COMPUTER MODELING

of

Phase Diagrams

Edited by L. H. Bennett

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Gaithersburg, Maryland

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Preface

The Symposium on Computer Modeling of Phase Diagrams was sponsored by the Alloy Phase Diagram Data Committee of the Materials Science Division of the American Society for Metals. It was presented as part of the Fall 1985 meeting of The Metallurgical Society of AIME in Toronto, Canada. All presentations were invited, and the authors were asked to combine both tutorial and research flavor in their manuscripts. In view of the general applicability of much of the activity to materials beyond alloys, there were presentations on computer modeling of ceramic and ionic salt phase diagrams as well as of alloys. The uses of the computer in the various presentations covered a wide range as well: 40 minutes of supercomputer time in order to calculate one input datum for phase diagrams (the bcc -fcc energy difference for elemental tungsten) to a few seconds on a personal computer to calculate an entire phase diagram (for a beginning student to gain insight into the meaning of a phase diagram).

Computer modelling has been applied to phase diagrams for at least a generation, predominantly in the form of thermodynamic optimization. Some of the pioneers of that work, which is formalized in the CALPHAD organization and journal of the same name, also took part in the present seminar and are represented in this volume. An earlier symposium and proceedings, "Calculation of Phase Diagrams and Thermochemistry of Alloy Phases", edited by Y. A. Chang and J. F. Smith (The Metallurgical Society of AIME, Warrendale, Pa 1979) focused primarily on that same aspect. Today, computer modelling is more encompassing and the present Symposium proceedings represents a wide variety of applications. In the foreword to an earlier Symposium, Theory of Alloy Phase Formation, edited by L. H. Bennett (The Metallurgical Society of AIME, Warrendale, PA 1980), the editor, referring to the 1979 and 1980 symposia, commented on the fact that "the two groups involved - quantum mechanics, statistical mechanics, and Hume-Rothery metallurgy on one hand, and thermodynamics on the other, unfortunately are still represented by two diverse communities." The present volume is evidence that this is no longer the situation.

Thermodynamic optimization remains important, of course, and was represented in several of the presentations. The importance of interactions between these optimization procedures and physical models was highlighted. Inclusion of magnetic terms was emphasized in several papers. The Cluster Variation Method (CVM) was very prominantly featured - this statistical mechanical procedure for finding the configurational entropy associated with ordering has become the leading method for determining order disorder transitions. The structural stability of the elements was addressed by a priori quantum mechanical calculations and by reasoning backwards from comparisons of optimized phase diagrams with experimental data. Classification of symmetry principles and of crystal structures, both important to the construction of phase diagrams, were addressed. Renormalization group theory was shown to be a useful newer technique for calculating phase diagrams.

There were a number of presentations concerned with computerization of the database, ranging from fundamental mathematical considerations (i.e., creation of an "incidence algebra") to very practical questions of how to establish the rules for a database for immediate daily use. Computer graphics presentations occupied a number of investigators, including how to present the most useful multicomponent diagrams when expensive computer systems are available, on the one hand, and how to produce binary diagrams quickly and inexpensively on computers likely to be available to users in far flung environments.

Thanks are due to the past and present chairmen of the Alloy Phase Diagram Data Committee, Dr. J. D. Livingston and Prof. J. B. Clark, for their aid and encouragement in organizing this symposium. Thanks are also due to Dr. L. J. Swartzendruber, Prof. J. F. Smith and Prof. Clark for service as session chairmen during the symposium.

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THERMODYNAMIC MODELING OF PHASE DIAGRAMS - A CALL FOR INCREASED GENERALITY

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Summary

A general thermodynamic databank would be a most valuable tool in research and technology. It could produce phase diagrams but also a large variety of thermodynamic quantities. It should be in the interest to all people interested in such information, chemists, metallurgists, ceramists etc., to start a large-scale collaboration in order to construct such a databank.

As a first step in this direction the SGTE group has been established·in Europe and is engaged in a joint project aimed at constructing a databank with some features of high generality. It is to be hoped that the result will be a demonstration that the concept of a general thermodynamic databank constructed through international collaboration, is realistic.

Coupling of phase diagrams and thermochemistry

It seems appropriate to start a symposium on Computer Modeling of Phase Diagrams by asking why we should like to model phase diagrams. Classically, phase diagrams have been determined by direct experimental measurements and the results were presented as diagrams drawn by hand. The assessment of the often conflicting pieces of information was no minor task and required a special talent. The outstanding example of this kind of work is the classical compilation of binary phase diagrams published by Hansen (1) in 1936, and one may add the current Data Program for Alloy Phase Diagrams run by ASM and NBS. It is typical of our time that this project makes use of computer techniques for storing the assessed phase diagram rather than relying on a printed picture. By this technique it is possible to update the collection of phase diagrams at any time and also to retrieve a phase diagram or any part of it and have it plotted with the axes most suitable for a particular application. As an example, the usual Gibbs triangle is not well suited for a practical application if one is interested in low contents of carbon and medium contents of chromium in iron. It is then better to choose a Cartesian coordinate system and to expand the scale for the carbon axis compared to the chromium axis.

It should be emphasized that this project does not involve modeling. The data base will simply store the lines of the phase diagram. It will contain no information on the properties of an alloy falling in a one-phase field except for the fact that it is in a single-phase state.

When assessing the information on a phase diagram it is of course necessary to keep in mind the general rules for the construction of phase diagrams, which can be derived from Gibbs' thermodynamics. These rules were explored in great detail by Bakhuis Roozeboom (2) and Schreinemakers (3,4) with some additions being made later by Masing (5) and Palatnik and Landau (6), for instance. However, thermodynamics does not only give general rules. It allows the quantitative calculation of phase equilibria from the thermodynamic properties of each one of the phases. A phase diagram may thus be regarded as a manifestation of the thermodynamic properties. Unfortunately, the thermodynamic properties are seldom known well enough to allow the calculation of a phase diagram. However, it is self-evident that, when assessing a phase diagram, one should make use of the thermochemical information available. As a simple example we can take van't Hoff's law for the depression of the freezing point. Knowing the heat of melting of a pure element A one may calculate the difference in slope of the liquidus and solidus at the A side of any A-B phase diagram. However, here we encounter the need for modeling because the freezing point depression depends upon the state of dissociation of the solute element. In alloys one can usually presume that it is dissociated in atoms and even without knowing the heat of melting of the pure element one could check one phase diagram against another if they have an element in common. A well-known example is the width of the so-called gamma loop in many binary Fe phase diagrams. Close to the Fe side the $\gamma+\alpha$ two-phase field should have a width determined by the temperature and independent of the nature of the alloying element. It is interesting to note that many of the binary Fe diagrams in Hansen's compilation were in conflict with each other in this respect. By applying the simple model of a solution of atoms to the assessment of a phase diagram one may considerably improve the result.

For silicate systems the situation is quite different. The freezing point depression of SiO_2 differs from the prediction given by the model for a solution of atoms and it even seems to depend upon the nature of the metal oxide added. This has given rise to many speculations regarding the structure of the silicate melts and various models have been proposed to explain the phase diagram information. These models primarily predict the thermodynamic

properties of the liquid phase and could have been constructed in order to explain experimental information on such properties. However, thermodynamical measurements are very difficult in SiO_2 rich melts and the best information available is the phase diagram information. In fact, in very many cases where information of both kinds is available, the phase diagram information is more reliable and more precise than the thermochemical information. As a consequence, one should not only use thermochemical information as a support when assessing a phase diagram. One should also allow the phase diagram information to influence the assessment of the thermodynamic properties. One should actually assess all the experimental information available on phase equilibria and thermodynamic properties in a single operation. It thus seems most appropriate that a journal devoted to the calculation of phase diagrams, CALPHAD, has the subtitle Computer Coupling of Phase Diagrams and Thermochemistry.

Physical models and mathematical models

We have thus found the answer to our question why we should like to model phase diagrams. Modeling is necessary if we want to couple phase diagrams and thermodynamics one way or another. The modeling primarily concerns the properties of the separate phases. From this point of view a more appropriate title of the present symposium would have been "Computer Modeling of Thermodynamic Properties of Phases." On the other hand, the phase diagram is at the center of our interest and we should not be satisfied unless we can treat at least the main features of the diagram. On the other hand, we may be willing to accept a very crude description of a phase if reliable information is not available. There are many cases where the thermodynamic properties of a phase are not well known and sometimes one does not even know the structure of a solution phase. Any model may then be applied and, if it is capable of describing all the information available, then it satisfies our immediate needs. A physical chemist may hesitate to work with such a model unless he feels that it is physically more realistic than alternative models and he is able to test this by comparing with experiments. As an example we may take the liquid phase in binary alloy systems with a strong, negative enthalpy of mixing. It has recently been modeled in two quite different ways. One model is based upon the hypothesis that the negative enthalpy is the manifestation of a strong tendency of the different atoms to form molecular-like aggregates, so-called "associates" (7). The other model is borrowed from the solid state where a strong negative enthalpy of mixing is typical of ordering systems, where the different atoms tend to go into different sublattices. This model is constructed by hypothesizing the existence of two sublattices in the liquid phase (8). It turns out that in the simplest case the two models give the same mathematical expression for the Gibbs energy. It is thus impossible to distinguish between them by comparing with experimental information on the thermodynamic properties. When we find that these models can successfully describe the experimental information on a certain system, then we have not gained any insight in the physical nature of the solution. It may be instructive to define the mathematical expression as a model in its own right, a "mathematical model". In our work it is legitimate to use such a model as long as it is capable of describing the information and it can then be used to predict the properties under conditions not studied directly by experiment. On the other hand, it would be hazardous to use it for predicting the physical state even though it may be based upon a physical model. In physical chemistry one is basically interested in understanding the physics of chemical systems and for the system being studied one would not be satisfied with a mathematical model if it is not intimately related to a physical model. On the other hand, the physical chemist may also be interested in applications either for a practical purpose or in his study of some other system.

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When the information on a phase is very meagre the phase diagram assessment may be performed with a very simple mathematical model for that particular phase. Such a model may not have any physical basis. It may still be useful for our purpose. However, if the adjustable parameters in the model have been evaluated from phase diagram information only, then one should be very cautious when using it for a prediction of thermodynamic properties. The sounder the physical model underlying a mathematical model is, the safer its predictions will be. In order to make predictions far away from experimental data points, i.e., in order to "extrapolate" the experimental information, one needs a model with a good physical basis.

Collaboration on a general database

Even though phase diagram people and physical chemists may have different ambitions it should be of mutual advantage if a scheme of collaboration for assessment work could be found. The ultimate goal would be a single, general database for the thermodynamic properties of all substances and solution phases. It should be administered by computers having access to computer software for all possible applications. As a first step in this direction a collaboration has been established in Europe under the name of SGTE (Scientific Group Thermodata Europe). The following organizations are members:

Laboratoire de Thermodynamique et Physico-Chimie
Métallurgiques ENSEEG, Domaine Universitaire
St Martin d'Hères Cedex, France

Association THERMODATA
Domaine Universitaire
St Martin d'Hères Cedex, France

IRSID
Maizières-les-Metz, France

Lehrstuhl für Metallurgie der Kernbrennstoffe und
Theoretische Hüttenkunde
Rheinisch Westfälische Technische Hochschule, Aachen, FRG

Royal Institute of Technology
Division of Physical Metallurgy
Stockholm, Sweden

National Physical Laboratory
MTDS, Division of Materials Applications
Teddington, UK

Atomic Energy Research Establishment, Harwell
MTDS
Harwell, UK

The immediate goal of the SGTE project is very restricted but an attempt is made to be as general as possible. In a sense this collaboration may be regarded as a feasibility study. The hope is to be able to demonstrate that a general database would be possible and useful. This is by no means self-evident. A number of difficulties will be discussed in the next section.

At the present stage the SGTE project concerns a number of different kinds of systems, Al-base alloys, Fe-base alloys, ionic aqueous solutions, salt systems and oxide systems.

As an example, the work on Fe-base alloys includes the most common alloying elements in steel and the goal is to obtain a dataset from which one could predict the constitution of any steel composition. A steel may

contain between 5 and 10 elements of significant importance. Only the binaries and a few of the ternaries are known reasonably well from direct experiments. Through the SGTE project quaternaries are now becoming available and by combination they may give a reasonable description of higher order systems.

The future extension of the database to cover most of the substances of practical importance will require an immense amount of work. It is necessary to extend the collaboration to include many more groups. The success of the ASM-NBS project indicates that a wide collaboration should be possible at least for alloys. Indeed, a considerable number of groups are already engaged in their own programs for assessment of phase diagrams by modeling. Unfortunately, there has not been a strong tendency for harmonizing these efforts. Each group has its own favourite models and different descriptions of the pure elements are being used. It is thus impossible to combine the results from different groups. This seems like a terrible waste of good work.

The crucial question is whether it would be possible to convince any group that it should give up its favourite models and forget the results they have already produced. Certainly, this will not happen unless some substantial advantages can be offered. A databank constructed to become very general in the future may be able to offer such advantages already during its stage of construction. One may hope that the current SGTE project will produce some attractive datasets and a rather general package of software and thus be able to act as a supercritical nucleus for a wide international collaboration.

Some of the SGTE efforts to increase the generality of its new databank will be described in later sections. Hopefully, these aspects will be attractive to other groups. On the other hand, there are many difficulties connected with a broad, international collaboration. Some of them will be discussed in the next section.

Difficulties of collaboration

1. First of all it must be agreed what thermodynamic function should be used for the storage of data. Three alternatives may be considered, $G(T,P,x_i)$, $F(T,V_m,x_i)$ and $U(S_m,V_m,x_i)$. In principle, all thermodynamic properties could be calculated from any one of them but that does not mean that all the thermodynamic properties can always be represented by any one of the functions. The problem appears as the system is approaching a critical point. A critical point connected with a separation in regions of different compositions, i.e. different x_i can be treated by all three. A critical point connected with a separation in regions of different densities, i.e. different V_m, can only be treated by F and U. A critical point related to S_m can only be treated by U. This is because U is the most basic quantity. However, it should immediately be mentioned that the latter kind of critical point will always occur inside the region of instability due to V_m and is thus of no practical importance. F would thus be suitable in all cases and it should be preferred to U because the variable T is more practical to use than S_m. By the same reason G should be preferred because the variable P is more practical to use than V_m. As an example, experimental data are often determined at a well controlled pressure whereas the V_m value is seldom controlled and rarely measured. The choice between F and G is thus a choice between generality and practicality. In this case the SGTE groups have decided to sacrifice generality and use G.

2. All the information contained in the database must be self-consistent. Consider for instance solutions of various elements in fcc Fe at a

temperature where the stable state of Fe is bcc. The relative stability of fcc Fe will thus enter into the assessment of all the binary systems with Fe. The results will be consistent only if the same description of pure Fe is used. If this is not the case, the results cannot be combined to form a basis for the assessment of higher order systems. By the same reason, when ternary systems are assessed, the same descriptions of the component binaries must be used in order to allow an extension to even higher order systems. When several groups collaborate on a common database they must reach an agreement at each stage in the assessment work. Once an agreement has been reached it will be very costly to modify it.

3. The thermodynamic properties of a phase must be stored as parameter values to be inserted in some mathematical model. However, in different systems one encounters different physical effects and may thus develop different models. In order to describe a higher order system, obtained by combining lower order systems, it is necessary to combine the models into a more general model. This can only be done if the models are compatible. This problem is particularly relevant for the liquid phase because very different kinds of melts may mix. Collaboration between different groups requires that agreement is reached regarding the models to be used. The models agreed on within the SGTE collaboration will be described in the following sections.

4. In order to obtain a satisfactory description of the thermodynamic effect in a binary system it is sometimes necessary to use a model which will rapidly grow very complex as one goes to higher order systems. Such a model will not be very practical for a database although it may be the only satisfactory model from the scientific point of view. The choice of a simpler but cruder model is not always easy to make.

5. In order to finance the assessment work for the database, it is necessary that practical results are being produced continuously and at a reasonable rate. It would be difficult to stop a line of activity while waiting for badly needed measurements or improvements of a model. In many cases one may be forced to accept a crude description of a lower order system in order to be able to proceed to a higher order system of great practical value. However, it will be very difficult to make such a decision in a collaboration involving several groups.

6. New information or the improvement of a model may justify a revision of the description of a lower order system. As a consequence, one must reassess all the higher order systems. It will be very difficult to take such a decision but sometimes it must be taken. It would be easier to carry out the reassessments if all the information on the primary assessment is saved and .preferably stored on a computer. However, that would mean that a significant part of the resources is spent without immediate practical results. In any case, it will be necessary to start up a new improved version of the database after not too many years. One would probably have to accept working on more than one generation of the database simultaneously. In fact, the first SGTE project concerned well defined, pure substances and it is still not completed. Nevertheless, in connection with the current SGTE project, which primarily concerns solution phases, it was considered necessary to start a new version of the dataset for pure substances.

7. The cost of a high degree of generality is substantial. A more general model will require more computer time than a simpler model chosen to fit the system under consideration. It will thus be cheaper to assess a phase diagram with a simple model but the result may not be useful as a basis for the assessment of a higher order system. It is to be hoped that our sponsors will appreciate the higher value of the results obtained with more general models. Anyway, decisions must be taken what is a reasonable degree of gene-

rality.

A more general package of software will also require more computer time
than a program written for a particular problem. On the other hand, the more
general package will be very economic when applied to a particular problem
which has not been considered earlier. Another advantage is that only the
expert may find his way through a forest of special programs whereas the
more general package can be used by a person with very limited expertice. For
some assessors of phase diagrams it may be cheaper to use special programs
but for people applying his results the more general package may be more
economic.

A high-generality databank

As an example of a databank constructed with a high degree of generality
in mind a databank called THERMO-CALC will now be desribed. It is a result
of the collaboration within SGTE and it is being used for an on line service
offering the datasets produced so far. This databank has recently been de-
scribed and many different applications have been reported (9). As a conse-
quence, only some of the main features will here be described.

The software for a databank of high generality must necessarily be very
large and once constructed it will be very difficult to change in particular
for new people. In an attempt to avoid making it too rigid SGTE decided to
recommend a modular system with well defined interfaces between the various
modules. It should then be possible for anyone to insert a new module which
obeys the rules defined by the interfaces. This principle has been followed
but not to the full extent, the reason being the limited effort that could
be put into the work. At the present time THERMO-CALC only has three main
modules connected by interfaces, a database module (10) a module for the
calculation of Gibbs energy values (11) and a module for the calculation of
equilibria and diagrams (12,13). The two interfaces were defined at an early
stage (14,15) but in order to minimize the work on the modules they were
slightly changed during the work.

The user defines his system interactively in the database module, i.e.,
he selects his phases, defines their sublattices and the species on each
sublattice. In the Gibbs energy module he can inspect the data and add his
own data when necessary. Furthermore, he can define his own expression for
the excess Gibbs energy if he is not satisfied with the standard expression.
A drastic change of the excess model may require new programming. However,
a change of the basic model requires that a new module is written.

Much effort has gone into making the equilibrium module as general as
possible. There the user defines the conditions for which he wants the equi-
librium to be calculated. The method of calculation is based upon a very
special minimization of the Gibbs energy which allows almost any conditions
to be used (16). This is partly due to the fact that the only information,
reaching this module from the database through the action of the Gibbs
energy module, comes in the form of values of Gibbs energy and its deriva-
tives with respect to the internal variables in each phase.

It is worth mentioning that two versions of the equilibrium module are
available and they are both able to interact with the interface attached to
the Gibbs energy module. The most recent version can handle the condition of
electroneutrality and molecular species (13).

A phase diagram is produced by a stepping procedure using one, two or
three variables, for producing two-, three- or four-dimensional diagrams. A

special feature is that sections through any many-dimensional diagram can be calculated directly.

In principle, the equilibrium module can handle any number of components and phases. The same program is used for the simplest one-component calculations and for the most complicated ones. To emphasize this fact the program has been given the name POLY.

A post-processor is included in the equilibrium module and it allows the results to be printed or plotted in any form. During the calculation of a system, all the variables are stored that define the equilibrium states calculated. From them the values of any thermodynamic quantity can be calculated afterwards and be presented in tables of diagrams.

It should be emphasized that a large number of different types of phase diagrams can be obtained but also diagrams that should be classified as property diagrams (17). The following examples of diagrams may be mentioned

. constitution and amounts of various phases in equilibrium at selected temperatures, compositions and activities,
. phase diagrams in binary, ternary and higher-order systems under auxiliary conditions such as constant temperature or pressure, constant amount of some components or constant chemical activities,
. predominance area diagrams,
. liquidus surfaces,
. calculation of equilibria when the set of stable phases is prescribed,
. property diagrams where a dependent quantity is plotted versus an independent.

It should be added that the THERMO-CALC package of software is constructed to be used as a subroutine in application programs. Two such programs deserve special mention. One is an optimization program for the assessment of systems (18). In principle, it can handle a system with many components and phases and it can accept experimental data of many different kinds. The other program (19) solves diffusion problems and through the interaction with THERMO-CALC it can take into account the changing conditions at phase interfaces and the effect of the thermodynamic properties on the diffusion constant (20).

Models in THERMO-CALC

It may be argued that a very general databank should permit any model to be used. On the other hand, in order to make possible the combination of descriptions of lower order systems to give a basis for the description of higher order systems it is necessary to restrict the choice of models. THERMO-CALC has been constructed for applications on higher order systems in mind and it has thus been necessary to choose a well defined set of models. They will be described in this section. A databank for binary systems could have been made with much less effort and could be much more flexible and would be much easier to collaborate on. However, already the extension to ternary systems would change the picture.

Temperature dependence

C_p for an element in each state (phase) is represented with a power series

$$C_p = -c - 2dT - 6eT^2 - 2fT^{-2} - 12gT^3 - 6hT^{-3} + --$$

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Several temperature ranges may be used but without discontinuities in C_P, H_m or G_m. The molar Gibbs energy will be expressed as

$$^oG_A - H_A^{SER} = a+bT+cT\ln T+dT^2+eT^3+fT^{-1}+gT^4+hT^{-2}+ --$$

This implies that the Gibbs energy is given relative to a reference called SER (stable element reference) which is defined with the use of H(298.15K) and S(0K) for the stable state of the pure elements at 298.15K and 1 bar.

The Debye theory is not applied and it is thus accepted that the data-bank will not cover the low temperature range. For reasonably low temperatures the Debye theory may be simulated by the T^{-3} term in C_P.

Extrapolation across the melting point is a problem. Much assessment work has been done in the past using a lattice stability of the type A+BT which implies that the heat and entropy of melting are constant, i.e. that the liquid and solid phases have the same C_P. It seems that one should at least make use of the difference in C_P at the melting point if it is known. A realistic extrapolation of this difference above and below the melting point does not seem possible today due to our limited knowledge. A particularly difficult problem is the glass transition in strongly supercooled liquids. SGTE has decided not to include this phenomenon and has agreed on the following convention which will ascertain that the liquid phase will not turn stable at low temperatures, nor the solid phase at high temperatures.

$$T>T_f : C_P^\beta = C_P^\ell(T)+[C_P^\beta(T_f)-C_P^\ell(T_f)](T/T_f)^{-10}$$

$$T>T_f : C_P^\ell = C_P^\alpha(T)+[C_P^\ell(T_f)-C_P^\alpha(T_f)](T/T_f)^6$$

T_f is the stable melting point independent of what solid phase is considered. α is the phase stable at 298.15K and 1 bar. For a magnetic element the magnetic contribution is added.

The method of extrapolation across solid state transition is decided by the assessor but he should take care not to make a phase come close to becoming stable where it should not be. He should be aware of the risk that a phase could otherwise become stable where it should not form in a higher order system.

Gaseous phase

Only the ideal model will be used for a gaseous phase at the present time. This means that a term RTlnP is added to the expression for $^oG_A - H_A^{SER}$. This term does not appear in C_P.

Molecules

Molecules may be used in the modeling of any phase. Each kind of molecule will then be defined as a species. The number of a certain kind of molecule is treated as an internal variable and its equilibrium value will be obtained by minimizing the Gibbs energy. The possibility of having frozen equilibria for molecules has not yet been included in the program.

Magnetic effects

Magnetic ordering is evaluated with respect to the completely disordered paramagnetic state and the following formula will be used in the pure ele-