

Demonstration of the Use of "BINGSS" With the Mg-Zn System as Example

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BINGSS is a program for least squares optimization of thermodynamic descriptions using experimental phase diagram and thermodynamic data. The number of measured values used is unlimited. Some special features and improvements since the first publication of this program are outlined.

The models for the thermodynamic description and their adjustable coefficients must be well selected. Missing parameters may disable the fit between experimental and calculated values. Too many coefficients may be undefined and may cause divergence of the calculation. Some ideas on how to handle these problems are demonstrated using the Mg-Zn system as an example.

1. Introduction

A knowledge of phase equilibria is fundamental to all aspects of materials science. A modern method of providing this knowledge for a particular application is by thermodynamic calculation of the equilibria using data stored in a computer data bank. Hence, the generation of reliable computer-readable thermodynamic data is very important.

For computer application, the data are stored as analytical expressions for the thermodynamic functions of state and as numerical values of the adjustable parameters of these expressions. The analytical expressions are derived from more-or-less simplified models of statistical thermodynamics. The most important descriptions as well as the methods for use of these data for the calculation of equilibria have been reviewed several times, for example by [82Luk].

For the determination of the adjustable coefficients of the analytical expressions, [77Luk] applied the least squares method using all kinds of experimental data giving quantitative information on thermodynamic properties. Besides calorimetric, emf, and vapor pressure data, all types of phase diagram measurements are valid for this purpose. The computer programs that perform this operation for binary and ternary systems are called BINGSS and TERGSS, respectively. The additional programs BINFKT and TERFKT are mainly tailored to calculate phase diagrams and pro-

duce plots of thermodynamic functions for testing the results of BINGSS and TERGSS. Less emphasis has been given to their use for calculations using data extracted from a data bank.

The least squares method has some limitations, which usually are not well satisfied by experimental thermodynamic data. This forbids the use of the method as a "black box" and demands a careful check of the quality of the results. The aim of this paper is to elucidate these problems and provide some hints on how to handle them using as an example the recently optimized Mg-Zn system [92Aga].

After selecting the appropriate model for the thermodynamic description of each phase, the user has to decide how many and exactly which of the adjustable coefficients will be used. With an insufficient number of coefficients, the description may be unable to reproduce experimentally well-established features of the thermodynamic properties. At the same time, too many coefficients may lead to bad results. The program uses these coefficients to smooth the experimental scatter, and it may produce strange results in areas that are not covered by experimental values. Thus the selection of the parameters to be adjusted is like navigation between Scylla and Charybdis, and each selected parameter must be justified by thermodynamic considerations. If insufficient experimental data are available, estimates may be necessary in order to provide a complete set of parameters. Examples of such estimates are enthalpies of formation calculated from the Miedema [76Mie] formulas or the use of a relationship between enthalpy and excess entropy of mixing first introduced by Kubaschewski [79Kub] and recently refined by Tanaka *et al.* [90Tan].

2. Least-Squares Method

To understand the problems arising in our application software due to the least squares method, the main steps of the method are repeated here.

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The purpose of the least squares method is to adjust variable coefficients of an analytical expression to experimental values. In our case, the analytical expression contains all thermodynamic functions of state, and the experimental values may be any thermodynamic or phase diagram measurements.

Starting with a set of approximate values for the adjustable coefficients, the analytical expressions enable a calculated value to be obtained for each measured value. The difference between the measured and this calculated value, multiplied by a weighting factor p , is called the "error":

$$(\text{measured value} - \text{calculated value}) \times p = \text{error} \quad (\text{Eq 1})$$

As the condition of best fit, the sum of the squares of these "errors" of all the m measurements should have a minimum value:

$$\sum_{i=1}^m (\text{error}_i)^2 = \text{Minimum} \quad (\text{Eq 2})$$

To solve this problem, the derivatives of this sum of the squares of the errors with respect to the adjustable coefficients are set to zero. The result is a set of n equations for the n unknown corrections of the adjustable coefficients:

$$\frac{\partial \sum_{i=1}^m (\text{error}_i)^2}{\partial \text{coeff}_j} = 0 \quad (j = 1 \dots n)$$

$$\frac{1}{2} \frac{\partial \sum_{i=1}^m (\text{error}_i)^2}{\partial \text{coeff}_j} = \sum_{i=1}^m \left(\text{error}_i \times \frac{\partial \text{error}_i}{\partial \text{coeff}_j} \right) = 0 \quad (j = 1 \dots n) \quad (\text{Eq 3})$$

To make these n equations linear, Gauss expanded the "error" into a Taylor series and truncated after the linear term:

$$\text{error}_i = \text{error}_i^0 + \sum_{k=1}^n \left(\frac{\partial \text{error}_i}{\partial \text{coeff}_k} \times \Delta \text{coeff}_k \right) \quad (\text{Eq 4})$$

This approximates the error by a linear function of the corrections, Δcoeff_k , of the adjustable coefficients. The derivative, $\partial \text{error}_i / \partial \text{coeff}_k$, is of course identical to $-p$ times the derivative of the calculated value, since the measured value does not depend on the coefficients.

Insertion of Eq 4 into Eq 3 generates a system of n linear equations of the n unknown corrections of the n adjustable coefficients:

$$\sum_{i=1}^m \left\{ \left[\text{error}_i^0 + \sum_{k=1}^n \left(\frac{\partial \text{error}_i}{\partial \text{coeff}_k} \times \Delta \text{coeff}_k \right) \right] \times \frac{\partial \text{error}_i}{\partial \text{coeff}_j} \right\} = 0 \quad (j = 1 \dots n)$$

or finally:

$$\sum_{k=1}^n \left(\sum_{i=1}^m \frac{\partial \text{error}_i}{\partial \text{coeff}_j} \times \frac{\partial \text{error}_i}{\partial \text{coeff}_k} \right) \times \Delta \text{coeff}_k = - \sum_{i=1}^m \text{error}_i^0 \times \frac{\partial \text{error}_i}{\partial \text{coeff}_j} \quad (j = 1 \dots n) \quad (\text{Eq 5})$$

This system of linear equations is solved for the corrections, Δcoeff_k , which are added to the starting values of the coefficients. The calculation is repeated iteratively until each of the corrections becomes smaller than a selected fraction ϵ of the corresponding coefficient.

There are two main problems associated with the application of this method for thermodynamic optimization: (1) The condition of best fit, Eq 1, is valid only if the errors satisfy a "Gaussian normal distribution" around the mean value. This is especially not the case when there are systematic errors in a series of experimental values. (2) The step of linearization in Eq 3 is problematic if the starting values of the adjustable coefficients are far from their final optimized values. In thermodynamic optimization this often cannot be avoided, and a divergence of the iteration after Eq 5 may result. This problem does not occur if the "equations of error," Eq 1, are already linear in the coefficients.

Due to the first point, the data must be carefully checked for systematic errors. Mostly, these are recognized from discrepancies between different sets of measurements. If the same quantity is measured several times and there is significant disagreement, a systematic error must be supposed, and one of the contradicting series of measurements must be omitted. If a discrepancy occurs between different types of data, then in general a check must be made to ascertain whether this contradiction is intrinsic to thermodynamic rules or is simply caused by an insufficient number of adjustable coefficients.

The second point illustrates that in the first iteration steps, equations of error (Eq 1) linear in the coefficients are better than nonlinear ones. For several types of data, BINGSS and TERGSS offer two different equations of error, one linear in the coefficients, the other one more exactly related to the measurement but nonlinear. An example is given in section 3.1.

3. Experimental Data

Most of the experimental data used in BINGSS are taken from the literature. Although there is a large variety of different types of measurements, they can be reduced to a few standard types, each of which is described by the same equation of error, *i.e.* the same formula for the "calculated value" of Eq 1. Within the three main types—phase diagram data, enthalpy data, and chemical potential data—the "calculated value" depends on the number of phases involved in the "measured value."

The different equations of error have already been discussed by [77Luk], but some of them have been improved upon in the present version of BINGSS. These are given in the following subsections.

3.1 Phase Diagram Data

A single two-phase equilibrium in a binary system can be measured in two different ways: (1) The concentration of one of the two phases is given, and the temperature of equilibrium is measured—for example the determination of the liquidus temperature by DTA on a sample with given composition. (2) The temperature is given and the concentration of one of the phases is measured—for example from the kink of a lattice parameter vs concentration plot of a series of samples annealed at the same temperature or by microprobe analysis of a single grain in an annealed sample. The equations of error of these two types of measurements are:

$$(T_{\text{meas}} - T_{\text{calc}}) \times p = \text{error} \quad (\text{Eq } 6)$$

$$(x'_{\text{meas}} - x'_{\text{calc}}) \times p = \text{error} \quad (\text{Eq } 7)$$

The “calculated values,” T_{calc} and x_{calc} of these two equations are the results of equilibrium calculations, which start from the slightly modified equilibrium conditions of Gibbs:

$$\begin{aligned} \mu'_1(x', T) - \mu_1^{\text{eq}} &= 0 \\ \mu'_2(x', T) - \mu_2^{\text{eq}} &= 0 \\ \mu''_1(x'', T) - \mu_1^{\text{eq}} &= 0 \\ \mu''_2(x'', T) - \mu_2^{\text{eq}} &= 0 \end{aligned} \quad (\text{Eq } 8)$$

where $\mu_j^{(i)}(x, T)$ are expressed by the analytical expressions containing the coefficients to be optimized. The five quantities— $x', x'', T, \mu_1^{\text{eq}}$, and μ_2^{eq} —are treated as unknowns. The set of equations (8) is usually nonlinear. It may be solved for the unknowns by an iteration method, for example the Newton-Raphson method. However, since there are five unknowns and only four equations, one of the unknowns has to be fixed, which formally is done by adding a fifth equation, either:

$$x' - x'_0 = 0 \quad (\text{Eq } 9)$$

or

$$T - T_0 = 0 \quad (\text{Eq } 10)$$

where x'_0 and T_0 are fixed values.

To calculate the value T_{calc} of Eq 6, the fifth equation added to the set of equations (8) is Eq 9. To calculate x_{calc} of Eq 7, Eq 10 is added to the set of equations (8).

In the paper by [77Luk], the equation of error for both cases is derived from the common tangent in a G vs x plot as condition for equilibrium:

$$G'(x', T) + (x'' - x') \times \left(\frac{\partial G'}{\partial x} \right)_{x', T} - G''(x'', T) = \text{error} \quad (\text{Eq } 11)$$

The three definitions of the error are illustrated in Fig. 1. In the upper part, two different measurements of a phase boundary are shown with the same calculated tie-line. The lower part of Fig. 1

explains Eq 11 in a G vs x plot. The first two terms of Eq 11 define the point corresponding to the concentration of the second phase, x'' , on the tangent of the $G'(x)$ curve taken at the measured concentration x'_{meas} . If the measured and calculated equilibrium concentrations coincide, this tangent is also tangent to the curve $G''(x)$ at x'' , and the error is zero. Equation 11 has the advantage that, if the Redlich-Kister description is used, the Gibbs energies G' and G'' are linear functions of the coefficients. Then, in Eq 11, the error is also related linearly to the coefficients, whereas in Eq 6 and 7 it is related nonlinearly. On the other hand, in Eq 11 the error depends on the concentration x'' , although this dependence is weak. Often x'' and x' are not measured in the same investigation, and x'' must be interpolated between measurements from another source. In any case, x'' must be given in the input file.

In the program BINGSS, values in the input file are defined as corresponding either to Eq 6 or 7, but by use of a switch variable in the program, Eq 11 may be selected as the equation of error. For the reasons given in section 2, Eq 11 is to be preferred if the starting values of the adjustable coefficients are rough estimates, since with the linearization involved in the least squares method, Eq 4, the nonlinear Eq 6 and 7 may cause divergence of the iteration. In the final steps, however, the dependence on x'' is a handicap for Eq 11, and Eq 6 and 7 should be preferred.

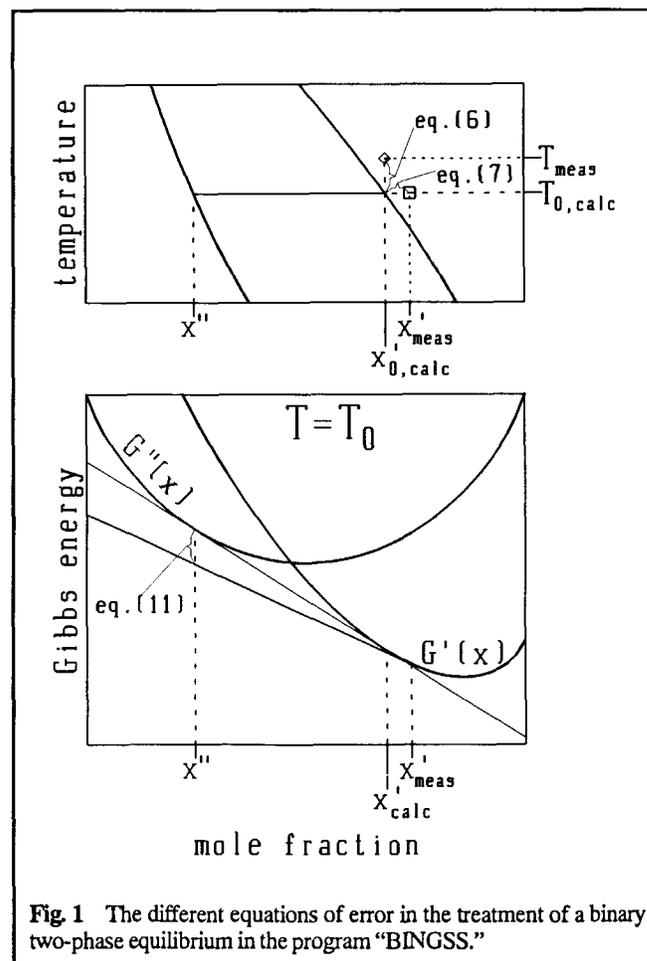


Fig. 1 The different equations of error in the treatment of a binary two-phase equilibrium in the program “BINGSS.”

The choice of Eq 6 or 7 depends on the slope of the measured phase boundary. This is demonstrated in Fig. 2. The nearly vertical solubility limit of the (A) solid solution cannot be measured by thermal analysis of a sample of known concentration of B, nor can it be treated using Eq 6. It *must* be treated using Eq 7 in the least squares optimization. The liquidus near a congruent melting point, however, cannot be determined by measuring the composition of a liquid subjected to equilibrium annealing at a fixed temperature. In this case, Eq 6 *must* be used. Most other equilibria can be treated by each of the two equations.

An invariant three-phase equilibrium in a binary system is treated using an equation of error identical to Eq 6, but here T_{calc} is the calculated three-phase equilibrium temperature. To the set of

equations (8), two more equations of the same type are added for the third phase, and the resulting set of six equations is solved for the unknowns $x', x'', x''', T, \mu_1^{eq}$, and μ_2^{eq} by the Newton-Raphson technique.

The concentrations of the phases in this three-phase equilibrium are usually extrapolated from the adjacent two-phase fields and therefore, contrary to [77Luk], are not treated as measured quantities of the invariant equilibrium. If they are to be considered, they are entered as an additional measurement of a two-phase equilibrium with one of the two other phases using Eq 7.

A linear equation of error for three-phase equilibria is also provided in BINGSS. It is based on the condition that the Gibbs energies of the three phases lie on a straight line in a G vs x plot, or that the following determinant is equal to zero:

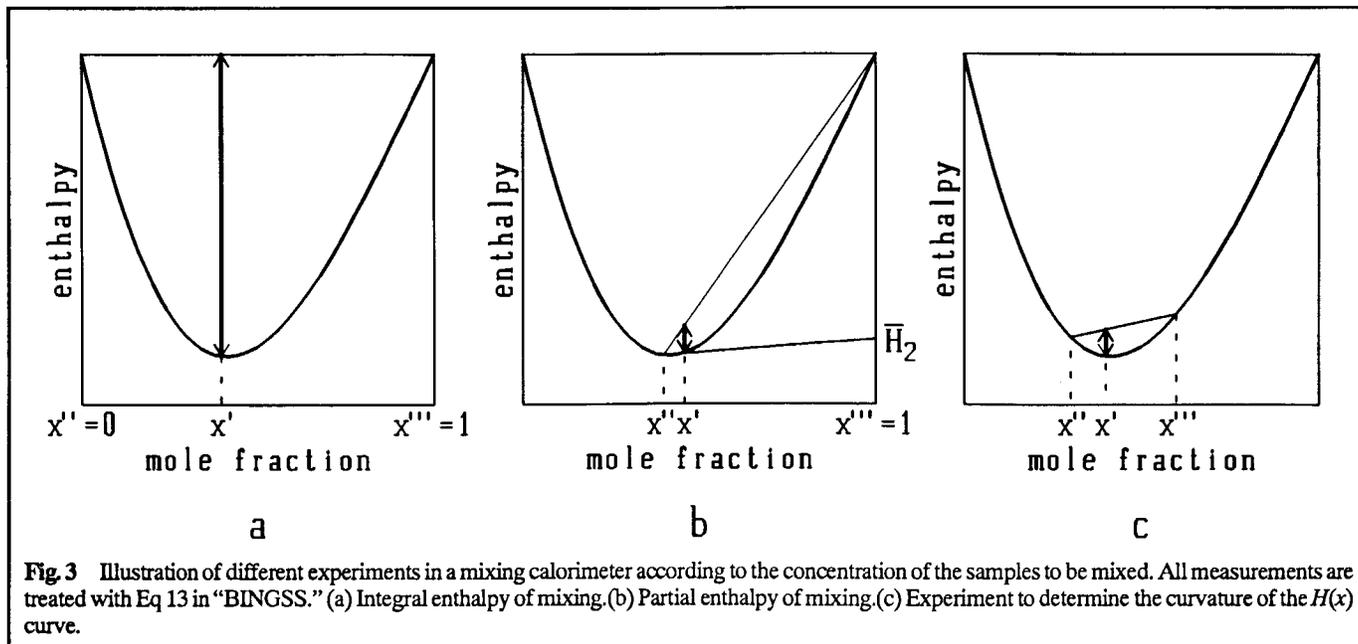
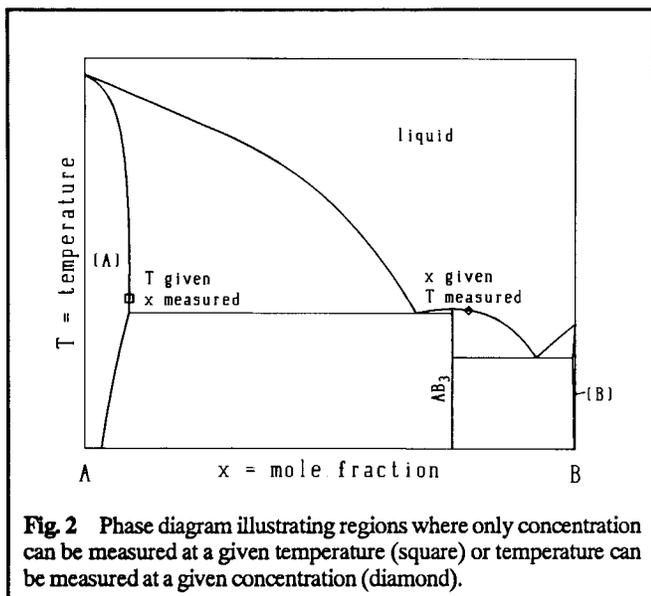
$$\begin{vmatrix} 1 & 1 & 1 \\ x' & x'' & x''' \\ G' & G'' & G''' \end{vmatrix} = 0 \quad (\text{Eq 12})$$

Analogous to Eq 11, Eq 12 depends on the concentrations x', x'' , and x''' of the three phases. In BINGSS, either Eq 6 or 12 can be selected by the switch variable "IVERS."

3.2 Enthalpy Data

Calorimetric enthalpy measurements are of two basic types: (1) values obtained using mixing calorimetry and (2) drop or scanning calorimetry data.

In case (1), the heat effect is measured when two separate samples, each characterized with respect to phase, temperature, and composition react in the calorimeter to form a single well-characterized sample. The corresponding calculated value is represented by the formula:



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$$H'(x', T_1) - [(1 - m) \times H''(x'', T_2) + m \times H'''(x''', T_3)] \quad (\text{Eq 13})$$

where $(1 - m)$ and m are the amounts of the two samples necessary to form 1 mol of atoms of the reaction product. The concentration of phase 1, x' , is calculated from m , x'' , and x''' . The three temperatures may be different, but in BINGSS either T_1 and T_2 or T_2 and T_3 are assumed to be equal, since in real experiments, usually not more than two different temperatures are used.

Equation 13 describes three types of measurement, which in experimental thermodynamics are usually treated as being different. This is explained in Fig. 3. If the two samples to be mixed are the two pure elements, the result is an integral enthalpy of mixing (Fig. 3a). If only one sample is a pure element ($x''' = 0$ or $x'' = 1$) and its amount, m , is small, the result can be expressed as the partial enthalpy of this pure element (Fig. 3b). The differential quotient defining the partial enthalpy, dH/dn , is in this case approximated as the quotient of differences, $\Delta H/\Delta n$, which is the measured value divided by the amount m . Finally, it is possible to mix two liquid solutions of different composition in the calorimeter. If the two concentrations are not very different, the result mainly reflects the curvature of the enthalpy vs concentration curve (Fig. 3c). This type of measurement is very seldom described in the literature as it cannot be connected directly with a commonly used thermodynamic function such as the integral or partial enthalpy. In the least squares optimization, however, it is very valuable, since the curvature of the $H(x)$ plot may show features that are hidden by the scatter of the measurements in integral or partial enthalpy plots. Entering these measurements directly into the calculation using Eq 13 forces the analytical expression to reproduce well the curvature of the $H(x)$ curve.

In the literature, measurements are often reported whereby successively small amounts of one element are added to a calorimetric bath consisting of the second pure element. The measured values are transformed to integral enthalpies by adding all the previous results. In Fig. 3b, this corresponds to the addition of the enthalpy of sample 2, $H(x'')$, multiplied by its amount, $(1 - m)$. This is a good procedure for the transformation of the results into a standardized thermodynamic function, but it must not be done for use in the least squares optimization. Each step must be treated as a separate measurement using Eq 13, otherwise the first measurement would have a much higher weighting than the last. The requirement that the least squares method have normal Gaussian distribution of the errors would in this case be violated. If the reported integral enthalpies allow recalculation of the measured quantities by subtracting the results of the previous steps, this must be done.

Another type of calorimetric measurement is that obtained from drop calorimetry. In this method, a single sample is dropped from a furnace or thermostat maintained at temperature T_1 into a calorimeter held at temperature T_2 . The measured heat is the enthalpy difference $H'(T_1) - H''(T_2)$, and the equation of error is therefore:

$$[\text{meas. value} - H'_{\text{calc}}(T_1) + H''_{\text{calc}}(T_2)] \times p = \text{error} \quad (\text{Eq 14})$$

At each of the two temperatures, the sample may be either single phase or a mixture of two phases in equilibrium. In the latter case, the value $H_{\text{calc}}(T)$ includes an equilibrium calculation.

Results of scanning calorimetry measurements are treated using the same Eq 14, but here the two temperatures T_1 and T_2 lie close together and the accuracy of the difference $\Delta T = T_1 - T_2$ is much better than that of T_1 or T_2 itself. In this case, the measurements give "true heat capacities," because $\Delta H/\Delta T$ approximates very well $dH/dT = C_p$. Drop calorimetry measurements also provide heat capacities if there are enough values to allow differentiation of the plotted $H(T)$ curve. However in drop calorimetry large changes of C_p in small temperature intervals are smoothed and therefore not well represented.

3.3 Gibbs Energy Data

Partial Gibbs energies or chemical potentials are measured using methods such as emf, vapor pressure, or solubility in a dilute solution with a third element as solvent. The results of measurements reported as Gibbs energies of formation of stoichiometric compounds are also really partial Gibbs energies of one element in a two-phase equilibrium between this phase and the nearly pure second element. Data reported as activities, a , are transformed to partial Gibbs energies using the relation $\Delta\mu = R \times T \times \ln a$. It has been argued that a normal Gaussian distribution of errors of the activity does not transform into a normal Gaussian distribution of errors of the partial Gibbs energy, μ . Although this is true, it is often difficult to judge which of the two quantities has an error distribution closer to a normal Gaussian distribution. In any case, the linearization step, Eq 3, results in the distinction between a and μ being lost.

4. Calculation Strategy

4.1 Data Entry Technique

The first stage in the optimization of a system is a literature research. All experimental data giving quantitative information on a thermodynamic function or on a boundary in a phase diagram are of interest. Qualitative information such as the statement "by micrography the sample was found to be single phase" cannot be used, whereas the information "at temperature T sample 1 is single phase α and sample 2 contains two phases α and β " can be interpreted as the $\alpha/\alpha+\beta$ boundary is at $x \pm \Delta x$, where x is the mean between the concentrations of the two samples and $2 \times \Delta x$ is the difference between these two concentrations.

Before the calculation can be started, it must be decided whether the system is to be denoted $A-B$ or $B-A$. Then all phases are numbered sequentially, and these numbers are used as codes for the phases. The input and output files of the programs are summarized in Fig. 4. Three input files are used in BINGSS. They have the FORTRAN file codes 01, 03, and 04. In the MS-DOS version, they have the common name "sys" and the different extensions .coe, .dat, and .bgl, respectively. The common name "sys" is usually composed of the chemical symbols of the two elements.

File 03 (sys.dat) contains all experimental data. An auxiliary program "BINDAT" assists in compiling the data from the various styles used in the literature to the standard formats used in the least

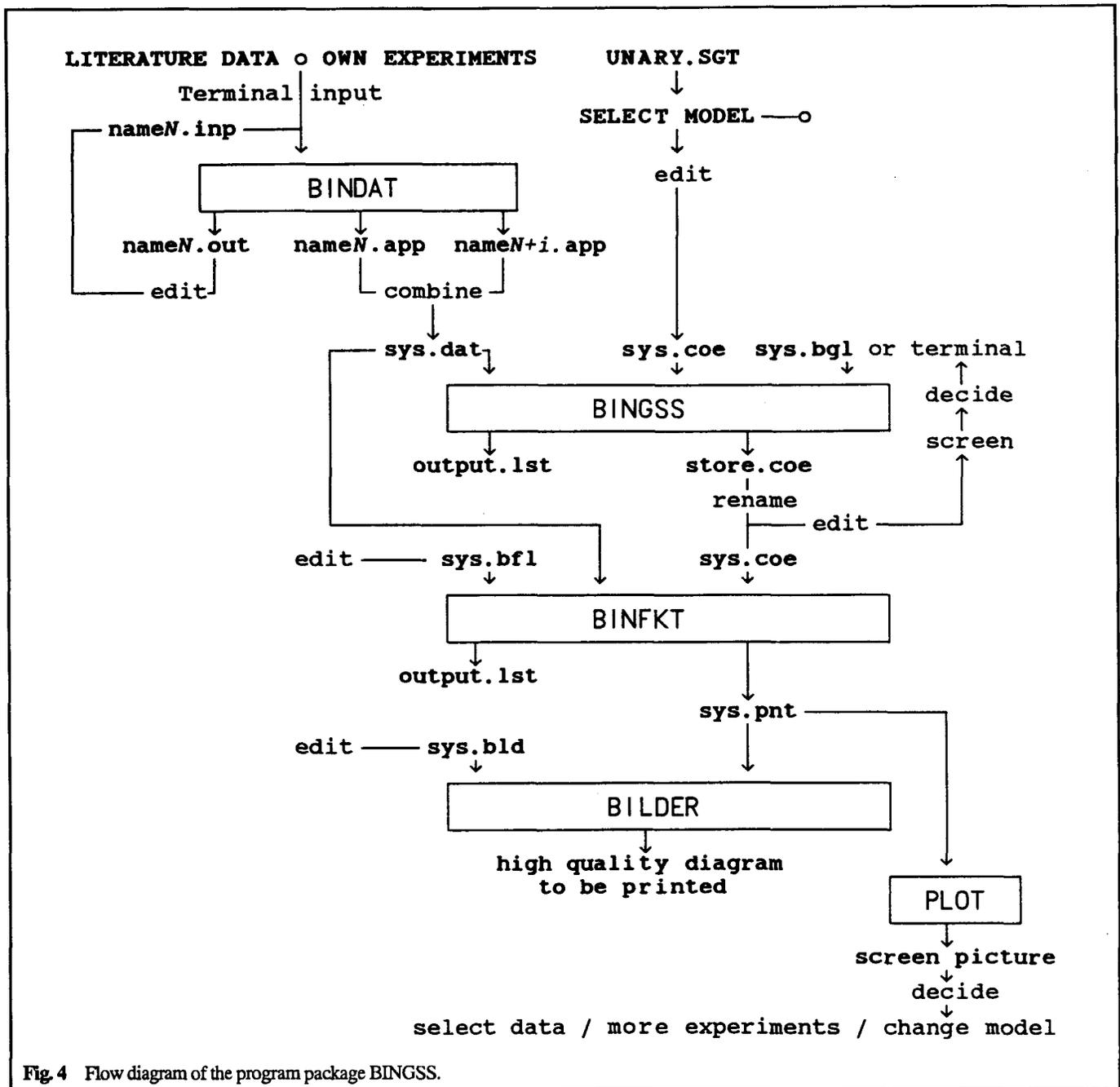


Fig. 4 Flow diagram of the program package BINGSS.

squares program. It also performs all necessary transformations such as mass fractions to mole fractions, cal to J, etc. The interactively entered data are stored in a file "nameN.out," which after correcting errors is taken as input for "BINDAT" without the necessity of typing all the data once more. The output file "namei.app" contains the data formatted for "BINGSS." Several of these files can be added to one file "sys.dat."

File 01 (sys.coe) is prepared by a text editor. For metallic systems, where the components are the elements, the unary data are copied from a file containing the already formatted data of [91Din]. The "excess term part" then is prepared choosing the model and the adjustable coefficients as described in the next sections.

File 04 (sys.bgl) may be replaced by terminal input. It decides how many iteration loops are calculated until the next input, what is the value of the switch variable "IVERS" discussed in section 3.1, and if the present result is put out. Also tables of either the "error" of each measurement or of the input, formatted to a better readable form, may be selected. A short output is given on the screen to enable selection of the next input from the terminal.

Besides printing on the screen, the BINGSS program has two output files. File 07 (store.coe) contains the adjusted coefficients; the rest of this file is identical to sys.coe. If the output is satisfying, this file is renamed to sys.coe, overwriting the old file sys.coe. Otherwise it may be edited, redefining the models and/or which coeffi-

Table 1 Matrix of Adjustable Coefficients of the Redlich-Kister Formalism

	1	T	T × lnT	
(x _{Mg} × x _{Zn}) ×	a ₀	b ₀	c ₀	1
	a ₁	b ₁	c ₁	(x _{Mg} - x _{Zn})
	a ₂	b ₂	c ₂	(x _{Mg} - x _{Zn}) ²

coefficients shall be adjusted. File 11, output.lst, contains details of the calculation including a table of the errors of each measurement.

The optimized file sys.coe is read into program BINFKT to calculate phase diagrams and plots or tables of thermodynamic functions vs temperature or vs concentration. The main purpose is to check the result of BINGSS with the input data. An additional file, sys.bfl, prepared using a text editor, gives details as to which functions or parts of the phase diagram shall be calculated. The output files contain tables in file 11, output.lst, and sequences of x-y pairs for curves to be plotted in file 08, sys.pnt.

Program BILDER finally transforms sys.pnt into plots, taking details for the layout from file 24, sys.bld. Program PLOT at PC's quickly transforms file sys.pnt into diagrams for different screen modes using a standard layout, which may be changed interactively.

4.2 Models

The choice of model for each phase in a system has a decisive influence on the quality of the optimized description. Several analytical descriptions can be found in the literature. The simplest is that used for a stoichiometric compound, which contains only temperature-dependent and no concentration-dependent terms. Such an expression is also used for phases with a small range of solubility if the experimental data are not sufficient to quantify the solubility range. Except for a few phases that require a magnetic contribution to the Gibbs energy, *G* is expressed as:

$$G - H^{\text{SER}} = a + b \times T + c \times T \times \ln T + d \times T^2 + e/T + f \times T^3 \quad (\text{Eq 15})$$

For solution phases, the most commonly used description is the Redlich-Kister formalism [48Red]. It is based on the regular solution model, which itself can be represented using only one coefficient. In the Redlich-Kister formalism this coefficient is replaced by a polynomial expression in the mole fractions. This can be considered as a curve fitting technique, which describes all the deviations from the regular solution model without modelling their physical basis. Because the regular solution is often a good first approximation for metallic systems, the Redlich-Kister formalism is particularly useful and leads to the following expression for the Gibbs energy:

$$G - H^{\text{SER}} = \left({}^0G_A - {}^0H_A^{\text{SER}} \right) \times x_A + \left({}^0G_B - {}^0H_B^{\text{SER}} \right) \times x_B + R \times T \left(x_A \times \ln x_A + x_B \times \ln x_B \right) + x_A \times x_B \times \sum_{v=0}^n K_v \left(x_A - x_B \right)^v \quad (\text{Eq 16})$$

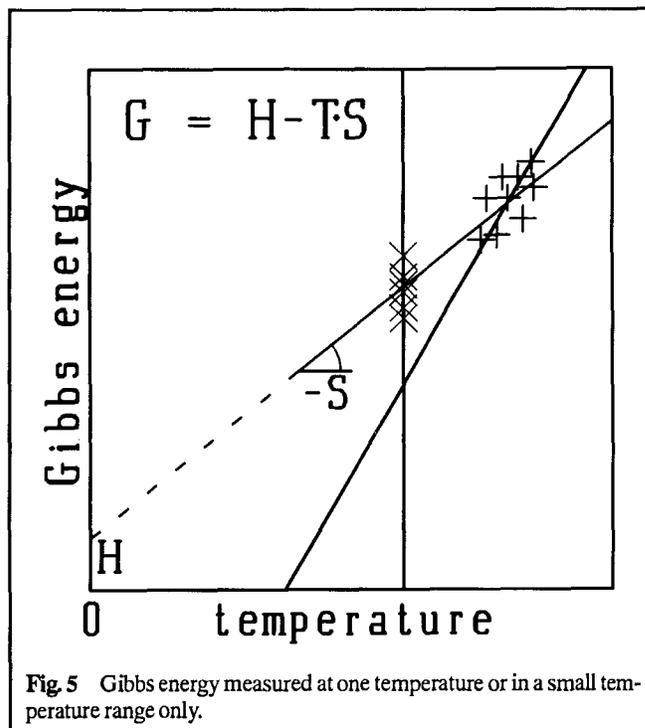


Fig. 5 Gibbs energy measured at one temperature or in a small temperature range only.

where the *K_v* are functions of temperature analogous to Eq 15:

$$K_v = a_v + b_v \times T + c_v \times T \times \ln T + \dots \quad (\text{Eq 17})$$

a_v, *b_v*, and *c_v* are the adjustable coefficients that form the matrix [77Luk] as it is shown in Table 1.

Other models implemented in BINGSS are the associated solution model [82Som] and several special cases of the Wagner-Schottky [30Wag, 52Wag] model, generalized as the "sublattice model" [76Hil]. The Gibbs energy descriptions derived from these models cannot be approximated well by a polynomial with only a few coefficients. They should therefore be used when adequate information is available. Since other models were not used in the optimization of the Mg-Zn system, they will not be discussed in more detail here.

4.3 Selection of the Adjustable Parameters

When the appropriate model for each phase has been chosen, the next important step is to select the coefficients to be adjusted. The main criterion for this selection is that only those coefficients that are determined by the experimental values should be adjusted. If insufficient experimental data are available, estimates must be used to obtain a complete description. For example, the *c_v* coefficients implicit in Eq 16 describe the excess heat capacity and should only be used if experimental heat capacity data obtained, e.g. by scanning or drop calorimetry or by measuring enthalpies of mixing at different temperatures, are available. If the *c_v* terms are not used, the Kopp-Neumann rule is implied. This is frequently the most appropriate estimate.

If the only available measurements for a particular phase are Gibbs energies measured in a narrow range of temperature, only one coefficient in each line of the matrix presented in Table 1 can

Table 2 Summary of Mg-Zn Experimental Data

Number	Phase	Phase equilibrium	μ	H	$H(T) - H(298)$
1.....	Liquid	Two phases -2,-6,-7,-8,-3 Three phases -2-4,-4-5, -5-6,-6-7, -7-8,-8-3	${}^1\mu_{\text{Mg}}(T), {}^1\mu_{\text{Zn}}(T)$ ${}^1\mu_{\text{Mg}}(x), {}^1\mu_{\text{Zn}}(x)$	${}^M H(x)$	${}^M H(T)$
2.....	Mg	-1,-4,-5			
3.....	Zn	-1,-8			
4.....	Mg ₇ Zn ₃	-2-5,-1-2,1-5	${}^{4-5}\mu_{\text{Mg}}(T_0)$		
5.....	MgZn	-1-6	${}^{5-6}\mu_{\text{Mg}}(T_0)$	$({}^F H)$	
6.....	Mg ₂ Zn ₃	-1-7	${}^{6-7}\mu_{\text{Mg}}(T_0)$		
7.....	MgZn ₂	Maximum -1 -1-6,-1-8	${}^{7-8}\mu_{\text{Mg}}(T_0)$	${}^F H$	
8.....	Mg ₂ Zn ₁₁	-1-7,-1-3	${}^{8-3}\mu_{\text{Mg}}(T_0)$	$({}^F H)$	

Note: As reported in the literature. The hyphen between numbers indicates that the phases represented by them are in equilibrium.

be independently adjusted. Figure 5 illustrates the possible consequences of using two coefficients, a and b . Expressing the Gibbs energy as $G = a + b \times T$, which is equivalent to $G = H - T \times S$, requires that straight line to be found which shows the best fit to the experimental points in a G vs T plot. Due to the scatter in the measurements, for the points (x) measured at a single temperature, this is a vertical line. Even if G has been measured in a narrow range of temperature (points +), values of H and S that are too large may result, although close to the temperature of the measurements, G will have reliable values.

A good method of estimation for this situation, first formulated by Kubaschewski [79Kub] and recently refined by Tanaka *et al.* [90Tan], makes use of a fixed ratio between excess entropy and enthalpy.

It is often much less clear than in the two examples given whether two or more coefficients are independently related to experimental values. A comparison of two calculations, with and without one of the coefficients may help, but a thermodynamic discussion of this problem is preferable. A better fit to the scatter of the experimental data may give the impression that a coefficient is well defined. In Fig. 5, for example, the line fitting the points "+" gives the impression that H and S are both well defined.

After a first run of BINGSS, the results are usually not satisfactory. The output of the programs BINFKT and BILDER may help to provide reasons. Most often, there are contradictions between different series of measurements, while bad selection of models or of the adjustable coefficients is also an important factor.

A contradiction between different measurements is easy to detect if the measured quantities are identical. Significantly different values for the same quantity imply that at least one experimental study suffers from systematic errors. Because the least squares method is unreliable in such cases, one of the contradicting series must be omitted from the calculation. A critical survey of the original studies must once more be carried out in order to decide, if possible, which series of measurements is more reliable. Virtual contradictions may occur due to typing errors during the preparation of file 03 (sys.dat). Data plots using "BILDER" help to detect such errors.

Contradictions between different types of data may be either intrinsically thermodynamic in origin or caused by incorrect selection of models and adjustable parameters. The outputs of BINFKT and BILDER may help in a thermodynamic discussion of this problem. General rules on how to proceed are rare, but examples are given below for the Mg-Zn system. If two different sets of data violate a law of thermodynamics, such as the relation between integral and partial quantities, the relation $d(G/T)/d(1/T) = H$, or the Gibbs-Konovalov rule [81Goo], the contradiction is intrinsically thermodynamic in nature. Other rules such as Raoult's law of freezing point depression, are model dependent. In such a case, a change of the model should be considered. For example, the freezing point depression changes with the number of atoms per associate in the associated solution model.

Sometimes the scatter of one series of experiments with many points overrides another series with only a few points. Here the weighting factor (p in Eq 1) may be changed for the two series. Each series of measured values in file 03 (sys.dat) is distinguished from the others by a label, a string with two characters. The weighting of all values with the same label can be changed without changing file 03 (sys.dat). This change of weighting uses a dimensionless number input either in file 04 (sys.bgl) or at the terminal. The number gives the ratio to the weighting, which is calculated as given by [77Luk].

A value of $p = 0$ for the weighting omits the corresponding series of measured data from the calculation, without removing it from file 03 (sys.dat). In the output of BINFKT and BILDER it can still be treated and compared with the calculations.

5. Application to the Mg-Zn Binary System

The recently optimized Mg-Zn binary system [92Aga] has been selected to illustrate the above-described calculation procedure because it presents very clearly some of the problems that occur in phase diagram optimization.

The data found in the literature for this system are summarized in Table 2. Data from all three of the main experiment categories dis-

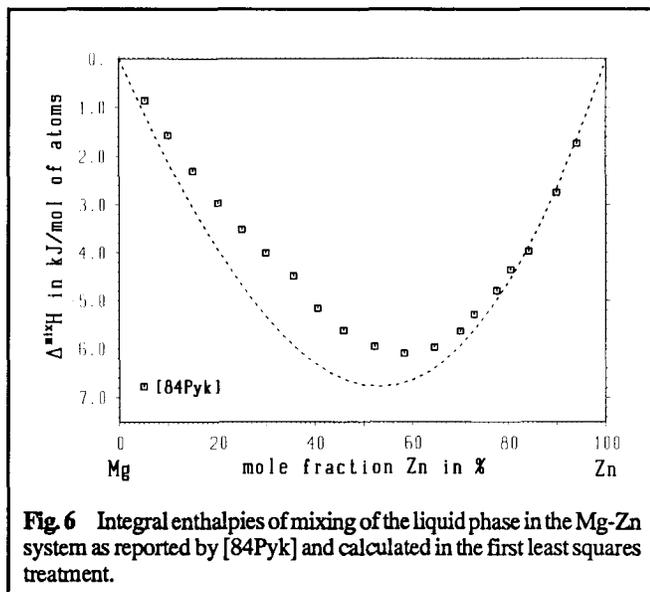


Fig. 6 Integral enthalpies of mixing of the liquid phase in the Mg-Zn system as reported by [84Pyk] and calculated in the first least squares treatment.

cussed in section 3 are available. The phases are referenced by numbers according to the sequence in file 01 (sys.coe).

There are five intermetallic compounds, each of which has a reported solubility range of ~1 mole%, but no quantitative results are available either for the width or for the nature of the departure from stoichiometry. They have therefore been treated as stoichiometric phases using Eq 15 to describe their temperature dependence.

As Mg-Zn is a metallic system, the Redlich-Kister formalism was used to model the concentration and temperature dependence of the excess term of the liquid phase. The solid solutions of Mg and Zn were also modelled using this formalism. As the latter two phases are both hexagonal close packed, they are treated as the same phase with a miscibility gap and are represented by a single description.

The next step is the selection of the adjustable coefficients for each phase. For the intermetallic compounds, no heat capacity measurements are reported in the literature. This automatically implies that c and higher coefficients in Eq 15 cannot be adjusted. Except for the phase $MgZn_2$, it is also impossible to adjust the coefficients a and b independently because the enthalpies of formation are not well known and the Gibbs energy of each phase is known only at the temperature of the three-phase equilibrium of its formation. For $MgZn$, Mg_2Zn_3 , and Mg_2Zn_{11} , the relationship $\Delta^F S \approx \Delta H^F / T_0$ with $T_0 = 3000$ K [79Kub] was used. Although this relationship was established with respect to liquid solutions only, we are not aware of a better estimation method for solid phases. It was therefore used to derive data for the solid phases in the present work.

For the liquid phase, a decision must be made as to which of the coefficients of Table 1 should be selected. ΔH values are available as a function of concentration as illustrated in Fig. 6, and these clearly show an asymmetry. The enthalpy of mixing was measured at three different temperatures, but no temperature dependence of ΔH was reported. As given in Table 2, μ values of liquid

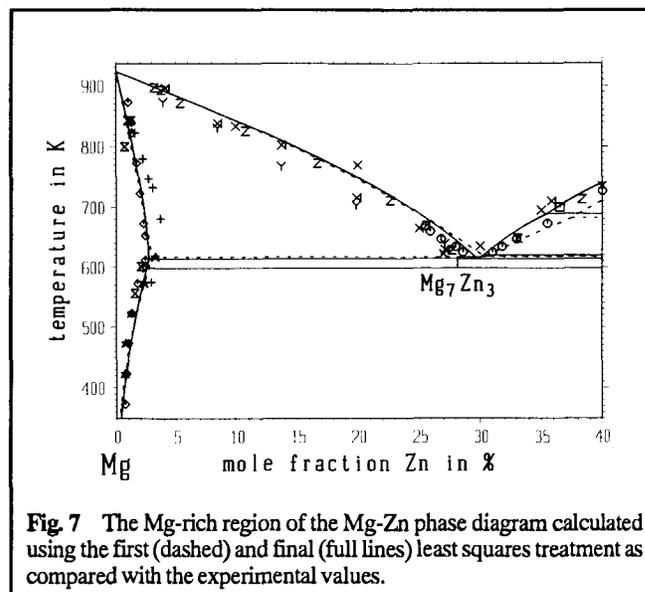


Fig. 7 The Mg-rich region of the Mg-Zn phase diagram calculated using the first (dashed) and final (full lines) least squares treatment as compared with the experimental values.

alloys are also known as a function of temperature and concentration. The analytical expression used for the liquid phase must be able to describe all these properties. Because ΔH and μ have both been measured, a and b coefficients are independently adjustable, and the asymmetric nature of the ΔH curve requires that at least two a coefficients, a_0 and a_1 , be used. No justification for use of a c coefficient seemed to be available.

A plot of the experimental data showed discrepancies between different measurements of the solidus and solvus of the Mg solid solution (see Fig. 7). In the calculation, the data denoted by "+" were not used.

The file mgzn.coe is now defined, and together with the file mgzn.dat the program BINGSS can start the optimization. In order to obtain rapid convergence, the linear equations of error are selected (Eq 11 and 12, IVERS=3) as discussed in section 3.1. After convergence, the more precise equations of error (Eq 6 and 7) can be used (IVERS=2).

With the selected models, the optimization was not yet satisfactory. The Mg-rich eutectic temperature was too high (Fig. 7), and the $H^{liq}(x)$ curve showed systematic deviation from the measured values (Fig. 6). It must now be decided whether there are contradictions between different data sets or an insufficient number of coefficients used to describe the phases well. The answer is given by the Gibbs-Konovlov rule [81Goo], which correlates the liquidus slope with the enthalpy. In order to obtain a steeper liquidus, it was necessary to have a more negative enthalpy of mixing for the liquid at the eutectic temperature. This is compatible with the measured $\Delta H^{liq}(x)$ of [84Pyk] if the enthalpy of mixing is temperature dependent. A c coefficient must therefore be introduced into the matrix of Table 1 for the liquid phase. To support this assumption, new experiments were required. Partial enthalpies of fusion were measured, and these provided evidence for the suggested temperature dependence. The result of the optimization is shown in Fig. 7.

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