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THE CORRECT CALCULATION OF SOME THERMODYNAMIC PARAMETERS OF NON-IDEAL SOLUTIONS FROM THEIR PHASE EQUILIBRIUM DATA

Abstract

A computational method has been proposed for calculating the correct interaction parameters from experimental phase diagrams, despite reports that this problem was believed to be a "thermodynamically incorrect" one. It has been shown that the presumed difficulties are not of fundamental importance. An original computer program has been applied to two well-known systems Bi-Sb (1) and Bi_2Te_3-Sb_2Te_3 (2), and a good agreement between calculated and observed values has been achieved. The values of interaction parameters Ω^s=7.1±0.4, Ω^l=1.56±0.09 kJ/mole for (1) and Ω^s =5.9±2.5, Ω^l =3.9±2.5 kJ/mole for (2) have been found. The results have been analysed and their statistical reliability has been established. In addition, the possibilities of calculating the liquidus curve from only the solidus experimental data the solidus from the liquidus experimental data have been demonstrated. It has been found that the prediction of liquidus from solidus is much more successful than predicting the solidus from the liquidus.

The results allow one to determine with reliance that the backward problem of modeling regular solutions for finding thermodynamic interaction parameters can be solved correctly. The calculated parameters can be used for both the computational restoration of missing pieces of the experimental phase equilibrium diagrams of binary and multinary systems and for the recognition of the physical nature of regular solutions.

1. INTRODUCTION.

One of the most effective techniques for investigating the numerous solid and liquid non-ideal solution systems is the calculation of their equilibrium compositions and the building of their phase diagrams by means of the *regular solutions* equations [1-6]. Models of regular solutions have been successfully applied to phase equilibrium calculations of binary systems having a continuous series of solid and liquid solutions. However, the equations describing the theory of regular solutions include the so-called thermodynamic interaction parameters that are often unknown, and direct ways calculating these values are labor intensive and are often not precise enough. Once experimental phase diagrams contain all of the necessary information for the derivation of exchange energies, the calculation of the exchange energy parameters from those diagrams by means of the numerical fitting of calculated and experimental liquidus and solidus curves can be achieved.

There have been earlier attempts to solve such a backward problem by other authors, to our knowledge, satisfactory solutions were not obtained. Moreover, the results strongly depend on chosen models, and no method has been proposed to suggest the preference of one model over another without considering real physical systems. As a result, this problem, and its solutions, have been proposed as "thermodynamically incorrect".

In contrast to the mathematically incorrect problems by Hadamard, the concept of "thermodynamically incorrect problems" has not been strictly formalized. It relies on the assumption that a chosen model's adequacy cannot be revealed from the solution itself without additional structural information. We have considered [7] that such an impossibility should not be postulated. In most cases the proof of the distribution of normal discrepancies, together with application of the "Occam's razor" for the rejection of exceedingly complicated models, may be sufficient to prove that a chosen model is adequate, and should offset the corresponding "incorrectness" problem. We suggest that some failures in the solution of the above problem were actually related to minimization and other calculational techniques and, sometimes, to bad experimental data. So we have decided to apply the following approach.

2. BASIC EQUATIONS.

The regular solutions theory is based on the assumption of zero excessive entropy. In the approximation considering only paired interactions between nearest atoms, the molar Gibbs energy of binary regular solutions can be described by following equations [2,4]:

$$G = x_1 G^0_1 + x_2 G^0_2 + RT\,(x_1 \ln x_1 + x_2 \ln x_2) + \Omega\, x_1 x_2\,, \qquad (1)$$

where G^0_1 and G^0_2 are Gibbs energies of pure components **1** and **2**, x_1 and x_2 are concentrations (mole fractions) of components **1** and **2**, and Ω is the interaction parameter. Unfortunately interaction parameters for most real systems are unknown. Consequently, the theory of regular solutions cannot be effectively used for non-ideal phase equilibrium simulations. The correlation between the exchange energy and various physical-chemical properties allows one to model Ω from experimental data resulting from enthalpies of mixing, vapour pressures, solubilities, composition and temperature of azeotropic and eutectic points, critical temperatures of stratification, and excessive volumes to name a few. However, most of these cited methods for evaluating Ω are laborious and indirect.

From eq. (1), liquidus and solidus curves of a binary system **1-2** can be described by following equations [4]:

$$\ln\frac{x_i^s}{x_i^l} = \frac{\Delta H_{m,i}}{RT} - \frac{\Delta S_{m,i}}{R} - \frac{\Omega^s\left(1-x_i^s\right)^2}{RT} + \frac{\Omega^l\left(1-x_i^l\right)^2}{RT}, \qquad (2)$$

where i (**1** or **2**) designates one of the components under consideration; $\Delta H_{m,i}$ and $\Delta S_{m,i}$ are melting enthalpy and entropy of the i-th component; x^s_i and x^l_i are the concentrations of the i-th component, corresponding to the solidus and liquidus curves respectively; Ω^s and Ω^l are thermodynamic interaction parameters for solid and liquid phases respectively. The following equations (3) derived from (2) appear to be very useful for calculating temperature values, T_{calc}, corresponding to given concentration values, which can then be compared with measured temperatures, T_{meas}, from the phase diagram:

$$f_1 = -RT\ln\frac{x_1^s}{x_1^l} + \Delta H_{m,1} - \Delta S_{m,1} + \Omega^s\left(1-x_1^s\right)^2 - \Omega^l\left(1-x_1^l\right)^2 = 0,$$
$$f_2 = -RT\ln\frac{1-x_1^s}{1-x_1^l} + \Delta H_{m,2} - \Delta S_{m,2} + \Omega^s\left(x_1^s\right)^2 - \Omega^l\left(x_1^l\right)^2 = 0. \qquad (3)$$

3. THE RELATIONSHIP TO INCORRECT PROBLEMS.

Often, the retrocalculation of parameters where some measured data are used to propose a set of physical parameters appears to be incorrect. An example of such an incorrect problem would be an attempt to solve the equation $\mathbf{T}_{calc}(\Omega, \mathbf{x})=\mathbf{T}_{meas}$ with respect to Ω directly. However, many such problems are reduced to a task of the minimization of the discrepancies $(T_{i,calc}-T_{i,meas})$; these are then governed by the properties of "correct problems" as proposed by Hadamard, *i.e.* requirements of solvability, unambiguity, and stability of the solution [8, 9]. The problem's **solvability** is assured by existence of the minimum and of the algorithm of its finding. As soon as the minimum is found the question is no longer relevant.

Assuming a minimum exists and is found, the Hessian matrix at that point should be defined as positive, which can be checked. This is enough for **stability** of the solution. Otherwise, if the number of parameters is not very large, say not more than 10 (in our case this number is only two) this condition can be usually and easily achieved by the appropriate selection of a sufficient number of experimental data points.

The **unambiguity** requirement in such problems is violated only in the case where several minima exist. This can often be avoided by the appropriate restriction of the search within parameter space; the choice of an appropriate mathematical model is of great importance in this respect. Consequently, excessively complicated models should be avoided (*i. e.* Occam's razor is applied). The unambiguity requirement for correct solutions is the most critical requirement. As it was shown by Tikhonov, unambiguity of solution itself, in many cases, assures the satisfaction of the stability condition [10, 11]. However, this requirement, being especially rigorous for mathematical problems, can often be softened for real physical problems and may be substituted by a requirement of physical meaning and, thus, adequacy of the solution. Therefore, the problem we are examining can be solved by appropriate fitting methods, in contrast to truly incorrect backward problems. For example, problems with a great number of parameters (hundreds or thousands) or distributed parameters are, in principle, impossible to solve by the usual minimization methods without incremental solutions such as Tikhonov's stabilizers.

A technical problem for realizing minimization by these methods arises. We observed that the choice of the minimization method affects not only the ability to achieve a solution, but also the possibility of evaluating the precision of the derived parameters and, therefore, a practical confirmation of the stability of the obtained solution. The solution is especially sensitive to the method chosen, particularly in the case of a poorly defined Hessian matrix. In our opinion, the failures of previous attempts had arisen mainly from the minimization methods selected. Usually, methods that rely on the direct search of a minimum were chosen. These methods do not rely on information based upon the functional form of the minimization, and as a result, lose their efficacy, especially in the presence of ravines and plateaus, leading to a poorly defined Hessian matrix. This could be interpreted as a singularity of the Hessian matrix and, therefore, leads to the "incorrectness" of the problem. In other cases the, linear Least Squares (LS) method was chosen. However, this method cannot be very useful in our selected model equations because of the nonlinearity of the discrepancies.

Another source of errors was discovered in reference [12], where an attempt was undertaken to calculate the thermodynamic functions of the Bi-Sb system. Two versions of

the Ω^S parameter calculation in the frame of the regular solutions resulted in two different values, and as it was acknowledged by the authors, a satisfactory description of the *(T, x)*-diagram could not be obtained. In our opinion, the main reason of the failure was that in the fitting procedure, the authors used a phenomenological model instead of the actual experimental values approximating regression equations *T(x)*, a model which did not exactly approximate the simulated system. In an attempt to plot the phase diagram using these regression equations, we discovered that the experimental points [4] not only lie far from the obtained curves but that the distribution of these deviations is very far from a normal one.

4. RESULTS.

In our approach we have chosen Powell's method of minimization of non-linear functions, intended specifically for the fitting of the least squares criterion under conditions of strong nonlinearity [13]. On the basis of this method we developed an original computer program PLESQ (Powell LEast SQuares), which allowed us to not only find optimal values of the desired parameters, but to analyze the reliability and precision of the obtained results and to establish the adequacy of the chosen model as well.

To analyze the validity of our approach, we selected the two well-known systems, Bi–Sb and Bi_2Te_3–Sb_2Te_3, which form continuous solid solutions [4, 5]. Thermodynamic parameters that we used in our calculations [4, 14] are given in Table 1.

Table 1. Experimental values of the melting parameters of the initial components.

Compound	ΔH_m, *kJ/mole*	T_m, *K*
Bi	10.87	544
Sb	19.80	903
Bi_2Te_3	120.50	859
Sb_2Te_3	98.95	891

Experimental data were taken from [4]. The calculated values of the interaction parameters together with their confidence intervals are shown in Table 2.

Table 2. Calculated values of the interaction parameters.

System	Ω^S, *kJ/mole*	Ω^l, *kJ/mole*
Bi-Sb	7.1±0.4	1.56±0.09
Bi_2Te_3-Sb_2Te_3	5.9±2.5	3.9±2.5

Standard deviations, *s*, and confidence values (95% reliability) were automatically found at the end of the search procedure from the diagonal elements of the co-variation matrix. It should be noted that the facts of existence and boundedness of the co-variation matrix demonstrated that the Hadamard requirement of stability for this problem was satisfied. The values obtained for the interaction parameters are positive and agree with the thermodynamic theory of solutions [2] and the values of corresponding parameters of related systems [15].

Good agreements of the calculated curves with the experimental data points on the melting phase diagrams of the Bi–Sb and Bi_2Te_3–Sb_2Te_3 systems were obtained and are shown in Figs. 1 and 2. The validity of these results are confirmed by the statistical data

given in Table 3. The average values of the discrepancies between the calculated and the measured temperature data for both systems are $6K$ and $1K$ respectively, which we consider to be an acceptable result. The control of discrepancies (ξ_i) matching the normal distribution law was used as a criterium of adequacy of the model.

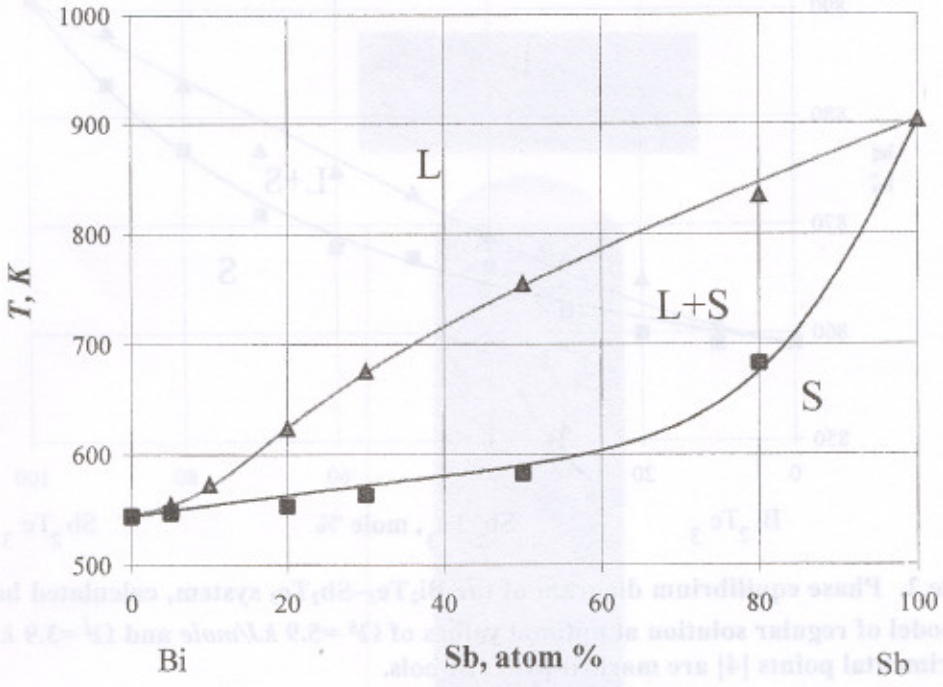

Figure 1. Phase equilibrium diagram of the Bi-Sb system, calculated based on the model of regular solutions at optimal values of Ω^S =7.1 *kJ/mole* and Ω^l =1.56 *kJ/mole*. Experimental points [4] are marked with symbols.

Several methods of checking this hypothesis are known. One of the most appropriate, in the case limited sample size n, is the evaluation of the normalized mean absolute deviation $d=(n\cdot s)^{-1}\Sigma|\xi_i|$. For the general population of normally distributed random values, this quantity is equal to $(2/\pi)^{1/2} = 0.798$. Our calculated value of d for the Bi-Sb system has been found to be 0.77 (see Table 4), which is rather close to the theoretical value and is within the d-statistics percentage points of 10% (d=0.890) and 90% (d=0.741) at n=11 [16]. Thus the discrepancies for the Bi-Sb system can be considered as normally distributed random values with zero mean value, and the chosen model is adequate. In the case of the Bi_2Te_3–Sb_2Te_3 system, the value of d (1.3) turned out to be large compared to the theoretical value. However, this may be due to systematic experimental errors, not necessarily from an inadequate model. The error in the measured temperatures appears large and the temperature range is very small. In other words, this is a case where the measurement techniques should first be improved and the new data reported and evaluated, rather than the model or the simulation method being refined.

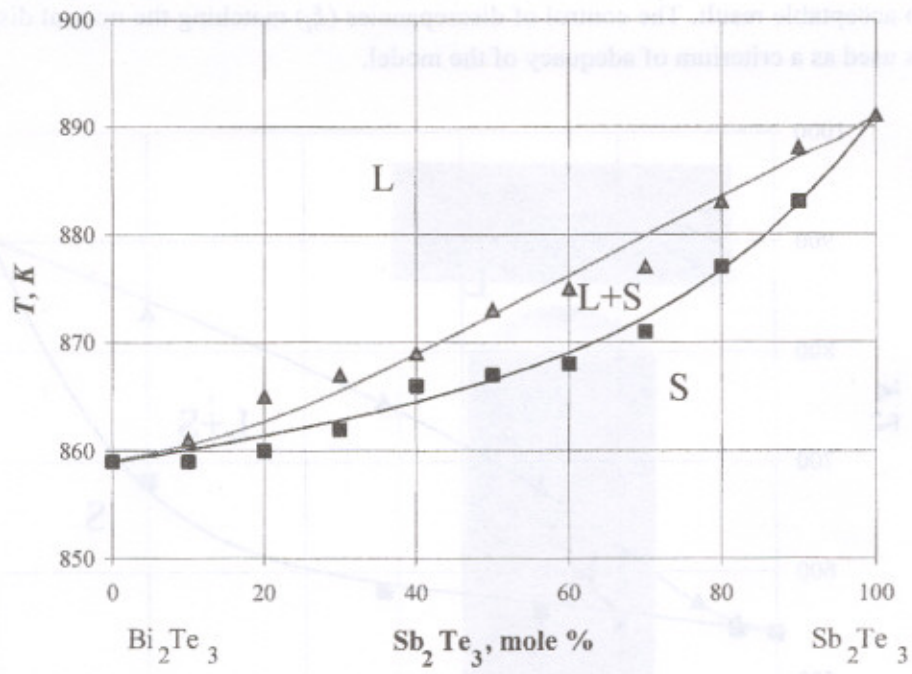

Figure 2. Phase equilibrium diagram of the Bi_2Te_3–Sb_2Te_3 system, calculated based on the model of regular solution at optimal values of Ω^S =5.9 *kJ/mole* and Ω^L =3.9 *kJ/mole*. Experimental points [4] are marked with symbols.

Table 3. Statistical properties of discrepancies (T_{calc}-T_{meas}) in degrees K, where appropriate.

Characteristics	Bi–Sb	Bi_2Te_3–Sb_2Te_3
Sample size	11	18
Sample average, *K*	-2.2	-0.1
Standard deviation of the average, *K*	1.8	0.3
Sample median, *K*	-0.3	0.26
Mean square discrepancy, *K*	6.2	1.2
Sample span, *K*	19.2	5.2
Normalized mean absolute deviation	0.77	1.3

The proposed approach can also be used to calculate the full diagram of the phase equilibrium if experimental information from only one of the two solidus or liquidus curves is available. We observed that the prediction of the solidus curve (or parameters) from the liquidus data is much more reliable than the prediction of the liquidus from the solidus data. For example, in the Bi-Sb system, we ignored the known liquidus data and obtained interaction parameters of Ω^S = 3±3 and Ω^L= –5±4 *kJ/mole*, which are far from correct. Taking into account the liquidus data and ignoring the solidus, we obtained values of Ω^S =

6.8±0.3 and Ω^l = 1.4±0.4 *kJ/mole*, which are practically identical to the results obtained from the full set of data (Table 2.) Comparing these results, we can conclude that in such systems, the liquidus data are much more informative for the calculation of interaction parameters are the solidus data. So, in spite of the fact established in reference [5], that the solidus experimental data are more reliable than the liquidus, the calculation of unknown interaction parameters should rely preferably on the liquidus data. This would make the problem more stable and the results more reliable.

5. CONCLUSIONS.

It has been shown that the "backward" problem of modeling regular solutions for the determination of thermodynamic interaction parameters, which was deemed as a "thermodynamically incorrect problem", can be solved correctly. A computational approach has been developed for the evaluation of thermodynamic interaction parameters in non-ideal solid and liquid solutions by means of a numerical fitting of the experimental solidus and/or liquidus curves for corresponding binary systems by using models of regular solutions. The advantages of the method have been demonstrated on the well-known systems Bi-Sb and Bi_2Te_3-Sb_2Te_3. An acceptable agreement has been obtained and numerical values of interaction parameters for liquid and solid phases have been found. It has been proven that the hypothesis of normal distribution is acceptable for the observed discrepancies and therefore, the model is adequate.

In addition, a numerical experiment has been performed for the modeling of the liquidus curve from only the solidus experimental data and *vice versa* for the sample system of Bi-Sb. It has been shown, that the prediction of liquidus data from the solidus is much more successful than in the opposite case.

By using concrete systems as examples, the possibility of thermodynamic calculations of phase diagrams without the need of data on thermodynamic phase properties has been demonstrated and the "correctness" of this method has been established. The proposed method of the calculation of interaction parameters in non-ideal solid and liquid solutions is especially useful when calculating the phase diagrams of multinary system is impossible due to the of lack of some thermodynamic properties.

LIST OF SYMBOLS

G	Gibbs energy	d	Normalised mean deviation
H	Enthalpy	n	Sample size
R	Universal gas constant	s	Standard deviation
S	Entropy	x	Mole fractions of components
T	Temperature (Kelvin)		

GREEK LETTERS

Ω	Thermodynamic parameter of interaction	ξ	Discrepancy value

SUBSCRIPTS		*SUPERSCRIPTS*	
i,1,2	designations of components	s	solid phase
i	counter of experimental point or discrepancy	l	liquid phase
m	melting	0	standard conditions

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