Chapter 1 Introduction

This chapter describes how to use this user's manual; outline of the CHD for Windows system will be given in the following sequence;

1. What can be done with CHD?
2. Commands
3. Menus
4. How to Use this manual

1.1 What can be done with CHD for Windows?

This program is for constructing the chemical potential diagram.

By the chemical potential diagram, the following diagrams are included;

1) Conventional diagrams such as the Pourbaix diagram
2) Generalized chemical potential diagrams

Detailed description on chemical potential diagram will be given in Chapter 2.

To draw a diagram, the following procedures should be adopted;

1) retrieve the thermodynamic data from the MALT database or read the thermodynamic data from a file;
2) change the specification of chemical system, if necessary;
3) define the diagram type, the diagram coordinates, and the fixation of chemical potential, if necessary.
4) calculate to construct the diagram.

To manipulate the diagram, the following functions are available;

1) change the location of the diagram in the display panel;
2) touch the point on the diagram to know the detailed thermodynamic information;
3) draw a continuous line by manually clicking;
4) change the location of the diagram and the text string or change rectangular shape;
5) zoom up or down;
6) rotate the three dimensional diagram;
7) make dissections of the diagram;
8) change colors or Fonts.

To transfer the diagram to other software or hardware, the following ways are prepared;

1) save the diagram as a file of bitmap, jpeg, or metafile;

2) copy the diagram to clipboard as metafile.

1.2 Commands

Commands in CHD for Windows will be made by selecting one of menus. Even so, typical commands can be listed below in relation with the given menus.

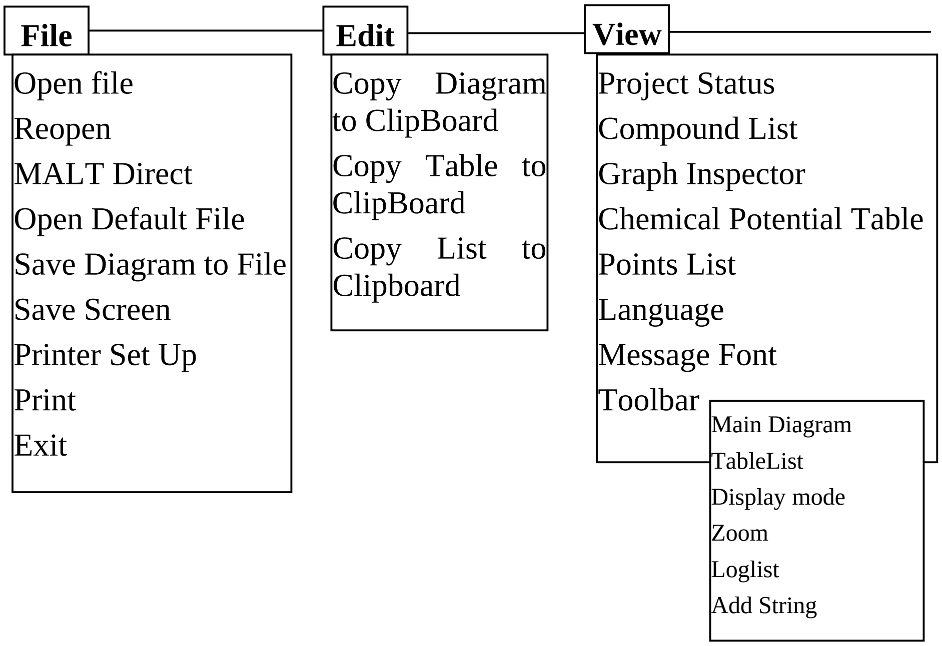
Read Data From Files (menu “File”)
Specify the Chemical System (menu “Project / Chemical System”)
Define the Diagram Type (menu “Project / Specify Diagram”)
Calculate (menu “Run / Calculate”)

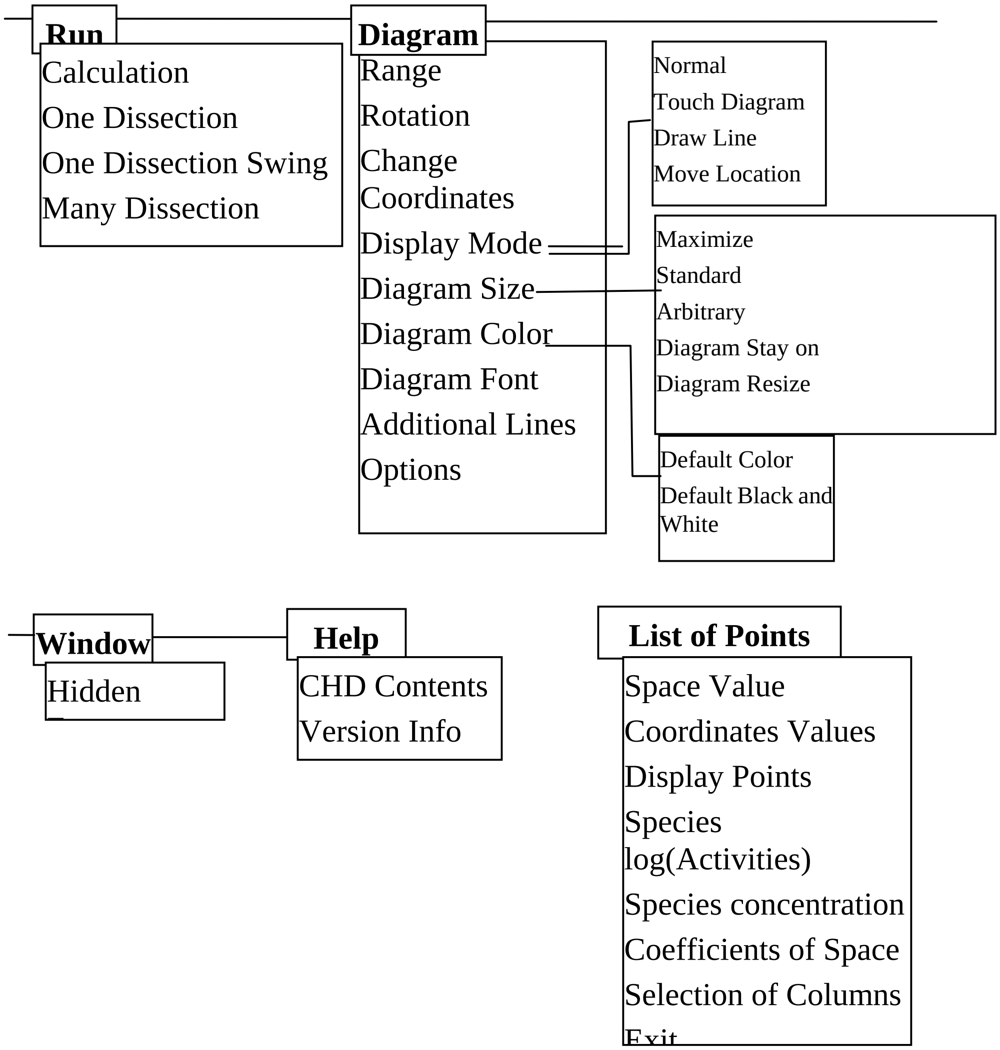
Save Diagram to File (menu “File / Save Diagram to File”)
Copy Diagram to Clipboard (menu “Edit / Copy Diagram to Clipboard”)

Manipulate the Diagram (menu “Diagram”)
Diagram Display mode (menu “Diagram / Diagram Display mode”)

1.3 Menus

CHD menus are organized as follows;





1.4 How to Use This Manual

CHD for Windows provides facilities for constructing generalized chemical potential diagrams.

This manual has been prepared by assuming that users are able to do the followings without any problems;

1. With adequate knowledge about Windows and related software to start Windows;
2. to have ability of writing computer programs in more than two computer languages;
3. to have proper knowledge about the thermodynamics to convert their own materials problems to thermodynamic problems.

Even so, the Chapter ***3*** is prepared for beginners in both applying thermodynamics and handling personal computers.

This manual consists of the following chapters;

chapter 1 : introduction

chapter 2 : Generalized chemical potentials diagrams

To use this CHD for Windows, it is essential to know the materials thermodynamics properly. In this chapter, a brief explanation will be given for generalized chemical potentials diagrams. Users are highly recommended to read review articles to know the whole features of the generalized chemical potentials diagram.

The followings are articles which give rather detailed description of generalized chemical potential diagrams,

1) H. Yokokawa, "Generalized Chemical Potential Diagram and its Applications to Chemical Reactions at Interfaces between Dissimilar Materials," ***J. Phase Equilibria.*** 20(3)**, 258-287 (1999).**

2) H. Yokokawa, "Fundamental and Applications of the Generalized Chemical Potential Diagram (in Japanese)," ***Materia (Journal of Metal. Society Japan)*** *35*, **1025-1030, 1133-1139 , 1250-1255 , 1345-1351 (1996).**

chapter 3 : Instruction   Let's run CHD for Windows

This chapter describes the most fundamental way of using CHD for Windows in an appropriate sequence. Please run MALT for Windows according to the instruction given in chapter 3 of the Manual for MALT for Windows. Then, try to touch CHD for Windows to draw different kinds of diagrams. This will give you interestingly interactive time with generalized chemical potentials diagrams.

chapter 4 : For full use of CHD for Windows functions

This chapter describes details of CHD for Windows menus and functions including those which are not described in chapter 3.

Chapter 2 Generalized Chemical Potential Diagrams

In this chapter, the generalized chemical potential diagram will be described in the following aspects:

1) Conventional vs. Generalized chemical potential diagram
2) Characteristic features of chemical potential diagram
3) A New Algorithm for Further Generalization
4) Applications of generalized chemical potential diagram

2.1 Conventional vs. Generalized chemical potential diagrams

2.1.1 Conventional chemical potential diagram

The conventional chemical potential diagram is a kind of stability diagram in which the redox element is selected and the stability area of its compounds are displayed as functions of chemical potentials that represent the chemical properties of environments. In Fig. 1, the chemical potential diagram for the Fe-O-S system at 800K is displayed. A typical chemical reaction for representing such a diagram is given as

$$2FeSO_4 = Fe_2O_3 + S_2 + 2.5O_2 \qquad [2.1]$$

The left hand side of this fundamental equation is always one compound of the selected redox element, whereas the right hand side consists of another compound of the redox element and species adopted for coordinates. Thus, two-phase-coexistence relation between $FeSO_4$ and Fe_2O_3 is given as a reaction with S_2 and O_2. This makes it possible to give the following relation to representing the phase boundary in the chemical potential diagram.

$$2\mu(FeSO_4) = \mu(Fe_2O_3) + \mu(S_2) + 2.5\mu(O_2) \qquad [2.2]$$

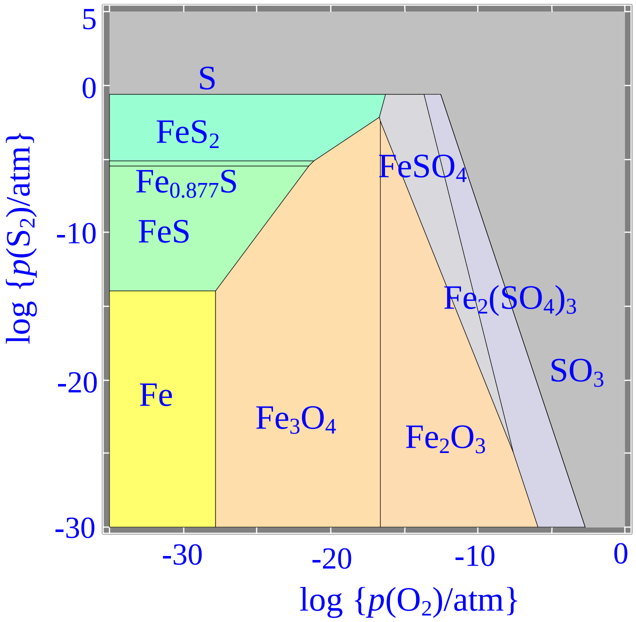


Fig. 2.1 Conventional chemical potential diagram for the Fe-O-S system at 800 K.

The coefficients of 1 and 2.5 for $\mu(S_2)$ and $\mu(O_2)$ provides a slope of the phase boundary in the chemical potential diagram.

The main features of such conventional chemical potential diagram can be summarized as follows;

1) In any cases, the redox element has to be determined.
2) The coordinate variables are selected from the chemical potential values which can characterize the chemical environments. For example, log $\{p(O_2)/\text{atm}\}$, log $\{p(S_2)/\text{atm}\}$, log $\{p(CO_2)/\text{atm}\}$, log $\{p(Na)/\text{atm}\}$ are usually used .

In many cases, the coordinate variable can be regulated by an appropriate experimental way. This makes this diagram valuable as the stability diagram or the predominant area diagram. This provides useful tools to understand the thermodynamic stability of materials in various chemical environments.

On the other hand, there are several demerits in the conventional chemical potential diagrams. These are

1) When there are several candidates for redox elements, it becomes difficult to select properly one redox element. This makes it difficult to apply the

conventional diagrams to those systems containing alloys or double oxides;

2) From a similar reason, it is difficult to extend to the multi-component systems. When the appropriate environmental coordinates could be selected, the stability diagram could be extended to the multi component systems. However, it is not easy to find out appropriate coordinates in actual material systems without difficulties;
3) The interface stability among different materials cannot be examined properly, just because more than two elements are always to be considered simultaneously.

2.1.2 Generalization

The above demerits are originated from the selection of the redox element and the coordinates corresponding to the environmental variables.

To overcome such demerits, it is essential to have the more generalized fundamental reaction to construct the chemical potential diagram. This can be given in the following relation:

$$2\mathrm{La} + 2\ \mathrm{Zr} + 7\mathrm{O} = \mathrm{La_2Zr_2O_7}$$

$$2\mu(\mathrm{La})+2\mu(\mathrm{Zr})+7\mu(\mathrm{O})=\Delta_f G^o(\mathrm{La_2Zr_2O_7}) \qquad [2.3]$$

Here, the Gibbs energy for formation of $La_2Zr_2O_7$ is correlated with the chemical potentials of elements La, Zr and O.

Strictly speaking, the above reaction should be corrected for the reference state for the elemental chemical potential. In the convention for the reference state adopted in the JANAF table, the reference state is selected at respective temperatures. In such a case, the above equation should be rewritten as follows;

$$2\{\mu(\mathrm{La})-\mu^o(\mathrm{La})\}+2\{\mu(\mathrm{Zr})-\mu^o(\mathrm{Zr})\}+7\{\mu(\mathrm{O})-\mu^o(\mathrm{O})\} = \Delta_f G^o(\mathrm{La_2Zr_2O_7})$$

where $\mu^o(\mathrm{La})$ ***is the chemical potential value at the reference state at a temperature. In another convention adopted in data book by Barin-Knacke, the reference state is defined only at 298.15 K. In such a case,***

$$2\{\mu(\mathrm{La})-\mu^o_{\mathrm{La}}\}+2\{\mu(\mathrm{Zr})-\mu^o_{\mathrm{Zr}}\}+7\{\mu(\mathrm{O})-\mu^o_{\mathrm{O}}\} = \Delta_f{}'G^o(\mathrm{La_2Zr_2O_7})$$

where μ^o_{La} ***is the reference chemical potential of La at 298.15 K and*** $\Delta_f{}'G^o(\mathrm{La_2Zr_2O_7})$ ***is the Gibbs energy change referred to the standard***

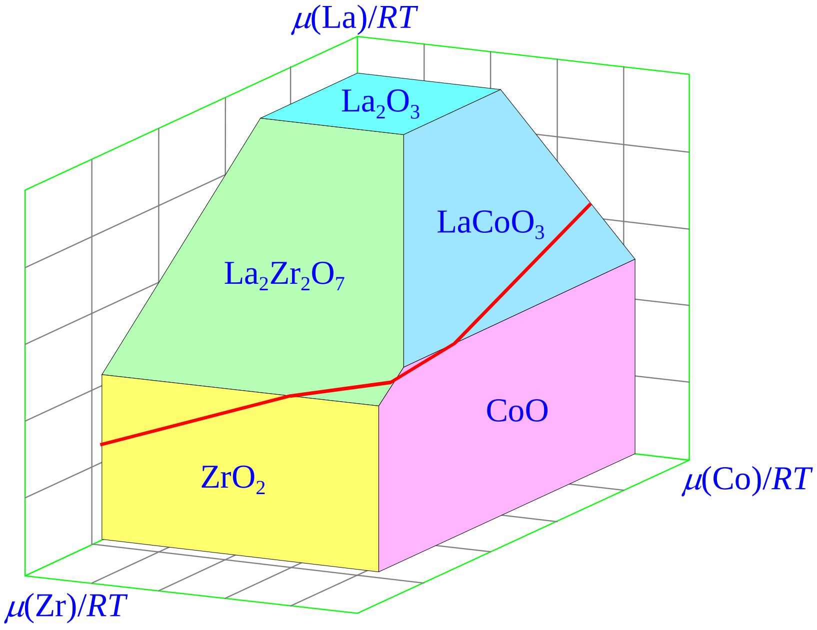


Fig. 2.2 Generalized chemical potential diagram for the La-Co-Zr-O system at 1273 K under $p(O_2)$ = 1 atm.

temperature. The difference between $\Delta_f G^o(La_2Zr_2O_7)$ and $\Delta_f' G^o(La_2Zr_2O_7)$ is described in details in the Manual of MALT for Windows.

In Eq. [2.3]. the references states are adopted as $\mu^o{}_{La}=\mu^o{}_{Zr}=\mu^o{}_O=0.0$ and $G^o=\Delta_f' G^o$. The equation [2.3] is a linear equation in the μ(La)- μ(Co)- μ(Zr)-μ(O) four dimensional space. When the phase relations under the condition of $p(O_2)$ = 1 atm are considered, the above equation has two variables in the μ(La)- μ(Co)- μ(Zr) space. Geometrically, this indicates the plane in the μ(La)- μ(Co)- μ(Zr) space that has a slope of (2,0,2) as shown in Fig. 2.2. When another compound, $LaCoO_3$, having the different stoichiometric numbers is considered, this phase corresponds to a plane having a different slope so that two compounds have a common edge. Furthermore, G^o in Eq.[2.3] determines the relative location of the plane to the origin, namely, the reference states of elements. Thus, the thermodynamic information of compounds all well appears as the geometrical features of the plane. By using Eq. [2.3] as the fundamental reaction for constructing the chemical potential diagram, the generalized chemical potential diagrams can be thus constructed without selecting any redox element or specifying the environmental chemical potentials.

Table 2.1 Comparison between conventional and generalized chemical potential diagrams.

Chemical potential diagrams	
Conventional	Generalized
Selection of one Redox Element As functions of chemical potentials for representing Environments (pH, log $p(O_2)$ etc) Difficult to apply to Alloys or Complex oxides	Free to Select Metals/Nonmetals As functions of any chemical potentials for representing the state of elements inside solid substances. (μ(M)/RT) Simultaneous considerations on Chemical Reactions and Diffusion Solid/gas, solid/solid interfaces

As shown in Fig. 2.2, three-phase coexistence can be represented as a corner of three planes. This corner represents a point in the chemical potential space so that the thermodynamic functions are uniquely determined as suggested from the Gibbs phase rule.

All stable compounds form a polyhedron consisting of planes having negative slopes. That is, this polyhedron is open to the negatively infinite directions. This corresponds to the fact that the stoichiometric number is always positive.

Comparison between the conventional and the generalized chemical potential diagrams is given in Table 2.1.

Since there is no need to select any redox element, it is possible to treat two elements in an equivalent way. This generalization makes it possible to examine the interface stability between two materials. In Fig. 2.2, the chemical stability between $LaCoO_3$ and ZrO_2 can be identified as unstable against the formation of $La_2Zr_2O_7$ and CoO. This corresponds to the following chemical reaction:

$$LaCoO_3 + ZrO_2 = 0.5\ La_2Zr_2O_7 + CO + 0.25\ O_2(g) \qquad [2.4]$$

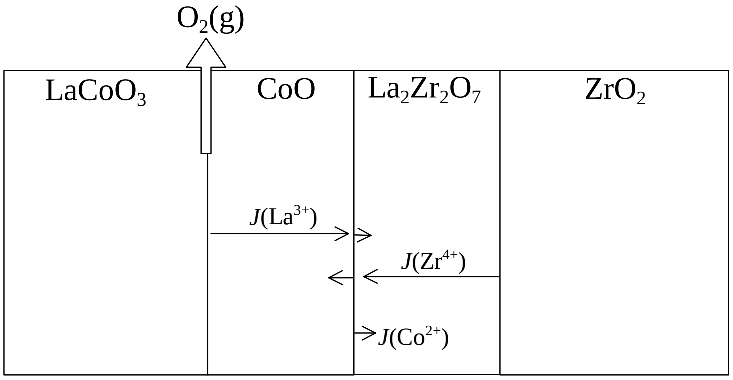


Fig. 2.3 Reactive diffusion path for interface reaction between $LaCoO_3$ and ZrO_2

The Gibbs energy change for this reaction can be found to be negative at 1273 K.

In solid involved reactions, diffusion plays important roles. Unlike gaseous reactions, homogeneous reaction cannot proceed in the solid-solid reactions. Since the driving force for diffusions is provided as the chemical potential difference, reaction diffusion path can be well represented in the chemical potential diagram. In other words, coordinates for the generalized chemical potential diagrams indicate the thermodynamic state inside solid materials which can be correlated with the reactive diffusion. In this sense, the generalized chemical potential diagram provides not only the stability of the substance but also the driving force for diffusion and resulting reactive diffusion path. For example, the chemical reaction between $LaCoO_3$ and ZrO_2 proceeds through diffusion shown in Fig. 2.3. The reaction products, CoO and $La_2Zr_2O_7$, form a layered structure; the sequence is given as $LaCoO_3/CoO/La_2Zr_2O_7/ZrO_2$. A key point is in that CoO appears just next to the $LaCoO_3$ not in between $La_2Zr_2O_7$ and ZrO_2. Since the oxygen potential is nearly constant throughout the reaction zone, this sequence is reasonable from the chemical potential point of view. That is, the chemical potential of Co should be maximum in CoO. This does not allow for Co ions to migrate to form CoO. Instead, CoO is formed as a result of diffusion of La ions in $LaCoO_3$ to migrate beyond the CoO phase. In such a case, La ions can diffuse through along the La chemical potential gradient. On the formation of CoO phase, the valence of Co ions changes so that oxygen may be evolved around the $LaCoO_3$ and CoO interface. On the other hand, Zr ions diffuse through $La_2Zr_2O_7$ phase. The La and Co ions meet at the CoO and $La_2Zr_2O_7$ interface.

These features in diffusion associated with solid-solid interface reactions can be represented as the reactive diffusion path in the chemical potential diagram

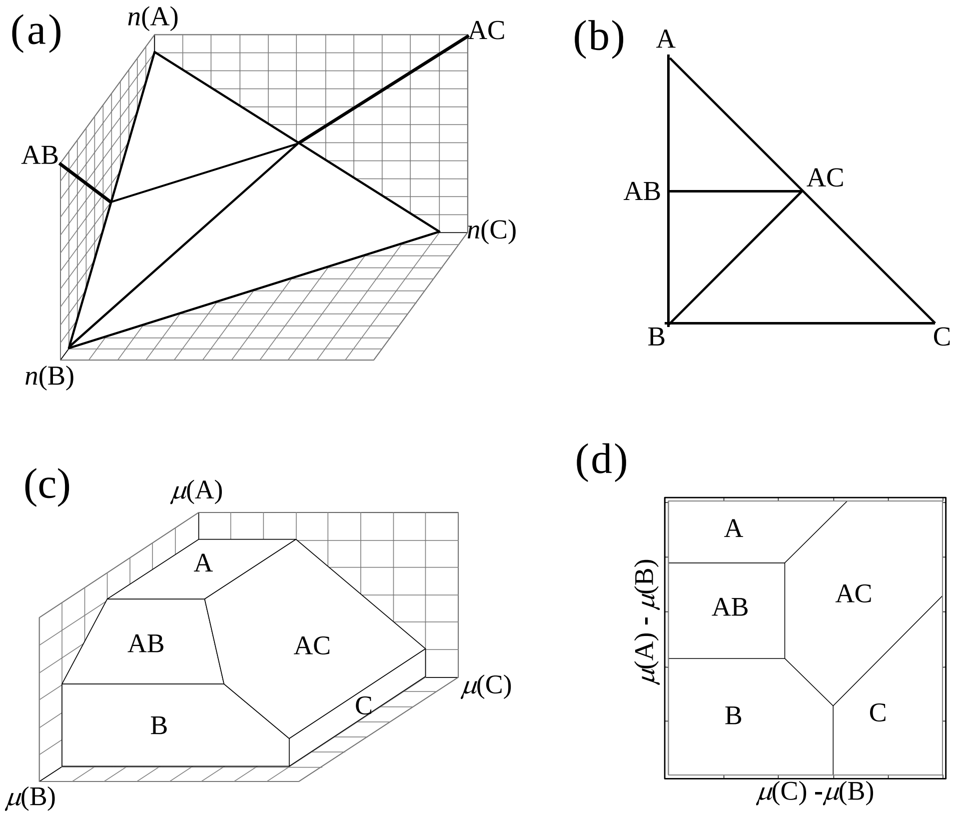


Fig. 2. 4 Type 1 diagram for the A-B-C system. (a) three dimensional molar space, $A_{1-x}B_{1-y}C_{x+y}$. Compound AB and AC are represented by lines which start from the origin and the slope corresponding to the stoichiometric numbers; (b) Composition diagram, (c) three dimensional chemical potential diagram, (d) two dimensional chemical potential diagram using two variables in the chemical potential difference type.

as shown in Fig 2.2. This is one of the characteristic features of generalized chemical potential diagram.

2.2 Characteristic features of generalized chemical potential diagrams

The generalization can be realized in many aspects.

Conventional chemical potential diagrams can be constructed from the polyhedron in the chemical potential space. For example, Fig. 2.1 was constructed from the same procedure as the generalized chemical potential

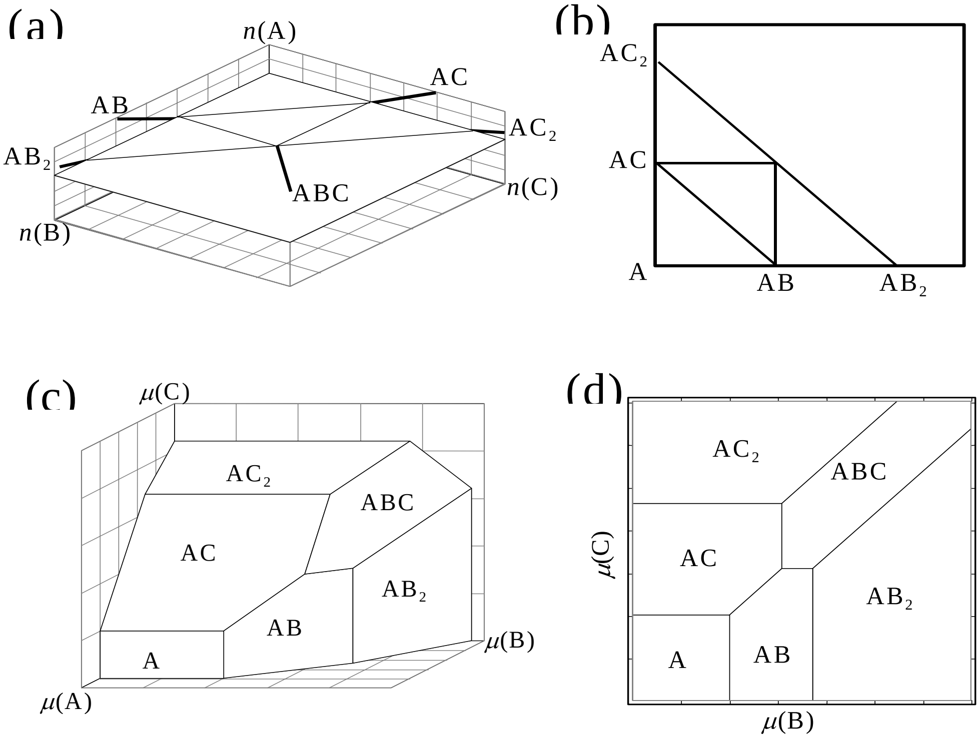


Fig 2.5. Type 2 diagram for the A-B-C system. (a) Molar space and system representation as AB_nC_m. (b) Compositional diagram where n and m in AB_nC_m are adopted as coordinates, (c) three dimensional chemical potential diagram, (d) two dimensional diagram with coordinates of elemental chemical potentials.

diagram. In Fig. 2.1, the thermodynamically inaccessible areas are displayed as a gray area. In this area, any sulfur – oxygen compounds are thermodynamically unstable and decomposed into S or SO_3. From the generalized diagram point of view, this corresponds to the fact that only on the surface of the convex polyhedron, thermodynamically meaning states are realized. In other words, spaces above the polyhedron are thermodynamically unstable. This space is displayed as gray in Fig. 2.1.

2.2.1 Three types of two dimensional chemical potential diagrams

To construct the two dimensional diagram, two chemical potentials should be selected as coordinate variables. This is a kind of the projection of polyhedron to a plane which is defined by the two coordinates. Here, one problem arises due to the convex nature of polyhedron; that is, in some cases, projected phase relations are doubly folded on the coordinate plane. To avoid

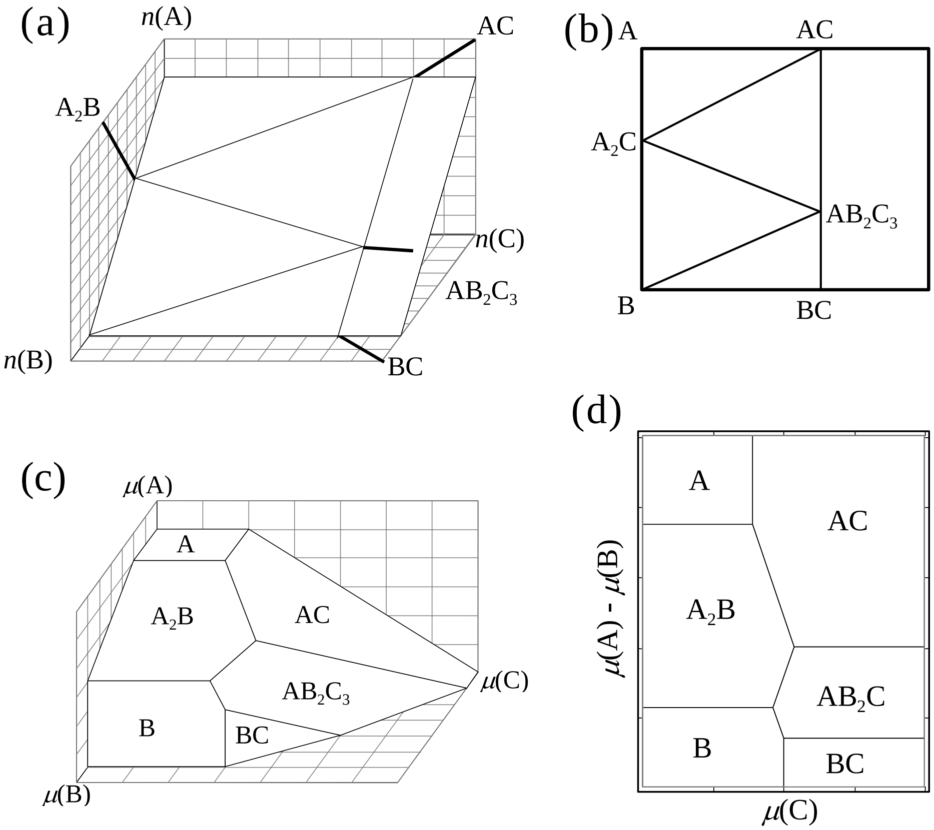


Fig. 2.6 Type 3 diagram for the A-B-C system. (a) Molar space for the system represented by $A_{1-x}B_xC_n$. (b) Compositional diagram for $A_{1-x}B_xC_n$ system, (c) three dimensional chemical potential, (d) two dimensional diagram with coordinates of elemental chemical potential and chemical potential difference.

this overlapping, there can be several ways of selecting the coordinate variables. For three component systems, the following diagrams can be constructed:

(1) Type 1 is for the three component system where the three components are equivalently treated as shown in Fig. 2.4. In the molar space, this system is represented as $A_{1-x}B_{1-y}C_{x+y}$. In the compositional space, a triangle diagram is appropriate for representing this system. This is frequently used for ternary alloys and ternary oxides systems. For the two dimensional chemical potential diagram, two chemical potential differences, $\mu(A)$-$\mu(B)$ and $\mu(C)$-$\mu(B)$, are used as coordinates. Use of the chemical potential difference is a key point in representing phase relations in the two dimensional plane. A sum of elemental chemical potentials, $\mu(A)+\mu(B)$, is

inappropriate as coordinate, because phase relations are always folded and overlapped.

(2) Type 2 is for the three component system where the element A and the elements B and C can be treated differently; for example, A is the metallic element and B and C are the non-metallic elements. For the two dimensional diagram, two elemental chemical potentials, μ(B) and μ(C), are used as coordinates. Since μ(A) is not used as coordinates, it is the same as the conventional diagram.

(3) Type 3 is for the three component system where the elements A and B and the element C are different. For example, A and B are metallic and C is non-metallic. For the two dimensional diagram, the elemental chemical potential difference, μ(A)- μ(B), and the elemental chemical potential, μ(C), are used.

Note that in any cases, the three dimensional chemical potential diagram shows properly the phase relations in the three-component system without further treatment. In this sense, the generalization of the three dimensional chemical potential diagram is extremely high.

Figs. 2.4 to 2.6 were constructed by using the test data which are stored as ABC1.abs, ABC2.abs, and ABC3.abs; see 4.3 Menu "File" and Fig.4.4.

2.2.3 Some features of two dimensional diagram

The geometrical features of the generalized two-dimensional diagrams are explained by using the type-3 two dimensional diagram for the La-V-O system and the Sr-V-O system shown in Fig. 2.7 and 2.8.

1) The phase relations in the La-V-O system are shown in the two dimensional diagram with coordinates of log [$p(O_2)$/atm] and log [a(V)/a(La)].
2) The phase relations in the V-O sub-binary system are shown in the upper part, those in the La-O sub-binary system being in the lower part. Phase boundaries of such systems are represented by vertical lines. The La-V sub-binary system is shown in the left hand side of the diagram. Here, no La-V intermetallic compounds are presented in the absence of their thermodynamic data. Phase boundaries in the La-V system are given as the horizontal lines.

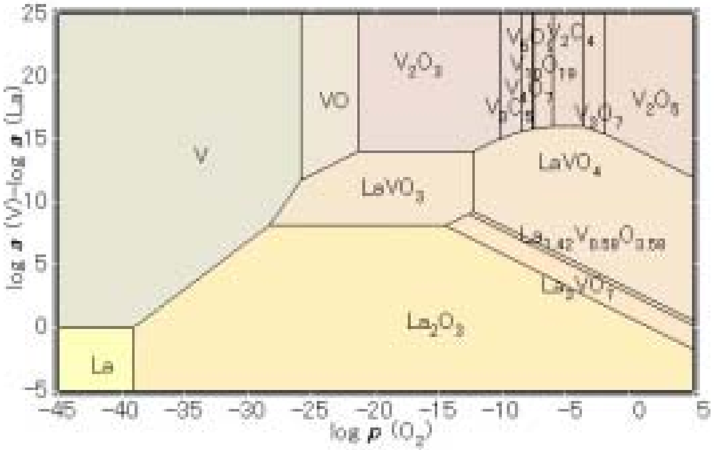


Fig. 2.7 Two dimensional diagram for the La-V-O system at 1273 with coordinates of log [$p(O_2)$/atm] and log [$a(V)/a(La)$].

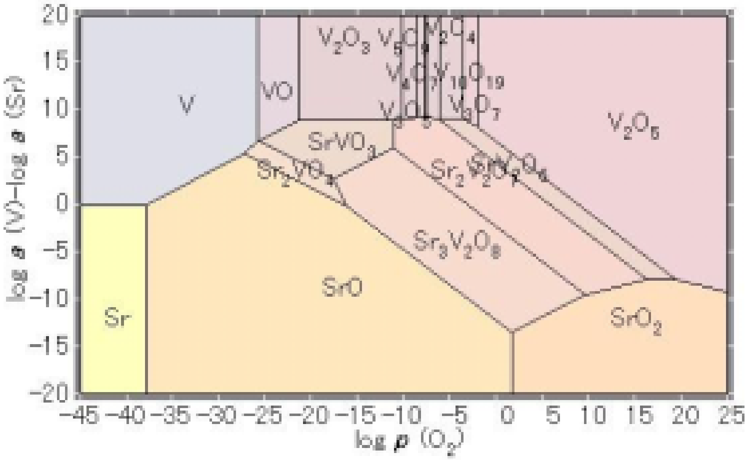


Fig. 2.8 Two dimensional diagram for the Sr-V-O system at 1273 with coordinates of log [$p(O_2)$/atm] and log [$a(V)/a(Sr)$].

3) Ternary compounds appear in the middle of the diagram. In the La_2O_3-V_2O_5 pseudo binary system, ternary compounds appear in parallel. Their borderlines have the slope of –1/2. Similarly, in the La_2O_3-V_2O_3 pseudo binary system, $LaVO_3$ appears with borderlines having the slope of zero.
4) Generally speaking, the slope of two adjacent phases is determined by their stoichiometric numbers.
5) Compounds belonging to a pseudo binary system appear in parallel having the same slope for borderlines. For example, the followings are in the same binary systems:

La_2O_3/$LaVO_3$/V_2O_3 (Fig. 2.7)

$La_2O_3/La_3VO_7/La_{1.42}V_{.58}O_{3.5}/V_2O_5$ (Fig 2.7)
$SrO/Sr_2VO_4/SrVO_3$ (Fig. 2.8)
$SrO/Sr_3V_2O_7/Sr_2V_2O_7/SrV_2O_6/V_2O_5$ (Fig. 2.8)

This is true even when the same valence number is not realized in a sub-binary system. For example,

$VO/SrVO_3/Sr_3V_2O_8/SrO_2$ (Fig. 2.8)

From the stoichiometric number point of view, these compounds belong to the VO-SrO_2 subsystem and appear in parallel, although the valence number of V ions changed from +2 to +6.

6) An interruption of a series of the compounds in parallel indicates that a compound in the pseudo-binary system decomposes into other compounds in the true ternary systems. For example, in the following reaction,

$$SrVO_3 + VO_2 = Sr_2V_2O_7 + V_2O_3 \qquad [2.5]$$

the vanadium tetravalent ions disproportionate into the trivalent ions and the double oxide of penta-valent V ions.

Many two-phase boundaries meet with other boundaries to form the three-phase coexistent points.

2.2.4 Extension to multi-component systems

Adopting the fundamental equation [2.3] for constructing a diagram makes it possible to extend to the multi-component systems.

Instead of three dimensional chemical potential space, the *n*-component chemical potential space can be setup for the *n*-component chemical systems. In such a space, the *n*-phase coexistence determines the chemical potentials uniquely, corresponding to a point in the space. The (*n*-1)-phase coexistence gives lines. In other words, any compounds can be represented by super planes in the space.

To represent such phase relations in a diagram, however, special means will be needed to reduce the dimensionality such as fixation of selected chemical potential; make a dissection; make some parts of diagram transparent.

Fixation of chemical potential

When the system has *n* (>3) components, the chemical potential diagram can be set up by fixing the (*n*-3) chemical potentials.

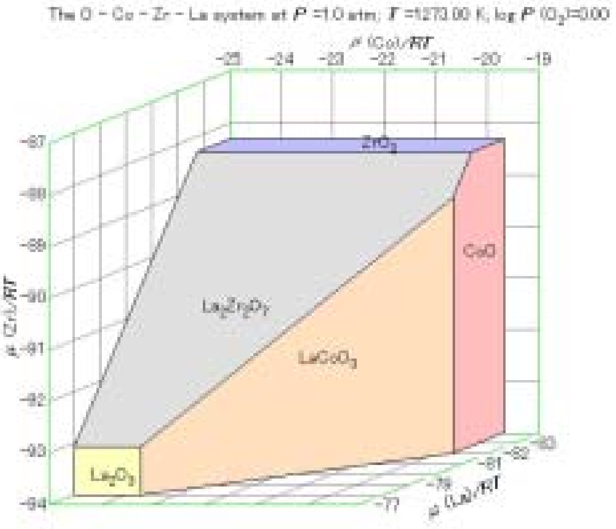


Fig. 2.9 Chemical potential diagram for multicomponent systems. The La-Zr-Co-O system at 1273 K and under a condition of $p(O_2)$ = 1 atm.

Fig 2.9 shows the chemical potential diagram for the La-Zr-Co-O system at 1273 K. Since the component number is four, one fixation of chemical potential makes it possible to draw the chemical potential diagram. In Fig. 2.9, the oxygen partial pressure is fixed at 1 atm. As coordinates, the three elemental chemical potentials are adopted. Geometrical features of this diagram is essentially the same as those in the three dimensional surface diagram for the three component systems. For example, binary oxides, instead of elements, appear as the planes perpendicular to the corresponding coordinates; that is, La_2O_3, ZrO_2, CoO are perpendicular to axes of μ(La), μ(Zr), μ(Co). Double oxides appear between the binary oxides in a similar manner.

This diagram should be compared with the triangle compositional diagram at $p(O_2)$= 1 atm. In pseudo ternary ceramic systems, phase relations provide the fundamental basis of understanding the chemical reactions and related phase behavior. Similarly, the chemical potential diagram like Fig.2.9 can provide the basis for chemical reaction among the ceramic materials. Particularly, Fig. 2.9 shows that $LaCoO_3$ and ZrO_2 can react to form $La_2Zr_2O_7$ and CoO as already given in Eq.[2.4].

Selection of chemical potential to be fixed is arbitrary. It is therefore very important to select the appropriate fixation of chemical potential in order to extract useful thermodynamic information. Fig. 2.10 compares the two three dimensional surface diagrams; (a) is for the La-Co-O system at 1273 K and (b)

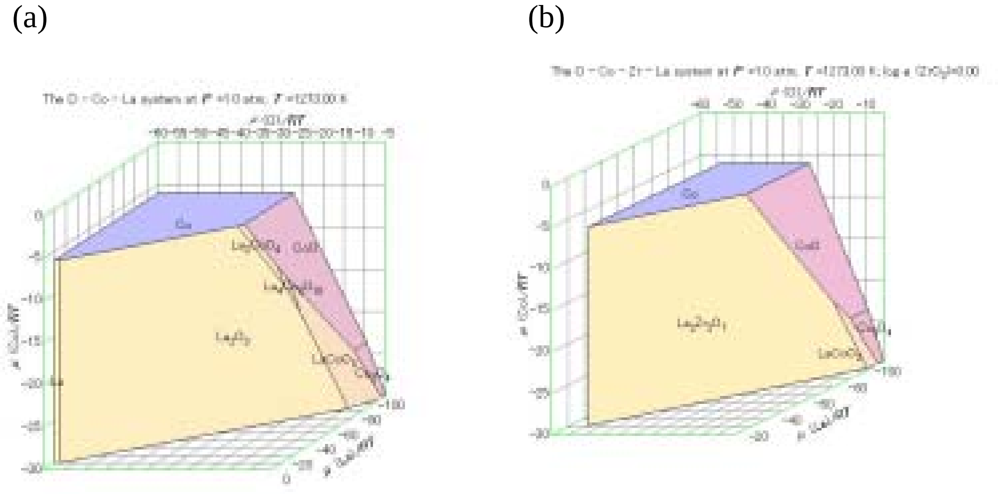


Fig. 2.10 Chemical potential diagram for multicomponent systems. The La-Zr-Co-O system at 1273 K and under a condition of $a(ZrO_2) = 1$ (b) is compared with the La-Co-O system at 1273 K (a).

is for the La-Zr-Co-O system at 1273 K under the condition of $a(ZrO_2)=1$. Since the zirconium oxide is used in fixation, it is natural to use other three elemental chemical potentials. This makes it possible to compare two diagrams directly. The condition of $a(ZrO_2)=1$ means that zirconia oxide is always present in an excess amount. In such a condition, La_2O_3 is no longer stable against the reaction with ZrO_2 to form $La_2Zr_2O_7$. The presence of $La_2Zr_2O_7$ in addition to ZrO_2 indicates that the chemical potential of the La_2O_3 component is lowered. In Fig. 2.10, the stability polygon for $La_2Zr_2O_7$ appears so as to cut off the stability polygons of La_2CoO_4 and $La_4Co_3O_{10}$. This means that these compounds are completely unstable against the reaction with ZrO_2.

$$La_2CoO_4 + 2ZrO_2 = La_2Zr_2O_7 + CoO \qquad [2.6]$$

$$La_4Co_3O_{10} + 4ZrO_2 = 2La_2Zr_2O_7 + 3CoO + 0.5\ O_2(g) \qquad [2.7]$$

There remains the stability region of $LaCoO_3$ although the area is narrowed by the presence of $La_2Zr_2O_7$. This suggests that the formation of $La_2Zr_2O_7$ and CoO from $LaCoO_3$ and ZrO_2 is governed by the oxygen potential, and only in the high oxygen potential region, $LaCoO_3$ is stable against reaction with ZrO_2.

Construction of three dimensional diagram with a function of dissection

For the ternary system, two dimensional diagram can be set up. This implies that a three dimensional diagram can be set up for the quaternary systems. Fig. 2. 11 shows one example for the Li-Fe-C-O system at 923 K. In the three dimensional chemical potential diagrams, the stable compounds are

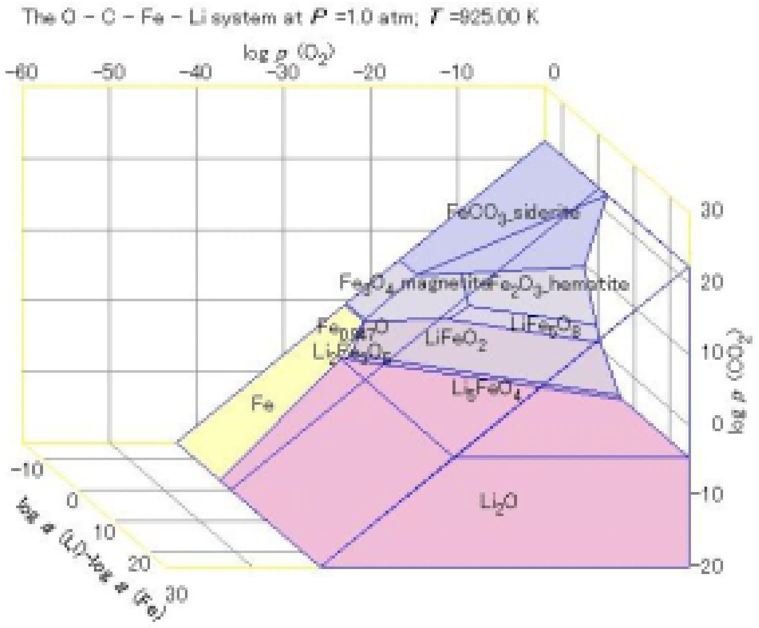


Fig. 2.11 Three dimensional chemical potential diagram for multicomponent systems. The Li-Fe-C-O system at 923 K. The stability polyhedrons of carbon and Li_2CO_3 are made transparent.

represented by polyhedrons instead of polygons in the three dimensional surface diagram. In this sense, it becomes difficult to display these polyhedrons in a visually understandable way.

One way to see the geometrical features of those polyhedrons is to make some polyhedrons transparent. In Fig. 2. 10, the polygon of carbon and the polyhedron of Li_2CO_3 are made transparent.

Another way is to make dissections for the three dimensional diagram to give the two dimensional diagram. Dissection is defined in a similar manner to the fixation; that is, selection of species chemical potential and their fixed value. This dissection diagram can be changed by adjusting the location of dissection plane in terms of the fixed value.

2.3 A New Algorithm for Further Generalization

CHD for Windows adopts a new algorithm of constructing a polyhedron corresponding to a chemical potential diagram. This algorithm is named as convex polyhedron method and is briefly explained here.

New features in chemical potential diagrams

The new algorithm is based on the polyhedron approach which proves new features of the chemical potentials as follows:

(1) Further generalization of coordinate axis.

The fundamental coordinates are based on the elemental chemical potentials. In principle, this can be easily extended to other intensive thermodynamic variables. Particularly, temperature and pressure are the most important intensive variables. In the present version of CHD, the following axes:

Temperature	Inverse Temperature
Pressure	logarithmic Pressure

are adopted.

Since the temperature dependence of chemical potential is not linear, this extension has to include the treatment for non-flat planes.

(2) Treatment for mixture phase

Initially, CHD was coded for treating only the stoichiometric compounds. However, treatment for mixtures is highly required particular when applications to practically important materials problems are concerned. As the simplest mixture, the ideal association model is adopted.

Algorithm for Constructing Chemical Potential Diagrams

Some twenty years ago, Linkson and coworkers summarized the computer methods for construction of the Pourbaix diagrams and categorized into three methods; that is, Point-by-Point method, Line elimination method and Convex polygon method.

P. B. Linkson, B. D. Phillips, and C. D. Rowles, "Computer Methods for the Generation of Eh-pH Diagrams," Minerals Sci. Engng., 14(2), 65-79(1979).

Since the convex polygon method is the most advanced and elegant algorithm, almost all recent methods are based on the convex polygon method.

Old CHD program for constructing the generalized chemical potential diagrams is also based on the polygon method. More generalization, however, has been achieved in our previous algorithm, that is, adoption of the formation reaction as basic equation, no need of selecting one redox element, generalized selection of coordinate axes and so on.

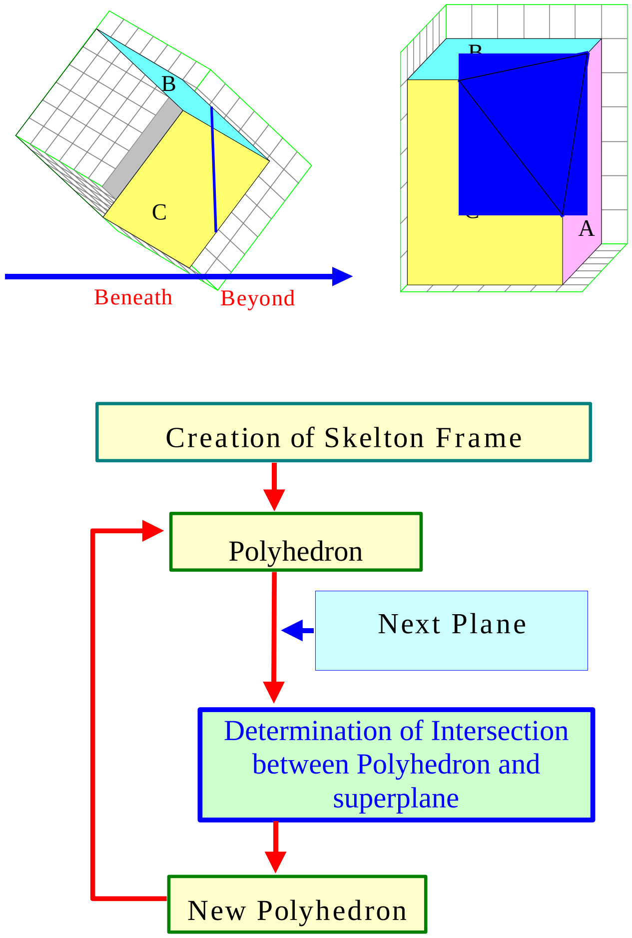


Fig. 2.12 Convex polyhedron approach to constructing the chemical potential diagram.

The present new method aims at extending this method to more flexible one and making applicable to multicomponent systems. Since the algorithm is based on the three dimensional polyhedron, this can be called as "Convex Polyhedron Approach."

The main point of the convex polyhedron approach is to obtain the intersection between a previously obtained polyhedron and a new plane. The intersection is obtained as follows;

1) a polyhedron consists of facets, edges and vertices.

2) For respective vertices, judgment will be made on whether the vertex is beneath or beyond the plane.

4) ***Between the beneath vertex and the beyond vertex, a new vertex point can be obtained as the intersection point of the edge and the new plane.***

5) ***New vertices can be connected with each other to form new edges and a facet. This facet forms the intersection.***

6) ***The beyond vertices can be deleted to form a new polyhedron having the new facet in it.***

Merits of Convex Polyhedron Approach

The present polyhedron approach has many merits as a computer algorithm. This can be briefly explained below.

Computer geometrical considerations are the basis of constructing chemical potential diagrams. This makes it possible to divide complicated procedures into two independent procedures:

(1) Geometrical procedures based on the features of vertices, edges and facets are common to any kind of diagrams. This is based on the geometrical features alone and does not need any numerical calculations.

The geometrical judgment is made by using the convexity of the two planes. As shown in Fig 2.13, the thermodynamic relations given in the Gibbs energy(chemical potential) vs. composition plot can be re-plotted in the chemical potential-chemical potential plot. In the Gibbs energy vs. composition plot, the stable phases are represented as lines which located at the lowest part, and those sable phases form convex relations in the downward direction. The same relations plotted in the chemical potential-chemical potential plot have the similar features; that is, the stable phase is represented by a line which dissects the lowest parts and the stable phases form the convex polygon.

This makes it possible to extend easily to multi component systems. The basic relations to be used in the geometrical considerations are the convexity of the intersected planes. When the n-component system is considered, the super plane is given by one equation and the intersection of the super planes is determined by two equations.

This is also makes it possible and easy to include the temperature or pressure as coordinate axes. As shown in Fig. 2.13, the same convexity can be applied to the temperature dependent phase. Here, the chemical potential can be given as a function of temperature. In a unary system, the chemical potential is equal to the Gibbs energy. In the chemical potential vs. temperature plot, the stable phase is always the lowest value at the given temperature. When the stable phase is changed, the convexity appears in this plot. The same geometrical features can be obtained in the chemical potential divided by RT vs. inverse temperature as given in Fig. 2. 13.

(2) Numerical Calculations

Several judgments are made by numerical calculations independently of the geometrical consideration. For example, the following procedures require the numerical calculations.

(a) Beneath-beyond criterion for a plane against respective points (Vertices) This is quite important judgment. Whenever one plane is considered in a geometrical convex polyhedron, this judgment is required.

(b) Derive an Intersection between An Edge and A Plane

This is the most frequently appearing procedure. This intersection point usually becomes a new vertex.

(c) Derive An Edge between Two Vertices

When all phases involved are stoichiometric compounds, this procedure is quite simple; this is the connection of two points by a straight line.

These features make it possible to treat mixture phases in a simple way. The above three calculations can be easily extended to include mixture phases.

For treatment of temperature dependent phase relations

Generalization can be made to extend to include the axes corresponding temperature and pressure by using the same geometrical considerations; that is, convexity and beyond – beneath criterion.

First, we check the equation for chemical potential. Here we have to recognize that there are two ways of adopting the reference state in representing Gibbs energy. First one is the following;

$$l\,(\mu(\mathrm{A}) - \mu^\circ(\mathrm{A})) + m\,(\mu(\mathrm{B}) - \mu^\circ(\mathrm{B})) + n\,(\mu(\mathrm{C}) - \mu^\circ(\mathrm{C})) = \Delta_\mathrm{f}G^\circ(\mathrm{A}_l\mathrm{B}_m\mathrm{C}_n) \qquad [2.8]$$

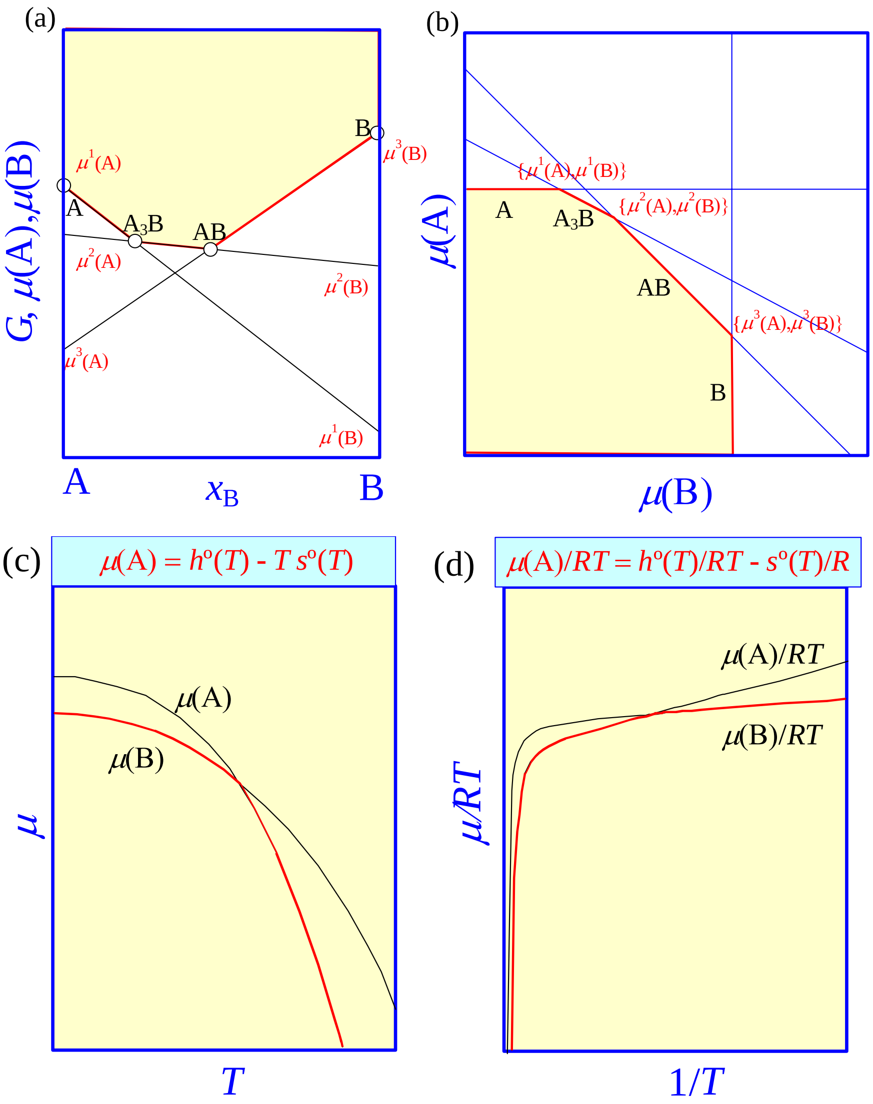


Fig. 2.13 Convexity in (a) Gibbs energy vs. composition space; (b) chemical potential space and (c,d) in the chemical potential – temperature space.

In this representation that the JANAF thermochemical table and other major data books adopt, the reference state is defined for each temperature; this can be expressed as $\mu°(A)$. Second way is

$$l\,(\mu(A) - \mu°_A) + m\,(\mu(B) - \mu°_B) + n\,(\mu(C) - \mu°_C) = G°(A_lB_mC_n) \qquad [2.9]$$

Here, the reference state is defined only at the standard temperature, 298. 15 K. This is adopted for example in the data book by I. Barin. To describe the phase relations as a function of temperature, the second method is appropriate. Note that in this representation, the element in the reference state has no longer zero Gibbs energy.

In the chemical potential diagram, usually the value of the chemical potential divided by RT is used. Correspondingly, the inverse temperature can be adopted to be consistent with the treatment of chemical potentials:

$$\begin{aligned}
&\{-h°(A_lB_mC_n)/R\} \quad \{1/T\} \\
&+ \quad \{l\} \quad \{(\mu(A) - \mu°_A)/RT\} \\
&+ \quad \{m\} \quad \{(\mu(B) - \mu°_B)/RT\} \\
&+ \quad \{n\} \quad \{(\mu(C) - \mu°_C)/RT\} = -s°(A_lB_mC_n)/R \qquad [2.10]
\end{aligned}$$

Here,

$$G°(A_lB_mC_n) = h°(A_lB_mC_n) - s°(A_lB_mC_n)\,T \qquad [2.11]$$

where $h°(A_lB_mC_n)$ and $s°(A_lB_mC_n)$ are the enthalpy and the entropy of the compound $A_lB_mC_n$.

In Fig. 2.13, the convexity is compared in various spaces; in the G-x plot (a), the convexity appears in the downward, whereas in the $\mu(A)$ - $\mu(B)$ plot, it appears in the right-upper direction. In the μ - T plot (c), it appears in the same manner as (b). In the last μ/RT- $1/T$ plot (d), it appears in the left – upper direction.

In Fig. 2.14, an example of the generalized chemical potential diagram including the inverse temperature as axis is shown for the Mn-O system. Oxygen gas is also included in this case. Its chemical potential divided by RT decreases increasing temperature; the same behavior can be seen for manganese. From the equation [2.10], it is easily understood that a slope in μ/RT- $1/T$ plot means minus enthalpy and the intersection at $1/T$=0 indicates minus entropy value. Always, entropy of elements increase with increasing temperature.

Binary oxides in the $\mu(Mn)/RT$-$\mu(O)/RT$- $1/T$ plot appear in a different manner. At a constant temperature, the chemical potential diagram behaves like in Fig. 2.13(b). In Fig. 2.14, this can be seen as the dissection at the lowest temperature. With increasing temperature (decreasing inverse temperature), the chemical potential values change with a positive slope in the plot. This corresponds to the fact that the enthalpy change for formation of compounds is usually negative.

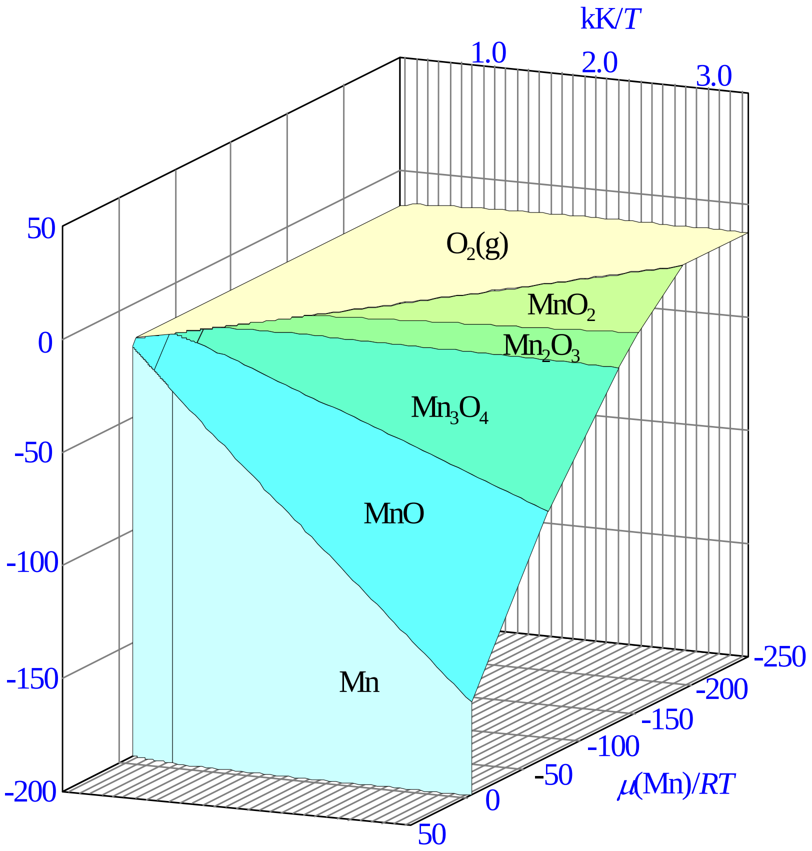


Fig. 2.14 Generalized chemical potential with inverse temperature for Mn-O system.

Along the boundaries with $p(O_2)$=1 atm, the manganese chemical potential decreases with lowering temperature. This is completely opposite behavior against the manganese chemical potential in Mn metal.

The decomposition of binary oxides can be represented by the geometrical feature that the stability region of one compound disappears at the higher temperatures. For example, in Fig. 2.14, the three phase point of $MnO_2/Mn_2O_3/O_2$(g) indicates that MnO_2 decomposes into Mn_2O_3 as follows;

$$MnO_2 = 0.5\ Mn_2O_3 + 0.25\ O_2(g) \qquad [2.12]$$

Similarly, the decompositions of Mn_2O_3, Mn_3O_4, MnO can be seen in Fig. 2.14.

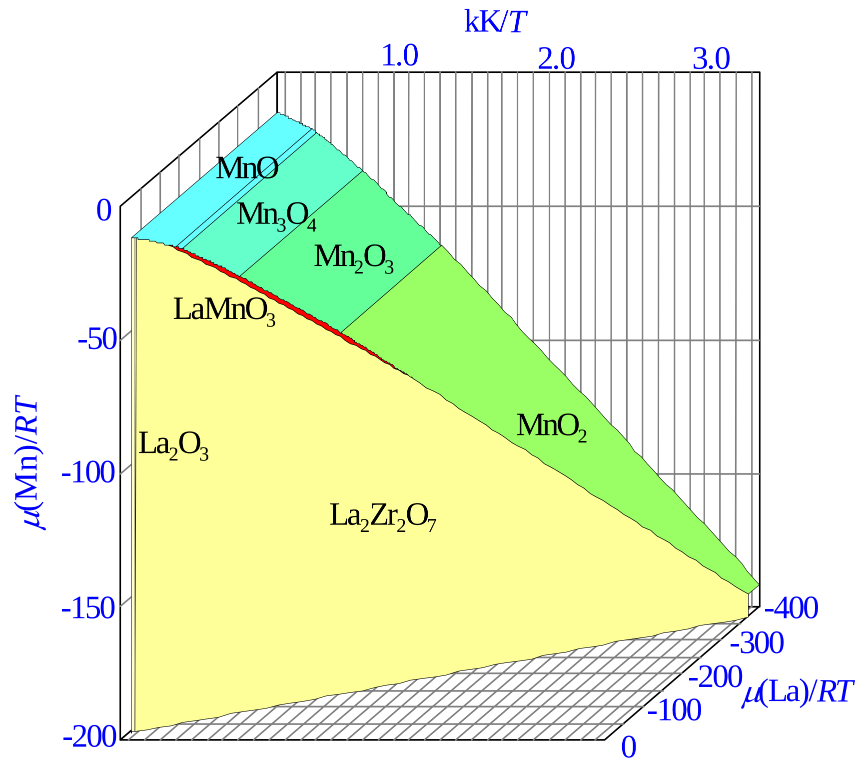


Fig. 2.15 Generalized chemical potential with inverse temperature for La-Mn-Zr-O system under the conditions of $p(O_2)=1$ atm $a(ZrO_2)=1$.

From the chemical potential point of view, there is an interesting feature in Fig. 2.14; that is, μ/RT-can be lowered with decreasing temperature in binary oxides, although this kind of behavior could not be seen in elements.

In Fig. 2.15, another example is shown for the generalized chemical potential diagram with inverse temperature. Since the La-Zr-Mn-O system has 5 freedom in the chemical potential – temperature space, two chemical potential values should be fixed to obtain the three dimensional surface chemical potential diagram. In Fig.2.15, oxygen partial pressure is fixed at 1 atm and also the activity of zirconium oxide is fixed at unity. This condition is convenient to see the reactivity of ZrO_2 with $LaMnO_3$.

In this figure, there are several points to b e noted :

1) $\mu(Mn)/RT$ in the manganese oxides decreases with decreasing temperature. This corresponds to the fact described above on the behavior along the MnO_n-$O_2(g)$ boundaries.

2) $La_2Zr_2O_7$ phase appears instead of La_2O_3 because ZrO_2 is always available to form the zirconate.

3) the stability area of $LaMnO_3$ appears between manganese oxides and $La_2Zr_2O_7$. This means that in this region, $LaMnO_3$ can stably coexist with

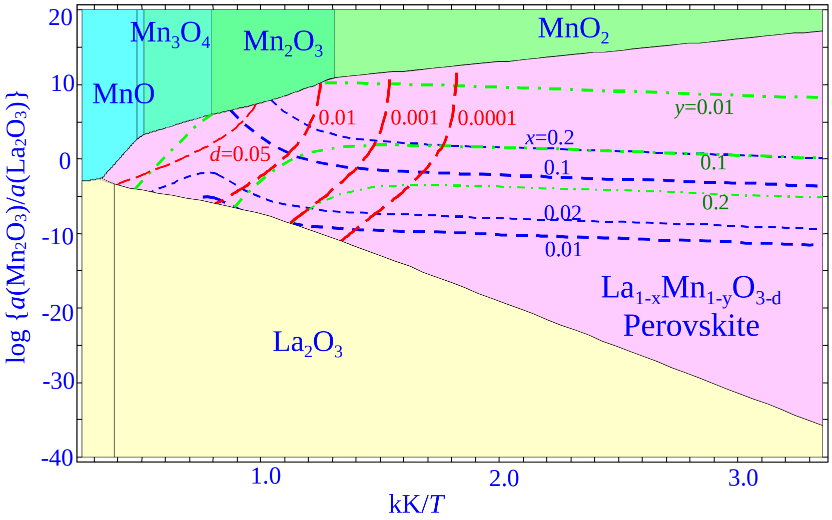


Fig. 2.16 Generalized chemical potential with inverse temperature for La-Mn-O system under the conditions of $p(O_2)=1$ atm with additional lines for constant substoichiometric values for La, Mn and O stoichiometry.

ZrO_2. Note that this area is limited at both high and low temperatures. This can be written down as follows;

$$LaMnO_3 + ZrO_2 + 0.25\ O_2(g) = 0.5\ La_2Zr_2O_7 + MnO_2 \qquad [2.13]$$

$$LaMnO_3 + ZrO_2 = 0.5\ La_2Zr_2O_7 + MnO + 0.25\ O_2(g) \qquad [2.14]$$

It is interesting to note that both reactions are related with oxidation or reduction of manganese ions.

Framework and Points in the stability region

The generalized chemical potential diagram consists of frames which gives the borders among the stable phases. This gives the information of phase equilibria and related chemical reactions.

On the other hands, each point inside stability polygons exhibits one thermodynamic state that should be characterized in terms of defects. Relation between defect concentration and the chemical potentials is not trivial so that it will be needed to have a simple model to correlate the defect properties and the chemical potentials. In such a case, it will be straight-fold that the diffusion properties will be discussed in the chemical potential space.

Fig.2.16 shows the chemical potential diagram for the La-Mn-O system in which the perovskite phase is treated with an ideal association model to represent the La, Mn, and oxygen nonstoichiometries. Each point inside the stable field of $LaMnO_3$ phase has the different stoichiometric numbers. It will give some information how those cations and anions have the vacancies and exhibit the diffusivities.

2.4 Applications of generalized chemical potential diagrams

Use as stability diagram, predominance area diagram

This is one of the conventional ways of utilization of chemical potential diagram. One element is selected; this is frequently called “redox element.” The diagram shows the stable chemical forms of these elements as functions of environmental chemical potential values. By “environmental” valuables, it means that these values are controllable. This implicitly assumes that the chemical species which represents the environmental conditions can easily interact with those substances which contain the redox element.

Fig. 2.17 indicates that the stability diagram or the predominance area diagram is based implicitly on the situation that the diffusion of oxygen gas and its interaction with the solid materials is sufficiently fast so that any gradient of oxygen chemical potential will appear in the system.

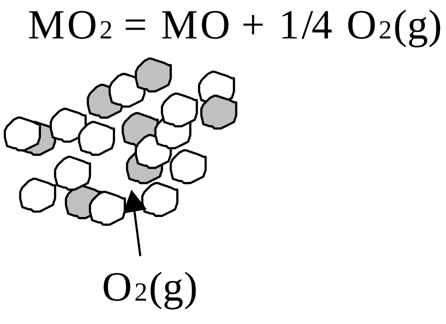


Fig. 2.17 Phase equilibria and environmental chemical potential. Oxygen gas can freely penetrate into any parts of the system to realize phase equilibria.

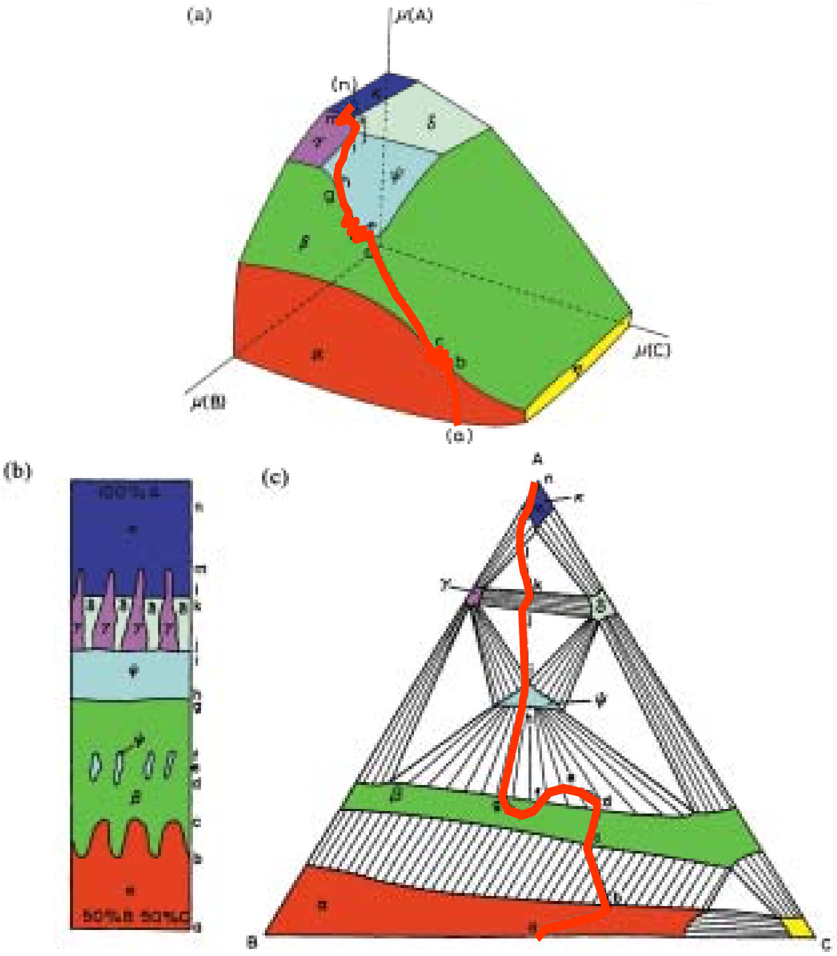


Fig. 2.18 Interface reaction and associated with reactive diffusion path in the compositional diagram and in the chemical potential diagram.

Use as Compatibility diagram or Reactive diffusion path plotter

The generalized chemical potential diagram can treat alloys or complex oxides as well. That is, the stability of such materials can be easily examined as functions of environmental valuables. In addition, this can be applied to examine the chemical compatibility of different materials. When two materials are in equilibrium with each other, their stability regions should be adjacent in the chemical potential space. It is a quite simple criterion.

When two materials are not in equilibrium, there appears driving force for chemical reactions and/or interdiffusion across the interface of two materials.

Chemical reaction and associated interdiffusion will provide a microstructure of a developed reaction zone as shown in Fig. 2.18. To examine how the chemical reaction and interdiffusion proceed at the interface, it becomes common to plot the reactive diffusion path in the compositional phase diagram particularly in the alloy systems. As shown in Fig. 2. 18, such reactive diffusion path exhibits quite complicated features in the compositional diagram. In some cases, elements diffuse against the compositional gradient. This is called up-hill diffusion and is expressed by the path having the backward direction.

In the chemical potential diagram, the reactive diffusion path can be drawn as well. Since the diffusion is driven from the chemical potential difference, it is reasonably understood that the reactive diffusion path in the chemical potential diagram becomes very simple as shown in Fig. 2. 18. Although there had been discussed many conventional points on how to represent the reactive diffusion path in the compositional diagram, it is essentially no need to set the conventions in the chemical potential diagram.

Chapter 3 Instruction

Let's Use CHD for Windows

In Chapter 3, the fundamental methods of running CHD for Windows will be described.

This chapter consists of the followings;
1. MALT/CHD Interface
2. Set up a Typical Diagram
3. Fixation of Chemical Potentials
4. Three Dimensional (Polyhedron) Diagram for Multicomponent System
5. Non-Chemical Potential Variables

3.1 MALT/CHD Interface

In order to utilize CHD for Windows, it is essential to be familiar with MALT for Windows. Almost all thermodynamic data to be used in CHD for Windows will be supplied from the MALT database and its facility for treating data. This data set is called a “compound system.” In this section, the essential part given in the manual for MALT for Windows will be reproduced.

MALT for Windows provides the computer programs, CHD for constructing chemical potential diagrams and gem for calculating complicated chemical equilibria. Compared with chemical equilibrium calculations, utilization of chemical potential diagrams is not popular. Even so, chemical potential diagrams are quite convenient for materials thermodynamics. Here, explanation will be made only on how to construct the chemical potential diagram by using the thermodynamic data stored in MALT.

1) prepare the thermodynamic data for a selected chemical system;
2) run the computer program, CHD;
3) specify the conditions to construct the chemical potential diagram for the selected system;

4) do calculation based on the polyhedron approach for constructing the generalized chemical potential diagrams;
5) display the obtained diagram;
6) manipulate the diagram upon some requirements for dissection, touch etc.

3.1.1 Preparation of the compound system in MALT for Windows

As an example to construct the chemical potential diagram, we will use the Ca-O-C system. To retrieve the thermodynamic data, you can do the same procedure given as Section 3.3 in the MALT user's manual; that is, select the "Get a Compound System" menu with the option of "Selection by Elements." Ca, O, C should be selected together with the mode of "compounds consisting of combination of elements." This retrieval mode is very convenient for the construction of chemical potential diagrams.

3.1.2 Run the computer program, CHD

Here, it is ready to run the CHD program. The easiest way of running "CHD" is the selection of the "CHD" command in the "Tools" main menu. This command is to execute the following command

```
"CHDWin.exe /md"
```

The meaning of the switch "/md" is that the command "MALT Direct" will be made after the initialization procedure.

Another way to run the CHD is to use the short cut. In the link field in the "property" dialog for short cut, the name of "CHDWin.exe" is usually given. In this field, "/md" can be added. In such a case, whenever CHDWin starts, the first command "MALT Direct" is performed. When it is succeeded, the thermodynamic data of the current compound system is transferred. When it is failed, the message of "MALT is not running" appears.

Fig. 3.1 shows the resulting "CHD" main form after executing the MALT Direct" command.

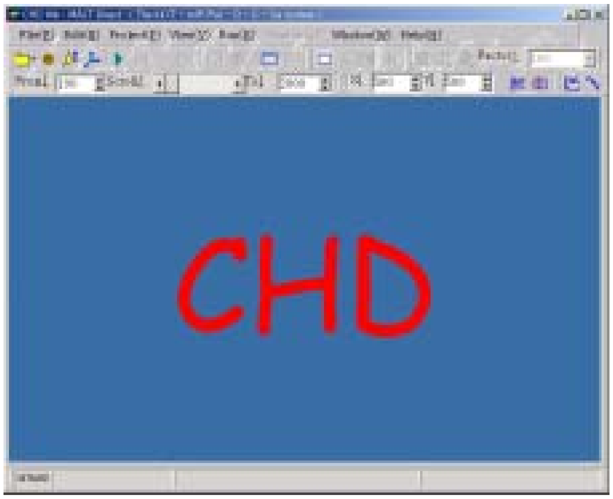
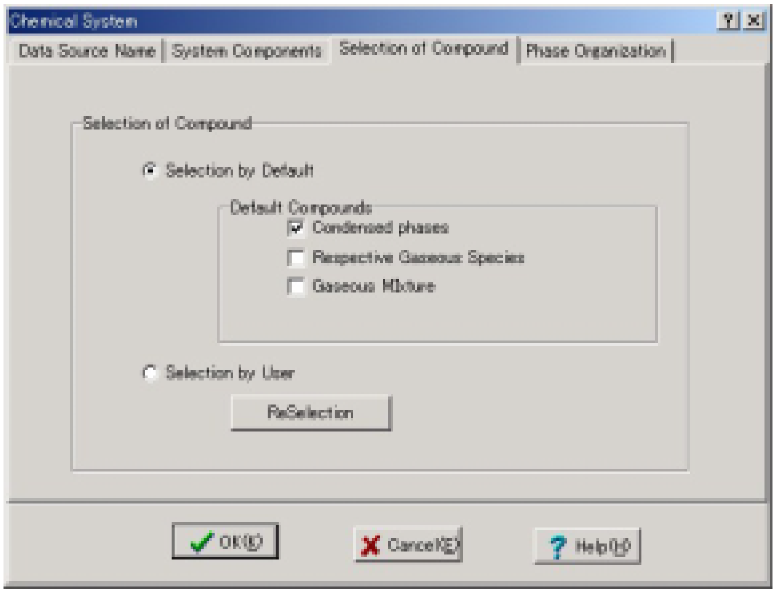


Fig. 3.1 CHD Main form after selecting “CHD” in the “Tools” menu.

In the title line of the Main Form, it is indicated that data are obtained by MALT Direct for the Ca-O-C system,

The next line is the menu bar, whereas the second line indicates the tool buttons for selected commands given in the menus. The status line is located in the bottom of the Main form.

The main menu consists of Files, Edit, Project, View, Run, Diagram, Windows



Selection of Compound

● Selection by Default

Default Compounds

☑ Condensed phases

☐ Respective Gaseous Species

☐ Gaseous Mixture

○ Selection by User

Fig. 3.2 Chemical System Form with the page for Selection of Compound.

and Help.

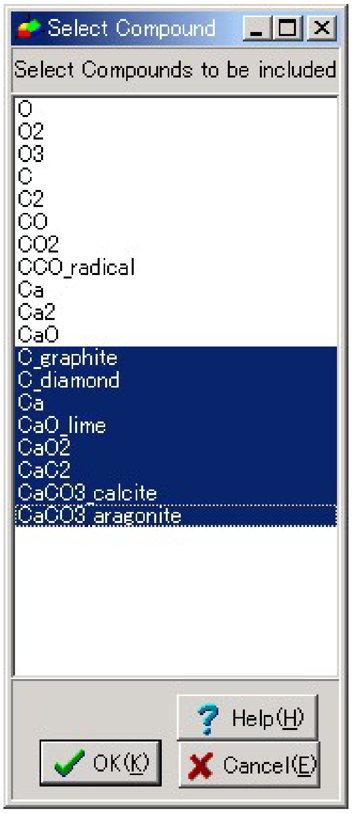
3.2 Set up a Typical Diagram

3.2.1 Specification of Chemical System

In order to construct a chemical potential diagram, many parameters should be defined. In the “CHD” program, such parameters are given as default values in many cases.

In the situation given in Fig. 3.1, the CHD is ready to construct a diagram by using default values given for this system. Even so, users may have some idea what kinds of diagrams they want to construct. This is made in the “Chemical system” submenu and the “Specify diagram” submenu in the “Project” main menu .

MALT Direct provides the chemical system that has already organized as a system consisting of the gaseous mixture, aqueous solution and condensed



O
O2
O3
C
C2
CO
CO2
CCO_radical
Ca
Ca2
CaO
C_graphite
C_diamond
Ca
CaO_lime
CaO2
CaC2
CaCO3_calcite
CaCO3_aragonite

Fig. 3.3 Select Compound for “Selection by User” for compounds to be included in construction of diagrams.

phases. Usually, the chemical potential diagram is constructed for condensed phases. In what follows, we accept this default setting for chemical system.

Even so, there are some needs to include gaseous mixture or respective gaseous species. This can be made in the page of “Selection of Compound” in the “Chemical System” Form as shown in Fig. 3.2.

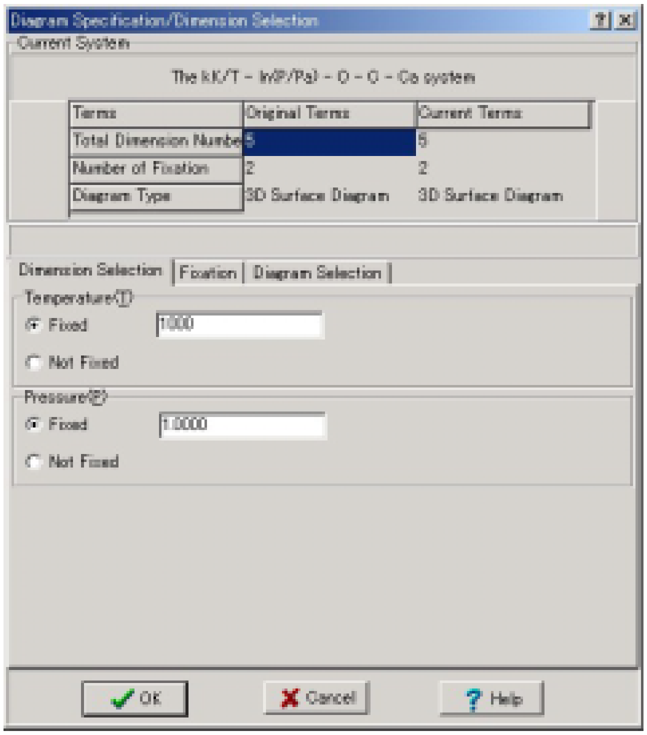
Selection can be made between “Default” treatment or “Selection by User." When “Default” is selected, compounds to be included can be selected from 1) Condensed phases, 2) respective aqueous species, 3) and gaseous mixture.

When some compounds are to be excluded or included, “Selection by User” can be selected. Clicking the “Reselection” button leads to the appearance of the Select Compound Form as shown in Fig.3.3.

This setting for the Default selection will be stored in “CHDWin.ini” file.

3.2.2 Specification of calculation conditions

When the “Specify Diagram” submenu in the “Project” menu is selected, the



Current System

The kK/T - ln(P/Pa) - O - O - Ca system

Terms	Original Terms	Current Terms
Total Dimension Numbe	5	5
Number of Fixation	2	2
Diagram Type	3D Surface Diagram	3D Surface Diagram

Temperature(T)

● Fixed 1000

○ Not Fixed

Pressure(P)

● Fixed 1.0000

○ Not Fixed

Fig. 3.4 Diagram Specification for giving the selected values for temperature and pressure.

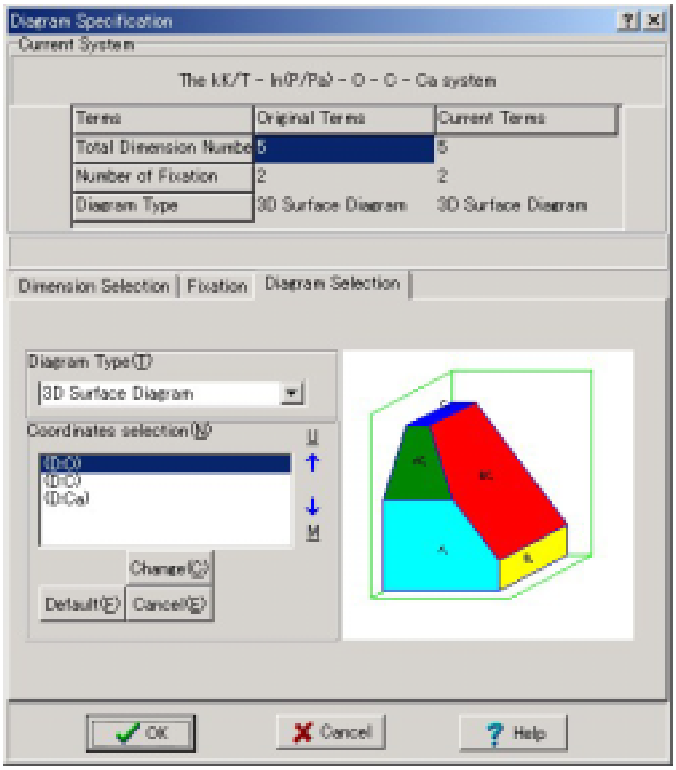
“Diagram Specification” Dialog will appear as shown in Fig. 3.4.

In the upper part of Fig. 3.4, the information of the current system is given to make a proper selection of the parameters. The current Ca-O-C system is the 5 component (dimension) system including temperature and pressure. For a system which has more than 5 dimensions, default setting of the fixation is made to fix temperature and pressure. Usually, pressure is set as 1 atm, whereas temperature is set at 298.15 K.

In Fig. 3.4, there are 3 tabsheets for specification of conditions.

The first tabsheet of “Dimension” is for determination of temperature and pressure. Since default temperature is 298.15 K, this value is changed to 1000 K in Fig. 3.4.

In the second tabsheet of “Fixation” is for further fixation of component (dimension) properties. In the current system, we have three free dimensions that is the appropriate number for constructing the chemical potential diagram for the Ca-O-C system. We do not need to specify in this tabsheet for the current system.



The kK/T – ln(P/Pa) – O – C – Ca system

Terms	Original Terms	Current Terms
Total Dimension Numbe	5	5
Number of Fixation	2	2
Diagram Type	3D Surface Diagram	3D Surface Diagram

Diagram Type(T): 3D Surface Diagram

Coordinates selection(N):
(D:O)
(D:C)
(D:Ca)

Fig. 3.5 Diagram Specification for giving the selected values for Diagram selection.

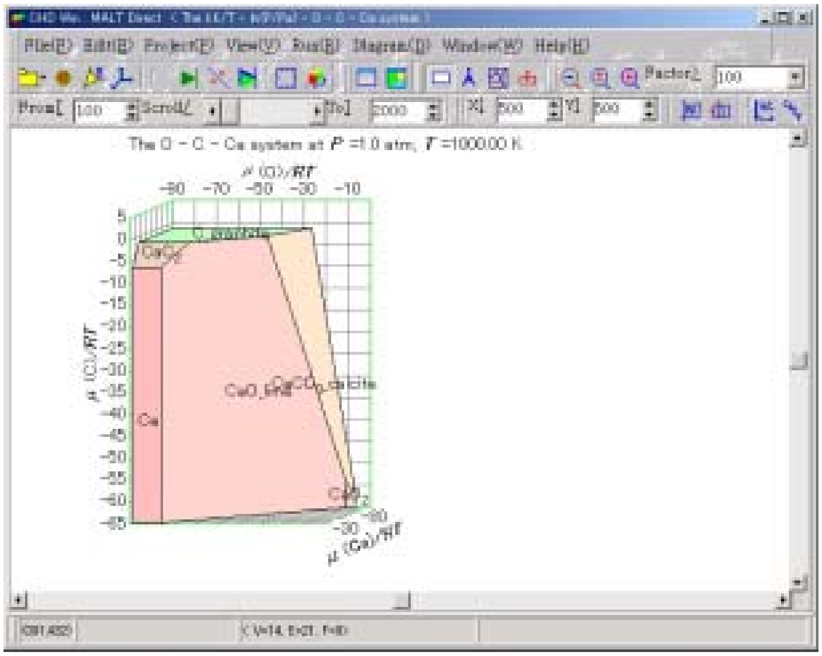


Fig. 3.6 Three dimensional surface diagram for the Ca-O-C system at 1000 K. This is the default type diagram.

The tabsheet of “Diagram Selection” is to specify the diagram type to be constructed. The default diagram type for the current system is the 3D surface diagram.

3.2.3 Calculation

By selecting the “Calc” submenu in the “Run” main menu, calculation starts and then a diagram will be shown, if calculation will be done successfully.

Fig. 3.6 shows the three dimensional surface diagram for the Ca-O-C system. “Three dimensional” indicates that there are three dimensions which can be changed. In this case, three dimensions mean the elemental chemical potentials of Ca, O and C. By “surface”, it means that the three chemical potentials have one relation like

$$\mu(\mathrm{Ca}) + \mu(\mathrm{C}) + 3\mu(\mathrm{O}) = \mu^{o}(\mathrm{CaCO_3}) \qquad [3.1]$$

for $CaCO_3$. This indicates that each stable compound has its own plane having the slope corresponding to its stoichiometry. Such planes form one polyhedron as shown in Fig. 3. 3. Surface in this polyhedron indicates the thermodynamic stable states. Inside polyhedron is thermodynamically inaccessible.

3.2.4 Diagram Rotation

For the three dimensional surface diagram, it is important to determine how to draw the three dimensional information on the two dimensional plane. This is made by adopting the conversion parameters as follows:

$$U = a_{11}\,x + a_{12}\,y + a_{13}\,z \qquad [3.2]$$

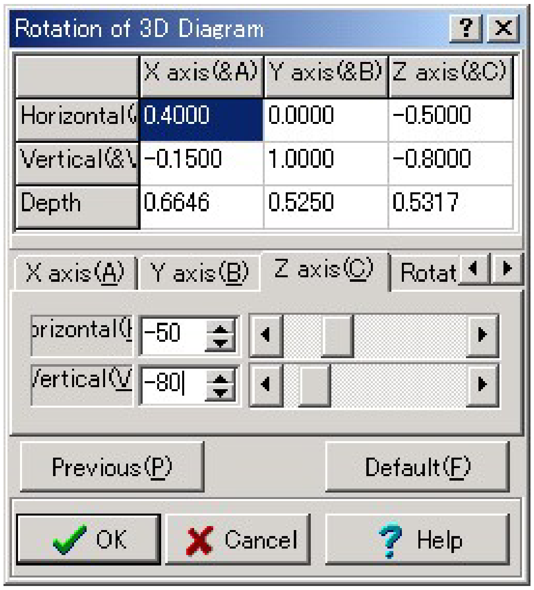
$$V = a_{21}\,x + a_{22}\,y + a_{23}\,z \qquad [3.3]$$

Where U and V are the coordinates of a new two dimensional display panel and x, y, z are the coordinates of the three dimensional surface diagram. This conversion is a part of the conversion from a three dimensional space to another three dimensional space. The invisible third coordinate can be called "Depth, w."

$$W = a_{31}\,x + a_{32}\,y + a_{33}\,z \qquad [3.4]$$

Rotation of the three dimensional surface diagram is realized by changing these coefficients. This is made in the "Rotation of 3D Diagram."

Fig. 3.7 shows the "Rotation of 3D Diagram" dialog, where the conversion coefficients are given in the upper part.



	X axis(&A)	Y axis(&B)	Z axis(&C)
Horizontal(	0.4000	0.0000	-0.5000
Vertical(&V	-0.1500	1.0000	-0.8000
Depth	0.6646	0.5250	0.5317

rizontal(-50

ertical(V -80

Fig. 3.7 Rotation of 3D Diagram

The coefficients can be changed by two different ways: the first is to change directly the coefficients in the upper part. When one of matrix cells is clicked, the corresponding edit field is focused among given spin edit fields. This field can be directly edited by inputting numerical keys or by clicking the upward or the downward arrow buttons. The second is to use scroll bars prepared for respective axes. Furthermore, scroll bas are prepared for rotations around respective axes.

Here, we change the coefficients as follows;

X-axis

Horizontal	100	=>	40
Vertical	0	=>	-15

Z-axis

Horizontal	-50	=>	-50
Vertical	-20	=>	-80

3.2.5 Diagram Color

The diagram can be draw in black/white mode or in color mode. In color mode, several ways can be adopted to give colors for respective polygons. These are

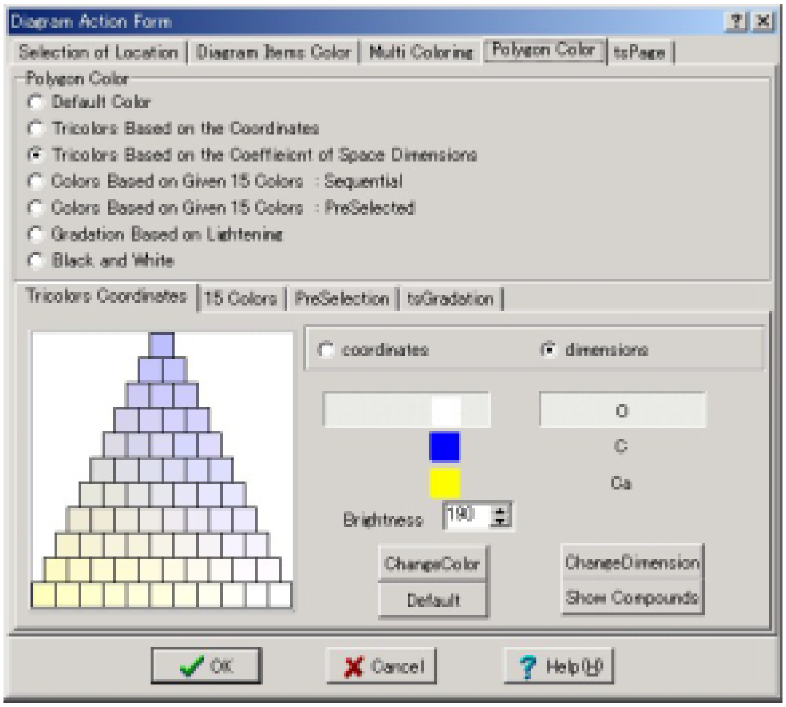
1) Tricolors based on the coordinates;
2) Tricolors based on the coefficients of space dimensions;
3) Colors based on Given 15 colors: Sequential
4) Colors based on Given 15 colors: Preselection.

Fig. 3.8 shows how to define the color in the diagram, where "Tricolor based on the coefficients of space dimensions" is adopted; In this particular diagram, the dimensions of μ(O), μ(C), μ(Ca) are used and the colors of "white", "blue" and "yellow" are attributed. By this attribution, respective polygons can be given according to their stoichiometric numbers. These colors can be shown by clicking the "Show Compound" button in the Form.

3.2.6 Summary of procedures

[Compound System]

Selection of <Ca,C,O> system



Polygon Color
○ Default Color
○ Tricolors Based on the Coordinates
● Tricolors Based on the Coefficient of Space Dimensions
○ Colors Based on Given 15 Colors : Sequential
○ Colors Based on Given 15 Colors : PreSelected
○ Gradation Based on Lightening
○ Black and White

○ coordinates ● dimensions

Brightness 190

Fig. 3.8 Diagram Action Form / Page for Polygon Color

Here, the same Ca-C-O system is used.

[Project / Chemical System]

<Chemical System> Dialog
{Selection of Compounds} Page
Selection by Default
x Condensed phases
o Respective Gaseous Species
o Gaseous mixture

[Project / Specify Diagram]

<Diagram Specification> Dialog
{Dimension Selection} Page
Temperature
x Fixed at 1000 K
o Not Fixed
Pressure
x Fixed at 1 atm

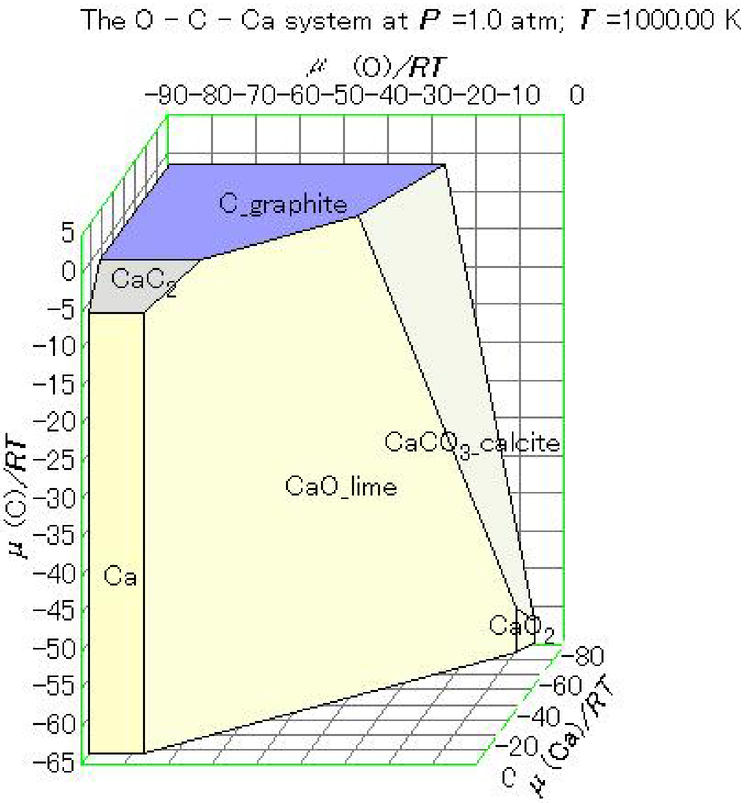


Fig. 3.9 Three Dimension Surface Diagram for the Ca-C-O system at 1000K after correction for Diagram Rotation.

o Not Fixed

[Run / Calc]

[Diagram / Rotate]

<Rotation of 3D diagram> Dialog

X-axis Horizontal 100 => 40

Vertical 0 => -15

Z-axis Horizontal -50 => -50

Vertical -20 => -80

As a result, the following matrix values are obtained

0.4 0.0 -0.5

-0.15 1.0 -0.8

[Diagram/Options]

<Diagram Action Form>

{Polygon Colors} Page

Tricolors based on the coefficients of space dimensions

“white”	O
“blue”	C
“yellow”	Ca

3.2.7 Diagram for the La-Mn-O system

This is given in Diagrams examples in CHD manual.

3.3 Fixation of Chemical Potentials

One of the merits of the generalized chemical potential diagram is that this can be applied to multicomponent systems with fixation of an appropriate number of chemical potentials. Here, we construct the chemical potential diagram for the La-Mn-Zr-O system at a constant temperature.

3.3.1 Obtain the thermodynamic data for the La-Mn-Zr-O system

In MALT for Windows, the chemical system of the La-Mn-Zr-O system is selected.

The thermodynamic data for the system is transferred into CHD by using “MALT Direct.”

3.3.2 Specification of chemical system

No further specification will be made in the calculation.

3.3.3 Fixation for Diagram construction

Temperature is fixed at 1273 K and pressure is fixed at 1 atm in the “Dimension Selection” page.

Then, “Fixation” page is selected. In Fig. 3.10, the appearance of “Fixation” page is shown. There are “List of Fixed values” box in the top and “Dissection to be created” box in the bottom. In the “List of Fixed Values box”, buttons for “Add”, “Change”, “Delete” and “Cancel” are available.

When “Add” button is selected, “Select Fixed” Dialog will appear like given in Fig. 3.10. First, selection is made among the “type of fixation.” Here, the

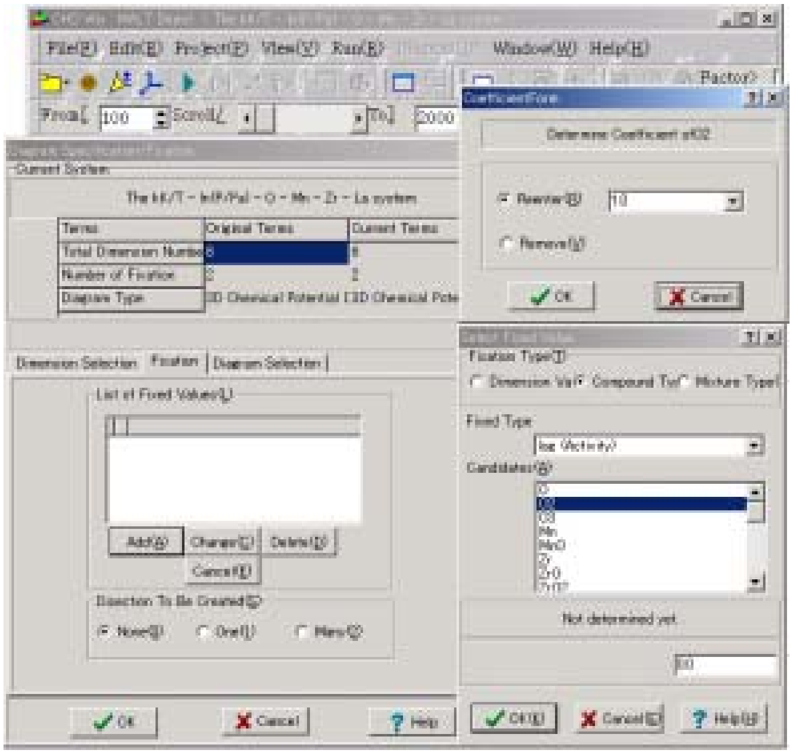


Fig. 3.10 Fixation of chemical potential is made by the following sequence:(1) click “Add” button;(2) Select the Fixation Type and corresponding dimension of species by double clicking (3) Determine the coefficient.

partial pressure of oxygen gas is to be fixed at one atmosphere. For this purpose, the “compound type” is first selected. After clicking the compound type , then, list of compounds is given. Fixed type can be selected among the given list. Usually, log(activity) is selected as default and there is no need to change it.

“O2 g” can be selected by moving the cursor with arrow keys and double clicking or hitting the “cr” key. The next dialog “Coefficient Form” appears as given in Fig. 3.10. Selection should be made among “Reenter” and “Remove”. This is for editing the linear combination of chemical potentials. Fixation can be made using the following linear equation:

$$a\,\mu(\mathrm{X}) + b\,\mu(\mathrm{Y}) + c\,\mu(\mathrm{Z}) + \ldots = A \qquad [3.5]$$

Here, X, Y, Z are the compound and *a b c* are the coefficients to be determined for respective chemical potentials. The value, *A*, should be determined at the bottom of in the “Select Fixed Value” dialog.

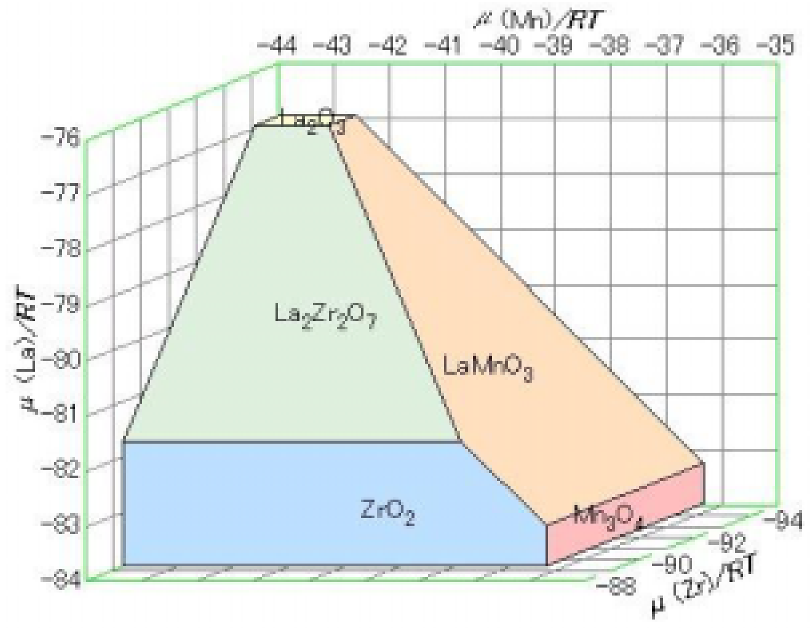


Fig. 3.11 The chemical potential diagram for the La-Mn-Zr-O system at 1273 K and under $p(O_2) = 1$ atm.

“Remove” in the “Coefficient Form” is given for the purpose to remove the already selected compound and its coefficient from the given linear combination.

“Reneter” means to define the coefficient for the selected compound.

Here, “Reenter” and “coefficient”=1.0 are selected.

After selection is made, this “Coefficient Form” disappears and the selected function of linear combination appears instead of the “Not determined yet” message. The default value for the “Fixed Value” is set as 0.0. This means that the logarithmic activity of selected compound is zero, that is, the activity is equal to unity.

“Diagram Selection” page can be then selected to define the diagram coordinates. The present system is the four-component system and already one chemical potential is fixed so that the normal three dimensional surface diagram can be constructed. Here, the default diagram type is selected, namely, the three dimensional surface diagram. The coordinates of this diagram can be selected. Candidates for selecting the coordinates are given as list. Since the oxygen gas is selected to fix the chemical potential, the element

"O" is already removed from the list. As a result, La, Mn and Zr can be selected as coordinates.

3.3.4 Run

The diagram can be constructed by clicking "Run." The resulting diagram is given in Fig. 3.11.

This is the* La-Mn-O-Zr *quaternary system at a constant temperature.

By fixing the oxygen partial pressure at 1 atm, the diagram is constructed as a normal three-dimensional diagram. Since the oxygen potential is fixed, three chemical potentials, μ(La)/RT, μ(Mn)/RT, μ(Zr)/RT, are selected as diagram axes.

In a* ZrO_2 *plane, the chemical potential of* ZrO_2 *is equal to unity. Since the oxygen potential is fixed, the chemical potential of Zr, μ(Zr)/RT, becomes constant. Thus, the plane of* ZrO_2 *is perpendicular to the axis of μ(Zr)/RT. Similarly, the slope of respective planes is determined in terms of the stoichiometry of other elements than oxygen.

Double oxides,* $La_2Zr_2O_7$ *and* $LaMnO_3$*, appear between the respective constituent oxides.

A reaction between* ZrO_2 *and* $LaMnO_3$ *can be checked as follows;

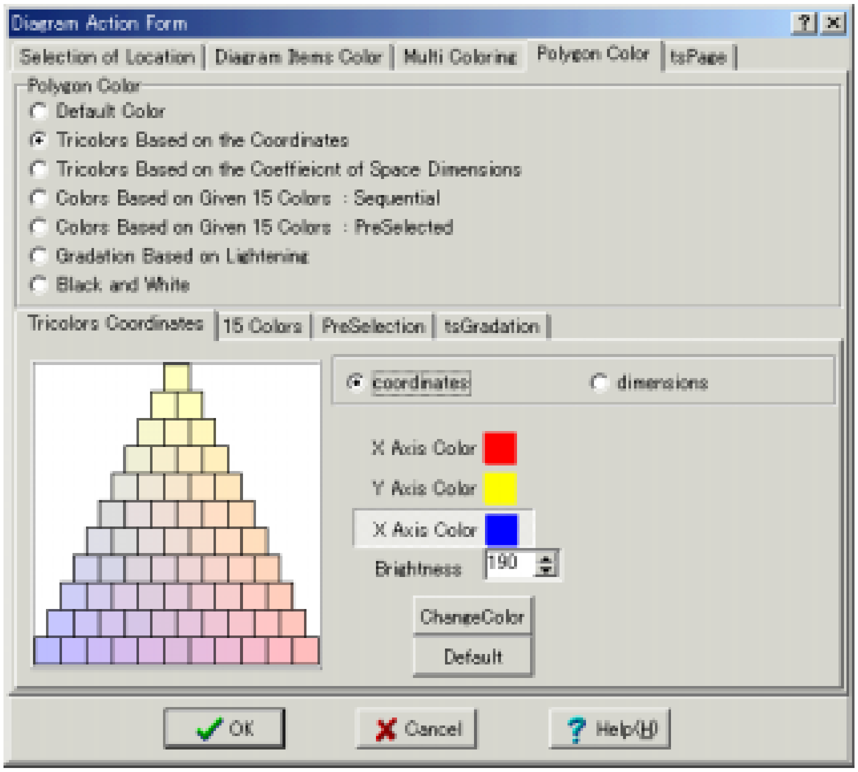
$$ZrO_2 + LaMnO_3 = 0.5\ La_2Zr_2O_7 + 1/3\ Mn_3O_4 + 1/12\ O_2(g)$$

The stability region of* ZrO_2 *is contacted directly with that of* $LaMnO_3$*, whereas the stability regions of products,* $La_2Zr_2O_7$ *and* Mn_3O_4 *are separated from each other. This means that the Gibbs energy change for the above reaction is positive.

3.3.5 Change Color

In Fig. 3.12, Tricolors based on the diagram coordinates is selected. In this option, the colors should be selected for the X-, Y-, Z- axes. By clicking on the X-, Y- or Z-axis field, the focus is moved to the field. By hitting the "Change" button, the dialog for selecting color appears. The same dialog can be also given by double clicking on the selected field.

Each flat polygon can be characterized as the coefficients of linear equation representing the flat plane;



Polygon Color

○ Default Color
● Tricolors Based on the Coordinates
○ Tricolors Based on the Coeffieicnt of Space Dimensions
○ Colors Based on Given 15 Colors : Sequential
○ Colors Based on Given 15 Colors : PreSelected
○ Gradation Based on Lightening
○ Black and White

● coordinates ○ dimensions

X Axis Color 🟥
Y Axis Color 🟨
X Axis Color 🟦
Brightness 190

Fig. 3.12 Diagram Action Form-Polygon Color page. The colors for respective polygons can be selected by choosing one mode.

$$a\,X + bY + c\,Z = 1 \qquad [3.6]$$

Color attributed from the coefficients of coordinates can be seen as triangle diagram in the left of the page.

3.3.6 Summary of procedures

[System] **Selection of <La,Mn,Zr,O> system in MALT**

[Project / Chemical System]]

<Chemical System> Dialog

{Selection of Compounds} Page

Selection by Default

x Condensed phases

o Respective Gaseous Species

o Gaseous mixture

[Project / Specify Diagram]

Diagram Specification> Dialog

{Dimension Selection} Page

Temperature
x Fixed at 1273 K
o Not Fixed
Pressure
x Fixed at 1 atm
o Not Fixed
{Fixation} Page
Add
<Select Fixed Value>Dialog
Select O2(g) Species
<Coefficient Form> Dialog
Select ReEnter 1.0
{Diagram Selection}Page
3D surface
Coordinates
(La)
(Mn)
(Zr)

[Run / Calc] ▶ ▷
[Diagram / Options]
<Diagram Action Form> Dialog
{Polygon Color} Page
(1)Tricolors based on the Coordinates
X-Axis red
Y-Axis yellow
Z-axis Blue

3.3.6 Fixation of activity of compound

There are many ways to fix the chemical potential in the multi component systems. The resulting diagram correspondingly provides the different features depending on the fixed condition. In the above section, the partial pressure of oxygen is fixed. Here, the activity of the compound is fixed.

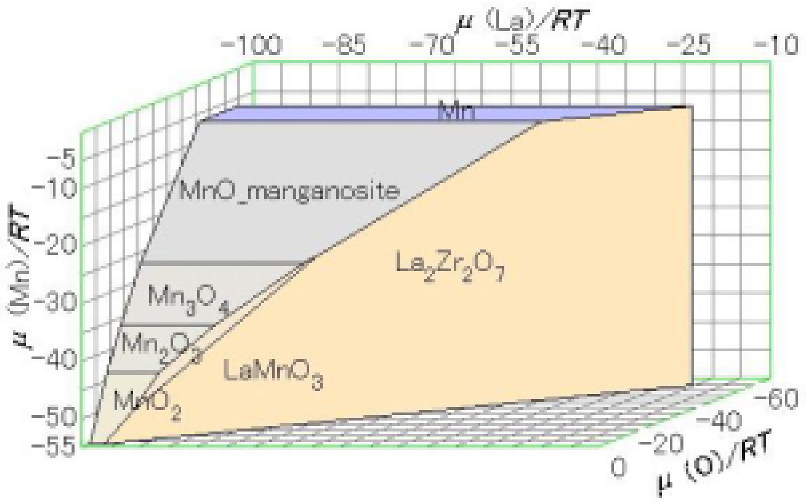


Fig. 3.13 The chemical potential diagram for the La-Mn-Zr-O system at 1273 K and under the condition of $a(ZrO_2) = 1$.

Procedures to retrieve the thermodynamic data for the La-Mn-Zr-O system and to select temperature and pressure are the same as the above section.

Fixation of the activity of ZrO_2 will be made in a similar way to the previous example. The compound type is selected in the fixation type of the "Select Fixed Value" diagram.

Construction of diagram can be made after selecting "Run" command. Fig. 3.13 shows resulting diagram.

Comparison is made with (2b) where the chemical potential diagram for* La-Mn-O *system is given.

The stability region of* La_2O_3 *is replaced by that of* $La_2Zr_2O_7$*. This corresponds to the following reaction;

$$La_2O_3 + 2ZrO_2 = La_2Zr_2O_7$$

Since the activity of* ZrO_2 *is equal to unity in the present diagram, the activity of* La_2O_3 *is fixed at a certain value in the* $La_2Zr_2O_7$ *stability region. This change in the activity of* La_2O_3 *compared with (2b) make a shift of the location of the* La_2O_3 *plane to the* $La_2Zr_2O_7$*. As a result, the three phase point of* MnO, $LaMnO_3$ *and* $La_2Zr_2O_7$ *is located at a point which has a lower* La_2O_3 *activity value. This point can be written down as

$LaMnO_3 + ZrO_2 = 0.5\ La_2Zr_2O_7 + MnO + 1/4\ O_2(g)$

Among the five chemical species involved in the reaction, three are shown as the stable phase plane, one is given as a species whose chemical potential is fixed and one is given as one of species which are used as axes of diagram.

The three phase point of **MnO_2, $LaMnO_3$** ***and*** **$La_2Zr_2O_7$** ***shows the following reaction;***

$LaMnO_3 + ZrO_2 + 1/4\ O_2(g) = 0.5\ La_2Zr_2O_7 + MnO_2$

3.4 Three Dimensional (Polyhedron) Diagram for Multicomponent System

The generalized chemical potential diagram makes it possible to construct the three dimensional diagram for the multicomponent system. Here, the La-Mn-Zr-O system is considered.

3.4.1 Construction of three dimensional diagram

When the four component system is considered, the chemical potential

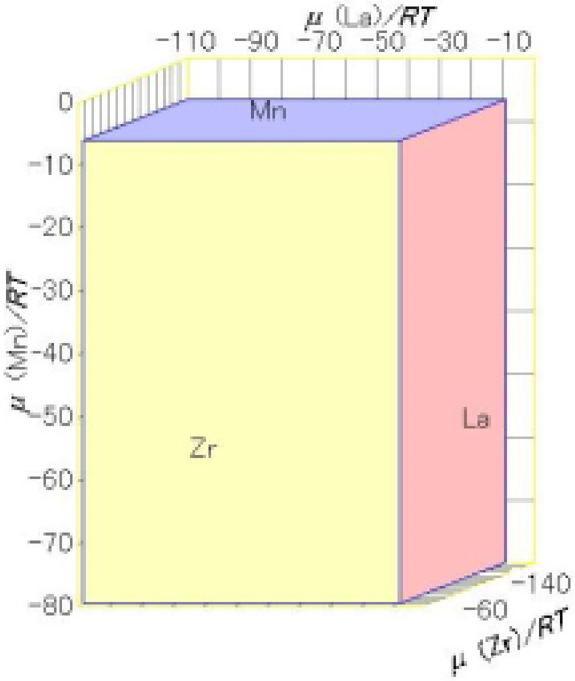


Fig. 3.14 The three dimensional chemical potential diagram for the La-Mn-Zr-O system at 1273 K. Note that other phases than Mn, La, Zr metals are not seen.

diagram can be displayed in the three dimensional manner.

The first example is the three dimension diagram with elemental chemical potential coordinates. Here, the four elemental chemical potentials are available. Out of four elements, three elements should be made. Since the La-Mn-Zr-O system consists of three metallic elements and oxygen, three metallic elements are selected as coordinates.

Fig. 3. 14 shows the three dimensional diagram for the La-Mn-Zr-O system at 1273 K. Only elements of Mn, La, Zr are visible. In any compounds, the activities of elements are lower than unity except for the cases where such compounds are in equilibrium with elements.

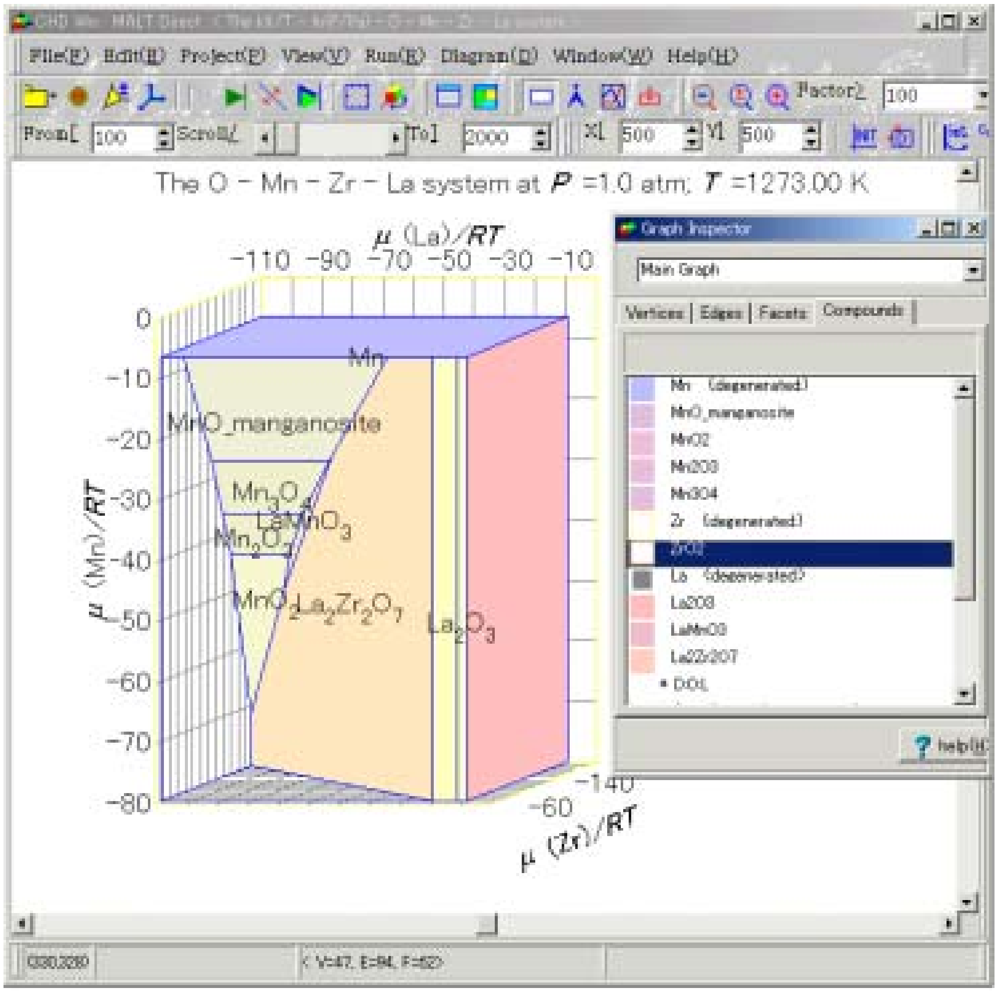


Fig. 3.15 The three dimensional chemical potential diagram for the La-Mn-Zr-O system at 1273 K under the option of Graph inspector which provides to make the phase polyhedron transparent.

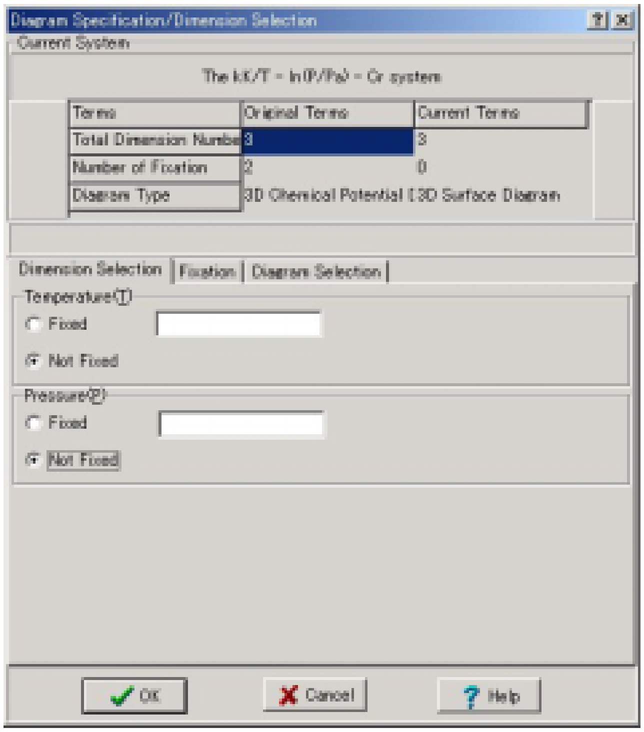
3.4.2 Non-visualization of phases

Since the three dimensional diagram consists of many polyhedrons for stable compounds, many compounds cannot be seen in the presence of other phases. Thus, the function of making the stable polyhedron transparent is necessary.

First, the “Graph inspector” dialog is selected in the “View” menu. The “compound” page is selected. The list of compounds appears with the indication of respective colors. Double clicking on the compound is switch for making the compound transparent or visible. In Fig. 3.15, Zr, La and ZrO_2 are double clicked and are turned to be transparent.

What are visible in Fig. 3.15 are the compounds which can stably exist in the presence of ZrO_2(in other words, $a(ZrO_2)=1$). Those compounds can be compared with those compounds presented in Fig. 3.13 which was obtained under the condition of $a(ZrO_2) = 1$.

3.5 Non-chemical potential variables



The kK/T - ln(P/Pa) - Cr system

Terms	Original Terms	Current Terms
Total Dimension Numbe	3	3
Number of Fixation	2	0
Diagram Type	3D Chemical Potential	3D Surface Diagram

Temperature(T)
○ Fixed
● Not Fixed

Pressure(P)
○ Fixed
● Not Fixed

Fig. 3.16 Selection of the three dimensional surface chemical potential diagram for the Cr system with coordinates of inverse temperature and with logarithmic pressure.

To select the non-chemical-potential coordinates, it is needed to select temperature and pressure as non-fixed dimension. This is made in the “Dimension selection” page in the “Chemical System” Form.

Fig. 3.16 shows the “Dimension selection” page for the Cr system. In the default setting of the system definition, temperature and pressure are fixed at 298.15 K and 1 atm. After clicking the “Non Fixed” radio buttons for temperature and pressure, the default diagram type changes to “ 3D surface diagram” in the top of the Form.

Since the Cr system contains only one condensed phase, the normal diagram contains only plane for condensed Cr phase. This diagram does not give any useful thermodynamic information. To avoid this, the Cr vapor is also included in the present construction. For this purpose, the Chemical System menu is selected and “Respective Gaseous Species” radio button should be checked in the default compound option.

Fig. 3.17 shows three dimensional surface diagram for the Cr system in the μ(Cr)-1/T-ln (P/atm) plot. In the present chemical potential diagram, there appear two stable species, namely, Cr metal (condensed phase) and Cr Vapor.

The stability region of Cr vapor is located below the stability region of Cr

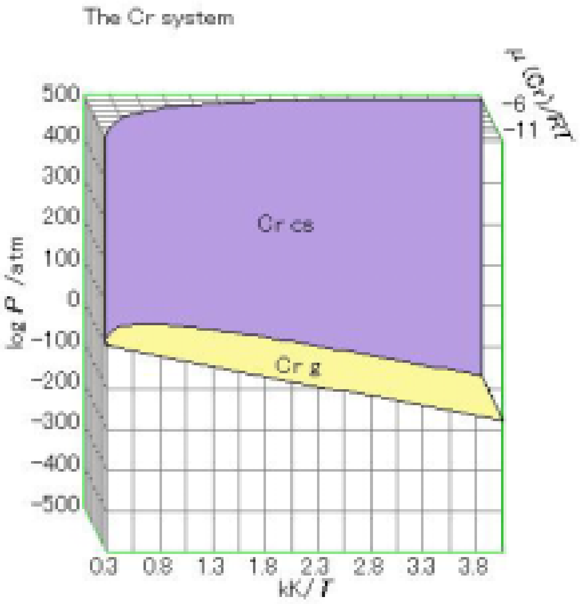


Fig. 3.17 The three dimensional chemical potential diagram for the Cr system with coordinates of inverse temperature and with logarithmic pressure.

metal. The borderline between two stability regions indicates the equilibrium vapor pressure of Cr vapor over Cr metal. In this sense, this diagram can be regarded as the generalized Arrhenius plot for the equilibrium vapor pressure. Generalization is realized in the point that the chemical potential of chromium is given for respective equilibrium point.

Next example is the Mn-O binary system. For this system, the three dimension surface diagram can be set up by adopting the inverse temperature as one coordinate and the fixed total pressure at 1 atm.

Fig. 3.18 shows the three dimensional surface diagram for the Mn-O system in the μ(Mn)-m (O)-1/T- plot

In the Mn-O systems, Mn metal, MnO, Mn_3O_4, Mn_2O_3, MnO_2 exist as stable phases. In the diagram, O_2(g), Mn(g) are also included as stable gas phases.

The intersect line between the O_2(g) plane and the frame plane at μ(Mn)/RT=-300 shows that μ(O)/RT decreases with increasing temperature (or with decreasing inverse temperature, 1/T). Similarly, decrease of μ(Mn)/RT is plotted in the frame plane of μ(O)/RT.

The chemical potential divided by RT is expressed in terms of enthalpy and entropy as follows;

$$\mu(O)/RT = (h/R)(1/T) - s/R$$

In the diagram, the enthalpy term, h/R, is expressed as a slope of the tangent plane, whereas the entropy term is expressed as intersect at 1/T=0. The values of h and s are always positive for elements so that μ(O)/RT is always going down with increasing temperature.

The borderline between Mn and Mn(g) indicates the vaporization temperature.

$$Mn = Mn(g)$$

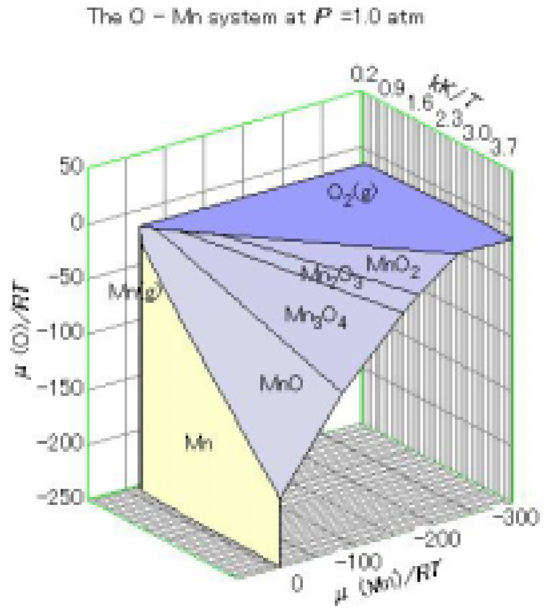


Fig. 3.18 The three dimensional chemical potential diagram for the Mn-O system with coordinate of inverse temperature.

The three phase point among $\mathbf{MnO_2}$, $\mathbf{Mn_2O_3}$, ***and*** $\mathbf{O_2(g)}$ ***indicates that*** $\mathbf{MnO_2}$ ***is reduced into*** $\mathbf{Mn_2O_3}$***. This corresponds to the following chemical reaction.***

$$\mathbf{MnO_2 = 0.5\ Mn_2O_3 + 0.25\ O_2(g)}$$

The plane of $\mathbf{MnO_2}$ ***has a negative slope for the 1/T axis. This corresponds to the negative enthalpy change for formation of*** $\mathbf{MnO_2}$***.***

Chapter 4. For Full Use of CHD

4.1 CHD Environments

CHD for windows uses “CHDWin.ini” for reading and saving the CHD environmental parameters.

When CHDWin.ini file is not available in the same directory as the CHDWin.exe file, a new CHDWin.ini file is created and will save the current setting of the parameters. If no apparent parameters were set during the session, the default setting values will be saved in the CHDWin.ini file.

Command Parameter

CHD will check the command line to examine whether “/md” parameter is included.   If so, the “MALT Direct” command will be executed first.

4.2 Main Form

The CHD Main Form contains the followings:

1) Title bar
2) menu bar
3) tool bars
4) main display panel
5) status bar
6) Dock panels at the right-hand side and at the bottom part

Fig. 4.1 shows the main form in which the three dimensional diagram for the La-Co-Zr-O system at 1273 K is displayed. In addition, one dissection is cut and displayed in another display panel which is docked in the left docking panel.

Size of Form

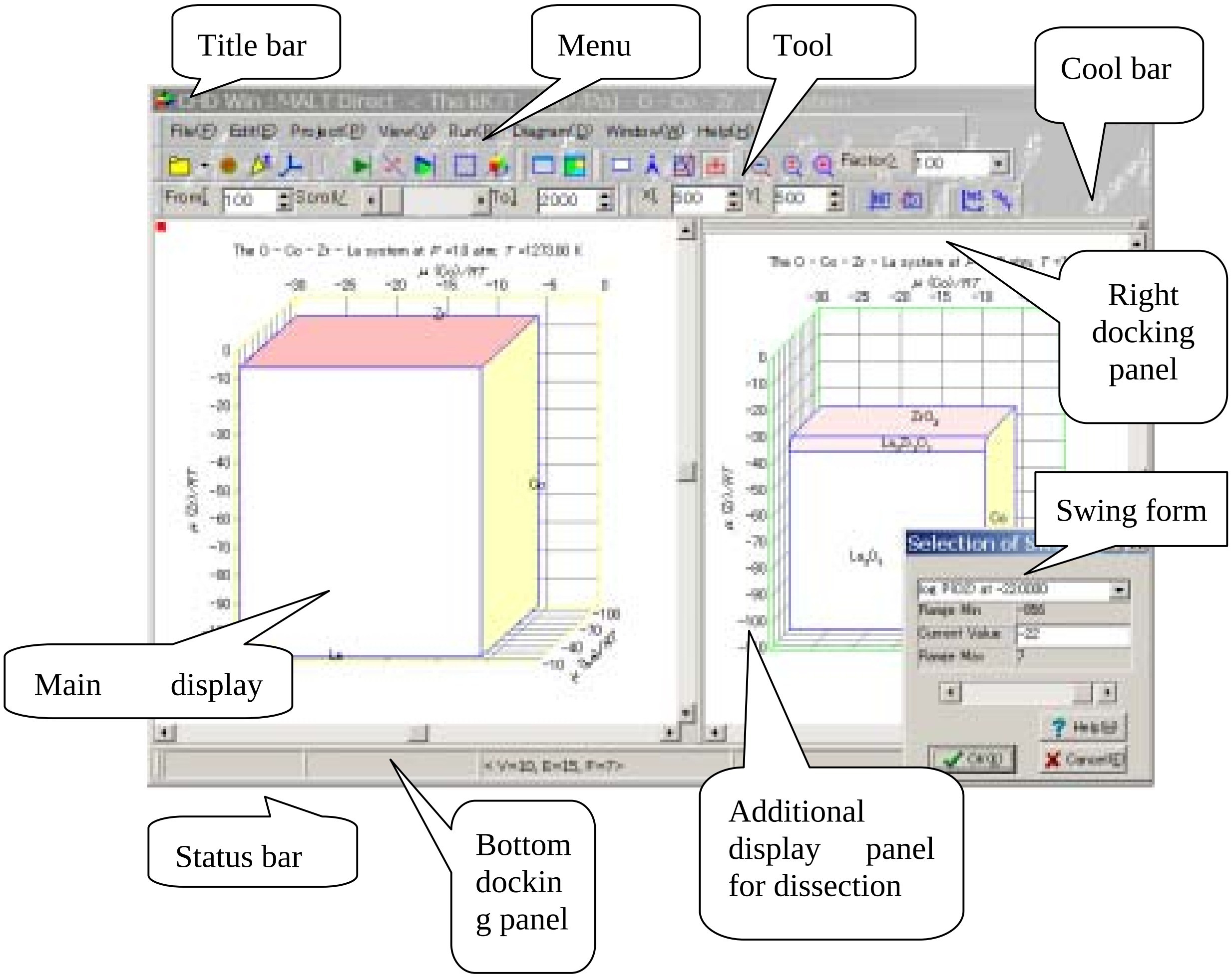


Fig. 4.1. MALT main form.

The Size of the Main Form can be changed by moving one of corners or one of edges by mouse.

Title bar

“CHD Win” is the short title. When the thermodynamic data are successfully read from the MALT database or from the file, the title for the chemical system will be added to the short title.

Menu bar

Main menus are given in Table 4.1. Menu bar is contained in the cool bar. But, this menu bar cannot be floated from the cool bar.

Table 4-1 Items in the main menu and their functions

Items	Functions
File(F)	Open File for thermodynamic data or save Chemical Potential Diagram
Edit(E)	Copy Diagram, Table items.
Project(P)	Define the chemical system and the conditions for constructing diagrams.
View(V)	Provides detailed data associated with the chemical potential diagram.
Run(R)	Create a polyhedron, cut dissections of the obtained polyhedron.
Diagram(D)	Provides the functions of manipulating diagram (coordinate range, polyhedron rotation, Select the display mode, size, Font, color)
Windows(W)	Display hidden forms.
Help(H)	Manual, version information

Tool bars

The main cool bar is a container for toolbars.

The toolbars to be displayed in this cool bar can be selected in the [View / Toolbar] menu or by right clicking on the Main Cool bar.

Although the menu bar cannot be floated, other toolbars can be floated. By dragging at the left side of each tool bar, the tool bar will be floated.

Display panel

This is for displaying a diagram which is constructed under the specified conditions. The Display Zoom factor can be changed by "Zoom" buttons; the location of Diagram in the Panel can be change by using the Horizontal Scroll bar or the Vertical Scroll bar.

Responsible Diagrams to Menus and tool buttons

Only in the main form, there are menus and tool buttons. Those menus and tool buttons are valid even for the diagram displayed in other display panels. The active form responsible to menus and buttons is indicated as red square mark shown in the top-right corner. In Fig. 4.1, the main panel is responsible.

MALT is not running. First run MALT

Fig. 4.2. Message for not running MLAT.

4.3 Menu “File”

Read Data from File

The following files can be read from the present CHD version:

1) MALT compound data file (*.mcd)
2) MALT Version 1. data file(*.sc)
3) CHD User Compound Data file (*.dat)
4) Test data (*.abs)

Even when the thermodynamic data will be read from the files, it is needed to run the mother MALT program. When the MALT system is not running, the message appears as given in Fig. 4.2.

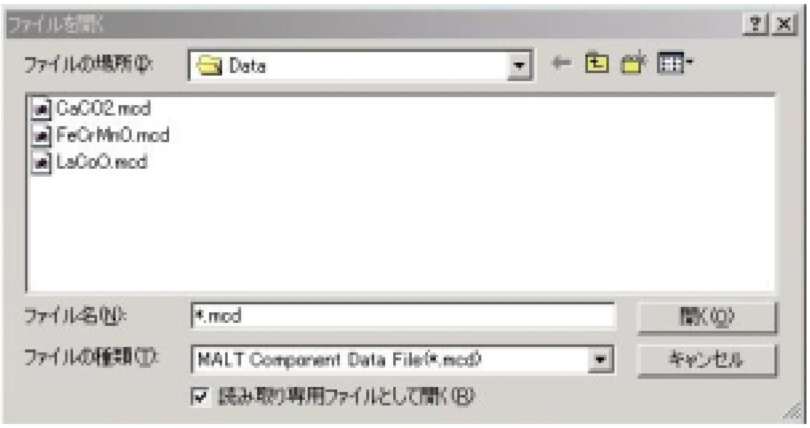
When the menu “Open File” is selected, the “Open File” Dialog appears as shown in Fig. 4.3. This is the Windows supplied dialog so that the message of this dialog is given in the Widows message language; note that Fig. 4.3 was given by Japanese windows.

The selection of File type is important because the subsequent procedure will be made according to the selected type. When the file name selected and the file type selected are not consistent, reading the thermodynamic data will fail.

Format of Respective Files

The format of respective files is determined as follows:

1) MALT compound data file



ファイルの場所(I): Data

CaCO2.mcd
FeCrMnO.mcd
LaCoO.mcd

ファイル名(N): *.mcd

ファイルの種類(T): MALT Component Data File(*.mcd)

☑ 読み取り専用ファイルとして開く(R)

Fig. 4.3. Open file dialog for reading thermodynamic data. This is Window’s dialog so that the message language is the same as OS’s language.

This file is created and managed within the MALT for windows system. This file is edited in the Menu “Tools” / “Data Format Conversion” and saved in the same menu items of the MALT for Windows.

2) MALT version 1. compound file (*.sc)

This option is prepared to keep the consistency with the earlier versions of MALT.

All data are given as ASCII text and the comma "," is used as delimiter. The first line is a comment line with the title of the file. This is necessary for properly reading data but will not be used in the present CHD. Thermodynamic data for respective compounds are followed sequentially. Data for one compound consists of 4 different lines;

(0) Comment line which starts with "*";
(1) Compound title line (one line) containing 6items;
(2) Stoichiometry(7lines) consisting two items;
(3) High Temperature Data No. 1
(4) High Temperature Data No. 2

Data lines (3) and (4) are repeated for respective high temperature phases

Table 4.2 Example of MALT version 1 compound file:

```
*  87/08/12  [87/08/12]
malt1.0,La,La,g,g, 1
La, 1
0, 0
0, 0
```

```
0. 0
0, 0
0, 0
0, 0
138.905 , 431 , 393.59 , 182.268 , 22.753 , 1
$,g, 298 , 2500 , 0 ,$,
32.372 , .282 ,-28.21 , 0 , 5.869 ,-15.8248 ,-.193013 , 11,
malt1.0,La,La,cs,sl, 4
La, 1
0, 0
0, 0
0, 0
0, 0
0, 0
0, 0
138.905 , 0 , 0 , 56.9 , 0 , 1
$,c1, 298 , 550 , .364 ,tp,
27.07 , 1.34 ,-.33 , 0 , 0 ,-8.24116 ,-.154819 , 5,
$,c2, 550 , 1134 , 3.121 ,tp,
17.66 , 15.02 , 3.93 , 0 , 0 ,-3.99622 ,-.101601 , 5,
$,c3, 1134 , 1193 , 6.197 ,mp,
39.54 , 0 , 0 , 0 , 0 ,-16.3762 ,-.235862 , 5,
$,l, 1193 , 3730 , 0 ,bp,
34.31 , 0 , 0 , 0 , 0 ,-3.93978 ,-.193617 , 5,
```

3) CHD User Compound Data file
This data file is based on the Gibbs energy representation.

1) All data are given in a proper sequence and in the formatted style for respective lines.
2) Comment line; all lines which start with the asterisk (*) are defined as comment lines and will be just read.
3) Lines without any string(that is, blank line) will be also read through.
4) All data lines are read and separated into several words using space as separator.

System Data lines consist of
- System Information
- Component(Element) Names
- Component(Element) atomic mass : This will not be used in CHD
- Gibbs energy Expression Information
- Additional Information This will not be used in CHD

Main Data Lines consist of
- Name of Mixture/Stoichiometric Compounds
- Type of Mixture
- ThermoData For respective compounds, which consists of
  - Name of compound
  - Data type, Number of phases, stoichiometric numbers

Table 4.3 Example of User Compound Data File

```
* Data File to be created by user
   2   1   5   3
  O           Co
     15.99940     58.93320
   6   1   2   3   4   5   6
   1   1
GAS
IDMX
O
4  1    1.0000    0.0000
2.5000000E+03  2.4328149E+05 -2.1885825E+01 -2.0845000E+01  8.5000000E-06
0.0000000E+00 -4.8550000E+04  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
O2 4       1    2.0000    0.0000
 2.5000000E+03 -1.4231317E+04  3.0877261E+01 -3.4350000E+01 -9.6000000E-04
 0.0000000E+00  9.2250000E+05 -6.7666667E+07  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
O3 4       1    3.0000    0.0000
 2.5000000E+03  1.1552677E+05  1.6258143E+02 -5.7780000E+01 -3.5500000E-04
 0.0000000E+00  2.1245000E+06 -1.2850000E+08  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
Co 4       1    0.0000    1.0000
2.5000000E+03  4.1556568E+05  2.1115903E+00 -2.6819000E+01  3.1500000E-05
0.0000000E+00  1.7010000E+05  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
CoO
4  1    1.0000    1.0000
4.0000000E+03  2.8028824E+05  1.4209312E+01 -3.6490000E+01 -2.6000000E-04
0.0000000E+00  2.6970000E+05  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
Co
4  4    0.0000    1.0000
7.0000000E+02 -6.7380728E+03  1.1042648E+02 -2.0280000E+01 -7.7800000E-03
0.0000000E+00  0.0000000E+00  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
1.3940000E+03 -1.2804053E+04  2.6397436E+02 -4.5270000E+01  2.3620000E-02
-6.4300000E-06  0.0000000E+00  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
1.7680000E+03  2.6707448E+05 -1.0849677E+03  1.2803000E+02 -3.2700000E-02
 0.0000000E+00 -7.8695000E+07  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
3.2010000E+03 -1.5016034E+03  2.4415313E+02 -4.0500000E+01  0.0000000E+00
0.0000000E+00  0.0000000E+00  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
CoO
4  2    1.0000    1.0000
2.0780000E+03 -2.5477621E+05  3.1589943E+02 -5.5100000E+01  2.3000000E-03
-9.9000000E-07  8.3500000E+04  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
2.5000000E+03 -2.0404540E+05  3.3456010E+02 -6.0670000E+01  0.0000000E+00
0.0000000E+00  0.0000000E+00  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
Co3O4
4  1    4.0000    3.0000
1.2200000E+03 -9.4106306E+05  8.3592218E+02 -1.3665000E+02 -1.3765000E-02
-7.9216667E-06  1.1445000E+06  0.0000000E+00  0.0000000E+00  0.0000000E+00
-2.0  0.0   0.0
```

4) Test Data file

This file is provided to construct a polygon in a normal (not thermodynamic) space. Respective planes in this space is represented by the following equation;

$$la + mb + nc = \mathrm{const} \qquad [4.1]$$

Here, the dimensional number is 3. The variables, a, b ,c, form the space. The coefficients, l, m, n, determine the slope of the plane, and the const determines the location of the plane.

The first line of the data file gives the dimensional number.

The data for respective planes consist of three lines;

1) Name of the plane
2) The data for the coefficients
3) The data for the constant value

Table 4.4 Example of test data file

```
3
A
1, 0, 0
0
B
0, 1, 0
0
C
0, 0, 1
0
AB
1, 1, 0
-10
AC
1, 0, 1
-20
```

Fig.4.4 shows a three-dimensional diagram corresponding to the test data given in the above file. This system consists of five planes, A, B, C, AB and AC.

Reopen the previously used files

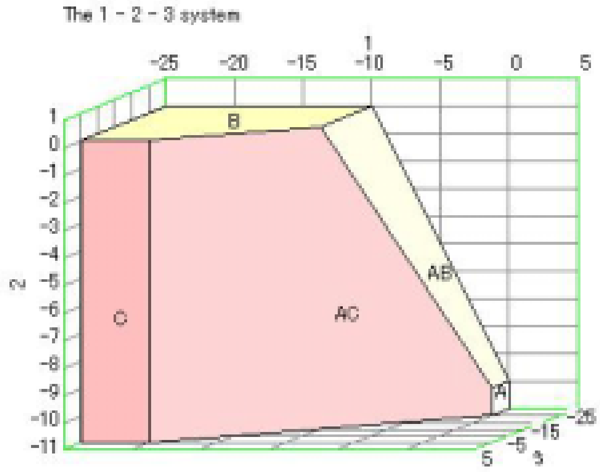


Fig. 4.4. Three Dimensional surface diagram corresponding to the test data given above.

The previously used files are stored with their data type. It is therefore not needed to specify the file type explicitly. These file names are always renewed so that old files will disappear.

When the file was moved from the previous directory after the previous use, such a file cannot be read again. In such a case, the menu item for the file reopen is changed to “not enable”.

MALT Direct

This consists of two procedures;

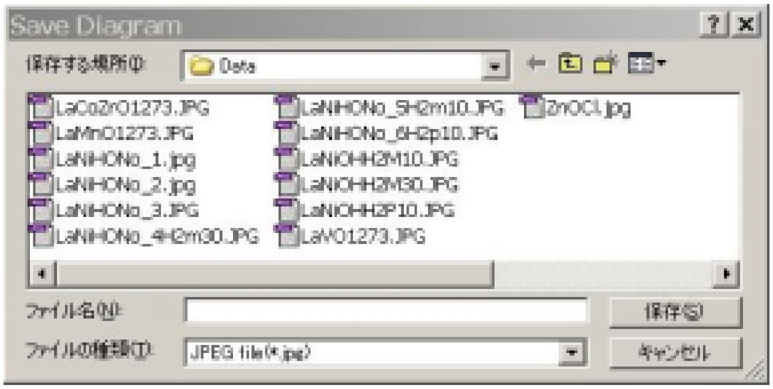
1) ask MALT to send the current retrieved data to CHD;
2) receive the thermodynamic data and prepare for utilization of CHD.

To use this function, the MALT has to be run. When MALT is not available, the message given in Fig. 4.2 will appear.

Open Default File

One file can be specified as the default file. This is made in the “Project / Set as Default File” menu. This file is read in this menu.

Save File



保存する場所(I): Data

LaCoZrO1273.JPG
LaMnO1273.JPG
LaNiHONo_1.jpg
LaNiHONo_2.jpg
LaNiHONo_3.JPG
LaNiHONo_4H2m30.JPG
LaNiHONo_5H2m10.JPG
LaNiHONo_6H2p10.JPG
LaNiOHH2M10.JPG
LaNiOHH2M30.JPG
LaNiOHH2P10.JPG
LaVO1273.JPG
ZnOCl.jpg

ファイル名(N):

ファイルの種類(T): JPEG file(*.jpg)

Fig. 4.5. Dialog for save the diagram. The file type can be selected from Window metafile, bitmap and jpeg.

When the thermodynamic data are supplied from the MALT for Windows by the MALT Direct, those data can be saved as the compound data file. This file can be only read but cannot be edited.

Save Diagram

The diagram in the CHD display panel can be saved in the following forms:

1) window meta file
2) bitmap file
3) jpeg file

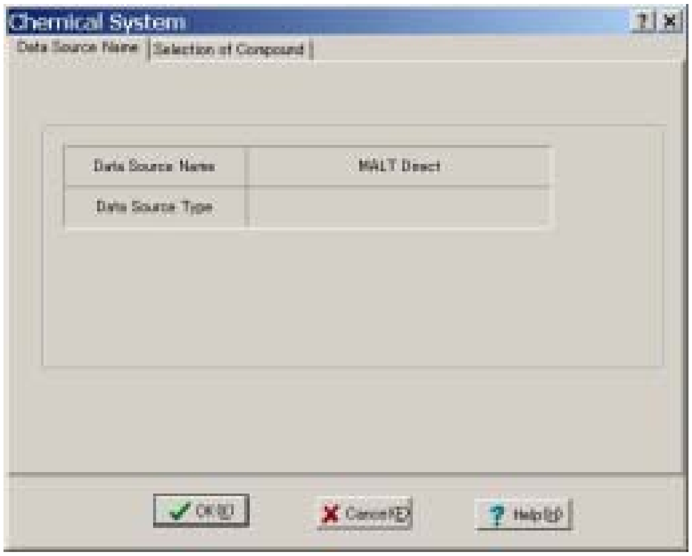
Fig. 4.5 shows the dialog for save the diagram. Here, jpeg type is selected. As a result, available files having the ".jpg" are displayed in the current folder. Note that Fig. 4.5 is the Window's providing dialog to that the message language is controlled by Windows.

Save Screen

The current screen will be save in a bitmap file or a jpeg file in a similar procedure to "Save Diagram."

Printer Set Up ; Print

Exit



Data Source Name	MALT Direct
Data Source Type	

Fig. 4.6. The Chemical System Dialog with a page of Data Source Name

CHD will be ended.

4.4 Menu “Edit”

Diagram in the display panel and table contents in the lists can be copied to clipboard

Copy Diagram to Clipboard

The format of the diagram is in the window metafile. If other graphic formats such as bitmap or jpeg files are preferred, the menu “Save Diagram” should be selected.

When there are many displayed panels, the diagram on the panel with red square mark on the top left corner will be copied.

Copy Table to Clipboard

Table contents in the Graph Inspector and other tables can be copied to clipboard. Such data are easily transferred to other software such as Microsoft Excel or Origin.

Copy List to Clipboard

CHD provides a list of text strings during its processes particularly in the followings:

1) reading data from file: data are read from file and stored in a list. When reading data was failed such a list will be given.
2) Creating a graph and constructing a diagram is also recorded for each process.

These lists can be shown by clicking the “List” tool button. Such list can be copied to clipboard.

4.5 Menu “Project”

Chemical System

The specification of the chemical system can be made in the “Project/Chemical System” as follows;

Selection of Compound

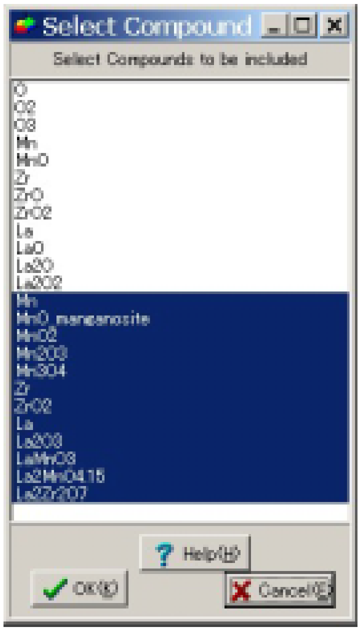
● Selection by Default

Default Compounds

☑ Condensed phases
☐ Respective Gaseous Species
☐ Gaseous Mixture

○ Selection by User

Fig. 4.7. The Chemical System Dialog with a page of Selection of Compound..



O
O2
O3
Mn
MnO
Zr
ZrO
ZrO2
La
LaO
La2O
La2O2
Mn
MnO_manganosite
MnO2
Mn2O3
Mn3O4
Zr
ZrO2
La
La2O3
LaMnO3
La2MnO4.15
La2Zr2O7

Fig. 4.8 Select Compound Form

1) Data Source Name

Name and Type of Data source will be displayed as Fig. 4.6.

2) Selection of Compound

Among chemical species, selection can be made for species to be examined in the construction of chemical potential diagram. Selection is made by choosing one option from the following two options;

i) Default
ii) Selection by user

As shown in Fig. 4.7, for default selection, the following items should be checked or unchecked:

Condensed phases
Respective gaseous species
Gas Mixture

In “Respective gaseous species,” each species in the standard pressure will be treated as one flat plane in diagrams, whereas in “Gas Mixture”, one phase under a given pressure is expresses as a curved plane.

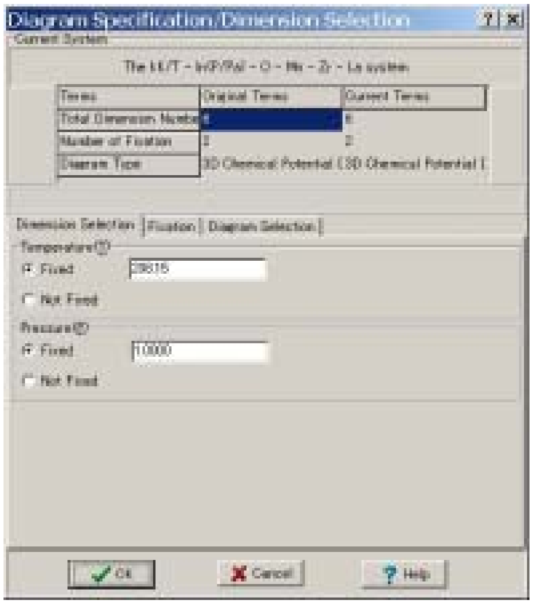
In the initialization of the current project, only condensed phases are taken for this purpose. After selection is made in this menu, however, the selection will be stored in the CHDWin.ini file and applied to any systems which will be read afterward.

When “selection by user” is selected, the Select Compound Form (Fig. 4. 8) will appear. The currently selected compounds are indicated by blue color. By double clicking on the selected compound, the selection can be changed between “selected” and “unselected” states.

Specification of Diagram

CHD can create different types of diagrams. This depends on the total number of components and the number of fixed variables in the system. These fundamental information on the current chemical system is given in the upper part of the Diagram Specification Form (Fig. 4.9).

As an example, the La-Zr-Mn-O system is retrieved through “MALT Direct.” This is the four-element system. By adding the temperature and pressure, total number of the components becomes 6. During the initialization of project, temperature is fixed at 298.15 K and pressure is fixed at 1 atm (101,325 Pa). In the upper table of the form, the initial terms and the current terms are



Terms	Original Terms	Current Terms
Total Dimension Number	6	6
Number of Fixation	2	2
Diagram Type	3D Chemical Potential (	3D Chemical Potential (

Temperature(T)
● Fixed 298.15
○ Not Fixed

Pressure(P)
● Fixed 1.0000
○ Not Fixed

Fig. 4.9 Diagram Specification Form

compared. The initial terms are set when this form is opened. Whenever specification will be changed during the current setting, new specification is shown in the current terms.

Whenever the current terms are changed, the default type of diagram will change according to the followings:

Table 4.5 Examples of diagram which can be constructed in various types; diagram with underline is the default type.

Total dimension number	Number of fixed variables	possible types	Examples
3	0	2D, 3D surface	Cr
4	1	2D, 3Dsurface	Mn-O at constant Pres.
5	2	2D, 3Dsurface	Ca-C-O at constant Pres. and Temp. La-Mn-O at constant Pres. and Temp.
6	3	2D, 3Dsurface	La-Mn-Zr-O at $p(O_2)$=1 atm
6	2	**3D**	

Pages

1. Dimension Selection

   The thermodynamic intensive variables can be divided into two categories; that is, the chemical potentials and others such as temperature and pressure. Here, non-chemical potential variables can be specified about whether those variables are fixed at selected values or not.

   Method:

   To fix at a value, check "fixed" and edit the field in the right hand side. To cancel the fixation, check "not fixed". Then, the text value in the edit field will disappear.

   (1) Temperature : Default = Fixed at 298.15 K.

   (2) Pressure : Default = Fixed at 1 atm.

2. Fixation

   The current list of “Fixed Values” is given in the Fixation page.

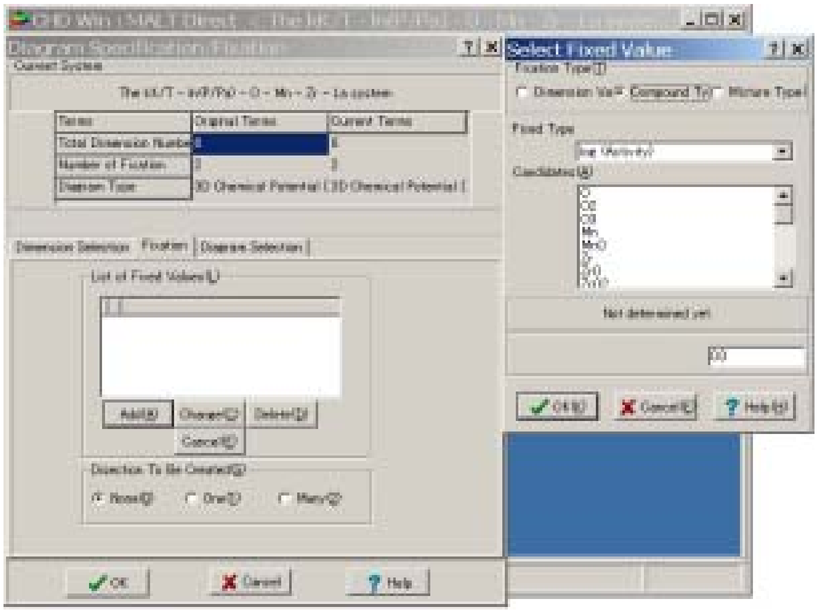


Fig. 4.10 Fixation of chemical potentials with dialog for Select Fixed Value.

Name : The specified species, a combination of species;

Type : Fixed Type.

Modification for the current setting can be made by clicking the buttons for “Add,” “Change,” “Delete,” and “Cancel.”

Add : "Select Fixed Value" Dialog appears as shown in Fig. 4.10. Fixation cam be selected from the Dimension variables, the Compound type.

When the Dimension variables are selected, only one dimension can be selected for one fixation.

When the Compound type is selected, a linear combination of chemical potentials of compounds can be selected. For this purpose, after selecting one chemical species, the Coefficient Form will appear and prompt to input a coefficient for a linear equation. After inputting the coefficient, the current linear equation will be given below the candidate species.

A fixed value is input at the bottom of the form.

Change : First, select the line in the list of the Fixed values to be changed. Then click the change button.

Delete : First, select the line to be deleted. Then click the delete button.

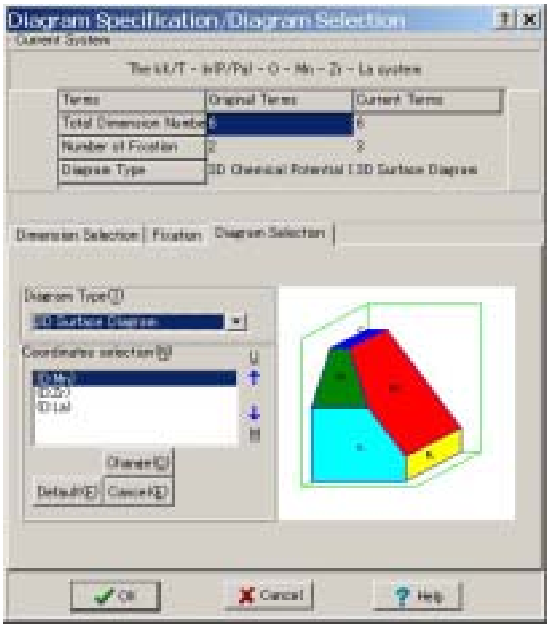


Diagram Specification /Diagram Selection

Current System

Terms	Original Terms	Current Terms
Total Dimension Number	6	6
Number of Fixation	2	3
Diagram Type	3D Chemical Potential / 3D Surface Diagram	

Fig. 4.11 Selection of Diagram.

Cancel : The currently modified fixed values are all canceled and the old values become valid.

On every change in fixation, the information of the current setting is renewed at the upper part of the “Diagram Specification” dialog.

Dissection to be created

If you want, the pages for dissections can be added in this [Diagram Type].

No dissection (default):

One Dissection:

Many Dissections:

To cancel "One Dissection" or "Many dissections", select No dissection.

It is highly suggested to specify the dissection condition after the Diagram selection is made first.

3. Diagram Selection

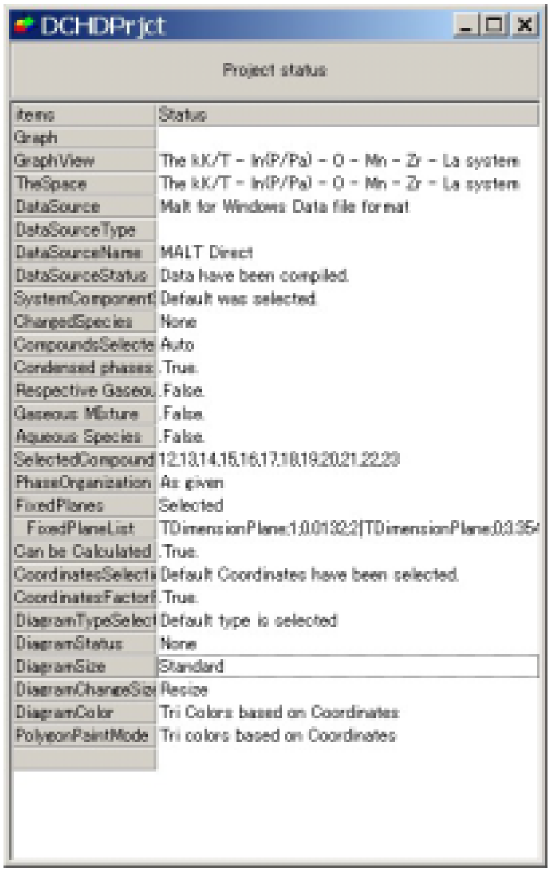
Diagram type and coordinates can be selected.

The chemical potential diagram type can be selected among the available types which are given in the combobox. A typical image is given for the selected diagram type.

Coordinates selection can be made by changing the default coordinates. Whenever the default diagram type is set, default coordinates are selected at the same time. The first coordinate is for the X axis and the second and the third are for the Y and the Z axis, respectively. Note that three coordinates are needed even for the two-dimensional diagrams. This is because the third coordinate is needed to determine the front and rear surfaces of the polygons. Change will be made by clicking one of the following buttons:

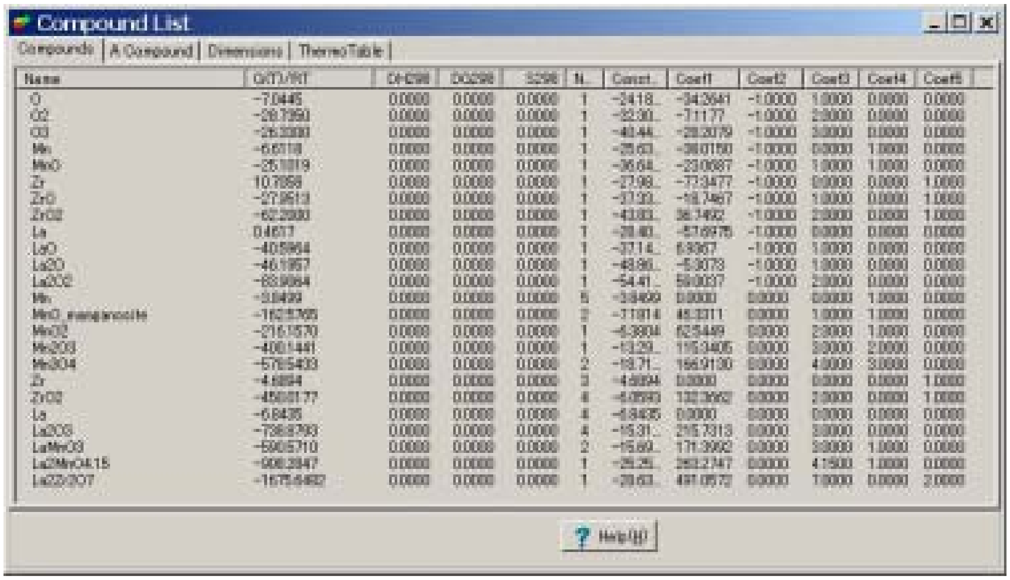
Change
Default
Cancel

Downward or upward arrows make exchange the selected line and the lower or the upper line, respectively.



items	Status
Graph	
GraphView	The kK/T - ln(P/Pa) - O - Mn - Zr - La system
TheSpace	The kK/T - ln(P/Pa) - O - Mn - Zr - La system
DataSource	Malt for Windows Data file format
DataSourceType	
DataSourceName	MALT Direct
DataSourceStatus	Data have been compiled.
SystemComponent	Default was selected.
ChargedSpecies	None
CompoundsSelecte	Auto
Condensed phases	.True.
Respective Gaseou	.False.
Gaseous Mixture	.False.
Aqueous Species	.False.
SelectedCompound	12,13,14,15,16,17,18,19,20,21,22,23
PhaseOrganization	As given
FixedPlanes	Selected
FixedPlaneList	TDimensionPlane;1;0.0132;2|TDimensionPlane;0;3.35
Can be Calculated	.True.
CoordinatesSelecti	Default Coordinates have been selected.
CoordinatesFactorI	.True.
DiagramTypeSelect	Default type is selected
DiagramStatus	None
DiagramSize	Standard
DiagramChangeSiz	Resize
DiagramColor	Tri Colors based on Coordinates
PolygonPaintMode	Tri colors based on Coordinates

Fig. 4.12 Project Status



Name	G(T)/RT	DH298	DG298	S298	N...	Const...	Coef1	Coef2	Coef3	Coef4	Coef5
O	-7.0445	0.0000	0.0000	0.0000	1	-24.18...	-34.2641	-1.0000	1.0000	0.0000	0.0000
O2	-28.7990	0.0000	0.0000	0.0000	1	-32.30...	-7.1177	-1.0000	2.0000	0.0000	0.0000
O3	-26.3300	0.0000	0.0000	0.0000	1	-40.44...	-28.2079	-1.0000	3.0000	0.0000	0.0000
Mn	-6.6118	0.0000	0.0000	0.0000	1	-25.63...	-38.0150	-1.0000	0.0000	1.0000	0.0000
MnO	-25.1019	0.0000	0.0000	0.0000	1	-36.64...	-23.0687	-1.0000	1.0000	1.0000	0.0000
Zr	10.7858	0.0000	0.0000	0.0000	1	-27.98...	-77.3477	-1.0000	0.0000	0.0000	1.0000
ZrO	-27.9613	0.0000	0.0000	0.0000	1	-37.33...	-18.7467	-1.0000	1.0000	0.0000	1.0000
ZrO2	-62.2880	0.0000	0.0000	0.0000	1	-43.03...	38.1492	-1.0000	2.0000	0.0000	1.0000
La	0.4617	0.0000	0.0000	0.0000	1	-28.40...	-57.6975	-1.0000	0.0000	0.0000	0.0000
LaO	-40.5964	0.0000	0.0000	0.0000	1	-37.14...	6.9367	-1.0000	1.0000	0.0000	0.0000
La2O	-46.1957	0.0000	0.0000	0.0000	1	-48.86...	-5.3073	-1.0000	1.0000	0.0000	0.0000
La2O2	-63.9864	0.0000	0.0000	0.0000	1	-54.41...	59.0037	-1.0000	2.0000	0.0000	0.0000
Mn	-3.8499	0.0000	0.0000	0.0000	5	-3.8499	0.0000	0.0000	0.0000	1.0000	0.0000
MnO_manganosite	-162.5765	0.0000	0.0000	0.0000	2	-7.1814	45.3311	0.0000	1.0000	1.0000	0.0000
MnO2	-216.1570	0.0000	0.0000	0.0000	1	-6.3804	62.5449	0.0000	2.0000	1.0000	0.0000
Mn2O3	-400.1441	0.0000	0.0000	0.0000	1	-13.29...	115.3405	0.0000	3.0000	2.0000	0.0000
Mn3O4	-576.5433	0.0000	0.0000	0.0000	2	-18.71...	166.9130	0.0000	4.0000	3.0000	0.0000
Zr	-4.6894	0.0000	0.0000	0.0000	3	-4.6894	0.0000	0.0000	0.0000	0.0000	1.0000
ZrO2	-450.0177	0.0000	0.0000	0.0000	4	-6.0593	132.3662	0.0000	2.0000	0.0000	1.0000
La	-6.8435	0.0000	0.0000	0.0000	4	-6.8435	0.0000	0.0000	0.0000	0.0000	0.0000
La2O3	-726.8793	0.0000	0.0000	0.0000	4	-15.31...	215.7313	0.0000	3.0000	0.0000	0.0000
LaMnO3	-590.5710	0.0000	0.0000	0.0000	2	-15.69...	171.3992	0.0000	3.0000	1.0000	0.0000
La2MnO4.15	-906.3947	0.0000	0.0000	0.0000	1	-25.25...	263.2747	0.0000	4.1500	1.0000	0.0000
La2Zr2O7	-1675.6482	0.0000	0.0000	0.0000	1	-28.63...	491.0572	0.0000	7.0000	0.0000	2.0000

Fig. 4.13 Compound Lists

One Dissection, Many Dissections, Additional Lines

These will be explained elsewhere (see 4.7).

Set as Default File

The current thermodynamic data can be defined as default file which can be read by selection of the menu "default file."

4.6 Menu "View"

Project Status

The present status of the project will be displayed in the dialog as shown in Fig. 4. 12. The fundamental selections for constructing diagrams are listed.

Compound List

The list of compounds and other properties related to the construction of the chemical potential diagram is given in this section. As given in Fig. 4.13, the Compound List Form has several pages for displaying the numerical data for the compounds. The first page of "Compounds" shows

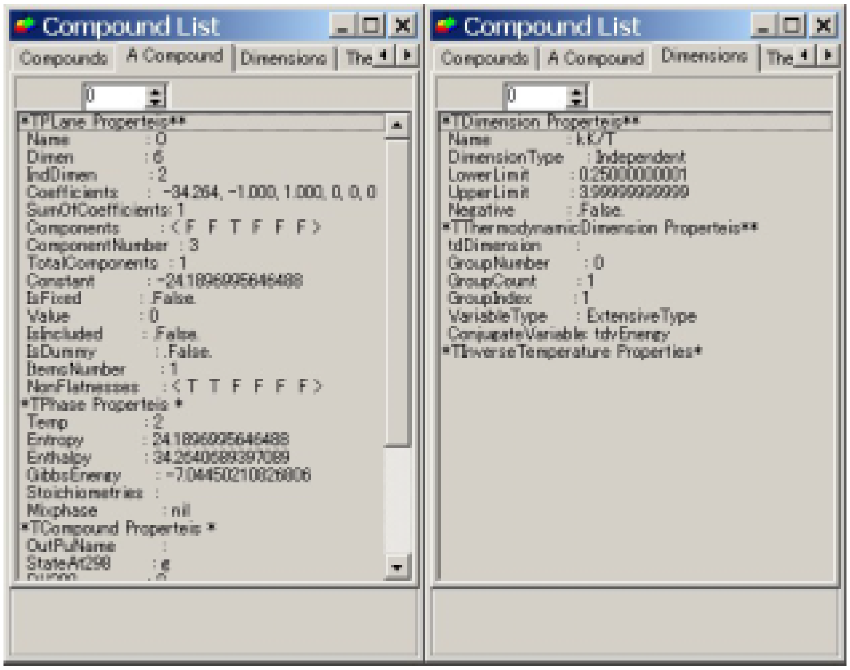
Name	Name of species
G(T)/RT	Gibbs energy value at previously selected temperature
DH298	Enthalpy change for formation at 298.15 K
DG298	Gibbs energy change for formation at 298.15 K
S298	Entropy at 298.15 K
N	Number of high temperature phases
Const	
Coef1 to Coef5	

For data obtained by MALT direct, the thermodynamic data at 298.15 K are not displayed.

Constant and coefficients are values for the following equation;

$$- s/R = (-\Delta H/R)\ 1/T - \log P\ + l\ \mu(\mathrm{A})/RT\ + m\ \mu(\mathrm{B})/RT + n\ \mu(\mathrm{C})/RT \qquad [4.1]$$

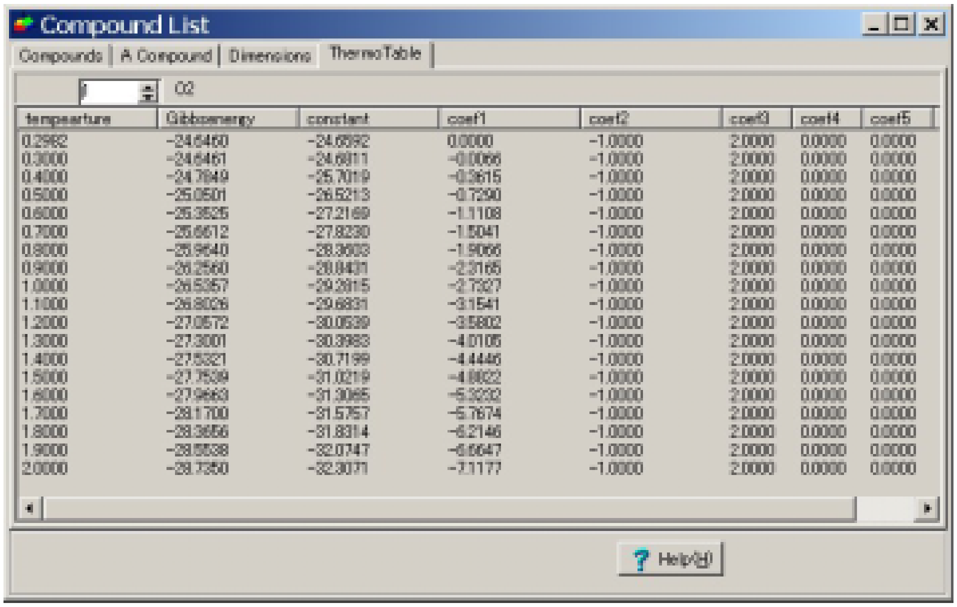
Here, - *s/R* is constant and -Δ*H/R* is the coef 1. Note that these values are for previously selected temperature. Coef 2 is 1 for gaseous species and zero for the condensed phase. Coef 3 and others are the stoichiometric numbers.



```
*TPLane Properteis**
 Name               : 0
 Dimen              : 6
 IndDimen           : 2
 Coefficients       :  -34.264, -1.000, 1.000, 0, 0, 0
 SumOfCoefficients: 1
 Components         : < F  F  T  F  F  F >
 ComponentNumber  : 3
 TotalComponents  : 1
 Constant           : -24.1896995646488
 IsFixed            : .False.
 Value              : 0
 IsIncluded         : .False.
 IsDummy            : .False.
 ItemsNumber        : 1
 NonFlatnesses      : < T  T  F  F  F  F >
*TPhase Properteis *
 Temp               : 2
 Entropy            : 24.1896995646488
 Enthalpy           : 34.2640589397089
 GibbsEnergy        : -7.04450210826806
 Stoichiometries  :
 Mixphase           : nil
*TCompound Properteis *
 OutPutName         :
 StateAt298         : g
```

```
*TDimension Properteis**
 Name               : kK/T
 DimensionType      : Independent
 LowerLimit         : 0.250000000001
 UpperLimit         : 3.99999999999
 Negative           : .False.
*TThermodynamicDimension Properteis**
 tdDimension        :
 GroupNumber        : 0
 GroupCount         : 1
 GroupIndex         : 1
 VariableType       : ExtensiveType
 ConjugateVariable: tdvEnergy
*TInverseTemperature Properties*
```

Fig. 4.14 Information of compound and Dimensions



tempearture	Gibbsenergy	constant	coef1	coef2	coef3	coef4	coef5
0.2982	−24.6460	−24.6592	0.0000	−1.0000	2.0000	0.0000	0.0000
0.3000	−24.6461	−24.6811	−0.0066	−1.0000	2.0000	0.0000	0.0000
0.4000	−24.7849	−25.7019	−0.3615	−1.0000	2.0000	0.0000	0.0000
0.5000	−25.0501	−26.5213	−0.7290	−1.0000	2.0000	0.0000	0.0000
0.6000	−25.3525	−27.2169	−1.1108	−1.0000	2.0000	0.0000	0.0000
0.7000	−25.6612	−27.8230	−1.5041	−1.0000	2.0000	0.0000	0.0000
0.8000	−25.9640	−28.3603	−1.9066	−1.0000	2.0000	0.0000	0.0000
0.9000	−26.2560	−28.8431	−2.3165	−1.0000	2.0000	0.0000	0.0000
1.0000	−26.5357	−29.2815	−2.7327	−1.0000	2.0000	0.0000	0.0000
1.1000	−26.8026	−29.6831	−3.1541	−1.0000	2.0000	0.0000	0.0000
1.2000	−27.0572	−30.0539	−3.5802	−1.0000	2.0000	0.0000	0.0000
1.3000	−27.3001	−30.3983	−4.0105	−1.0000	2.0000	0.0000	0.0000
1.4000	−27.5321	−30.7199	−4.4446	−1.0000	2.0000	0.0000	0.0000
1.5000	−27.7539	−31.0219	−4.8822	−1.0000	2.0000	0.0000	0.0000
1.6000	−27.9663	−31.3065	−5.3232	−1.0000	2.0000	0.0000	0.0000
1.7000	−28.1700	−31.5757	−5.7674	−1.0000	2.0000	0.0000	0.0000
1.8000	−28.3656	−31.8314	−6.2146	−1.0000	2.0000	0.0000	0.0000
1.9000	−28.5538	−32.0747	−6.6647	−1.0000	2.0000	0.0000	0.0000
2.0000	−28.7350	−32.3071	−7.1177	−1.0000	2.0000	0.0000	0.0000

Fig. 4.15 Thermodynamic Table as a function of temperature

Pages for “A Compound” and “Dimensions” give the information on respective compounds and dimensions as shown in Fig. 4.14. This is used in the construction of diagrams. Target compound or target dimension can be selected by changing the number of compounds or dimensions.

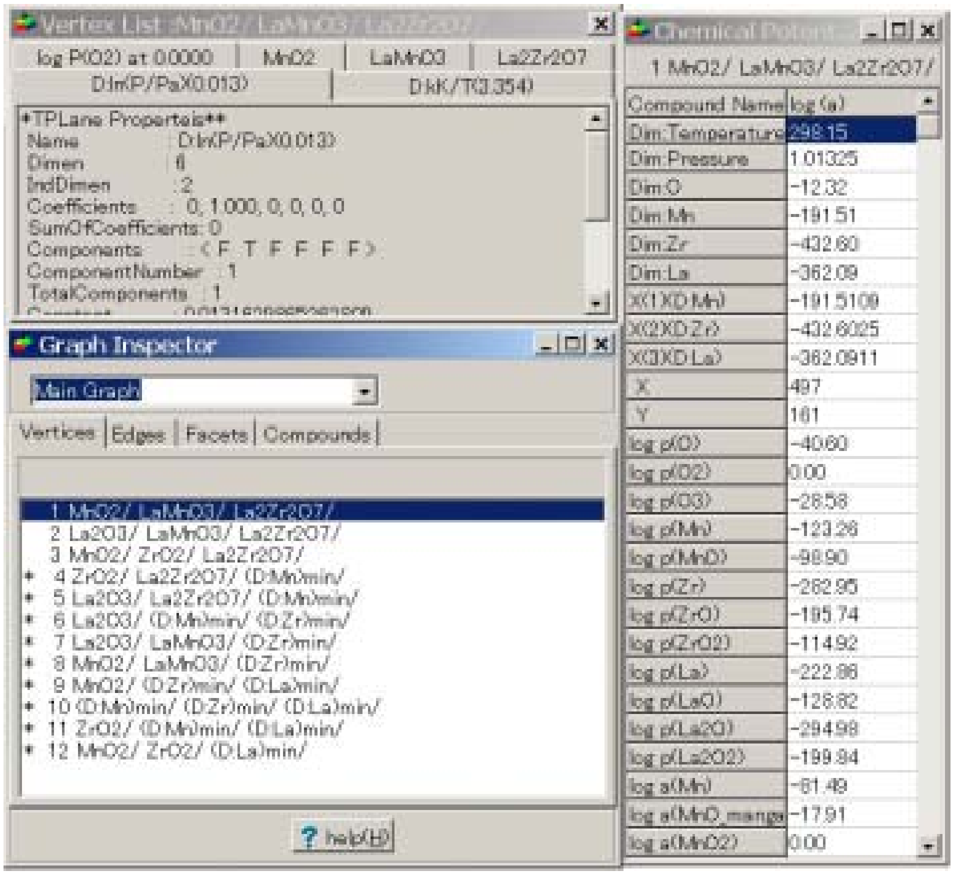
Page for “Thermo Table” gives the Gibbs energy and constant and coefficients in equation 4.1 as a function of temperature. Target compound can be selected in terms of number in the compound list.

Font of those lists can be changed by changing font in the “Message Font “ Menu, which is described below in this section.

Graph Inspector

Construction of any diagram is based on the graph in the chemical potential space. Graph is characterized in terms of vertices, edges, and facets. In addition, the information of planes (compounds) is also given.

Vertices can be characterized in terms of planes which form respective vertices and the chemical potential values which are determined uniquely.



```
*TPLane Propertels**
Name              : D:ln(P/Pa)(0.013)
Dimen             : 6
IndDimen          : 2
Coefficients      : 0, 1.000, 0, 0, 0, 0
SumOfCoefficients: 0
Components        : ( F  T  F  F  F  F )
ComponentNumber   : 1
TotalComponents   : 1
```

```
   1 MnO2/ LaMnO3/ La2Zr2O7/
   2 La2O3/ LaMnO3/ La2Zr2O7/
   3 MnO2/ ZrO2/ La2Zr2O7/
*  4 ZrO2/ La2Zr2O7/ (D:Mn)min/
*  5 La2O3/ La2Zr2O7/ (D:Mn)min/
*  6 La2O3/ (D:Mn)min/ (D:Zr)min/
*  7 La2O3/ LaMnO3/ (D:Zr)min/
*  8 MnO2/ LaMnO3/ (D:Zr)min/
*  9 MnO2/ (D:Zr)min/ (D:La)min/
* 10 (D:Mn)min/ (D:Zr)min/ (D:La)min/
* 11 ZrO2/ (D:Mn)min/ (D:La)min/
* 12 MnO2/ ZrO2/ (D:La)min/
```

1 MnO2/ LaMnO3/ La2Zr2O7/

Compound Name	log (a)
Dim:Temperature	298.15
Dim:Pressure	1.01325
Dim:O	-12.32
Dim:Mn	-191.51
Dim:Zr	-432.60
Dim:La	-362.09
X(1)(D:Mn)	-191.5109
X(2)(D:Zr)	-432.6025
X(3)(D:La)	-362.0911
X	497
Y	161
log p(O)	-40.60
log p(O2)	0.00
log p(O3)	-28.58
log p(Mn)	-123.26
log p(MnO)	-98.90
log p(Zr)	-262.95
log p(ZrO)	-195.74
log p(ZrO2)	-114.92
log p(La)	-222.86
log p(LaO)	-126.82
log p(La2O)	-294.98
log p(La2O2)	-199.94
log a(Mn)	-81.49
log a(MnO_manga	-17.91
log a(MnO2)	0.00

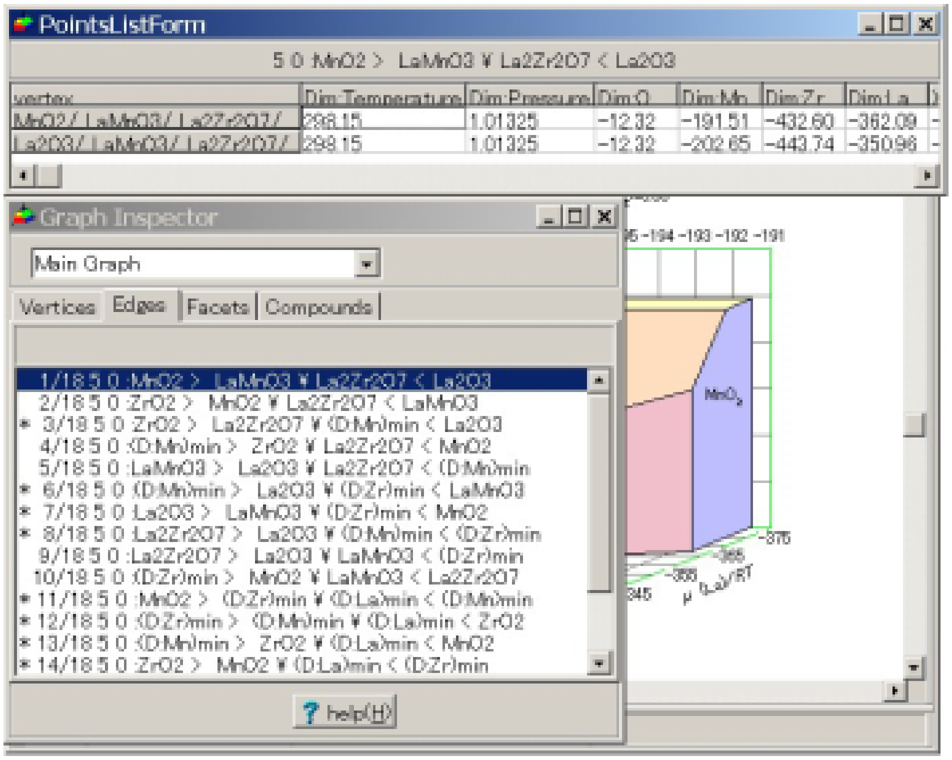
Fig. 4.16 Graph Inspector/ Vertices together with the chemical potential table and Vertex List Form.

Fig. 4.16 shows the list of vertices which give the name of compounds involved. By double clicking on the line, more detailed information appears in the "Vertex List" Form and the "Chemical Potential" Table like in Fig. 4. 16.

The "Vertex List" Form gives the properties of respective compounds, whereas the "Chemical potential" Table gives the numerical values as will be explained below.

Those lines with asterisk (*) are artificial vertices which contain hypothetical planes like the lowest limits of the space.

"Edge" list is given in Fig. 4.17. By double clicking on the line selected, the point list form gives the list of the chemical potential values as shown in Fig. 4.17. By double clicking on the line in the "Points List" Form, the information of the vertex will be shown in the "Chemical Potential" Table and the "Vertex List" Form in the same manner as the above case.



5 0 :MnO2 > LaMnO3 ¥ La2Zr2O7 < La2O3

vertex	Dim:Temperature	Dim:Pressure	Dim:O	Dim:Mn	Dim:Zr	Dim:La
MnO2/ LaMnO3/ La2Zr2O7/	298.15	1.01325	-12.32	-191.51	-432.60	-362.09
La2O3/ LaMnO3/ La2Zr2O7/	298.15	1.01325	-12.32	-202.65	-443.74	-350.96

```
  1/18 5 0 :MnO2 >  LaMnO3 ¥ La2Zr2O7 < La2O3
  2/18 5 0 :ZrO2 >  MnO2 ¥ La2Zr2O7 < LaMnO3
* 3/18 5 0 :ZrO2 >  La2Zr2O7 ¥ (D:Mn)min < La2O3
  4/18 5 0 :(D:Mn)min >  ZrO2 ¥ La2Zr2O7 < MnO2
  5/18 5 0 :LaMnO3 >  La2O3 ¥ La2Zr2O7 < (D:Mn)min
* 6/18 5 0 :(D:Mn)min >  La2O3 ¥ (D:Zr)min < LaMnO3
* 7/18 5 0 :La2O3 >  LaMnO3 ¥ (D:Zr)min < MnO2
* 8/18 5 0 :La2Zr2O7 >  La2O3 ¥ (D:Mn)min < (D:Zr)min
  9/18 5 0 :La2Zr2O7 >  La2O3 ¥ LaMnO3 < (D:Zr)min
 10/18 5 0 :(D:Zr)min >  MnO2 ¥ LaMnO3 < La2Zr2O7
* 11/18 5 0 :MnO2 >  (D:Zr)min ¥ (D:La)min < (D:Mn)min
* 12/18 5 0 :(D:Zr)min >  (D:Mn)min ¥ (D:La)min < ZrO2
* 13/18 5 0 :(D:Mn)min >  ZrO2 ¥ (D:La)min < MnO2
* 14/18 5 0 :ZrO2 >  MnO2 ¥ (D:La)min < (D:Zr)min
```

Fig. 4.17 Graph Inspector/ Edges together with the Points List Form

“Facets” page in Graph Inspector provides lists of facets. Since the facets are painted with colors which are attributed for respective polygons, such colors are also given in the list. By clicking on the line of facets, the facts in the target diagram will be transparent. When another facet is clicked, that facet becomes transparent and the previous facet is colored again. When the diagram is repainted, such specification for transparency will be cancelled and all facets are painted properly.

Compounds in Graph Inspector give the list of compounds which are displayed in the diagram. For respective compounds, color is attributed. By clicking on the compound in the list, the whole area associated with the compounds becomes transparent except for the framework for the graph, that is, edge parts.

In the three dimensional diagram, this function becomes powerful in inspecting the geometrical features of the polyhedrons in the diagram. This specification for transparency will hold for the rest of displaying diagram. In a typical procedure in inspecting the three dimensional diagram, this option as well as rotation can be used simultaneously to see geometrical features deep inside the diagram.

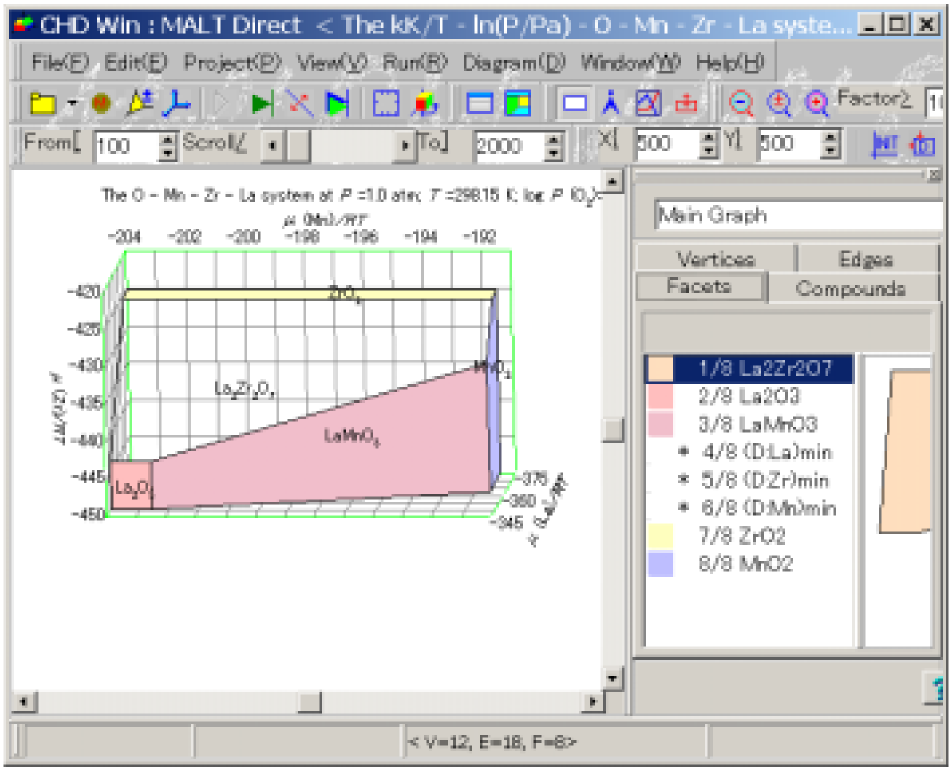


Fig. 4.18 Graph Inspector/ Facets docked at the Main Form

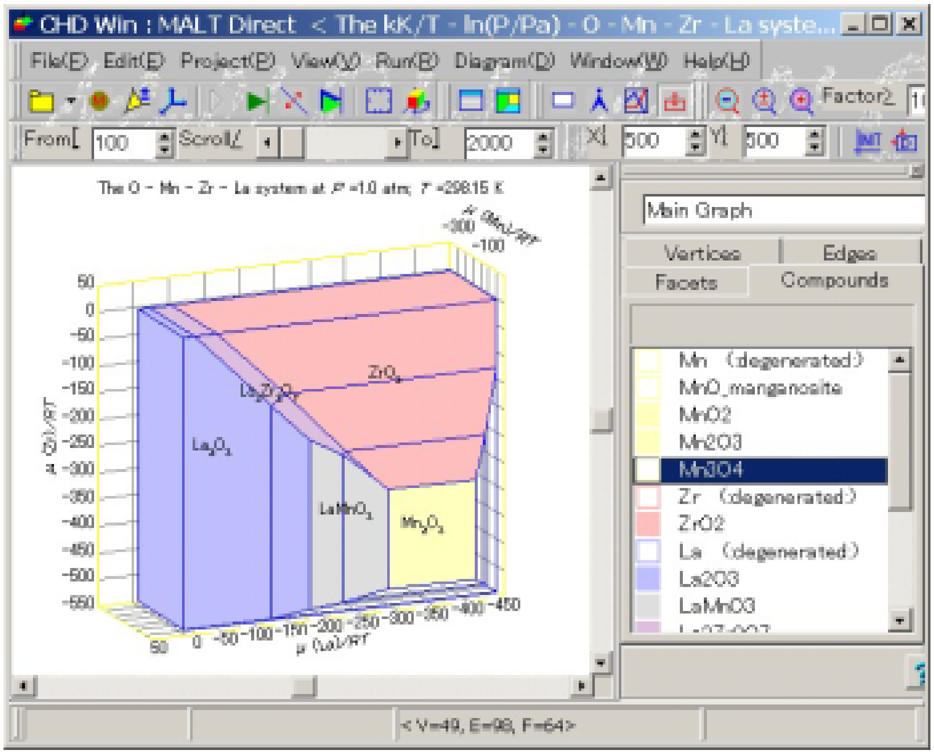
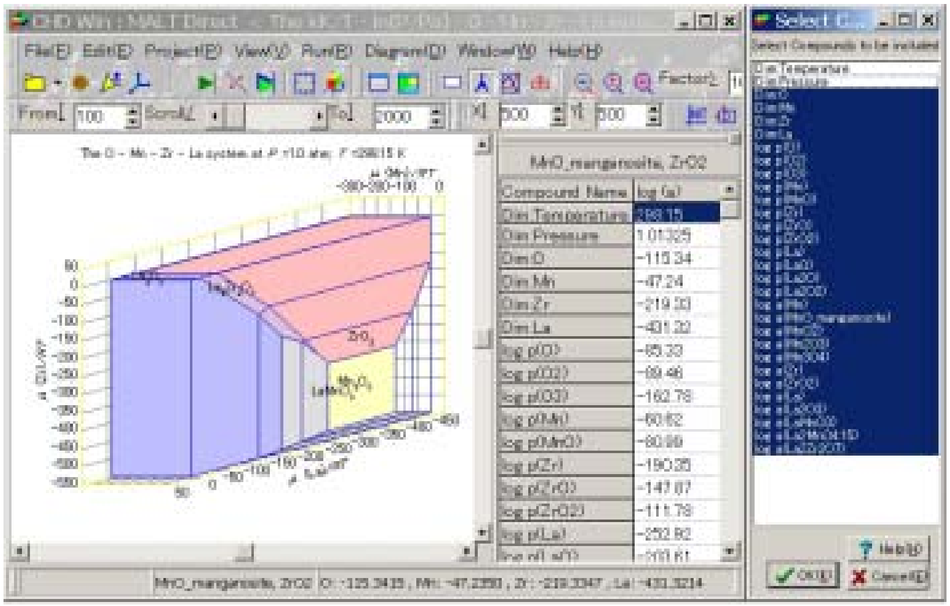


Fig. 4.19 Graph Inspector / Compounds docked in the Main Form.



MnO_manganosite, ZrO2

Compound Name	log (a)
Dim Temperature	298.15
Dim Pressure	1.01325
Dim O	-115.34
Dim Mn	-47.24
Dim Zr	-219.33
Dim La	-431.22
log p(O)	-65.33
log p(O2)	-69.46
log p(O3)	-162.78
log p(Mn)	-60.62
log p(MnO)	-60.69
log p(Zr)	-190.25
log p(ZrO)	-147.67
log p(ZrO2)	-111.78
log p(La)	-252.82

MnO_manganosite, ZrO2 O : -115.3415 , Mn : -47.2350 , Zr : -219.3347 , La : -431.3214

Fig. 4.20 Chemical potential table with selection of columns option /the Select compound Form.

Chemical Potential Table; Points List Form

The Chemical Potential Table can be called from the touch diagram mode of displaying diagram and also from the selection in the Graph Inspector.

The listing items of the chemical potential table can be selected by two ways; one is checking among the following groups;

Space values
Coordinates values
Display Points
Species log(activity)
Species concentration
Coefficients of space;

the other being the selection of columns. When selection is made on this option, the Select Compound Form will appear like in Fig. 4.20. The currently selected items are shown as blue lines.

The "Points List" Form has about the same function as the "Chemical Potential" Table except that the Points list form can display several points at the same time. The way of selection of display items is the same. When the selection is made in the chemical potential table, this is sent to the Points List Form

Language

Message language can be selected as Japanese or English. After change language option, please restart CHD.

Message Font

Windows dialog for font will appear for message font. This font will be used for Font in the main form and other forms having lists etc. Font used in drawing diagrams can be changed in “Diagram Font” submenu (see 4.8).

Toolbar

Options for tool bars are the followings:

1) Include or exclude the tool bars in the cool bar.
2) Add strings to tool buttons or exclude strings.

4.7 Menu “Run”

Calculation

In many cases, the default setting is made just after reading the thermodynamic data in the chemical system so that “Calculation” can be made without further specification.

When calculation was made with success, a graph is created and the graph inspector becomes available. Here, by graph, it means the geometrical and numerical information on vertices, edges and facets. When a diagram can be drawn, the diagram will be displayed after the calculation. When any diagram cannot be drawn, just new graph is available. Further procedures associated with diagram cannot be available.   This is particularly for those systems consisting more than 4elements. For full use of the functions of CHD, it is highly recommended to decrease the freedom by making further fixation so as to be able to draw a diagram.

One Dissection

Dissection is available only when a diagram is available.

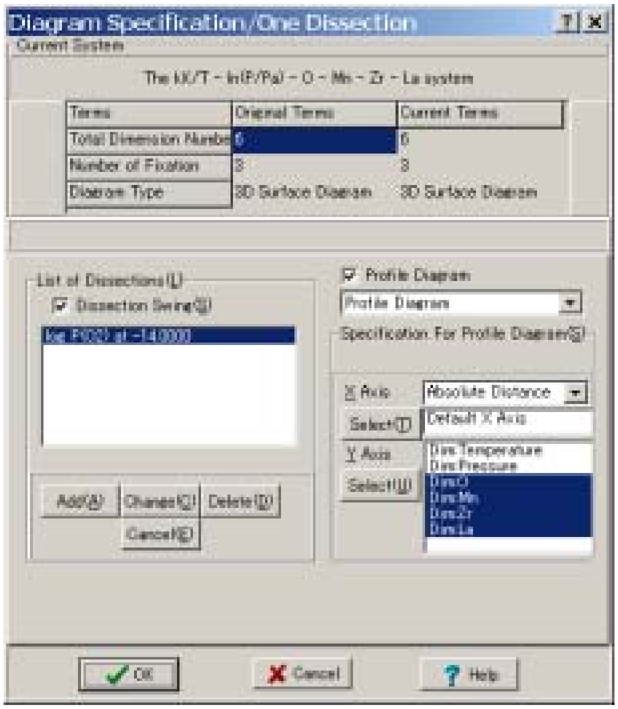


Diagram Specification/One Dissection

Current System

The kK/T – ln(P/Pa) – O – Mn – Zr – La system

Terms	Original Terms	Current Terms
Total Dimension Number	6	6
Number of Fixation	3	3
Diagram Type	3D Surface Diagram	3D Surface Diagram

List of Dissections(L)

☑ Dissection Swing(S)

log P(O2) at -14.0000

☑ Profile Diagram

Profile Diagram

Specification For Profile Diagram(S)

X Axis: Absolute Distance

Default X Axis

Y Axis: Dim.Temperature, Dim.Pressure, Dim.O, Dim.Mn, Dim.Zr, Dim.La

Fig. 4.21 One dissection for three-dimensional surface diagram.

By specifying another chemical potential at a selected value, one dissection diagram can be cut off from the original diagram. This specification of chemical potential decreases one dimension of the chemical potential diagram.

Fig. 4.21 shows the one dimension page in the Diagram Specification Form. This consists of two parts; the left side is for determination of the dissections. Editing dissections can be made by clicking the buttons of “Add”, “Change”, “Delete” and “Cancel.”

The way of determining a dissection is similar to that of determining fixation. That is, the determination is made by selecting dimension variable or compound type. For dimension variable, only one dimension can be select. For compound type, the linear combination can be selected. In addition, constant value should be selected.

The results of dissection can be drawn in two different ways;

1) A specified dissection is displayed on the target diagram.
2) An additional diagram is created in an additional panel. For this purpose, the “profile diagram” should be checked.

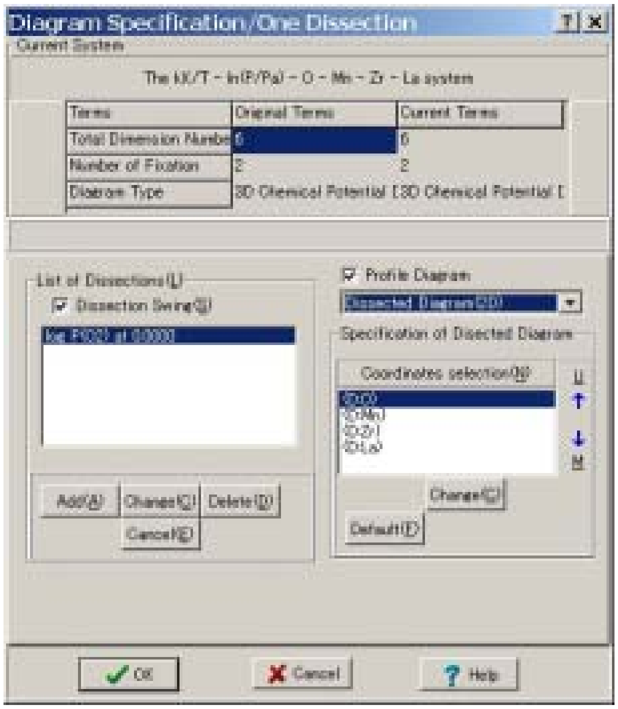


Diagram Specification/One Dissection

Current System

The kK/T – ln(P/Pa) – O – Mn – Zr – La system

Terms	Original Terms	Current Terms
Total Dimension Numbe	6	6
Number of Fixation	2	2
Diagram Type	3D Chemical Potential	3D Chemical Potential

☑ Dissection Swing(S)

☑ Profile Diagram

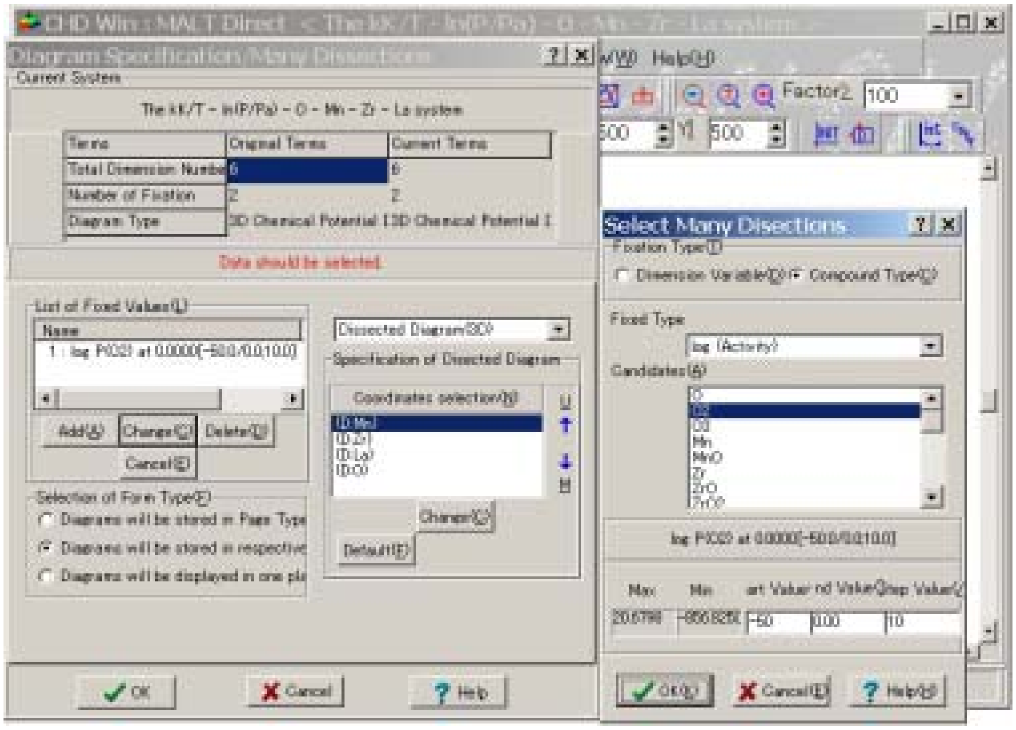
Fig. 4.23 One dissection for three dimensional diagram.

The dissected line can be drawn only on the three dimensional surface diagram. When “Dissection swing” checkbox is checked, a small form for changing the value of dissection will appear.

The value for dissection can be changed by moving the scroll bar in the Dissection Swing Form. This scroll bar can be changed in the given range maximum and minimum. These Maximum and minimum values can be changed by right clicking on the Dissection Swing Form.

Profile diagram

Additional diagram for three dimensional surface diagram can be called as “Profile Diagram.” This provides the change of chemical potentials as a function of chemical potential. As “X” axis, one of the chemical potentials can be selected. Selection is made in the “Select” button. Alternatively, the distance in the chemical potential space can be selected. In this case, distance is automatically calculated and there is no need to specify further.



The kK/T - ln(P/Pa) - O - Mn - Zr - La system

Terms	Original Terms	Current Terms
Total Dimension Number	6	6
Number of Fixation	2	2
Diagram Type	3D Chemical Potential	3D Chemical Potential

Data should be selected

Name
1 : log P(O2) at 0.0000[-50.0/0.0/10.0]

Coordinates selection:
(D:Mn)
(D:Zr)
(D:La)
(D:O)

○ Diagrams will be stored in Page Type
● Diagrams will be stored in respective
○ Diagrams will be displayed in one pla

Factor2: 100
X: 500 Y: 500

○ Dimension Variable(D) ● Compound Type(C)

Fixed Type: log (Activity)

Candidates(A):
O
O2
O3
Mn
MnO
Zr
ZrO
ZrO2

log P(O2) at 0.0000[-50.0/0.0/10.0]

Max	Min	Start Value	End Value	Step Value
20.6798	-856.8285	-50	0.00	10

Fig. 4.24 Many dissections for three dimensional diagram.

For “Y” axis, several values can be selected and plotted against the X axis. Selection can be made by clicking the “select” button to show the following popup menu:

Space value
Coordinates values
Display Point
Species log (Activity)
Species concentration
Coefficients of Space
Selection of Column
Exit

This is the same popup menu for the Chemical Potential Table. When some of the above menu items are clicked, candidate properties are renewed. The target properties are shown as blue lines. This can be changed by double clicking on the target line.

Dissection Diagram

When the target diagram is the three-dimensional diagram, the dissection diagram can be constructed instead of the profile diagram. As shown in Fig. 4.23, the dissection 2D diagram or the dissection 3D diagram can be used.

As coordinates, any coordinate can be selected as in the target diagram. Even so, it is recommended to select one of the shown coordinates in the list in the right-hand side. For such a case, no anomalous appearance will be given.

One Dissection Swing

The Dissection Swing Form will appear and then the dissection value can be changed.

Many Dissections

A number of dissection diagrams can be setup. The dissection values are specified in terms of the minimum and the maximum values with a step value.

Resulting diagrams are displayed in respective Forms. These Forms can be docked with each other or on the main form.

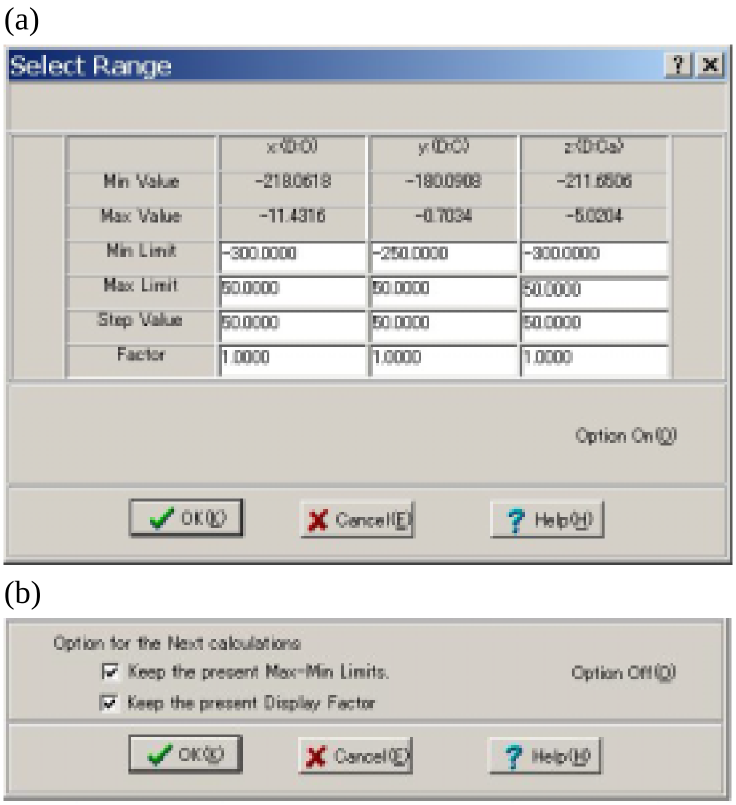
To delete these forms for dissection diagrams, the target dissection in the list can be deleted by clicking the “delete” button.

4.8 Menu “Diagram”

Range

In the normal procedure, range is automatically given so as to show all vertices calculated in a proper range. Such range can be edited by using “Range” menu.

Fig. 4.25 shows the Range Dialog. “Max value” and “Min value” are calculated from the obtained vertices. Min limit, Max limit, step value and display factor are to be edited for respective axes. The display factor is automatically determined so as to display diagram in an appropriate ratio among axes.



(a)

Select Range

	x:(D:O)	y:(D:C)	z:(D:Ca)
Min Value	-218.0618	-180.0908	-211.6506
Max Value	-11.4316	-0.7034	-5.0204
Min Limit	-300.0000	-250.0000	-300.0000
Max Limit	50.0000	50.0000	50.0000
Step Value	50.0000	50.0000	50.0000
Factor	1.0000	1.0000	1.0000

(b)

Option for the Next calculations

☑ Keep the present Max-Min Limits.

☑ Keep the present Display Factor

Fig. 4.25 Range Dialog (a) with Option off, (b) with Option on.

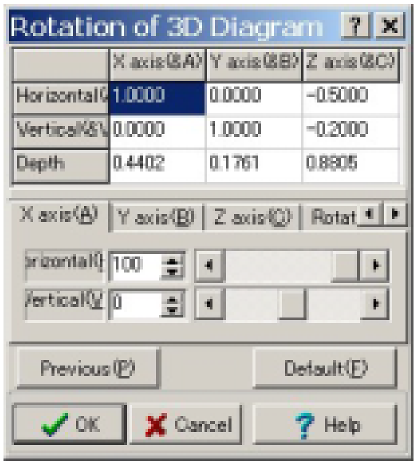
In bottom of the dialog, “Option On/off” button is available. When the “Option on” button is clicked, the options are displayed as shown in Fig. 4.25(b). Two options are available. One is about the range limits, the other being the display factor. When these options are clicked, this option becomes valid in the subsequent construction of diagrams. Otherwise, the range limits and the display factor will be automatically determined and renewed.

Rotation

The three dimensional diagram is plotted on the display panel by using the conversion matrix from the diagram coordinates[u, v, w] to the screen coordinates[X,Y];

$$\begin{bmatrix} X \\ Y \end{bmatrix} = \left(\begin{bmatrix} a11 & a21 & a31 \\ a12 & a22 & a32 \end{bmatrix} \right) \begin{bmatrix} u \\ v \\ w \end{bmatrix} \qquad [4.2]$$

The default matrix values are



	X axis(&A)	Y axis(&B)	Z axis(&C)
Horizontal(	1.0000	0.0000	−0.5000
Vertical(&V	0.0000	1.0000	−0.2000
Depth	0.4402	0.1761	0.8805

rizontal(: 100

Vertical(V: 0

Fig. 4.26 Rotation Dialog

$$\begin{pmatrix} 1 & 0 & -0.5 \\ 0 & 1 & -0.2 \end{pmatrix} \qquad [4.3]$$

Rotation of the diagram can be made by changing this matrix values. As shown in Fig. 4.26. the matrix values are shown in the top of the dialog and also in the two spin edit field for respective axis. This spin edit value can be also changed by scroll bar in the right hand side. On every action for changing value, the information is transferred to the current display panel and the target diagram is repainted.

In the “Rotation” page, rotation along the X, Y, or Z axis will be made on the presently displayed diagram.

The “previous” button resets the values to the previously restored values.

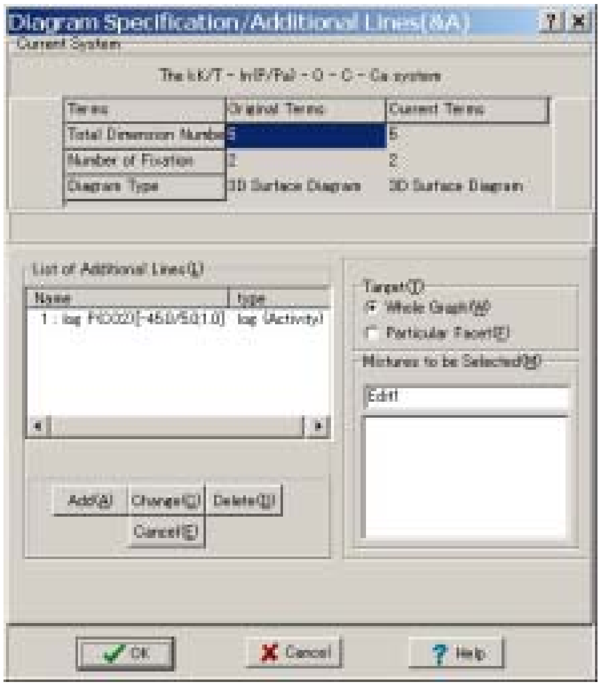
The “default” button resets the values to the default values given in Eq. [4.3]

Change Coordinates

The “Diagram Selection” page in the “Diagram Specification” Form will appear and the coordinates can be changed.

Display Mode

When a diagram is displayed in a display panel, there are several display



The kK/T - ln(P/Pa) - O - C - Ca system

Terms	Original Terms	Current Terms
Total Dimension Number	5	5
Number of Fixation	2	2
Diagram Type	3D Surface Diagram	3D Surface Diagram

Name	type
1 : log P(CO2)[-45.0/5.0/1.0]	log (Activity)

Fig. 4.27 Additional lines page in the Diagram Specification Form.

modes available.

The normal mode is to inform only the cursor position in the status line.

The "Touch Diagram" mode is to give the chemical potential table associated with the touched point on the diagram. This is only valid inside the visible facets. The space values are given in the status line and other more detailed properties are given in the chemical potential table.

The "Draw Line" mode is to draw a line on the three dimensional surface diagram. Each point is collected and can be shown as profile diagram. Single clicking on the surface adds a new point and double clicking ends the line. The profile diagram is shown after ending the lining. Collected points are shown in the points list form. To delete drawn lines, the "One dissection" menu is selected and items in the list can be deleted by clicking the "delete" button.

The "Move Location" mode is to move the location of the diagram itself or the string text associated with the diagram. After selecting this mode, cursor can be moved to the target diagram or text string. For the case of the diagram, a blue box appears along the diagram frame. On the top bar of the box, the cursor shape changes to finger and dragging can be made by left click and move mouse. By double clicking on the top bar, the diagram is maximized.

On double clicking on the maximized diagram, the previous size is recalled. On the corners, the shape of the box can be changed. For text string, only the change of location can be made. Instead, size of text string can be changed in “Diagram Font.”

Diagram Size

Diagram size relative to the display size is selected among maximize, standard and arbitrary.

“Maximize” makes full use of display panel in whatever shape.

“Standard” is based on a typical ratio between height and width.

“Arbitrary” starts the display mode of “Move location”.

Diagram Stayon / resize

Diagram size responsible to the resize of the display panel is selected between stay on or resize.

In “Resize,” the diagram size is always resized on change of the display panel size. For example, when diagram size is selected as standard, the diagram size is always resize to have the standard size for new display panel. On the other hand, In “Stay on,” no scaling will be made and the diagram size stay unchanged even on the change of the display panel. As a result, some parts of diagram can be masked by the frame. In such a case, scroll bar in the horizontal and vertical sides can be used to look the masked parts.

Diagram Zoom

In the normal procedure, the size is determined relative to the display panel size. This can be defined as the size having the factor of 100. The display factor can be changed in different ways;

1) Zoom down : Select the zoom down mode by clicking the Zoom down tool button, or select the “Zoom down” menu first and then clicking on the diagram gives rise to contraction to half size. The second click gives rise to another contraction. To stop it, the Zoom down tool button should be clicked again.
2) Zoom up : This mode gives rise to double size.
3) Zoom Plus Minus: After clicking this tool button, the display factor can be changed by manipulating the scroll bar for display factor which is prepared in the main tool bar. On clicking on the diagram, the center of the display

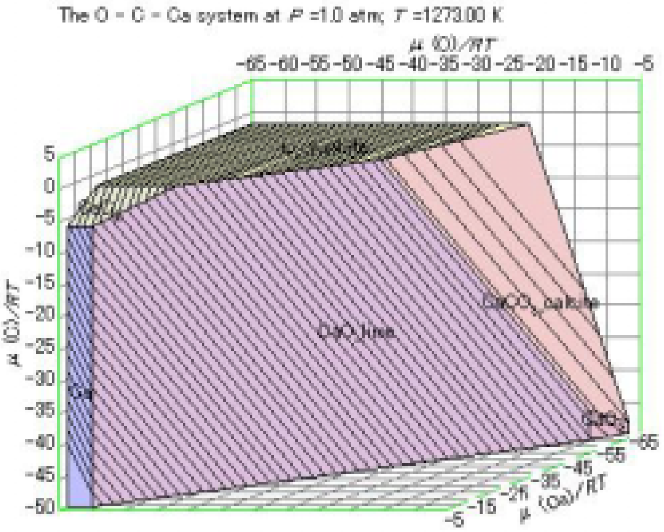


Fig. 4.28 Ca-O-C system with iso-partial pressure lines of CO_2

area moves to that clicked point. To zoom up in the vicinity of some point, first click that point. This leads to making the point at the center. Then manipulating the scroll bar gives rise to the zoom up and down at the point.

4) In the “Zoom” tool bar, the combobox for display factor is available. By selecting one of the listed factors, the diagram size can be changed.
5) To recover from undesired treatments on the zooming, there are two tool buttons are available. One is the initial tool button, the other being the “Default” tool button. Whenever the display mode is adopted among Zoom Down, Zoom up or Zoom plus minus, the initial position and size of the diagram is stored. The “Initial” tool button recalls the stored data. Note that this position and size are always renewed when Zoom mode is quitted. The “Default” tool button is to recall the normal position and size.

Diagram Color

Basically, the polygons in the diagram are colored in two ways: one is color, the other being in black and white. This is selected in the Diagram Color menu.

Diagram Font

Window’s dialog for Font appears for the diagram font. The selected font is common for all diagrams and will be saved in CHDWin.ini.

Additional Lines

When the two dimensional diagram or the three dimensional surface diagram are displayed, additional lines can be added on such diagrams. Fig. 4.27 shows the “Additional lines” page in the Diagram Specification Form.

When the “Add” button is clicked, the Select Additional Lines Form appears. This is essentially the same as the Many Dissections Form. Specification cam be made by using the elemental chemical potential or a linear combination of chemical potentials of compounds. When target chemical potential is selected, the default values for maximum, minimum, and step value are given. These values can be edited by users.

Additional lines are displayed all over the diagram. However, when mixture phases are included in the system, the additional lines can be limited in a selected mixture phase or drawn for whole system. This can be selected in the right hand side of the page.

Options

At present, options are available for painting mode of polygons. As shown in Fig. 4.29, there are five modes:

1) tricolors based on the coordinates values
2) tricolors based on the coefficients of space dimensions
3) color based on given 15 colors : sequential
4) color based on given 15 colors : preselected,
5) black and white

Tricolors are determined by pre-selected three colors and three coefficients associated with polygon. For Tricolors based on the coordinates values, the slope of the polygon plane in the coordinates is used. For tricolors based on the coefficients of space dimensions, the stoichiometric numbers of associated compounds are used instead. In this mode, the compound is displayed always in the same color

Change color can be made by double clicking on the color to be revised, or by clicking the “Change Color” button.

Brightness of colors can be adjusted by changing “brightness” index between 0 to 255.

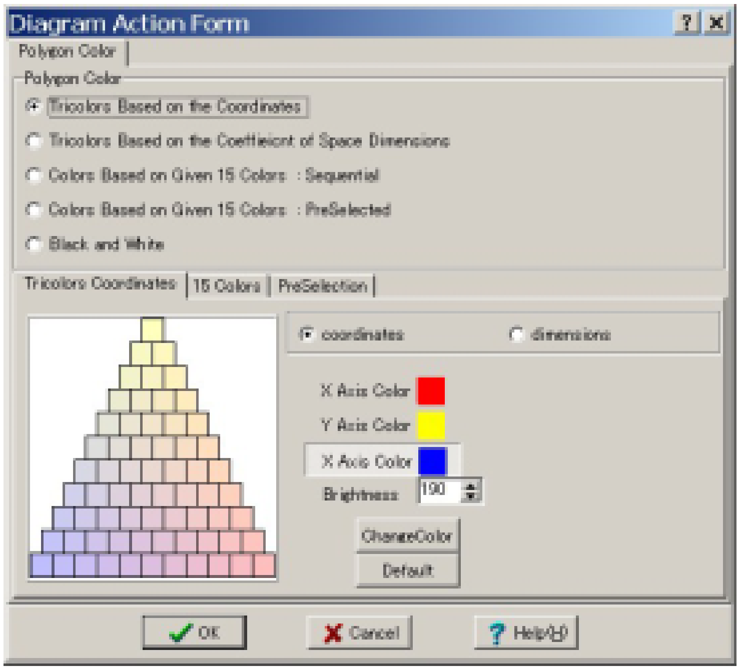


Diagram Action Form

Polygon Color

Polygon Color

● Tricolors Based on the Coordinates

○ Tricolors Based on the Coefficient of Space Dimensions

○ Colors Based on Given 15 Colors : Sequential

○ Colors Based on Given 15 Colors : PreSelected

○ Black and White

Tricolors Coordinates | 15 Colors | PreSelection

● coordinates ○ dimensions

X Axis Color 🟥

Y Axis Color 🟨

X Axis Color 🟦

Brightness 190

Fig. 4.29 The Diagram Options Form for determining polygon colors. No.1, Tricolors based on the coordinates values.

When the second mode is selected, each compound can have the same color throughout the series of construction. As shown in Fig. 4.30, “Show Compounds” button is used to show the present color for respective compounds in the left part.

Given 15 colors can be prepared by users. Its default values are determined from the following colors ;clGreen, clBlue, clRed, clYellow, clAqua, clFuchsia, clLime, clMaroon, clNavy, clOlive, clPurple, clSilver, clTeal, clMoneyGreen, clSkyBlue, clCream.

User’s determined colors are saved in CHDWin.ini file.

The “Sequential” mode is to give colors for list of polygons step by step. This mode does not check what compound is related to the polygon.

When you want to give a selected color for respective compounds, it is better to adopt the “Preselected” mode. In this mode, two buttons are available. The “Default Given colors” button gives the given 15 colors for compounds in the system sequentially.

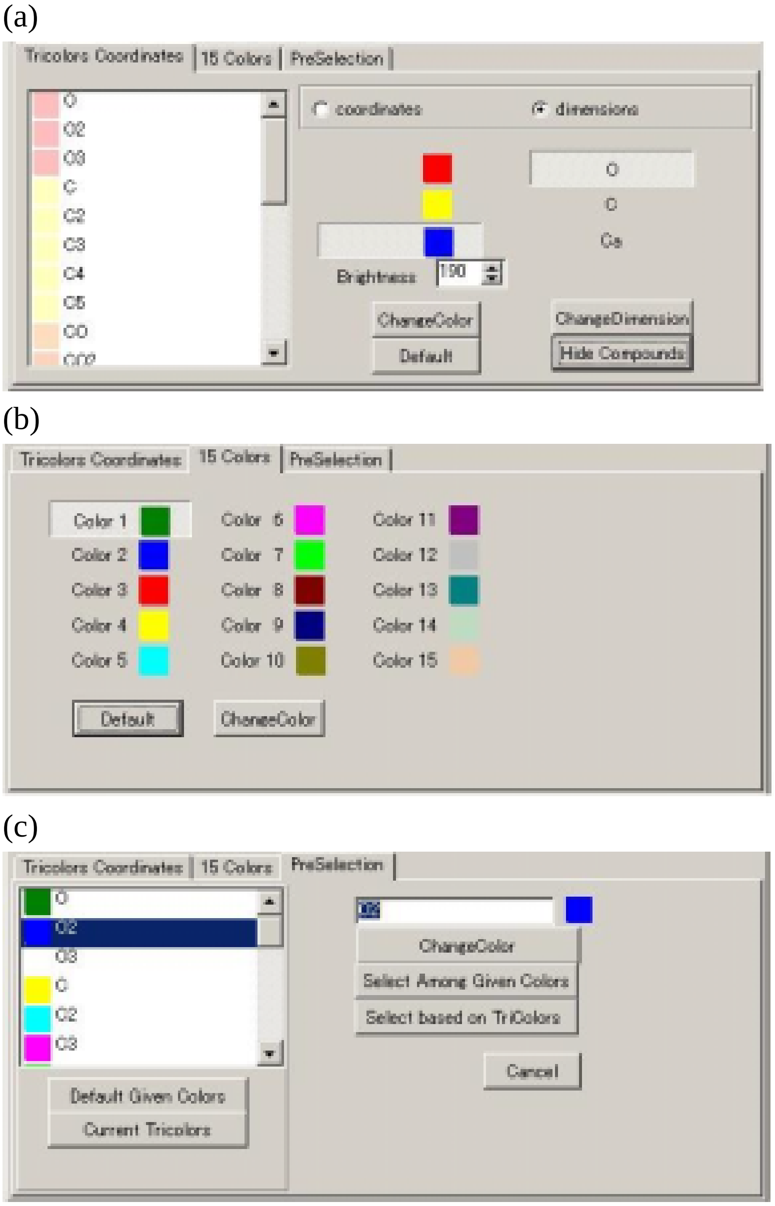


Fig. 4.30 The Diagram Options Form for determining polygon colors. (a) No.2, Tricolors based on the coefficients of space dimensions, (b) No. 3 Given 15 colors : Sequential, (c) Given 15 colors : Pre-Selected.

The "Preselected" mode is useful when you want to paint the special compound with a selected color.

4.9 Menu "Window"

Hidden forms

CHDWin uses several forms. Some of these forms will be hidden by other forms, particularly by the main form. By clicking the "Hidden Forms" menu, the list of the forms appear as menu items. On clicking the menu item, the hidden form will be shown on other forms. When the form was docked to other place, the form will be undocked.

4.10 Menu "Help"

CHD Help

Help system for the CHD for Windows consists of three ways:

1) start the CHD Help from the main menu;
2) click the help button on respective forms;
3) click the F1 key.

Version Info

Version information will be displayed.

4.11 Popup Menu

Popup menus are available for several cases;

1) When the display mode is normal, the popup menus for diagram cam be used after right clicking.
2) On the selection of compounds, popup menus for the following items can be selected;
    - Space Value
    - Coordinates Values
    - Display Points
    - Species log(Activities)
    - Species Concentration
    - Coefficients Of Space
    - Selection Of Column
    - Exit

3) On right clicking on the coolbar in the main from, the popup menus for toolbars will appear.
4) When clicking the downward arrow in the right side of file open tool button, the popup menus for reopen files will appear.

Appendix For Setup Pourbaix Diagrams

A.1Pourbaix diagrams and MALT/CHD

At present, the thermodynamic database MALT does not contain any aqueous species in its main database. Even so, the thermodynamic data for some aqueous species are available at 298.15 K and those data can be utilized in constructing the Pourbaix diagram. On the other hand, the present CHD for windows can provide a basis of constructing such Pourbaix diagrams, although this has been developed originally for constructing high temperature chemical potential diagrams.

Here, a method of constructing Pourbaix diagrams will be explained by using the user's data file, "FeSAqueous.txt" which store the thermodynamic data for aqueous species in the Fe-S-H-O system. This appendix is based on the following paper:

H. Yokokawa, N. Sakai, T. Kawada, and M. Dokiya, "Generalized Electrochemical Potential Diagrams for Complex Aqueous (M-X-H-O-e$^-$) Systems," J. Electrochem. Soc. 137(2)**, 388 (1990).**

Another example is the Li-Mn-O-H system which appears as the important system for the positive electrode for lithium batteries. This will be based on the user's data file, "LiMnOHAqueous.txt."

User's DataBase: FeSAqueous.udb

In this appendix, the compounds and aqueous species listed in Table A. 1 are used in constructing Pourbaix diagrams. The condensed compounds are those retrieved from the thermodynamic database MALT. Data source "udb" means the FeSAqous.udb which are compiled from the user data file "FeSAqueous.txt." The data source of the aqueous species are the NBS thermodynamic properties published in 1982 which are the main parts of the MALT database so that the consistency of the data in the FeSAqueous.udb with the Main Database is obvious.

In the NBS tables, some data are lack in the absence of the experimental data. For the construction of chemical potential diagram, only the Gibbs energy data are used. On the other hand, the Gibbs energy in MALT Direct is calculated from the enthalpy data and the entropy data. When enthalpy and entropy are lack but Gibbs energy is available in the NBS table, the NBS data could not be used directly. In such a case, user data are treated as follows as a convenient method although this has no physical meaning, that is, the enthalpy value is assumed to be the same as the Gibbs energy and the entropy is calculated to reproduce the Gibbs energy value from thus assumed enthalpy.

In addition, the heat capacity of all aqueous species is assumed to be zero. Apparently, this is not correct.

Thus, please note that the present data set of the aqueous species are not valid at temperatures other than 298.15 K.

Table A.1 Gibbs energy change for formation of compounds and their data sources

Compound	state	$\Delta_f G^o/RT$	source
H_2S	g	-13.53	MALT
SO_2	g	-121.14	MALT
Fe^{2+}	ao	-31.84	udb
Fe^{3+}	ao	-1.90	udb
$HFeO_2^-$	ao	-176.82	udb
S^{2-}	ao	34.63	udb
SO_4^{2-}	ao	-300.49	udb
HS^-	ao	4.87	udb
HSO_4^-	ao	-305.11	udb
$FeSO_4^-$	ao	-311.91	udb
H_2S	ao	-11.24	udb
H_2O	l	-95.72	MALT
H_2O_2	l	-48.69	MALT
$H_2SO_4*6.5H_2O$	l	-922.66	MALT
Fe	c	0.00	MALT
Fe_2O_3	c	-299.55	MALT
Fe_3O_4	c	-409.85	MALT
FeS	c	-40.52	MALT
FeS_2	c	-67.36	MALT
$FeSO_4$	c	-331.31	MALT
$Fe_2(SO_4)_3$	c	-909.78	MALT
$FeSO_4*7H_2O$	c	-1012.99	MALT

What are Pourbaix Diagrams

Usually, the Pourbaix diagrams can be used for different types of diagrams.

One is the predominance area diagram, in which the dominant aqueous species will be given as a function of pH and pE, where pH means –log *a*(H^+) and pE is the corresponding variable for electrical potential. Resulting area of each aqueous species can be expressed in terms of convex polygons.

The second, important diagram is the normal diagram in which the equilibria between the aqueous species and the condensed phases are shown as chemical potential diagrams.

Here, these two types of diagrams will be reproduced using the CHD for Windows.

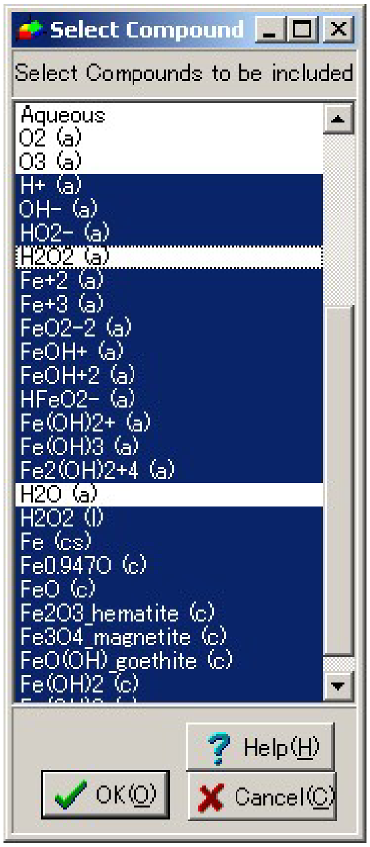
Fe-O-H-e^- system

In the MALT for Windows, the thermodynamic data should be retrieved in the following manner.

1) User data file, FeSAqueous.txt, should be selected and compiled (menu Tool/User data/compile user data text file).
2) In the menu of Tool/MALT options, check should be made on the option for including aqueous species in the options in searching.
3) In the menu of “Get compounds by elements”, “Compounds consisting of combinations of elements” should be selected as the mode of searching compounds. When the element sets of O,H, Fe will be selected, the compounds and aqueous species in the Fe-O-H-e^- system will be retrieved.

In CHD for Windows, these thermodynamic data will be transferred from MALT by means of MALT Direct.

Note again here that the present thermodynamic data for aqueous species stored in the user database: FeSAqeous.udb does not include the high temperature heat capacity data. Calculation at temperatures other than 298.15 K leads to serious errors so that this should never be attempted.



Select Compound

Select Compounds to be included

Aqueous
O2 (a)
O3 (a)
H+ (a)
OH- (a)
HO2- (a)
H2O2 (a)
Fe+2 (a)
Fe+3 (a)
FeO2-2 (a)
FeOH+ (a)
FeOH+2 (a)
HFeO2- (a)
Fe(OH)2+ (a)
Fe(OH)3 (a)
Fe2(OH)2+4 (a)
H2O (a)
H2O2 (l)
Fe (cs)
Fe0.947O (c)
FeO (c)
Fe2O3_hematite (c)
Fe3O4_magnetite (c)
FeO(OH)_goethite (c)
Fe(OH)2 (c)

Fig. A1.1 Selection of Species to be included in the chemical potential diagram.

Chemical System

The first diagram to be constructed is the Pourbaix diagram for the Fe-O-H-e^- system. Species to be included are determined as followed:

1) Menu Chemical System is selected:

   Selection of compounds is made by "selection by Default" with checking on the "Condensed phases" and "Aqueous species."
2) Then, "Reselection" button is clicked.
3) Among the listed species, the following species are excluded.

   O2(a), O3(a), H2O2(a)

Fig. A1.1 shows the resulting form for selecting compounds. The focused species and compounds are to be included in the diagram construction.

Diagram Specification

Dimension Selection :

No further specification is needed; that is, 298.15 K is selected.

Fixation

Since the Pourbaix diagram is constructed under the condition of $a(H_2O)$ = 1. For this purpose, the following is made:

1) Select the species, H2O a, in the list of species and compounds.
2) Select the coefficient of 1.

Diagram Selection

Here, the three dimension surface diagram is selected as diagram type.

As Coordinates, the followings are listed:

(D:O)
(D:Fe)
(D:pE)

Here, (D:pE) is the coordinate corresponding to the electric charge. In the present treatment of CHD, the charge is treated as pseudo element. As a result, working variable for the electrical potential is defined as follows,

$$\mathrm{pE} = \phi / 2.303\, kT \qquad \text{(A1.1)}$$

where ϕ is the electrical potential. This is well related with the pH defined as

$$\mathrm{pH} = -\mu(\mathrm{H}^+) / 2.303\, kT = -\log a(\mathrm{H}^+) \qquad \text{(A1.2)}$$

To modify the coordinates appropriate for the Pourbaix diagram,

1) pH is selected as X axis. For this purpose, first focus is moved on the first line of (D:O) and double click on this line. A species, H+ (a), is first selected and the coefficient of –1 is selected in the Coefficient Fom.
2) pE is selected as Y axis. For this purpose, focus is moved on the (D:pE) and then click the upward arrow to move the (D:pE) to the second line.
3) The coordinate (D:Fe) is not changed.

Equilibria between condensed phases and aqueous species I generalized diagram

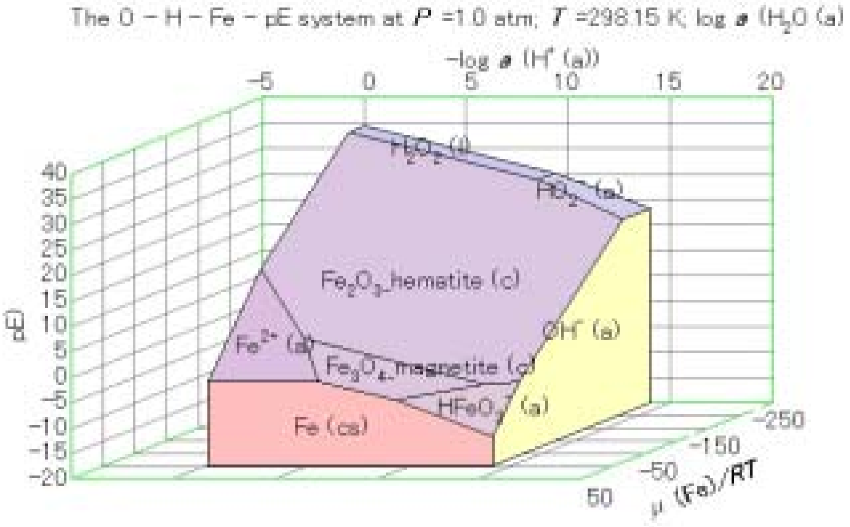


Fig. A1.2 The generalized electrochemical potential diagram for the Fe-O-H-e^- system at 298.15 K under the condition of $a(H_2O) = 1$.

Fig. A1.2 shows the generalized electrochemical potential diagram for the Fe-O-H-e^- system at 298.15 K under the condition of $a(H_2O) = 1$. The important point as the generalized diagram is that the chemical potential or the activity of Fe is explicitly expressed in the diagram. In this diagram, the condensed phase and the aqueous species are respectively shown as stable polygon.

There are several points to be noted here:

1) Aqueous species are presented as the condition that their activity is equal to unity.
2) On the other hand, those species or compounds which do not contain the iron component form the frame within which the iron compounds can be displayed as stable compounds; namely, H^+, H_2O_2(l), HO_2^-, and OH^- form such a frame as shown in Fig. A1.2.

Equilibria between condensed phases and aqueous species II Pourbaix diagram

Fig. A1. 3(a) and 3(b) are the diagram to reproduce the Pourbaix diagram.

Fig. A3(a) is the two dimensional chemical potential diagram which is constructed under the same calculation conditions as Fig. A1.2. When compared with the normal Pourbaix diagram, the regions beyond pH=0 or 14 are lacked. This is because the H^+ and OH^- species are explicitly included as

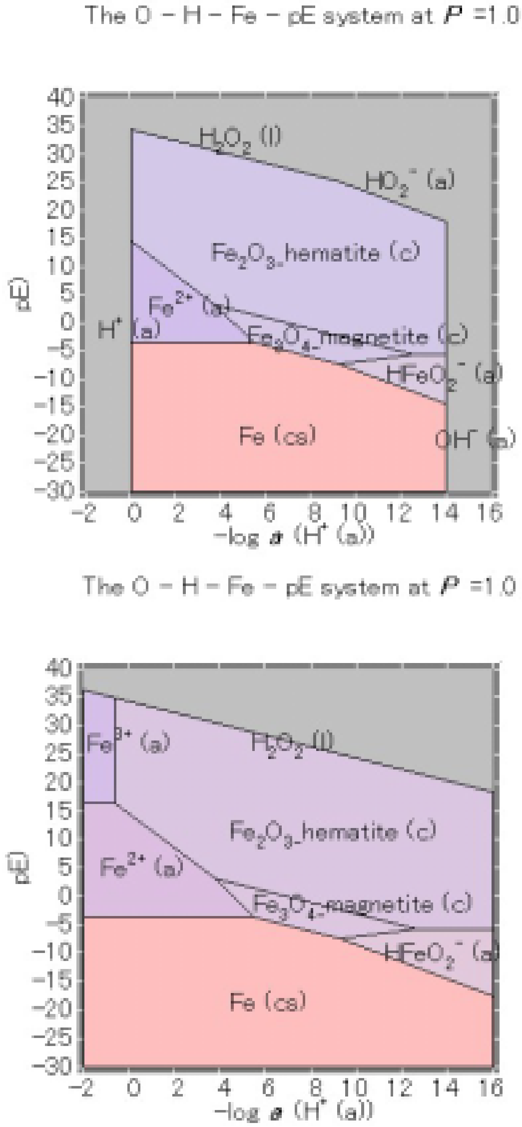


Fig. A1.3 The generalized electrochemical potential diagram for the Fe-O-H-e^- system at 298.15 K under the condition of $a(H_2O) = 1$. (a) with and (b) without H^+, HO_2^-, and OH^- species.

target compounds to be included as stable species and their activity is defined as unity.

To reproduce the Pourbaix diagram which shows the equilibria beyond these limits, the following can be made.

1) In the menu of “Chemical System / Selection of compounds,” “ReSelection” button is clicked and the species, H^+, HO_2^- and OH^-, are excluded.

2) Other conditions are the same as before.

Resulting diagram is shown in Fig. A1. 3(b). The species, Fe^{3+}, appears as stable species.

Predominant area diagram

Pourbaix also proposed to use the predominant area diagram which indicate what aqueous species is predominant in the given thermodynamic conditions in terms of pH and pE.

To reproduce the predominant area diagram, the following setting can be made:

1) In the menu of “Chemical System / Selection of Compounds, the default setting is made only on the aqueous species.
2) Then, “ReSelection” button is clicked and those species which do not contain the iron component will be excluded; namely, O_2, O_3, H^+, HO_2^-, OH^-, H_2O_2 will be excluded.

Fig. A1. 4 shows the predominant area diagram in which only the iron containing aqueous species are presented as predominant species.

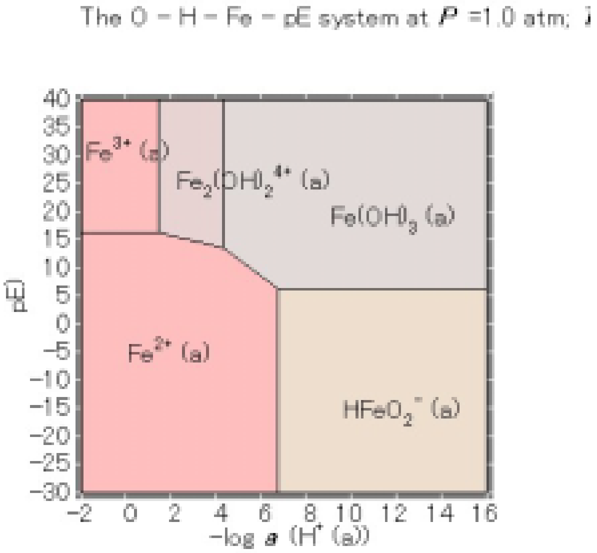


Fig. A1.4 The predominant area diagram for the Fe-containing species at 298.15 K.

S-O-H-e^- System

Chemical System:

The same user database is used to retrieve the thermodynamic data for the S-O-H-e^- system.

The Pourbaix diagram and the predominant area diagram for the S-O-H-e^- system can be constructed in the same procedures as those in the Fe-O-H-e^-

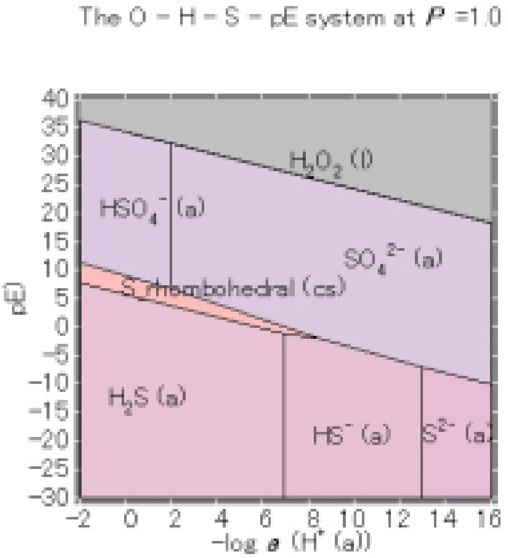


Fig. A1.5 The Pourbaix diagram for the S-O-H-e^- system at 298.15 K.

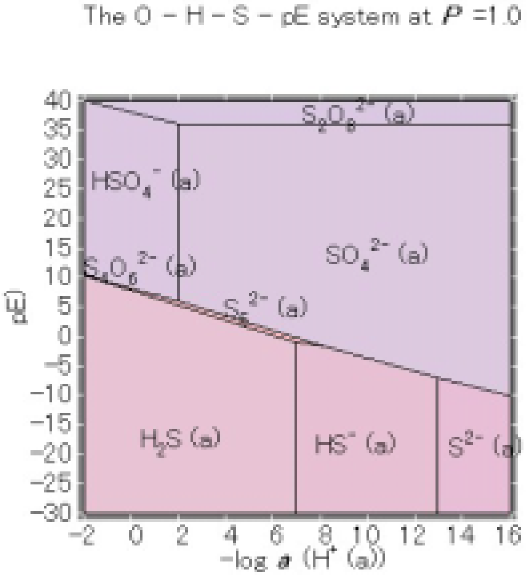


Fig. A1.6 The predominant area diagram for the S-containing species at 298.15 K.

system.

Fig. A1.5 shows the two dimensional chemical potential diagram for the S-O-H-e^- system. As sulfur compounds, only S appears as stable compounds.

Fig. A1. 6 shows the predominant area diagram for the sulfur aqueous species. This is very similar to Fig. A1. 5 where except S, aqueous species are the stable ones.

Fe-S-O-H-e^- System

The most powerful point of the present CHD program is to construct the Pourbaix diagram for the multicomponent system without any difficulty. As described above, we do not need to have any other algorithms for constructing the Pourbaix diagram or the predominant area diagram. What is needed in constructing such diagrams is only the following:

1) Select the species to be included in construction of diagram.
2) Specify the condition that $a(H_2O) = 1$.
3) Select the coordinates appropriate for the Pourbaix diagrams. Particularly, pH and pE should be correctly selected.

The same procedures will be adopted below to construct the Pourbaix diagram for the Fe-S-O-H-e^- multicomponent system.

Chemical System

The thermodynamic data for the Fe-S-O-H-e^- system are retrieved from the MALT main database and the user database: FeSAqueous.udb.

Three Dimensional Chemical Potential Diagram

Selection of Compounds

Condensed phases and also aqueous species are included, although species in the O-H-e^- system are excluded to eliminate the limits derived from H^+ etc.

Fixation

Only the activity of water is fixed at unity.

Diagram Coordinates

$-\log a(H^+)$ (=pH)

pE
log *a*(Fe) – log *a*(S)
(D:Fe)

After execute the command Run, the range limits are modified as follows:

	-log *a*(H^+)	pE	log *a*(Fe)-log *a*(S)
min	-2	-40	-100
max	16	40	150
step	2	10	50
factor	1	0.25	0.125

Fig. A1.7 shows the three dimensional Pourbaix diagram for the Fe-S-O-H-e^- system ate 298.15 K under *a*(H_2O)=1. As the third axis, we select the valuable of log *a*(Fe) – log *a*(S). The type of axis variable is convenient for treating two metals in equivalent manner. Here, we are treating two elements, iron and sulfur.

In Fig. A1.7, the phase equilibrium information for the Fe-O-H-e^- subsystem appears in front of the diagram. On the right hand side, the dissection at pH=16 appears as a function of log *a*(Fe)-log *a*(S).

Conventional diagram for the Fe-S-H_2O system

Traditionally, the Pourbaix diagram for the Fe-S-H_2O system has been constructed under the assumption that the redox element of the target diagram is Fe so that only species which contain the iron component will appears in the diagram.

To reproduce such a diagram in CHD, the following should be made:

1) the third axis is changed to – log *a*(Fe) + log *a*(S). This is to present the sulfur containing compounds before the iron containing compounds which do not include sulfur.
2) In the menu of rotation of 3D diagram, the conversion matrix is changed to as follows;

	X-axis	Y-axis	Z-axis
Horizontal	1.0	0.0	0.0
Vertical	0.0	1.0	0.0
Depth	0.0	0.0	1.0

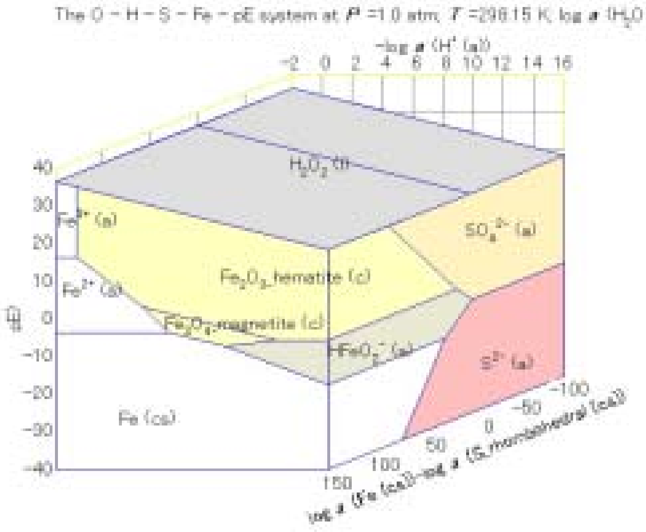


Fig. A1.7 The Three Dimensional Pourbaix diagram for the Fe-S-O-H-e^- system at 298.15 K.

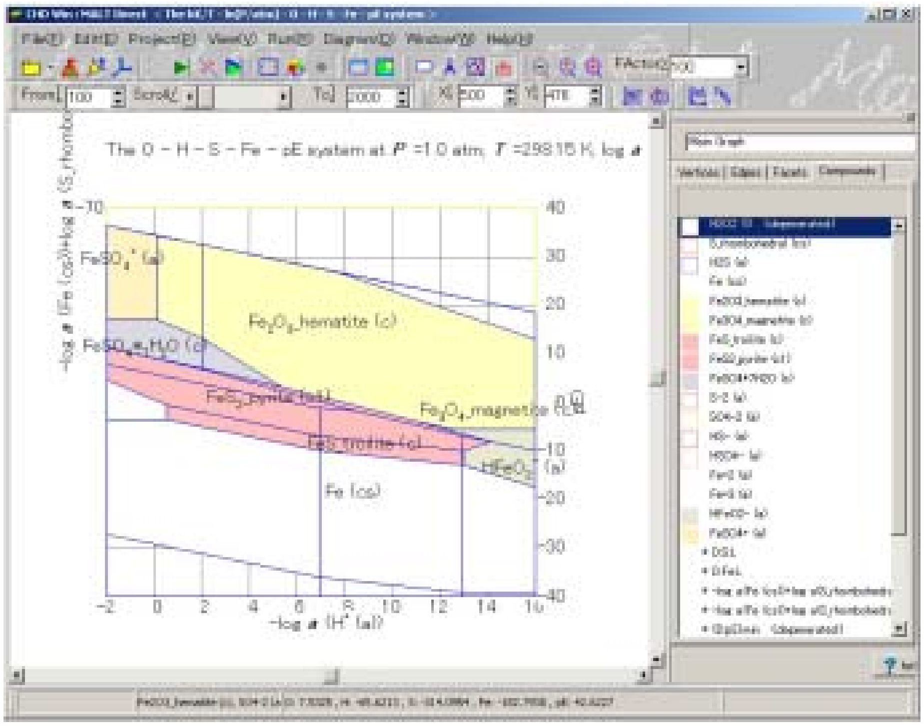


Fig. A1.8 The Three Dimensional Pourbaix Diagram projected on the pH-pE plane.

3) In the menu of Graph Inspector / “Compounds” page, the transparency of

the displayed compounds is changed in the following compounds:

- H2O2 (l)
- S_Rhombohedral (cs)
- H2S (a)
- S-2(a)
- SO4- (a)
- HS-(a)
- HSO4- (a)

Fig. A1. 8 shows the three dimensional diagram which is rotated so as to give the normal two dimensional Pourbaix diagram. There are several blue lines which are not related with the stable polygons of the species. These are borderlines for species which are converted to be transparent.

The phase equilibria become complicated so that it is not easy to distinguish the respective stable area. For example, in Fig. A1. 8, it is not easy where the stability region of Fe_3O_4. To make clear the relative relations among the stability areas, the option of zoom can be used. Fig. A1.9 shows the enlarged diagram; here, the stability region can be well recognized in relations to other stability areas.

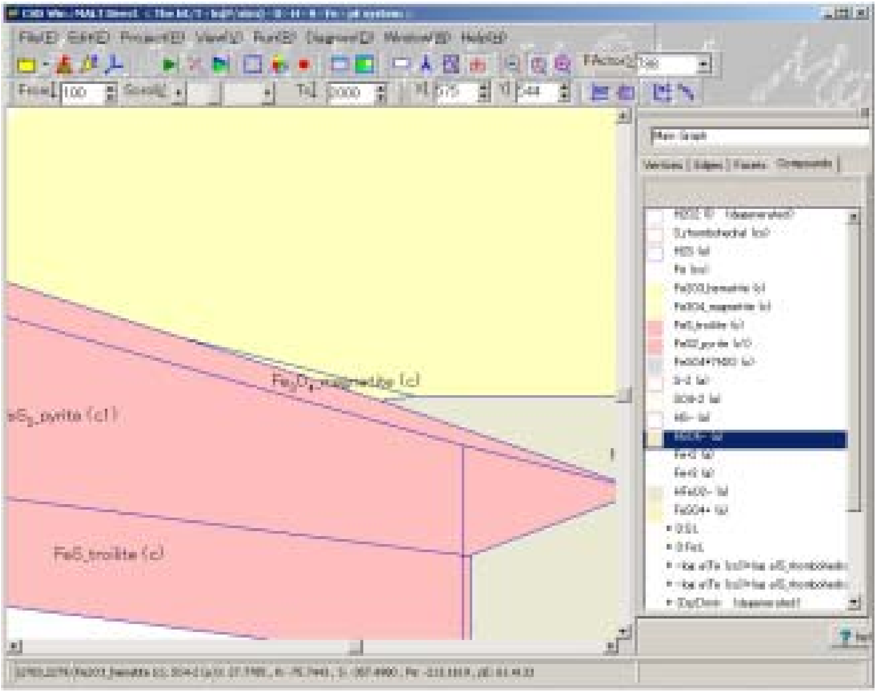


Fig. A1.9 The Three Dimensional Pourbaix Diagram projected on the pH-pE plane. This is enlarged diagram to show clearly the stability area of Fe_3O_4.

Dissections

There are many ways to specify another fixation to obtain the two dimensional diagram or the three dimensional surface diagram. One of the most attractive ways is to make a dissection on the three dimensional diagram.

Fig. 1A.10 shows the dissection diagram which was constructed on the basis of the previously constructed three dimensional diagram (Fig.A1. 8,9).

The menu of Run / Dissection is selected. The dissection plane is defined by selecting the variable of pH, that is, H^+ is selected and the coefficient of –1 is selected.

“Dissection Swing” should be checked.

“Profile Diagram” should be also checked. The diagram type is specified as dissected diagram(2D). The coordinates are selected as follows;

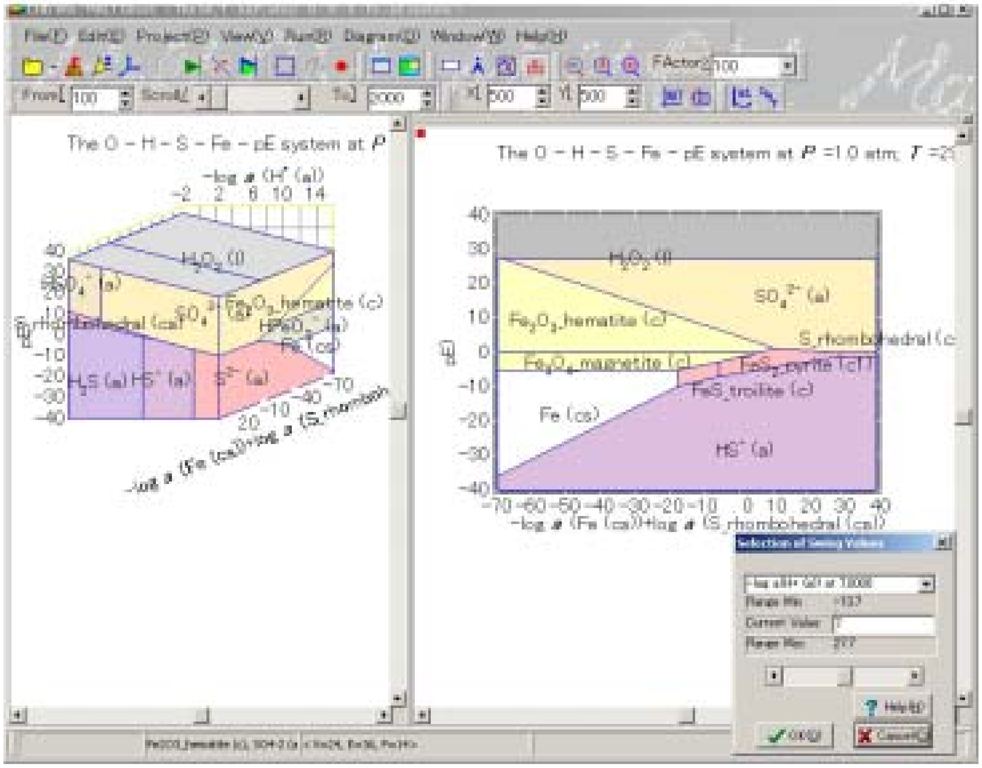


Fig. A1.10 The dissection diagram at pH=7 for the three Dimensional Pourbaix Diagram at 298.at K.

1) The axis variable, –log *a*(Fe) + log *a*(S), is moved to the x-axis.
2) The axis variable, pE, is moved to the y-axis.
3) As a result, the working variable pH is moved to the z-axis that will not be used in 2D dissection diagram.
4) When the Selection of Swing Values appears, the range limits are changed by right-hand-mouse click; the new values should be changed from –2 to 16.

Fig. A1. 10 shows the dissection at pH=7. In the left hand side, the phase relations in the Fe-O-H-e^- system are presented, whereas the phase relations in the corresponding sulfur system are shown in the right hand side. In between, those species which contain both iron and sulfur appear.

Relation among diagrams for dry, hydrated and wet systems

Since the chemical potential diagram for the Fe-S-O system and the electrochemical potential diagram for the Fe-S-O-H-e^- system can be constructed by the same algorithm and the same program, it is very easy to compare those diagrams under the same conditions. One interesting comparison from the chemical point of view is the construction of diagrams with the same coordinates for the dry, the hydrated and the wet systems. By hydrated system, the diagram is constructed for the Fe-S-O-H system without any aqueous species. Even so, the activity of water is fixed at unity in the system, some hydrated compounds can be formed. By wet system, the diagram can contain the aqueous species in addition to the compounds appearing in the hydrated system.

Fig.A1.11 compares three diagrams for the Fe-S-O (-H-e^-) systems. As wet systems, pH=7 is adopted.

In the hydrated system, $FeSO_4$ disappears and instead, $FeSO_4$*7H_2O appears. In addition, H_2SO_4*H_2O appear in the upper-right corner.

In the aqueous system, the aqueous species, SO_4(a), appears instead of $FeSO_4$, $FeSO_4$*7H_2O or H_2SO_4+H_2O. In addition, the aqueous species, HS^-, appears in the left hand side. This diagram should be compared with the Pourbaix-type dissection diagram in Fig. A2.10.

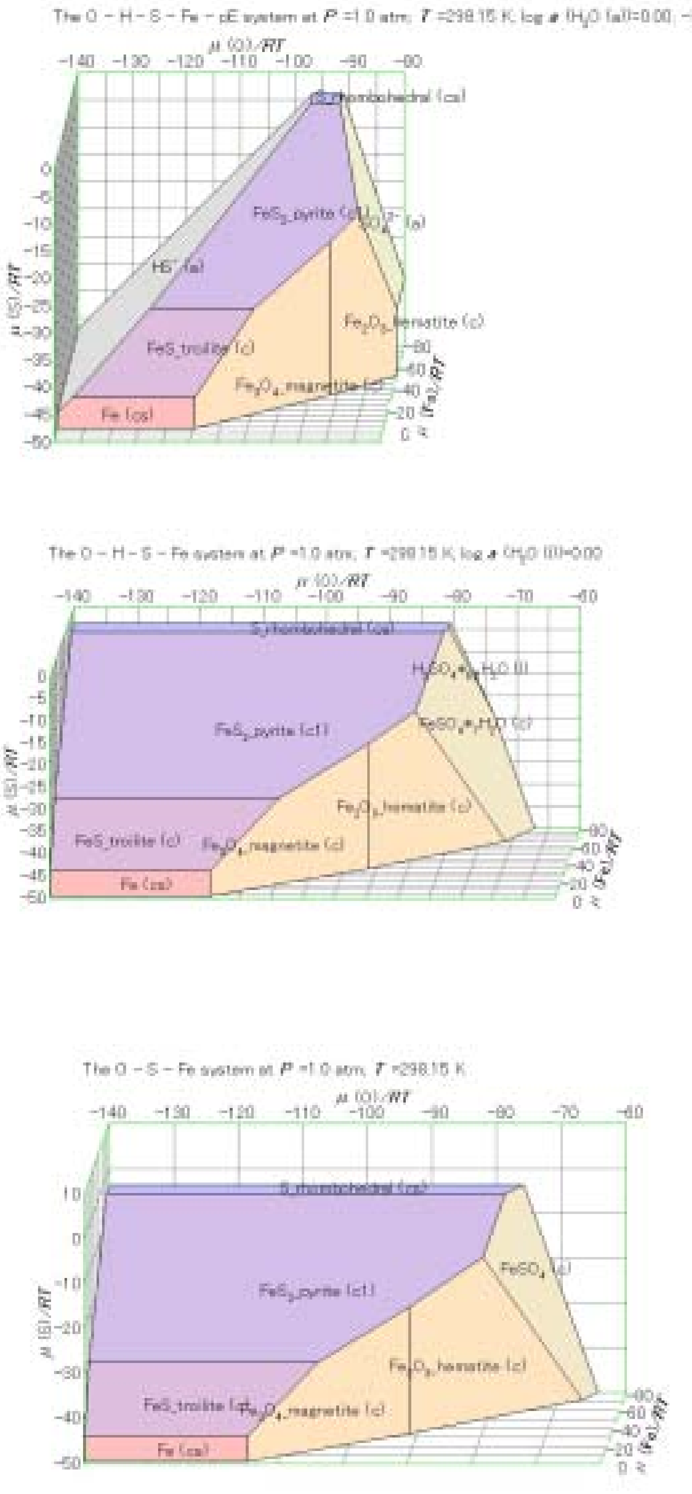


Fig. A1.11 The chemical potential diagrams for the Fe-S-O system: (a) wet system, (b) hydrated system (c) dry system

A2 Electrochemical potential diagrams for Li-Mn-O-H-e$^-$ system

The present electrochemical potential diagram can be applied to many materials issues associated with the electrochemical devices. One of such applications is the lithium batteries.

Here, an attempt will be made to construct the electrochemical potential diagram for the Li-Mn-O-H-e$^-$ system. Although the electrolyte for lithium battery does not contain water in it, it will be interesting to know the phase equilibria associated with the Li-Mn-O-H system because it has been already pointed out that the presence of a small amount of acidic water that is caused by the oxidation of the electrolyte may enhance the manganese dissolution.

Chemical System

The thermodynamic data for the Li-Mn-O-H-e$^-$ system can be completed when the user database, LiMnOHAqueous.txt is used.

Pourbaix diagram for the Mn-O-H-e$^-$ system

The thermodynamic data for the Mn-O-H-e$^-$ system are retrieved as follows:

1) user database “LiMnOHAqueous.udb” is loaded in the menu “Options / User data /load user database.”
2) In the menu “Tools / Customize MALT Setting ,” check should be made for the “including Aqueous species” in the Options for Search in “General” page.
3) In the menu “Search Compounds,” “Get compounds” with “Search by Elements” is selected. In the form of “Search Compounds by Elements,” the mode of “Compounds consisting of combination of the elements” is checked and then “Mn,” “O,” and “H” are selected.
4) After preparing the thermodynamic data in MALT with above procedures , the “MALT Direct” is used to transfer the data to CHD.

In a similar manner described in Appendix 1, the two dimensional Pourbaix diagram for the Mn-O-H-e$^-$ system can be constructed as in Fig. A2.1.

5) In the chemical system, the selection of compounds is made by first selecting the “Select by Default” with check on the condensed phases and the aqueous species and then by clicking “ReSelction” button to remove the species of O2(a), O3(a), H$^+$(a), OH$^-$(a), HO2$^-$(a), H2O2(a).

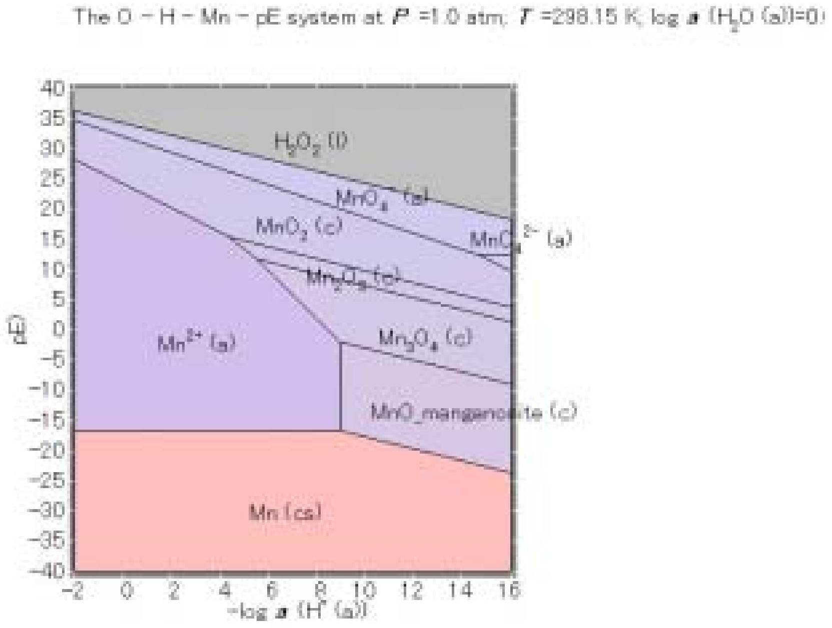


Fig. A2.1 The Two Dimensional Pourbaix Diagram for the Mn-O-H-e^- system at 298.15 K.

6) In the menu "Project / Specify Diagram," the fixation is made to select the water, H2O(a), with the fixed value at unity and the diagram type of 2D chemical potential diagram with the coordinates of -log $a(H^+)$ as the x axis and the (D:pE) as the y axis and (D:Mn) as the z-axis.
7) Since the resulting diagram has a display range wider than the normal, the display range of diagram should be changed by selecting the menu "Diagram / Range." The proper range for the x- and the y-axes are the followings

	-log $a(H^+)$	pE
min	-2	-40
max	16	40
step	2	10
factor	1	0.25

The chemical feature of the Pourbaix diagram for Mn is that the aqueous species Mn^{2+} as well as MnO_4^- and MnO_4^{-2} are present.

Pourbaix Diagram for the Li-O-H-e^- system

In the same manner, the Pourbaix diagram for the Li-O-H-e$^-$ system can be constructed as given in Fig. A2.2. In this system, only Li$^+$ species apears as the stable species. However, the stability region of Li$^+$ is quite wide compared with the corresponding species in the Mn-O-H system.

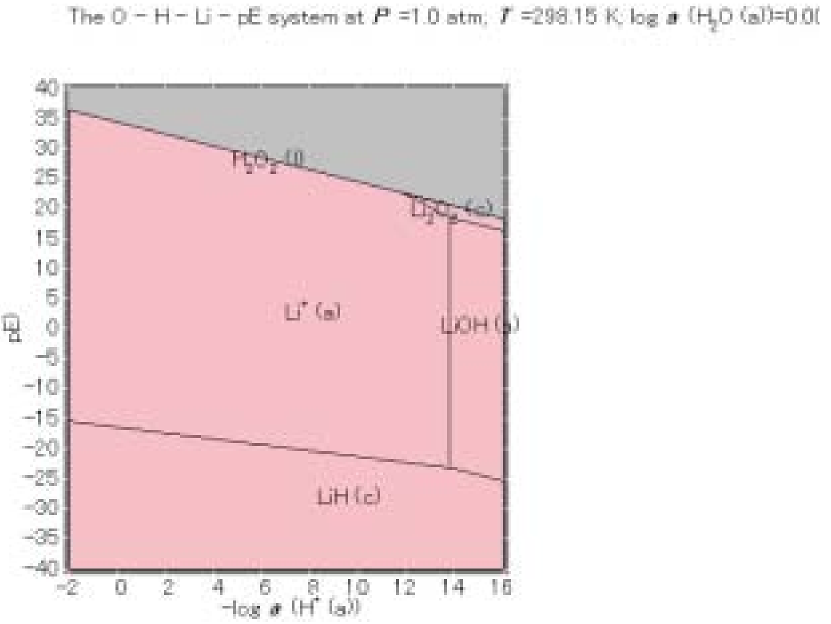


Fig. A2.2 The Two Dimensional Pourbaix Diagram for the Li-O-H-e$^-$ system at 298.15 K.

Three dimensional Pourbaix diagram for the Li-Mn-O-H e$^-$ system

The three dimensional Pourbaix diagram can be set up by the following procedures:

1) Data retrieval for the Li-Mn-O-H-e$^-$ system from the MALT main database and the user database: LiMnOHAqueous.udb.
2) Remove of aqueous species which do not include Li or Mn.
3) Fixation of water, H2O, at the activity of unity
4) The diagram type of 3D chemical potential diagram
5) Change of the coordinates as follows:

X axis : -log $a(H^+)$ (=pH)

Y-axis : pE

Z-axis : log *a*(Mn) – log *a*(Li)

6) Diagram Range is defined as

	-log *a*(H^+)	pE	log *a*(Mn)-log *a*(Li)
min	-2	-40	-90
max	16	40	60
step	2	10	10
factor	1	0.25	0.125

Fig. A2.3 shows the resulting diagram. Phase equilibria in the Mn-O-H-e^- subsystem shown in Fig. A2.1 appears in the front plane in Fig. A2.3, whereas in the right hand side plane, the phase equilibria at *pH*=16 appear.

Since this is the three dimensional diagram so that some additional procedures are needed to know more detailed information of the target chemical equilibria.

The followings are the possible procedures

1) To make some compounds transparent.

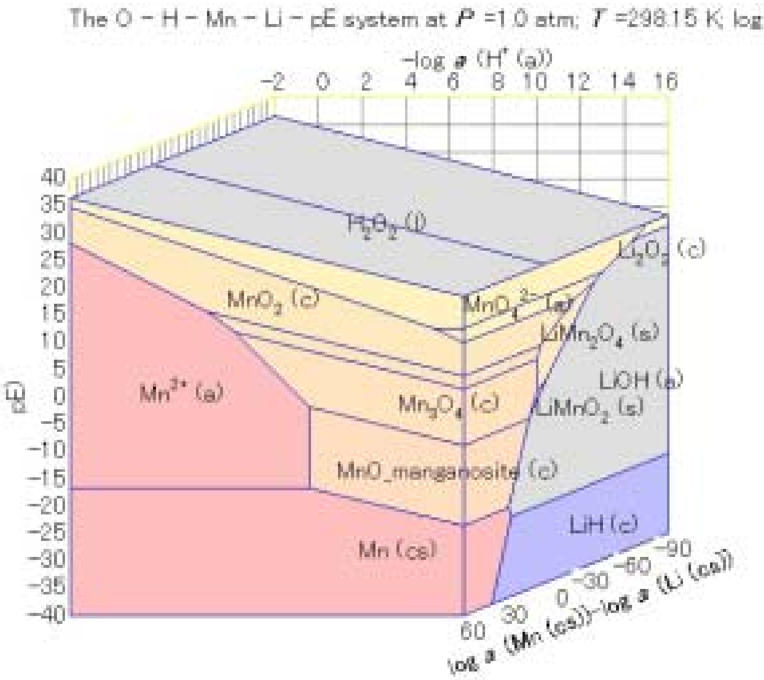
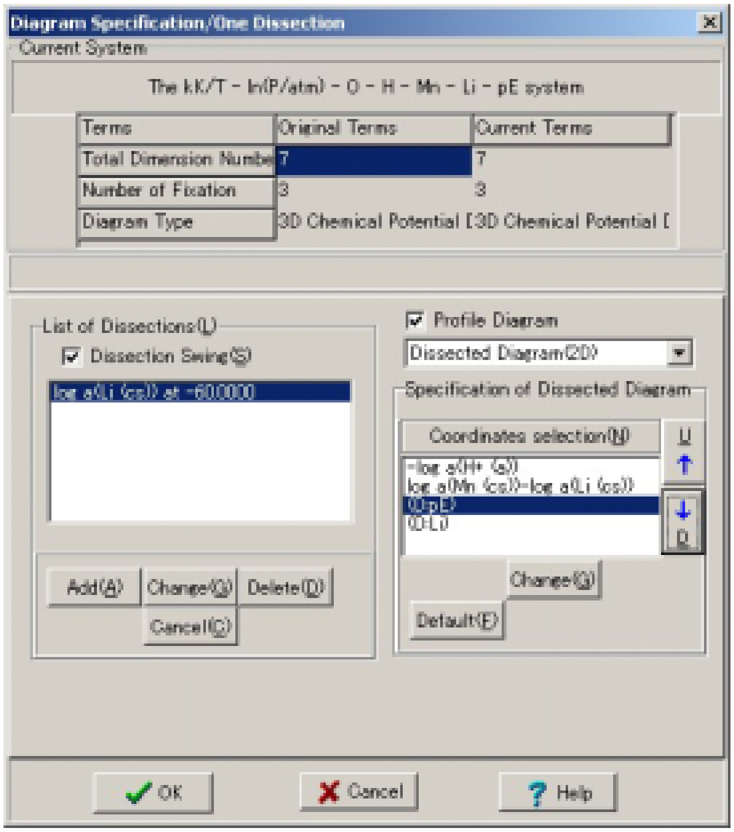


Fig. A2.3 The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e^- system at 298.15 K.



Current System

The kK/T - ln(P/atm) - O - H - Mn - Li - pE system

Terms	Original Terms	Current Terms
Total Dimension Numbe	7	7
Number of Fixation	3	3
Diagram Type	3D Chemical Potential [	3D Chemical Potential [

List of Dissections(L)

☑ Dissection Swing(S)

log a(Li (cs)) at -60.0000

☑ Profile Diagram

Dissected Diagram(2D)

Specification of Dissected Diagram

Coordinates selection(N)

-log a(H+ (a))
log a(Mn (cs))-log a(Li (cs))
(O:pE)
(O:Li)

Fig. A2.4 The Diagram Specification / One Dissection for the three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e^- system at 298.15 K.

2) To make one dissection and to swing the dissection value.
3) To make a series of dissections

<u>One dissection at log *a*(Li) = -60</u>

Here, an attempt is made to make a dissection by fixing the lithium activity.

The menu “Dissection” is selected. Thus, the dialog for the Diagram Specification / One Dissection page will appear as Fig. A2.4. One dissection plane is selected by clicking the Add button and the Li(cs) is selected among the Compound candidate. At this time, the fixed value is input as –60.

When profile diagram is checked, the diagram can be selected between the dissected diagram (2D)or the dissected diagram (3D). Here, the dissected diagram (2D) is selected. In Fig. A2.4, the X-axis for the 2D dissection diagram is defined as –log $a(H^+)$, the Y-axis being log a(Mn) – log a(Li).

A resulting dissection diagram is shown in Fig. A2.5. In this diagram, the display form for the dissection diagram is docked in the right-hand side docking panel.

The CHD Main form has the two docking panels; that is, the right-hand panel and the bottom-side panel. When the top frame of the display form is dragged by putting the control key and left click of mouse, the position of cursor appearing with the dragging square frame can be adjusted between the Right-hand frame of the Main Form and the scroll bar of the Main Display Panel. Then, the Dissection Display Form will be docked to the panel as shown in Fig. A2.5. The relative size of the main display panel and the additional display panel can be adjusted by manipulating the position of splitting bar adjacent to the vertical scroll bar of the main display panel.

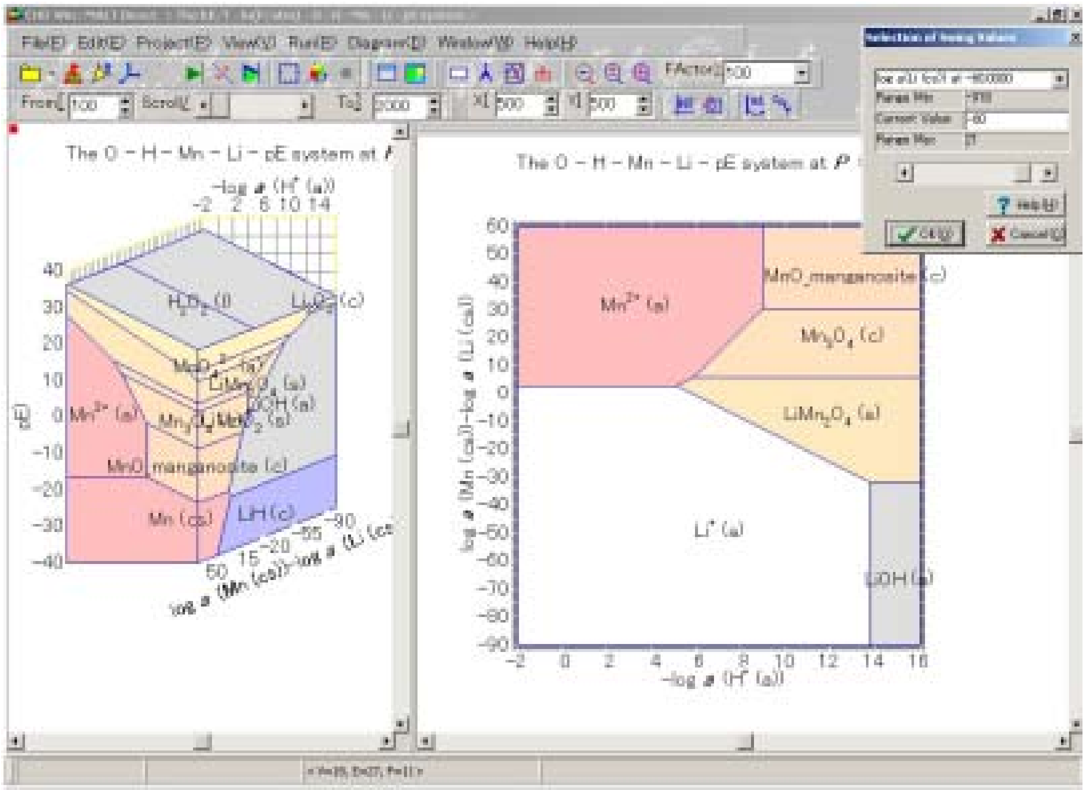


Fig. A2.5 The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e^- system at 298.15 K with the dissected diagram (2D) at log *a*(Li)=-60. In the upper right corner, the Form for Selection of Swing values appears. The dissected value can be changed by manipulating the scroll bar.

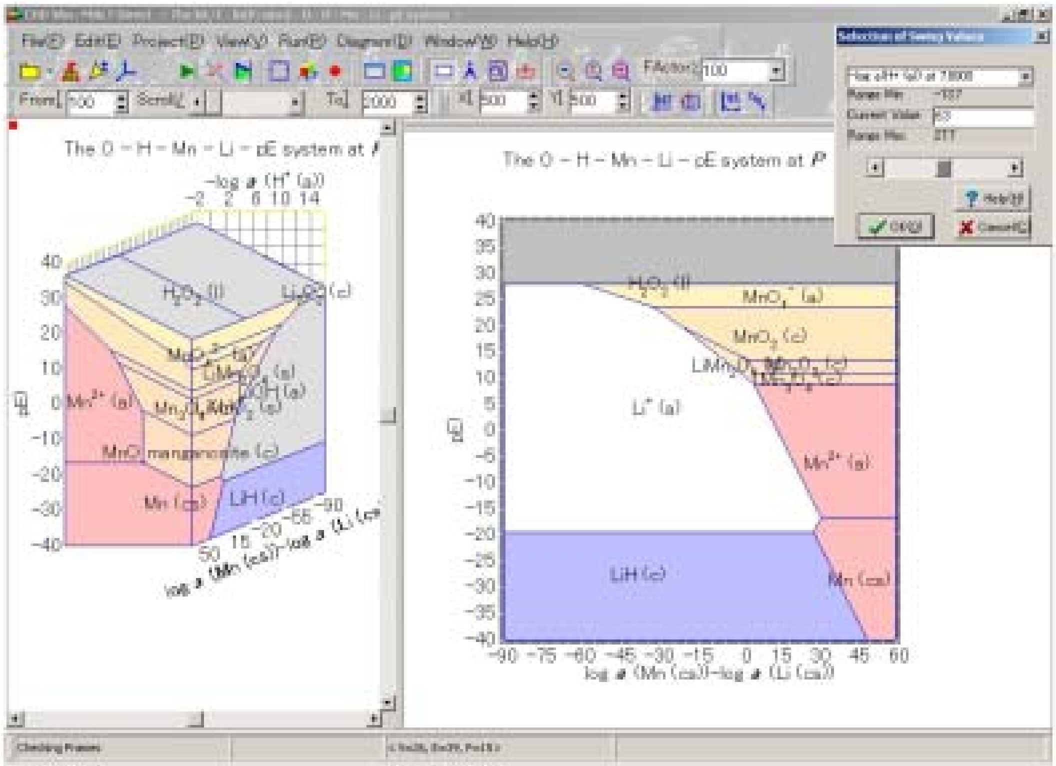


Fig. A2.6 The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e^- system at 298.15 K with the dissected diagram (2D) at -log $a(H^+)$=6.3.

When the Dissection Swing option is checked, the small form for selecting the swing value appears as in Fig. A2.5. Whenever the dissection value is changed, a new diagram is constructed and updated in the same display panel.

Fig. A2. 6 shows the dissection diagram for another dissection. Here, the pH, that is, -log$a(H^+)$, is defined as a dissection at 6.3. As the X-axis, the logarithmic activity difference, log a(Mn)-log a(Li), is adopted. The equilibria in the manganese system appear in the right-hand side, whereas those in the lithium system are given in the left-hand side.

In the chemical potential diagrams shown in Figs. A2.5 and 6, the chemical stability of $LiMn_2O_4$ against the dissolution into aqueous solutions can be discussed by using the following considerations.

First, the electrode reaction of $LiMn_2O_4$ can be written as follows;

$LiMn_2O_4 = Li^+(a) + Mn_2O_4 + e^-$ (A2.1)

The right-hand side direction is the charging process and the left-hand side direction is the discharging process. In Fig. A2.5, the lithium activity is fixed at log *a*(Li)=-60, and the equilibria between $LiMn_2O_4$ and $Li^+(a)$ is shown.

Since E/V = -(2.303 RT / F) log a(Li), log a(Li)=-60 corresponds to E=3.55 V

This indicates that this lithium activity corresponds to the discharging process where $Li^+(a)$ is inserted into Mn_2O_4 phase. In Fig. A2.6, the three phase combination of $Li^+(a)$ / $LiMn_2O_4$/Mn_2O_4 corresponds well the above electrode reaction.

In addition to the normal electrode reaction, there is some possibility that side reactions can occur during the charge/discharge processes. The manganese dissolution is one of the most important side reactions. It has been pointed out that the manganese dissolution is enhanced by the acidic environments caused from the oxidation of electrolyte component. Since $LiMn_2O_4$ is dissolved into Li^+ and Mn^{2+}, this reaction can be written as follows:

$LiMn_2O_4 + 8H^+ + 3e^- = Li^+(a) + 2Mn^{2+}(a) + 4\ H_2O(a)$
(A2.2)

In Fig.A2.5, the stability regions of Li^+ and Mn^{2+} appear in the low values of pH=–log *a*(H^+), whereas $LiMn_2O_4$ appears in the high pH region. This well corresponds to the fact that $LiMn_2O_4$ is dissolved under the acidic condition.

This is the reaction that consumes the electron so that this can be regarded as discharge-process-enhancing reaction. Actually, during the discharge process, the lithium activity increases (the electrode potential value decreases); In Fig. A2.5, the dissection value can be changed from –60 to –58. This corresponds to a change in lithium activity on discharge. On this change in the lithium activity, the stability area of $LiMn_2O_4$ becomes small. In other wards, the three-phase point of Li^+/$LiMn_2O_4$/Mn^{2+} shifts to the more basic side; that is, the manganese dissolution is enhanced.

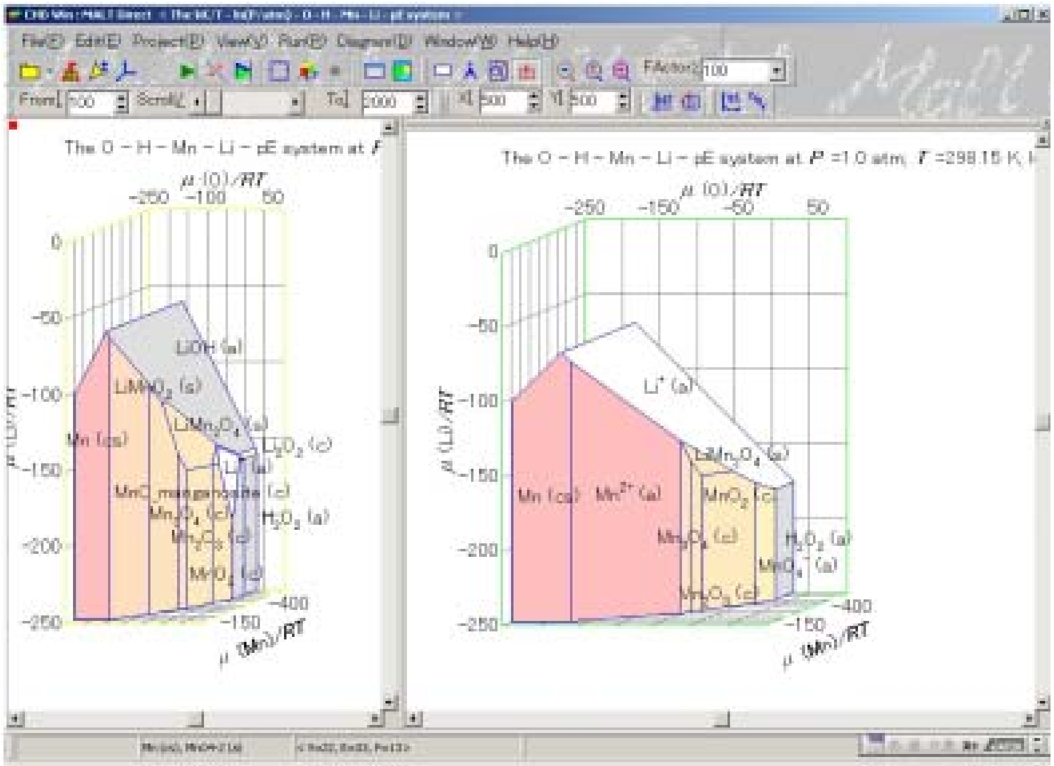


Fig. A2.7 The Three Dimensional Pourbaix Diagram for the Li-Mn-O-H-e^- system at 298.15 K in the normal high temperature coordinates for the Li-Mn-O systems.

In Fig. A2. 6, the interesting phase equilibria are plotted. Here, three-phase point of Li^+/$LiMn_2O_4$/Mn^{2+} is represented as the vertex point of their stability polygons. There is however, a new feature appearing in this diagram. That is, the spinel phase, Mn_3O_4, becomes very close to that three-phase point. This thermodynamically implies that the dissolved manganese ions, Mn^{2+}, can be precipitated as the spinel phase. Since the $LiMn_2O_4$ itself has the spinel structure, it is suggested that there is no kinetic barrier for Mn_3O_4 to be precipitated.

$$3Mn^{2+} + 4H_2O = Mn_3O_4 + 8H^+ + 2e^- \qquad (A2.3)$$

By combining with (A2.1), the following reaction can be written:

$$3LiMn_2O_4 + 8H^+ + 5e^- = 3Li^+ + 2Mn_3O_4 + 4H_2O \qquad (A2.4)$$

By comparing Eqa. (A2.4) and (A2.1), the following is obvious: The manganese ions remain without change in the ionic configuration after the lithium ion is removed in (A2.1), whereas the manganese ions in (A2.4) can be regarded as reconstructed from aqueous solution; in such a case, there are no lithium sites in the new spinel precipitate.

Thus, these diagrams can give the reasonable explanation for the following facts in the lithium batteries.

1) Manganese dissolution is enhanced in the acidic situation after the oxidation of electrolyte component.
2) Manganese dissolution becomes more severe on discharge process.
3) Even so, the manganese dissolution tends to be mild on heavily discharge state.
4) The capacity loss is also associated with the manganese dissolution. The loss of the lithium site due to the occupation of manganese ions should be the reason for the capacity fading.

Relation among the Pourbaix diagram for the multi-component system and the high temperature chemical potential diagram.

Since the Li-Mn-O system is one part of the subsystems of the Li-Mn-O-H-e^- system, it can be possible to compare the phase relation appears in Fig. A2. 5 and 6 with those chemical potential diagrams proposed for high temperature use.

The main chemical potential diagram in Fig. A2.7shows the three dimensional diagram for Li-Mn-O-H-e^- system at $a(H_2O)=1.0$. Although the aqueous species are shown in this diagram, they are not well shown because the axis of *pH* now disappears. In other wards, the phase equilibria developing along the pH axis are degenerated into the non-pH axis. Actually, there should be many species at one point in the three chemical potential diagram.

To display the diagram in Fig.A2.7, the species of MnO_4^- and MnO_4^{2-} are changed to be transparent.

The comparison is made in Fig. A2. 7 where the same phase equilibria as in Fig. A2. 6 are plotted in the normal three dimensional diagram. In this diagram, the stable polygons for Li^+ and Mn^{2+} appear in addition to the non-aqueous species. This clearly shows how the aqueous species affect on the normal phase equilibria.