Copper – Indium – Tin

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Introduction

The Cu-In-Sn system is of great importance for development of Pb free solders.
The first extensive investigation of phase equilibria was carried out in the Cu rich part of the system by [1972Koe] at 400 - 900°C. On the base of the results of [1972Koe] the phase equilibria of system were critically assessed by [1979Dri]. The phase equilibria over the whole concentration range at 110 - 900°C were studied by [2001Liu]. Experimental works of [1956Kle, 2001Ita] were devoted to studing of thermodynamic properties of liquid alloys. The experimental works are summarized in Table 1.
The thermodynamic assessment of the whole diagram in the framework of CALPHAD method was presented by [2001Liu].

Binary Systems

Assessments of the Cu-In system by [2003Bah], of the Cu-Sn system by [Mas2], and of the In-Sn system by [Mas2] are accepted.
In [1972Koe] binary systems were taken from [H]. For the Cu-Sn and In-Sn as well as for Cu-In system at temperatures above 400°C, they are in good agreement with [Mas2].
In the thermodynamic assessment of ternary system [2001Liu] the binary descriptions are accepted from the following sources: [2002Liu] for the Cu-In system, [2004Liu] for the Cu-Sn system, and [1996Lee] for the In-Sn system. These works are in reasonable agreement with [Mas2]. There is one exception for Cu-Sn system. Authors of [2001Liu] and [2004Liu] have recently reported that a two-stage ordering reaction *A*2-*B*2-*D*03 in the bcc phase region takes place, rather than a β/γ_1 two phase equilibria. In [2001Liu] a simplified description of the Gibbs energy of the bcc phase was made, were the ordering reactions of the bcc phase was not considered. It should be mentioned that all phase diagrams of the ternary system included in the present evaluation are checked and corrected for consistency with the accepted binary systems [2003Bah, Mas2].

Solid Phases

The crystallographic data on the Cu-In-Sn phases and their temperature ranges of stability when available are listed in Table 2. In and Sn are markedly dissolved in Cu, but solution of Cu in (In) and (Sn) is negligible. The high temperature bcc β and hexagonal η phases (NiAs type) form a continuous range of solid solutions between the Cu-In and Cu-Sn sides. A weak relative stabilization of β solid solution in the ternary system is found. The β phase decomposes in the ternary system via a eutectoid reaction at 568°C that is slightly lower than the eutectoid decomposition of the β phase in both binary systems (e_5 in Cu-Sn system is at 586°C and e_6 in Cu-In system is at 576.5°C). The high temperature Cu-Sn and Cu-In based cubic γ_1 and γ_2 solid solutions essentially extend into the ternary forming two-phase equilibria in the central part of the concentration triangle. Dissolving a third component decreases the decomposition temperature of both phases down to 517 and 509°C for γ_1 and γ_2, respectively. As a result, γ_1 and γ_2 solid solutions exist in the ternary system as separate ternary phases in the temperature intervals of 517 to 520°C and 509 to 618°C, respectively, after [1972Koe].
The existence of the second ordering reaction of the bcc β phase rather than the β (bcc) + γ (*D*03) two-phase equilibrium in the Cu-Sn binary system is accepted by [2001Liu] (referring to own unpublished data) in contradiction to the Cu-Sn phase diagram accepted in the current assessment and by [1972Koe]. This question is open so far and further investigation is required.
The Cu-Sn based ζ and ε phases as well as Cu-In based δ_2 phase exhibit the wide homogeneity ranges. The solubility of a third component essentially increases with decreasing temperature. The high temperature binary ζ phase is stabilized by In additions down to 400°C and possibly below according to [1972Koe].

Below 582°C, the decomposition temperature of the ζ phase in the Cu-Sn system, the ζ ternary solid solution exists as a separate ternary phase like the above mentioned γ phases. The Cu-Sn based δ_1 phase exists in a narrow composition range close to the Cu-Sn side from ~590°C (temperature of the peritectoid reaction of its formation in the Cu-Sn system after [1972Koe]) to ~350°C (temperature of the eutectoid decomposition of the ternary δ_1 solid solution).
Liu *et al.* [2001Liu] reported the Cu-Sn based ζ phase in ternary alloys only at 600°C. Instead, a wide composition range of the δ_1 phase is proposed, for example, at 500°C up to about 16 mass% (10.5 at.%) In at 19 mass% (12.2 at.%) Sn in equilibrium with δ_2 and ε phases. This contradicts the results of [1972Koe]. The authors of [2001Liu] did not discuss this contradiction and it will not be discussed in the current assessment because of the lack of information on the original experimental data in both works. The interpretation of phase equilibria proposed by [1972Koe] seems to be preferable since more alloys in this range of compositions were studied and an XRD method was used in addition to metallography and DTA (DSC in [2001Liu]) methods. A diffusion couple method for establishing an of equilibrium state seems to be less reliable compared to conventional metallurgical methods even if long-time equilibrated couples are used.
Two ternary compounds, τ_1 and τ_2, exist in the system. Compound τ_1 ($Cu_{11}In_2Sn$) found by [1972Koe] forms by a peritectoid reaction at 585°C. At 400°C, its homogeneity range continues from 3 to 10 at.% Sn at almost constant content of Cu. This phase was confirmed by [1993Mor] and [2001Liu]. According to [2001Liu] the τ_1 phase has composition $Cu_{16}In_3Sn$ and disappears at a temperature below 400°C. The decomposition reaction for the τ_1 phase based on the ternary phase diagram after [1972Koe] may be assumed as $\tau_1 \rightleftharpoons (Cu) + \delta_2 + \zeta$. The τ_2 phase was reported by [1984Rom]. This phase was also found by [2001Liu] at 110°C. Its composition after [2001Liu] is Cu_2In_3Sn. According to calculations and DSC data of [2001Liu] this compound exists below 156°C. The crystal structure of both τ_1 and τ_2 phases is not established.

Invariant Equilibria

The data on the invariant equilibria are given in Table 3. Reaction scheme is given in Fig. 1. For the composition range from 50 to 100 at.% Cu equilibria U_1 to U_{10}, P_1, E_1, E_2, and E_3 are taken from the experimental work of [1972Koe]. For the copper poor part of the system four calculated invariant equilibria involving the liquid phase U_{11}, U_{12}, E_6 and $L + (In) \rightleftharpoons \chi + \eta$ (marked as P_3 in [2001Liu]) are reported by [2001Liu]. However, reactions involving the τ_2 phase formation are not presented by [2001Liu]. It should be noted that the original experimental data on the phase composition of equilibrated at 110°C alloys, DSC data and vertical sections at 10, 20, and 30 mass% Cu of [2001Liu] indicate the equilibrium of the τ_2 phase with liquid. However, according to calculations of [2001Liu] liquid is not stable at 110°C. The τ_2 formation reaction may be assumed from the reaction scheme above 150°C as $L + \eta + (In) \rightleftharpoons \tau_2$, P_2. To connect the reaction P_2 with the reaction E_6 calculated by [2001Liu] two invariant equilibria U_{13} and U_{14} should be assumed. The equilibria U_{11}, U_{12}, and E_6 are taken from [2001Liu].
To reach agreement between isothermal section at 110°C and vertical sections at 10, 20, and 30 mass% Cu presented by [2001Liu] the invariant reaction between solid phases $\eta + \chi \rightleftharpoons \tau_2 + \theta$ at ~109°C, U_{15}, should be supposed.
The calculated temperatures of the invariant equilibrium of the liquid, β, η and γ_2 phases (651.6°C) and of the invariant equilibrium of the liquid, β, ε and η phases (612.4°C) by [2001Liu] are close to the temperatures of the transition reactions U_2 and U_3, respectively, after [1972Koe]. However instead of the β phase, the γ_1 phase participates in these reactions according to [1972Koe].
The eutectoid decomposition, E_4, of the τ_1 ternary compound is proposed in the current assessment taking into account the phase equilibria at 400°C (and higher temperatures) after [1972Koe] and the experimental data of [2001Liu], who found, that the τ_1 phase is stable at 400°C and disappears in alloys equilibrated at 250°C.
[1972Koe] considers the possibility of the eutectoid decomposition of the δ_1 phase via the reaction $\delta_1 \rightleftharpoons (Cu) + \zeta + \varepsilon$, E_5. The existence of such an invariant reaction is in good agreement with the isothermal section at 400°C after [1972Koe]. The temperature of this decomposition should be very close to the

temperature of the eutectoid reaction $\delta_1 \rightleftharpoons$ (Cu) + ε in the binary Cu-Sn, since the solubility of In in δ_1 is low. It was shown to be less than 1 at.% at 400°C. The phases η, η' and η'' are undistinguished in discussing the ternary system, and the corresponding equilibria are not considered here and below, although they should exist at low temperatures.

Liquidus Surface

The partial liquidus surface projection for the copper rich part of the ternary diagram investigated by [1972Koe] (50 to 100 at.% Cu) is given in Fig. 2. Figure 3, taken from [2001Liu] does not present stable equilibria and may be considered reflecting the metastable crystallization of the alloys, excluding the formation of τ_2. It should be mentioned that, reaction U* in Fig. 3 (P_3 according to [2001Liu]) is metastable, because experiments indicate the formation of τ_2 phase and therefore it should be involve in the reactions with the liquid phase.

Isothermal Sections

Experimental isothermal sections for Cu rich alloys at 900°C according to [2001Liu] and at 650, 600, 555, and 400°C after [1972Koe] are given in Figs. 4 to 8. It should be mentioned that equilibrium of η phase with liquid is shown in Fig. 8 according to experimental data of [2001Liu]. Continuous solid solutions of β phase at 650 and 600°C (Figs. 5 and 6) and η phase at 400°C (Fig. 8) from the Cu-In to the Cu-Sn side are exposed. An important feature of the phase equilibria in this system is the high solubility of a third component in the Cu-In and Cu-Sn based phases γ_2, γ_1, δ_2, and ζ (Figs. 5 to 8). Another feature is that the high temperature binary phases γ_2, δ_2, and ζ are stabilized to lower temperature by picking up a third component, as demonstrated in Figs. 6 to 8. Very low solubility of In in the δ_1 phase is shown in Figs. 7 and 8 after [1972Koe] in contradiction with [2001Liu].
Experimental sections at 650, 600, 500, 400 and 250°C, in the whole concentration range, and at 180 and 110°C below 40 mass% Cu as well as the calculated ones at 650, 400, 180, and 110°C in the whole concentration range, are presented by [2001Liu]. The comparison of experimental data of [1972Koe] and [2001Liu] reveals several contradictions. According to [2001Liu] at 600°C the ζ phase containing 1.9 mass% (1.25 at.%) In is in equilibrium with ε and β (instead of γ_1 after [1972Koe]). Also [2001Liu] considered the bcc based phases in the Cu-Sn system as a single β phase field inconsistent with the two phase field β + γ_1 accepted by [1972Koe] and in the current assessment. According to [2001Liu] the δ_1 phase presents extended solid solution at 500 and 400°C being in equilibrium with the (Cu), ε, η, and γ_2 phases that is inconsistent with the data of [1972Koe]. In the calculated sections at 180 and 110°C by [2001Liu], the δ_1 phase coexists with the η phase in contradiction with data of [1972Koe] indicating a low solubility of In in δ_1. The results of [1972Koe] for a high temperature range, including 650, 600 and 400°C, are preferred because they are based on investigation of more alloys using an XRD method for identification of phases additionally to metallography and DTA (DSC in [2001Liu]) methods. Only the low Cu region of the isothermal sections at 180 and 110°C are accepted in the present assessment according to [2001Liu]. The rest can not be accepted because of the above mentioned contradictions with the data of [1972Koe].
The isothermal section at 180°C in the composition range 0 to 50 mass% Cu according to experimental data of [2001Liu] is shown in Fig. 9. The section at 108°C shown in Fig. 10 is derived from the experimental data of [2001Liu] for the temperature-composition sections at 10, 20, and 30 mass% Cu and for the isothermal section at 110°C. The section at 110°C after [2001Liu] differs from the one given in Fig. 10 in the central part of the composition range by the existence of the η + χ equilibrium instead of the alternative τ_2 + θ. According to the proposed reaction scheme, the section at 110°C falls into a very narrow temperature range between solid state reaction U_{15} (109°C) and the eutectic E_6 (111.2°C). The isothermal section presented in Fig. 10 is more representative, because the topology will be preserved at wider temperature range below the U_{15} reaction. The tie line η + χ at 110°C is shown by a dashed line in Fig. 10. Difficulties in the realization of the equilibrium state especially for Cu poor alloys complicate investigation of phase equilibria very essentially. The disagreement in interpretations of the phase equilibria in different works arises from this fact. Further work is needed for clearing the situation not only near the In-Sn side of the system but in the whole composition range at low temperatures.

Temperature – Composition Sections

Nine experimental temperature-composition sections are reported by [1972Koe]. Seven of them parallel to the In-Sn side in the whole concentration range are shown in Figs. 11 to 16. The section at 60 at.% Cu in the composition range 0 to 25 at.% In is given in Fig. 17. The wide homogeneity ranges of the γ_1, ζ, ε, τ_1, β, and η phases are cut by the sections. No vertical section of the ternary system is quasibinary, including ones through the β and η solid solutions. At 400°C the τ_1 phase is in equilibria with the (Cu) and ζ phases in the section at 4 at.% In (Fig. 18) and in equilibria with (Cu) and δ_2 phases in the section at 2 at.% Sn (Fig. 19). The vertical sections at 10 and 30 mass% Cu are given in Figs. 20 and 21, respectively, partially based on the calculations of [2001Liu]. However, it is found in the present assessment that several phase boundaries are missed in the calculations of [2001Liu]. On the other hand, the topology of the vertical sections in the temperature range of 112 - 150°C obtained by [2001Liu] is in contradiction with the presented reaction scheme. Therefore, the phase relations in this temperature range are corrected in the present assessment to correspond to the accepted reaction scheme. Several data points obtained by DSC in [2001Liu] are in agreement with the vertical sections presented in Figs. 20-21. These sections demonstrate the coexistence of the τ_2 compound with the liquid together with η, (In) and χ phases. However it should be pointed out that the vertical sections presented in Figs. 20-21 are tentative in the temperature range 100-300°C and the composition range from 0 to 40 mass% Sn.

Thermodynamics

The mixing enthalpies of the liquid Sn_xCu_{1-x}-Sn_xIn_{1-x} alloys at $x = 0.84$ were measured callorimetrically by [1956Kle] by direct mixing of liquid Sn_xCu_{1-x} and Sn_xIn_{1-x} alloys in a calorimeter at 450°C. The results are presented in Table 4. The thermodynamic properties of the liquid solution between these terminal binary alloys are characterized by slight positive deviations from ideality.

The thermodynamic activity of indium was measured by [2001Ita]. Measurements were carried out by emf method along $x_{Cu}/x_{Sn} = 4$, $x_{Cu}/x_{Sn} = 1$, and $x_{Cu}/x_{Sn} = 0.25$ sections at 727, 827, and 927°C, respectively. Results obtained are presented graphically in Figs. 22a, 22b and 22c. The positive deviations of thermodynamic properties of the liquid alloys from ideality increase with increasing copper contents. Results of [2001Ita] were used by [2001Liu] in the thermodynamic assessment of the system.

The assessments of thermodynamic parameters in the ternary system are available from works [1997Lee, 2001Liu]. The isothermal section of the Cu-In-Sn ternary system at 250°C calculated using only the binary thermodynamic parameters is reported by [1997Lee]. Due to the lack of information on thermodynamics, the ternary compounds τ_1 and τ_2, as well as the homogeneity ranges of binary phases were not included in the calculation. This results in a serious disagreement of the calculations of [1997Lee] with the experimental and calculated phase diagram of [2001Liu] at 250°C. The assessment of [2001Liu] takes into account homogeneity ranges of solid phases as well as formation of τ_1 and τ_2 phases. However the calculated isothermal and vertical sections of [2001Liu] seem to be very contradictory (see chapters Isothermal Sections and Temperature–Composition Sections). Obviously more careful Calphad assessment is necessary to get quantitative character of isothermal and vertical sections at 110 - 250°C.

Notes on Materials Properties and Applications

The study of dispersion-hardening pastes containing copper, indium, and tin was carried out by [1981Mak]. It was reported that after heat treatment of the pastes at 200°C the alloys with a melt point of 600 - 800°C were obtained.

The isothermal section of the Cu-In-Sn phase diagram at 250°C and metastable phase equilibria between (Cu) and liquid at the same temperature were calculated by [1997Lee] by CALPHAD method using the only binary thermodynamic parameters. The results obtained were used for prediction of interface reaction products between copper and In-Sn solder alloys. These predictions were extended by [2003Jeo] to the case of formation of ternary compounds in the system using thermodynamic assessment [2001Liu].

The growth kinetics of intermetallic compound layers formed between In-48 at.% Sn solder and Cu substrate were investigated by [2002Som] and [2005Kim]. In [2002Som] the diffusion reaction process in

Cu/In-48 at.% Sn/Cu joints were investigated between 180 and 400°C. Electron microprobe analysis revealed the presence of one or two intermetallic layers in the interaction zone. A layer of the η phase formed below 200°C. Layers of the η and ζ phases formed above 200°C. According to [2005Kim], in the solder joint Cu/In-48 at.% Sn at 70 to 100°C, the intermetallic compound layer was composed of two phases: τ_2 adjacent to the solder and η which was the dominant phase. A quantitative analysis of the intermetallic compound layer thickness as a function of time shows a constant growth rate at constant temperature [2002Som, 2005Kim].
The selective formation of intermetallic compounds in Sn-20In-0.8Cu (mass%) ball grid array solder joints with Au/Ni [2004Wu] and Au/Ni/Cu [2004Chi] surfaces was investigated.

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Table 1: Investigations of the Cu-In-Sn Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1956Kle]	High temperature calorimetry	450°C, Sn_xCu_{1-x} - Sn_xIn_{1-x}, $x = 0.84$
[1972Koe]	Optical microscopy, X-ray analysis; differential thermal analysis	$x_{Cu} > 0.5$, four isothermal sections at 650, 600, 555, 400°C; nine vertical sections at 83.5, 80, 77, 75, 70, 65, 60 at.% Cu, 4 at.% In, 2 at.% Sn
[2001Ita]	Admittedly emf method with zircona solid electrolyte	a_{In}, 727-927°C, $x_{Cu}/x_{Sn} = 4$, $x_{Cu}/x_{Sn} = 1$, $x_{Cu}/x_{Sn} = 0.25$
[2001Liu]	Diffusion couple method; differential scanning calorimetry (heating curve), metallography, energy dispersive X-ray spectroscopy, thermodynamic assessment using the CALPHAD method	Eight isothermal sections at 900, 650, 600, 500, 400, 250, 180, 110°C; eight vertical sections at 10, 20, 30, 40, 50, 60, 70, 80 mass% Cu.

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
α, (Cu)	*cF*4 $Fm\bar{3}m$		dissolves 11.0 at.% In at 576.5°C and $y = 0$ [2003Bah]
$Cu_{100-x-y}In_xSn_y$ < 1084.62	Cu		dissolves 9.1 at.% Sn at 520-586°C and $x = 0$ [Mas2]
		$a = 361.46$	pure Cu, 25°C [Mas2]
(In) < 156.634	*tI*2 *I*4/*mmm* In	$a = 325.3$ $c = 497.70$	dissolves 12 at.% Sn at 0°C [Mas2] pure In, 25°C [Mas2]
(βSn) < 231.9681	*tI*4 $I4_1/amd$ βSn	$a = 583.18$	dissolves several at.% In [Mas2] pure Sn, 25°C [Mas2]
β, $Cu_{100-x-y}In_xSn_y$ 798 - 568	*cI*2 $Im\bar{3}m$		
$Cu_{13}Sn_3$ 798 - 586	W		$13.1 \le y \le 16.5$ at $x = 0$ [Mas2] $13.1 \le y \le 27.5$ and 798-520°C at $x = 0$ in [2001Liu]
		$a = 302.61$	at 14-25 at.% Sn, $x = 0$ and 710°C [V-C2]
$Cu_{100-x}In_x$ 711.3 - 576.5		$a = 298.0$ to 299.0	$18.5 \le x \le 23.7$ at $y = 0$ [2003Bah] at $16 \le x \le 18$ and $y = 0$ [1992Che]
γ_1, $Cu_{100-x-y}In_xSn_y$, 755 - 517	*cF*16 $F\bar{4}3m$		
Cu_4Sn 755 - 520	$CuHg_2Ti$	$a = 611.76$	$15.5 \le y \le 27.5$ at $x = 0$ [Mas2] at 14-25 at.% Sn, $x = 0$ and 710°C [V-C2]
δ_1, $Cu_{100-x-y}In_xSn_y$, $Cu_{41}Sn_{11}$ 590 - 350	*cF*416 $F\bar{4}3m$ $Cu_{41}Sn_{11}$	$a = 1798.0$	$20 \le y \le 21$ at $x = 0$ [Mas2] [V-C2]
ζ, $Cu_{100-x-y}In_xSn_y$, 640 - 400	*hP*26 $P6_3$ $Cu_{10}Sn_3$		
$Cu_{10}Sn_3$ 640 - 582		$a = 733.0$ $c = 786.40$	$20.3 \le y \le 22.5$ at $x = 0$ [Mas2] [V-C2]
ε, $Cu_{100-x-y}In_xSn_y$, Cu_3Sn < 676	*oC*80 *Cmcm* Cu_3Sn	$a = 552.9$ $b = 4775.0$ $c = 432.3$	$24.5 \le y \le 25.9$ at $x = 0$ [Mas2] [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
η, $Cu_{100-x-y}In_xSn_y$, Cu_6Sn_5	*hP*4		
	*P*6$_3$/*mmc*		43.5 ≤ *y* ≤ 45.5 at *x* = 0 [Mas2]
415 - 186	NiAs	*a* = 419.2	[V-C2]
		c = 503.7	
		γ = 120°	
η, $Cu_{100-x}In_x$			33.1 ≤ *x* ≤ 36.2 at *y* = 0 [2003Bah]
670.2 - 276.6		*a* = 426.9	at *x* = 35.6 [V-C2]
		c = 523.9	
		γ = 120°	
η', $Cu_{100-y}Sn_y$	-		44.8 ≤ *y* ≤ 45.5, hexagonal [Mas2]
< 189	-		
	based on NiAs?		
γ_2, $Cu_{100-x-y}In_xSn_y$,	*cP*52		
684.1 - 509	*P*$\bar{4}$3*m*		
Cu_9In_4	$InMn_3$		27.9 ≤ *x* ≤ 32.2 at *y* = 0 [2003Bah]
684.1 - 617.8		*a* = 925.03	at *x* = 29.6, *y* = 0 and 650°C [V-C2]
δ_2, $Cu_{100-x-y}In_xSn_y$,	*aP*40		
Cu_7In_3	*P*$\bar{1}$		29.1 ≤ *x* ≤ 31.2 at *y* = 0 [2003Bah]
< 632.2	Cu_7In_3	*a* = 1007.1	at *x* = 30 and *y* = 0 [V-C2]
		b = 912.6	
		c = 672.4	
		α = 90.22°	
		β = 82.84°	
		γ = 106.81°	
η'', $Cu_{100-x}In_x$	-	-	33.3 ≤ *x* ≤ 36.6 [2003Bah]
< 388.3	-		
	Ni_2In		
φ, $Cu_{11}In_9$	*mC*20		[2003Bah]
< 305.8	*C*2/*m*	*a* = 1281.4	at 280°C [V-C2]
	AlCu	*b* = 435.4	
		c = 735.3	
		β = 54.49°	
χ, $In_{100-x}Sn_x$	*tI*2		12 ≤ *x* ≤ 44 [Mas2]
< 140.0	*I*4/*mmm*	*a* = 346.3	at *x* = 25 [V-C2]
	In	*c* = 440.4	
θ, $In_{100-x}Sn_x$	*hP*5		72 ≤ *x* ≤ 98.5 [Mas2]
< 224	*P*6/*mmm*	*a* = 320.5	at *x* = 80 [V-C2]
	-	*c* = 299.5	
		γ = 120°	
* τ_1, $Cu_{11}In_2Sn$	?	-	[1972Koe]
585 - (325 ± 75)°C			$Cu_{16}In_3Sn$ in [2001Liu]
* τ_2, Cu_2In_3Sn	?	-	[2001Liu]
< 156°C			

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)[a]		
				Cu	In	Sn
$L + \beta \rightleftharpoons \gamma_1 + \gamma_2$	676	U_1[b]	L	76 (62)	17 (25.5)	8 (12.5)
$L + \gamma_2 \rightleftharpoons \gamma_1 + \eta$	648	U_2[b]	L	66.5 (51.9)	19.5 (27.7)	14 (20.4)
$\beta + \gamma_1 + \gamma_2 \rightleftharpoons \tau_1$	585	P_1[b]	-	-	-	-
$L + \gamma_1 \rightleftharpoons \varepsilon + \eta$	583	U_3	L	58.5 (43.2)	13 (17.4)	28.5 (39.4)
$\beta + \gamma_2 \rightleftharpoons \delta_1 + \tau_1$	578	U_4	-	-	-	-
$\gamma_1 + \varepsilon \rightleftharpoons \eta + \zeta$	575	U_5	-	-	-	-
$\beta + \delta_2 \rightleftharpoons \alpha + \tau_1$	571	U_6	-	-	-	-
$\beta \rightleftharpoons (Cu) + \gamma_1 + \tau_1$	568	E_1	-	-	-	-
$\gamma_1 + \eta \rightleftharpoons \zeta + \gamma_2$	562	U_7	-	-	-	-
$\gamma_1 + \gamma_2 \rightleftharpoons \zeta + \tau_1$	552	U_8	-	-	-	-
$\gamma_2 + \eta \rightleftharpoons \zeta + \delta_2$	551	U_9	-	-	-	-
$\gamma_1 + \tau_1 \rightleftharpoons (Cu) + \zeta$	540	U_{10}	-	-	-	-
$\gamma_2 \rightleftharpoons \zeta + \delta_2 + \tau_1$	509	E_2	-	-	-	-
$\gamma_1 \rightleftharpoons (Cu) + \delta_1 + \zeta$	517	E_3	-	-	-	-
$\tau_1 \rightleftharpoons (Cu) + \delta_2 + \zeta$	325±50	E_4	-	-	-	-
$\delta_1 \rightleftharpoons (Cu) + \varepsilon + \zeta$	~350	E_5	-	-	-	-
$L + (\beta Sn) \rightleftharpoons \eta + \theta$	218.5	U_{11}[c]	L	1.18 (0.64)	5.08 (4.95)	93.74 (94.41)
			(βSn)	0.02 (0)	1.56 (1.53)	98.42 (98.47)
			η	56.17 (40.91)	12.47 (16.42)	31.36 (42.67)
			θ	0 (0)	2.93 (2.83)	97.07 (97.17)
$L + \varphi \rightleftharpoons \eta + (In)$	154.1	U_{12}[c]	L	0.57 (0.32)	99.43 (99.68)	$1.4 \cdot 10^{-3}$ ($1.5 \cdot 10^{-3}$)
			φ	55 (40.35)	45.0 (59.65)	0.0 (0.0)
			η	60.61 (87.96)	35.13 (48.07)	4.26 (6.02)
			(In)	0 (0)	99.999 (99.999)	0.001 (0.001)
$L + \eta + (In) \rightleftharpoons \tau_2$	~150	P_2	-	-	-	-
$L + (In) \rightleftharpoons \tau_2 + \chi$	~140	U_{13}	-	-	-	-

Reaction	T [°C]	Type	Phase	Composition (at.%)[a)]		
				Cu	In	Sn
$L + \tau_2 \rightleftharpoons \eta + \chi$	~112	U_{14}	-	-	-	-
$L \rightleftharpoons \eta + \chi + \theta$	111.2	E_6[c)]	L	1.28 (0.75)	53.78 (53.23)	44.94 (46.02)
			η	57.1 (36.64)	23.81 (31.68)	19.09 (26.26)
			χ	0 (0)	56.55 (55.73)	43.45 (44.27)
			θ	0 (0)	23.44 (22.85)	76.56 (77.15)
$\eta + \chi \rightleftharpoons \tau_2 + \theta$	~109	U_{15}	-	-	-	-

a) mass% are given in brackets;
b) coordinates are taken from Fig. 2;
c) calculated by [2001Liu].

Table 4: Thermodynamic Data of Reaction or Transformation

Reaction or Transformation	T [°C]	Quantity, per mol of compound [J·mol^{-1}]	Comments
$Sn_xCu_{1-x}(L) + Sn_xIn_{1-x}(L) \rightleftharpoons Sn_xCu_yIn_z(L)$	450	83	$x = 0.8354$ $y = 0.1123$ $z = 0.0523$
	450	73	$x = 0.8466$ $y = 0.0962$ $z = 0.0572$

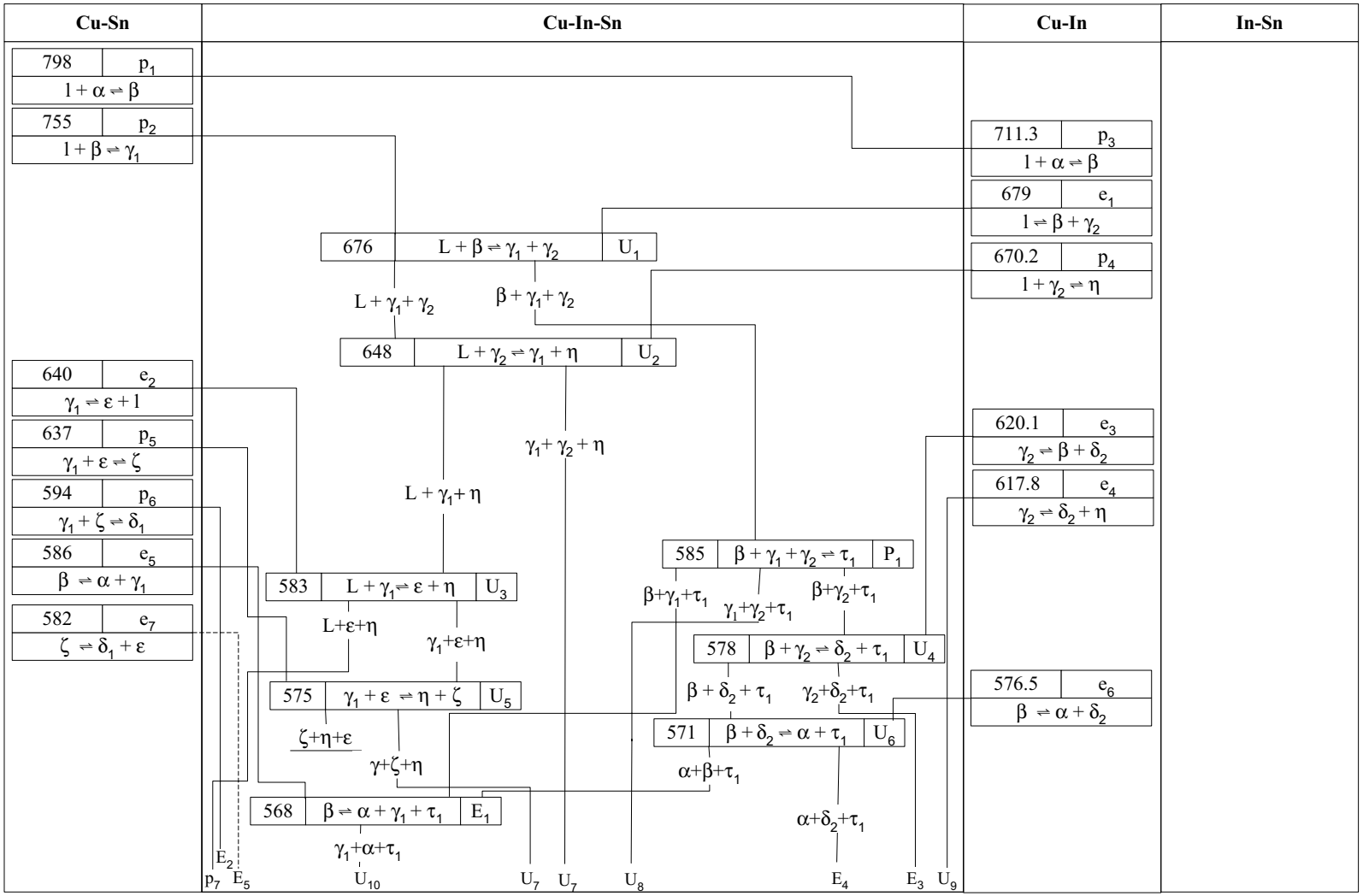

Fig. 1a: Cu-In-Sn. Reaction scheme, part 1

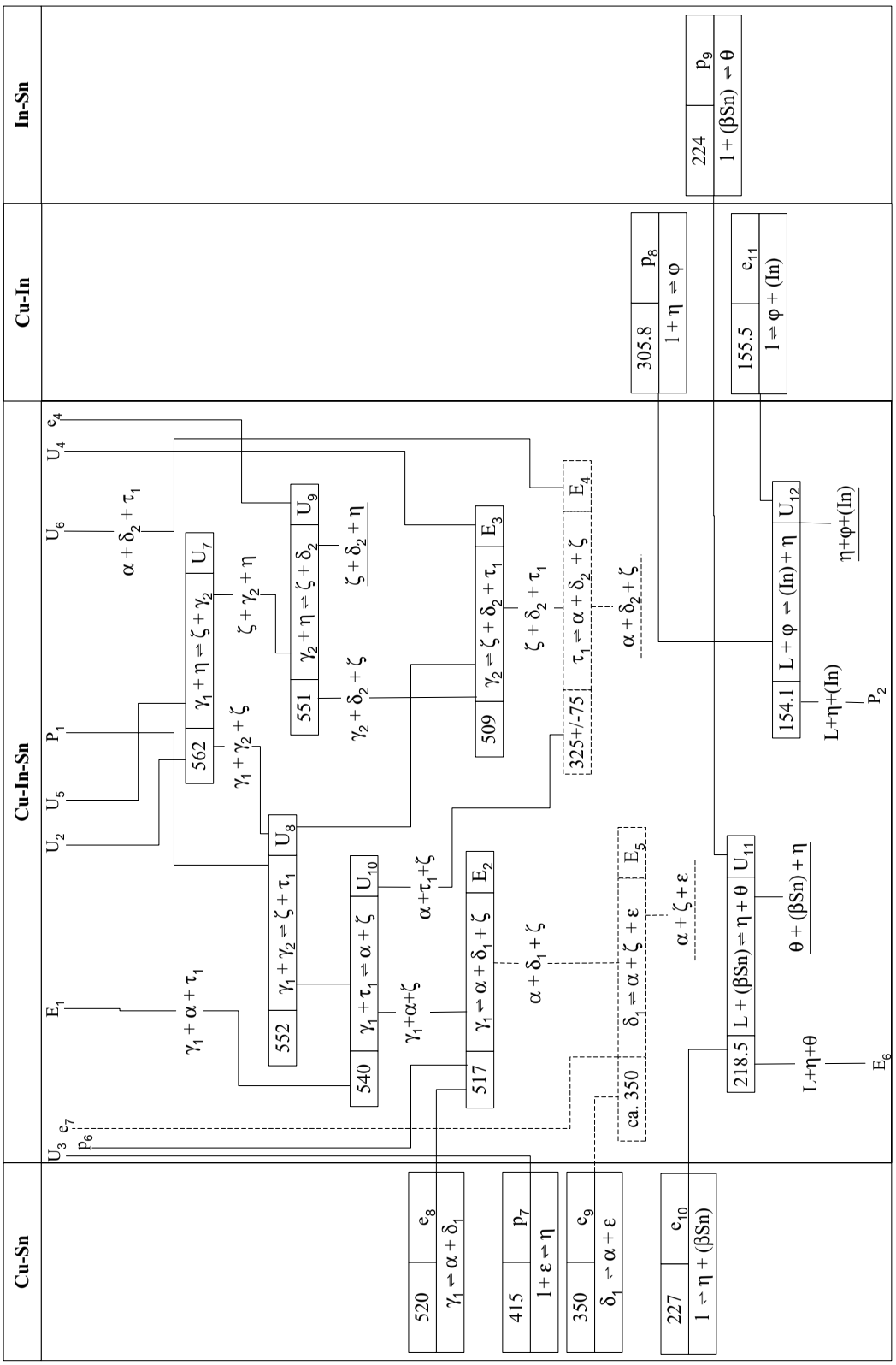

Fig. 1b: Cu-In-Sn. Reaction scheme, part 2

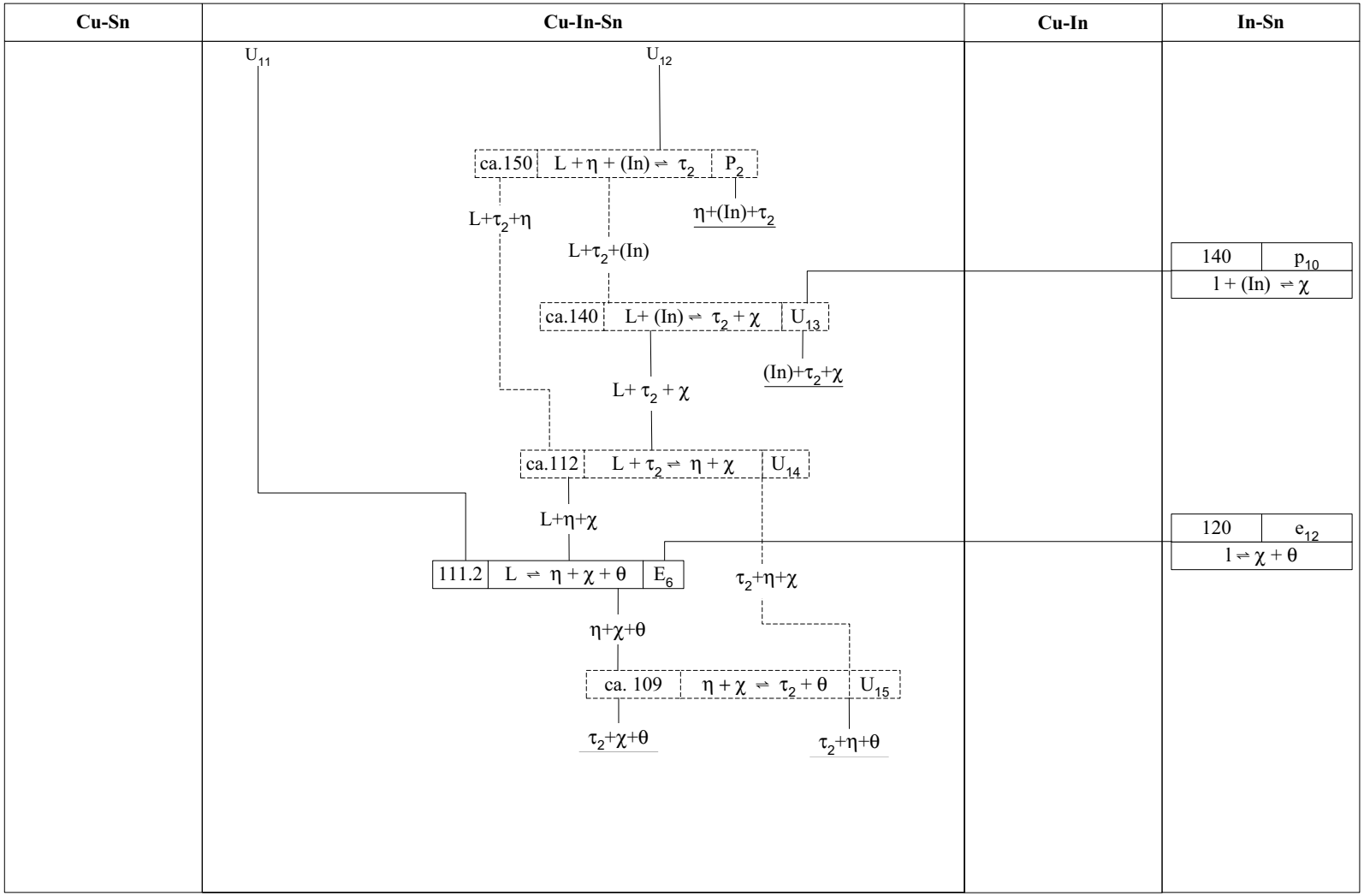

Fig. 1c: Cu-In-Sn. Reaction scheme, part 3

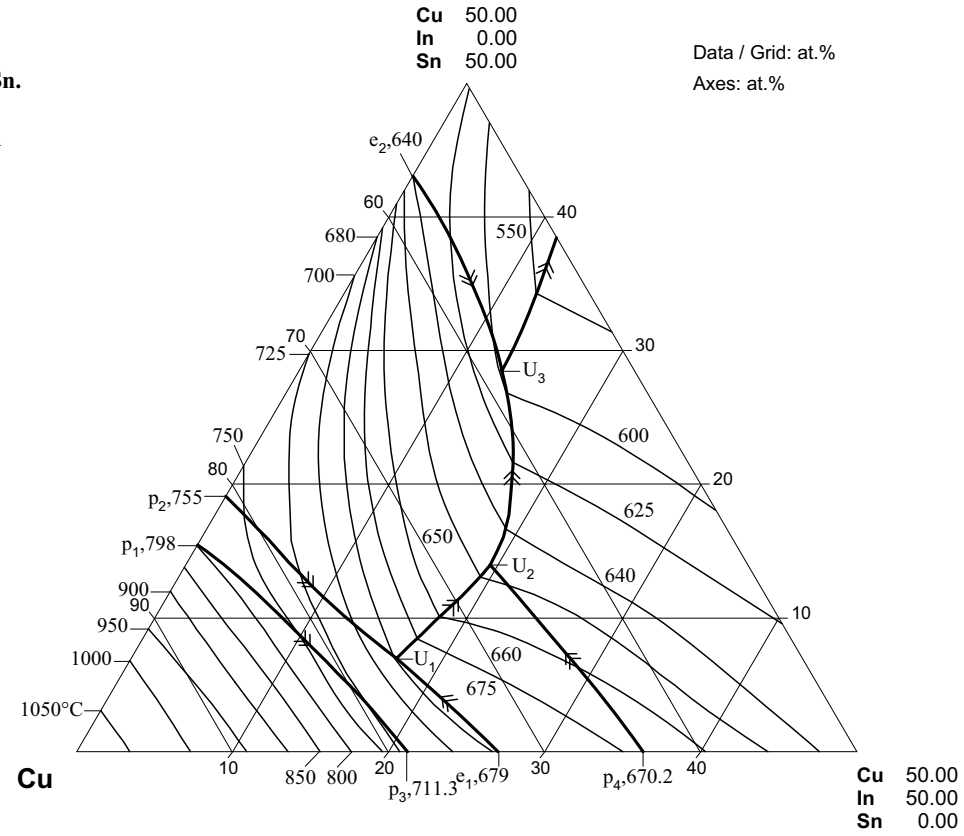

Fig. 2: Cu-In-Sn. Partial liquidus surface projection

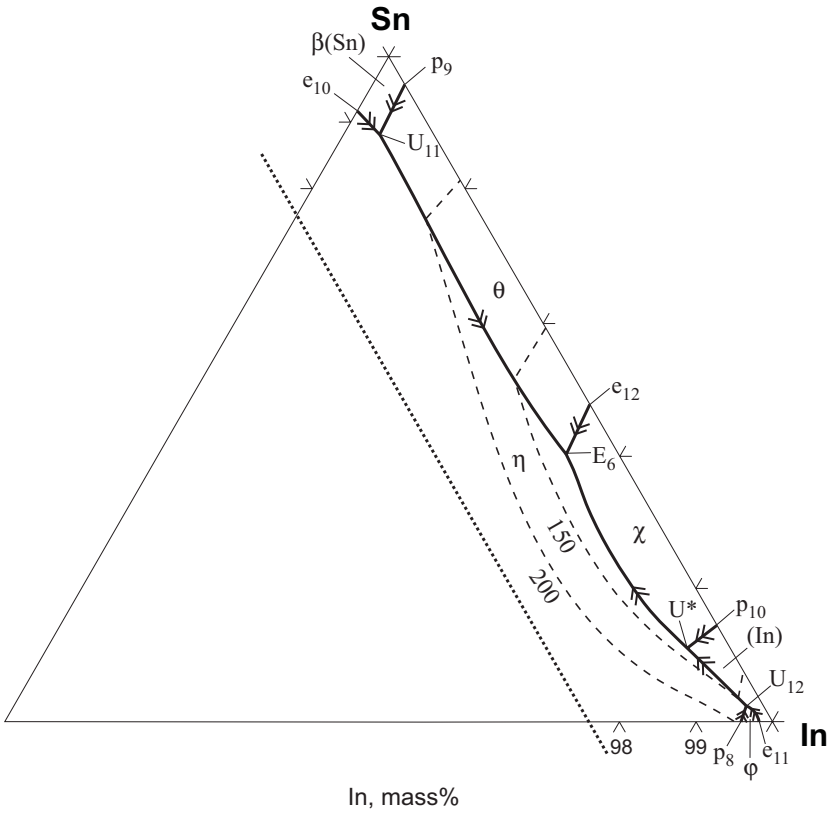

Fig. 3: Cu-In-Sn. Partial liquidus surface projection near the In-Sn side calculated without considering τ_2 phase

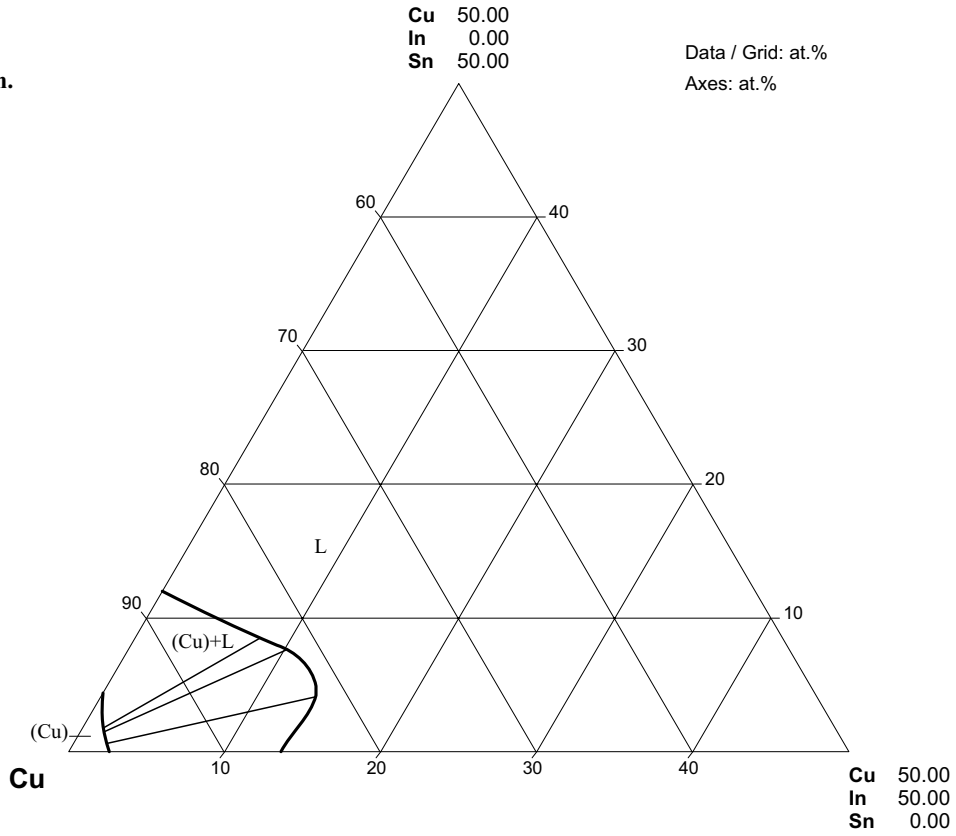

Fig. 4: Cu-In-Sn. Isothermal section at 900°C

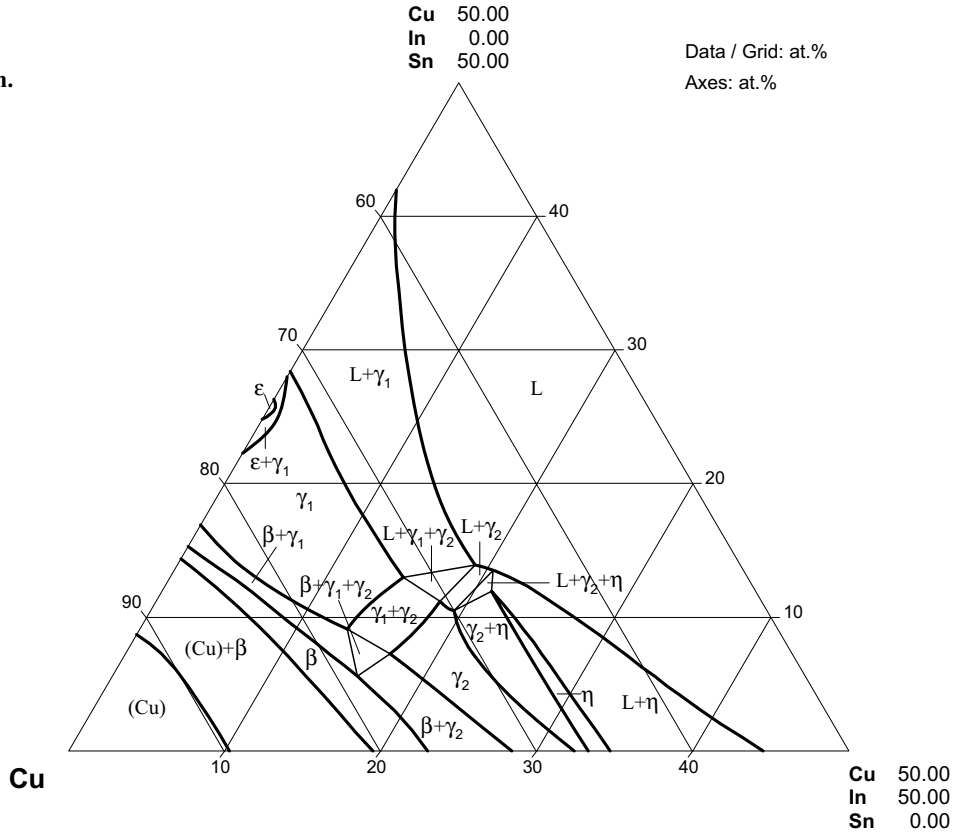

Fig. 5: Cu-In-Sn. Isothermal section at 650°C

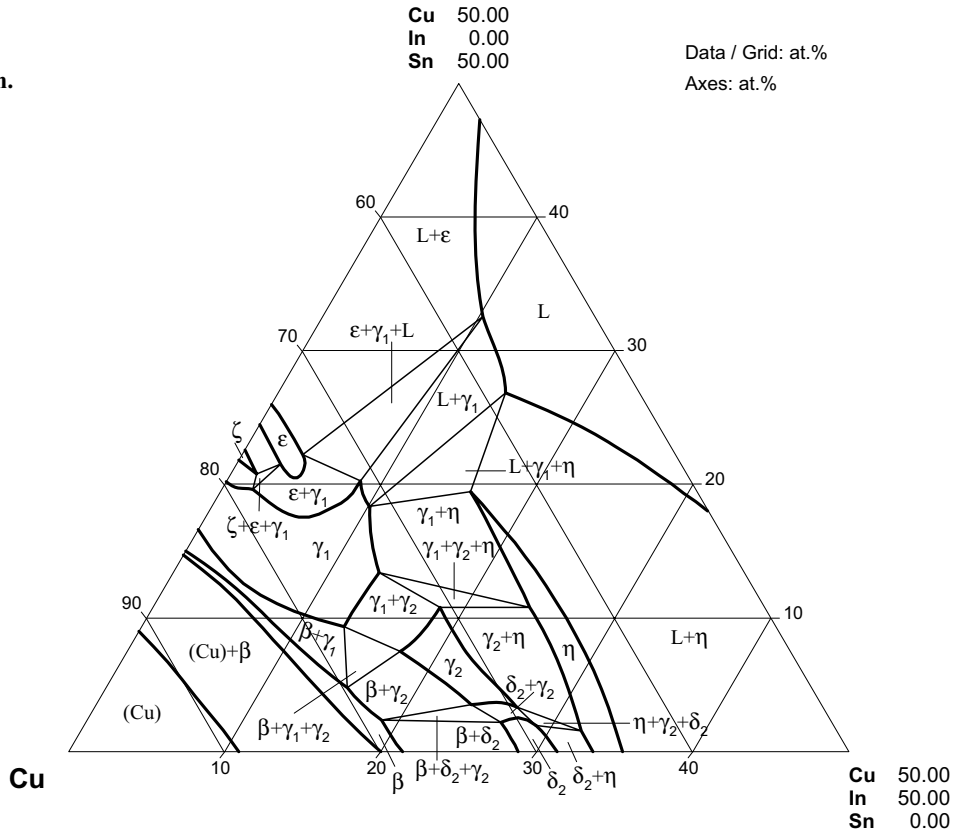

Fig. 6: Cu-In-Sn. Isothermal section at 600°C

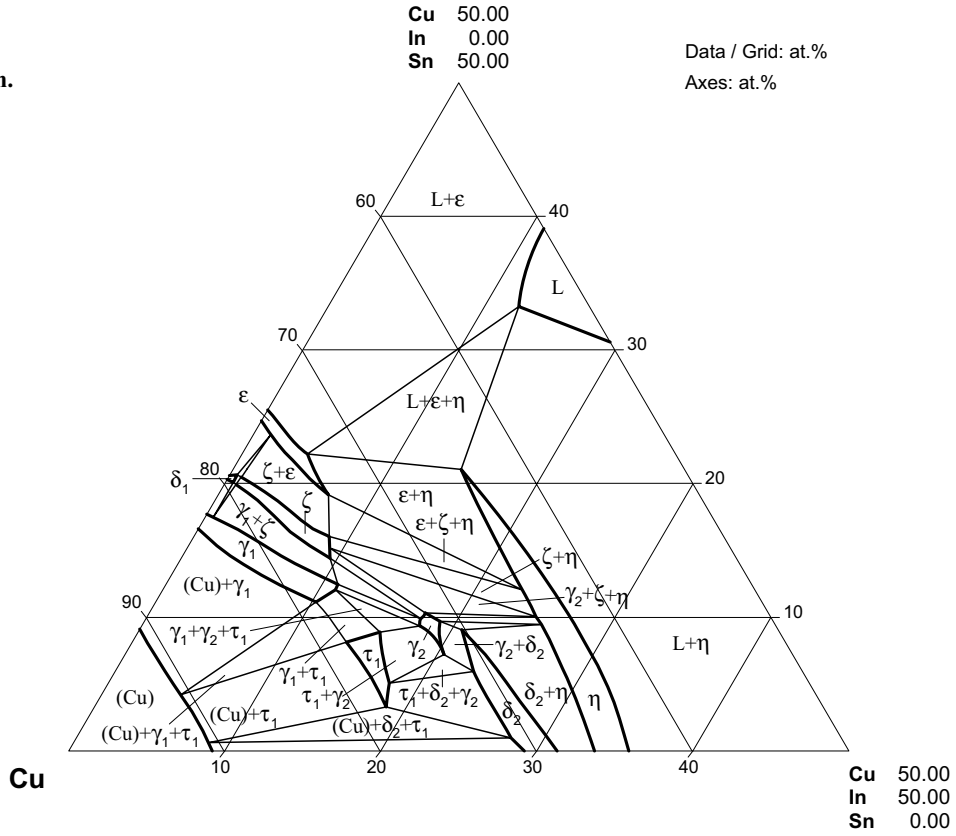

Fig. 7: Cu-In-Sn. Isothermal section at 555°C

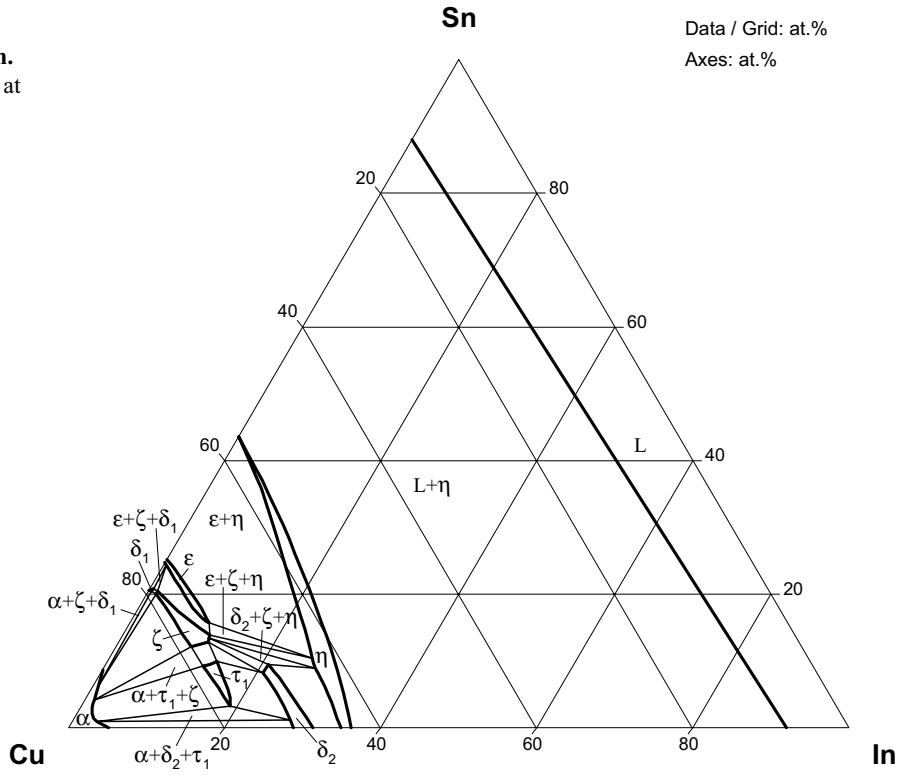

Fig. 8: Cu-In-Sn. Isothermal section at 400°C

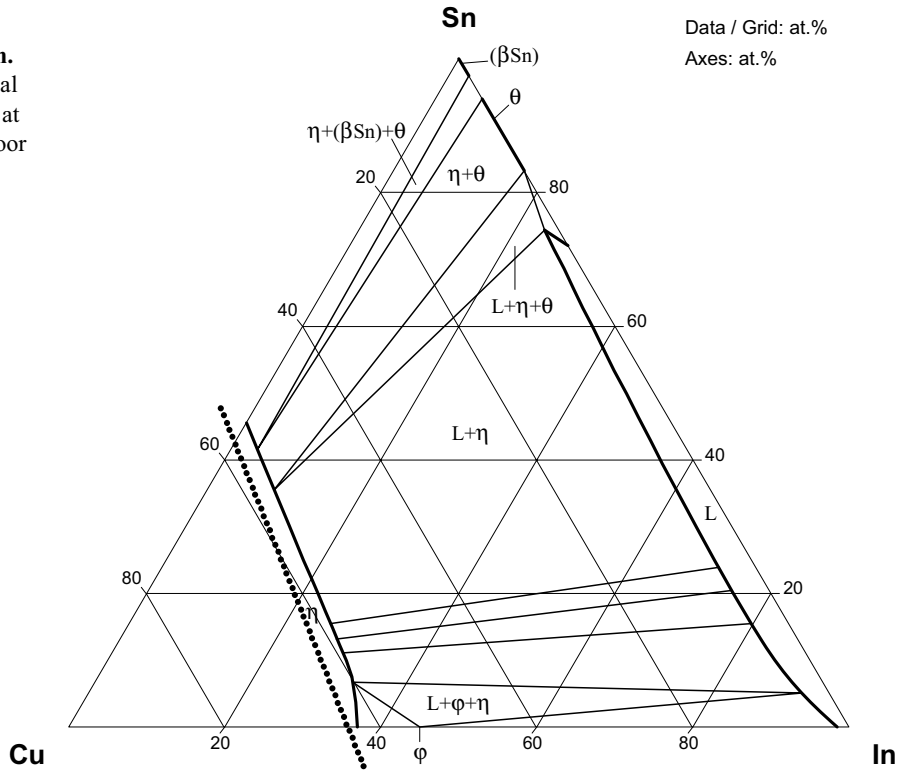

Fig. 9: Cu-In-Sn. Experimental partial isothermal section at 180°C in the Cu poor region

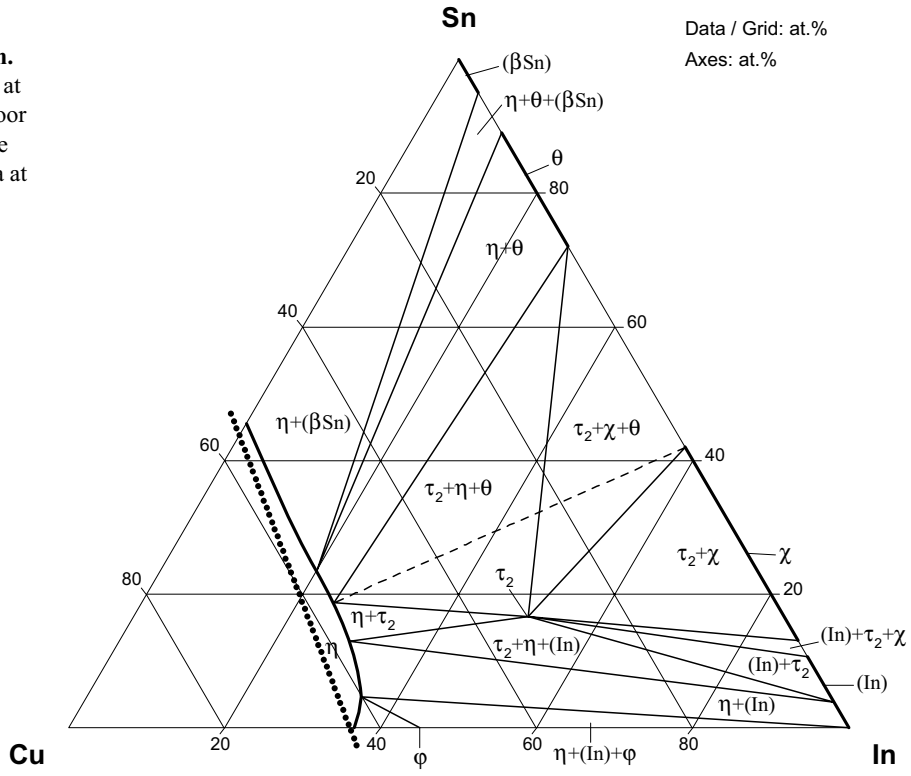

Fig. 10: Cu-In-Sn. Isothermal section at 108°C in the Cu poor region. Dashed line indicates equilibria at 110°C

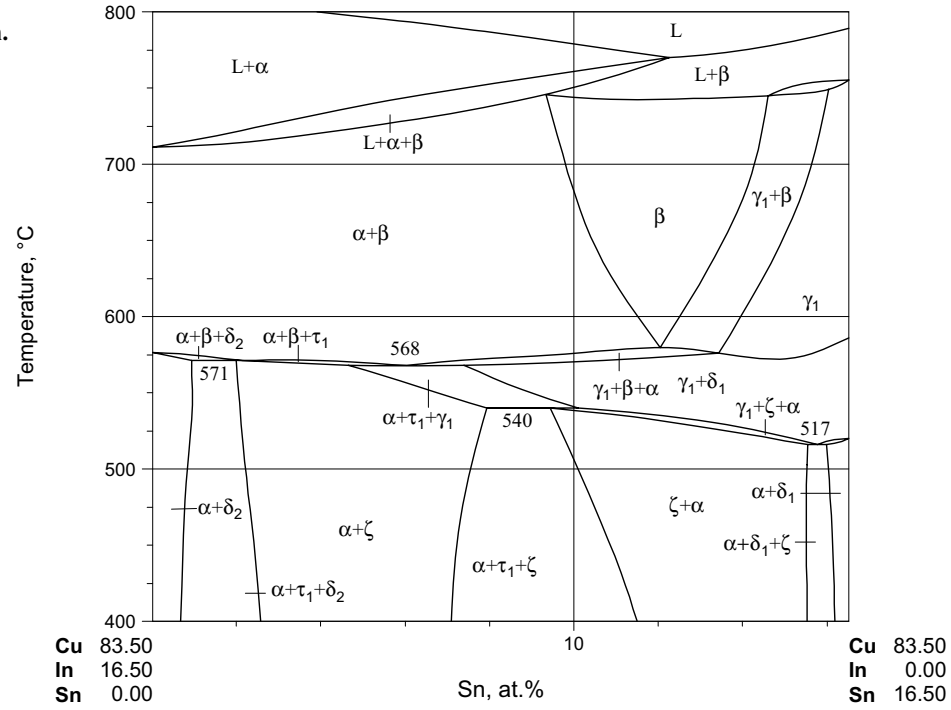

Fig. 11: Cu-In-Sn. Vertical section at 83.5 at.% Cu

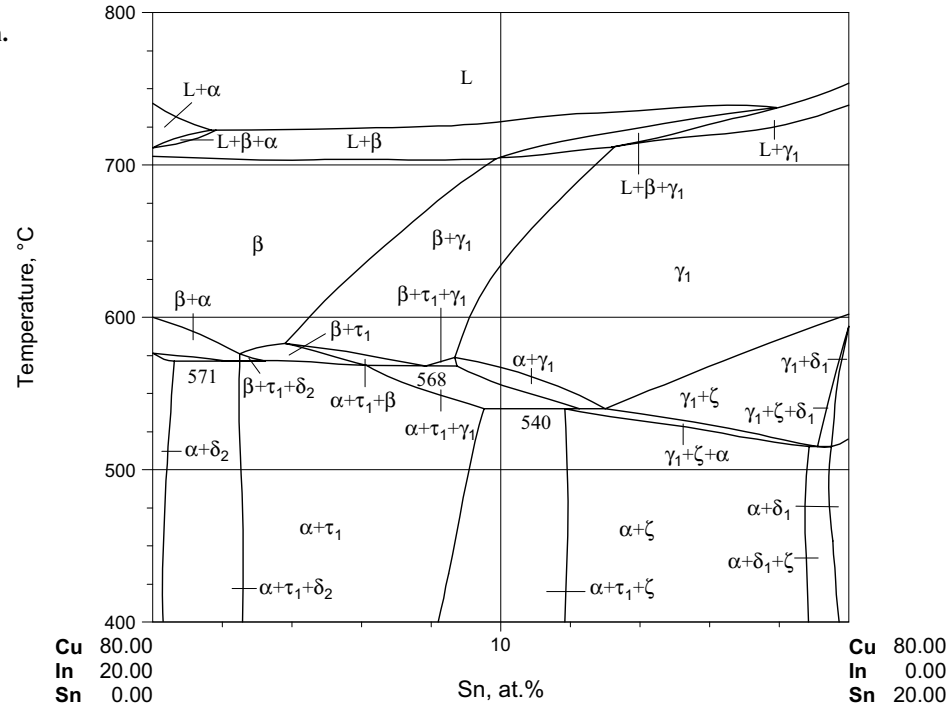

Fig. 12: Cu-In-Sn.
Vertical section
at 80 at.% Cu

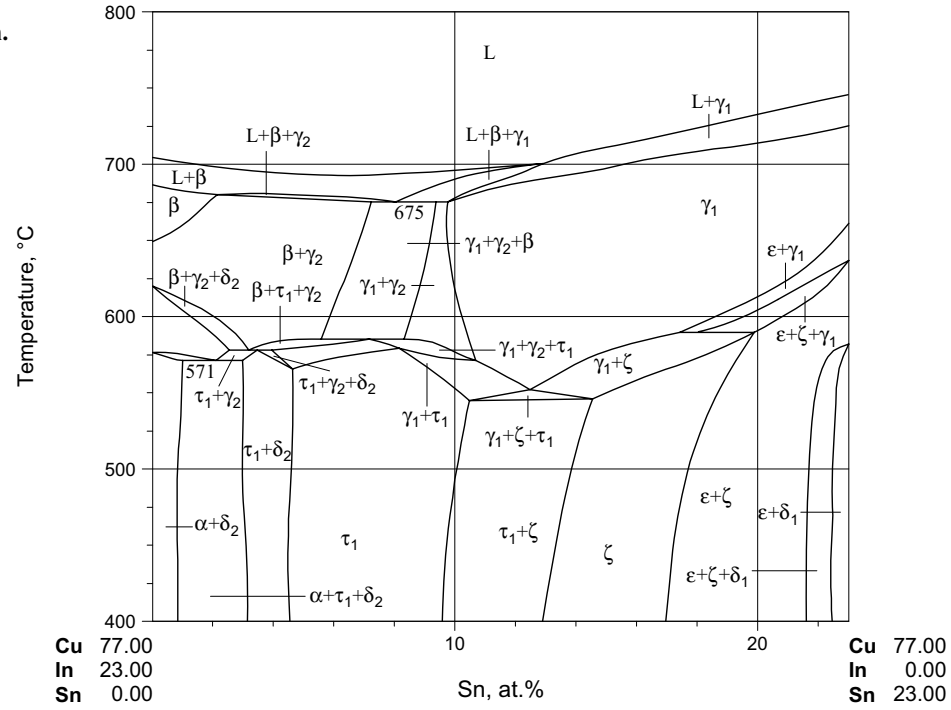

Fig. 13: Cu-In-Sn.
Vertical section
at 77 at.% Cu

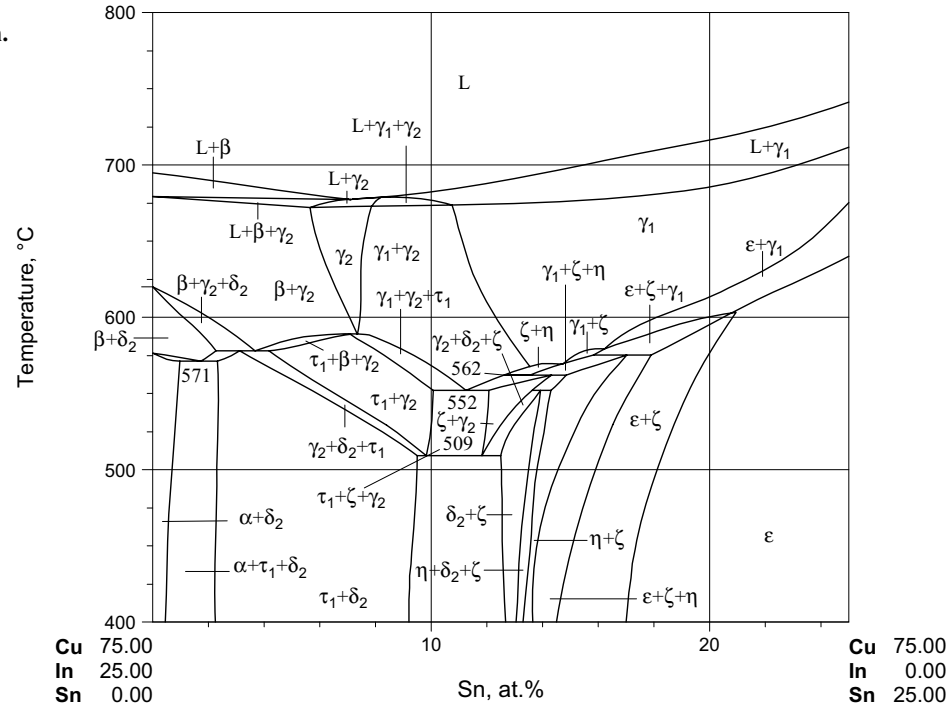

Fig. 14: Cu-In-Sn.
Vertical section
at 75 at.% Cu

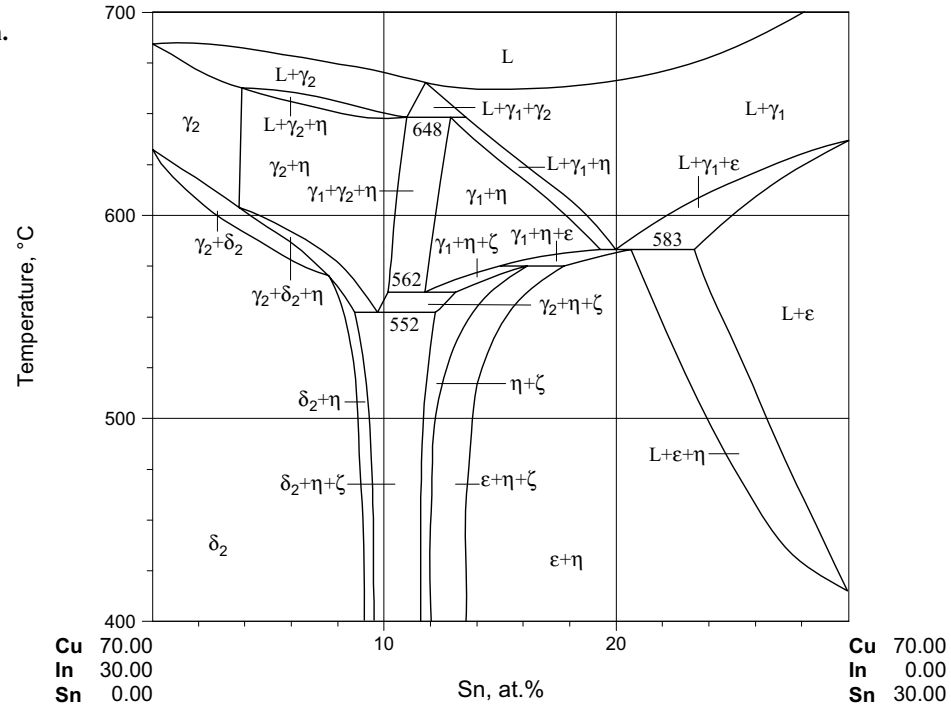

Fig. 15: Cu-In-Sn.
Vertical section
at 70 at.% Cu

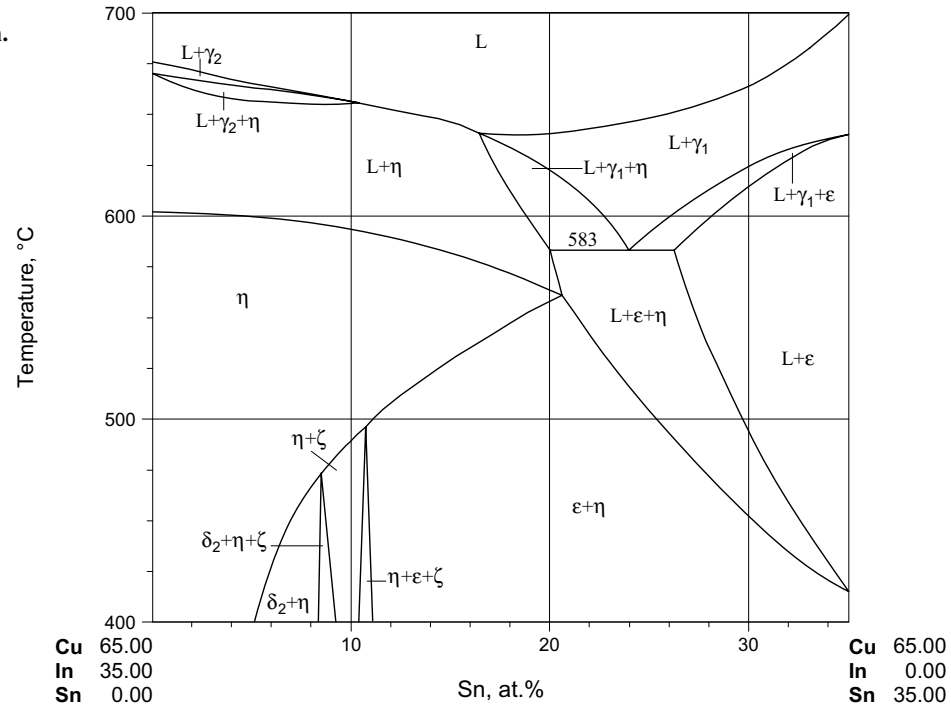

Fig. 16: Cu-In-Sn.
Vertical section
at 65 at.% Cu

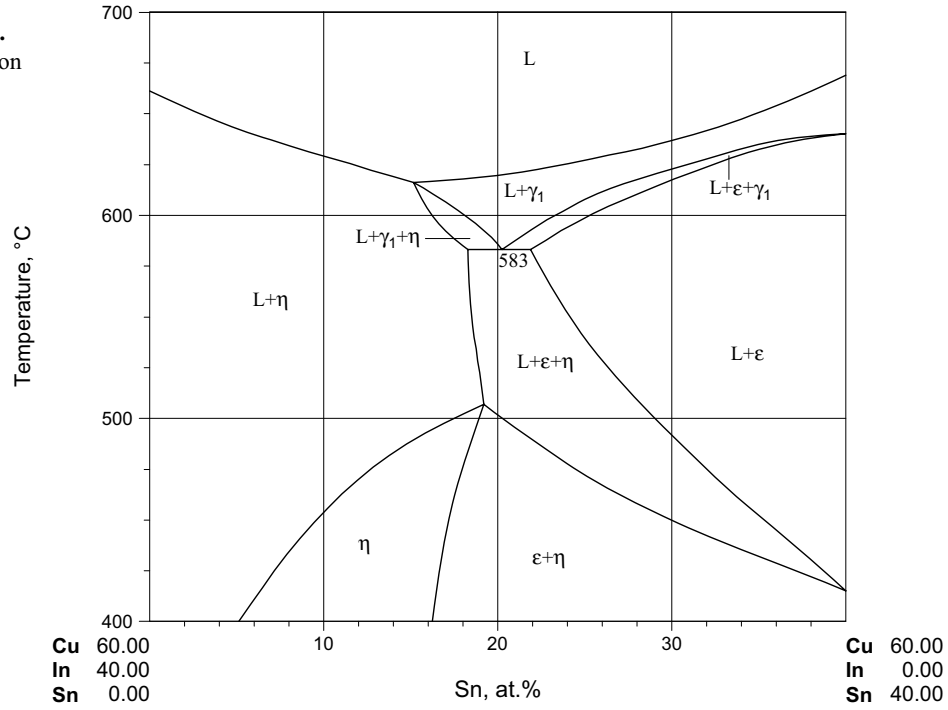

Fig. 17: Cu-In-Sn.
Partial vertical section
at 60 at.% Cu

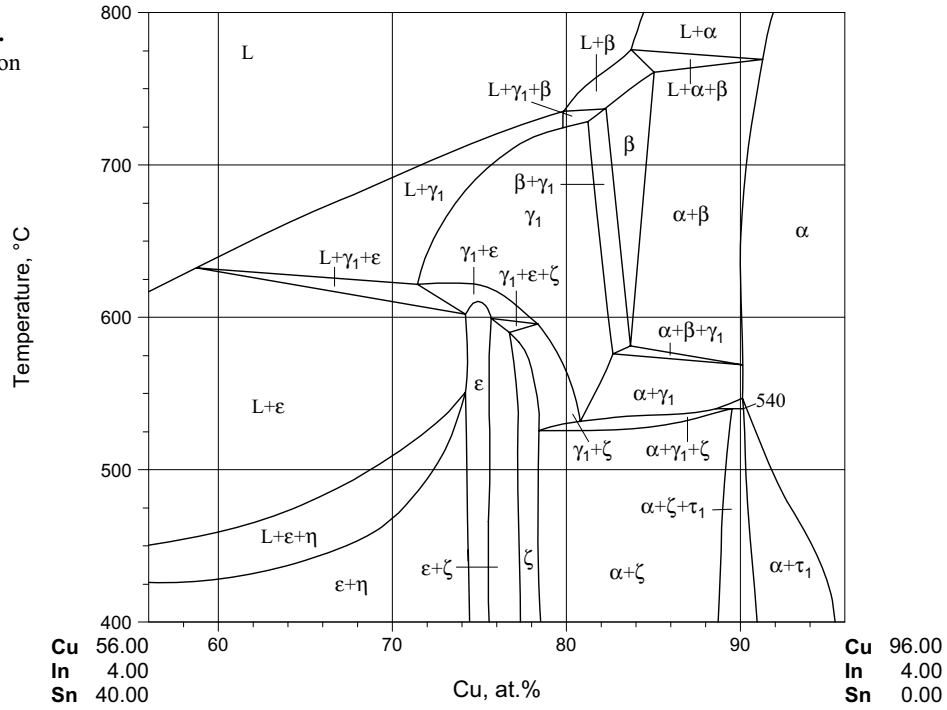

Fig. 18: Cu-In-Sn.
Partial vertical section at 4 at.% In

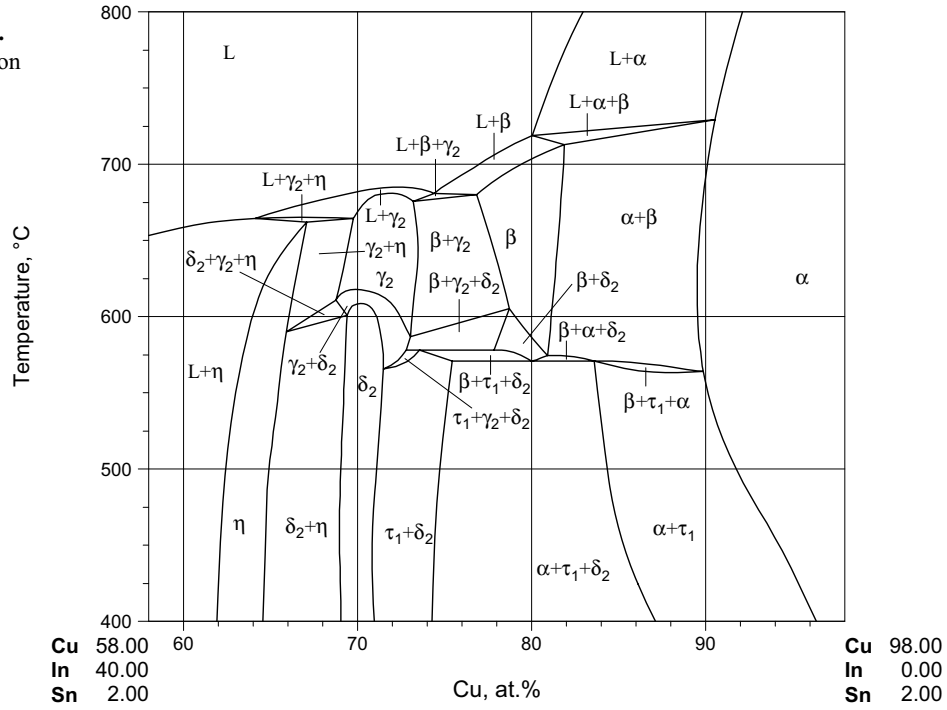

Fig. 19: Cu-In-Sn.
Partial vertical section at 2 at.% Sn

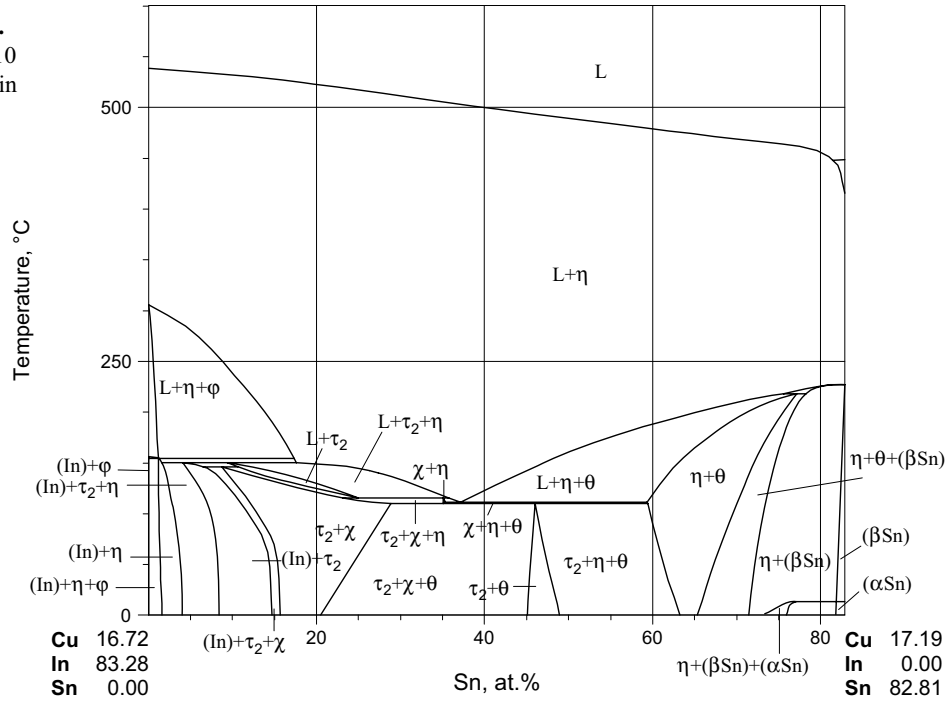

Fig. 20: Cu-In-Sn. Vertical section at 10 mass% Cu, plotted in at.%

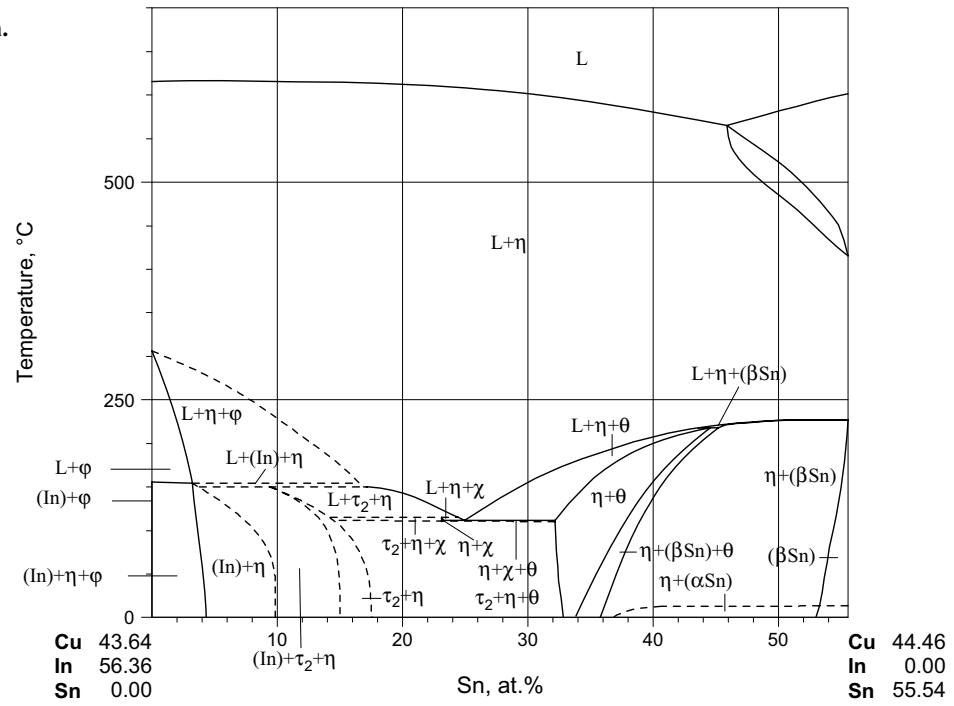

Fig. 21: Cu-In-Sn. Vertical section at 30 mass% Cu, plotted in at.%

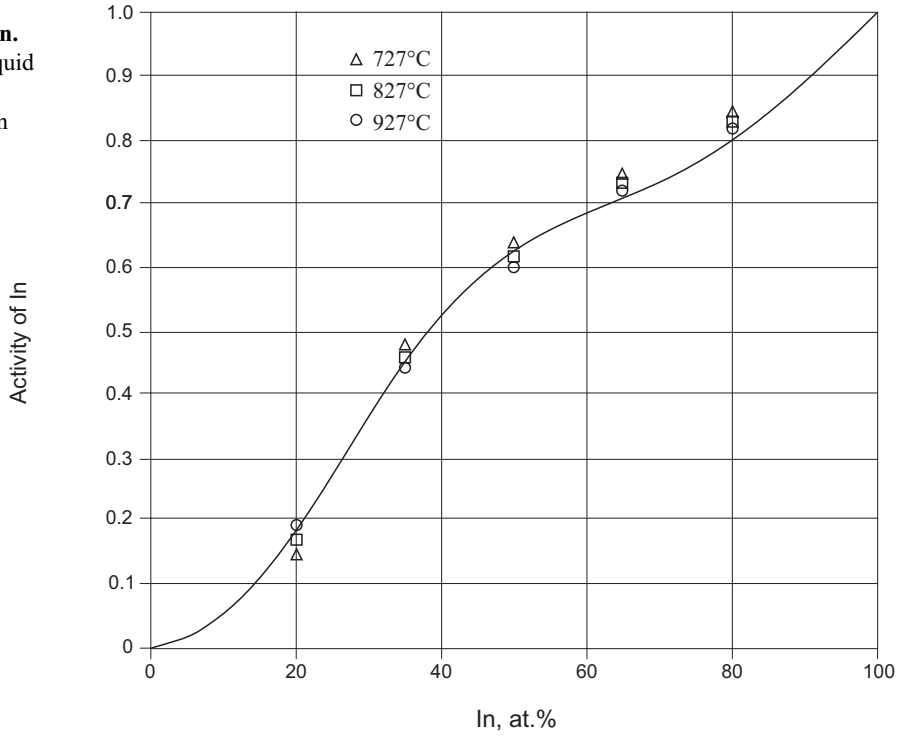

Fig. 22a: Cu-In-Sn. Activity of In in liquid alloys along $x_{Cu}/x_{Sn} = 4$ section

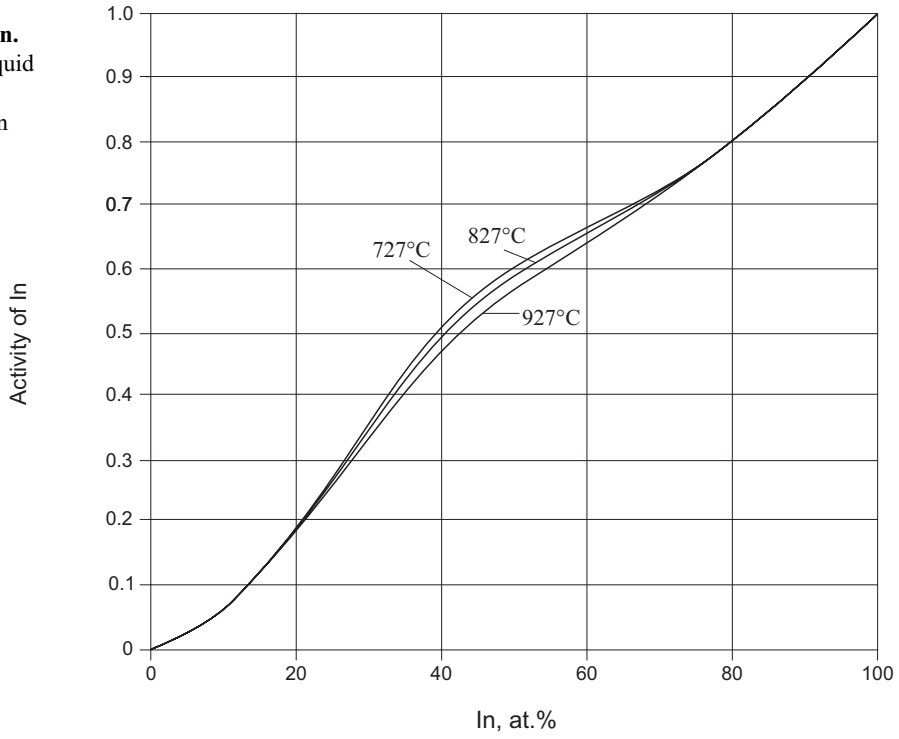

Fig. 22b: Cu-In-Sn. Activity of In in liquid alloys along $x_{Cu}/x_{Sn} = 1$ section

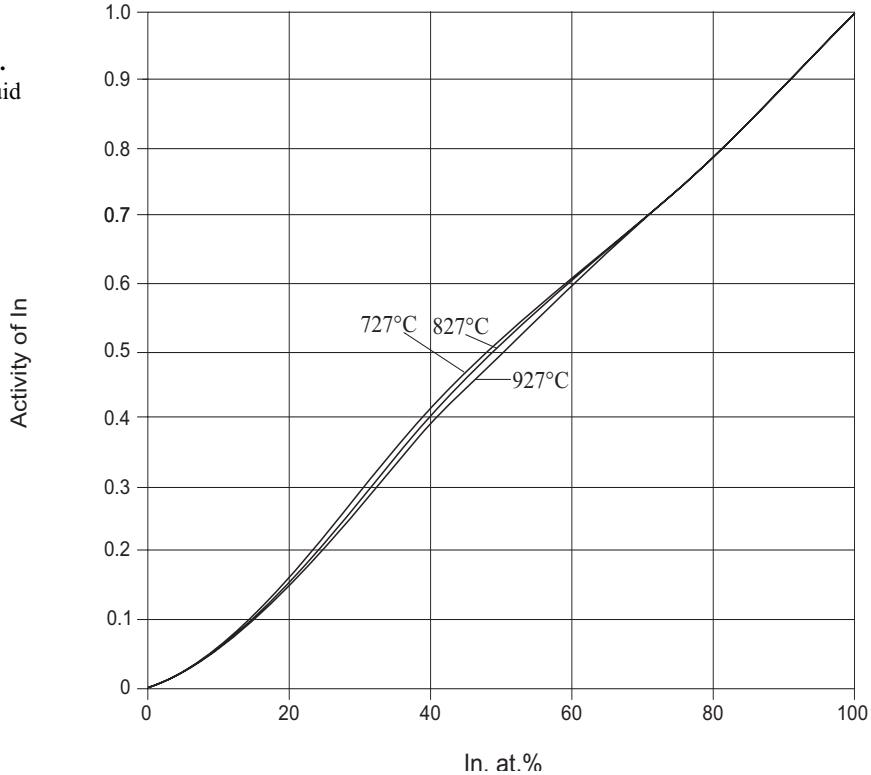

Fig. 22c: Cu-In-Sn. Activity of In in liquid alloys along $x_{Cu}/x_{Sn} = 0.25$