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Thermodynamic database MALT2 and its applications to high temperature materials chemistry [☆]

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Abstract

The revised thermodynamic database MALT2 and associated computer programs are described and discussed in terms of requirements for a thermodynamic database from the viewpoint of materials chemistry. The equilibrium approach is discussed from three different aspects; Gibbs energy minimization, mass action law and associated enthalpy considerations, and the construction of chemical potentials. In particular, application of generalized chemical potential diagrams to reactions between condensed materials is discussed with an emphasis on materials compatibility and long term stability such as electrolyte–electrode chemical interactions in high temperature electrochemical cells.

Keywords: Chemical potential; Database; EVD; MALT2; Program

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1. Introduction

Materials chemical problems associated with high temperature processes should be examined from both kinetic and equilibrium aspects. Generally speaking, with increasing temperature, the equilibrium properties become important [1] because

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the kinetic barrier becomes relatively low compared with thermal energy. This makes it complicated to carry out kinetic analyses at high temperatures, since many factors such as nucleation, surface reaction and diffusion may contribute and compete with each other. Furthermore, kinetic data sometimes behave sensitively to impurities which makes it difficult to prepare, by experiment or by estimation, a whole set of kinetic data for a multicomponent system. However, thermodynamic considerations can easily be applied to multicomponent systems, since thermodynamic data have been evaluated with an emphasis on the thermochemical network among a huge number of compounds [2] and also because there has been great advance in computer software for calculating complicated equilibrium properties in multicomponent systems [3]. This difference between the kinetics and equilibrium approaches in treating high temperature multicomponent systems makes it attractive to adopt the following strategy: first, thermodynamic considerations should be regarded to gain insight into what chemical processes dominate the system to be considered; then, the kinetic approach can be focused on the dominant process. For this purpose, it is desirable to clarify the interrelation between thermodynamic and kinetic considerations because the driving force of any kinetic phenomenon can be given by the chemical potential differences.

In this paper, we report on the thermodynamic database MALT2 which has been designed for use primarily in materials science: its applications to practical materials problems are also described with an emphasis on solid–solid reactions.

2. Requirements in materials chemistry

Thermodynamic database activities first started in the field of metallurgy and have been developed into integrated systems combined with powerful software [4]. At present, such thermodynamic databases are widely used in many fields. Even so, additional requirements arise for utilization of thermodynamic databases in materials chemistry; these can be summarized as follows.

(1) Enlargement of the database. Many databases have been constructed mainly from the metallurgical standpoint and as a result, some important materials have not been included in them. Because the thermodynamic properties of some high temperature materials have been investigated experimentally, it will be necessary to compile them into databases.

(2) Appropriate method of estimation and confirmation. When materials screening is carried out for a large number of compounds, the chemical stability of such compounds becomes one of the key criteria. In such a case, it will be necessary to estimate thermodynamic data of complex compounds. It will also be necessary to examine how sensitive the calculated results are to different estimates for thermodynamic data.

(3) Appropriate correlation between thermodynamic data and other chemical or physical measurements. The materials' design approach will be fruitful when the relation between chemical reactivity and controlling factors for critical properties is available; usually, doping and other techniques for materials optimization can be

achieved using ideas of valence control, size effects or chemical bonds. If the chemical reactivity of materials can be correlated with such chemical concepts, materials optimization is made easier.

(4) Appropriate analytical method for kinetically slow processes. Although chemical equilibria calculations have been demonstrated to be quite powerful [5] for chemical processes in which gaseous species contribute to homogenize the system, it will be necessary to carry out thermodynamic analyses on rather slow processes including nucleation, surface reaction, and diffusion associated with solid–solid reactions. This is particularly important when materials compatibilities and long term stabilities of interfaces are considered for high temperature processes.

3. Thermodynamic database MALT2

The Materials-oriented Little Thermodynamic (MALT) database was first constructed in 1986 by the thermodynamic database task group organized by the Society of Calorimetry and Thermal Analysis, Japan [6]. The main objective at that time was to provide people in industry with good quality thermodynamic data for a large number of compounds and to help them carry out thermodynamic calculations on their practical problems. For easier access to the database, we have adopted personal computers as host machines, although some disadvantages (limited memories and slow calculating speed) were obvious compared with mainframe computers.

In 1992, this system was revised as MALT2 by retaining the policy of using personal computers. However, recent advances in the hardware and software associated with personal computers have provided more comfortable circumstances in their use for the thermodynamic database.

The main features of MALT2 are the following:

(1) Database. In the present enlargement, efforts have been focused on double oxides, especially the transition metal oxides, because of their great importance in industrial use. The thermodynamic data of some organic compounds have been also added. The total number of species becomes 4931, compared with 3000 in MALT.

(2) User's data. The present MALT2 database does not provide functions for estimating the thermodynamic data. Instead, users can input their own data and can use them together with data in the database.

(3) Use of resident data. MALT2 provides, in addition to a retrieving function, a function of calculating the thermodynamic properties associated with a selected reaction. To facilitate the utilization of thermodynamic data for the user's own purpose, MALT2 provides a new function of making data resident in the main memory of computers. These data can be accessed from the user's program using the software interrupt technique. This can be done in any computer language; actually, sample programs written in several computer languages are provided.

(4) To make thermodynamic analyses on materials problems, the equilibrium properties of multicomponent systems are required. Because it is difficult and time consuming for general users to write such a program for calculating complicated

equilibria, MALT2 provides the following sophisticated computer programs for general use as examples of using residentialized thermodynamic data: (i) Chemical equilibria calculation, *gem* [7]; this program is based on the Gibbs energy minimization. To search the minimum point of the Gibbs energy of system, its gradient is projected into the space that satisfies the mass balance condition, which makes it possible to obtain the equilibrium point with high reliability and stability. (ii) Chemical potential diagram, *CHD* [8–11]; this is based on a convex polygonal approach for constructing generalized chemical potential diagrams. The thermodynamically stable phase combinations are selected out of all possible combinations in a multicomponent system. Results are displayed in two or three dimensional diagrams. As coordinates of the two dimensional diagram, any combination of chemical potentials can be selected.

4. Use of equilibrium properties

"Equilibrium" is the most fundamental concept in high temperature materials science. Even so, there are several ways of applying this concept to practical materials systems. In principle, the equilibrium state can be defined in the following three different ways: (1) the state in which a system containing a fixed amount of reactants has the minimum Gibbs energy value; (2) the Gibbs energy change for any reactions among species in a system becomes zero; and (3) the state in which the chemical potentials of any species are constant throughout a system. Although these three definitions are thermodynamically equivalent, some different characteristic features appear when they are applied to multicomponent systems.

4.1. Gibbs energy minimization

In multicomponent systems in which a large number of reactions may happen, it is very hard, at a glance, to gain insight into what reactions may occur. Even so, the chemical equilibria calculation based on the Gibbs' energy minimization can provide one solution for giving starting materials. This uniqueness of solution is a great help in obtaining the chemical nature of the high temperature compatibilities of materials. This merit of the equilibrium approach becomes indispensable with increasing number of components or compounds. A good example of an application to materials chemistry is the chemical vapor deposition (CVD) diagram [12].

4.2. *Mass action low* ($RT \ln K = \Delta_r G^\ominus$)*: enthalpy consideration*

Equilibrium constants at high temperatures are characterized in terms of the standard Gibbs energy changes. Since the entropy term can roughly be given from change in mole number of gaseous species in a considered reaction [1], the enthalpy term plays a key role in determining the chemical nature of equilibria characteristic for a particular system. There are two different ways of utilizing the enthalpy term in materials chemistry.

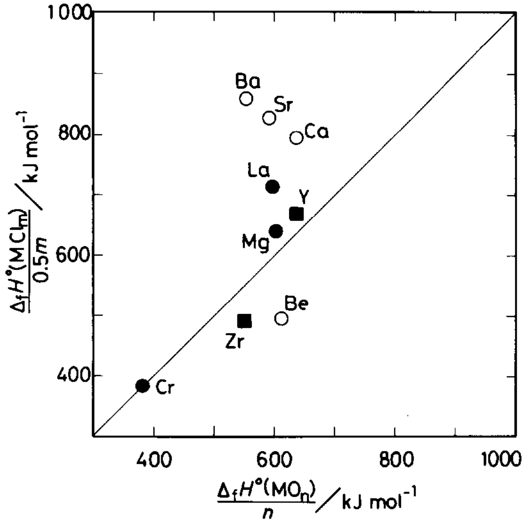

Fig. 1. Enthalpy versus enthalpy plot for elements (solid symbols) to be used in the electrochemical vapor deposition (EVD) technique. Ba, Sr and Ca (open symbols) cannot be used in the EVD process because their chlorides are thermodynamically more stable than their oxides under the EVD conditions.

(i) The enthalpy change for formation from elements usually exhibits a variety of changes which are not easily correlated with appropriate chemical scales such as electronegativity. This in turn makes it possible to characterize the chemical nature of a particular element and its compounds in terms of their enthalpy values. Such information should be useful in optimization of materials selection. For example, Fig. 1 shows an enthalpy versus enthalpy plot for elements to be used in the electrochemical vapor deposition (EVD) process [13] by which a dense film can be fabricated on a porous support tube. Basic reactions are

$$M_{n/2}Cl_2(g) + H_2O(g) = M_{n/2}O(s) + 2HCl(g) \qquad (1)$$

where n is the valence number of element M. Since the entropy changes for the above reaction are about the same among the various elements, the thermodynamic features of the reaction are determined by the enthalpies of chlorides and oxides. Fig. 1 shows that points corresponding to the respective elements are distributed over a wide area. Points in the upper and left-hand side show that the chloride is more stable than the oxide under the same conditions. In the formation of doped lanthanum chromites (La,M)CrO_3 (where M is Ca, S) or La(Cr,M′)O_3 (where M′ is Mg), only magnesium doping can be adopted in the EVD process, although strontium doping is more suitable in view of other material requirements such as electrical conductivity or thermal expansion coefficient. The difference in enthalpy appearing in Fig. 1 is in the order of several 100 kJ mol^{-1}; this magnitude of difference cannot be overcome by usual materials modification. Conclusively, Fig. 1 tells that as far as the EVD process is concerned, strontium cannot be used.

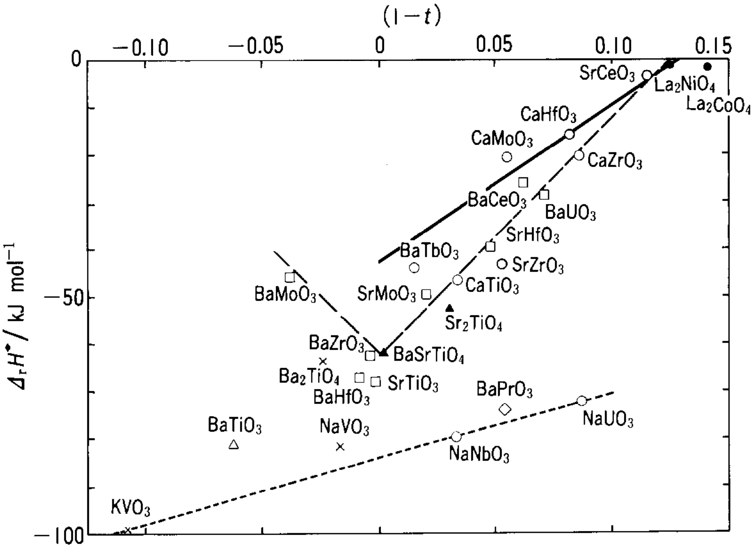

Fig. 2. The stabilization energy of perovskite oxides as a function of tolerance factor derived from Shonon's ionic radii. Good correlation can be obtained for the alkaline earth (dashed line) and the rare earth (solid line) perovskites, respectively [14]. The alkali perovskites (dotted line) exhibit a different correlation.

(ii) For the complex oxides, the enthalpy change for formation from the constituent oxides becomes important; this term can be called the "stabilization energy". Since this originates from changes in the electrostatic energy by rearrangement of ions, this shows good correlation with ionic radius or related properties. For example, Fig. 2 shows the stabilization energy of perovskite oxides [14,15] as a function of tolerance factor t, which can be derived only from the ionic size. Such a correlation can provide the basis of understanding the relative stabilities among a family of compounds having a similar crystal structure such as Ruddlesden–Popper phases [16]. This correlation is also useful for estimation of the thermodynamic properties associated with doping or solid solution among perovskite phases.

4.3. *Construction of chemical potential diagram*

The chemical potential diagram is usually constructed by envisaging the chemical form of a particular element as functions of chemical potentials of nonmetallic species. This is suitable for cases when the chemical behavior of a particular element in a large chemical medium such as an aqueous solution or a gaseous mixture will be examined using those chemical potentials which can characterize the thermodynamic state of the medium. In such a case, the amount of medium is not important information, while the medium can be characterized reasonably by constant chemical potentials. Note that species representing the key chemical potentials can move rather fast in aqueous solution or gaseous mixtures.

Another merit of utilizing the chemical potential diagram can be found in its applications to condensed phase reactions in which more than two metallic elements are involved and their diffusion takes place slowly. Due to slow rates of reaction and diffusion, some chemical potential gradients may arise in the system considered. Although this is a non-equilibrium state, it can be expected that a local equilibrium approximation can hold in small areas and chemical potentials may change smoothly with some discontinuous points at phase boundaries.

To ensure this kind of utilization, it is necessary to construct a generalized chemical potential diagram in which any elements (either metallic or nonmetallic) can be treated equivalently. The MALT2 related program *CHD* has been developed to construct generalized chemical potential diagrams for multicomponent systems. Since the chemical potential diagram is constructed by checking all possible phase combinations, this provides visualized information on the types of chemical reactions which may occur in a whole range of compositions in a considered system. The resulting diagrams are similar to the equilibrium activity diagrams which are utilized in geology [17].

This generalized chemical potential diagram is quite useful for the following case.

(i) When a large number of compounds are involved, the diagram gives an overall feature of reactivity or stability for the many compounds involved. It is fairly useful when the transition metal double oxides are considered, because double oxides with different valences make phase relations quite complicated.

(ii) Checking validity of estimated thermodynamic data. Because the stability of a particular compound is displayed by the geometrical arrangement of related stability polygons, the effect of changing the Gibbs energy to be used can also be visualized by growth or contraction of the stability polygon of the compound under consideration.

(iii) Thermodynamic stability of interface. In particular, the chemical stabilities of interfaces between dissimilar materials such as semiconductor–metal, ceramics–metal, and electrolyte–electrode interface can easily be examined in terms of the geometrical arrangement of the stability fields of compounds.

(iv) Drawing a reaction path. A reaction path representing the arrangement of reaction products can be drawn as a continuous smooth line in the chemical potential diagrams. After plotting, further information can be derived about what is the major diffusion species and how different the diffusion rate is among the elements involved. This means that use of the chemical potential diagram gives a basis for comparing the equilibrium properties with the kinetic properties.

5. Applications to practical materials problems

Applications of thermodynamic analysis to materials problems in the energy-related fields are quite important, because chemical stability is one of the major materials required in this field; actually, many new high temperature processes in the energy-related fields have encountered severe materials problems. Without solving materials problems, their industrialization cannot be achieved. Applications have been made mainly by the National Institute of Materials and Chemical Research for the following materials problems in high temperature fuel cell technology.

Solid oxide fuel cells consist of many materials with different electrical properties and geometrical shape. The electrolyte (yttria stabilized zirconia, YSZ) should be a dense ionic conductor, while the electrodes (lanthanum manganites for cathode and Ni/YSZ cermet for anode) should be porous electron (or mixed) conductors; furthermore, the interconnection (lanthanum chromite) should be a dense electron conductor. In fabricating solid oxide fuel cells it is important to consider the following materials problems [18]: (i) to avoid electrolyte–electrode interactions; (ii) to achieve an air sinterability of the lanthanum chromite interconnection; (iii) to establish an appropriate way of sealing of edges of planar cells. All are related to possible chemical reactions and mass transfer across the interface between different materials. In view of this, the thermodynamic analyses can provide an appropriate way of rationalizing experimental results and gaining insight into the chemical nature involved in the phenomenon. This will make it possible to obtain a research and development policy about what should be done next to overcome the materials problems.

The electrolyte–electrode interaction is a good illustrative example [16,19]. To obtain an interface between adjacent materials with a good electrical contact, high temperature treatment is usually needed. During this process of preparing the interface, there is a great possibility of some chemical reactions occurring at the interface.

The thermodynamic analysis and its comparison with experimental results revealed interesting features about the reaction between perovskite oxide electrodes and YSZ electrolyte. First, the analysis based on the Gibbs energy change for the following reactions gives a good explanation of the fundamental difference between $LaCoO_3$ and $LaMnO_3$.

$$LaMO_3 + ZrO_2 = 0.5La_2Zr_2O_7 + MO + 0.25O_2(g) \qquad (\text{M is Co, Mn}) \qquad (2)$$

As shown in Fig. 3, at 1273 K this reaction does not proceed for $LaMnO_3$ but it does for $LaCoO_3$ [16]. Since the stabilization energies of $LCoO_3$ and $LaMnO_3$ are about the same, this difference originates from that in the valence stability of Co^{3+} and Mn^{3+}. Usually, Co^{3+} is not stable, while the large stabilization energy of the perovskite makes it possible for Co^{3+} ions to exist in the perovskite phases. However, the above consideration shows that such stabilization of Co^{3+} is destroyed by chemical reactions in which La_2O_3 is extracted from the perovskite to form another double oxide with a relatively large stabilization energy.

This consideration roughly corresponds to the experimental electrochemical activity results. Even so, some experiments indicate that lanthanum manganite actually reacted with YSZ. This contradicts the consideration based on Eq. (2). Thus, a second analysis has been made to clarify this phenomenon. Fig. 4 shows the chemical potential diagram for the La–M–Zr–O (M is Co, Mn) system at $P(O_2) = 1$ bar [20]. When M is Co, the Gibbs energy of Eq. (2) is negative; this is represented in Fig. 4 where it is seen that the stability polygons of $LaCoO_3$ and ZrO_2 are separate because those of $La_2Zr_2O_7$ and MO intervene. When M is Mn,

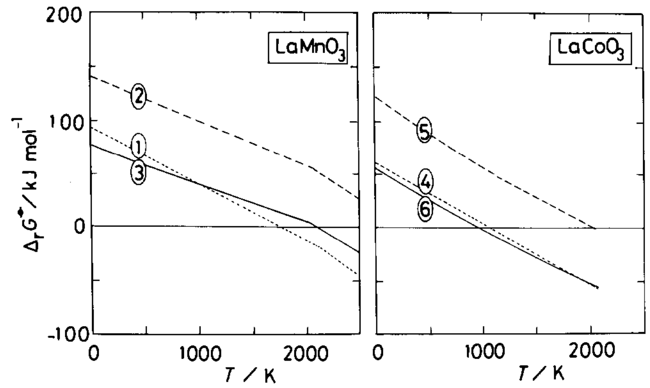

Fig. 3. The Gibbs energy change for reactions between $LaMO_3$ (M is Co, Mn) and ZrO_2. (1) $0.5Mn_2O_3 = MnO + 0.25O_2(g)$, hypothetical; (2) $LaMnO_3 = 0.5La_2O_3 + MO + 0.25O_2(g)$; (3) $LaMnO_3 + ZrO_2 = 0.5La_2Zr_2O_7 + MnO + 0.25O_2(g)$; (4) $0.333Co_3O_4 = CoO + 0.167O_2(g)$; (5) $LaCoO_3 = 0.5La_2O_3 + CoO + 0.25O_2(g)$, hypothetical; (6) $LaCoO_3 + ZrO_2 = 0.5La_2Zr_2O_7 + CoO + 0.25O_2(g)$.

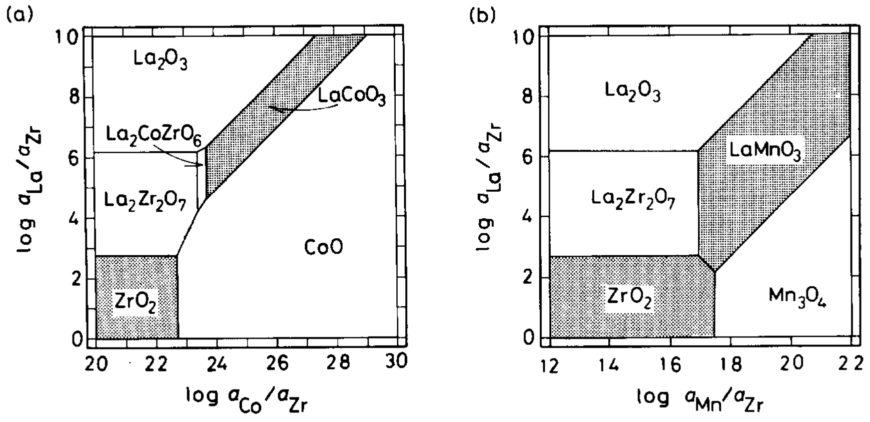

Fig. 4. Chemical potential diagram for the La–M–Zr–O ((a) M is Co; (b) M is Mn) systems at 1273 K and $P(O_2) = 1013$ hPa [20].

the stability polygons of $LaMnO_3$ and ZrO_2 are in contact with each other, indicating that Eq. (2) does not apply. Even so, detailed examination of Fig. 4 suggests that there is a possibility of the formation of $LaMnO_3/La_2Zr_2O_7/ZrO_2$. This can be well understood by taking into account the nonstoichiometry of $LaMnO_3$. Since Mn^{4+} is relatively stable even in a perovskite structure, this gives rise to La nonstoichiometry, resulting in $La_{1-y}MnO_3$. This is shown in the compositional diagram in Fig. 5 [21]. Using this diagram, the reaction between lanthanum manganite and YSZ can be ascribed to the formation of $La_2Zr_2O_7$ due to the large La stoichiometry. In other words, the La deficient manganite can be in equilibrium with ZrO_2; this provides a good basis for rationalizing various experimental facts concerning the lanthanum manganite electrodes.

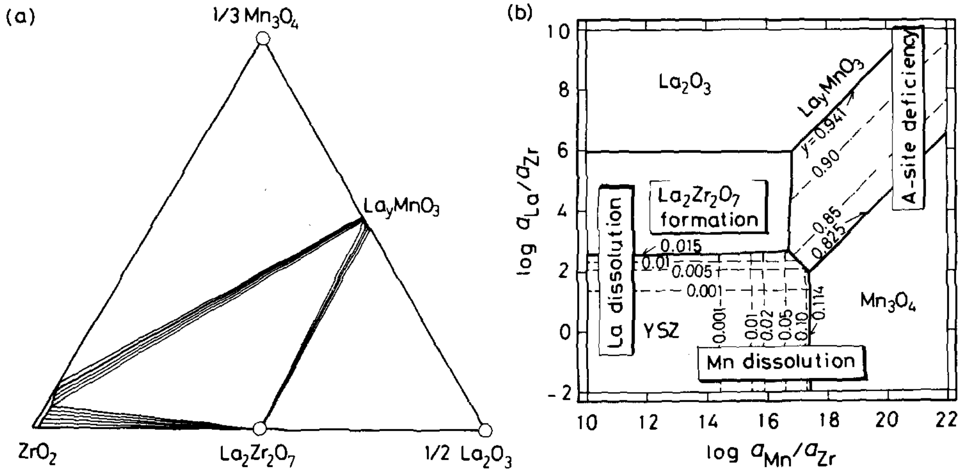

Fig. 5. Effect of lanthanum nonstoichiometry on the compositional diagram and on the chemical potential diagram [21].

6. Concluding remarks

Applications of thermodynamics in the materials science field have been widely and successfully made in high temperature processes such as CVD. However, applications to solid–solid reactions have not been utilized extensively for a long period of time, just because chemical potential diagrams for systems containing more than two metallic elements are not easily drawn. The present approach based on generalized chemical potential diagrams make it easy to apply the thermodynamic idea to systems containing many complex compounds. This will be particularly useful for thermodynamic analyses on stabilities of interfaces between dissimilar materials which are of great technological importance. Such an advance in the utilization of thermodynamic data gives rise to strengthened requirements for a thermodynamic database suitable for materials' science.

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