Thermodynamic equilibrium calculation is sometimes difficult in a system when minor but important species are present, when only stoichiometric condensed phases are stable and the gas phase is absent, and when multiple minima are present in the Gibbs energy of some non-ideal solution phases. A new program is being developed to overcome these problems. The Gibbs energy minimization method has been implemented to determine the thermodynamic equilibrium similar to other conventional programs. When the system is singular, however, the chemical potentials of the system components are uniquely determined by taking additional minimization of the molar Gibbs energy of the gas phase. Accordingly, the vapor pressure, for instance, is always determined even when only pure condensed phases are active and the gas phase is absent at equilibrium. Furthermore, an automatic routine that introduces multiple phases of different compositions and checks their stability has been implemented to detect possible phase splitting in non-ideal solution phases.

One of the issues is related to the singularity in the stoichiometric matrix that is most exemplified by the system of 1 mol H$_2$O at 300 K under 0.1 MPa. Under this condition, all the elements go into the single-species water phase, and the gas phase is absent, so that the chemical potentials for elements are not uniquely determined by the Gibbs energy minimization. The problem was described in detail in the book of Smith and Misen. Among the commercial packages mentioned above, only FactSage seems to have a limited ability to handle the problem, which properly works in the present H$_2$O problem, though sometimes fails when a ternary compound is involved. Namely, when solid MgAl$_2$O$_4$, for instance, is the only stable phase, the chemical potentials and vapor pressures are not correctly determined even by FactSage. Thus, the problem is old, but still remains to be solved. In such cases, the system is singular, and the state of the system cannot be fully determined only by the Gibbs energy minimization. It would be common practice in such cases to add a small amount of an inert gas to the system, or to take the Helmholtz energy minimization instead, though some care must be taken, and the trick is not always effective. For instance, the equilibrium of the system of 1 mol SiO$_2$ with 1 mol of inert Ar at 300 K under 0.1 MPa cannot be calculated due to the numerical singularity in this case. Except for experts in the field, such difficulty is hardly manageable in a correct fashion. A similar problem arises when trace but important components are involved in the system, which is related to the round-off error commonly associated with numerical calculations.

The other problem is the well-known difficulty in finding the global minimum of the system when multiple local minima are present in some of the non-ideal solution phases. Though global minimization is one of the fundamentally difficult numerical problems, it is of very practical importance, so that the conventional programs are all prepared with a special function to cope with it. For instance, in ThermoCalc, MTData, and FactSage, several phases that are the same but of the different composition, i.e., split-phases, can be introduced in the calculation. In particular, only the number of split-phases must be specified in the latter two programs. PanDAT is much more superior to the others.
in this respect, as the detection of phase splitting is fully automatic. As discussed in detail by Chang et al., the procedure taken by the former three software necessitates more-or-less deep knowledge, skills and experiences about the subject, and therefore, they are not for non-expert users. Furthermore, except for a few component systems, verification is practically impossible. Thus, like PanDAT, an automatic check for phase splitting is an indispensable function in the equilibrium calculation software for non-expert users.

The present study has been undertaken to primarily improve these two difficulties with the conventional programs. We have also tried to develop software, which is reliable as much as possible, easy to use, and needs only basic thermodynamic knowledge.

2. Equilibrium Calculation

2.1 Basic algorithms

The basic algorithm of the present program is based on an analysis similar to that by Smith et al. Other conventional programs would also use a similar analysis in this respect, though there would be more-or-less important differences in the actual implementations. The principle of the equilibrium calculation is rather simple as shown below. Refer to Refs. 16, 1 and 1 for details.

The total Gibbs energy of the system is minimized:

$$G = \sum_n Y_n \mu^n = \text{min},$$

under the constraints:

$$\sum_n Y_n A_{i,n} \chi_i^n = B_i, \quad (2)$$
$$\sum_i \chi_i^n = 1, \quad (3)$$
$$Y_n \geq 0, \quad (4)$$

where $Y_n$ and $\mu^n$ are the molar amount of the $n$-th phase and the molar Gibbs energy, respectively, $\chi_i^n$ is the mole fraction of the $i$-th species in the $n$-th phase, $A_i$ is the stoichiometric matrix which represents the chemical formula of the species, and $B_i$ is the element abundance vector. Equation (2) is the mass-balance equation, which represents the overall composition of the system. Usually, temperature, $T$, pressure, $P$, and the composition vector, $B_i$, are assigned as the initial conditions for the calculation. Non-ideal thermodynamic models, such as the sublattice model, the regular solution model, etc. may be employed for the solution phases, in which interactions are usually expressed by Redlich–Kister polynomials, with Muggianu extrapolation to a multi-component system as follows:

$$\mu = \sum_i \chi_i \mu_i^0 + RT \sum_i \chi_i \ln(\chi_i) + \sum_{i,j} \chi_i \chi_j \sum_k L_{i,j}(\chi_i - \chi_j)^k + \cdots, \quad (5)$$

where $L_{i,j}^{(k)}$ represents the $k$-th binary interaction parameter, for instance.

Minimization of eq. (1) can be attained by the usual Lagrange’s undetermined multiplier method as follows. Note that eq. (3) is the “internal” condition for each phase, so that it does not manifest itself in the conditions for the total system, as clearly shown in Ref. (16). By letting $\lambda_i$ and $\theta_n$ be the corresponding Lagrange’s multipliers for eqs. (2) and (4), respectively, we have

$$L = \sum_n Y_n \mu^n + \sum_i \lambda_i (B_i - \sum_n Y_n A_{i,n} \chi_i^n) - \sum_n \theta_n Y_n \quad (6)$$

By taking variations, we obtain the minimization condition with the constraints as follows:

$$\theta_n = \mu^n - \sum_{i,j} A_{i,j} \lambda_i \chi_i^n, \quad (7)$$

the following relation holds:

$$\text{if } Y_n > 0, \text{ then } \theta_n = 0, \quad (8)$$
$$\text{else if } Y_n = 0, \text{ then } \theta_n \geq 0.$$

This is the so-called Kuhn-Tucker Condition. In eq. (7), $\theta_n$ depends on the composition, so that condition (8) must hold for $\theta_n^m$, which is the minimum of $\theta_n$ with respect to the composition, $\chi$. Here, in general, $\theta_n$ may have several local minima that give rise to phase splitting. Lagrange’s multiplier, $\lambda_i$, becomes equal to the chemical potential of the $i$-th element, and $\theta_n^m$ is the minimum distance between the Gibbs energy surface, $\mu^n$, and the plane spanned by $\lambda$. The distance is zero for the active phases, so that $\theta_n^m$ is called the tangent plane distance. Furthermore, the activity of a phase is defined by $\alpha_n^0 \equiv \exp(-\theta_n^m)$ in the present program, though normalization of $\theta_n^m$ for 1 mole element is made for condensed phases.

Minimization of the total Gibbs energy is thus divided into two procedures, i.e., the phase-internal minimization of $\theta_n$ in eq. (7) for each phase under the condition of eq. (3), and the assignment of the conditions, eqs. (2), (4) and (8). In the present program, $\lambda_i$ and $Y_n$ are considered basic independent variables of the system. The composition, $\chi$, of each phase is, then, the dependent variable of the chemical potentials, $\lambda_i$, which is determined by the minimization of eq. (7). Thus, the present program consists of double loops. The Quasi-Newton minimization method is employed in the inner loop for the minimization of eq. (7) for a fixed $\lambda$. The Newton–Raphson method, on the other hand, is employed in the outer loop, where $\lambda$ and $Y_n$ are iteratively optimized to satisfy the mass-balance condition, eq. (2), and the stability conditions, eqs. (4) and (8). When there are other inner freedoms in a phase model as in the case of a sublattice model or ionic phases, other constraints, such as the charge balance constraint, are necessary except for eq. (3).

The initial values for the variables and initial working set of phases are determined by the Linear Simplex method, so that the necessary input by the user is the calculation conditions such as temperature, pressure, and the overall composition of the system. In the outer loop, the activities of the phases that are not currently included in the calculation are evaluated at the appropriate interval by the minimization of eq. (7). When some phases are found to be active, they are then included in the subsequent iterations. In this active phase detection procedure, split phases are also examined. Thus, all
of the active phases including the split-phases are efficiently determined.

One of the features of the present program is the adoption of the Quasi-Newton minimization in the inner-loop. When the check for phase splitting is perfect, then the method constitutes a true Gibbs energy minimization. This method is found much more reliable than the usual procedure that employs the chemical potentials of the constituent species. The latter method was also examined in detail, but, as it only determines extrema fundamentally, it sometimes gives a false convergence to the local maxima or saddle-points, and therefore, the reliability is rather low when the phase has multiple minima. The Quasi-Newton minimization method is the reliable alternative in such cases, since downhill stepping is fundamentally guaranteed.

The problem associated with trace-species or that of round-off error is related to the mass-balance eq. (2), and is also related to the problem of singularity. By using the usual matrix operations, equivalent but different expressions can be easily obtained for eq. (2). Thus, a selection algorithm of the appropriate expression for eq. (2) that does not suffer from round-off errors or singularities is one of the key-points that was elaborated in the present program.

### 2.2 Calculation in a singular system

As noted before, the mass-balance equation, eq. (2), sometimes becomes singular depending on the conditions. As some of the mass-balance conditions virtually disappear, the state of the system cannot be fully determined. The occurrence of such a singularity depends on the system and the calculation conditions, but often occurs when only some stoichiometric condensed phases are active, and not likely to occur when solution phases are active. However, for instance, in oxide systems such as SiO$_2$–CaO, only a liquid solution phase is generally stable at high temperatures. Only the chemical potentials for the end-members are, then, determined, and not for all the component elements, so the system is singular. Thus, the singular situation is rather common in thermodynamic equilibrium calculations.

FactSage/ChemSage invokes additional minimization steps in such situations in which the “phase-dependent” $\lambda$ is determined by assuming the same composition for each phase as that of the total system$^8$ (details not available). However, the physical meaning of the procedure is rather obscure, and, as noted before, the algorithm generally works properly only when there are two system elements or less. Accordingly, we have done a detailed study on the subject, and the result is found to be simple as follows:

In the equilibrium constant method, which is the alternative method to find thermodynamic equilibrium, the gas phase of the saturation vapor pressure is assumed to be present, which is in equilibrium with the active condensed phases, when the assigned pressure is high and the gas phase is absent. The correct vapor pressure is accordingly determined. The condition, i.e., the assumed presence of the gas, constitutes the difference between the equilibrium constant method and the conventional Gibbs energy minimization method. It must be noted that the gas phase can be assumed to contain all the elements of the system, and becomes active when the pressure is sufficiently low. The condition of the assumed presence of the gas phase with a saturation pressure has a clear physical meaning, and is realized by the minimization of the molar Gibbs energy of the gas phase, as explained below.

The gas phase is unstable and inactive when the assigned pressure is higher than the equilibrium pressure. However, its composition must be the same as that of the gas under the equilibrium vapor pressure. This is just the physical proposition of the Kuhn-Tucker condition for inactive phases, where the composition is determined by the minimization of $\theta_{\text{gas}}$ in eq. (7). Furthermore, the molar Gibbs energy of the equilibrating gas phase is at a minimum, and the same gas composition gives the minimum Gibbs energy even under higher pressures. This is simply because the pressure difference gives the overall shift, $RT\Delta \ln(P)$, for the Gibbs energy. Namely, the assumed gas phase must be at the minimum of the molar Gibbs energy. Therefore, when there is singularity and there remains undetermined freedoms in the system, they must be determined by the same principle, i.e., the minimization of the molar Gibbs energy of the gas phase through minimization of eq. (7). Thus, the minimization of the Gibbs energy is fully achieved with respect to all the freedoms of the system, so that the present algorithm may be regarded as the full Gibbs energy minimization. The chemical potentials, thus determined, are equal to those that are determined under the condition where the gas phase becomes active by adding an inert gas, for instance.

Conventional programs lack this additional minimization procedure, so that when the system happens to be singular, all the constituent chemical potentials are not determined, and some problems may result. In the present program, as shown in Table 1, the correct vapor pressures, and also the correct chemical potentials, are always determined.

### Table 1 Equilibrium calculation results at 1300 K with initial feed of 1 mol Al$_2$Si$_3$O$_6$ (mullite). Only the major species are listed in the table. TP indicates the calculation under a constant pressure of 1 bar, and TV under a constant volume of 1 L. The FACT-DB database was adopted in the calculation by FactSage, and data taken from the JANAF tables$^{25,26}$ and by Barin$^{27}$ were employed in the calculation by CaTCalc. The gas activity corresponds to the vapor pressure in the present case. The vapor species from mullite are mainly due to the SiO$_2$ vaporization, so that the relation, $P_{\text{SiO}} = 2P_{\text{SiO}_2} + P_{\text{O}_2}$, approximately holds between the partial pressures of SiO, O$_2$ and O. As the result, the solid Al$_2$O$_3$ becomes active.

<table>
<thead>
<tr>
<th>Gas</th>
<th>CaTCalc (TP)</th>
<th>CaTCalc (TV)</th>
<th>FactSage (TV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(g)</td>
<td>0.61566</td>
<td>0.61566</td>
<td>0.61739</td>
</tr>
<tr>
<td>O$_2$(g)</td>
<td>0.23923</td>
<td>0.23923</td>
<td>0.24195</td>
</tr>
<tr>
<td>O(g)</td>
<td>0.13720</td>
<td>0.13720</td>
<td>0.13350</td>
</tr>
<tr>
<td>SiO$_2$(g)</td>
<td>7.9036E-03</td>
<td>7.9036E-03</td>
<td>7.1600E-03</td>
</tr>
<tr>
<td>AlO(g)</td>
<td>4.5185E-09</td>
<td>4.5185E-09</td>
<td>4.3277E-09</td>
</tr>
<tr>
<td>Al(g)</td>
<td>1.8474E-10</td>
<td>1.8474E-10</td>
<td>1.6908E-10</td>
</tr>
<tr>
<td>Al$_6$Si$_3$O$_9$ Amount</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Al$_2$O$_3$ Amount</td>
<td>0</td>
<td>3.4433E-15</td>
<td>3.6865E-15</td>
</tr>
</tbody>
</table>
2.3 Phase-splitting

In a non-ideal solution phase, multiple-minima are a common feature. Although only active split phases are important and their actual number may be few in practice, possible split phases are many and increase with the number of components. Therefore, manual checking is impractical when the component is more than a few, and automatic checking is indispensable in such a calculation software.

In the present program, a set of phase-internal minimizations of eq. (7) from several different initial compositions is automatically executed for every non-ideal solution phase. The procedure implementation is easy due to the double-loop minimization in the present program. Thus, the active split phases are efficiently and automatically detected.

As no split phases are initially assumed, failure to detect active split-phases simply results in nonconvergence of the whole calculation. This point becomes serious when the compositions are very close, for instance, near the consolute point, since it is not then easy to distinguish and detect the active split phases. A special routine has been developed to detect even very close split phases in the present program. With such more or less special routines, a reasonable ability to detect all the active split phases is attained. The procedure is, however, a probabilistic procedure that does not assure global minimization, though it mostly works effectively in practice. Further study is certainly needed, but the reliability would be substantially better compared to the conventional programs except for PanDAT.

Figure 1 shows 4-phase splitting automatically detected by the present program in the BCC single-phase system of Fe–Cr–V–C. An almost identical result was obtained with FactSage by assuming three split-phases except in the range of 640–750 K. The reason for the difference is simply due to the limitation of FactSage that at most three split-phases are allowed in the calculation.

2.4 Data, thermodynamic models and other features

For practical use, the supplied database is often not sufficient even when the most developed packages are employed. Thus, the data should be easily added, modified or amended. Therefore, the data is to be given in a text format in the present program, which almost follows the rules of the SGTE text database.

Thermodynamic models that are currently supported are the sublattice model, the ionic two sublattice liquid model, the Inden magnetic model, the split-sublattice model for ordering, and the associated solution model. Other models, such as the quasi-chemical model and some aequous models, are planned to be supported, after developing facilities to draw phase diagrams and property diagrams.

Another feature of the program is that there are no predetermined limitations on the number of elements, species, phases, sublattices, interaction parameters, their orders, etc. This is due to the full adoption of the dynamic memory allocation for variables.

A necessary procedure for the calculation is the system definition, either by elements specification or by feed species specification, and the conditions, such as temperature and pressure. After the calculation, a templated graph is automatically displayed. The results and the calculation conditions can be transferred into spreadsheet software through a clipboard.

At present, the failure rate is estimated to be less than $10^{-4}$ which is roughly determined by extensive trial calculations. Final public release is planned at the end of the year after critical beta-testing by some experts.

The thermodynamic database, especially for solution phases, will be separately presented which would be a mere collection of the published data in the open literature. The program has no optimization routines for thermodynamic data from experimental data at present.

3. Conclusion

A detailed study has been conducted on two problems regarding thermodynamic equilibrium calculations. One is concerned with the difficulty that there remain undetermined freedoms even after minimization of the total Gibbs energy of the system. An equilibrating gas phase is assumed to be present with a zero amount, as in the equilibrium-constant method, to fully determine the thermodynamic state of the system. The algorithm is also effective for problems in which minor but important species cause some numerical problems. The other problem is the automatic examination of the possible phase splitting in non-ideal solution phases. As a result of the study, new software has been developed.

REFERENCES