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What will be done in the future with O.J. Kleppa's enthalpy data set?

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Abstract

A survey of Kleppa's complete literature allows us to distinguish five different periods in his work. Each period is linked to another type of the calorimeter device increasing the temperature range at each step. Starting from the study of low melting binary alloys during his thesis period, Prof. Kleppa measured the enthalpy of formation of many refractory compounds in the last period. More than 200 binary systems were studied providing an unrivalled enthalpy data set of crucial interest for the phase diagram optimisation. Thanks to the computer efficiency it is yet possible to use these data in multicomponent systems modeling for real industrial applications. The quinary Cu–In–Pb–Sn–Zn system for which Prof. Kleppa established many binary enthalpy data illustrates the method.

Keywords: Enthalpies of formation; Metallurgical thermodynamics; Multicomponent alloys; Cu, In, Pb, Sn, Zn system; Kleppa work; Phase diagram calculation

1. Introduction

After nearly 50 years of uninterrupted experimental work devoted to thermochemisty of materials it is time to wonder what will be done in the future by the young scientists community, of the patrimony of data I have obtained? This question is of special importance for Prof. Ole J. Kleppa with his unrivalled set of consistent enthalpy data.

The progress of phase diagram calculation of multicomponent systems, is significant as far as industrial applications for new material development and metallurgical processes are now in due course. That will probably be the main topic of the next future metallic thermodynamics. That means that simple models are used: the Redlich-Kister multicomponent model, coming from the petroleum industry, is generalised for the large solubility metallic phases and the Hillert sub-lattice model for the intermediate phases. Together they provide a very large domain of applications, useful for estimating the main multicomponent metallic systems.

In the 80^{ies} we trusted the progress of band theory of physical quantum mechanics to provide a lot of «ab initio» or semi-fitted energetic data sets. Unfortunately the relative phase stability in a multicomponent alloy depends on only some thousandth of eV and the actual precision of the calculated cohesive energy will not attain 0.01 eV in the most accurate situations. This part of the physical thermochemistry remains interesting in order to understand the philosophy of the metallic bonding, but it is yet far from any practical applications.

The phase diagram calculation of a multicomponent alloy cannot start out of nothing, but out of consistent thermodynamic data used to fit first the binary systems, then the ternaries. Higher order terms are generally not needed. The enthalpy of mixing of all the binary liquid phase and the enthalpy of formation of compounds are of crucial interest to obtain a set of coherent multicomponent data bank.

In this lecture first we would like to commend the complete work of Prof. Ole J. Kleppa, then choose a sole quinary metallic system, recently optimised in our lab, (which many Kleppa binary enthalpy data have been used for), to illustrate the future interest of the Kleppa data patrimony.

2. A survey of the Kleppa work

Fig. 1 is the histogram of the main Kleppa publications up to December 1999, that means 208 referred papers

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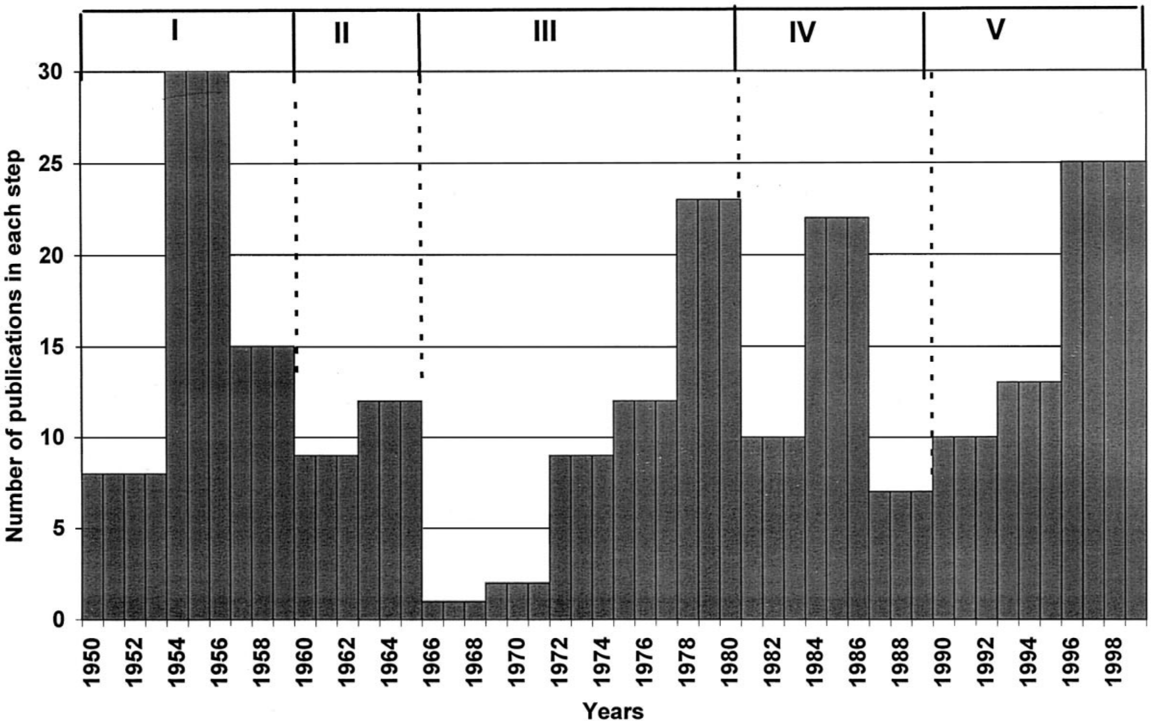


Fig. 1. Histogram of Prof. Kleppa's main publications, describing five different periods in his work, each one linked to a particular calorimeter device.

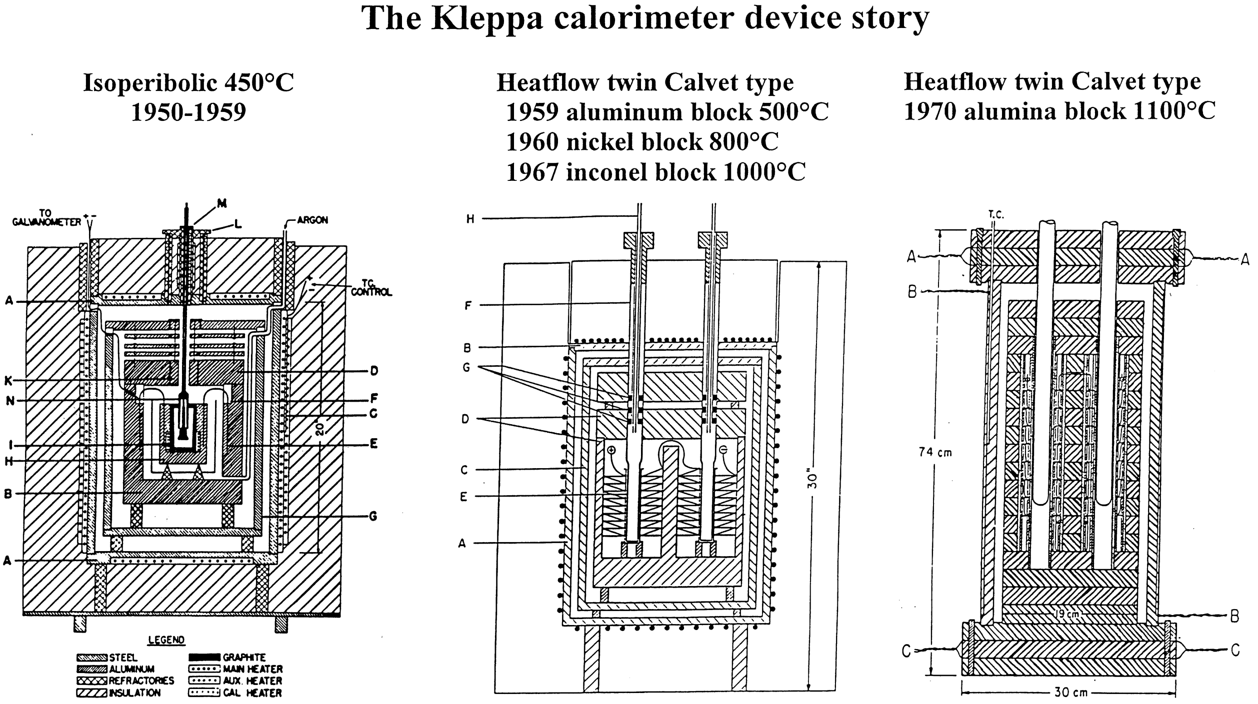
essentially devoted to the enthalpy measurements of almost 200 binary systems. It is clear when examining this histogram that the Kleppa work can be divided into five different periods, each one corresponding to an inflow of publications. It is also obvious that the complete description of the Kleppa work would need a bibliography list containing over 200 Kleppa references. For this reason we have decided to publish this article with only a few Kleppa references. Each period of his work is characterised by a particular type of his calorimeter device, by a temperature range of experiments and by one or more scientific goals. It can be noticed that the continuous increase of the temperature range of the Kleppa calorimeters (see Figs. 2 and 3), was linked to the evolution of his subject of research, starting from the low melting metallic binary systems and finishing with refractory materials like borides, silicides, carbides or intermetallic high melting transition compounds. Vice versa the possibility of reaching higher temperatures influenced the choice of his new goals. Table 1 summarises the main characteristics of each period of the Kleppa work.

2.1. The Thesis period and its extension

This first period started in 1950 and continued up to 1959. When he was a student Kleppa built his first original high temperature calorimeter during the preparation of his Thesis. It was an isoperibolic calorimeter with one sole crucible (in graphite). The isothermal block was made of aluminum, which has a high heat-conductivity, its design was influenced by the adiabatic calorimeter of Kubaschewski and Walter. This calorimeter had a stirrer and was appropriate for dissolution calorimetry (like liquid tin calorimetry) and for any mixing calorimetry in a low melting metallic liquid phase. At 450°C the heat transfer from crucible to the isothermal block did not exceed 10–15% of the total reaction-heat, even after a 40 min long dissolution. The correction of the heat transfer was of the Regnault type. The accuracy of the device was estimated to 1% of the result after correction. During the preparation of his thesis [1] the future doctor Kleppa measured the enthalpy of mixing of five binary liquid phases at 450°C: Bi–Pb, Cd–Pb, Pb–Sn, Sn–Zn, Cd–Sn and the enthalpy of formation of compounds of the noble metals Cu, Ag and Au with Cd, In, Sn, Tl, Pb, Bi. Dr Kleppa continued the same program for 3 years after his thesis defense, (introducing also the Ga and Hg components), with the study of the systems Ag–Zn, Bi–Cd, Bi–Hg, Bi–Zn, Cd–Hg, Cd–In, Cd–Tl, Cd–Zn, Ga–Zn, and Hg–Tl.

2.2. The second binary alloys period

Starting in 1960 with his first Calvet type calorimeter Prof. Kleppa introduced Ge, Mg, Ni, Sr and also the alcaline metals in his programs. But the general philosophy remained the same as during the first period of his work.



A furnace core with main heater, B and D isothermal aluminum block, I graphite crucible and calibration heater, N graphite charging or stirring device, C stell shield.

A main heater, B top heater, C heavy shield, D block jacket, E calorimeter cell with differential thermopile between the two cells and the jacket, H introducer, G anti radiation shields

A top heater, B main heater, C bottom heater, T.C. temperature control.

Fig. 2. The Kleppa calorimeter device story before 1990.

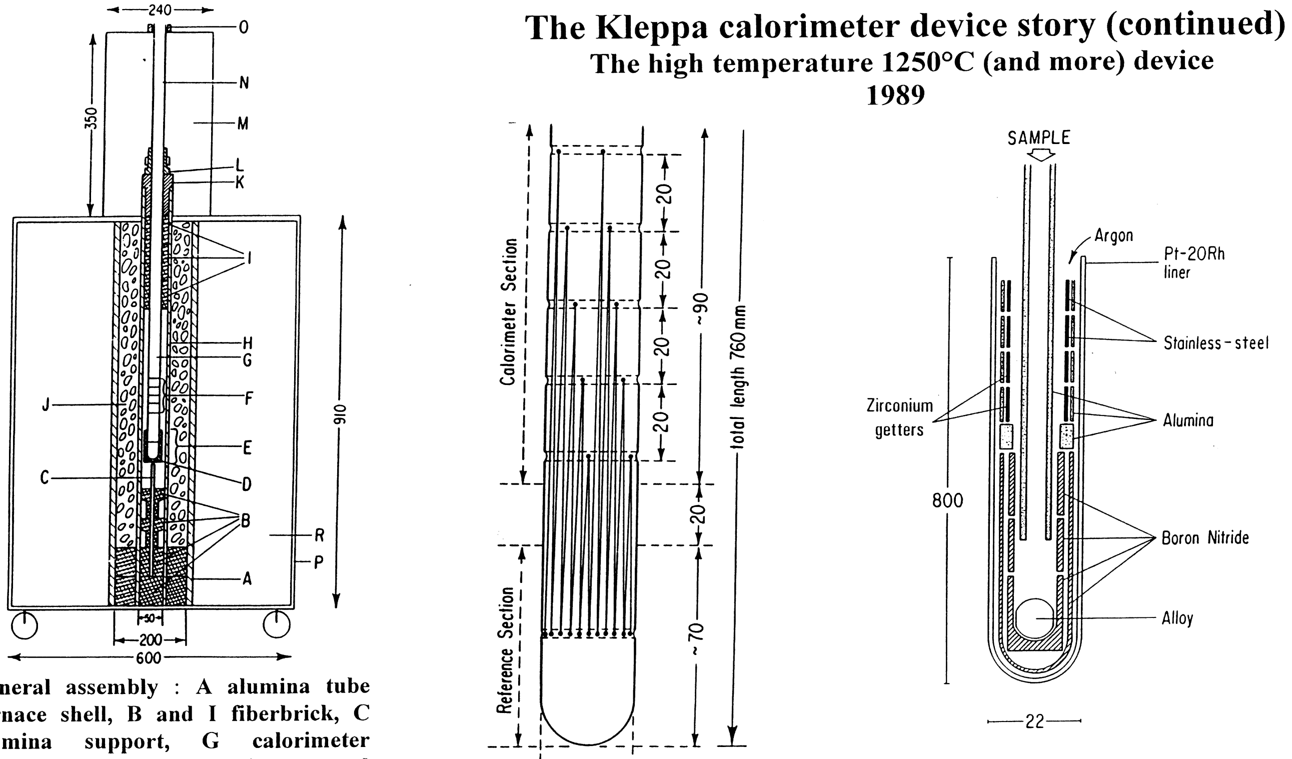
Probably for 5 years he used the old and the new calorimeters simultaneously. During this period he studied the following systems: Cu–Ga, Cu–Ge, Cu–Zn, Cs–Rb, Hg–In, Hg–Sn, Hg–Zn, K–Na, K–Rb, Na–Rb, Mg–Ni, Mg–Sn, Mg–Sr and Mg–Zn.

2.3. The third period: increasing the temperature range of the Calvet-type calorimeters

During the third period Prof. Kleppa developed intensive efforts to increase the temperature range of his calorimeters. He collaborated also with Prof. Darby at the Argonne National Laboratory on that purpose. The scientific program of Prof. Kleppa changed drastically during this period. For about 15 years he left the binary alloys studies and engaged on new programs in the field of binary salt systems: fluorides, chlorides, bromides, iodides nitrates and tungstates. The study of these binary liquid systems required higher temperatures than the low melting metallic alloys and Prof. Kleppa was now able to work at 800°C and above. During the same period also Prof. Kleppa measured various enthalpy of combustion of pure metals and studied the hydrides and deuterides enthalpies of formation of metallic systems: Ta–H, Ta–D, Pd–H, Pd–Ag–H, Pd–Cu–H, Pd–H, Au–H, Pd–D.

2.4. The fourth period with the alumina block Calvet-type calorimeter working up to 1100°C. The Topor-Kleppa solute–solvent method in Chicago and the Gachon-Hertz direct synthesis method at 1500°C in Nancy

The preceding programs concerning the binary salt mixtures and also the hydrides were continued and extended after 1980 but the interest of Prof. Kleppa came back to the binary metallic systems when he was able to melt new series of metallic alloys like Cu–Ti, Cu–Zr, Cu–Hf, Cu–Ni, Cu–Ag, Cu–Au . . . In the 1980s the progress of the band theory became significant and there was a strong demand from physicists to measure the enthalpy of formation of intermetallic binary transition compounds so as to verify the new theoretical methods of prevision of the cohesive energy. The same pressing demand from physicists was felt in Chicago and in Nancy but the technical answers were completely different in our two laboratories. The melting temperature of these intermetallic transitions



The Kleppa calorimeter device story (continued)
The high temperature 1250°C (and more) device
1989

General assembly : A alumina tube furnace shell, B and I fiberbrick, C alumina support, G calorimeter alumina tube, H alumina furnace and PtRh40 electrical coil, E reference zone, F measuring zone with 5 thermocouple rings, P water jacket.

The thermopile :the reference ring at the bottom and the five calorimeter rings around the crucible.

The cell assembly :inside the Pt-20Rh liner, the boron nitride protectors, the boron nitride crucible and the zirconium getters.

Fig. 3. The Kleppa calorimeter device story (continued after 1990): the high temperature device for direct synthesis drop calorimetry.

compounds were often superior to 2000°C. In the same period Prof. Kleppa was requested to measure the enthalpy of formation of the LaB_6 compound: Topor and Kleppa [5] had the idea to synthesise a ternary eutectic with platinum, $Pt_{0.72}B_{0.24}La_{.04}$ which was liquid at 1100°C, in the calorimeter cell. Starting the drop calorimetry the first time with the lantanum boride and the platinum and the second time with the pure B, La and Pt components the difference of the measured enthalpies provided the enthalpy of formation of the lantanum boride. A similar method (called the solute–solvent calorimetry) was used afterwards in Chicago by Topor and Kleppa to measure the enthalpy of formation of many intermetallic transition compounds. At the same time (1980) I decided with my coworker Jean-Claude Gachon to start a program of very high temperature (up to 1500°C) powder synthesis to measure the enthalpy of formation of the intermetallic transition compounds directly in the cell of the calorimeter. The two programs were developed for 10 years independently in Chicago and Nancy and provided quite equivalent results and a lot of publications from both sides of the Atlantic Ocean including sometimes the same binary systems like Pd–Ti, Pd–Zr, Pd–Hf, Co–Hf, Ni–Hf, Pt–Ti, Pt–Zr, Pt–Hf, Rh–Zr, Rh–Hf, Ir–Ti, Ir–Zr, Ir–Hf, Ru–Hf . . .

2.5. The fifth period: direct synthesis calorimetry in Chicago

In 1990 Prof. Kleppa was still the same young enterprising man and he decided to build his own very high temperature calorimetric device (Fig. 3). At the same period he invited a young student of Prof. Gachon's, Najim Selhaoui, to undertake a postdoctoral work in Chicago. With the help of Susan Meschel a kind of collaboration between the two labs started (in particular for the study of the Ru–Y system [3]). The production of the Kleppa's laboratory is still increasing today (Fig. 1) with the direct synthesis method applied to carbides, borides silicides and many intermetallic binary compounds!

3. The method of optimisation and the multicomponent system previsions

Kleppa wrote in his thesis in 1956 [1]: "Of particular interest to the solution chemist are the changes in free energy, in enthalpy and in entropy, which are associated with the formation of the mixture . . . It is sufficient to establish two of them in order to obtain a complete

Table 1
The five main periods of the Kleppa work

Period number	I	II	III	IV	V
Dates	1950–1959	1960–1966	1966–1982	1983–1990	1990–2000 and more
Title	Thesis period and extension	First Calvet Type 500°C	New Calvets 800°C to 1100°C	* = Solute–solvent drop calorimetry	Direct-reaction calorimetry
Calorimeters	Isoperibolic 450°C	Twin symmetric fluxmetric aluminum block	Twin symmetric fluxmetric: silver, nickel, inconel, alumina blocks	Twin symmetric fluxmetric alumina block 1100°C	High temperature 1500°C device
Subjects	1. Low melting binary liquids 2. Intermetallic compounds by tin dissolution	1. Low melting binary liquids 2. Intermetallic compounds by tin dissolution	1. Binary metallic liquid and solids 2. H and D in binary alloys 3. Molten salts	1. Cu, Ag, Au liquid alloys (continued) 2. Borides* 3. Silicides* 4. Intermetallic transition compounds*	1. Intermetallic transition and rare earth compounds 2. Carbides silicides germanides stannides borides . . . 3. High melting binary liquids
Main coworkers (each one cited once only in his arrival period)	Ole J. Kleppa alone up to 1956 M. Kaplan	C.E. Thalmayer R.C. King T. Yokokawa	M.E. Melnichak P.G. Dantzer G. Boureau K.C. Hong C. Picard S. Sato M. Shamsuddin H. Yokokawa R.C. Phutela S. Watanabe	L. Topor W.G. Jung K. Fitzner	S.V. Meschel N. Selhaoui Q. Guo

thermodynamic description''. This statement is still completely true. Any multicomponent optimisation starts from a data set (enthalpy and entropy) concerning first the pure components (the SGTE unary data bank), then the binary mixtures and finally the ternaries. Higher terms are generally not needed. It is absolutely necessary to optimise the different contributions in the increasing order of complexity: no ternary term could correct any discrepancy in the binary evaluations and no binary term could compensate any error in the unaries. For the binary systems there is the SSOL data bank in the Thermo-Calc program. But this bank is sometimes partially right and often incomplete.

In the early years of his work, Kleppa, considering the different experimental possibilities (like e.m.f., vapor pressure, calorimetry . . .) to obtain thermodynamic accurate data, concluded [2]: ''my experimental approach to the systematic study of the thermodynamic of binary alloys should be based on calorimetry and more specifically on high temperature mixing and reaction calorimetry. While I recognised that calorimetric measurements would not give me all the desired thermodynamic information, I inferred that in most cases it would provide the leading terms in the Gibbs energy of alloys formation.''

This is true: an accurate knowledge of the enthalpies is necessary to any good optimisation. Nevertheless it is not sufficient, the entropy terms also are significant, particularly in three situations:

- At high temperature when the entropy contribution becomes prominent.
- When the enthalpy term is weak, like in the In–Sn binary where the solid intermediate phases appear only by their entropy contribution.
- For the order–disorder transformations linked to the balance between the enthalpy and the entropy.

The calorimetry data have to be completed by any Gibbs function information like e.m.f., vapor pressure measurements or mass-spectrography, or simply by the phase diagram which is a real Gibbs meter if the enthalpies are well known.

The phase diagram optimisation is realised in a melting-pot called PARROT, (in the Thermo-Calc program), where all experimental information can be used: partial or integral enthalpies, activities, integral Gibbs functions, e.m.f. measurements, phase boundaries, tie-lines . . . Parrot is able to optimise the adjustable parameters of the different phases in order to obtain the best fit of all the experimental data. The final result gives a description of the Gibbs function of any phase modelised in the system.

For the disordered solution, wide in the composition scale, the polynomial model of Redlich-Kister which is a variant of the Margules approach, is the most appropriate way of modelising the Gibbs functions of the multicomponent phases. (This model came from the petroleum industry and was only supported by empirical intuitive considerations). For a binary system the x_2 mole fraction is equal to the $(1 - x_1)$ variable, but this is wrong in a multicomponent system, whereas $(x_2 - x_1)$ is a variable which remains independent of the complexity of the system. The sole binary terms of a Redlich-Kister multicomponent development will represent 80–90% of the total excess Gibbs function. The ternary terms only give a minor contribution and the higher order terms are generally not needed if the binary and ternary terms are well optimised.

For the ordered phases, which stoichiometric or semi-stoichiometric compositions Hillert and Staffanson [4] have proposed the sublattice model which is a close variant of the associated model description.

Both the Redlich-Kister and the sublattice models are implemented in the Thermo-Calc program, giving any facilities to simply modelise very complex systems. In each of these two models any adjustable parameter contains the enthalpic and the entropic contribution.

4. The quinary Cu–In–Pb–Sn–Zn system as an illustration of the calculation method

4.1. The binary sub-systems

In a quinary system there are 10 binary sub-systems, namely:

Cu–In Cu–Pb Cu–Sn Cu–Zn In–Pb
In–Sn In–Zn Pb–Sn Pb–Zn Sn–Zn

all these binaries must be well optimised before any multicomponent calculation. Kleppa published many data concerning nine of these systems. All these binary sub-systems were revised and optimised in our lab during this work, even the systems which the Thermo-Calc SSOL databank gave an optimisation for. New calorimetric or e.m.f. measurements were performed when necessary. In the following paragraphs we have selected the more significant original optimisations or improvements.

4.1.1. Cu–In data

Kleppa studied this system during the first period of his work in 1956 [5], using his isoperibolic calorimeter. He established the first data concerning the enthalpy of formation of the Cu_7In_3 and the η compounds by dissolution in a tin bath at 450°C. He measured also the enthalpy of mixing of the liquid phase for $x_{In} > 0.92$ at the same temperature.

Subramanian and Laughlin [6] established in 1989 an up to date complete compilation of this system containing the phase diagram and all the available thermodynamic data. Their phase diagram is generally accepted as the final version. It is based on the original works of Weibke and Eggers [7], Hume-Rothery et al. [8], Reynolds et al. [9] and Jones and Owen [10]. The η phase exhibits some complicated ordering transitions at low temperature. In 1994 Okamoto [11] proposed a simplified version of this phase diagram. Our optimisation was built according to this last phase diagram and taking into account all the available thermodynamic data. Fig. 4 displays both Subramanian and Laughlin's and Okamoto's phase diagrams. Fig. 5 is a comparison between our final optimised phase diagram and the version of the Hultgren et al. [12] compilation (we did not take into account any ordering of the η phase).

4.1.2. Cu–In discussion

According to the calorimetry measurements of Kang et al. [13] there exists a very important excess heat capacity in the liquid phase, linked to some short-distance order. Nevertheless it was easier to describe the liquid phase without any excess Cp and add the enthalpy of the liquid disordering to the melting enthalpy of the solids. That was our philosophy when optimising this system. For the mixing enthalpy of the liquid phase we have accepted the measurements of Itagaki and Yazawa [15] at 1073 K which are consistent with those of Kang et al. [13] at 1129 K. Fig. 6 is a comparison between the experimental enthalpy of mixing of the liquid phase and our own optimisation. For the liquid phase also we take into account the e.m.f. measurements of Kang et al. [14] and those of Azakami and Yazawa [16]. For the solid phases we take into account the Kleppa's results [5].

Fig. 7 shows that our calculation for the liquid phase is consistent with the e.m.f. data of Kang et al. [13] reproduced as in a mirror (for the temperature scale). Fig. 8 explains why it was possible to modelise the liquid phase without any excess Cp: recently Bahari et al. [17] measured with a high precision the Cp of the Cu_7In_3 alloy from room temperature in the δ solid structure up to 1000°C in the liquid and crossing the γ structure. The restitution by the model of the enthalpy of the alloy is accurately consistent with the experiment in the two solid

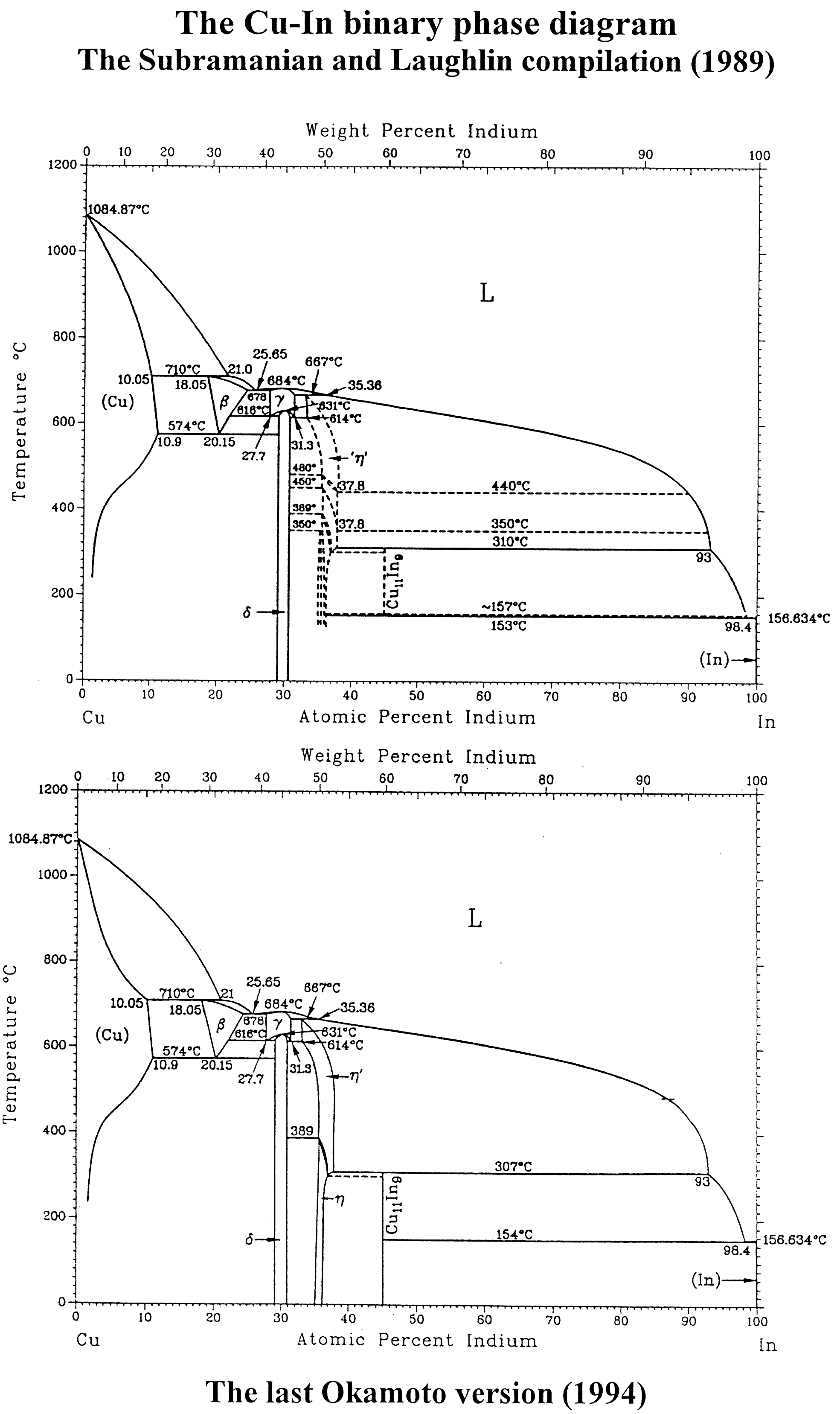


Fig. 4. The Cu–In phase diagram according to Subramanian and Laughlin's compilation [6] and Okamoto's last modifications [11].

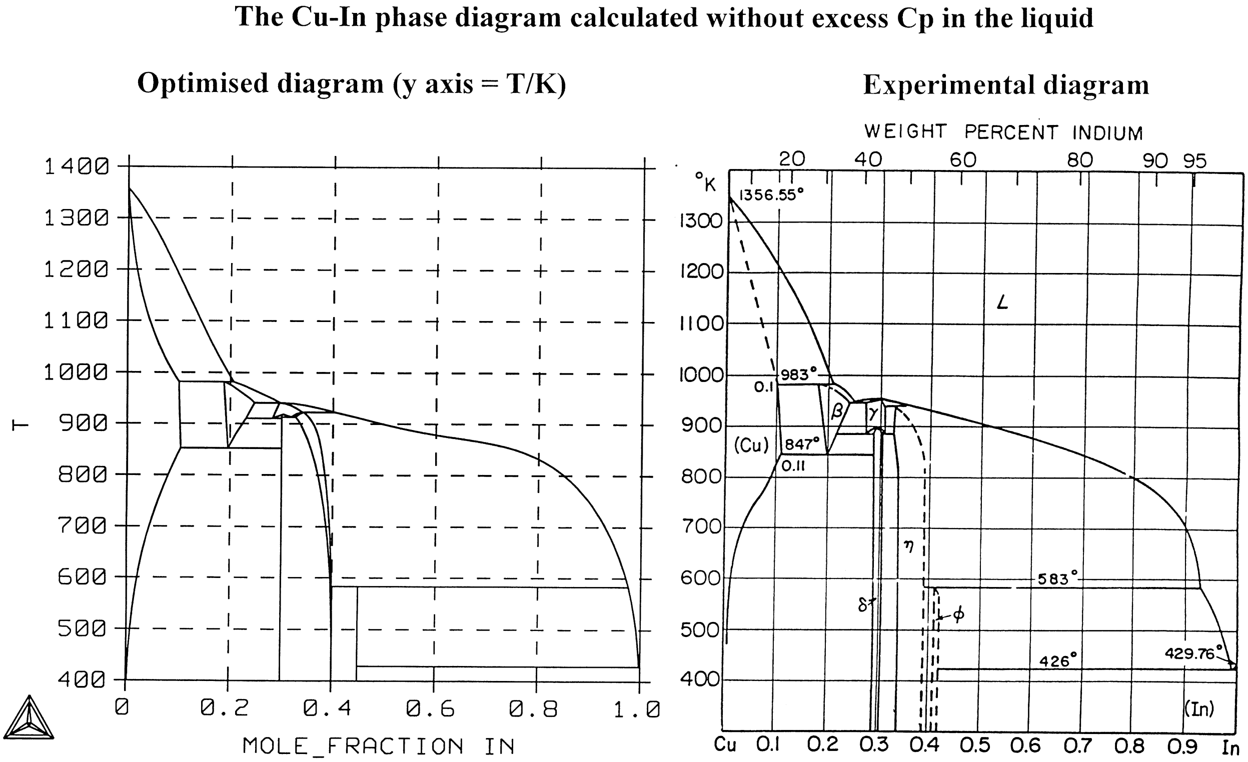


Fig. 5. Comparison (on the same scale) between our modelised Cu–In phase diagram and the experimental diagram according to Hultgren et al. [12].

domains. At high temperature the calculated liquid enthalpy also meets the experimental values. In between the total disordering energy of the liquid is added to the melting enthalpy of the γ phase. The work of Bahari et al. confirms the existence of an excess Cp in the liquid phase but shows that the Kang et al. enthalpies are overvalued at low temperature, above the liquidus line.

The enthalpy of formation of the solid phases are quite consistent with the Kleppa results: for the δ phase ($x_{\mathrm{In}} = 0.30$) Kleppa found −8535 J/mol and the calculation gave

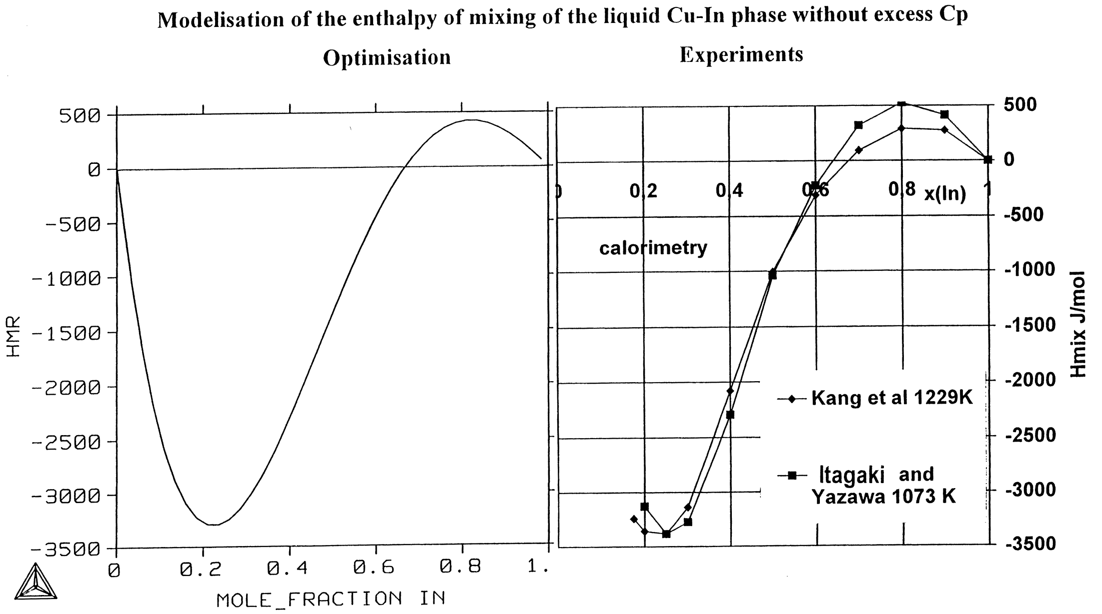


Fig. 6. Modelisation of the enthalpy of mixing of the Cu–In liquid phase without excess heat capacity. Comparison with two different experimental results [13,15].

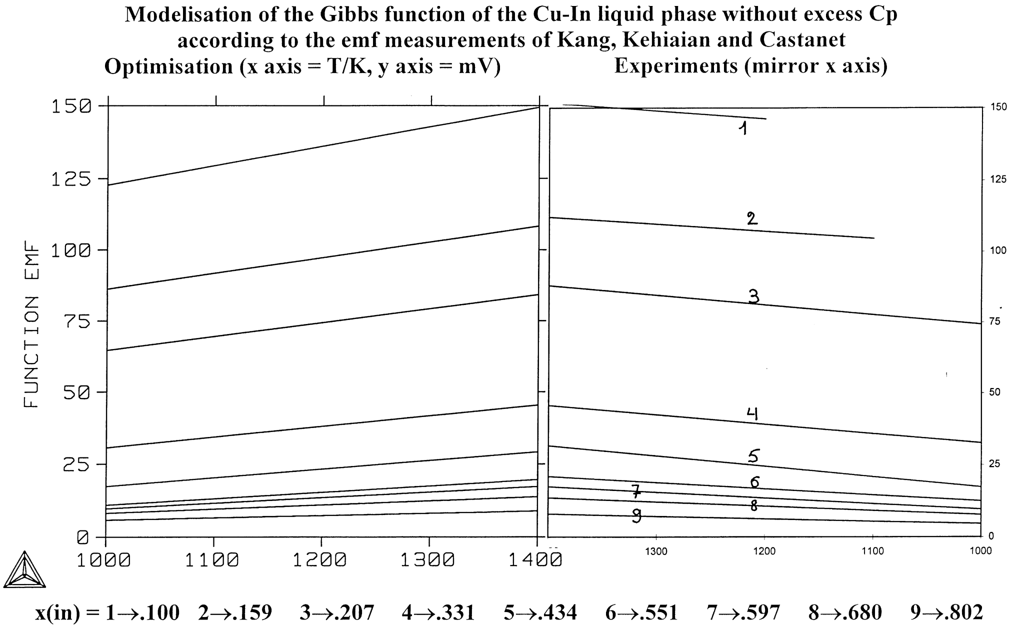


Fig. 7. A Thermo-Calc optimisation without excess Cp based on the e.m.f. measurements of both Kang et al. [14] and Azakami and Yasawa [16]. The e.m.f. value is proportional to the indium chemical potential in the Cu–In liquid phase. Comparison, (as in a mirror), between the model and the experimental results [14].

−8520 J/mol and for the η phase ($x_{In}=0.39$) Kleppa found −7531 J/mol whereas the modelisation gave −6540 J/mol.

4.1.3. Cu–Sn

Kleppa studied this system during the first period of his work in 1956 [5,18], using his isoperibolic calorimeter. He established the first data concerning the enthalpy of formation of the solid α, δ and ε phases by tin calorimetry at 450°C and the enthalpy of mixing of the liquid for $x_{Sn}>0.84$. A first Thermo-Calc optimisation was published in 1996 by Shim et al. [19], after some tests we accepted

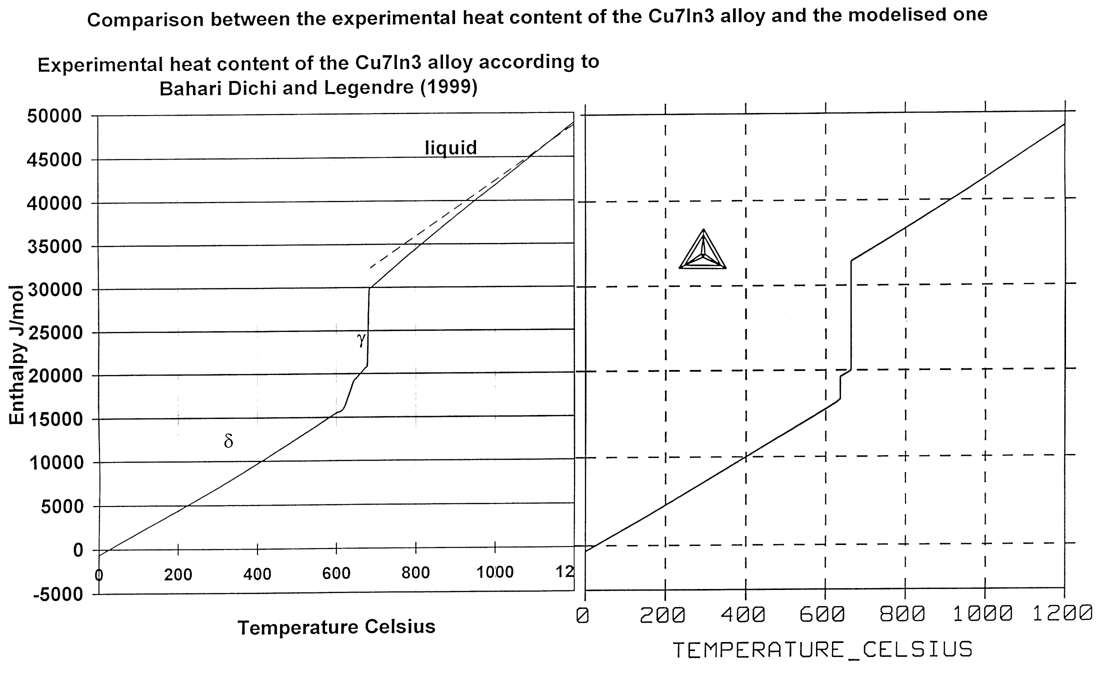


Fig. 8. Molar heat content of the Cu_7In_3 alloy according to the Cp measurements of Bahari et al. [17]. Comparison with our Thermo-Calc model neglecting the excess Cp in the liquid phase: the total disordering enthalpy of the liquid phase is added to the melting enthalpy of the γ phase.

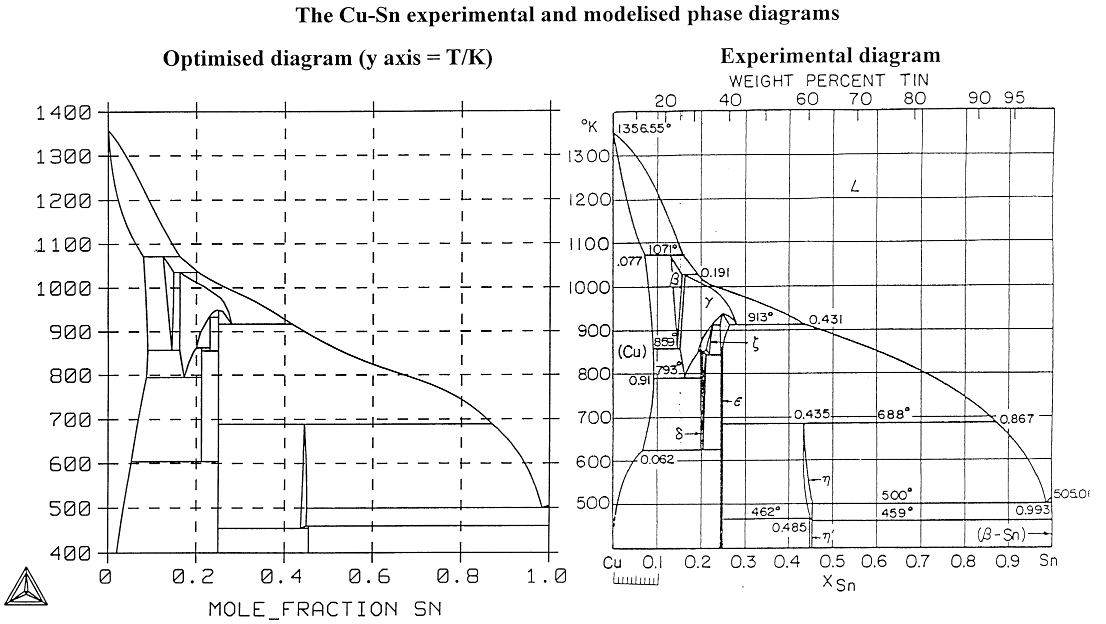


Fig. 9. Comparison (on the same scale) between our modelised Cu–Sn phase diagram and the experimental diagram according to Hultgren et al. [12]. The Gibbs functions of the liquid, α and β phases are those of Shim et al [19], all the other phases are changed.

their modelisation for the liquid, α and β phases. But we modified the other solid phases, in particular our Cu–Sn–η phase is isomorphic of the Cu–In–η phase and gives a complete ternary solubility. For our optimisation we used the critical compilation of Saunders and Miodownik [20]. Fig. 9 is the comparison between our calculated phase diagram and the experimental original diagram of Raynor [21] taken in the Hultgren et al. compilation [12]. The consistency between the optimised enthalpy of formation of the Cu_3Sn–ε phase and the Kleppa measurement is 2%.

4.1.4. Cu–Zn

This binary was modelised in 1993 by Kowalski and Spencer [22] and introduced in the Thermo-Calc SSOL databank. More recently Liang and Chang [23] optimised the Al–Cu–Zn ternary system. To allow the ternary modelisation of the γ-brass phase, they simplified the γ-model of Kowalski and Spencer (a four sublattices model) and chose a disordered single sublattice model. The same problem appeared in our multicomponent system and we adopted the γ disordered model of Liang and Chang.

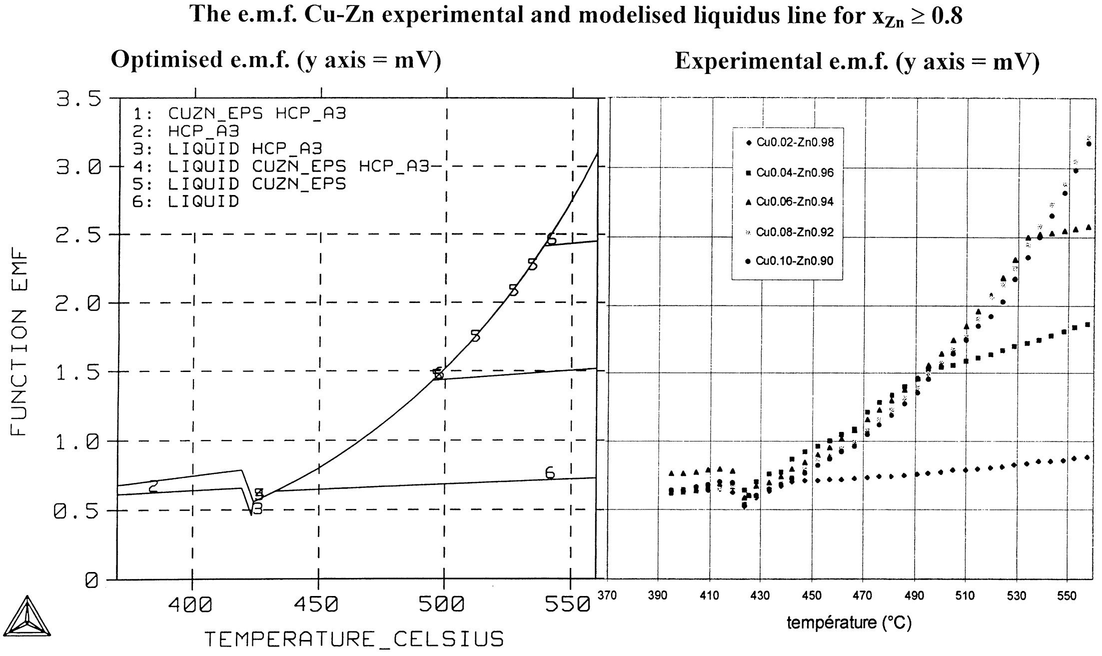


Fig. 10. An e.m.f. accurate determination of the Cu–Zn liquidus line for $x_{Zn} \geq 0.90$: experimental and new Thermo-Calc modelisation.

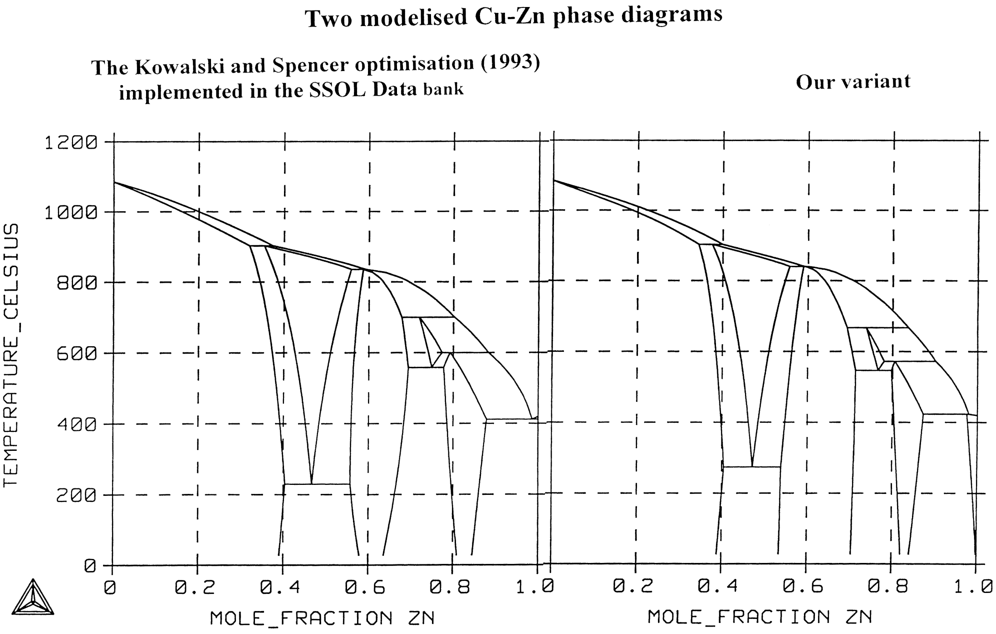


Fig. 11. Comparison between the Kowalski and Spencer [22] Cu–Zn Thermo-Calc phase diagram and our new variant.

We observed that the liquidus line in the high Zn content area was not completely true. For this reason we modified the three ε, zinc and liquid phases in this region. We undertook an accurate e.m.f. study with the following alloys, $Cu_{10}Zn_{90}$, Cu_8Zn_{92}, Cu_6Zn_{94}, Cu_4Zn_{96} and Cu_2Zn_{98}. It should be noticed that, (in the first period of the Kleppa work), Kleppa and Thalmayer [24] also studied the Cu–Zn liquid phase for $0.8 \leq x_{Zn} \leq 0.92$ by e.m.f. Our own study is situated in continuity with this study, at higher zinc content. Fig. 10 is the comparison between our experimental results and our new model. In this optimisation we also detected an excess Cp in the liquid phase at low temperature (450–550°C), but it was easier to modelise the liquid phase without excess Cp. Fig. 11 is a comparison between the diagram of this new modelisation and those of Kowalski and Spencer.

4.1.5. In–Sn

A first complete Thermo-Calc optimisation of this system was published in 1996 by Lee et al. [25]. Unfortunately the indium activity measurements taken into account in this optimisation were those of Terpilowski and Przezdzieka-Mycielska [26], which were at variance with the recent accurate e.m.f. study of Vassiliev et al. [27], concerning nine alloys $0.20 \leq x_{Sn} \leq 0.95$. For this reason we undertook a new optimisation of this binary in 1999 [28]. The enthalpy of mixing of the liquid phase was measured by different authors but Kleppa was the first one in 1956 [18]. All the enthalpy results are consistent with an accuracy of ±25 J/mol. With the new model the indium chemical potentials measured by Vassiliev et al. were restituted with an average accuracy of ±90 J/mol for all the alloys (Fig. 12). The new phase diagram was identical to the Lee et al. phase diagram (Fig. 13) but the thermodynamic functions of all the phases of the system were something different.

4.1.6. Pb–Zn

This system was the most difficult system to optimise while it exhibited a strange shape miscibility gap up to 800°C in the liquid domain. For this reason the literature data concerning the mixing enthalpy of the liquid is completely inconsistent: Fig. 14 gives an idea of the various results it is possible to find in the literature. In fact at low temperature the liquid is biphased and at high temperature the vapor pressure of zinc is too high to allow easy experiments. To obtain a reliable evaluation of this mixing enthalpy we decided to study two ternary liquid

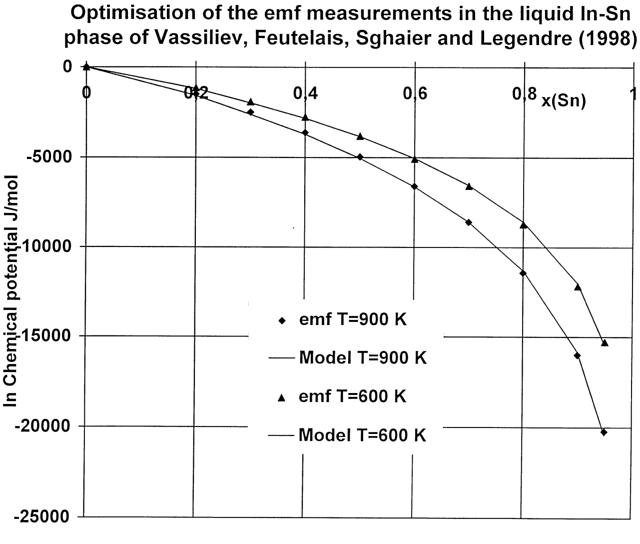


Fig. 12. New Thermo-Calc optimisation of the In–Sn liquid phase according to the e.m.f. study of Vassiliev et al. [27].

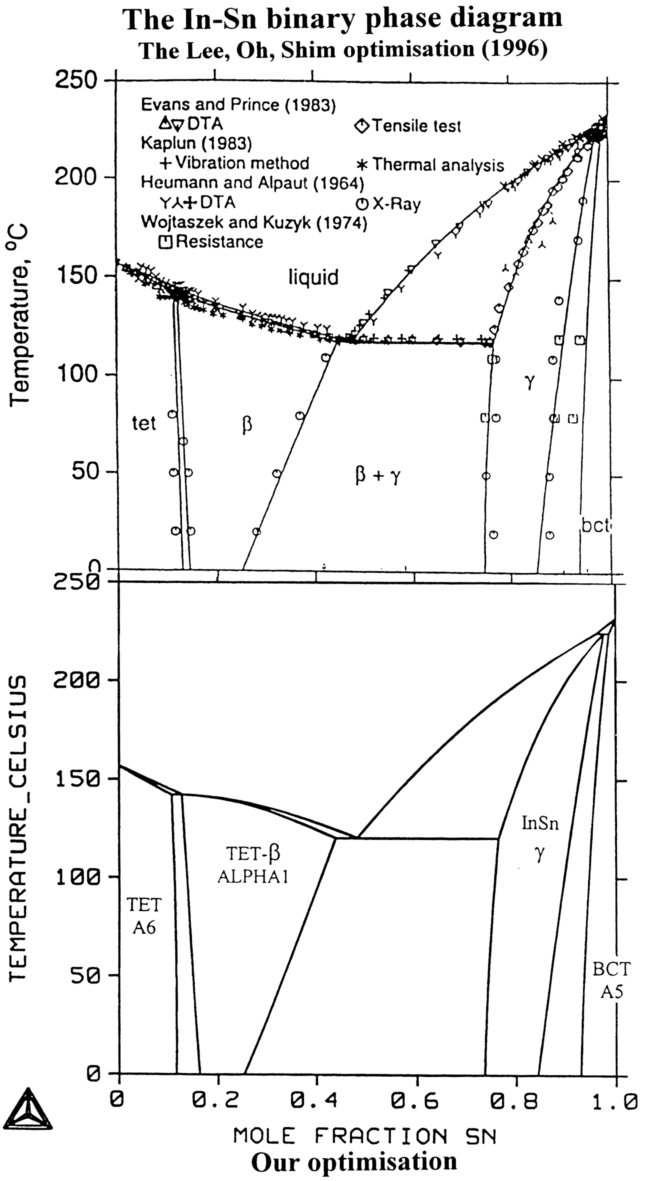


Fig. 13. Comparison between the Lee et al. [25] In–Sn Thermo-Calc phase diagram established with the e.m.f. measurements of Terpilowski and Przedzieka-Mycielska [26] and our variant based on the e.m.f. study of Vassiliev et al. [27].

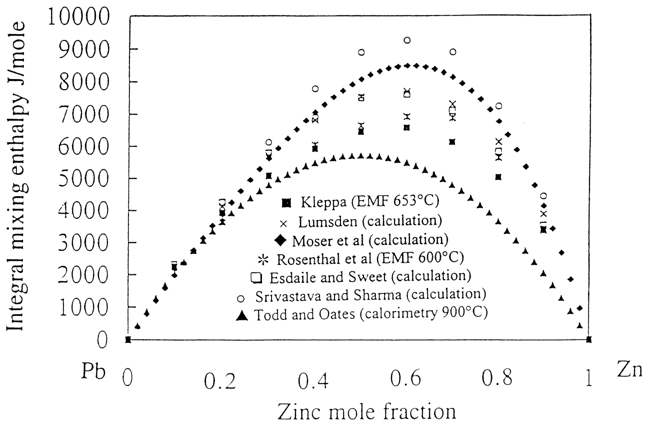
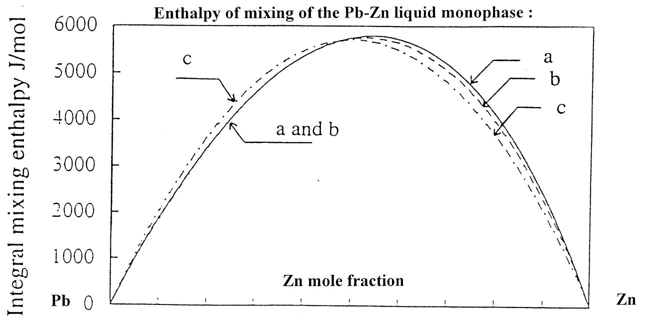


Fig. 14. Enthalpy of mixing of the Pb–Zn liquid phase: a survey of the extremely scattered literature.

phases linked by the same Pb–Zn binary border: we chose the In–Pb–Zn and the Pb–Sn–Zn systems. It was possible to obtain reliable ternary enthalpies by calorimetry outside the miscibility gap at 480°C and to modelise the liquid phase. An extrapolation of the formula up to the Pb–Zn binary gave two independent evaluations of the binary mixing enthalpy. The two results we got were surprisingly close [29,30]. Fig. 15 is a comparison between our two Pb–Zn mixing enthalpy evaluations. Our evaluation also proves that the regular enthalpy model of Todd and Oates [31], was almost right. It was obtained from drop calorimetry of demixed solid, taken at room temperature, and heated in the cell of the calorimeter up to the liquid monophase at 900°C. In fact the maximum enthalpy is shifted close to $x_{Zn} = 0.55$. During these two studies we observed a very nice consistency of our own results for the In–Zn and Pb–Zn mixing enthalpy with the Kleppa results obtained during the first period of his work [32,33]: for these two systems the difference between Kleppa's and ours was less than ±50 J/mol (the maximum enthalpy is about 3000 J/mol).

Our Thermo-Calc optimisation of this binary was based on this mixing enthalpy, together with the activity measurements by e.m.f. of Kleppa [34] and those of Rosenthal et al. [35], and the miscibility gap phase diagram obtained by Trahan and Lacy [36] and also by Esdaile and Sweet [37]. Fig. 16 shows that the optimisation of all these data gives a final enthalpy of mixing hardly different for the



a) extrapolation of our calorimetric measurements (outside the miscilbility gap) in the ternary Pb-Sn-Zn system at 444 °C
b) extrapolation of our calorimetric measurements (outside the miscilbility gap) in the ternary In-Pb -Zn system at 483 °C
c) Todd and Oates drop calorimetry (1964)
from solid demixed phases at room temperature to monophase liquid at 900°C

Fig. 15. Enthalpy of mixing of the Pb–Zn liquid phase: extrapolation of our calorimetric measurements obtained outside the miscibility gap in the ternary Pb–Sn–Zn system at 444°C (curve a) and in the ternary In–Pb–Zn system at 480°C (curve b). The calorimetric results of Todd and Oates [31] (curve c) obtained by dropping demixed solid phases taken at room temperature in the calorimeter cell at 900°C are consistent with our extrapolations.

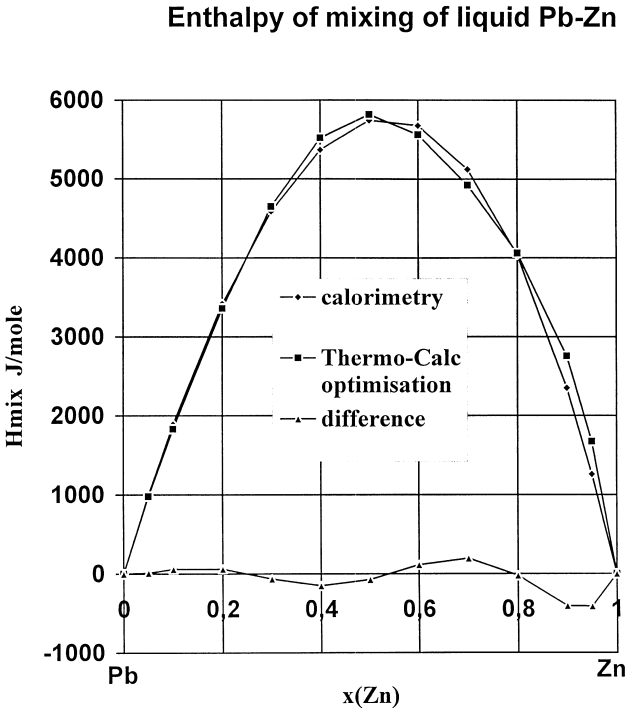


Fig. 16. Enthalpy of mixing of the Pb–Zn liquid phase: after the complete Thermo-Calc optimisation of the phase diagram the calculated enthalpy is hardly different from the experimental result in the zinc rich part.

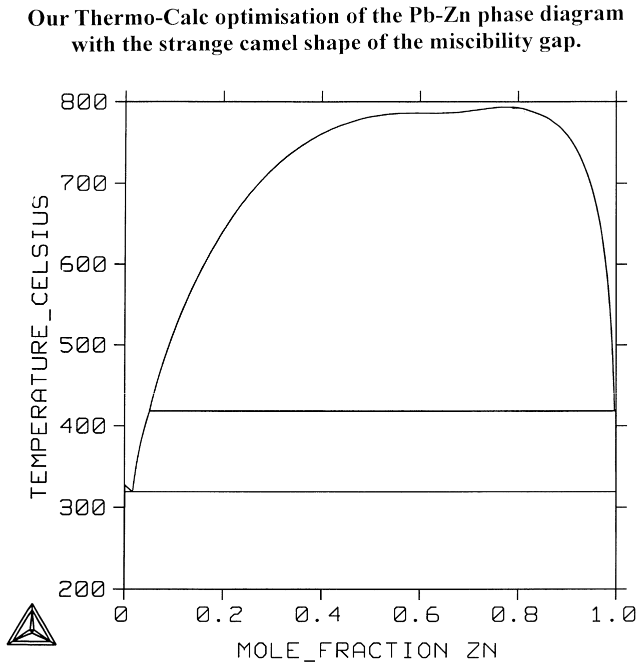


Fig. 17. Our new Pb–Zn phase diagram Thermo-Calc optimisation with its strange camel shape.

highest zinc content. On the other hand the miscibility gap we got (Fig. 17) exhibits a camel shape, not far from a double maximum (with two different critical compositions). This shape has to be compared (Fig. 18) to the more recent study of Okajima et al. [38] by e.m.f. It will be noticed that the existence of two different critical points will give an invariant plateau with three different binary

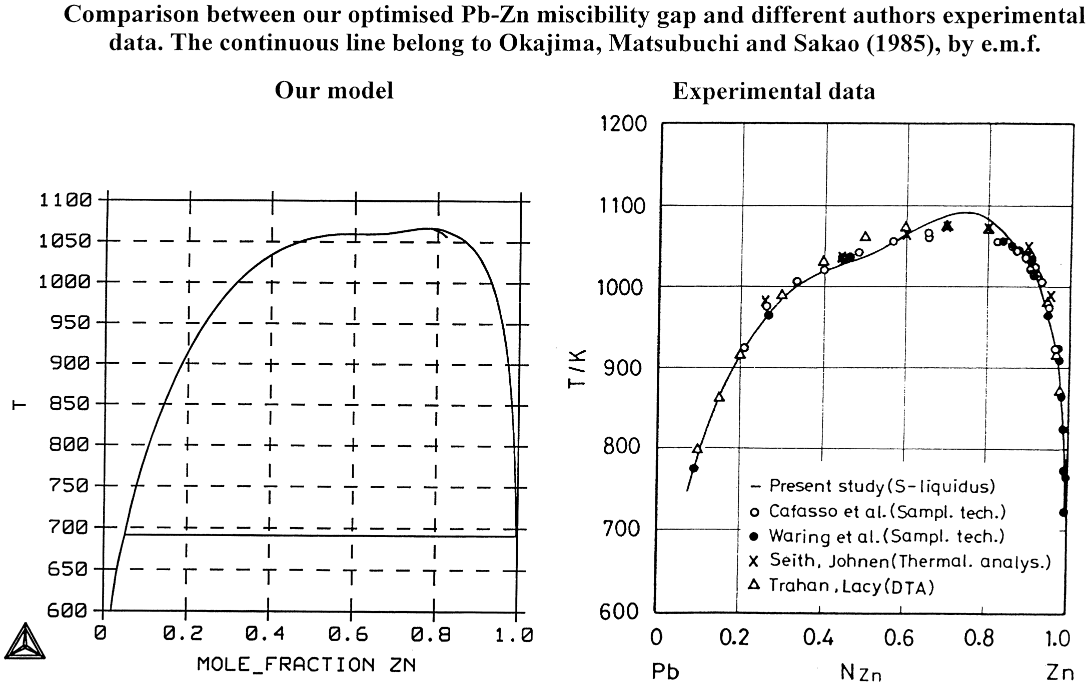


Fig. 18. Comparison between our Pb–Zn calculated phase diagram and the main literature experimental data according to Okajima et al. [38] (continuous line).

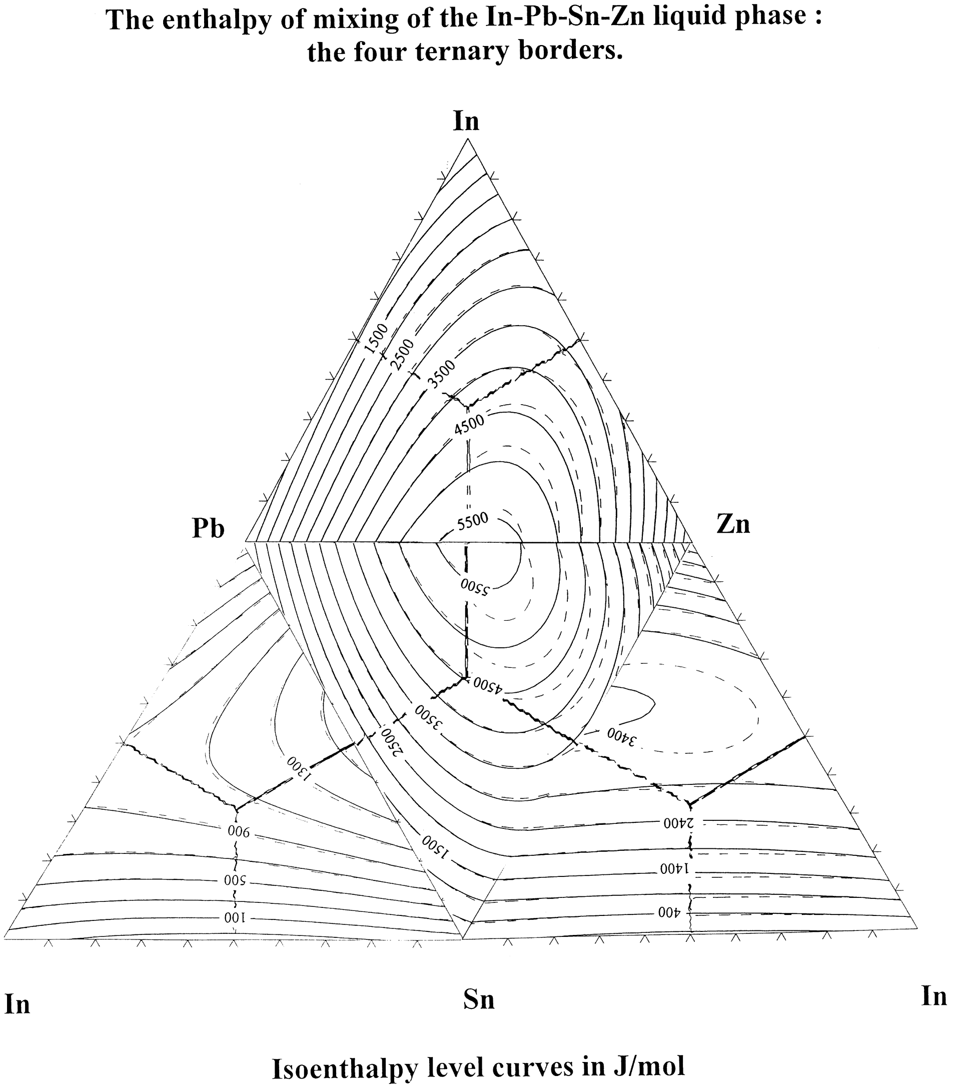


Fig. 19. Enthalpy of mixing of the In–Pb–Sn–Zn liquid phase: the four ternary borders obtained by drop calorimetry [39]. The continuous lines are the Redlich-Kister model and the dotted lines the Darken model.

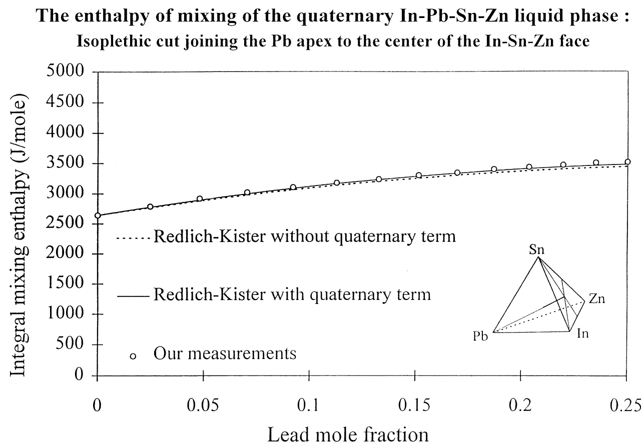


Fig. 20. Enthalpy of mixing of the In–Pb–Sn–Zn liquid phase: isoplethic cut joining the Pb apex to the center of the In–Sn–Zn face. No quaternary term is needed in the Redlich-Kister model considering the estimated experimental uncertainty ±200 J/mol.

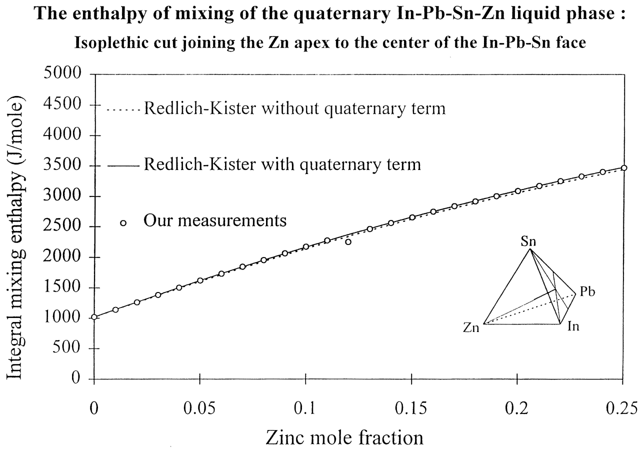


Fig. 21. Enthalpy of mixing of the In–Pb–Sn–Zn liquid phase: isoplethic cut joining the Zn apex to the center of the In–Pb–Sn face. No quaternary term is needed in the Redlich-Kister model considering the estimated experimental uncertainty ±200 J/mol.

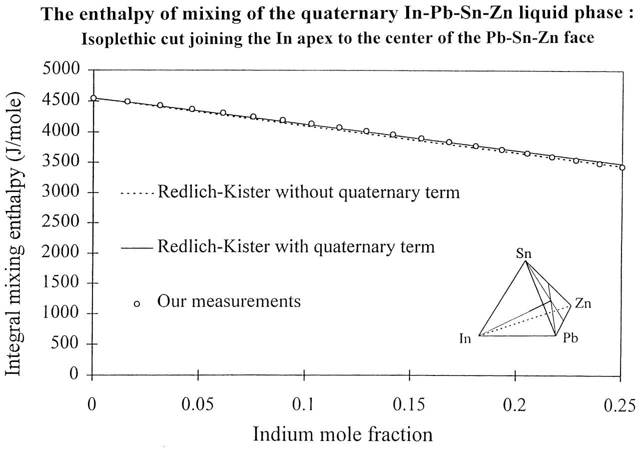


Fig. 22. Enthalpy of mixing of the In–Pb–Sn–Zn liquid phase: isoplethic cut joining the In apex to the center of the Pb–Sn–Zn face. No quaternary term is needed in the Redlich-Kister model considering the estimated experimental uncertainty ±200 J/mol.

liquids in equilibrium. This binary Pb–Zn system is not far from this surprising situation.

4.2. The ternary and quaternary sub-systems

A five components system generates 10 ternary subsystems. In the present case:

Cu–In–Pb Cu–In–Sn Cu–In–Zn Cu–Pb–Sn Cu–Pb–Zn Cu–Sn–Zn In–Pb–Sn In–Pb–Zn In–Sn–Zn Pb–Sn–Zn.

It is more difficult to find good thermodynamic data in the literature for ternary systems. Nevertheless the ternary term in the Redlich-Kister model still remains a relatively small part of the total excess Gibbs function. This is the exact answer when the three binary borders functions are three regular solutions. This is also approximately true when the three binary interactions are close to regular interactions or when they are all repulsive, which means that no ternary cluster may be expected. The ternary term becomes very significant when two or three binary border interactions are attractive as in Cu–Sn–Zn or Cu–In–Zn.

In the following paragraphs we'll give a quick survey of the quaternary In–Pb–Sn–Zn phase diagram and of some copper ternaries for which some literature data are available for comparison.

4.2.1. In–Pb–Sn–Zn

For the four ternary liquid phases generated by the components In, Pb, Sn, Zn we made our own complete calorimetric study [29,30,39], even the quaternary system was investigated [39] proving that an accurate optimisation can be obtained without any quaternary term. Fig. 19 summarizes the results we got in the four ternary borders. Figs. 20–22 show the three quaternary isoplethic cuts joining one of the In, Pb or Zn apex to the center of the opposite ternary face: considering the experimental uncertainty (≈ ±200 J/mol) the ternary modelisation is accurate enough to modelise the mixing enthalpy.

Fiorani and Oleari [40] have studied the Pb–Sn–Zn liquid phase by the e.m.f. method, we have also explored an area of this ternary by the same method when finding some incompatibilities in their data. Moser and Fitzner

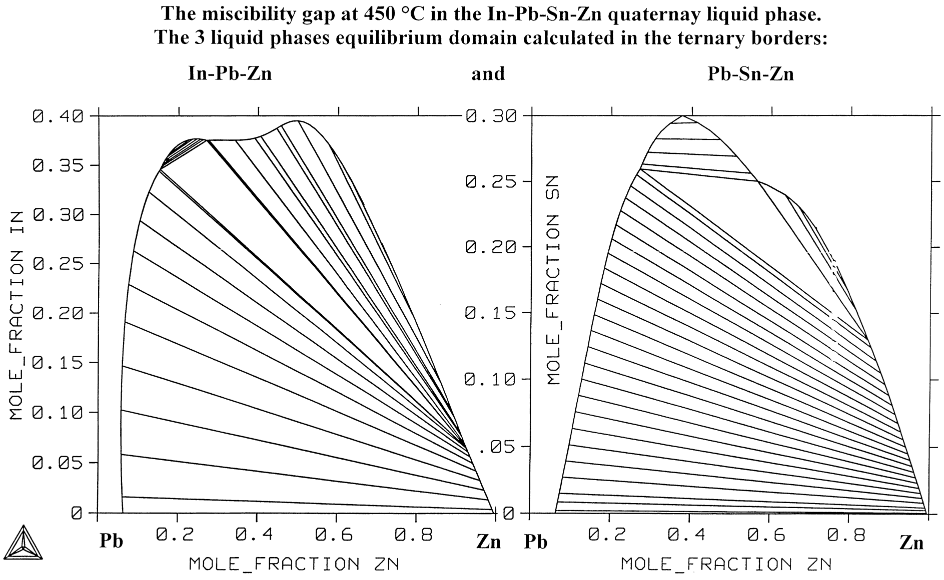


Fig. 23. The calculated miscibility gap in the In–Pb–Sn–Zn liquid phase: the two Pb–Sn–Zn and In–Pb–Zn ternary borders. According to the model there should exist a three liquid phases equilibrium domain. In fact we have no direct experimental proof of this strange phase diagram.

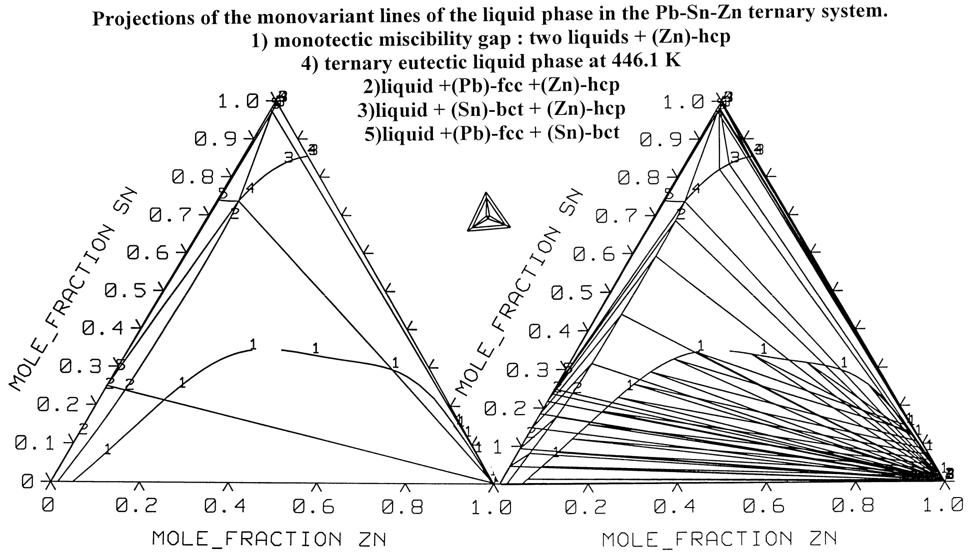


Fig. 24. Projections of the monovariant lines of the liquid phase calculated in the Pb–Sn–Zn ternary system: (1) monotectic miscibility gap: two liquids+(Zn)-hcp; (2) liquid +(Pb)-fcc +(Zn)-hcp; (3) liquid+(Sn)-bct+(Zn)-hcp; (4) ternary eutectic liquid phase at 446.1 K; (5) liquid +(Pb)-fcc+(Sn)-bct. The eutectic lines are consistent with the experimental study of Levi-Malvano and Ceccarelli [42].

[41] have studied the In–Pb–Zn system by the e.m.f. method and we have also realised some e.m.f. measurements in this ternary. Finally we also studied 19 quaternary In–Pb–Sn–Zn compositions by e.m.f. to measure the zinc activities and to determine some quaternary points on the miscibility gap hypersurface. The ternary border sub-systems and the quaternary liquid phase were optimised (without quaternary term), taking into account all these data. It was very surprising to find that the camel-shape of the Pb–Zn miscibility gap was more pronounced in the multicomponent system. Fig. 23 is a calculation of the ternary Pb–Sn–Zn and Pb–In–Zn miscibility gaps at 450°C where a large three liquid equilibrium domain was found, generating two different critical compositions. There is not yet any experimental proof of such coexistence of three metallic phases in these ternaries and in the quaternary. To our knowledge such situations are unheard of in metallic systems, but have been well observed in

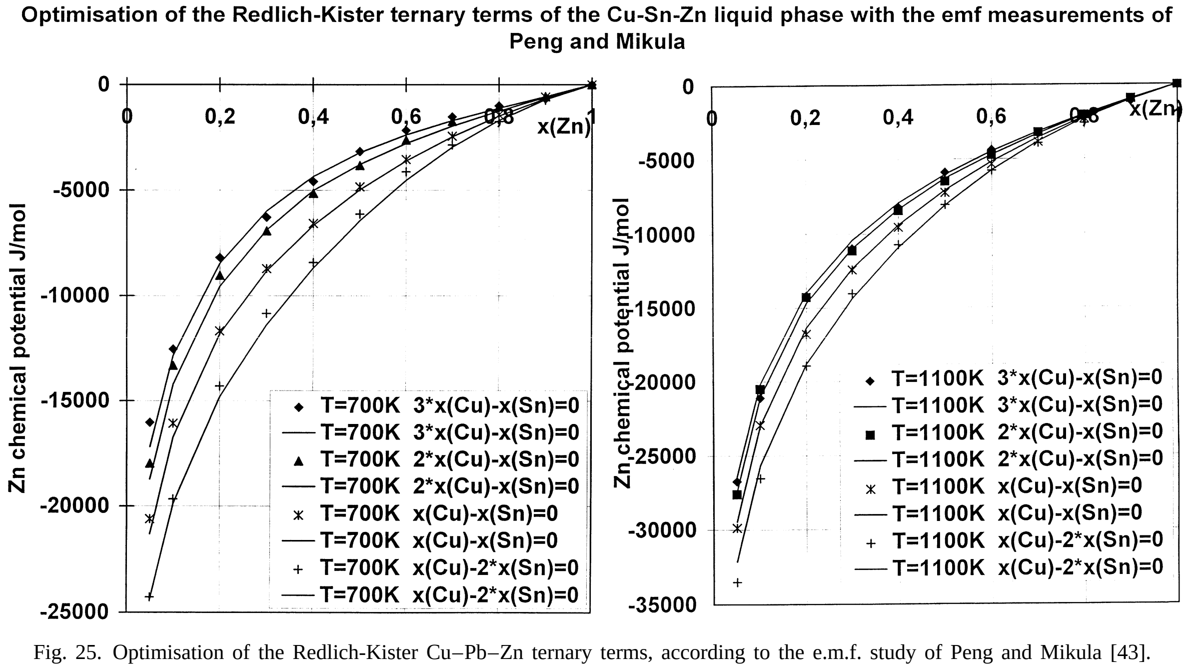
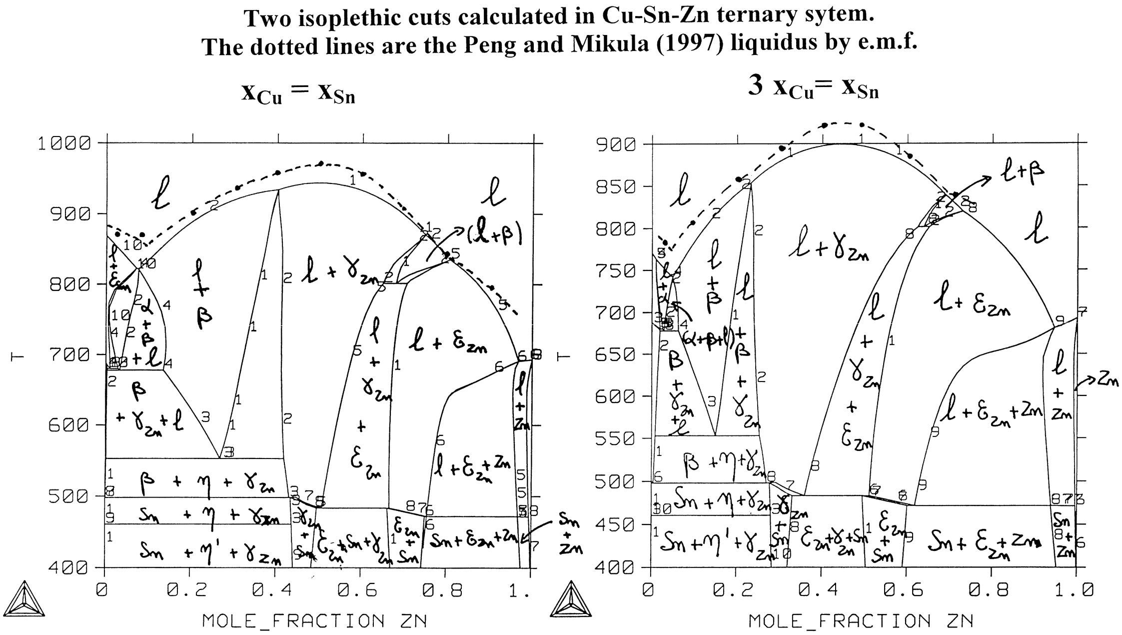


Fig. 25. Optimisation of the Redlich-Kister Cu–Pb–Zn ternary terms, according to the e.m.f. study of Peng and Mikula [43].



Two isoplethic cuts calculated in Cu-Sn-Zn ternary sytem.
The dotted lines are the Peng and Mikula (1997) liquidus by e.m.f.

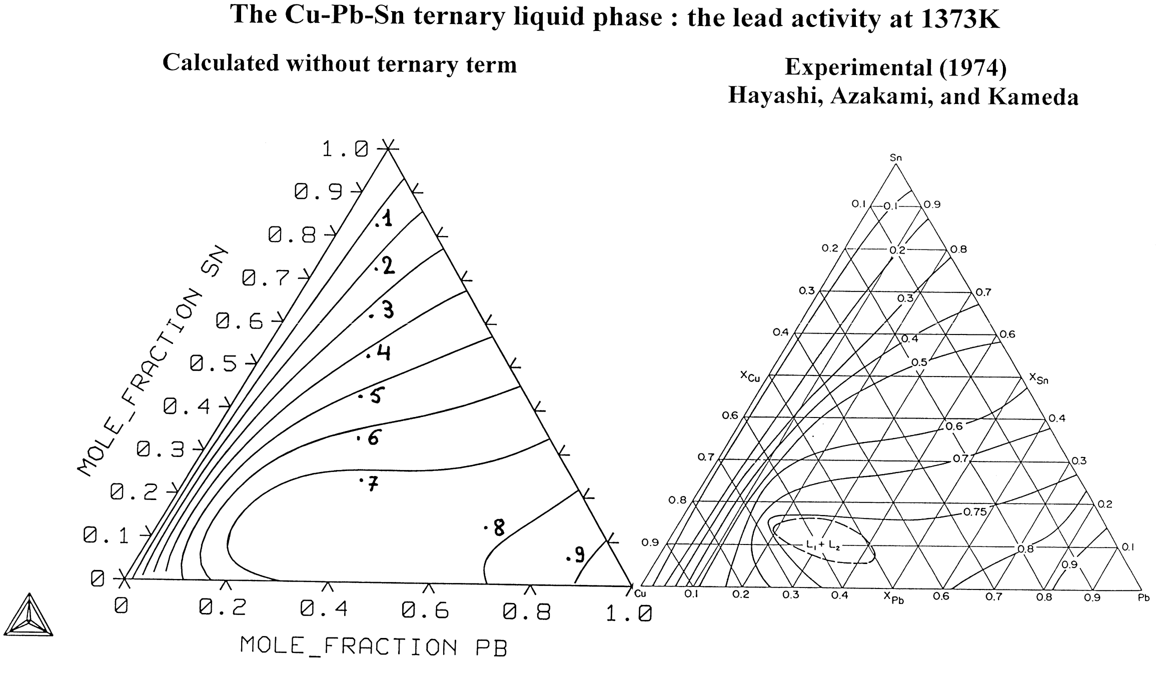
$x_{Cu} = x_{Sn}$ $3\,x_{Cu} = x_{Sn}$

Fig. 26. Two isoplethic cuts calculated in Cu–Sn–Zn ternary system. The dotted lines are the Peng and Mikula [43] ternary liquidus by e.m.f.

hydro-organic mixtures like $CH_3OH/H_2O/CO_2$ at high pressure. Fig. 24 is the complete projection of the monovariant lines generated by the liquid phase in the Pb–Sn–Zn system, exhibiting an eutectic ternary invariant (consistent with the experimental observations of Levi-Malvano and Ceccarelli [42]) and a monotectic miscibility gap showing two liquids in equilibrium with the zinc solid phase.

4.2.2. Cu–Sn–Zn

The thermodynamic functions of mixing of the Cu–Sn–Zn liquid phase were well established in 1997 by Peng and



The Cu-Pb-Sn ternary liquid phase : the lead activity at 1373K

Calculated without ternary term

Experimental (1974)
Hayashi, Azakami, and Kameda

Fig. 27. the lead isoactivity curves in the Cu–Pb–Sn liquid phase calculated at 1373 K without ternary term. Comparison with the experimental results of Hayashi et al. [46].

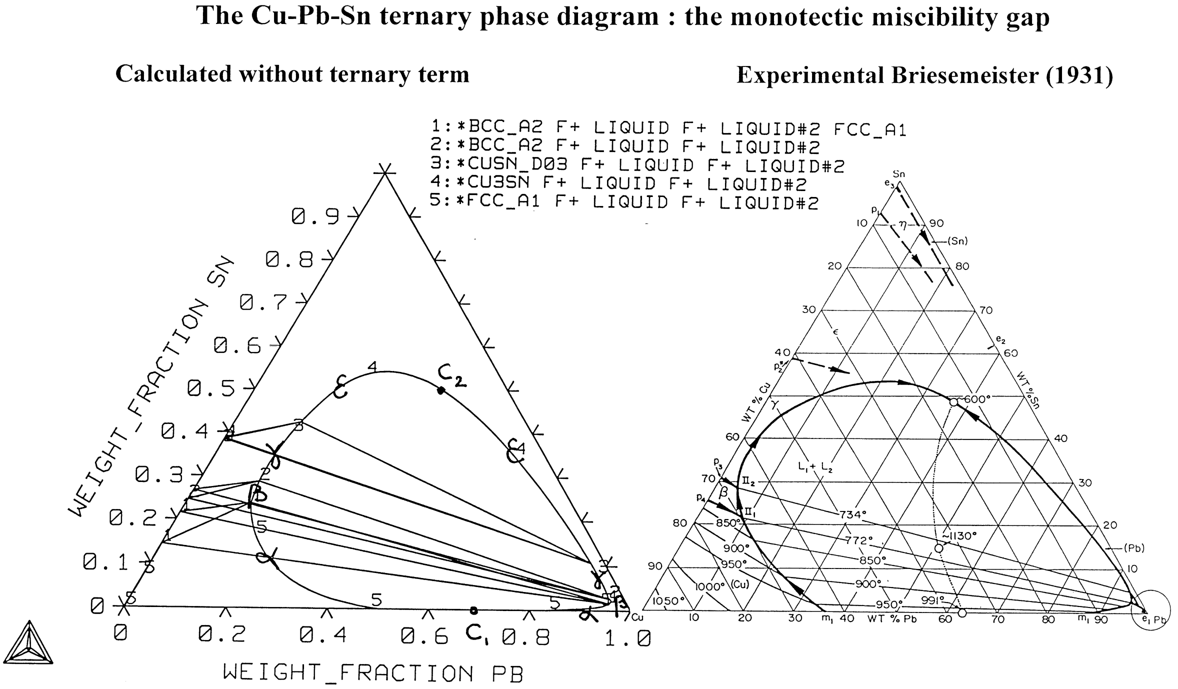


Fig. 28. The monotectic Cu–Pb–Sn line calculated without ternary term. Comparison with the experimental Briesemeister's phase diagram [44].

Mikula by the e.m.f. method [43]. Using three ternary Redlich-Kister coefficients it was easy to modelise this liquid phase: Fig. 25 shows the consistency between the measured zinc chemical potential at 1100 K and 700 K (by extrapolation) and the calculated ones. Fig. 26 is the calculated phase diagrams in the two isoplethic cuts $x_{Cu} = x_{Sn}$ and $2x_{Cu} = x_{Sn}$ together with the experimental liquidus points measured by Peng and Mikula: the solid phases were not optimised, nevertheless the discrepancy on the liquidus surface is less than 20°C.

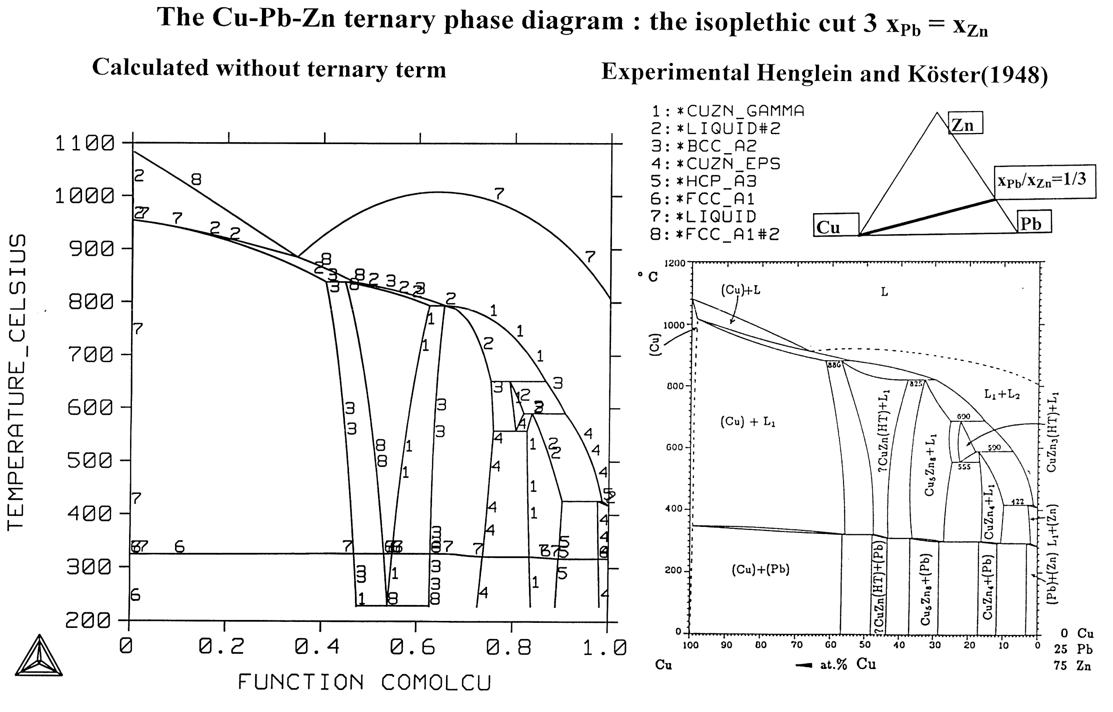
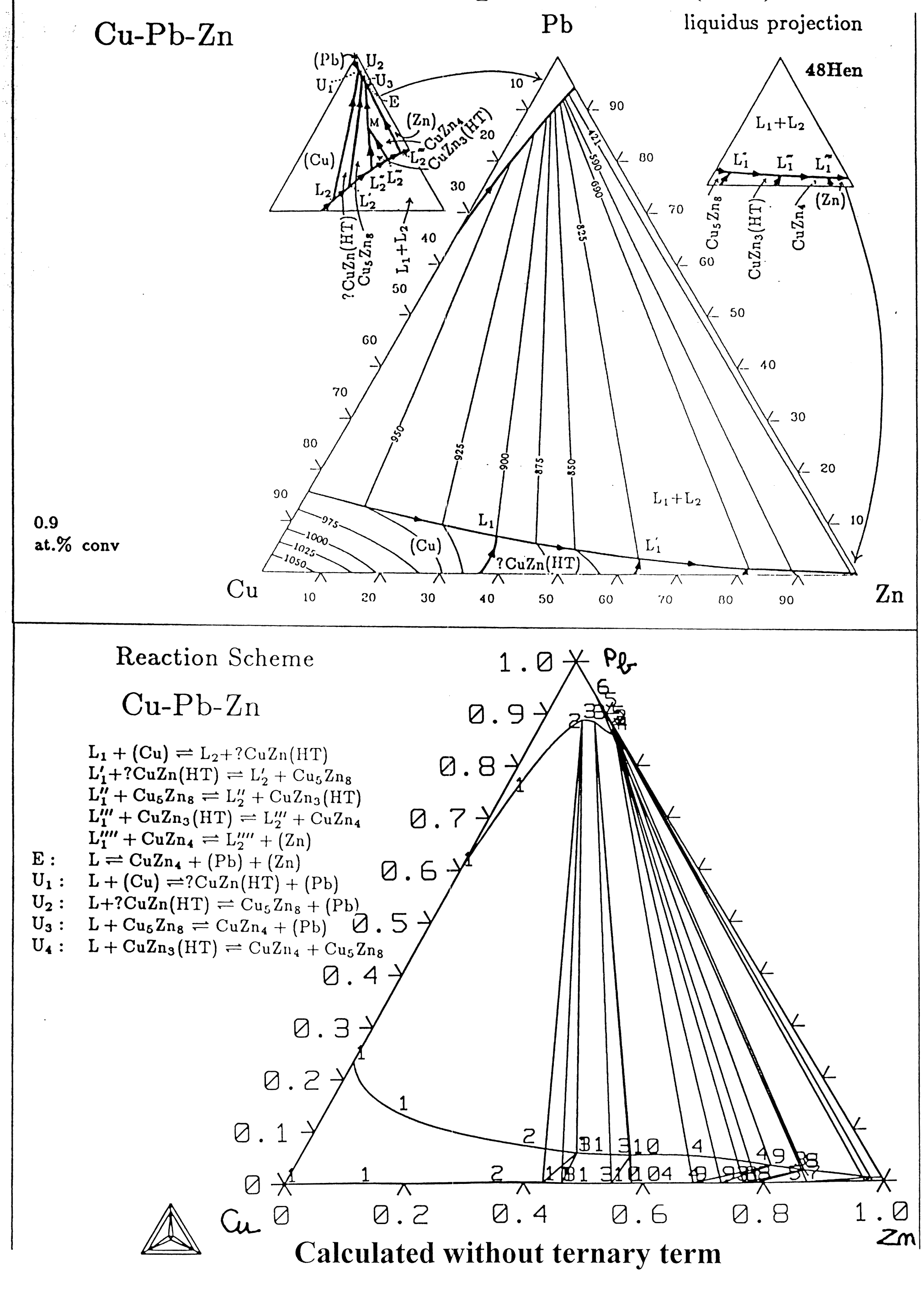


Fig. 29. The isoplethic cut $x_{Zn} = 3x_{Pb}$ calculated without ternary term in the Cu–Pb–Zn phase diagram. Comparison with the experimental result of Henglein and Köster [47]. The thermodynamic mistake in the liquidus slopes drawn by Henglein and Köster at 825°C is corrected by the model.

Projections of the monovariant lines with liquid in the Cu-Pb-Zn ternary phase diagram

Experimental Henglein and Köster(1948)



Reaction Scheme

Cu-Pb-Zn

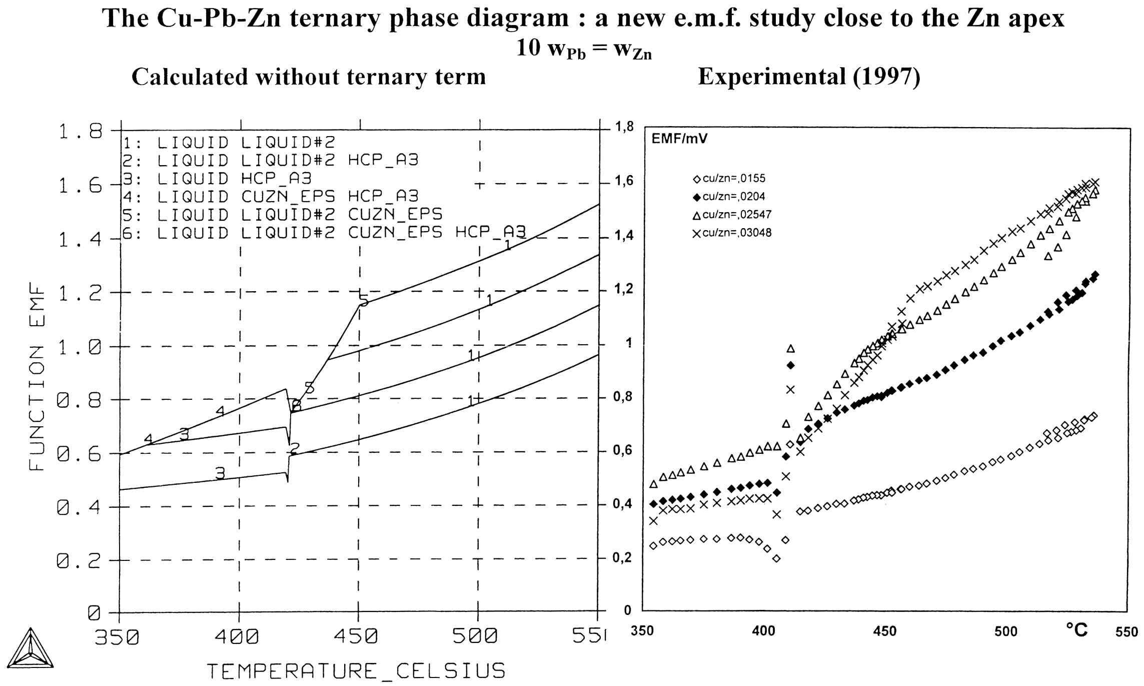
$L_1 + (Cu) \rightleftharpoons L_2 + ?CuZn(HT)$
$L_1' + ?CuZn(HT) \rightleftharpoons L_2' + Cu_5Zn_8$
$L_1'' + Cu_5Zn_8 \rightleftharpoons L_2'' + CuZn_3(HT)$
$L_1''' + CuZn_3(HT) \rightleftharpoons L_2''' + CuZn_4$
$L_1'''' + CuZn_4 \rightleftharpoons L_2'''' + (Zn)$
E : $L \rightleftharpoons CuZn_4 + (Pb) + (Zn)$
U_1 : $L + (Cu) \rightleftharpoons ?CuZn(HT) + (Pb)$
U_2 : $L + ?CuZn(HT) \rightleftharpoons Cu_5Zn_8 + (Pb)$
U_3 : $L + Cu_5Zn_8 \rightleftharpoons CuZn_4 + (Pb)$
U_4 : $L + CuZn_3(HT) \rightleftharpoons CuZn_4 + Cu_5Zn_8$

Calculated without ternary term

Fig. 30. Projection of the monotectic curves of the two liquid phases in the Cu–Pb–Zn phase diagram: calculation without ternary term and experimental phase diagram according to Henglein and Köster [47].

4.2.3. Cu–Pb–Sn

The ternary phase diagram was studied by Briesemeister in 1931 [44], and more recently the lead activity of the liquid phase was measured by Azakami [45] and by Hayashi et al. [46]. Two binary interactions in this system are repulsive and consequently the ternary interactions are weak. We have neglected the ternary terms and Fig. 27 shows the consistency between the experimental lead


The Cu-Pb-Zn ternary phase diagram : a new e.m.f. study close to the Zn apex

$10\ w_{Pb} = w_{Zn}$

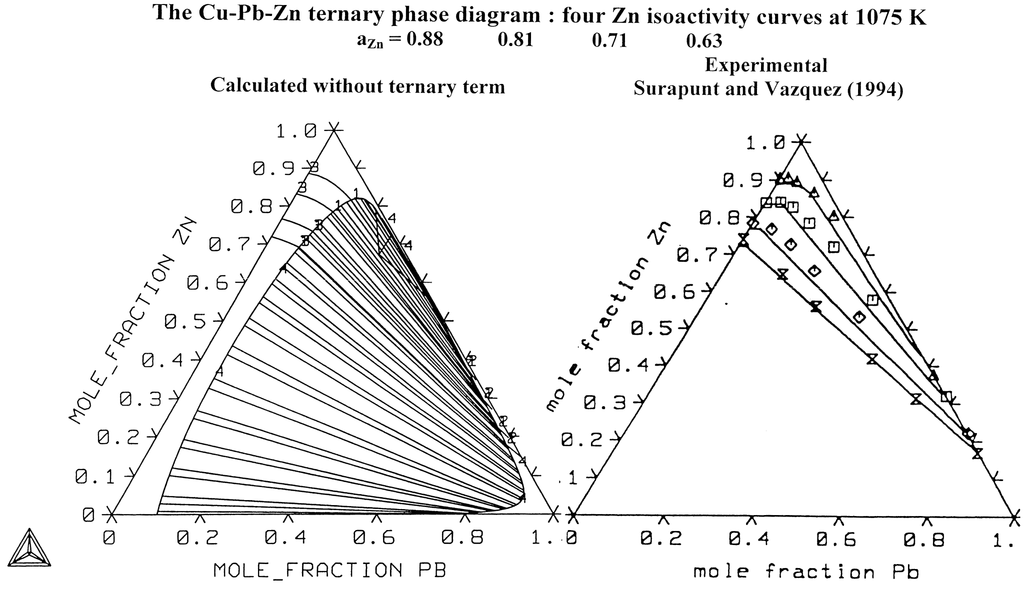
Calculated without ternary term **Experimental (1997)**

Fig. 31. Experimental e.m.f. study of the Cu–Pb–Zn liquid phase in the zinc rich part: the model is calculated without ternary term.

activities and the calculated ones at 1373 K. Fig. 28 is a comparison between the monotectic ternary miscibility gap (two liquids + one solid phase) calculated by the model and the experimental Briesemeister proposal, which are very close.

4.2.4. *Cu–Pb–Zn*

The ternary phase diagram was studied by Henglein and Köster in 1948 [47]. In this system also two binary interactions are repulsive and the ternary terms are weak. Fig. 29 compares the isoplethic cut $x_{Pb}/x_{Zn} = 1/3$ obtained by Henglein and Köster to our calculation (obtained without any ternary term): the consistency is rather good and the calculated phase diagram avoids the wrong shape of the liquidus line proposed by Henglein and Köster at the peritectic (liquid $+\beta+\gamma$) equilibrium. Fig. 30 is the projection of the monotectic lines calculated and compared to the experimental proposal. We have also, studied the


The Cu-Pb-Zn ternary phase diagram : four Zn isoactivity curves at 1075 K

$a_{Zn} = 0.88$ 0.81 0.71 0.63

Calculated without ternary term **Experimental Surapunt and Vazquez (1994)**

Fig. 32. Comparison between the experimental results of Surapunt and Vazquez [48] and the isoactivity curves calculated in the Cu–Pb–Zn ternary system at 1075 K.

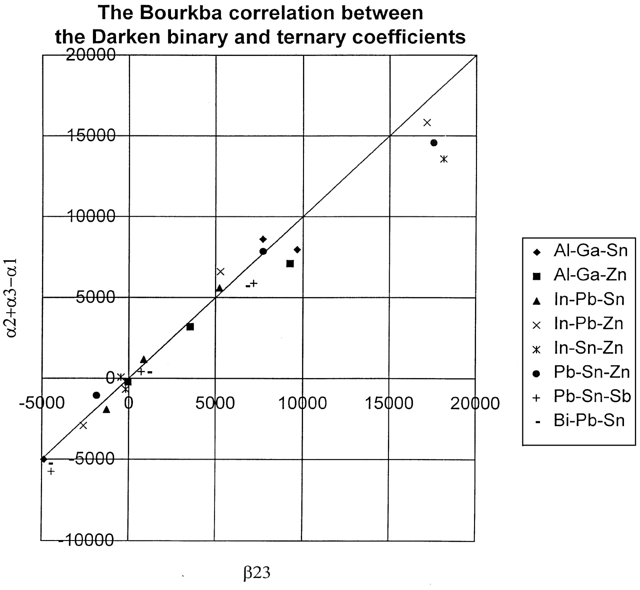


Fig. 33. An experimental correlation established by Bourkba [50] between the ternary and the binary interaction coefficients of the Darken model [49].

high-rich zinc part of this system by the e.m.f. method: Fig. 31 shows the good answer of the model by comparison to the experimental values. Fig. 32 is a comparison between four Zn isoactivity curves calculated at 1075 K without ternary terms and the experimental data of Surapunt and Vazquez [48]: the consistency is excellent.

5. Evaluation of the ternary terms when no experimental ternary data is available

When no ternary thermodynamic data is available, as actually in the Cu–In–Zn system it is also possible to use the Darken ternary dilute model [49], to obtain a reasonable evaluation of the ternary term. The Darken dilute solution equation is written (when 2 and 3 are the two solutes and 1 is the solvent):

$$G^{\text{exs}} = x_2RT\ \ln(\gamma_2) + x_3RT\ \ln(\gamma_2) - (\alpha_2x_2^2 + \alpha_3x_3^3 + 2\beta_{23}x_2x_3)$$

α_2 and α_3 are the binary Darken functions of the solutes 2 and 3 in solvent 1. According to Darken the β_{23} coefficient can be written $2\beta_{23} = \alpha_2 + \alpha_3 - \alpha_1$ where α_1 is the Darken binary function of an hypothetical 2–3 system. In fact Bourkba [50] established that the α_1, α_2 and α_3 terms could simply be considered as the binary regular terms of the Redlich-Kister developments in the 2–3, 3–1 and 1–2 systems respectively. The Bourkba formula is linked to the first neighbour Bragg-Williams statistical model. Fig. 33 shows this empirical correlation obtained with 8 ternary systems generating 24 dilute solutions.

6. Conclusion and acknowledgements to my coworkers in this work

The primary source of knowledge for realistic evaluation of metallic multicomponent phase diagram will remain good experimental binary and ternary data: enthalpy and chemical potential measurements are needed to calibrate the two contributions of the Gibbs-functions enthalpy and entropy. Experimental equilibrium lines and tie-lines in phase diagrams could also be considered as equivalent to Gibbs-data, when accurate calorimetric data are available. For these two reasons the large Kleppa's binary enthalpy data set will remain of crucial interest for a very long future period.

Thanks to computer efficiency it is yet possible to apply the chemical thermodynamics directly in the field of real industrial processes: but such a goal could not be obtained without the measurement of precise enthalpies and Gibbs functions. The binary system data have to be considered as a world patrimony and nothing in this field should become any industrial secret: Kleppa's work is a fabulous source of primary data implicitly included inside the Thermo-Calc SSOL bank of many binary systems.

Ternary data are also increasing and will develop more and more in the future, but probably all these data will not appear immediately in the general literature because of some industrial constraints.

Young scientists are now challenged to being both expert thermodynamists (for computer optimisation), but also excellent experimenters to establish the data they need by themselves. The new job in our labs will consist of a perpetual exchange between experiments and Thermo-Calc optimisation.

Acknowledgements

I'd like to acknowledge my coworkers' last 7 years contribution in the calculations I have presented and in the experimental calorimetry and e.m.f. studies which were simultaneously engaged, whenever it appeared that there was a lack of thermodynamic data.

Professor Ole J. Kleppa (without himself knowing):	**Now in this audience**
Mouhsine Azzaoui	Now in cement-industry in Morocco
Abdelhamid Bourkba	Now in University of Agadir in Morocco
Christophe Naguet	Now informatist in UK
Khadija El Assaoui	Now in Administration in Morocco
Valery Vassiliev	University Lomonossov, Moscow

Bo Sundman	Royal Institute of Technology, Stockholm
Jean Marc Fiorani	University of Nancy
Nicolas David	Actual Thesis student, University of Nancy

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