Bismuth – Tin – Zinc

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Introduction

Experimental investigations of the Bi-Sn-Zn phase diagram date from the end of the nineteen century when composition of two coexisting liquids was determined by chemical analysis of separated layers [1891Wri, 1892Wri]. However these results should be considered as semi-quantitative, because later is was shown by [2000Mal1] that immiscibility can not take place above 600°C. A first part of the ternary miscibility gap for this solder system was given by [1949Jae1] at 650 and 750°C. [1949Jae2] showed a liquidus surface which was based on the earlier experimental work of [1923Muz]. [1923Muz] measured thermal arrests of 104 liquid alloys using cooling curves. The first and second recorded arrests could be identified as two- and three-phase equilibria, while the third one corresponded to eutectic equilibrium. Microscopic analysis was also applied by [1923Muz]. [1987Mal] reviewed the experimental data of the Bi-Sn-Zn based on activity determination from emf measurements of [1959Ole], [1966Pta] and calculations of [1977Pel]. A complete thermodynamic calculation of the ternary system is given by [2000Mal1]. This work included a detailed summary of the experimental work. The experimental works of the Bi-Sn-Zn system are summarized in Table 1.

Binary Systems

The phase diagrams for binary systems are taken from [1994Oht] for Bi-Sn, from [2000Mal2] for Bi-Zn and from [1999Oht] for Sn-Zn according to recommendation of [2000Mal1]. Phase diagram of the Sn-Zn is of simple eutectic type. The phase diagram of this binary system calculated in [1999Oht] is similar to the latest recommendation of [2002Per]. However, the temperature of eutectic reaction $l \rightleftharpoons (Zn) + (Sn)$ according to calculation of [1999Oht] is 6 degrees lower than in [2002Per]. The differences between phase diagram of [1999Oht] and [2002Per] are within uncertainty limit of experimental data on phase equilibria.

Solid Phases

In this system no ternary phase is known. The crystallographic data of the phases in the Bi-Sn-Zn system and their ranges of stability are listed in Table 2.

Invariant Equilibria

The ternary system contains only one invariant reaction: $L \rightleftharpoons (Bi) + (Sn) + (Zn)$ found experimentally at 130°C by [1923Muz] and calculated by [2000Mal1]. The compositions of the phases are listed in Table 3. It should be mentioned that there is an inconsistency between the results published in table 2 of [2000Mal1] and figure 7 published in the same work. It is proved in the present evaluation that published thermodynamic parameter reproduce data from table 2 of [2000Mal1], but give slightly different phase diagrams. Therefore, all figures presented in the present evaluation are re-calculated with thermodynamic parameters of [2000Mal1].

Liquidus Surface

[1923Muz] presented the first experimental liquidus surface. The calculated liquidus surfaces are given by [1977Pel, 2000Mal1, 2003Moe] and [2004Oht]. The experimental and calculated liquidus surfaces are in a quite reasonable agreement. Liquidus surface calculated using thermodynamic parameters published by [2000Mal1] is presented in Fig. 1.

Isothermal Sections

Figures 2 to 4 show isothermal sections at 135°C, 170°C and 250°C calculated using thermodynamic description of [2000Mal1]. Experimental isothermal sections are not available so far.

Temperature – Composition Sections

Vertical sections at constant 5 mass% Sn and constant 40 mass% Sn calculated from thermodynamic data of [2000Mal1] are given in Figs. 5 and 6. They are in a good agreement with experimental data of [1923Muz].

Thermodynamics

The activity of Zn in liquid phase of the Bi-Sn-Zn system was derived from emf measurements in works of [1959Ole, 1966Pta, 1967Glu, 1968Lou, 1985Mat] and from vapor pressure of Zn measured by Knudsen's effusion method [1961Yok]. The Zn activities at 450, 551 and 641°C calculated from thermodynamic data of [2000Mal1] are reproduced in Figs. 7 to 9. They are in a good agreement with experimental data of [1959Ole] and [1966Pta].
[1986Zha1] and [1986Zha2] calculated the vertical section at constant 5 at.% Zn using the theorem of corresponding relations between neighbor phase regions. [1971Pta] calculated limited solubility of metals at 441, 484, 532 and 569°C based on measurements from [1966Pta]. First thermodynamic calculations of the entire ternary system by the Calphad method was made by [1977Pel], based on emf measurements of [1966Pta] for the ternary system and emf data of [1977Bal] for the quaternary Bi-Cd-Sn-Zn system. [1986Mat] calculated infinite dilution properties using a new approach, based on free volume theory and in extension of Kapoor's model for binary substitutional molten metallic solutions. The calculated excess energies were in a good agreement with experimental data obtained by emf method in the same work [1986Mat]. [1999Ohn] and [2000Mal1] presented a thermodynamic calculation which reproduced all available experimental data. [2003Moe] and [2004Oht] present a Calphad-type calculation based on different thermodynamic descriptions of binary data. However, both thermodynamic descriptions [2003Moe] and [2004Oht] reproduce quite similar liquidus surface for the Bi-Sn-Zn system as thermodynamic parameters of [2000Mal1].

Notes on Materials Properties and Applications

Numerous efforts have been undertaken in recent years to develop Pb-free substitutes for the lead-tin soldering alloys widely used in microelectronics. System containing Ag, Bi, Cu, In, Sb, Sn, Zn and other elements have been experimentally and thermodynamically studied [1977Pel, 1997Hua, 1997Yoo, 1999Ohn, 2003Moe, 2004Oht]. The candidates for Pb-free solders should fulfill many requirements such as wettability of substrate, formation of strong chemical bonds with substrate, low melting temperature, good mechanical properties, corrosion resistance, safe for health and environment and so on [2003Moe].
[2001Lee] examined the effects of Zn addition on the interfacial and mechanical properties and the of the solder joint with the Cu substrate. [2003Lin] investigated morphology and growth kinetics of this joint.
Jointing properties including joint strength ant interfacial structure of Bi-Sn-Zn solders were given by [2003Sug]. [2004Sho] investigated tensile properties of low-melting solders of the Bi-Sn-Zn system. For the alloy Sn-8Zn-3Bi an approximately double tensile strength was found in the investigated strain-rate and temperature range compared with those of commercial Sn-37Pb alloy. Microhardness of the Sn-9Zn and Sn-8Zn-3Bi solders was experimentally measured and compared with Sn-37Pb solder in [2005Isl]. Micro-hardness of Sn-37Pb and Sn-9Zn (eutectic) decreases with increasing reflow temperature while it decreases for Sn-8Zn-3Bi (non-eutectic). It was shown by SEM investigation that the formation of Pb rich islands in Sn-37Pb, formation of Zn rod from spheroids in Sn-9Zn and precipitation of Bi rich phase in Sn-8Zn-3Bi are the important features that contribute to different hardness nature [2005Isl].

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Table 1: Investigations of the Bi-Sn-Zn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1891Wri, 1892Wri]	chemical analysis of separate melts	600 to 800°C
[1923Muz]	thermal analysis, microscopy	104 alloys
[1959Ole]	emf	450, 500, 550°C, activity of Zn
[1961Yok]	Knudsen effusion method	317 to 387°C
[1966Pta]	emf	441 to 641°C, activity of Zn
[1967Glu]	emf	450 to 650°C, activity of Zn
[1968Lou]	emf	450 to 650°C, activity of Zn
[1971Pta]	emf	427 to 627°C, activity of Zn
[1985Mat]	emf	500°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Bi) < 271.442	*hR*6 $R\bar{3}m$ αAs	*a* = 454.613 *c* = 1186.152	at 31°C [Mas2]
(Sn) 231.9681 - 13	*tI*4 $I4_1/amd$ βSn	*a* = 583.18 *c* = 318.18	at 25°C [Mas2]
(Zn) < 419.58	*hP*2 $P6_3/mmc$ Mg	*a* = 266.50 *c* = 494.70	at 25°C [Mas2]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				Bi	Sn	Zn
L ⇌ (Bi) + (Sn) + (Zn)	130	E	L	39.39	54.35	6.25
			(Bi)	95.75	3.44	0.81
			(Sn)	14.03	85.41	0.56
			(Zn)	$6.03 \cdot 10^{-4}$	$4.23 \cdot 10^{-4}$	99.999

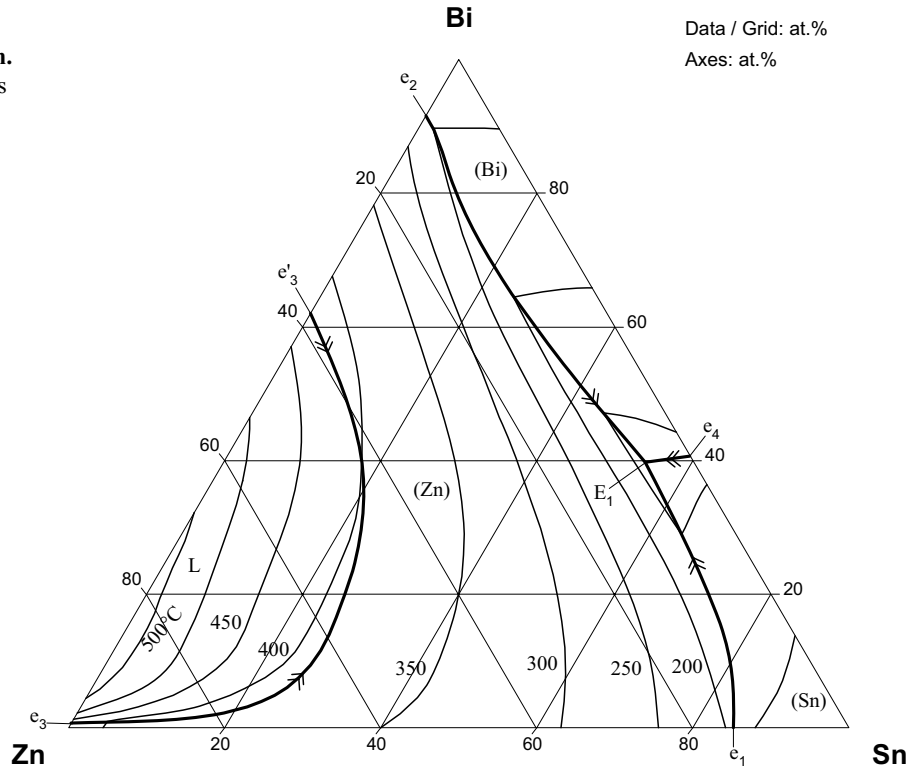

Fig. 1: Bi-Sn-Zn. Calculated liquidus surface projection

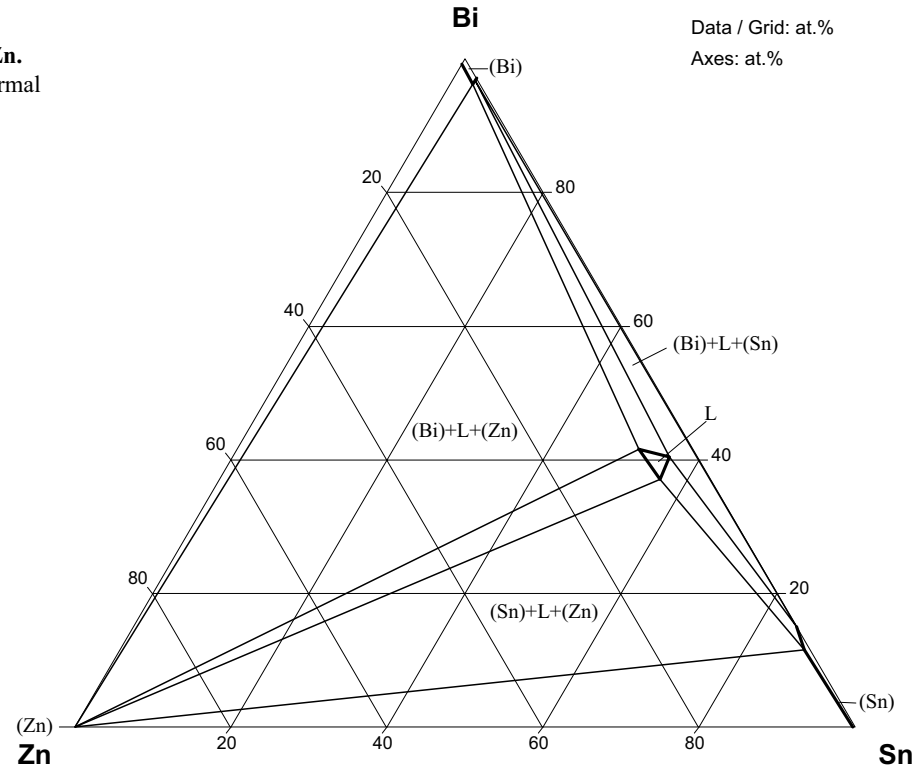

Fig. 2: Bi-Sn-Zn. Calculated isothermal section at 135°C

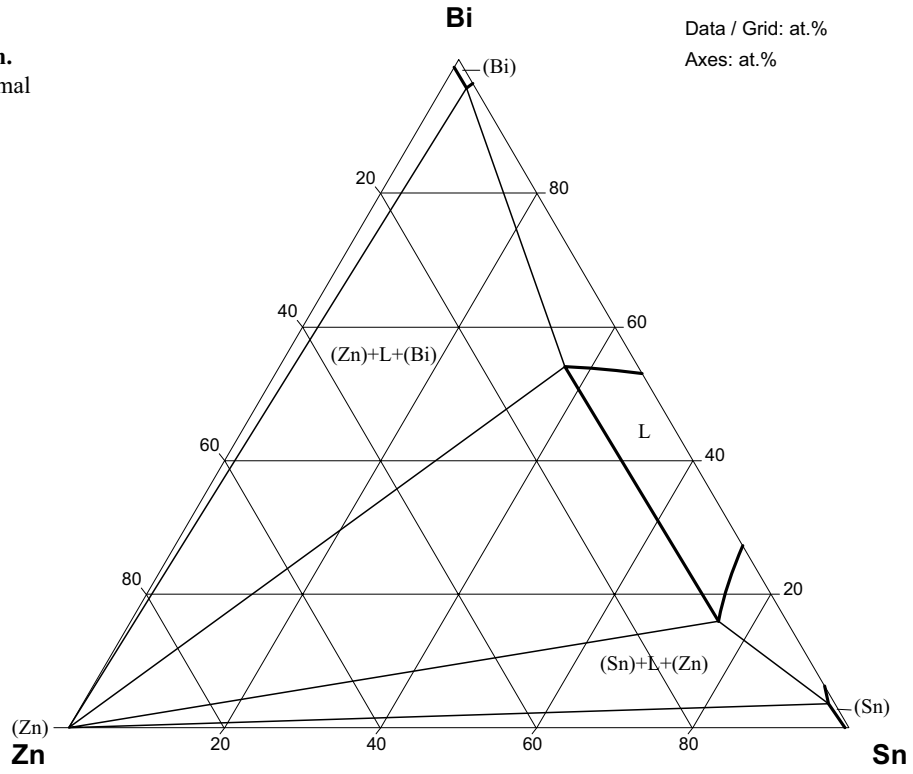

Fig. 3: Bi-Sn-Zn. Calculated isothermal section at 170°C

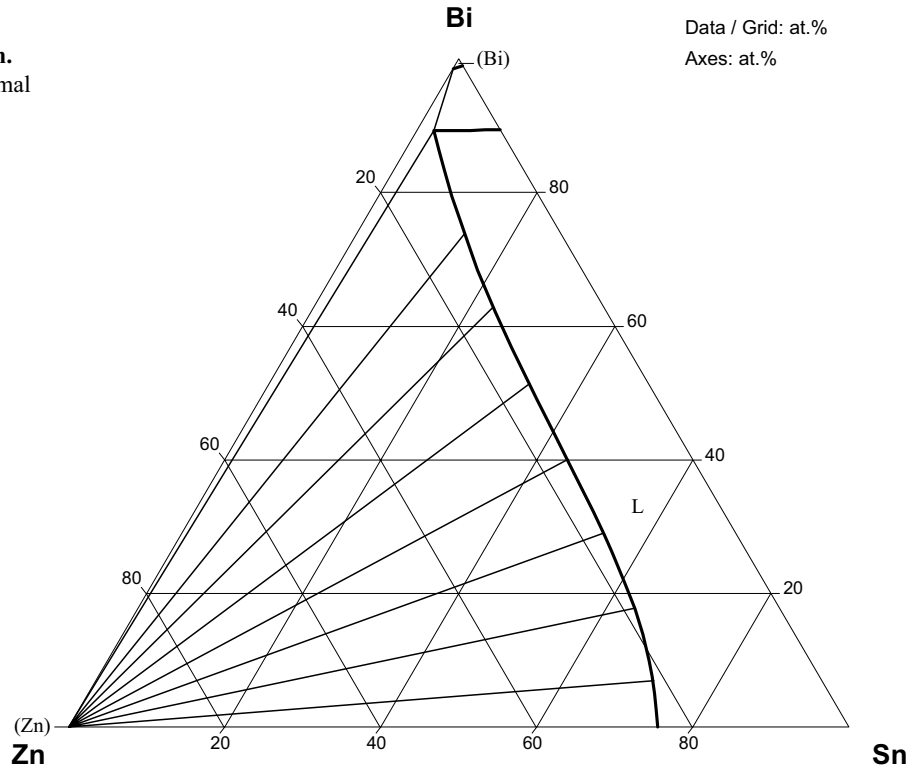

Fig. 4: Bi-Sn-Zn. Calculated isothermal section at 250°C

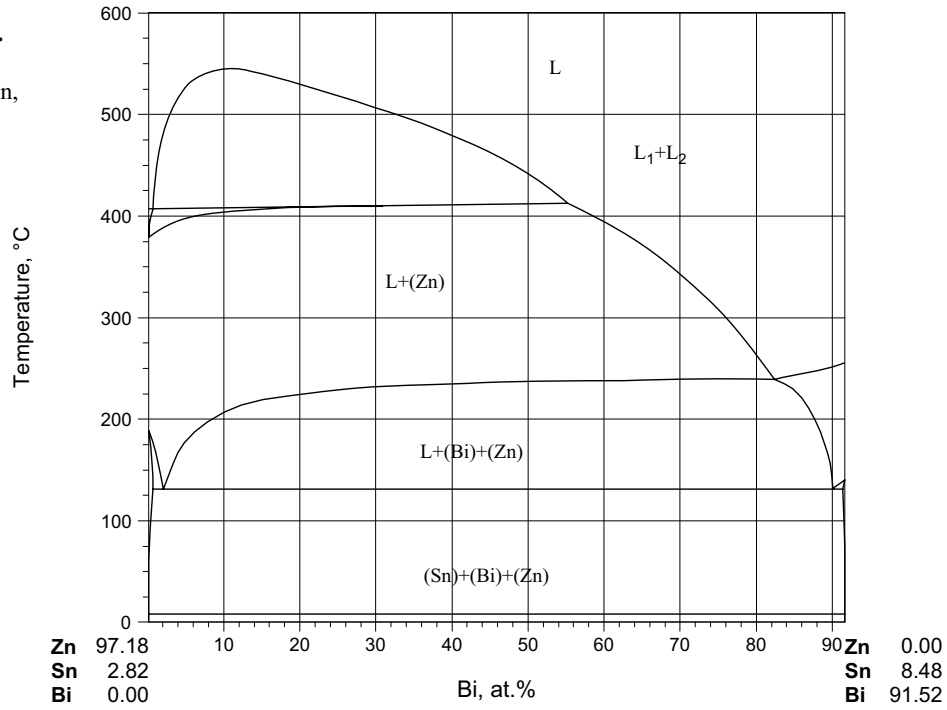

Fig. 5: Bi-Sn-Zn. Vertical section at constant 5 mass% Sn, plotted in at.%

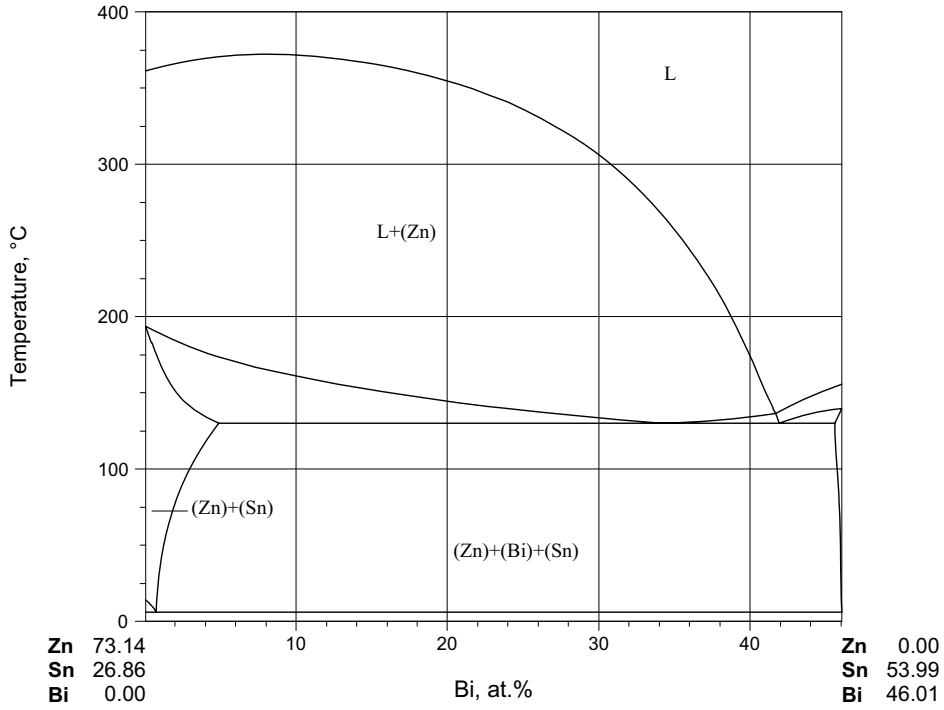

Fig. 6: Bi-Sn-Zn. Vertical section at constant 40 mass% Sn, plotted in at.%

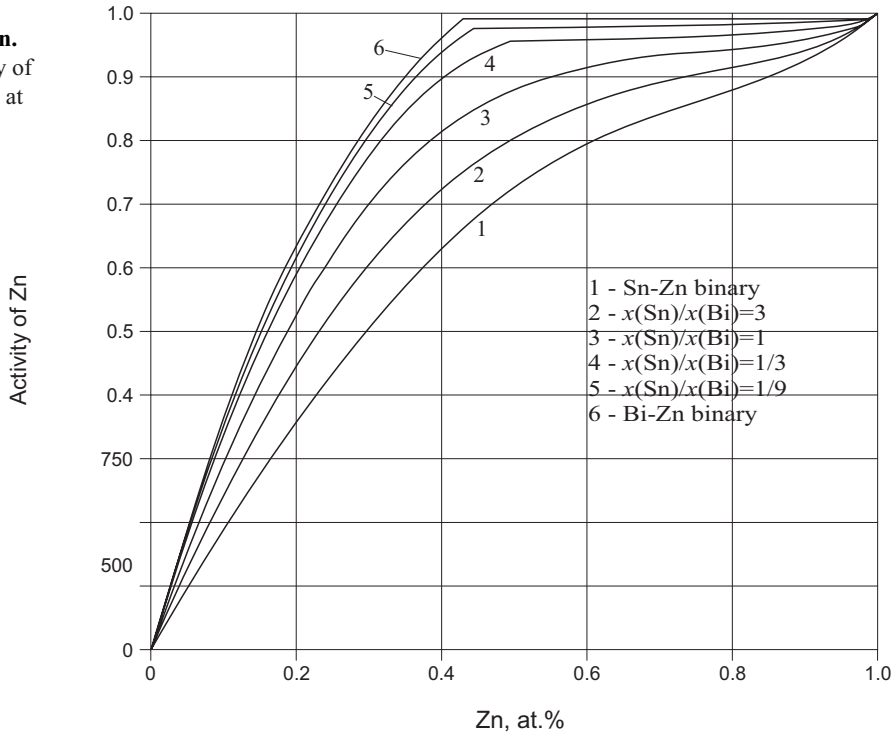

Fig. 7: Bi-Sn-Zn. Calculated activity of Zn in liquid phase at 450°C at fixed x(Sn)/x(Sb) ratio

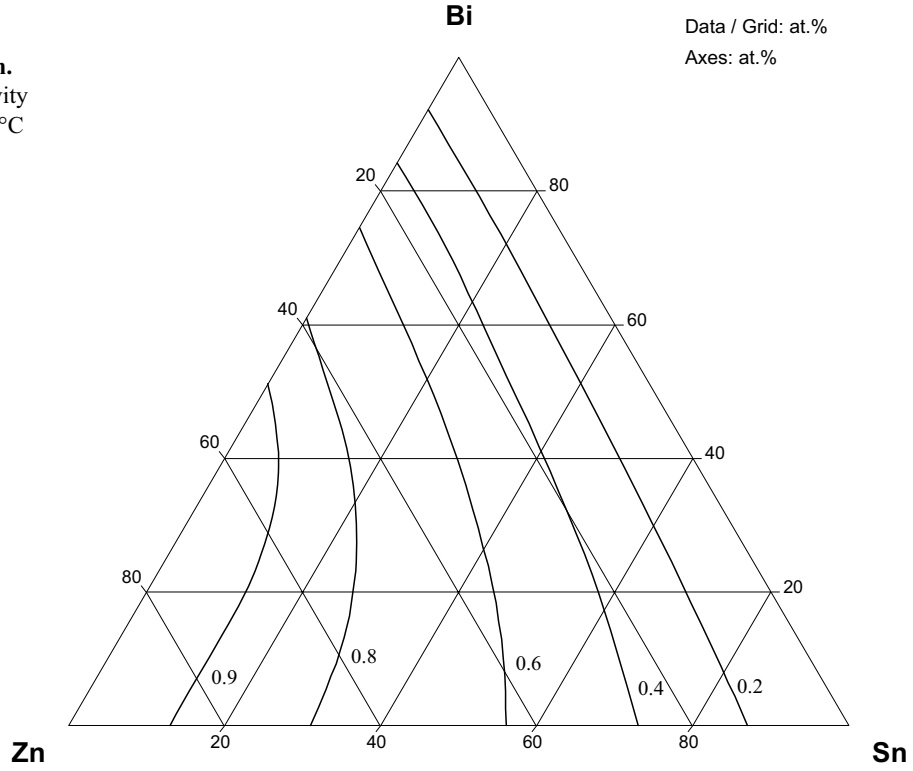

Fig. 8: Bi-Sn-Zn. Calculated isoactivity lines for Zn at 551°C

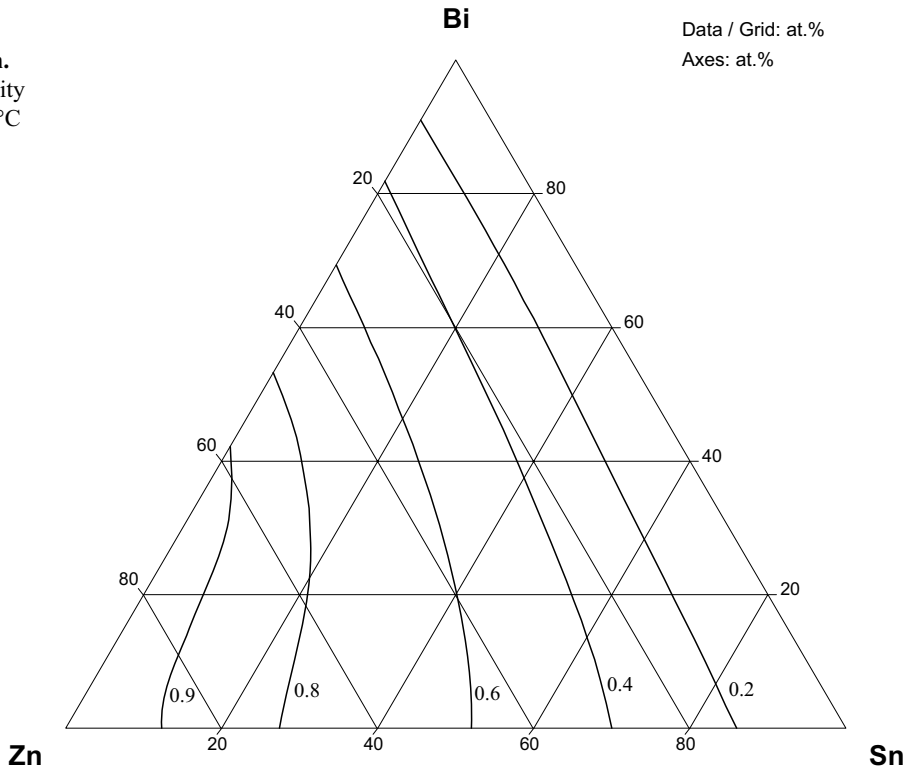

Fig. 9: Bi-Sn-Zn. Calculated isoactivity lines for Zn at 641°C