The Cu-Th (Copper-Thorium) System

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The Cu-Th phase diagram is characterized by the occurrence of four congruently melting intermediate phases that are essentially line compounds, two terminal solid solution phases, (Cu) and (Th), with negligible homogeneity ranges, and five eutectic transformations. A metastable phase, as well as metastable extension of solubility of Cu in (Th), were observed on splat cooling. Reports on the crystal structures were available. Thermodynamic measurements presented negative enthalpy and Gibbs energy of formation values for the compounds, indicating strong compound forming tendencies in this system.

Equilibrium Diagram

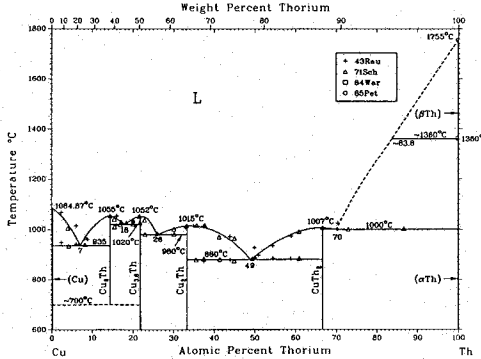
The assessed equilibrium diagram of the Cu-Th system is presented in Fig. 1. The equilibrium phases in this system include:

- the fcc terminal solid solution, (Cu), stable below 1084.87 °C, with solubility of Th of less than 0.01 at.% at 900 °C
- the fcc terminal solid solution, (αTh), stable below about 1363 °C, with presumably negligible solubility of Cu
- the bcc terminal solid solution, (βTh), stable between 1758 and approximately 1363 °C
- the orthorhombic phase Cu_4Th; stable below 1055 °C
- the hexagonal phase $Cu_{19}Th$, stable below 1052 °C
- the hexagonal phase Cu_2Th, stable below 1015 °C
- the tetragonal phase $CuTh_2$, stable below 1007 °C

The crystal structure and lattice parameter values for Cu-Th phases, accepted from [71Sch], are listed in Tables 1 and 2. All the intermediate phases appear to have negligible homogeneity ranges and have been represented as line compounds in this evaluation.

Literature on the Cu-Th system has been contradictory with regard to both the compounds and the associated transformation reactions (see [Hansen, Elliott, 58Rou]). This controversy arises from the extreme reactiveness of metallic Th with O and other elements, and from the resulting contamination effects during specimen prepa-

Fig. 1 Assessed Cu-Th Equilibrium Diagram



Temperatures shown for experimental data are as reported and have not been corrected to the 1968 temperature scale (IPTS-68).
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ration and processing. Th-rich compounds are pyrophoric and disintegrate in air, or even under partial vacuum (10^{-4} Torr) [61Bro], and react with SiO_2 tubes at high temperatures to form stable oxides. Progressive changes in composition also occur during annealing, chemical analysis, or XRD, because of oxidation. [65Tho] observed a lowering of the eutectic temperature in a Th-rich Cu-Th alloy by 50 °C because of a 2% Fe impurity. Melting specimens either under inert atmosphere or in a non-reacting liquid metal was used to avoid contamination [61Bro, 72Ber].

Temperature and composition values for transformations in this system, reported by various authors, are presented in Table 3.

The assessed Cu-Th diagram has been based primarily on the detailed and careful studies of [71Sch]. Alloys were made from 99.999% Cu and 99.97% Th in a gettered Ar atmosphere by arc melting, and were annealed in a Ta crucible under vacuum (5×10^{-5} Torr). The liquidus and the solidus isotherms were determined by DTA, and the eutectic points, by DTA and metallography. The accuracy of the DTA data is hard to judge, because both the scanning rate and whether the measurements were done during heating or during cooling are not mentioned. The crystal structure and lattice parameters were obtained from single-crystal and powder data, and the solid solubility of Th in (Cu), by the X-ray parametric method. Solidus and liquidus data from [71Sch] are presented in Table 4.

[72Ber] studied the formation of the Cu-Th compounds by powder and single-crystal XRD and by isothermal equilibration between 200 and 700 °C. The alloys were made from Cu and Th, both of 99.9% purity, in liquid Na. According to [72Ber], the solubility of Na in both (Cu) and (Th) is negligible. Thermodynamically, however, complete immiscibility is not possible, and the impurity effects, if very sensitive, can still alter the phase equilibria. Whether this was responsible for the observation of the compound Cu_3Th (see Table 5), as opposed to $Cu_{3.6}Th$, reported by [71Sch] and [74Bai], is not clear. [43Rau] made one of the earliest detailed studies of the Cu-Th phase diagram, based on thermal analysis, XRD, and metallography. The solid solubility of Th in (Cu) was studied by XRD, resistivity, and microhardness. Their reported invariant temperatures and compositions, shown in Table 3, are in close agreement with those of [71Sch]. However, the proposed stoichiometry of the compounds, except for Cu_6Th, differed considerably from those of [71Sch] (see Table 5). Selected liquidus data from their thermal studies are shown in Table 4, and Fig. 1. The eutectic transformation for the most Th-rich liquid, which was also very reactive, was studied by [65Tho], based on the metallography of annealed and quenched samples made from iodide Th and spectrographic grade Cu by arc melting (see Table 3). [42Gru] studied the system up to 21.5 at.% Th by thermal analysis. Phase diagram studies were also reported by [61Bro], [46Wil], and [40Gue].

Intermetallic Compounds. Like many other metals, Th forms a number of compounds with Cu. A list of these compounds in the chronological order of their reporting is shown in Table 5. Based on the present state of knowledge, the following four compounds are believed to be stable in this system:

- Cu_6Th, reported by [43Rau] and confirmed by [70Bus], [71Sch], and [72Ber]
- $Cu_{3.6}Th$, reported by [71Sch] and confirmed by [73Bai]

Table 1 Cu-Th Crystal Structure Data

Phase	Approximate homogeneity, at.% Th	Pearson symbol	Space group	Strukturbericht designation	Prototype
(Cu)	0	*cF*4	*Fm*3*m*	*A*1	Cu
Cu_6Th	14.29	*oP*28?	*Pnma*(a)	···	$CeCu_6$(b)
$Cu_{3.6}Th$	21.74	Hexagonal	*P*6/*m*(c)	···	$GdAg_{3.6}$
Cu_2Th	33.33	*hP*3	*P*6/*mmm*(d)	*C*32	AlB_2(e)
$CuTh_2$	66.67	*tI*12	*I*4/*mcm*(c)	*C*16	Al_2Cu(e)
(β Th)	100	*cI*2	*Im*3*m*	*A*2	W
(α Th)	100	*cF*4	*Fm*3*m*	*A*1	Cu
Metastable phase					
CuTh	50	*oC*8	*Cmcm*	B_f	CrB(f)

(a) [60Cro]. (b) [70Bus]. (c) [81Chi]. (d) [61Bro]. (e) [52Flo]. (f) [74Gie].

Table 2 Cu-Th Lattice Parameter Data

Phase	Approximate composition, at.% Th	Lattice parameters, nm *a*	*b*	*c*	Comment	Reference
(Cu)	0	0.36147	···	···	At 18 °C	[Landolt]
Cu_6Th	14.29	0.81103(7)	0.50817(3)	1.01046(6)	···	[71Sch]
$Cu_{3.6}Th$	21.74	1.1812(8)	···	0.8844(9)	···	[73Bai]
Cu_2Th	33.33	0.4383(4)	···	0.3496(3)	···	[71Sch]
$CuTh_2$	66.67	0.730(1)	···	0.580(2)	···	[71Sch]
(β Th)	100	0.411	···	···	(a)	[54Chi]
(α Th)	100	0.50845	···	···	···	[Pearson2]
Metastable phase						
CuTh	50	···	···	···	···	[74Gie]

(a) At 1400 ± 25 °C, 99.8% pure Th.

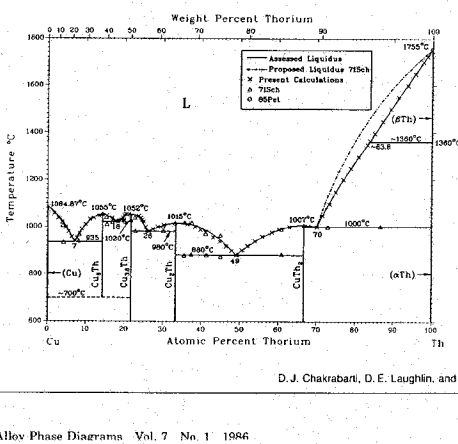
Table 3 Reported Temperatures and Compositions of Cu-Th Reactions

Reaction	Reaction type	Temperature, °C	Liquid composition, at.% Th	Method	Reference
$L \rightleftarrows (Cu) + Cu_6Th$	Eutectic	935 ± 5	7 ± 1	DTA, optical microscopy	[71Sch]
		946	~8(a)	Thermal analysis, X-ray, optical microscopy	[43Rau]
		940	7.6(b)	Thermal analysis	[42Gru]
$L \rightleftarrows Cu_6Th + Cu_{2.6}Th$	Eutectic	1020 ± 10	18 ± 0.5	DTA, optical microscopy	[71Sch]
		1020	19.5(c)	Thermal analysis	[43Rau]
$L \rightleftarrows Cu_{2.6}Th + Cu_2Th$	Eutectic	980 ± 5	26 ± 0.5	DTA, optical microscopy	[71Sch]
		970	29(d)	Thermal analysis	[43Rau]
$L \rightleftarrows Cu_2Th + CuTh_2$	Eutectic	880 ± 5	49 ± 0.5	...	[71Sch]
		883	50.8(e)	Thermal analysis	[43Rau]
$L \rightleftarrows CuTh_2 + (\alpha Th)$	Eutectic	1000 ± 5	70 ± 0.5	DTA, optical microscopy	[71Sch]
		1002	...	...	[43Rau]
		940	...	...	[46Wil]
		940	75	...	[58Rou]
		1037	75	...	[65Tho]
$L \rightleftarrows Cu_6Th$	Congruent	1055 ± 5(?)	14.29	DTA	[71Sch]
		1062	...	Thermal analysis	[43Rau]
$L \rightleftarrows Cu_{2.6}Th$	Congruent	1052 ± 5	21.74	DTA	[71Sch]
$L \rightleftarrows Cu_2Th$	Congruent	1015 ± 5	33.33	DTA	[71Sch]
$L \rightleftarrows CuTh_2$	Congruent	1007 ± 5	66.67	DTA	[71Sch]
		960	...	...	[58Rou]
$\beta Th \rightleftarrows L + \alpha Th$					
$L + \beta Th \rightleftarrows \alpha Th$	Metatectic/peritectic	~1363	~83	...	[This work]
$Cu_6Th \rightleftarrows (Cu) + Cu_{2.6}Th$	Eutectoid	~700	...	...	[This work](f)

Note: Accepted results have been taken from [71Sch].

(a) Indicated as 8.4 at.% Th in the figure and as 7.6 at.% Th in the text by [43Rau]. (b) The coexisting phases are L, (Cu), and Cu_6Th. (c) Between L, Cu_6Th, and Cu_2Th. (d) Between L, Cu_2Th, and Cu_5Th_9. (e) Between L, Cu_5Th_9, and unidentified Th-rich compound. (f) Based on the experimental data of [74Bai].

Fig. 2 Cu-Th Phase Diagram with Selected Experimental and Calculated Data



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- Cu_2Th, reported by [48Run] and confirmed by [52Flo], [55Mur], [56Bae], [61Bro], [71Sch], and [72Ber]
- $CuTh_2$, reported by [47Run] and confirmed by [52Flo], [55Mur], [56Bae], [61Mat], [71Sch], and [72Ber]

Each of the four compounds was observed to melt congruently, and the melting temperatures accepted in this evaluation have been taken from [71Sch] (see Fig. 1 and Table 3).

The phases in the two-phase fields in the solid state were identified by [71Sch] with XRD and microscopy.

Liquidus and Solidus. The accepted liquidus boundaries and the four compounds have been based on the thermal data of [71Sch], a few selected data from [43Rau], and the calculated results of thermodynamic modeling performed in this evaluation. The (Cu) liquidus is ill defined because of the limited and scattered nature of the thermal data, and the (Th) liquidus has not been determined experimentally. In both, the accepted boundaries have been estimated with the thermodynamic model discussed below. The liquidus curves have also been constrained to be compatible with the thermodynamically predicted initial slope values at the pure metal limits (see "Thermodynamics" section for details). The melting point of Cu (1084.87 °C) is taken from [Melt], and Th (1755 °C) is taken from [85Pet]. The allotropic transition temperature of Th (1360 °C) has been taken from [84War]. The (Th) liquidus proposed by [71Sch] is at variance with the calculated liquidus and the theoretical limiting slope requirements (see Fig. 2). The liquidus data from thermodynamic calculations in this evaluation are presented in Table 4. For the eutectic points occurring in this system, the temperatures and compositions of the corresponding eutectic liquids have been taken from [71Sch] (Table 3).

Solidus boundaries, representing the reaction isotherms, have been obtained from [71Sch] and are shown in Table 3. A metatectic, or alternatively, a peritectic transformation

Table 4 Cu-Th Liquidus and Solidus Data

Experimental			Calculated [This work]		
Composition, at.% Th	Liquidus temperature, °C	Solidus isotherm, °C	Boundary	Liquidus temperature, °C	Composition, at.% Th
From [71Sch]			L + (Cu)	935	7.1
4.1	1005	933		960	6.3
8.1	965	938		1000	4.7
14.3	1055	···		1040	2.9
15.4	1040	1010	L + Cu_6Th	935	7.0
17.1	1030	1018		950	7.5
18.3	···	1025		990	8.9
20	1035	1020		1020	10.4, 18.4
21.5	1052	1025		1030	11.1, 17.7
22.9	1031	980		1050	13.5, 15.1
26	···	981	L + $Cu_{3.6}Th$	980	26.3
30	1000	982		1020	18.6, 25.0
33.3	1015	···		1040	19.5, 24.1
35.7	1015	879		1050	20.0, 23.6
37.5	1014	880	L + Cu_2Th	880	49.0
41.3	970	880		920	46.3
45.1	965	872		960	43.1
49.3	···	881		980	26.2, 41.1
60.8	990	881		1000	28.5, 38.5
66.7	1007	···		1010	30.2, 36.5
73	···	1000	L + $CuTh_2$	880	49.0
86.8	···	1000		920	51.9
From [43Rau]				960	55.7
2.3	1067	946		980	58.4
6	1012	942		990	60.2
8.7	959	···		1000	62.8
15.8	1051	1019	L + (αTh)	1000	70.0
19.8	1026	1023		1100	73.3
35	1016	···		1200	76.9
37.3	1012	870		1300	80.9
43.8	970	876	L + (βTh)	1400	85.2
50	925	884		1500	89.2
54.5	931	881		1600	93.4
59	970	880		1650	95.5
70.5	1027	1002		1700	97.6
				1725	98.7
From [Melt]					
0	1984.87	···			
From [85Pet]					
100	1755	···			

Note: The accepted liquidus boundaries have been drawn based on the calculated results [This work], complemented by the thermal data of [71Sch], [43Rau], and melting point data from [Melt] and [85Pet], shown in bold-face type. For the $Cu_{3.6}Th$ liquidus, only the data of [71Sch] have been used.

Table 5 Reported Cu-Th Compounds

Reference	Compound
[40Gue]	Cu_3Th
[42Gru]	Cu_4Th
[43Rau]	Cu_4Th, Cu_6Th, Cu_8Th_5, Th-rich compound
[47Run, 48Run]	$CuTh_2$, Cu_4Th
[71Sch]	Cu_6Th, $Cu_{3.6}Th$, Cu_4Th, $CuTh_2$
[72Ber]	Cu_6Th, Cu_5Th, Cu_2Th, $CuTh_2$

occurs, depending on whether the βTh $\rightleftarrows$ αTh transformation temperature in (Th) is lowered or raised, respectively, relative to that of pure Th [83Mas] (see Fig. 1).

Solid Solubilities. The solid solubility of Th in (Cu) was studied by [40Gue], [42Gru], [43Rau], and [71Sch]. [40Gue] and [42Gru] reported a maximum solubility of 0.56 to 0.84 at.% Th and 1.1 at.% Th at 900 °C, respectively; these values are very high and must have been caused by impurities. [43Rau] reported a maximum solubility of 0.03 at.% Th at the eutectic temperature, which they reported as 946 °C. This compares well with the results of [71Sch], who obtained, from X-ray parametric measurements on samples quenched from 900 °C, a maximum solubility of less than 0.01 at.% Th. No data pertaining to the solubility of Cu in (Th) were available, but the solubility is expected to be very restricted, as represented in the phase diagram presented by [71Sch].

Metastable Phases

Metastable phase formation and phase extension in the Cu-Th system were studied by splat cooling. [74Gie] observed the formation of the metastable compound CuTh, having the CrB type of structure. The terminal solid solution phase, (Th), was found to extend to 15 at.% Cu.

Some of the reported compounds that do not appear in the equilibrium diagram could also be metastable phases, unless they were the product of stabilization by impurities or resulted from compositional changes during chemical analysis.

Crystal Structures and Lattice Parameters

Crystal structure information and lattice parameter values for the different phases are listed in Tables 1 and 2. The lattice parameters of the compounds were measured by several authors. These compare well with the data of [71Sch], as shown in Table 6.

Cu_6Th. The phase was first identified by [43Rau], but no structure related data were presented. [70Bus] reported the crystal structure as $CeCu_6$ type [60Cro]. This was confirmed by [71Sch] and [72Ber].

$Cu_{3.6}Th$. The crystal structure of this phase was identified by [73Bai] to be analogous to that of $GdAg_{3.6}$ [71Bai]. This interpretation was based on a comparison by [73Bai] of Debye-Scherrer patterns of samples provided by [71Sch] with those of $GdAg_{3.6}$, which showed good agreement.

Cu_2Th and $CuTh_2$. [52Flo] suggested that Cu_2Th is isostructural with AlB_2, and $CuTh_2$ is isostructural with $CuAl_2$. No lattice parameter data were given for either phase. These structures were confirmed by [56Bae], and by [55Mur], who also measured lattice parameter values.

Table 6 Reported Lattice Parameters of Cu-Th Compounds

Compound	Lattice parameters, nm			Reference
	a	*b*	*c*	
Cu_6Th	0.81103(7)	0.50817(3)	1.01046(6)	[71Sch]
	0.81063(4)	0.50672(3)	1.01193(6)	[72Ber]
	0.8115	0.5078	1.0122	[70Bus]
$Cu_{3.6}Th$	1.1812(8)	···	0.8344(9)	[73Bai]
Cu_2Th	0.4383(4)	···	0.3496(3)	[71Sch]
	0.43789(6)	···	0.34877(9)	[72Ber]
	0.4387(1)	···	0.3472(1)	[61Bro]
	0.437(1)	···	0.345(1)	[55Mur]
	0.435	···	0.347	[56Bae, 48Run]
$CuTh_2$	0.730(1)	···	0.580(2)	[71Sch]
	0.73120(3)	···	0.57944(4)	[72Ber]
	0.728(1)	···	0.575(1)	[61Mat]
	0.728(1)	···	0.575(1)	[55Mur]
	0.728	···	0.574	[56Bae, 47Run]

These and other values, obtained by several other authors ([71Sch, 72Ber, 61Bro, 61Mat, 48Run, 47Run]), are listed in Table 6.

Thermodynamics

Thermodynamic Measurements. The Gibbs energies ($\Delta_f G^0$), enthalpies ($\Delta_f H^0$), and entropies ($\Delta_f S^0$) of formation of Cu-Th compounds were studied by solid electrolyte (CaF_2) emf by [69Mag] and [74Bai]. [69Mag] reported data for the phase assumed to be Cu_4Th at 973 K. [71Ske] recalculated these results for the revised stoichiometry Cu_6Th, because Cu_4Th was shown not to be a stable phase in this system. [74Bai] made detailed measurements in the temperature range 729 to 1219 K and reported data on all four compounds: Cu_6Th, $Cu_{3.6}Th$, Cu_2Th, and $CuTh_2$. The alloys were made from 99.999% Cu and 99.97% Th by arc melting under purified Ar. The $\Delta_f H^0$ and $\Delta_f S^0$ values were estimated from the slopes and intercepts of the temperature variations of the Gibbs energy of formation curves. These, as well as the $\Delta_f G^0$ values at the average temperature (973 K), relative to pure solid Cu and pure solid Th as standard states, are presented in Table 7. Similar results for $\Delta_f G^0$ at 1000 K, plus the corresponding partial molar quantities for $\Delta_f H^0$ and $\Delta_f S^0$, were also presented in the compilations of [81Chi].

Thermodynamic Modeling. Although $\Delta_f H^0$ and $\Delta_f S^0$ values were known for the various compounds in the Cu-Th system, the liquid phase thermodynamic functions were not known. For the modeling analysis in this evaluation, the known liquidus in equilibrium with (Cu) and (Th) has been used to model thermodynamic parameters for the liquid. These results, in conjunction with other phase diagram data, have been used to calculate the thermodynamic parameters for the four compounds, which have been then compared with the experimental results of [74Bai]. The model parameters have been used to reproduce the [(Cu) + (Th)] liquidus and solidus curves as a check for self-consistency, and also to calculate unknown regions of the liquidus.

Because both the (Cu) and (Th) phases display virtually zero solubility, they have been assumed to be line phases, and their molar Gibbs energies represented by their respective lattice stability parameters. The latter value for (Cu) has been taken from [Hultgren, E]; those for (Th) have been chosen from the drop calorimetry data of

Table 7 Thermodynamic Properties of Cu-Th Compounds at 973 K

Compound	Reference	Gibbs energy, liquid $(-\Delta G(L))$, kJ/mol	Gibbs energy, solid $(-\Delta G(s))$, kJ/mol	Enthalpy, liquid $(-\Delta H(L))$, kJ/mol	Enthalpy, solid $(-\Delta H(s))$, kJ/mol	Entropy (ΔS), J/mol · K
Cu_6Th	[74Bai]	···	13.68 ± 0.04	···	10.46 ± 0.50	3.31 ± 0.54(b)
	[This work]	17.01	12.60	22.07	8.40	−5.20(a)
$Cu_{24}Th$	[74Bai]	···	20.88 ± 0.08	···	17.24 ± 0.67	3.68 ± 0.84(b)
	[This work]	19.61	14.84	18.60	4.60	1.04(a)
Cu_5Th	[74Bai]	···	26.36 ± 0.17	···	25.68 ± 1.46	0.29 ± 1.84(b)
	[This work]	27.99	22.64	40.08	25.57	−12.43(a)
$CuTh_2$	[74Bai]	···	26.78 ± 0.21	···	27.24 ± 0.21	−0.46 ± 2.65(b)
	[This work]	24.85	17.85	39.40	23.45	−14.96(a)

(a) Referred to pure liquid Cu and pure liquid Th as standard states. (b) Referred to pure solid Cu and pure solid Th as standard states.

[66Lev], as accepted by [76Oet] and [84War], in preference to the corresponding values in [Hultgren, E] (see Table 8). The Gibbs energy of the liquid has been approximated by a polynomial:

$$\Delta G^{ex}(L) = X(1-X)\sum_{i=1}^{N}(a_i^H X^{i-1} - T\cdot b_i^S X^{i-1}) \qquad \text{(Eq 1)}$$

where a_i^H and b_i^S are, respectively, the coefficients of the enthalpy and entropy functions of the liquid and X is the atomic fraction of Th. The coefficients have been assumed to be independent of temperature. The number of a^H and b^S terms derived from the standard multiple least-squares regression analysis of the phase coexistence data has been limited to a minimum, as a compromise between the reproducibility of the calculated diagram and the simplicity of the model.

For the initial analysis, the experimental (Cu) liquidus and the proposed (Th) liquidus [71Sch] were used to model the thermodynamic parameters for the liquid and, in turn, for the compounds. However, comparison of the $\Delta_f H^0$ and $\Delta_f G^0$ values for the compounds with the experimental results of [74Bai] showed large discrepancy. Apparently the liquidus, in particular for the (Th) end, was not correct. This interpretation was confirmed further from a consideration of the limiting slope of the liquidus near pure Th.

Because the (Cu) and (Th) phases have negligible homogeneity fields, the limiting slopes for the liquidus in both cases should obey van't Hoff's relation:

$$\Delta T/X_j^L = -[R(T_j^m)^2]/\Delta H_j^{m\to L} \qquad \text{(Eq 2)}$$

where $\Delta T/X_j^L$ is the limiting slope of the liquidus, T_j^m is the melting point; and $\Delta H_j^{m\to L}$ is the enthalpy of fusion for the component j. The value of $\Delta T/X_{Th}^L$, calculated from Eq 2 with $T_{Th}^m = 2031$ K, $\Delta H_{Th}^{m\to L} = 13\,807$ J/mol [66Lev] and $R = 8.314$ J/mol · K, is −24.8 K/at.% Cu, compared with −12 ± 2 K/at.% Cu, obtained from the liquidus proposed by [71Sch]. The corresponding value of $\Delta T/X_{Cu}^L$ for $T_{Cu}^m = 1358$ K and $\Delta H_{Cu}^{m\to L} = 13\,054$ J/mol is −11.8 K/at.% Th, which is slightly lower than that obtained from the experimental liquidus of [71Sch]. Therefore, the (Cu) liquidus has been modified to be compatible with the theoretical limiting slope, by imposing an additional small negative curvature. The Th end of the liquidus proposed by [71Sch] has been rejected, except for the data point at the eutectic temperature, 1000 °C. Instead, two liquidus temperatures in the dilute range (<1 at.% Cu) consistent with the limiting slope have been used, along with other liquidus data from the Cu end, to model the enthalpy and entropy of the liquid. Approximation of the liquid by a subregular solution model has been adequate to reproduce the phase diagram satisfactorily. The resultant expression for the $\Delta G^{ex}(L)$ is given in Eq 3:

$$\Delta G^{ex}(L) = X(1-X)(-94\,200 + 50\,050\,X) \quad \text{J/mol} \qquad \text{(Eq 3)}$$

The minimum value of $\Delta H^{ex}(L)$ according to Eq 3 is −17 827 J/mol at $X = 0.417$, and the corresponding $\Delta G^{ex}(L)$ value, estimated at 1000 K, is −23 475 J/mol.

The Gibbs energy of Cu_6Th, expressed in the form $A + BT$, has been estimated from a least-squares fit of the coexistence data for Cu_6Th + L at 935, 1055, and 1020 °C, corresponding to the liquid compositions 7, 14.29, and 18 at.% Th, respectively. For these calculations, Cu_6Th has been assumed to be a line compound. In a similar manner, the Gibbs energies of formation for $Cu_{3.5}Th$, Cu_2Th, and $CuTh_2$ have been estimated from a least-squares fit of the liquidus data at the following temperatures:

- **$Cu_{24}Th$:** 1020, 1052, and 980 °C
- **Cu_5Th:** 980, 1015, and 880 °C
- **$CuTh_2$:** 880, 1007, and 1000 °C

The Gibbs energy expressions for these phases, relative to pure liquid Cu and pure liquid Th, are presented in Table 8. For comparison with the measured data of [74Bai], the estimated $\Delta_f G^0$ at 973 K and $\Delta_f H^0$ values for all the compounds were normalized relative to pure solid Cu and pure solid αTh, as shown in Table 7. The calculated $\Delta_f H^0$ values agree within 2 to 20% of the measured values, except for the $\Delta_f H^0$ of $Cu_{3.5}Th$. The large discrepancy in

Table 8 Cu-Th Thermodynamic Parameters, J/mol, T in K

Lattice stability parameters	
$\Delta G_{Cu}^{fcc\to L} = 13\,054 - 9.613\,T$	[Hultgren, E]
$\Delta G_{Th}^{fcc\to L} = 13\,807 - 6.80\,T \pm 1255$	[66Lev]
$\Delta G_{Th}^{bcc\to L} = 17\,405 - 9.00\,T$	[66Lev]
$\Delta G_{Th}^{\alpha\to\beta} = 3\,600 - 2.20\,T \pm 120$	[66Lev]
Gibbs energy	[This work]
$G(L) = X(1-X)(-94\,200 + 50\,050\,X) + RT[X\ln X + (1-X)\ln(1-X)]$	
$G(Cu_6Th) = -22\,065 + 5.20\,T$	
$G(Cu_{3.5}Th) = -18\,600 - 1.04\,T$	
$G(Cu_2Th) = -40\,075 + 12.425\,T$	
$G(CuTh_2) = -39\,400 + 14.355\,T$	

Note: X = atomic fraction of Th; mol for compounds refers to respective atomic units as elementary entities; standard states are pure liquid Cu and pure liquid Th.

the latter case implies some uncertainty in either the phase equilibrium or the thermodynamic data associated with this compound. It is otherwise difficult to explain such an isolated large variation in the calculated result. No comparison has been attempted for the $\Delta_f S$ parameters, because of the large variations and uncertainties in their reported values [74Bai]. Interestingly, the enthalpy and the Gibbs energy values for the four compounds, calculated using the lattice stability parameters for αTh and βTh [Hultgren, E], were an average 2 to 6% nearer to the experimental values of [74Bai] than those obtained when using the parameters of [66Lev].

The calculated liquidus is shown by plus (+) marks in Fig. 2, and is tabulated in Table 4, for quantitative comparison with the measured data. The agreement among these results is very good.

The mutual stabilities of the four compounds with respect to the (Cu) and (αTh) phases has been examined by considering the relative changes with temperature of the Gibbs energies of these phases. For this analysis, the experimental data of [74Bai] have been used in preference to the calculated results in the present evaluation, because of uncertainties in the calculated thermodynamic parameters for $Cu_{24}Th$. The calculations have shown that the Cu_4Th phase decomposes at about 700 °C into (Cu) + $Cu_{2.6}Th$, in agreement with similar conclusions by [81Chi], who estimated the decomposition temperature of Cu_4Th to be 679 °C. The eutectoid transformation is indicated in Fig. 1 and 2 and in Table 3.

Suggestions for Future Experimental Work

- The (αTh) liquidus and the (βTh) liquidus should be determined. This will help in assessing the reliability of the calculated liquidus obtained in this evaluation, and also in deriving a more accurate thermodynamic expression for the liquid.
- The (βTh) → (αTh) transition temperature for the Cu-Th alloys should be determined accurately. This would indicate whether a peritectic or a metatectic type of transformation occurs.
- The experimental liquidus should be checked in the region of $Cu_{3.6}Th$, to ascertain if the observed inconsistency in $\Delta_f H°$ for the compound is because of inaccuracies in the experimentally determined liquidus.
- The predicted decomposition temperature of Cu_5Th should be investigated to check for accuracy of the experimentally determined $\Delta_f H°$ and $\Delta_f S°$ values of the compounds Cu_6Th and $Cu_{3.6}Th$.

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*Indicates key paper.
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