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Thermodynamic activities of alloys

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Abstract

The concept of activity is discussed briefly. Emphasis is placed on the principles of activity measurement and recent experimental developments as well as on temperature and concentration dependences, thermodynamic modeling, and modern thermodynamic evaluation. The activities as well as mixing properties of all types of alloys, even including metallic melts showing short-range ordering, can be represented algebraically by means of a simple concept. Using just one common set of parameters allows a straightforward description of combined temperature and concentration dependences. An extended temperature dependence of the excess Gibbs energy, as necessary for this purpose, has been derived. The presented concept makes possible putting together all activity measurements of a multicomponent alloy system for performing one algebraic overall best-fit. In connection with a personal computer this forms a very convenient, interactive evaluation tool yielding a considerable reduction of both, the experimental work and the time spent on evaluation. © 1998 Elsevier Science B.V.

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1. Introduction

Metallurgical thermodynamics is concerned with the equilibrium states of existence available to alloys, and with the effects of external influences on the equilibrium state. The most common molar thermodynamic functions of alloy systems are the Gibbs energy G, the enthalpy H and the entropy S which are connected by the well-known relation

$$G(x,T) = H(x,T) - TS(x,T) \tag{1}$$

where x is the mole fraction, and T the temperature in K. The molar functions Z (Z=G, H, S) of alloy systems are characterized by means of the contributions made by the alloy constituents k which are called partial molar functions Z_k (K being the number of components):

$$Z(x,T) = \sum_{k=1}^{K} x_k Z_k(x_k,T). \tag{2}$$

Thermodynamics has been developed without knowledge of the atomistic structure of matter. It is a macroscopic theory, and even in Boltzmann statistical mechanics ‘‘particles’’ are classical particles, that means geometrical figures only, despite the fact that they are now named ‘‘molecules’’. The physical properties are only linked to them by ‘‘imagination’’. Think of the laminar flow of fluids: the classical particles are producing parallel flow lines, whereas the real molecules are following the Brownian movement. It is not surprising, therefore, that no theory has been developed to explain all the observed thermo-

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dynamic mixing behavior of alloy systems. We are forced to determine the accurate thermodynamic data from experimental investigations, and to employ pseudo-theoretical expressions for the molar functions.

By common modeling, the difference between the molar quantities Z of alloys, and the contributions of the pure constituents, $Z^0(x,T)$, are defined as molar properties of mixing $Z^M(x,T)$,

$$Z^M(x,T) := Z(x,T) - Z^0(x,T). \tag{3}$$

If the mixing process does not involve a change in enthalpy, then the partial pressures of the alloy constituents k, $p_k^{id}(x_k,T)$, are simply the products of the vapor pressures of pure species k, $p_k^0(T)$, and of the corresponding mole fractions x_k:

$$p_k^{id}(x_k,T) = p_k^0(T)x_k. \tag{4}$$

Eq. (4) is an expression of Raoult's law and metal alloys, conforming with this behavior, are said to exhibit Raoultian ideal behavior. The quantities of mixing $Z^M(x,T)$ which do not exhibit this computable Raoultian ideal behavior are dealt with by introducing the concept of activity.

2. The concept of activity

The thermodynamic activity a_k of an alloy constituent k is defined as the ratio of its partial vapor pressure p_k to the vapor pressure of pure species k, p_k^0,

$$a_k(x_k,T) = p_k(x_k,T)/p_k^0(T) \tag{5}$$

where x_k is the mole fraction of the species k. We notice from Eq. (4) that, in case of ideal mixing behavior, the activity a_k becomes identical with the mole fraction x_k.

Practically speaking, the introduction of the concept of activity has the advantage that, if we substitute for the mole fractions x_k in the thermodynamic equations of ideal systems, the activities a_k, these equations are valid for real systems. In other words, all the deviations from the ideal behavior can be lumped into a single factor which is called the activity coefficient f_k, defined as the ratio of this activity a_k to the corresponding mole fraction x_k,

$$f_k(x_k,T) := a_k(x_k,T)/x_k = p_k(x_k,T)/(p_k^0(T)x_k), \tag{6}$$

and, in the characterization of real metal alloys, our attention is focused on it and its dependence on composition and temperature.

Although activities are thermodynamic functions of state, their magnitudes are assumed to be determined by the interactions among the constituent "particles" of the system which, in turn, determine bond energies and influence the spatial configurations assumed by the "particles". Thus, measurement of activities within a class of similar simpler systems can be expected to provide, at least, a basis for correlation of the behavior, which can then be used for extrapolation of the behavior of more complex systems.

2.1. *Gibbs energy of mixing and activity*

The activities a_k, are connected with the partial Gibbs energies of mixing G_k^M (or, chemical potential of mixing μ_k^M) by Eqs. (7a) and (7b) (R is the gas constant)

$$G_k^M(x_k,T) := \mu_k^M(x_k,T) = RT\ln a_k(x_k,T), \tag{7a}$$

$$a_k(x_k,T) = \exp\left(G_k^M(x_k,T)/RT\right). \tag{7b}$$

Combining Eq. (7a) and Eq. (2) makes it possible to determine the molar Gibbs energy of mixing $G^M(x,T)$ from activity measurement:

$$G^M(x,T) = \sum_{k=1}^{K} x_k G_k^M(x_k,T) = RT\sum_{k=1}^{K} x_k \ln a_k. \tag{8}$$

As the various phase equilibria occurring in a materials systems are determined by the variations, with composition, temperature and pressure, of the relative Gibbs energies of the various phases, such equilibria can be most precisely determined by accurate measurement of activity. Also, the activity of a component in the solution is a measure of the minimum Gibbs energy required to convert the component from its state in solution to the pure state in any proposed extraction or refining process.

In the majority of experimental methods, the activity of only one component is measured. In such cases, the activities of the other components can be obtained by means of the Gibbs–Duhem equation. For constant temperature and total pressure, this expression is

$$RT\sum_{k=1}^{K} x_k\,\mathrm{d}\ln a_k \equiv \sum_{k=1}^{K} x_k \mathrm{d}G_k^{\mathrm{M}} = 0. \tag{9}$$

2.2. Enthalpy of mixing, entropy of mixing, and activity

The relationship between the activity and the molar Gibbs energy of mixing, G^{M}, also allows to determine the enthalpy of mixing, H^{M}, and the entropy of mixing, S^{M}, from activity measurements: Differentiation of Eq. (1), in terms of the molar mixing quantities Z^{M}, with respect to the inverse temperature $1/T_1$ yields for the molar enthalpy of mixing H^{M} (or heat of mixing):

$$H^{\mathrm{M}}(x,T) = \partial(G^{\mathrm{M}}(x,T)/T)/\partial(1/T), \tag{10}$$

and, with respect to the temperature T for the molar entropy of mixing S^{M},

$$S^{\mathrm{M}}(x,T) = -\partial G^{\mathrm{M}}(x,T)/\partial T. \tag{11}$$

3. Experimental determination of activity

The activities of an alloy system can be determined by measuring the partial vapor pressures either by means of electrochemical measurements, or by determining the chemical equilibria. Concerning activity measurements by studying chemical equilibria, the review articles by Richardson and Alcock [1], as well as the articles by Grieveson, Lange and Schenck, and Schwerdtfeger and Turkdogan (all in Ref. [2]) should be consulted. Several effective experimental ways are known for investigating at temperatures lower than 1000 K, but there is a tremendous lack of convenient methods applicable at higher temperatures: The experimental difficulties increase considerably with the temperature of the condensed samples, e.g. at temperatures higher than 1500 K materials are limited to make inert, but still compact cell liners. Also applicable sensors are rare, as well as suitable materials for supporting-, handling-, and protecting-systems.

For general information on experimental techniques, the book by Kubaschewski et al. [3], the proceedings of the NATO Advanced Study Institute on Thermochemistry of Alloys [4] and the review articles by Kubaschewski [5] and Predel [6] are recommended. A brief overview on recent experimental developments has been given by Komarek [7].

3.1. Determination of activity by vapor-pressure measurement

Alloy systems show at actual temperatures "small" vapor pressures (<20 Pa) which will not obey any more the laws of hydromechanics, but must be described by the kinetic theory. The measurement of low vapor pressures requires, therefore, techniques entirely different to those employed for determining "common" vapor pressures. One of the few methods, still applicable at temperatures >1500 K, is that of molecular effusion after Knudsen, which has been dominant in the study of vapor pressures.

In this way, low vapor pressures are determined by means of the effusion of vaporized sample out of an isothermal vessel which is called the "Knudsen cell". This is a (cylindrical) crucible with a small knife-edge shaped orifice (0.5–1.5 mm diameter) in the lid. If, inside the Knudsen cell, thermodynamic equilibrium is established between the condensed sample and its vapor phase, then the pressure of the escaping molecular beam can be calculated from the equation for steady-state effusion of dilute gases,

$$p_k(x_k,T) = \mathrm{d}m_k/\mathrm{d}t\,A_0^{-1}(2k_{\mathrm{B}}T/M_k)^{1/2} \tag{12}$$

where $\mathrm{d}m_k/\mathrm{d}t$ is the mass rate of effusion, A_0 and k_{B} the orifice area and the Boltzmann's constant, respectively, and M_k is the mass of a molecule of the species k (see Ref. [8]). A block diagram of the variants, as have been proposed in literature as well as a brief review of modern Knudsen techniques, is given in Ref. [9]. In the last two decades, the PENKER technique (*Pen*dulum electronically balanced *K*nudsen-*e*ffusion *r*ecoil) [8] has been introduced as a new automatic null-method based on the recoil technique. Further advancement was less due to radically new techniques and more to automated control, data acquisition, and processing.

A particularly powerful tool is the Knudsen-cell mass spectrometry [9–11]. Following this method, the Knudsen cell is employed as the "gas source" of a high-temperature mass spectrometer, and the effusing vapor beam is directed into the ionization chamber of the mass spectrometer. The ion-current intensities J_k^{j} of the characteristic isotopes 'j' of the appropriate vapor species k are connected with the partial pressure by

$$p_k(x_k, T) = J_k^{\mathrm{j}}(x_k, T)T/(D_k^{\mathrm{j}} D_{\mathrm{I}}) \tag{13}$$

where D_k^{j} is an isotope specific constant (see Refs. [10,11]). The instrument-geometry constant sensitivity factor D_{I} in Eq. (13) depends strongly on the actual position of the Knudsen cell with respect to the ion source. This precludes the accurate determination of activity by measuring the vapor pressures in two different experiments, one with the alloy and the other with the pure component. For an overview on the various methods to overcome this difficulty, the article by Neckel [10] should be consulted. Following the variants of the "algebraic-intensity ratio" (AIR) technique [10,12], it is possible to determine the excess chemical potential of two alloy components without any additional effort. Many alloy systems have been investigated already by means of these techniques (compare [12,13]). The most recent review of mass spectrometric studies of metallurgical systems has been published by Kato [11].

3.2. *Electrochemical measurement of activity*

Performing a reaction in an electrolytic cell under reversible conditions at constant temperature, the electromotive force (emf) it produces can be related to the Gibbs energy; e.g. in case of symmetrical cells, which contain the component under investigation as the pure element in one and as an alloy in the other electrode, the measured emf is equal to the decrease in Gibbs energy for the cell reaction per unit charge:

$$\begin{aligned} G_k^{\mathrm{M}}(x_k, T) = \mu_k^{\mathrm{M}}(x_k, T) &= RT \ln a_k(x_k, T) \\ &= -n_k F\, E_k(x_k, T) \end{aligned} \tag{14}$$

where n_k is charge number, F the Faraday constant, and E_k the measured reversible cell voltage E_k of the formation cell. Thus, the activity $a_k(x_k,T)$ is given by

$$a_k(x_k, T) = \exp\left(-n_k E_k(x_k, T)F/RT\right). \tag{15}$$

Both, liquid and solid electrolytes are frequently used to determine thermodynamic properties of alloys. Of most importance for all types of emf measurements in alloys are the criteria for reversibility, because an emf cell will give correct results only if it operates reversibly, i.e. if it does not show drift or polarization effects. More and more solid electrolytes are used, and the reliability of such emf cells has increased considerably [7,14]. Experimental aspects and limiting factors are discussed by Schaller [14]. Various aspects of electrolytes are discussed also in a book edited by Geller [15].

The emf measurement for determining the activity also covers a wide field of application. An overview is given by Komarek [16]. Concerning hot corrosion of metals by fused salts, the article of Rapp [17] should be consulted.

4. Short-range ordering in liquid alloys

In a number of metallic melts it has been observed that the molar mixing properties show some anomalies in the concentration dependence: peculiarities in the shapes of the activity curves for dilute liquid alloys as well as a temperature dependence and/or a more or less distinct triangular shape of the molar enthalpy of mixing, H^{M}. The origin of abnormal mixing behavior, occurring in metallic melts, will be assumed commonly in short-range order effects. The concept of something like associates as complex, hypothetical molecule-like particles in metallic melts, has existed in chemical thermodynamics since the beginning of the twentieth century [18], and Wagner was the first to discuss the thermodynamics of such a behavior. Nevertheless their basic ideas have been applied to the thermodynamics of liquid alloys only in the last twenty-five years (compare Ref. [19]).

While direct evidence for these "compounds" is lacking, several authors reported successful use of such solution models which account for compound formation for representing various molar functions. Compound stoichiometry can be inferred from an examination of phase diagrams, chemically similar systems, thermodynamic and transport properties. However, the various models of short-range ordering in the liquid phase (compare Refs. [18,20,21]) yield extensive expressions for the mixing properties which cannot be transformed to formulas used commonly in mixing thermodynamics. An additional disadvantage may be that emphasis is seen on modeling the enthalpy of mixing [22].

It is also not possible to incorporate these representations into reasonable descriptions of multicomponent liquid alloys, because the results would be confusing. On the other hand, the interest on multicomponent metallic melts has increased considerably. At least with respect to a uniform description of multicomponent liquid alloys, it would be preferable to describe the mixing behavior of melts showing anomalies in the concentration dependence by means of simpler formulas than the above-mentioned ones [23].

5. Excess mixing behavior and activity coefficient

All deviations from the ideal behavior of alloy systems are lumped into the activity factor as defined in Eq. (6), and the characterization of real alloys as required in praxis is focused on it and its dependence on composition, and temperature. As the properties of mixing of ideal alloys are computable, it is common to define the deviations of the functions of mixing Z^{M} of real alloy systems from the ideal quantities Z^{id} as the molar excess functions, Z^{E}, which describe directly the contributions of the intermolecular forces:

$$Z^{\mathrm{E}}(x,T) = Z^{\mathrm{M}}(x,T) - Z^{\mathrm{id}}(x,T). \qquad (16)$$

The partial excess Gibbs energy (chemical excess potential μ_k^{E}) is connected with the activity coefficient f_k in a manner similar to the relation between the G_k^{M} and the activity a_k, Eqs. (7a) and (7b),

$$G_k^{\mathrm{E}}(x_k,T) := \mu_k^{\mathrm{E}}(x_k,T) = RT\ln f_k(x_k,T), \qquad (17)$$

The excess Gibbs energy $G^{\mathrm{E}}(x,T)$, the right form of the Gibbs–Duhem equation, and the excess entropy S^{E} are obtained by corresponding substitution in Eqs. (8),(9) and (11), respectively. As the ideal enthalpy of mixing H^{id} is zero, the enthalpy of mixing is identical with H^{E}.

The models, as suggested in literature for describing the concentration dependence of the excess mixing behavior of alloys, may be divided into pure algebraic formulas, and into equations based on a pseudo-theoretical background [24].

5.1. Pseudo-theoretical modeling

The various authors preferably introduced terms like "effective molar volumes", and/or "effective volumetric fractions" of the alloy species. However, none of these models offers any additional advantage over pure algebraic formulas either with respect to representing the molar mixing properties or for prediction purposes [24,25]. On the contrary, for an evaluation of experimental investigations on more complex alloy systems, the flexibility of these pseudo-theoretical equations is not sufficiently high [24].

The proposed variety of different expressions for the molar excess quantities often renders difficult the application and/or compilation of literature data. Altogether, it seems less meaningful, therefore, to employ any of these equations in metallurgical thermodynamics.

5.2. Algebraic formulas

Margules [26] was the first to propose a comprehensive, very efficient, yet still simple expression for the concentration dependence of the partial pressures of a binary mixture. He used a separate set of parameters for the description of the partial pressure of each component of binary alloys with the consequence of introducing a separate set of parameters for each alloy constituent. It has been shown recently [27], that the Margules concept can be unified to a common set of parameters for representing all component properties by approximating the excess Gibbs energy G^{E} instead of the partial vapor pressures.

In mathematics, the quality of polynomial approximations depends only on the powers of the variables employed, and not on any special combinations or splitting of variables. This follows simply from the validity of the associative law of addition of real numbers [25]. Thus, all polynomial series complying with the thermodynamic boundary conditions of alloys, as proposed in literature, are mathematically equivalent for representing the binary excess quantities [25]. e.g. no best fit based upon any polynomial of power n in $(2x-1)$ can yield results differing from the best fit curves obtained by means of the corresponding power series of the same power n in x.

Mathematical clarity can be enhanced and computational effort saved by using the simplest of all possible polynomials. In the late seventies and beginning of the eighties, the present author proposed the expansion after Redlich–Kister for this purpose. This yielded the broad application of this expansion, especially for phase-diagram calculations. However, some years later, it has been proved [28] that the simplest possible polynomial is the "thermodynamic adapted power" (TAP) series. In [13], it is demonstrated that the use of TAP series, instead of the Redlich–Kister expansion, yields considerably reduced computational effort in case of ternary alloys.

6. The multicomponent TAP series concept of excess quantities

6.1. Concentration dependence

6.1.1. Binary alloys

The binary excess functions ${}^{\mathrm{j,k}}Z^{\mathrm{E}}$ (j,k components) are represented by (N is the number of adjustable parameters ${}^{\mathrm{j,k}}C_n$) [28]:

$$ {}^{j,k}Z^{\mathrm{E}}(x) = x_j \sum_{n=1}^{N} {}^{j,k}C_n x_k^n. \tag{18a} $$

$$ {}^{j,k}Z_j^E(x_j) = x_k^2 \sum_{n=1}^{N} {}^{j,k}C_n x_k^{n-2}(1-n+nx_k), \tag{18b} $$

$$ {}^{j,k}Z_k^E(x_k) = x_j^2 \sum_{n=1}^{N} {}^{j,k}C_n x_k^{n-1} n. \tag{18c} $$

The customary classification of binary alloys with respect to the complexity of their excess properties may be performed with more clarity: The TAP parameter ${}^{j,k}\mathrm{C}_1$ and ${}^{j,k}C_2$ characterize the regular and subregular solution contributions as pointed out in Ref. [27]. Interchange of the components, as well as conversion among various literature proposals for polynomial represention of the ${}^{j,k}Z^{\mathrm{E}}(x)$ may be performed by means of a simple modular procedure developed in Ref. [25].

6.1.2. Ternary and multicomponent alloys

All prediction techniques as proposed in literature are based upon the assumption of ternary regular solution, where the excess quantities are geometry-dependent functions of the concentrations x_{k}, and of the excess properties of the three binary boundary systems j–k (j,k=1,2,3). Lück et al. [29] presented a survey of the most common algorithms to extrapolate the binary into ternary properties. None of these algorithms yields better prediction data for the ternary alloys than the simple sum of the binary boundary systems, ${}^{\mathrm{BBS}}Z^{\mathrm{E}}$ [23],

$$ {}^{\mathrm{BBS}}Z^{\mathrm{E}}(x) = {}^{1,2}Z^{\mathrm{E}}(x) + {}^{2,3}Z^{\mathrm{E}}(x) + {}^{3,1}Z^{\mathrm{E}}(x). \tag{19a} $$

Extrapolation for alloys containing K components are performed after [27] by:

$$ {}^{(K-1)BS}Z^E(x) = \sum[\text{all } Z^{\mathrm{E}} - \text{terms with } (K-1) \text{ components}]. \tag{19b} $$

Following [27], the ternary interaction is described by a polynomial in all mole fractions x_k,

$$ {}^{t}Z^E(x) = x_1x_2x_3[C_1 + ({}^{t}C_2x_1 + {}^{t}C_3x_2 + {}^{t}C_4x_3) + \ldots], \tag{20a} $$

where ${}^{\mathrm{t}}C_n$ are adjustable parameters (n=1,2,...). The general K-component interaction term is then:

$$ {}^{K}Z^E(x) = x_1 \ldots x_K[{}^{K}C_1 + ({}^{K}C_2x_1 + \ldots + {}^{K}C_{K+1}x_K) + \ldots], \ (K = 3, 4, \ldots). \tag{20b} $$

Combining the extrapolation formulas Eqs. (19a) and (19b), with Eqs. (20a) and (20b) yields, finally, for the molar ternary excess functions

$$ Z^E(x) = x_1x_2x_3[{}^{t}C_1 + \ldots] + x_1 \sum_{n=1}^{N_1} {}^{1,2}C_n x_2^n + x_2 \sum_{n=1}^{N_2} {}^{2,3}C_n x_3^n + x_3 \sum_{n=1}^{N_3} {}^{3,1}C_n x_1^n, \tag{21a} $$

and for the general form of the molar excess quantities of K-component alloys:

$$ Z^E(x) = {}^{K}Z^{E}(x) + {}^{(K-1)BS}Z^{E}(x), \ (K = 3, 4, \ldots) \tag{21b} $$

6.2. Temperature dependence

Within temperature ranges, in which the logarithms of the partial pressures of all constituents can be assumed to be proportional to the inverse temperature, the enthalpy of mixing as well as the excess entropy turn out to be temperature-independent. According to Eq. (1), the temperature dependence of the TAP parameters of the excess Gibbs energy is given by Eq. (22)

$$C_n^G(T) = C_n^H - TC_n^S \ (n = 1, 2, \ldots N) \tag{22}$$

which is equivalent to the assumption of vanishing molar excess heat capacity (ΔC_p=0), expressed by the rule of Neumann and Kopp, according to which the difference between the heat capacity of an alloy and the heat capacities of the corresponding amounts of the pure species at the same temperature is zero.

The temperature dependence of the enthalpy of mixing is given generally by means of a composite exponential function [30]. In metallic melts, this temperature dependence will be determined in relative small intervals, only. For this purpose the general formula can be substituted by a polynomial in the inverse temperature [30],

$$H^E = H_0 + D_1T^{-1} + D_2T^{-2} + \ldots, \tag{23}$$

with the temperature-independent adjustable parameters H_0 and D_i (i=1,2,...). Substituting in Eq. (10), and performing the integration yields a formula for an extended temperature dependence of the excess Gibbs energy of alloys,

$$G^E(T) = H_0 - TS_0 + (D_1/2)T^{-1} + (D_2/3)T^{-2} + \ldots. \tag{24a}$$

The corresponding relation for the TAP parameters is:

$$C_n^G(T) = C_n^H - TC_n^S + (D_{1,n}/2)T^{-1} + (D_{2,n}/3)T^{-2} \ldots \ (n = 1, 2, \ldots N) \tag{24b}$$

6.3. Combination of temperature and concentration dependence

Substituting all TAP parameters, C_n, in Eqs. (18a),(18b),(18c),(19a),(20a),(21a) and (21b) by the corresponding temperature-dependent TAP parameters Eq. (22) or Eq. (24b) yields the desired straightforward description of combined temperature and concentration dependence of the molar excess quantities of multicomponent alloys. With the additional advantage of necessary consistency between the excess properties as required by the Eqs. (1),(2),(10),(11) and (16). This TAP concept is applicable for all types of alloys, including metallic melts showing short-range ordering (compare Refs. [22,23,30]).

7. Algebraic evaluation of activity measurement

The activities $a_k(x_k,T)$ and/or the chemical excess potentials $\mu_k^E(x_k, T)$ of the investigated components k are obtained by regression of the experimental data. Following traditional evaluation techniques, the temperature dependence is determined by linear best fit, and in a second step the concentration dependence is determined graphically. The activities of the other alloy constituents are then obtained by graphical integration of the corresponding Gibbs–Duhem equations (Eq. (9)). Concerning multicomponent alloys, this restricts the evaluation to investigations along sections with constant ratios of the mole fractions of two components.

Thus, the traditional evaluation techniques are not only time consuming with respect to the graphical integration, and beset with problems relating to consistency of the determined data. No overall descriptions of the ternary or more component mixing behavior can be obtained, and the necessary experimental work, even for ternary alloys, is so extensive that it is rarely undertaken.

These difficulties can be solved by using the TAP series concept: Representing the excess Gibbs energy by means of a TAP series makes possible the substitution of each excess function of an alloy system by means of one common set of parameters. The TAP parameters will be considered to be adjusted by algebraic best fit of suitable experimental measurements. The required regression formulas are obtained by the simple substitution of the chemical excess potentials by the corresponding TAP expressions; e.g. in case of binary alloys the TAP parameters are obtained from EMF measurement by substituting from Eq. (18c) and (6) in Eq. (14)

$$\mu_k^E(x_k, T) \equiv x_j^2 \sum_{n=1}^{N} C_n^G(T) x_k^{n-1} = -n_k F E_k(x_k, T) - RT \ln x_k. \tag{25}$$

Following the AIR technique, the TAP parameters will be determined from the mass spectrometric measurements by means of the ratio of the chemical excess potentials of the two alloy constituent: Employing Eqs. (6),(7a),(13),(18b) and (18c), and combining all isotope specific factors in one additional adjustable parameter $C_0(T)$ yields the required best fit formula:

$$\begin{aligned}&\mu_k^E(x_k,T)/\mu_j^E(x_j,T)\\&\quad=\sum_{n=1}^{N} C_n^G(T)x_k^{n-1}(n-x_k(1+n))+C_0(T)\\&\quad=RT\ln\,[J_k^i(x_k,T))/J_j^l(x_j,T)]-RT\ln\,[x_k/x_j].\end{aligned} \tag{26}$$

Considering ternary alloys, the total activity measurements along all investigated constant-ratio sections can then be evaluated together by one algebraic overall best fit of the concentration dependence. All parameters in the right-hand side of Eq. (21a) – the ternary interaction terms ${}^tC_n$ as well as the binary ${}^{j,k}C_n$ parameters – can be assumed as adjustable best-fit parameters. However, at least two of the three binary boundary systems should be already investigated to obtain accurate ternary data [23]. If the mixing behavior of all binary boundary alloys are well known, then it is only necessary to perform the best fit for the ternary interaction parameter ${}^tC_n$:

$$\begin{aligned}&(\mu_k^E(x_k,T)-{}^{\mathrm{BBS}}\mu_k^E(x_k,T))\\&\quad=x_1x_2x_3[{}^tC_1^G(T)+\ldots].\end{aligned} \tag{27}$$

Employing the temperature-dependent TAP parameters $C^{\mathrm{G}}(T)$, Eqs. (22) and (24b), respectively as adjustable parameters makes it possible to perform an overall best fit of both the temperature and the concentration dependence of the chemical excess potentials; e.g. the adjustable parameters of the best-fit formulas (25) to (27) must be substituted from Eqs. (22) and (24b), respectively. Then, all experimental data at each temperature and composition of an alloy system can be utilized in one overall best fit. Details concerning the reliability, and powerfulness of the overall best-fit techniques are given in Refs. [13,22, 27,30,31].

8. Discussion and conclusion

The activity measurement makes possible the determination of the thermodynamic mixing behavior of alloys: The Gibbs energy of mixing is related directly to the activity. The enthalpy and entropy of mixing can be determined from its temperature dependence. And finally, the thermochemical equilibrium conditions enable computing the phase equilibria from the chemical potentials.

Thus, the main task in alloy thermodynamics is the determination of the activity of the alloy constituents. In recent years, the technique of computational determination of Gibbs energy data suitable for generating phase equilibria boundaries has become so convenient that more and more authors produce their own sets of assessed data, and ignore experimental investigations. As the phase-diagram calculations require only the differences among the chemical potentials of the involved phases, this technique may also produce artificial activity data.

And indeed, the discrepancies between experimental data and calculations of the phase equilibria of more component alloys can be increasingly tracked back to assessments of lower order systems based on those non-realistic thermodynamic data. Thus, it seems to be meaningful to base compilations of thermodynamic-mixing behavior on accurate activity measurement. This technique yields a more effective algebraic description of the ternary-mixing behavior than the results of pure phase equilibria analysis [13].

The TAP series concept makes possible the algebraic representation of the activity as well as all mixing properties of all types of alloys, including metallic melts showing short-range ordering by the same algorithm. Best-fit formulas as well as extrapolation from lower component alloys are incorporated. Using only one common set of parameters makes possible straightforward description of combined temperature and concentration dependence. An extended temperature dependence of the excess Gibbs energy as necessary for this purpose has been derived.

The new concept allows putting together all activity measurements of a multicomponent alloy system for performing one algebraic overall best-fit. In connection with a personal computer a very convenient, interactive evaluation tool yielding a considerable reduction both of the experimental work, and of the time spent on evaluation.

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