types of phase diagrams. Pressure, volume, enthalpy, entropy, chemical potential, *u*-fraction, etc. can be used for such phase diagram calculations. Interested readers are invited to read articles by Hillert [1] and Pelton [2], respectively.

In the present paper, a new application of phase diagram calculation is presented. It is attempted to calculate various properties of solutions, to plot the properties automatically using the method for the phase diagram calculation. In other words, the calculation of thermodynamic or physicochemical property obeys rules for the phase diagram calculation in a special case. In the following sections, principles of phase diagram calculation and automatic plotting are briefly explained. And *auxiliary phase(s)* and its Gibbs energy are introduced in order to plot the property diagram as the special case of phase diagram. A number of examples are presented: iso-oxygen bar, iso-activity, iso-activity coefficient, iso-sulfide capacity, surface tension, and iso-surface tension. Among those, the calculation of surface tension was already presented by one of the authors [3,4], where surface of a solution was explicitly considered as a separate phase. In the context of the present study, the surface phase is considered as the auxiliary phase of the solution.

All the phase diagram calculations in the present study were carried out using PHASEDIAGRAM module of FactSage software [5,6], which has been developed by Christopher W. Bale and his colleagues.

<sup>☆</sup>This paper is based on a presentation made in "Thermodynamic Applications, Optimizations, and Simulations in High-Temperature Processes: An EPD Symposium in Honor of Christopher W. Bale's 70th Birthday", TMS 2016, Nashville, TN.

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## 2. Zero-Phase Fraction line of conventional phase diagram

A phase diagram is composed of a number of lines separating stable phase regions. The lines are indeed phase boundaries. Morral and coworkers realized that each phase boundary appeared in a phase diagram represents fraction of a phase being zero, respectively. An example is shown in Fig. 1. This is an quaternary isobaric ( $P=1$  bar) – isothermal ( $T=850$  °C) – isoplethal ( $[pct C]=0.3$ ) section of Fe–Cr–V–C system. Gibbs energy equations for all the phases were taken from Lee and Lee [7]. Each line represents fraction of MC, fcc, bcc,  $M_7C_3$ , and  $M_{23}C_6$ , respectively, being zero. These lines are called as Zero-Phase Fraction (ZPF) lines [8]. Most computational phase diagram calculations use the concept of ZPF line [5,6,9].

Pelton and Schmalzried categorized various phase diagrams on two-dimensional domain in three types: “Type I” using potential–potential axis variables, “Type II” using potential–composition axis variables, and “Type III” using composition–composition axis variables [10]. Later, Hillert and Pelton, respectively, discussed proper choices of the axis variables which make a true phase diagram [1,2]. Once axis variables are chosen, two dimensional area is mapped in order to find various sets of lines representing ZPF of all phases. In the course of the mapping, minimization of Gibbs energy of the system is carried out. Overlapping all the ZPF lines results in a phase diagram such as that shown in Fig. 1. For example, the line A–A’ in Fig. 1 represents the ZPF line of fcc phase. Above this line, the fcc phase is not stable. Below this line, the fcc phase is stable. Therefore, phase fraction of the fcc phase on the line A–A’ is zero, and this is why the line is called ZPF line of fcc. Commercial software for phase diagram calculation actually calculates these ZPF lines in order to draw the phase diagram.

## 3. Auxiliary phase, its gibbs energy, and ZPF line of the auxiliary phase

Purpose of the present article is to show that same principle of the ZPF line and software can be used in order to calculate/plot thermodynamic and physicochemical properties. The properties to be shown in the present paper are listed in Table 1. These are only examples, and the present approach is not only limited to those properties.

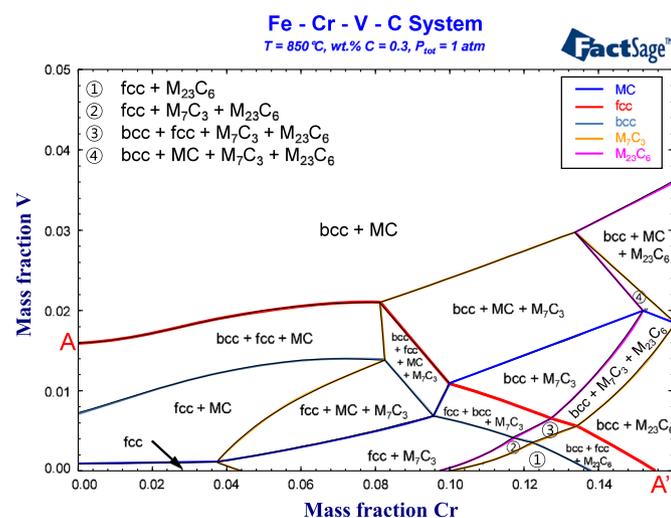


Fig. 1. (Color online) An isothermal section of Fe–Cr–V–C system at 850 °C, mass pct. C=0.3, taken from Pelton [19]. All lines were calculated using Gibbs energy equations proposed by Lee and Lee [7]. Those are ZPF lines of each phase listed in a box (MC, fcc, bcc,  $M_7C_3$ , and  $M_{23}C_6$ ). Line A–A’ represents a ZPF line of fcc phase.

## 3.1. Property diagram

One of the examples to be shown is iso-bar of gas components superimposed on a phase diagram. Typical example is shown in Fig. 2(a). This is a part of binary phase diagram of Mn–O system (from MnO to  $Mn_2O_3$ ). All phase boundaries are shown by thick lines. In the figure, several oxygen iso-bars are shown by thin dashed lines. It is a common to superimpose oxygen iso-bars on the diagram where O is a system component.

The other example is an iso-activity line superimposed on a phase region. Shown in Fig. 3(a) is the iso-activity line of MnO in MnO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> slag. For a clear presentation, only one iso-activity line ( $a_{MnO}=0.1$  with respect to pure solid MnO) is shown by a thick line. Conventionally, iso-activity lines were usually drawn by hand (by passing through experimentally determined compositions of known activity values) or by employing ternary Gibbs–Duhem equation [11].

Another example is an iso-activity coefficient of MnS in MnO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–MnS slag, shown in Fig. 4. An iso-activity coefficient line of MnS (with respect to pure solid MnS) is shown by a thick line. Conventionally, iso-activity coefficient line was usually drawn by hand (by passing through experimentally determined compositions of known activity coefficient values).

Those lines shown in Figs. 2–4 have not been considered as part of conventional phase diagram. However, in this paper, it is shown how such lines can be calculated automatically using phase diagram software.

## 3.2. Auxiliary phase and its Gibbs energy

In a A–B binary system, a phase equilibrium between two phases ( $\alpha$  and  $\beta$ ) can be described by Gibbs energies of these phases, as shown in Fig. 5 at constant  $T$  and  $P$ . When these two phases are in equilibrium, equilibrium composition in each phase is  $X_B^\alpha$  and  $X_B^\beta$ , respectively. Chemical potentials of A and B ( $\mu_A$  and  $\mu_B$ ) are also shown on both vertical axes. Here, the phase  $\alpha$  is a real phase, and its Gibbs energy is supposed to be known. Property of this real phase is to be calculated.

The other phase  $\beta$  is now considered as an auxiliary phase. Depending on its Gibbs energy,  $X_B^\alpha$ ,  $X_B^\beta$ ,  $\mu_A$ , and  $\mu_B$  are all determined. A closed circle on the Gibbs energy of  $\alpha$  represents a condition where fraction of the auxiliary phase  $\beta$  is zero (ZPF of  $\beta$ ). Therefore, the idea of the present study is to utilize the relationship between Gibbs energy of the auxiliary phase  $\beta$  and any property to be obtained, which may be obtained as  $X_B$  or  $\mu_B$  of the equilibrium condition.

One of simplest examples is shown in Fig. 2 for the oxygen iso-bar on Mn–O liquid. Fig. 2(b) shows a Gibbs energy of the slag phase (liquid Mn oxide) at  $P=1$  bar and  $T=1700$  °C as a function of composition ( $X_O$ ) by a solid curve. This is a Gibbs energy of the real phase. On the other hand, an auxiliary phase  $\beta$  is considered that O<sub>2</sub> is the only component. First, the oxygen iso-bar of 1 bar is discussed (A). Gibbs energy of the auxiliary phase  $\beta$  is formulated as:

$$g^\beta = g_{O_2}^\circ \quad (1)$$

where  $g_{O_2}^\circ$  is a Gibbs energy of pure O<sub>2</sub> gas at  $P_{O_2}=1$  bar. The Gibbs energy at 1700 °C is marked by a solid circle on a vertical axis. Equilibrium between the slag and the  $\beta$  is obtained by constructing a common tangent line between the curve and the circle, or minimizing Gibbs energy of the system composed of these two phases. The other solid circle on the horizontal axis tells the equilibrium composition of O ( $X_O$ ) in the slag phase when it is in equilibrium with the O<sub>2</sub> gas. Next, the oxygen iso-bar of 0.1 bar is discussed (B). Gibbs energy of the corresponding auxiliary phase  $\beta$

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