The As-Cu (Arsenic-Copper) System

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Equilibrium Diagram

Extensive investigations have been reported for the Cu-As system. This system has also been reviewed by [Hansen] and [Elliott]. The liquidus accepted by [Hansen] is based on the differential thermal analysis (DTA) data of [05Fri], [06Hio], [08Fri], and [10Ben]. [Elliott] revised the liquidus in the light of the more recent investigation of [57Hum]. Phase relationships in the Cu-As system have been the subject of numerous investigations.

[Hansen] and [Elliott] accepted the following phases and reactions: the terminal solid solution, (Cu), with a large solubility range: congruently melting Cu$_3$As, in eutectic equilibrium with (Cu); a high-temperature compound tentatively identified as Cu$_5$As$_2$, forming peritectically from the liquid and Cu$_3$As and subsequently decomposing eutectoidally into Cu$_3$As and an As-rich phase; and the eutectic reaction between Cu$_5$As$_2$ and an As-rich phase of unknown composition. In addition, the diagram of [Elliott] shows the peritectoid formation of Cu$_9$As. The stoichiometry of the most Cu-rich compound was given as Cu$_9$As by

[57Sch], Cu$_8$As by [60Hey], and Cu$_6$As by [72Nau]. Cu$_5$As$_2$ was subsequently designated Cu$_{19}$As$_8$ by [68Juz]. The phase diagram proposed by [72Nau] shows the existence of two additional compounds, Cu$_{15}$As$_4$ and Cu$_2$As. More recently, [82Ble] reported the formation of Cu$_3$As$_4$. Most of the Cu-As compounds also have been found to correspond crystallographically to naturally occurring minerals (see below).

General Features

The proposed equilibrium diagram for the Cu-As system (Fig. 1) follows the essential features of [Hansen] and [Elliott], with certain revisions based on more recent experimental investigations. The phases accepted are: (1) the liquid, L; (2) the fcc terminal solid solution, (Cu), with a maximum solid solubility of 6.83 at.% As at the eutectic temperature of 685 °C; (3) Cu-rich cph β (A3, Mg type), forming peritectoidally from (Cu) and γ' at 325 °C; (4) hexagonal γ (D0$_{18}$, Na$_3$As type), forming congruently from the liquid at 26.25 at.% As and 827 °C; (5) hexagonal γ' (Cu$_3$As type), existing over the maximum composition range of ~25.5 to 27.8 at.% As and undergoing an allotropic transfor-

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Fig. 1 Assessed Cu-As Phase Diagram
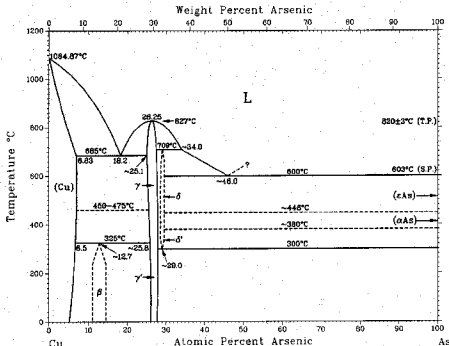
PR. Subramanian and D.E. Laughlin, 1988.

mation to hexagonal γ at temperatures between 450 and 475 °C; (6) cubic δ ($D0_3$, BiF_2 type), forming peritectically from L and γ at 709 °C and ~29 at.% As and undergoing an allotropic transformation to orthorhombic δ' at ~380 °C; (7) orthorhombic δ' (Cu_5As_2 type), existing over the limited temperature range 300 to 380 °C and decomposing eutectoidally into γ' and (αAs) at 300 °C and ~29 at.% As; and (8) pure As phases (αAs) and (ϵAs), with no reported solid solubility of Cu. (Pure As is dimorphic; rhombohedral (αAs) is stable at lower temperatures, and high-temperature orthorhombic (ϵAs) is stable above 448 °C.)

The various invariant reactions reported for the Cu-As system are summarized in Table 1, where the melting point of pure Cu is accepted from [Melt] as 1084.87 °C. Under atmospheric pressure, pure As sublimes at 603

°C [Melt]. The triple point of As exists near 820 ± 3 °C and at 3.71 MPa [Hultgren,E].

Liquidus and Solidus

Liquidus and invariant temperatures reported in the early investigations of [05Fri], [08Fri], and [10Ben] are in remarkably good agreement. All three investigations agree with regard to the existence of the Cu-rich and As-rich eutectic reactions and the congruently melting γ (or Cu_3As). [05Fri] and [08Fri] reported the peritectic formation of δ (or Cu_5As_2) and its subsequent decomposition through a eutectoid reaction; the phase relationships proposed for δ by [10Ben] are erroneous.

After a gap of almost half a century, the Cu-As phase diagram was redetermined completely by [57Hum] from DTA, microscopy, and X-ray analysis. Liquidus temperatures for compositions up to 30 at.% As were

Table 1   Special Points of the Assessed Cu-As Phase Diagram

Reaction	Compositions of the respective phases, at.% As			Temperature, °C	Reaction type	Reference
L ↔ (Cu)	0.0			1084.87	Melting point	[Melt]
L ↔ (Cu) + γ	18.8	0	26.6	685	Eutectic	[05Fri]
	16.8	0	25.1	685	Eutectic	[06Hio]
	18.4	3.4	25.4	689	Eutectic	[08Fri]
	18.4	2.6	25.1	685	Eutectic	[10Ben]
	18.2	6.83	25.5	685	Eutectic	[57Hum]
	18.2	6.83	25.1	685	Eutectic	Assessed
(Cu) + γ' ↔ β	6.5	~25.8	12.7	325	Peritectoid	(a)
γ' ↔ γ	25.5-27.3	25.5-27.3	...	450-475	Allotropic	[69Ben]
L ↔ γ		26.6		830	Congruent	[05Fri]
		25.1		747	Congruent	[06Hio]
		25.7		830	Congruent	[08Fri]
		25.1		830	Congruent	[10Ben]
		25.3		...	Congruent	[13Pus]
		26.25		827	Congruent	[57Hum]
				830		[71Guk]
		25.0		827		[72Uga]
δ' ↔ δ	28.6-29.6	28.6-29.6	...	~380	Allotropic	[71Lie]
L + γ ↔ δ	35.7	26.6	28.6	711	Peritectic	[05Fri](b)
	34.2	26.3	28.6	709	Peritectic	[08Fri](b)
	33.1	27.1	30.0	709	Peritectic	[57Hum](b)
	33.3	26.7	28.6	710	Peritectic	[72Uga]
	34.0	27.3	29.0	709	Peritectic	Assessed
δ' ↔ γ' + (αAs)	28.6	26.6	100	310	Eutectoid	[05Fri](c)
	28.6	26.3	100	300	Eutectoid	[08Fri](c)
	28.7	25.1	100	305	Eutectoid	[10Ben](c)
	31.0	27.1	100	300	Eutectoid	[57Hum](c)
	28.6	26.7	100	300	Eutectoid	[72Uga]
	29.0	27.8	100	300	Eutectoid	Assessed
L ↔ δ + (ϵAs)	43.4	28.6	100	600	Eutectic	[05Fri]
	44.9	28.6	100	600	Eutectic	[08Fri]
	42.9	28.7	100	600	Eutectic	[10Ben]
	46.0	31.0	100	600	Eutectic	[57Hum]
	45.8	29.6	100	600	Eutectic	[72Uga]
	46.0	29.0	100	600	Eutectic	Assessed
(ϵAs) ↔ As(vap)	100			603	Sublimation	[Melt]
(ϵAs) ↔ (αAs)	100			448	Allotropic	[King4]

(a) Eutectoid temperature obtained from [60Hey] and [66Mae]. (b) Peritectic phase designated Cu_5As_3. (c) Inferred from DTA data, although the authors did not indicate the eutectoid reaction.

determined from alloys prepared by conventional methods, whereas temperatures for compositions greater than 30 at.% As were obtained from alloys prepared in sealed silica tubes to prevent loss of As by vaporization. The resulting phase diagram is in excellent agreement with those proposed by [05Fri], [08Fri], and [10Ben]. In all these investigations, liquidus temperatures were not determined beyond the As-rich eutectic reaction, presumably because of the difficulties associated with the evaporation of As. More recently, [72Uga] determined the Cu-As phase diagram in the region 23.7 to 100 at.% As and in the temperature range 250 to 850 °C by DTA, X-ray diffraction, and optical metallography. Their liquidus temperatures are in close accord with the earlier investigations.

The assessed liquidus (Fig. 1) is based on the composite data of [05Fri], [08Fri], [10Ben], [57Hum], and [72Uga]. Figure 2 compares the assessed Cu-As phase diagram with the available experimental data. The liquidus data of [72Uga] beyond 46 at.% As are applicable only under constrained conditions, because pure As sublimes at 603 °C. As such, these data were rejected, and the proposed phase relationships are sketched schematically in Fig. 3. Table 2 lists the liquidus data of [05Fri], [08Fri], [10Ben], [57Hum], and [72Uga]. The Cu-As system is characterized by two terminal eutectics—L ↔ (Cu) + γ and L ↔ δ + (εAs). Reported eutectic temperatures are in good agreement (see Table 1). The accepted values in Fig. 1 are based on the data of [57Hum].

Solubility of As in (Cu)
The (Cu) solidus was determined by [57Hum] from metallographic examination of samples quenched after annealing at various temperatures. Because there have been no other determinations of the (Cu) solidus, the accepted boundary in Fig. 1 is from [57Hum].

The solid solubility of As in (Cu) has been investigated by metallography [10Ben, 27Han, 34Hum], electrical resistivity [13Pus], and lattice parameter measurements [37Mer, 39Owe, 40Owe, 49Owe]. [49Hum] indicated that the measurements of [27Han] and [34Hum] are erroneous because of insufficient annealing periods. The lattice parameter measurements of [37Mer] indicate a linear decrease in solubility from 6.8 at.% As at 680 °C to 6.4 at.% As at 300 °C. [40Owe] reported a discontinuous decrease in solubility at ~380 °C. More recent investigations confirm this discontinuity to be associated with the peritectoid formation of Cu-rich β, not a result of a polymorphic transition in γ (or Cu₃As), as was interpreted in the review of [Hansen]. Solubility data of [37Mer], [40Owe], and [49Owe] show good agreement and blend in with the room temperature solubility value of [13Pus]. Solubility data from these investigations are presented in Table 3 and shown as the (Cu) solvus curve in Fig. 1.

Intermediate Phases
β
The exact stoichiometry of this most Cu-rich intermediate phase is a subject of controversy. Although its

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Fig. 2 Assessed Cu-As Phase Diagram with Experimental Data

□ 05Fri	▽ 40Owe	
◇ 08Fri	▲ 49Owe	
● 10Ben	+ 57Hum	
■ 13Pus	× 72Nau	
△ 37Mer	▼ 72Uga	
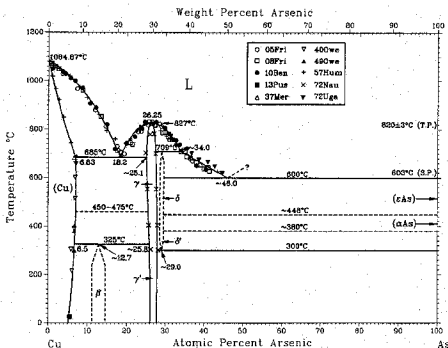
Table 2   Experimental Cu-As Liquidus Data

Composition, at.% As	Temperature, °C	Composition, at.% As	Temperature, °C	Composition, at.% As	Temperature, °C	Composition, at.% As	Temperature, °C
[05Fri]		21.1	737	10.1	930	8.14	969
0	1084	23.0	791	10.1	932	9.94	928
3.28	1030	24.8	823	10.5	905	12.66	860
7.39	966	24.8	825	11.3	885	14.75	794
11.82	878	25.7	826	11.5	888	16.91	735
14.62	810	25.7	830	12.9	860	18.23	687
17.39	726	26.5	828	14.7	820	20.85	757
18.34	702	26.7	823	17.1	715	22.70	795
19.42	697	27.2	818	19.6	742	24.10	815
23.60	790	29.5	787	19.8	740	25.42	826
25.57	818	29.8	787	22.0	770	26.25	827
26.56	830	31.2	759	23.2	790	28.69	798
27.73	827	34.2	710	23.8	800	30.16	772
28.62	822	34.7	707	24.8	832	30.52	763
29.0	812	35.6	688	25.1	830	36.70	684
29.47	787	36.3	685	26.3	830	40.10	653
31.63	757	37.9	665	26.9	830	43.40	626
34.54	716	40.0	697	27.4	830	**[72Uga]**	
36.94	669	40.2	641	27.8	830	23.7	804
37.90	661	41.0	642	29.8	807	27.3	804
39.0	651	41.3	629	32.0	760	28.6	800
[08Fri]		**[10Ben]**		32.6	755	30.7	779
0.9	1072	0	1084	33.7	740	31.3	772
1.7	1059	0.8	1065	35.4	700	32.7	731
2.6	1051	1.1	1050	38.0	650	37.0	697
4.3	1030	3.4	1035	40.4	635	38.7	676
8.6	959	4.1	1030	**[57Hum]**		41.0	666
13.0	851	4.4	1030	0.91	1072	43.7	645
17.5	711	5.8	1012	1.74	1064	44.7	621
19.3	699	6.7	1000	2.59	1053	**[Melt]**	
20.8	742	8.1	863	5.21	1017	0	1084.87
		8.6	970				

Note: Temperatures are reported as published and are not corrected to the 1968 temperature scale (IPTS- 68).

structure has been identified to be cph Mg-type, the stoichiometry has been given as Cu₉As [57Sch], Cu₅As [60Hey, 66Mae, 71Lie], and Cu₆As [72Nau]. According to [57Sch], Cu₅As is stable only below 400 °C. Cu₅As was observed by [60Hey] to be isostructural with the Cu₅As reported by [57Sch] and to be analogous to the ε phases of Cu-Sb, Ag-As, and Ag-Sb systems. The inability of [60Hey] to prepare single-phase specimens of this phase was speculated to be due either to slow transformation kinetics or to the presence of a limited temperature range of stability. Additionally, [60Hey] observed that β forms peritectoidally between ∼ 300 and 350 °C.

From experimental DTA, metallographic and X-ray investigation of the ternary Cu-As-Sn system, [66Mae] independently confirmed the peritectoid formation of the β at 325 ± 25 °C. Because this phase was stabilized by the addition of Sn, extrapolation to 0% Sn revealed its composition to be Cu₅As, in agreement with [60Hey]. The data of [40Owe] show an inflection in the (Cu) solid solubility curve at 380 °C, which could be attributed to the peritectoid formation of β. However, there is some uncertainty in the reported temperature at the inflection, because the (Cu) solid solubility curve

was determined by X-ray lattice parameter measurements. The existence of Cu₅As was further confirmed by [71Lie], who observed the presence of Cu₅As in a 25 at.% As alloy that had been quenched following annealing at 350 °C for 28 h. The X-ray and DTA investigation of [72Nau] assigned the stoichiometry Cu₆As to this phase. Moreover, [72Nau] observed the peritectoid formation of this phase to be between 450 and 500 °C, which is much higher than the values reported by earlier workers. In this review, β is shown to have the range of stability ∼11.1 to 14.3 at.% As, based on the reported extrema in the stoichiometries. The peritectoid formation temperature of β is accepted tentatively as 325 ± 25 °C.

γ and γ′

The congruent formation of γ (or Cu₃As) was established by [05Fri], [06Hio], [08Fri], [10Ben], and [57Hum]. There is some scatter in the composition of the observed congruent maxima, although the reported temperatures are in remarkably good agreement, with the exception of the data of [06Hio] (see Table 1). Additionally, γ has been confirmed to have a range of homogeneity. The data of [08Fri] showed a

Fig. 3 Schematic Phase Relationships for the As-Rich Region of the Cu-As System
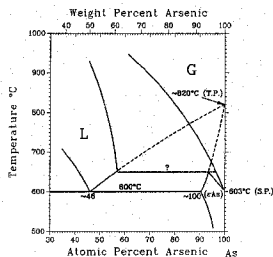
The L + G ↔ (εAs) reaction is shown at an undetermined temperature. The dashed lines show, under constrained pressure conditions, the extrapolation of the L + (εAs) phase-field boundaries to the triple point for pure As which lies at ~ 820 °C at 3.71 MPa [Hultgren,E]
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Table 3 Solid Solubility of As in (Cu)

Reference	Temperature, °C	Solubility limit, at.% As	Method
[13Pus]	25	5.1	Resistivity
[37Mer]	300	6.4	X-ray
	680	6.8	
[40Owe]	215	6.00	X-ray
	300	6.10	
	387	6.65	
	514	6.70	
	603	6.75	
	659	6.85	
[49Owe]	200	5.90	X-ray
	384	6.63	
	400	6.64	
	686	6.83	

homogeneity range of 25.4 to 26.3 at.% As. This was subsequently confirmed by [30Kat], who indicated that the homogeneity range is independent of temperature. [57Hum] observed a homogeneity range of ~ 1 at.% between 450 and 575 °C.

[60Hey] reported values of 24.94 and 26.88 at.% As for the Cu-rich limit and As-rich limit, respectively, at 560 °C. From DTA, X-ray, and optical metallography, [65Wan] determined the stoichiometry range to be 25.65 to 27.35 at.% As at 580 °C. Finally, [72Nau] determined the homogeneity field for γ as a function of temperature in the range 300 to 780 °C from lattice parameter measurements. The assessed phase boundaries for γ are based on the data of [72Nau], whereas the composition and temperature at the congruent point are from [57Hum].

[Hansen] had suggested that γ is dimorphic, based on a discontinuity in the phase boundary of (Cu) at 380 °C. It was later established by [60Hey] that this inflection is not due to a polymorphic transition, but to the peritectoid formation of Cu-rich β. According to [60Hey], this conclusion was supported further by the absence of any phase transitions following 2 to 3 weeks' annealing at temperatures below 400 °C. However, the later report of [69Ben] indicated the formation of a high-temperature hexagonal polymorph of

γ at temperatures between 450 and 475 °C. The formation of this high-temperature polymorph could have been overlooked by [60Hey], because these authors were looking for a phase transition at temperatures below 400 °C. In this review, the high-temperature and low-temperature modifications reported by [69Ben] are accepted, and are designated γ and γ', respectively.

γ (or Cu₃As) is also present in nature as the mineral domeykite (see below). Artificial synthesis of cubic α-domeykite has also been reported in the literature. [03Koe] (as quoted in [30Kat]) reported the synthesis of Cu₃As by passing As vapor over hot Cu. [50Bol] reported the high-pressure synthesis of cubic Cu₃As, and [51Wei] reported the synthesis of this compound at ordinary pressures.

δ and δ'

The peritectic formation of As-rich δ has been observed by several investigators [05Fri, 08Fri, 57Hum, 60Hey, 68Juz, 71Lie]. Almost all the investigations assumed the stoichiometry of this phase to be Cu₅As₂. However, the high-temperature X-ray investigation of [68Juz] showed δ to have the stoichiometry of Cu₉.₅As₄ or Cu₁₉As₈, comparable to the 29.42 at.% As composition that was reported by [72Nau]. Reported melting temperatures (Table 1) are in excellent agreement. The data of [06Hio] and [10Ben], showing a congruent melting maximum for δ, can be discarded.

[10Ben] also observed a thermal effect at 710 °C, which they erroneously assumed to be due to a polymorphic transition in δ, whereas in fact, this temperature is confirmed to be the peritectic melting temperature of Cu₅As₂. The data of [05Fri], [08Fri], [10Ben], and [72Uga] show δ to be a high-temperature phase, as indicated by its decomposition through a eutectoid reaction at lower temperatures (310 °C [05Fri], 300 °C [08Fri, 72Uga], and 305 °C [10Ben]). Subsequently, [60Hey], [66Mae], and [68Juz] confirmed the eutectoid decomposition of this phase near 300 to 305 °C.

Table 4 Cu-As Crystal Structure Data

Phase	Composition, at.% As	Pearson symbol	Space group	Strukturbericht designation	Prototype	Reference
(Cu)	0 to ~6.83	cF4	$Fm\overline{3}m$	A1	Cu	[Massalski]
β	11.1 to 14.3	hP2	$P6_3/mmc$	A3	Mg	[57Sch, 60Hey, 72Nau]
γ(HT)	25.0 to 27.8	hP8	$P6_3/mmc$	$D0_{18}$	Na₃As	[69Ben]
γ'(LT)	25.5 to 27.8	hP24	$P\overline{3}c1$	...	Cu₃As	[Pearson3]
δ(HT)	28.6 to 29.6	cF16	$Fm\overline{3}m$	D03	BiF3	[71Lie, Pearson3]
δ'(LT)	28.6 to 29.6	oI28	Ibam	...	Cu₅As₂	[Pearson3]
(αAs)	100	hR2	$R\overline{3}m$	A7	αAs	[Massalski]
(εAs)	100	oC8	Cmca	A11	αGa	[Massalski]
Metastable phases						
Cu₂As	~33.3	tP6	$P4/nmm$	C38	Cu₂Sb	[72Nau, Pearson3]
Cu₃As₄	~57.14	oI28	Immm	...	Cu₃As₄	[82Ble]

Note: LT = low temperature; HT = high temperature.

High-temperature X-ray and DTA studies of [68Juz] revealed that δ is dimorphic, with the high-temperature form stable between ~395 °C and the peritectic melting temperature and the low-temperature form stable between 300 and 315 °C. In the intermediate range, [68Juz] assumed that δ is in equilibrium with (As). DTA and X-ray investigations of [71Lie] confirmed the existence of the two forms of δ, together with the allotropic transformation to the high-temperature form at 380 °C. The high-temperature and low-temperature allotropic modifications are designated δ and δ', respectively, in this evaluation.

The maximum homogeneity range of δ and δ' is accepted provisionally as extending from the Cu₅As₂ composition to the Cu₁₉As₈ composition in this review. The proposed phase relationships for this phase in Fig. 1 are based tentatively on the data of [68Juz], [71Lie], and [72Uga], although further investigations definitely are required in this region.

Metastable Phases

Cu₂As

[06Hio] described the preparation of Cu₂As by heating an arsenite or arsenate of Cu with charcoal. [58Joh] reported the preparation of Cu₂As by artificial synthesis; however, the exact method of preparation was not revealed. Metallography and X-ray analysis by [58Joh] revealed the resulting alloy to be identical to the naturally occurring mineral koutekite. More recently, [72Nau] reported the synthesis of Cu₂As by selective wet oxidation of a Cu-As alloy with a higher starting Cu content. Selective dissolution of Cu by the action of oxidants such as ferric ions resulted in the formation of homogeneous Cu₂As. [72Nau] observed that Cu₂As decomposes to Cu₅As₂ and (As) on heating to 179 °C. On the other hand, DTA and X-ray studies of [68Juz] gave no evidence of the existence of Cu₂As. It

is likely that this synthetic Cu₂As is metastable, and as such, does not exist in the equilibrium diagram.

Other Reported Compounds

[06Hio] reported the preparation of Cu₃As₂ by passing As-containing hydrogen over dry cupric chloride. The occurrence of the compound Cu₃As₄ with an orthorhombic structure was reported recently by [82Ble]; however, no preparation details were given. There are no other reports of the existence of Cu₃As₂ and Cu₃As₄.

Crystal Structures and Lattice Parameters

Table 4 lists the crystal structures for the equilibrium and metastable phases in the Cu-As system. Lattice parameters of the terminal solid solution, (Cu), and the various phases are shown in Table 5. Lattice parameters of (Cu) at various temperatures and compositions are given in Table 6.

β

Cu-rich β has cph Mg-type structure [57Sch, 60Hey, 72Nau]. This phase has been called ε by [60Hey] and [72Nau], by virtue of its similarity to the ε phases of Cu-Sb, Ag-As, and Ag-Sb systems. Lattice parameters reported by [57Sch], [60Hey], and [72Nau] for β are in excellent agreement.

γ and γ'

[69Ben] reported high-temperature hexagonal γ to be isotypic with Na₃As ($P6_3/mmc$, hP8), with lattice parameters $a = 0.417$ and $c = 0.732$ nm at 490 °C. This is the only report of the existence of a high-temperature form for γ. The low-temperature modification of γ, designated γ' in this review, crystallizes in the hexagonal Cu₃As prototype structure, with space group $P\overline{3}c1$. Lattice parameters reported by [69Ben] for low-temperature γ' ($a = 0.7124$ and $c = 0.7296$ nm

at 23 °C) are in fair agreement with those reported by other investigators (see Table 5). The very early reports of [03Ste] (as quoted in [30Kat]) and [36Gre] indicated an orthorhombic structure and a bct structure, respectively, for the γ' phase. The fact that no recent authors have confirmed the existence of the orthorhombic and bct structures leads us to disregard the reports of [03Ste] and [36Gre].

δ and δ'

[60Hey] tentatively reported tetragonal structure for δ, with lattice parameters $a = 0.748$ and $c = 0.312$ nm. Subsequent studies by [68Juz] and [71Lie] indicated that this phase is dimorphic, with a cubic structure for the high-temperature form and a body-centered orthorhombic structure for the low-temperature modification (designated δ and δ', respectively, in this assessment). [68Juz] obtained a linear relationship between the lattice parameter of cubic δ and the temperature in the range 400 to 600 °C. [71Lie] reported the structure of the high-temperature cubic form to be isotypic with Fe₃Si (DO_3, $Fm\bar{3}m$, BiF₃ type)

and that of low-temperature modification to be isotypic with Mg₅Ga₂ ([Pearson3]) assigned a new prototype Cu₅As₂ for low-temperature δ'). Lattice parameters reported by [68Juz] and [71Lie] are in good agreement.

Cu₂As

According to [72Nau], their synthetic Cu₂As has the same structure as the tetragonal Fe₂As phase with space group $P4/nmm$. (According to [Pearson3], the prototype structure is Cu₂Sb.)

Cu₃As₄

[82Ble] reported the formation of orthorhombic Cu₃As₄ with a columnar structure and with lattice parameters $a = 0.354$, $b = 1.345$, and $c = 1.372$ nm; no atomic positions or prototype structure were given. However, [Pearson3] listed Cu₃As₄ as a new prototype (*oI28, Immm*).

[Pearson3] reported the existence of orthorhombic CuAs₂, with FeS₂-type structure and space group

Table 5 Cu-As Lattice Parameter Data

Phase	Composition, at.% As	Lattice parameters, nm a	b	c	Comment	Reference
(Cu)	0	0.36146	...	...	At 25 °C	[Massalski]
β	14.29(a)	0.2586	...	0.4229	c/a = 1.635, (b)	[38Ste]
		0.2590	...	0.4234	c/a = 1.635, (b)	[52Pad]
		0.259	...	0.424	c/a = 1.64	[57Sch]
		0.2588	...	0.4226	c/a = 1.633, (c)	[60Hey]
		0.2587	...	0.4225	c/a = 1.63	[72Nau]
γ(HT)	26.11	0.417	...	0.732	c/a = 1.76	[69Ben]
γ'(LT)	25.0	0.7215	...	0.7493	c/a = 1.039	[30Mac]
	(d)	0.7136	...	0.7323	c/a = 1.024	[30Kat]
	25.8	0.7132	...	0.7294	c/a = 1.023	[30Kat]
	(e)	0.7109	...	0.7282	c/a = 1.024	[30Kat]
	(f)	0.7117	...	0.7247	c/a = 1.020	[38Ste]
	(f)	0.711	...	0.727	c/a = 1.022	[52Pad]
	24.92(d)	0.7132	...	0.7304	c/a = 1.024	[60Hey]
	26.87(e)	0.7113	...	0.7272	c/a = 1.022	[60Hey]
		0.7143	...	0.7324	c/a = 1.025	[65Man]
		0.7124	...	0.7296	c/a = 1.024	[69Ben]
		0.7102	...	0.7246	c/a = 1.020	[71Guk]
	25.0(d)	0.7141	...	0.7310	c/a = 1.024	[72Nau]
	27.78(e)	0.7121	...	0.7310	c/a = 1.027	[72Nau]
δ(HT)	29.63(a)	0.5811	...	...	At 20 °C	[68Juz]
		0.5856	...	...	At 420 °C	[68Juz]
		0.582	...	...	...	[71Lie]
δ'(LT)	29.63(a)	0.5992	1.1603	0.5504	...	[68Juz]
		0.5977	1.1577	0.5491	...	[71Lie]
(αAs)	100	0.41319	...	...	At 25 °C α = 54.12° (g)	[Massalski]
(εAs)	100	0.362	1.085	0.448	At > 448 °C	[Massalski]
Metastable phase						
Cu₂As	33.33	0.3788	...	0.5942	c/a = 1.57	[72Nau]

Note: LT = low temperature; HT = high temperature. **(a)** Composition is from the assessed phase diagram (Fig. 1) and need not correspond with the stoichiometry reported by the authors. **(b)** For the mineral algodonite. **(c)** Alloy was not single phase. **(d)** At Cu-rich limit. **(e)** At As-rich limit. **(f)** For the mineral β-domeykite. **(g)** The hexagonal cell as $a = 0.37598$ and $c = 1.0547$ nm [Pearson3].

As-Cu

Pnnm and with lattice parameters $a = 0.4789$, $b = 0.5790$, and $c = 0.3537$ nm. They attributed this information to data from [40Pea]; however, it is clearly evident from [40Pea] that these data are for the nickel arsenide $NiAs_2$ and *not* for $CuAs_2$, as erroneously interpreted by [Pearson3].

Naturally Occurring Minerals

Algodonite

X-ray diffraction studies performed by [29Ram], [38Ste], [52Pad], and [60Hey] indicated that the mineral algodonite corresponds crystallographically to the most Cu-rich compound. There is, however, some variation in the reported composition, with the stoichiometry reported as Cu_7As [52Pad] (for a sample containing 16.9 at.% As), Cu_6As [29Ram, 60Hey], and Cu_4As [38Ste]. According to the reports of [19Bor], [29Ram], and [29Mac1], algodonite decomposes on heating into (Cu) and Cu_3As, which is in accordance with the Cu-As equilibrium diagram. [60Hey] indicated that algodonite is a high-pressure modification of β that dissociates into (Cu) and Cu_3As on heating to 250 °C. This dissociation temperature is in accordance with the observation of [38Ste]. [60Hey] attributed the apparent uncertainty in the composition of algodonite to the variation in the ambient pressures involved in the formation of this mineral. [38Ste] reported lattice parameters $a = 0.2586$ and $c = 0.4229$ nm. [52Pad] reported lattice parameters on the basis of a pseudohexagonal cell as $a = 0.2590$ and $c = 0.4234$ nm for a sample with 16.9 at.% As. [52Pad] also reported an orthorhombic cell for algodonite, with lattice parameters $a = 0.2594$, $b = 0.4561$, and $c = 0.4230$ nm for a sample containing 15.88 at.% As.

Table 6   Lattice Parameters of (Cu) vs Composition at Various Temperatures

Reference	Composition, at.% As	Annealing temperature, °C	Annealing period, h	Lattice parameters, nm
[30Kat]	0	...	...	0.3615
	1.7	...	...	0.3636
	(a)	...	...	0.3647
[37Mer]	1.57	680	1100	0.36226
	2.64	680	1100	0.36281
	3.72	680	1100	0.36335
	5.57	680	1100	0.36421
	6.27	680	1100	0.36452
		650	900	0.36454
		600	700	0.36452
		500	550	0.36453
		400	600	0.36452
		300	600	0.36451
	8.4(b)	680	1100	0.36486
		650	900	0.36481
		600	700	0.36479
		500	550	0.36475
		400	600	0.36470
		300	800	0.36464
[39Owe](c)	0.79	...	...	0.36183
	2.47	...	...	0.36287
	3.38	...	...	0.36298
	4.22	...	...	0.36347
	5.29	...	...	0.36398
	5.94	...	...	0.36426
[40Owe](c)	7.2	659	...	0.36470
		603	...	0.36465
		514	...	0.36463
		387	...	0.36457
		300	...	0.36432
		215	...	0.36429
[60Hey]	(d)	...	...	0.3647

(a) Solubility limit at room temperature. (b) Two-phase alloy. (c) At 18 °C. (d) Saturated (Cu) for alloys quenched between 350 and 660 °C.

Table 7 Lattice Parameter Data for Cu-As Minerals

| Mineral | Phase | Structure | Lattice parameters, nm | | | Comment | Reference |
			a	b	c		
Algodonite..........	...	Hexagonal	0.2604	...	0.4223	(a)	[29Mac2]
	Cu₄As	Hexagonal	0.2586	...	0.4229	$c/a = 1.631$	[38Ste]
	Cu₇As	Hexagonal	0.2590	...	0.4234	16.9 at.% As	[52Pad]
		Orthorhombic	0.2594	0.4561	0.4230	15.88 at.% As	[52Pad]
α-Domeykite......	Cu₁₅As₄(b)	Cubic	0.9611	...	...	...	[38Ste]
			0.980	...	...	...	[51Wei]
			0.962	...	...	24.88 at.% As	[52Pad]
			0.9612	...	...	...	[62Ber]
	Cu₃As	Cubic	0.9619	...	...	...	[77Igl]
β-Domeykite......	Cu₃As	Hexagonal	0.7117	...	0.7247	$c/a = 1.020$	[38Ste]
			0.711	...	0.727	$c/a = 1.022$	[52Pad]
Koutekite..........	Cu₂As	Hexagonal	1.151	...	1.454	...	[60Joh]
Paxite	Cu₂As₃	Orthorhombic	1.284	1.150	0.7654	35.8% As	[61Joh]

(a) Contains less Cu than the formula Cu₅As. (b) Composition suggested by [Pearson1].

Whitneyite

According to [16Bor], [19Bor], and [29Ram], the mineral whitneyite consists of a mixture of algodonite and (Cu).

Domeykite

The mineral domeykite is reported to exist in two forms [29Ram, 38Ste, 52Pad, 60Hey]. One of the forms of domeykite has cubic structure and has been called "mineral domeykite" [38Ste] or "α-domeykite" [52Pad, 60Hey], whereas the other form has hexagonal structure and has been called "artificial domeykite" [38Ste] or "β-domeykite" [52Pad, 60Hey]. [Pearson1] assigned the formula Cu₁₅As₄ to α-domeykite because of its structural similarity to the D8₆-type Cu₁₅Si₄. In contrast, the crystallographic studies of [77Igl] indicated that the formula of α-domeykite is Cu₃As, not Cu₁₅As₄ as proposed by [Pearson1]. [50Bol] and [60Hey] showed α-domeykite to be a high-pressure phase, which dissociates into hexagonal Cu₃As and Cu₅As on heating to 225 °C [38Ste]. The phase diagram proposed by [72Nau] shows the peritectoid formation of Cu₁₅As₄ at 225 °C; this presumably is based on the data of [38Ste] and [60Hey]. [51Wei] reported the preparation of "α-domeykite" or cubic Cu₃As at ordinary pressures. On this basis, [77Igl] concluded that α-domeykite is a low-pressure phase that forms at 1 to 1000 bar. The authors described the structure of this mineral as a distortion of the A15 structure (formerly called βW or W₃O) and speculated that this mineral may undergo a second-order phase transition to A15-type at high pressure. [77Igl] made no attempt, however, to correlate their observations with the phase relationships reported for Cu₃As in the equilibrium diagram. α-domeykite was assigned the space group I43d [Pearson1, 77Igl]. The mineral β-domeykite was found to correspond crystallographically to the equilibrium γ phase (or Cu₃As) [38Ste, 52Pad]. As such, it is isostructural with Cu₃As, with Pearson symbol hP24 and space group P3c1. Reported lattice parameters for domeykite (Table 7) are in good agreement.

Koutekite

[58Joh] reported that the mineral koutekite has the composition Cu₂As. [60Joh] reported hexagonal structure both for the mineral and for synthetic Cu₂As, with lattice parameters $a = 1.151$ and $c = 1.454$ nm. In contrast, [72Nau] reported that their synthetic Cu₂As is isostructural with tetragonal Fe₂As (P4/nnm, Cu₂Sb type).

Paxite

The mineral paxite (or Cu₂As₃) was shown by [61Joh] to be isostructural with the orthorhombic Sb₂S₃ structure, with lattice parameters $a = 1.284$, $b = 1.150$, and $c = 0.7654$ nm for a mineral sample of composition 35.8 wt.% Cu. [Pearson2] disagreed with the conclusion of [61Joh] that Cu₂As₃ is Sb₂S₃ type. Paxite appears to be a metastable phase, and as such, should not occur in the Cu-As equilibrium diagram.

Lattice parameters reported for the various Cu-As minerals are summarized in Table 7.

Thermodynamics

Thermodynamic investigations of the Cu-As system consist of determinations of elemental activities in Cu-rich liquid Cu-As alloys and in the terminal solid solution, (Cu). Activities in liquid Cu-As alloys have been determined by emf [69Aza] (also see [76Aza]), vapor transport [71Bod, 79Jon], isopiestic [81Hin, 85Hin1], and Knudsen cell mass spectrometric methods [85Hin2]. Activity data for Cu and As in liquid Cu-As alloys are summarized in Table 8. From emf data, [69Aza] obtained the following relationship for the activity coefficient of Cu (γCu) at 1000 °C for compositions greater than 15.8 at.% As:

$$\log \gamma_{Cu} = -5.285 X^2_{As} + 0.0853 \qquad (Eq\ 1)$$

where X_{As} is the atomic fraction of As. According to [69Aza], normal Gibbs-Duhem integration of this equation did not yield reliable values for γ_As, especially

As-Cu

for $X_{As} > 15.8$ at.% As. Using an alternate Gibbs-Duhem integration based on a single data point for a_{As} at $X_{As} = 0.27$, [69Aza] obtained values for γ_{As}, that show better agreement with the experimental trend for γ_{Cu}. Using a transport or carrier gas technique, [79Jon] determined the activities of As in solution in molten Cu at 1100 °C. As_4 was assumed to be the predominant vapor species at 1100 °C. The results indicate a negative deviation from Raoult's law. [79Jon] reported the following relationship for γ_{As} in the composition range $X_{As} = 0.22$ to 0.27:

$$\log \gamma_{As} = -15.39\, X^2_{Cu} + 3.78 \qquad (Eq\ 2)$$

[80Lyn] and subsequently [83Dab] re-evaluated the data of [69Aza] and [79Jon] on the basis of more recent information on the vapor pressure of As. Based on the reported data for As from [Hultgren,E], [83Dab] determined the saturation vapor pressures of

the pure As species (As_4, As_3, As_2, and As) at various source temperatures. From these data, the author redetermined the activity coefficients of As at 1100 °C from the raw data of [79Jon] and fitted them to the following equation for $X^2_{Cu} \leq 0.68$:

$$\log \gamma_{As} = 1.99 \times 10^{-2} (X^2_{Cu})^{-6.64} - 2.60 \qquad (Eq\ 3)$$

As seen in Table 8, a_{As} values calculated from the revised activity coefficients from Eq 3 are three orders of magnitude greater than the original data of [79Jon]. In a similar manner, [83Dab] obtained the following equation for γ_{As} at 1000 °C from the data of [69Aza]:

$$\log \gamma_{As} = -5.24\, X^2_{Cu} + 1.70 \;(X^2_{Cu} \leq 0.71) \qquad (Eq\ 4)$$

The activity coefficients from Eq 4 are fairly comparable to those from Eq 3. In effect, [80Lyn] and [83Dab] showed that the data of [69Aza] and [79Jon]

Table 8   Reported Activities of Cu and As in Liquid Cu-As Alloys

Reference	Temperature, °C	Composition, at.% As	Activity a_{Cu}	a_{As}	Method
[69Aza]	1000	0.27	...	2.48×10^{-4}	Vapor transport emf
[69Aza](a)	1000	0.05	0.947	7.75×10^{-6}	
		0.10	0.880	1.66×10^{-5}	
		0.15	0.800	2.82×10^{-5}	
		0.20	0.610	6.12×10^{-5}	
		0.25	0.400	1.76×10^{-4}	
		0.27	0.357	...	
		0.30	0.293	...	
[71Bod]	1300	0.0178	...	1.9×10^{-8}	Vapor transport
		0.0255	...	2.6×10^{-8}	
[79Jon]	1100	0.174	...	1.40×10^{-7}	Vapor transport
		0.197	...	2.20×10^{-7}	
		0.217	...	5.50×10^{-7}	
		0.228	...	8.70×10^{-7}	
		0.250	...	2.85×10^{-6}	
		0.263	...	5.88×10^{-6}	
		0.267	...	8.34×10^{-6}	
		0.270	...	1.17×10^{-5}	
[83Dab](b)	1100	0.174	...	7.94×10^{-4}	Vapor transport
		0.197	...	1.09×10^{-3}	
		0.217	...	1.96×10^{-3}	
		0.228	...	2.66×10^{-3}	
		0.250	...	5.07×10^{-3}	
		0.263	...	9.11×10^{-3}	
		0.267	...	1.14×10^{-2}	
		0.270	...	1.40×10^{-2}	
[85Hin1](a)	1000	0.05	0.945	0	Isopiestic method
		0.10	0.870	0	
		0.15	0.797	0.003	
		0.20	0.600	0.017	
		0.25	0.420	0.052	
		0.30	0.307	0.110	
		0.35	0.232	0.186	
[85Hin2](a)	1150	0.03	...	0.00032	Mass spectrometry
		0.05	...	0.00061	
		0.10	...	0.00220	

(a) Activity data read from graph in the original paper. (b) Revised values based on the data of [79Jon].

Fig. 4 Excess Gibbs Energy of Mixing of Liquid Cu-As Alloys at 1000 °C

Legend:
- ○ 69Aza
- □ 83Dab(a)
- × 85Hin1
- — 83Nie

Y-axis: $G^{ex}(L)$, kJ/mol

X-axis: X_{As}
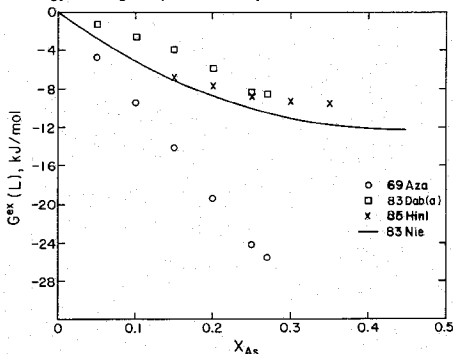
Note: Data from [80Lyn] based on revised data of [69Aza] (see text). Optimized $G^{ex}(L) = X(1-x)[-56\ 268 - 24\ 207\ (2x-1)]$.

P.R. Subramanian and D.E. Laughlin, 1988.

are closer to one another than was originally reported by [79Jon]. Cu activities calculated by [85Hin1] from their isopiestically determined As activities are in good agreement with those obtained directly by [69Aza] from emf measurements. Table 9 lists the reported values for the activity coefficient of As at infinite dilution. Figure 4 shows the $G^{ex}(L)$ values calculated from the original activity data of [69Aza] and [85Hin1] at 1000 °C, as well as those from [83Dab] based on the revised data of [69Aza].

Based on the semiempirical model of [80Mie], [83Nie] predicted the heats of solution of As in liquid Cu as –58 kJ/mol and of Cu in liquid As as –40 kJ/mol. These values were used in conjunction with a subregular solution model to determine the excess Gibbs energy of mixing of liquid Cu-As alloys as follows:

$$G^{ex}(L) = X(1-X)[-49\ 000 + 9000(2X-1)] \qquad (Eq\ 5)$$

where X is the atomic fraction of As. The G^{ex} vs X trend from this equation is compared in Fig. 4 with the experimental data.

[83Lud] determined the activity of As in the terminal solid solution, (Cu), at 695 °C, based on vapor pressure measurements by a pseudo-isopiestic method—based on nonisothermal conditions, but at constant pressures (also see [83Heh]). The authors observed that the vapor species above alloys with low As concentration is predominantly As₂, whereas for alloys near the terminal solubility, the species As₄ is increasingly

Table 9 Reported Activity Coefficient of As at Infinite Dilution in Liquid Cu-As Alloys

Reference	Temperature, °C	Activity coefficient γ°_{As}
[69Aza]	1000	1.45×10^{-1}
	1300	8.00×10^{-5}
[71Bod]	1300	1.0×10^{-5}
[79Jon]	1100	5.0×10^{-7}
[83Dab](a)	1000	3.98×10^{-3}
[83Dab]	1100	2.63×10^{-3}
[81Hin]	1150	4.0×10^{-4}
[85Hin1]	1000	1.0×10^{-3}
	1150	6.8×10^{-3}
[85Hin2](c)	1150	7.3×10^{-3}

(a) Revised values based on the data of [69Aza]. (b) Revised values based on the data of [79Jon]. (c) Determined by [85Hin2] from their activity coefficient data, as well as those of [85Hin1].

present. The resulting activity data, listed in Table 10, show significant negative deviation from Raoult's law.

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Table 10 Activity of As in (Cu) at 695 °C

Composition, atomic fraction As x_{As}	Activity a_{As}	Composition, atomic fraction As x_{As}	Activity a_{As}
0.030	0.0017	0.045	0.0077
0.030	0.0030	0.047	0.0077
0.032	0.0029	0.050	0.0094
0.034	0.0022	0.051	0.0093
0.035	0.0044	0.054	0.0116
0.036	0.0047	0.056	0.0151
0.040	0.0077	0.059	0.0192
0.042	0.0075		

(a) From [83Lud]; data read from graph in the original paper.

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*Indicates key paper.
#Indicates presence of a phase diagram.

As-Cu
Mg-Nd