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EXPERIMENTAL THERMODYNAMICS AND PHASE EQUILIBRIA COMPUTATIONS

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Abstract

Emphasis is placed on the actual experimental situation as well as on the advantages and risks of various optimization techniques, especially on those of analysis and synthesis of phase equilibria curves. Computer calculations permit the synthesis of the phase diagrams of real alloys over a wide range of temperature and composition by computation combined with thermodynamic analysis of the experimental data.

However, more and more authors are producing their own sets of „Gibbs energy data" by means of „trial and error" techniques, therefore. This development yielded not only advantages, and so it is more and more required to put more physics into CALPHAD solution models. There is reason to be concerned that CALPHAD had reached a stage where its future scientific status might be in danger.

Advantages and disadvantages of several proposals are discussed briefly, and some suggestions are presented for a realistic synthesis of experimental investigations and mathematical evaluations by means of which both, the experimental work as well as meaningful assessment techniques may be stimulated.

Keywords: multicomponent alloys, solutions, phase diagram computations, experimental techniques, approximation formulas, mixing effects.

1. Introduction

Thermodynamic description of binary and more component solution systems as metal alloys, electrolytic solutions, organic mixtures, etc., covers both the thermodynamic mixing behavior as well as the coexisting equilibrium states, and the effects of external influences on these equilibria. The thermodynamic mixing effects are described by means of the dependences on temperature T and concentration x both of the thermodynamic activities a_j of the constituents j, and of the so-called thermodynamic functions Z - especially the Gibbs energy G, the enthalpy (heat) H and the entropy S.

The knowledge of these data is of great importance for industry as well as for basic science: The solutions of many problems as those concerning the reactions used in process metallurgy and heat treatment depend on the availability of accurate thermodynamic mixing properties. This shows again that there is no discrepancy between basic science and the efforts of practical industry. Only the main goal of interest is different, but neither the theoretical background nor efficient tools for solving arising problems.

2. Phase equilibria curves

The construction of phase equilibria curves of solution systems has been a domain exclusively of experimental investigations for a long time. But, e.g. concerning metal alloys, the synthesis of a phase diagram on the basis of metallographic information alone requires a great deal of time, materials, and labor. Particularly in case of more component alloys even the powerful techniques of vacuum-deposition of three kinds of metals from three corners, and the more component diffusion couple technique do not yield phase equilibria lines within reasonable effort of experimental time.

But phase equilibria boundaries can also be established computationally employing the thermochemical equilibrium conditions that at constant temperature T the partial Gibbs energy $G_k^{\alpha}(T,x_k^{\alpha})$ for each component k (x_k are the mole fractions) must be equal in each of the coexisting phases α, β, ... (ζ_k^{α}, ζ_k^{β} are the equilibrium compositions):

$$G_k^{\alpha}(T,\zeta_{Fe}^{\alpha}, \zeta_{Ni}^{\alpha}, \zeta_{Cr}^{\alpha}) = G_k^{\beta}(T,\zeta_{Fe}^{\beta}, \zeta_{Ni}^{\beta}, \zeta_{Cr}^{\beta}) = \ldots \quad (k = Fe,Ni,Cr), \ldots\ldots (1)$$

Explicit assessment of phase equilibria based upon Eq. (1) are connected with enormous amounts of computations, however. This way was prohibited therefore before the industrial development of powerful and cheaper electronic data-processing machines (EDP) took place in the sixties. In the seventies it was especially the merit of the CALPHAD group to push forward the developments of suitable EDP programs for analysis and synthesis of the phase diagrams by means of computer calculations. Additional advantage is the possibility to determine the phase diagrams of real alloys over a wide range of composition and temperature by computation combined with thermodynamic analysis of experimental properties of the molar Gibbs energy G, enthalpy H, and entropy S.

The computational techniques require the molar Gibbs energy G in all coexisting phases over the whole employed temperature ranges – even at temperatures at which the various phases are not stable any more. Consequently, no phase equilibrium can be computed by means of experimentally determined data only. Data additionally necessary have to be estimated and/or derived by means of more or less suitable extrapolation techniques.

3. Molar thermodynamic functions Z

Even binary solution systems show already such a varied and complex behavior that no physical explanation has been found yet, which is extensive enough to describe all appearing mixing behavior. Not surprisingly, because thermodynamics has been developed without knowledge of the atomistic structure of matter. As we know all, it is a macroscopic theory, and even in Boltzmann's statistical mechanics „particles" are classical particles that means geometrical figures only, despite they are named now „molecules" [1]. The physical properties are only linked to them by „imagination". The laminar flow of fluids may be a good illustration for this concept: The classical particles are building parallel flow lines whereas the real molecules are following the Brownian movement.

Neither traditional techniques nor newer considerations may improve these basic difficulties. The first principle computations as fashionable at

present, e.g., uses only very simple assumptions and require several parameters which have to be calibrated by comparison with experimental reality. We could develop arbitrary theories using only a single one of these calibration parameters, namely the difference between the computed value of the theory and the real value of the alloy property experimentally determined. Of course, half-theoretical considerations may help one day to find better descriptions of the thermodynamic mixing behavior, but we have to improve extremely our theory of chemical bond first!

Thus accurate numerical data of the thermodynamic mixing quantities of binary and multicomponent alloys require therefore experimental investigations. However, thermodynamic investigations at higher temperatures of above 1200 K are often beset with serious difficulties: Even a series of binary and ternary alloys show broader concentration ranges within which no experimental investigations can be performed with respect to the high evaporation-losses, and to chemical reactions between the sample and the crucible materials. Beside these problems accurate measurements, and their thermodynamic evaluation are very time-consuming. Furthermore the unavoidable scattering of the experimental results prohibits consistent thermodynamic data, and because of the discrete measurements no continuous description of the thermodynamic mixing behavior can be obtained. A realistic synthesis is needed, therefore of experimental investigations and mathematical evaluations.

4. Splitting of the molar functions Z

Applied thermodynamics characterizes the molar functions Z of K-component systems commonly by means of the contributions made by the alloy constituents k which are called partial molar functions Z_k:

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

In the phase α the molar partial properties $Z_k^{\alpha}(T,x^{\alpha})$ (Z = G, H, S) are split by common modeling as following:

$$Z_k^{\alpha}(x^{\alpha},T) = Z_k^{\alpha,0}(T) + Z_k^{\alpha,id}(x_k^{\alpha},T) + Z_k^{\alpha,E}(x_k^{\alpha},T) + Z_k^{\alpha,mag}(x_k^{\alpha},T), \quad \ldots\ldots (3)$$

where Z_k^0, and Z_k^{id} denote the contributions of the pure species, and of the „ideal" alloy constituents, respectively (phase index α omitted):

$$Z_k^{\alpha,id}(x_k^\alpha,T) = RT\ ln\ (x_k^\alpha) \quad (4)$$

In Eq. (3) the terms Z_k^E, and Z_k^{mag} are assumed commonly to be due to the intermolecular and magnetic forces, respectively.

Conversion among the various thermodynamic data sets of computational synthesized phase equilibria curves is often beset with difficulties due to the different extrapolation techniques used [2]. The problem would be simplified a bit by establishing unified reference levels of partial molar properties - the $Z_k^0(T)$ term in Eq. (3). Therefore it is really meaningful to employ the reference data as developed by SGTE [2] for this purpose.

4.1. The magnetic correction term $Z_k^{mag}(x_k,T)$

The introduction of a magnetic term Z_k^{mag} in Eq. (3) is always problematically, because experimental investigations will only yield the deviation between the "ideal" solution property ($Z_k^0+Z_k^{id}$) and the molar property Z. This difference has to be determined experimentally, and is nothing else than the total excess term ($Z_k^E+Z_k^{mag}$). However, especially the databanks offered by the ThermoCalc group are based upon the use of magnetic terms Z_k^{mag} as expressed by the model of Sundman and Agren [3] .

With respect to support the efforts of establishing a general data base for the reference states of the elements it is meaningful to employ the elementary magnetic contributions, nevertheless. But considering binary systems, no reasons may be found to support the problematical splitting of the deviation from the ideal solution model into two terms. Furthermore, description of assumed magnetic influence, Z_k^{mag}, by polynomials in temperature up to the power 25 (!) as employed in the model of [3] looks a bit strange from a physico-chemical point of view.

There is suspicion that use of a magnetic correction neither will simplify the thermodynamic description nor improve the quality of binary phase diagram, except in cases of incorrect excess data employed. Recently in the binary systems Fe-Ni [4], Fe-Cr [4] and Co-Cr [5] better

agreement with the experimental phase equilibria data have been obtained by means of computations based upon experimentally determined data without any binary magnetic correction than from previous assessments employing these binary magnetic contributions.

4.2. The excess term $Z_k^E(x_k,T)$

Since the contributions of ideal solutions are well defined and computable, the sum of magnetic contributions Z_k^{mag} and of the molar excess properties Z_k^E are responsible for the complexity of real metal melts behavior. As pointed out above, using a magnetic term is problematically with respect to the arbitrary splitting of the proper excess contribution into two arbitrary parts. Therefore, be careful in combining experimental excess data with assumed magnetic properties, it may yield data terrible wrong!

The proposed variety of different expressions for the molar excess quantities makes difficult often the application and/or compilation of literature data. For detailed review and discussion of the literature suggestions see [6,7]. As proved in [7] all polynomial series complying with the thermodynamic boundary conditions of alloys, as proposed in literature, are mathematically equivalent for representing the binary excess quantities [7]. This follows simply from the validity of the associative law of addition of real numbers.

Mathematical clarity can be enhanced and computational effort saved by using the simplest of all possible series. In the late seventies and beginning of the eighties the author proposed the Redlich-Kister series for this purpose which yielded the broad application of this series especially for phase diagram calculations. However some years later in [8] the simpler TAP series has been developed: As demonstrated in [9], the use of the TAPS concept instead of the Redlich-Kister series yields in case of ternary solutions considerable reduced computational effort. The formalism of the multicomponent TAPS concept is summarized in Table 1.

Table 1. The multicomponent TAPS concept of excess quantities Z^E

A1. Concentration dependence $Z^E = Z^E(x)$ For interchange of the components, as well as for conversion among various literature proposals for polynomial representing of $Z^E(x)$ see [7].		
A1.1. Binary systems (j,k: constituents; N: number of adjustable parameters ${}^{j,k}C_n^Z$; ${}^{j,k}C_1^Z$: regular solution; ${}^{j,k}C_2^Z$: sub-regular solution)	${}^{j,k}Z^E(x) = x_j \sum_{n=1}^{N} {}^{j,k}C_n^Z x_k^n$,	(A1a)
	${}^{j,k}Z^E{}_k(x_k) = x_j^2 \sum_{n=1}^{N} {}^{j,k}C_n^Z x_k^{n-1} n$,	(A1b)
	${}^{j,k}Z^E{}_j(x_j) = x_k^2 \sum_{n=1}^{N} {}^{j,k}C_n^Z x_k^{n-2}(1-n+nx_k)$.	(A1c)
A1.2. K-component systems (K = 3,4,...)		
A1.2-1 Extrapolation formulas	${}^{(K-1)BS}Z^E(x) = \Sigma$ [all Z^E-terms with (K-1) components]	(A2)
	Ternary systems: ${}^{2\text{-}BS}Z^E(x) = {}^{1,2}Z^E(x) + {}^{2,3}Z^E(x) + {}^{3,1}Z^E(x)$.	
A1.2-2 K-component interaction included (${}^KC_j^Z$: adjustable parameters of the K-component interaction).	$Z^E(x) = {}^KZ^E(x) + {}^{(K-1)BS}Z^E(x)$,	(A3a)
	${}^KZ^E(x) = x_1 \ldots x_K[{}^KC_1^Z + ({}^KC_2^Z x_1 + \ldots + {}^KC_{K+1}^Z x_K) + \ldots]$.	(A3b)
	Ternary systems: $Z^E(x) = {}^tZ^E(x) + {}^{2\text{-}BS}Z^E(x)$, ${}^tZ^E(x) = x_1x_2x_3\,[C_1^Z + ({}^tC_2^Z x_1 + {}^tC_3^Z x_2 + {}^tC_4^Z x_3) + \ldots]$.	

A2. Temperature dependence $Z^E = Z^E(T)$		
A2.1 Heat of mixing $H^E(T)$	$H^E = H_0 + D_1 T^{-1} + D_2 T^{-2} + ...$ *(H_o and D_i (i=1,2,...): temperature-idependent adjustable parameters)*	(A4)
(C^H_n, C^{Ho}_n: adjustable parameters)	$C^H_n = C^{Ho}_n + D_{1,n} T^{-1} + D_{2,n} T^{-2} + ...$,	(A5)
A2.2. Excess Gibbs energy $G^E(T)$ (n = 1,2,...N)	**Always:** $C^G_n(T) = C^H_n(T) - T\, C^S_n(T)$.	(A6)
	H^E and S^E temperature independent: $C^G_n(T) = C^H_n - T\, C^S_n$	(A7)
	H^E and S^E temperature dependent : $C^G_n(T) = C^{Ho}_n - T\, C^{So}_n + (D_{1,n}/2)\, T^{-1} + (D_{2,n}/3)\, T^{-2} ...$	(A8)

A3. Combined temperature and concentration dependence $Z^E = Z^E(x,T)$
(i) **For all types of solution systems:** Substitute in Eqs. (A1) - (A3) the TAP-parameters by the corresponding temperature dependent TAP parameters (Eqs. (A5) - (A8)), only.
(ii) **Necessary consistency** between the excess properties as required by the Eqs. (9) to (11) is guaranteed
(iii) **Applicable** not only for all of metal alloys including metallic melts showing short range ordering, but also for all other types of multi-component systems.

4.3. Molar mixing functions Z^M, and activity a_k

Another type of modeling is a bit different, but also common in applied thermodynamics: The differences between the molar quantities Z of the solutions, and the contributions of the pure constituents, $Z°(x,T)$, are defined as quantities of mixing $Z^M(x,T)$,

$$Z^M(x,T) := Z(x,T) - Z°(x,T). \quad (5)$$

The properties of mixing $Z^M(x,T)$ which do not exhibit Raoult's ideal behavior are dealt with by introducing the concept of activity: The activity a_k of a constituent k is defined as the ratio of its partial vapor pressure p_k to the vapor pressure of pure constituent k, $p°_k$,

$$a_k(x_k,T) = p_k(x_k,T)/ p°_k(T). \quad (6)$$

This type of modeling shows the advantage that we can employ the same structure of equations for both the ideal solutions as well as for real solution systems: In latter case we have only to substitute the mole fractions x_k in the thermodynamic equations of ideal systems by the activities a_k. In other words all the deviations from the ideal behavior can be lumped into one 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,

$$f_k(x_k,T) := a_k(x_k,T)/x_k = p_k(x_k,T)/ (p°_k(T)x_k), \quad (7)$$

and in the characterization of real solution systems our attention is focused on it and its dependence on composition and temperature. Corresponding to Eq. (4) the activity coefficient f_k, is connected with the partial excess Gibbs energy G^E_k by Eq. (8)

$$G_k^E(x_k,T) := RT \ln f_k(x_k,T) = RT [\ln a_k(x_k,T) - \ln x_k]. \quad (8)$$

This common and convenient concept is employed successfully in experimental thermodynamics, especially for the evaluation of measurements on the thermodynamic mixing effects since many, many years. But it is consistent with Eq. (3) only by omitting the magnetic term - additional reason against the arbitrary splitting of the excess contributions on the mixing effects: Introducing of a mixing magnetic correction term require at least meaningful adapting of the concept of activity, at first.

4. Computational synthesis of phase equilibria

As obvious from Eq. (1), computational construction of phase equilibria curves require only the differences of the molar Gibbs energy G, and not their absolute values. This makes possible not only basically different strategies of assessment, but also the use of many different sets of thermodynamic parameters to describe more or less satisfactorily the phase diagrams of alloy systems. The assessment techniques as employed in literature may be divided into two main classes: (i) Those involving the so-called lattice stability functions (compare [10]), and (ii) assessments using the common modeling of the partial molar properties $Z^{\alpha}(T,x^{\alpha})$ as presented in Eq. (3). Concerning details of the various techniques the book of Saunders and Miodownik [10] should be consulted.

4.1. Phase equilibria functions

The thermodynamic parameters used for the phase diagram calculations based upon lattice stability functions are called in literature as "Gibbs energy", nevertheless they are basically different to the physical notion of the molar Gibbs energy. This seduces into misapplications over and over again. Therefore "Gibbs energy" should not be used in context with lattice stability functions any longer. May be a notion like "phase equilibria function" should be introduced instead to characterize apparently that these functions are only employable for phase diagram computations – and not for any other application in alloy thermodynamics.

4.2. Risks of Data Generating

In the last years computational determination of molar Gibbs energy data for generating phase equilibria boundaries has become so convenient that more and more authors are employing it. However, very often there is a lack of reliable experimental data. In case of more component alloy systems including the three binary boundary systems the experimental determination of reliable molar Gibbs energy data is very time-wasting, and usually beset with considerable difficulties. Therefore it may be understandable that more and more authors are ignoring the lack of experimental investigations, and produce their own sets of assessed data.

These authors have not obeyed always the risks of the pure assessment-technique: As the synthesis of phase equilibria curves by using Eq. (1) requires only the differences between the chemical potentials of the involved phases α, optimization of thermodynamic parameter sets especially for binary systems has been performed in increasing number of cases more or less arbitrarily. With the consequence, that discrepancies between calculations and experimental data of phase equilibria in higher order systems more and more can be tracked back to assessments of lower order systems based upon those non-realistic thermodynamic data [11].

Recently also Oates et al. [12] required to put more physics into CALPHAD solution models. And even Hillert, the founder and mentor of the ThermoCalc group, regretted some developments in the phase diagram engineering at the CALPHAD XXVI Conference. He was concerned that CALPHAD had reached a stage where its future scientific status might be in danger [13]. Omitting the problematic splitting of the excess contribution in favor of employing thermodynamic mixing properties more experimentally proved, may be the right way doing this.

5. Experimental thermodynamics

The block diagram in Fig.1 gives an overview of the possibilities for the determination of the molar excess Gibbs energy G^E, the excess enthalpy (heat of mixing) H^E, and the excess entropy S^E which are connected by the well-known relation:

$$G^E(x,T) = H^E(x,T) - T\,S^E(x,T). \quad (9)$$

The molar Gibbs energy of multicomponent solution systems can be determined either (i) by measuring the partial vapor pressures, (ii) by means of electrochemical measurements, or (iii) by determining the chemical equilibria. The latter method is very time-consuming and not plotted in Fig.1. Concerning G^E-measurements by studying chemical equilibria, the articles by Richardsen and Alcock [14], as well as several articles in [15] are recommended (Grieveson, Lange and Schenck, Schwerdtfeger and Turkdogan) .

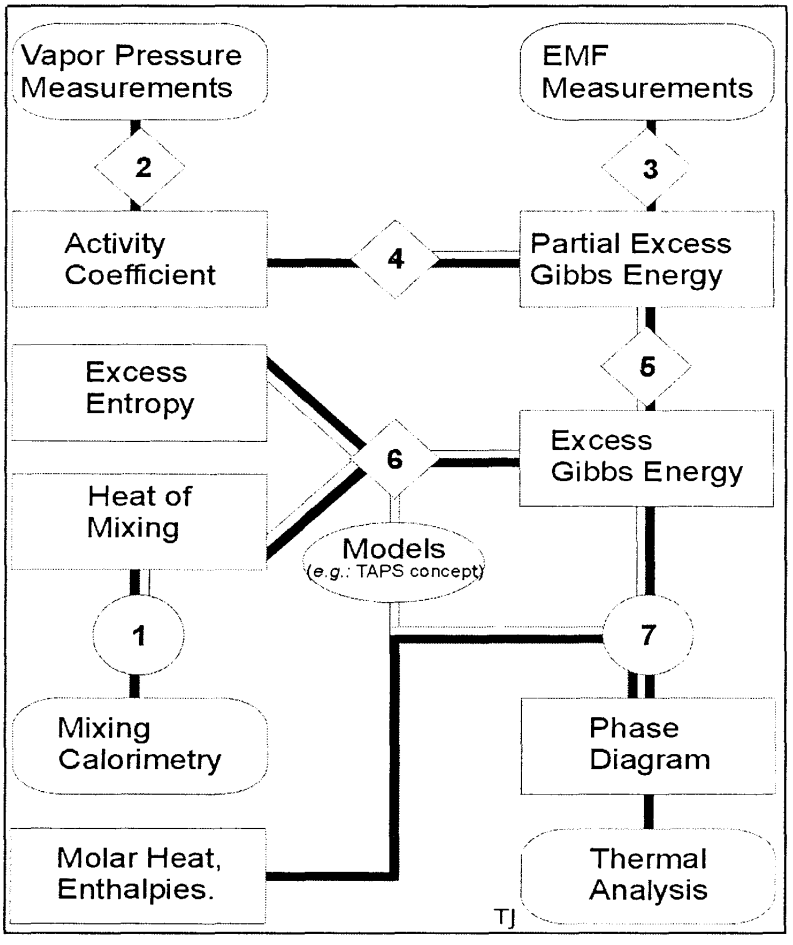

Fig. 1. Determination methods of excess mixing effects.
1: Eq.(13), in case of negligible mass-loss Eq. (12); 2: Eq. (7) combined with Eq. (15) and Eq. (16), respectively; 3: Eq.(17); 4: Eq.(8); 5: Eq.(2); 6: Eqs. (9) - (11), combined with suitable models as the TAPS concept (see Table 1); 7: Eq.(1).

As Fig. 1 indicates the heat of mixing H^E may be measured directly by calorimetric methods, but it can also be determined from the temperature dependence of the excess Gibbs energy G^E, because differentiation of Eq. (9) with respect to the inverse temperature T^{-1} yields the excess heat of mixing H^E:

$$H^E(x,T) = \partial [G^E(x,T)/T] / \partial [T^{-1}]. \quad (10)$$

Concerning the excess entropy we do not know any experimental technique for direct measurements, and so we are forced to determine the S^E-values by computations only (compare Fig. 1): Either from separate measurements of G^E and H^E using Eq. (9) or from the temperature dependence of the excess Gibbs energy GE, as differentiation of Eq. (9) with respect to the temperature T yields the excess entropy S^E:

$$S^E(x,T) = -\partial G^E(x,T) / \partial T. \quad (11)$$

For general information on experimental techniques consult the book by Kubaschewski et al. [16], the proceedings of the NATO advanced study institute on Thermochemistry of Alloys [17] and the review articles by Kubaschewski [18], Predel [19], and Komarek [20].

5.1. Mixing Calorimetry

The quantitative differential thermal analysis is based on the phenomenon that each thermochemical reaction as the mixing of a molten charge with a sample is accompanied by a heat effect, either by producing or by consuming a special quantity of heat. For investigations with non-measurable small evaporation rates and with a pure species as the starting sample, the heat of mixing may be assumed as the simple sum of all heat effects ΔQ_l of the chargings (n number of moles, j number of chargings):

$$H^E(x_j) = \sum_{l=1}^{j} \Delta Q_l / n_j, \quad (12)$$

The constituents of many actual alloy systems show, at higher temperatures, considerable vapor pressures, and so the evaporation rates of the composing species of those metal alloys cannot be neglected anymore. in these cases the determination of the heat of mixing has to be based upon a generalized calorimeter formula as derived in [21]:

$$H^E(x_j) = [\Delta Q + n'_{j-1} H^E(x'_{j-1})] / n'_j, \quad (13)$$

where n' and x' are the number of moles and the mole fractions, respectively, of the samples at the end of the fore periods of the actual charging j.

The data of the "starting-points" (that is the end of the fore-periods) in alloy systems with measurable evaporation losses cannot be measured directly. Following the way as suggested in [21] the heats of mixing at the end of the fore-periods, $H^E(x')$, will be determined by interpolation, whereas the required values of the mole fractions x' and of the number of moles n' will be obtained by applying the evaporation formula as derived in [21] to calculate the mass losses due to evaporation dm_j of the constituents of a sample at the temperature T during the interval of timer dt:

$$dm_j = dt\, F_{vap}\, a_j(T)\, p^\circ_j\, (T)\, (M_j/T)^{1/2}, \quad (14a)$$

where F^{vap} is vaporization factor, and Mj is mole mass of the species k. The vaporization factor itself is composed of various constants, the effusion orifice F, and of an experimentally determined correction factor f_p^{cor} of the actual sample crucible [1]

$$F^{vap} = f_p^{cor}\, F\, (2\pi R)^{-1/2}. \quad (14b)$$

Detailed explanations are given in [21]. Concerning general experimental techniques of mixing calorimetry see [16-20,22], e.g.

5.2. Vapor pressure measurements

The gas phase of a substance in thermodynamic interaction (exchange of energy and mass) with a condensed phase (liquid or solid) of the same substance may be called "vapor phase". Over each condensed sample exists a vapor phase which contains pressures of the vapors of each component of the sample. The partial pressure of each component vapor changes therefore with temperature and composition of the sample, maintaining the vapor-condensed phase equilibrium.

Many interesting substances - specifically metal alloys - show even at higher temperatures vapor pressures lower than 20 Pa. Such "small" vapor pressures will not obey any more the laws of hydromechanics, and their behavior must be described by means of the kinetic theory. The measurement of small vapor pressures require therefore techniques entirely different to those employed for determining „common" vapor pressures. Several effectful experimental ways are known for investigations at temperatures lower than 1000 K, but there is a tremendous lack of convenient methods applicable at higher temperatures. One of the few methods, still applicable at temperatures higher than 1500 K is the molecular effusion after Knudsen which has been dominant in the study of vapor pressures.

Following this way, small vapor pressures are determined by means of the effusion of vaporized sample out of an isothermal vessel which is called "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,

$$p_k(x_k,T) = dm_k/dt\ A_o^{-1}\ (2\ k_B\ T/M_k)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ (15)$$

where dm_k/dt is the mass rate of effusion, A_o and k_B are the orifice area and the Boltzmann's constant, respectively, and M_k is the mass of a molecule of the species k (see [23]).

A block diagram of the various variants as have been proposed in literature is given in Fig. 2. In the last two decades the PENKER technique (*Pen*dulum electronically balanced *K*nudsen-*e*ffusion *r*ecoil) [23] has been introduced as a new automatic null-method based on the recoil technique. Other advancement was less due to radically new techniques but more to automated control, data acquisition, and processing. For a brief review of modern Knudsen techniques see [24].

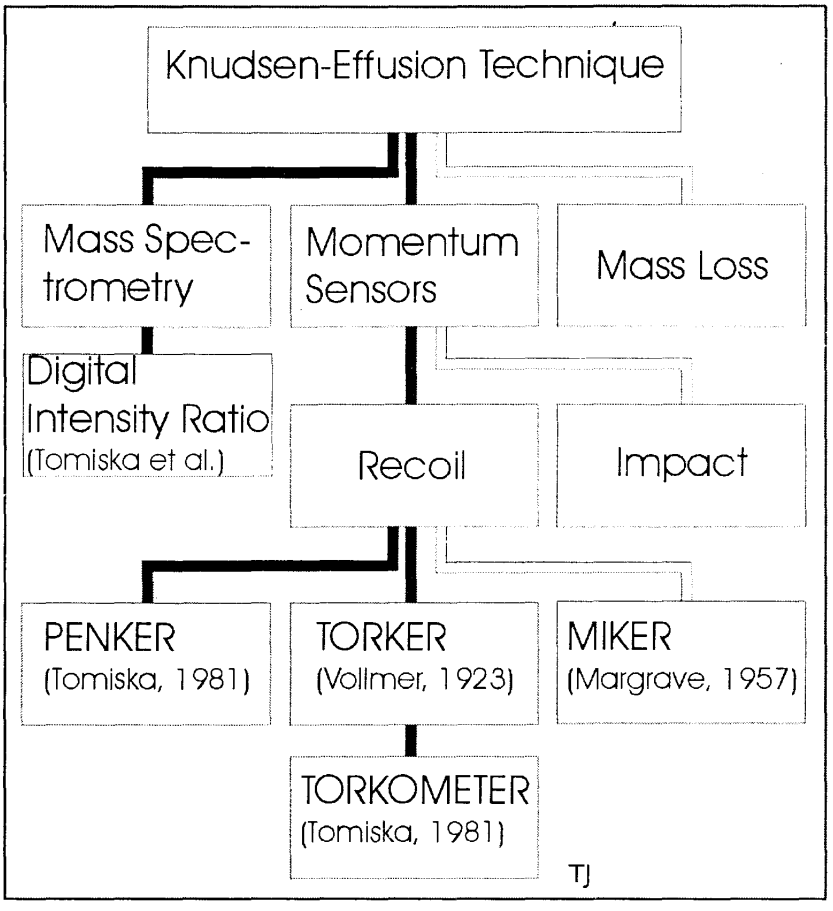

Fig. 2. Block diagram of Knudsen effusion techniques.

A particular powerful tool is the Knudsen cell mass spectrometry [24-26]. 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

$$p_k(x_k,T) = J_k^j(x_k,T)\, T /(D_k^j\, D_I) \quad \text{..... (16)}$$

where D_k^j is an isotope specific constant (see [25,26]). The instrumental geometric constant sensitivity factor D_I in Eq. (16) 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 [25] should be consulted. Following the various variants of the „Algebraic Intensity Ratio" (AIR) technique [25,27] 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 [27,4]). The most recent review of mass spectrometric studies of metallurgical systems has been published by Kato [26].

5.3. Electrochemical measurements

The determination of excess Gibbs energy G^E from electrochemical measurements employs its connection to the electromotive force (EMF) which is produced by performing a reaction in an electrolytic cell under reversible conditions at constant temperature. In case of symmetrical cells which contains 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:

$$G^E_k(x_k,T) = RT \ln f_k(x_k,T) = -n_k F E_k(x_k,T) - RT \ln x_k. \quad (17)$$

where n_k is charge number, and F is the Faraday constant, and E_k is the measured reversible cell voltage E_k of the formation cell.

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 [20,28]. Experimental aspects and limiting factors are discussed by Schaller [28]. Various aspects of electrolytes are discussed also in a book edited by Geller [29]. Concerning hot corrosion of metals by fused salts the article of Rapp [30] should be consulted. An overview over the wide field of application of EMF measurements is given by Komarek [31].

5.4. Algebraic evaluation of experimental measurements

The thermodynamic excess properties $Z^E_k(x_k,T)$ of the investigated solution systems 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. 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 wasting with respect to the graphical integration, and beset with problems concerning the 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 big that it is rarely undertaken.

Powerful evaluation techniques are obtained by putting together all experimental measurements to one algebraic overall best-fit employing the TAPS concept as given in Table 1 [32-34]. E.g., if all (K-1)-component boundary systems are well-known, then it is only necessary to determine the best-fit values of the K-component interaction terms ${}^{K}C_n^{Z}$. This tool of modern experimental thermodynamics makes possible a combined, simple and consistent description of both the temperature, and the concentration dependence of the excess mixing behavior of multicomponent solutions systems by means of one set of parameters. The concept allows the representation of all types of solutions, and includes even liquid alloys showing short range ordering.

6. Discussion and Conclusion

A rough overview has been presented on the situation of applied thermodynamics. It has been carried out that there is no chance to obtain a theory in nearer future powerful enough to derive the thermodynamic mixing effect or reasonable phase equilibria curves. On the other hand the experimental effort of investigations especially on ternary and morecomponent solution systems is very large, partly such experimental measurements are even impossible, and evaluation of the measured data is

very time-consuming. Pure experimental constructions of phase equilibria are also connected with tremendous need on experimental time.

Nevertheless, in future computational synthesis of phase diagram should not be based upon sets of „Gibbs energy data" achieved by means of „trial and error" techniques. The problematic splitting off a "magnetic" term from the excess contribution of the thermodynamic mixing effects should be prohibited entirely with respect to reasons of consistency of the formulism. Furthermore there is founded suspicion that this additional correction term will only help to correct binary excess data assessed wrongly.

The enormous diversity on experimental techniques and suggestions indicate that practical requirement to minimize experimental investigations by means of suitable evaluation and assessment techniques. May be convenient online methods as suggested in literature will yield the right direction in future.

References

1. J. Tomiska, , Thermochimica Acta, 314 (1998) 145.
2. A.T. Dinsdale, CALPHAD, 15 (1991) 317.
3. B. Sundman and J. Agren, J.Phys.Chem.Solids, 42 (1981) 297.
4. J. Tomiska and J. Vrestal, Thermochimica Acta, 314 (1998) 155.
5. J. Havrankova, J. Vrestal and J. Tomiska, Ber. Bunsenges.Phys.Chemie, 102 (1998) 1225.
6. J. Tomiska, CALPHAD, 4 (1980) 63.
7. J. Tomiska, Thermochim. Acta, 151 (1989) 145-158; 159.
8. J. Tomiska, CALPHAD, 10 (1986) 91.
9. J. Tomiska and A. Neckel, J. Phase Equilibria, 17 (1996) 11.
10. N. Saunders and A.P. Miodownik: CALPHAD Calculation of Phase Diagrams. Oxford, Pergamon, 1998.
11. B.J. Lee, CALPHAD, 17 (1993), 251.
12. W.A. Oates, H. Wenzl and T. Mohri, , CALPHAD, 20 (1996), 37.

13. M. Hillert, Proc. of CALPHAD XXVI Conference, Palm Coast, Florida, May 11-16, 1997, 6e.

14. F.D. Richardson and C.B. Alcock, in J.O'M. Bockris, J.L. White and J.D. Mackenzie (Eds.), Physicochemical Measurements at High Temperatures. New York, Academic Press, 1959, 135.

15. R.A. Rapp (Ed.), Physicochemical Measurements in Metal Research. Vol. IV, Part I, of R.F. Bunshah (Ed.), Techniques of Metal Reasearch. New York, Interscience Publ., 1970.

16. O. Kubaschewski and C.B. Alcock, Materials Thermochemistry. New York, Pergamon Press, 1993.

17. H. Brodowsky and H.-J. Schaller (Eds.), Thermochemistry of Alloys. Dordrecht, Kluwer Academic, 1989.

18. O. Kubaschewski, Physica, 103B (1981) 101.

19. B. Predel, CALPHAD, 6 (1982) 199.

20. K.L. Komarek, Ber. Bunseng., 87 (1983) 709.

21. J. Tomiska, R. Lück, and B. Predel, Z. Metallkd., 75 (1984) 311-316; 373.

22. Th. Heumann and B. Predel, Z. Metallkd., 51 (1960) 509.

23. J. Tomiska, J. Phys. E: Sci. Instrum., 14 (1981) 421.

24. J. Tomiska, in [17], 247.

25. A. Neckel, in [17], 221.

26. E. Kato, J. Mass Spectrom. Soc. Jpn., 41 (1993) 297.

27. J. Tomiska, K. Kopecky, M.S. Belegratis and A. Neckel, Z. Metallkd., 84 (1993) 619.

28. H.-J. Schaller, in [17] 329.

29. S. Geller (Ed.), Solid Electrolytes. Top. Appl. Phys., 21, 1977.

30. R.A. Rapp, in [17] 481.

31. K.L. Komarek, Z.Metallkd., 64 (1973) 325.

32. J. Tomiska and H. Wang, Ber. Bunsenges. Phys. Chemie, 99 (1995) 633.

33. J. Tomiska, CALPHAD, 5 (1981) 81.

34. J. Tomiska, J. High Temp.-High Pressures, 14 (1982) 417.