Cu – S (Copper – Sulphur)

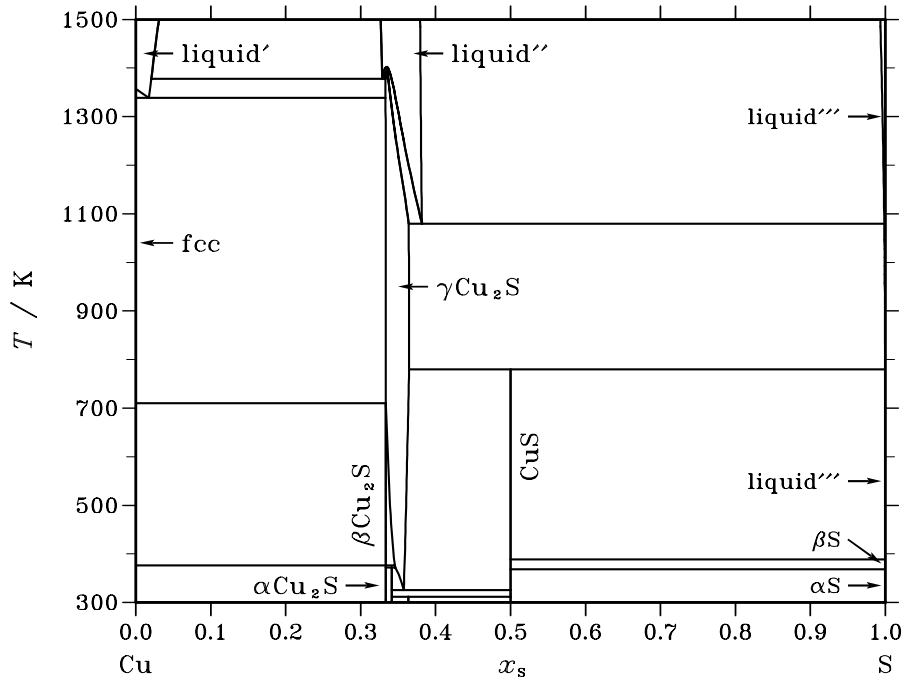

Fig. 1. Calculated phase diagram for the system Cu-S.

The Cu-S system is important for the production of Cu from ore. The solubility of S in solid and liquid Cu is small. Due to the preferred valences of Cu and S, +1 and -2 respectively, the liquid and several solid compounds are stable around the composition Cu_2S. Between the Cu-rich liquid and the liquid around Cu_2S there is a miscibility gap. At high temperature the only solid compound is diginite (γCu_2S) with a narrow composition range. At higher temperatures this melts congruently at 1403 K and forms a liquid with only slightly broader composition range.
At higher sulfur compositions solid or liquid sulphur or sulphur gas become stable. The calculated phase diagram in the figure is without the gas phase showing a second miscibility gap between almost pure liquid sulfur and liquid around the Cu_2S composition.
At lower temperatures there are several stoichiometric phases stable. The covellite phase is stoichiometric CuS. α and β chalcocite are stoichiometric αCu_2S and βCu_2S which are stable up to 376 K and 710 K, respectively. Djurlite has the stoichiometry $Cu_{1.93}S$ and anilite Cu_7S_4 and they are stable up to less than 373 K and 312 K, respectively. Diginite is not stable below 325. A magnification of the phase diagram in the range of the copper sulphides at lower temperatures is shown in Fig. 2.
There is no publication for this assessment [92Sun] but it gives a good fit to all experimental data up to 1991 for phase diagram, enthalpy, activities and heat capacities.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_LIQ	$(Cu^{+},Cu^{2+})_p(S^{2-},S,\Box)_q$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Cu,S)_1$
αCu_2S	$\cdots$	$\cdots$	$mP144$	$P2_1/c$	A_CHALCO	Cu_2S_1
βCu_2S	$B8_2$	Ni_2In	$hP6$	$P6_3/mmc$	B_CHALCO	Cu_2S_1
γCu_2S	$C1$	CaF_2	$cF12$	$Fm\overline{3}m$	DIGINITE	$(Cu,\Box)_2(Cu,\Box)_1S_1$
$Cu_{193}S_{100}$	$\cdots$	$\cdots$	$oP*$	$\cdots$	DJURLEITE	$Cu_{193}S_{100}$
Cu_7S_4	$\cdots$	$\cdots$	$oP44$	$Pnma$	ANILITE	Cu_7S_4
CuS	$B18$	CuS	$hP12$	$P6_3/mmc$	COVELLITE	Cu_1S_1
αS	$A16$	αS	$oF128$	$Fddd$	FC_ORTHO	S_1
βS	$\cdots$	βS	$mP48$	$P2_1/a$	MONOCLIN	S_1

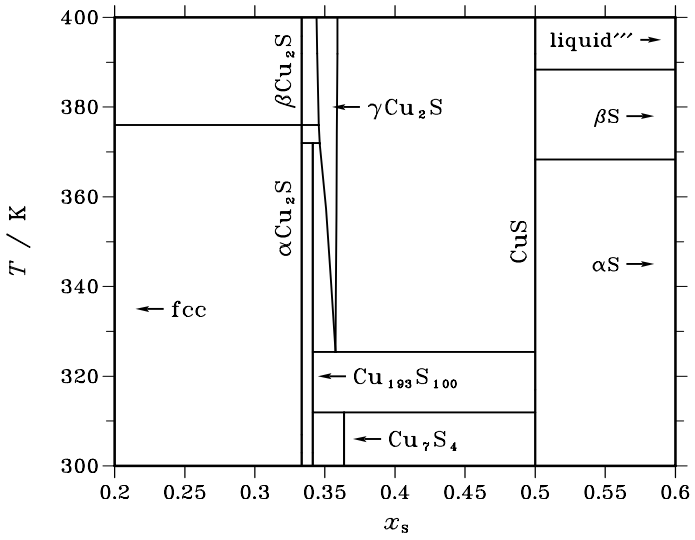

Fig. 2. Partial phase diagram for the system Cu-S.

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_S			$\Delta_r H$ / (J/mol)
liquid″ $\rightleftharpoons$ γCu_2S	congruent	1402.8	0.335	0.335		−4262
liquid″ $\rightleftharpoons$ liquid′ + γCu_2S	monotectic	1377.5	0.329	0.021	0.333	−4262
liquid′ $\rightleftharpoons$ fcc + γCu_2S	eutectic	1338.7	0.017	0.000	0.333	−13624
liquid″ $\rightleftharpoons$ γCu_2S + liquid‴	monotectic	1079.7	0.382	0.364	0.998	−3067
γCu_2S + liquid‴ $\rightleftharpoons$ CuS	peritectic	779.7	0.365	1.000	0.500	−3242
fcc + γCu_2S $\rightleftharpoons$ βCu_2S	degenerate	710.3	0.000	0.333	0.333	−392
liquid‴ $\rightleftharpoons$ CuS + βS	degenerate	388.3	1.000	0.500	1.000	−1721
βCu_2S $\rightleftharpoons$ αCu_2S	polymorphic	376.0	0.333	0.333		−1292
αCu_2S + γCu_2S $\rightleftharpoons$ $Cu_{193}S_{100}$	peritectoid	372.0	0.333	0.346	0.341	−851
CuS + βS $\rightleftharpoons$ αS	degenerate	368.3	0.500	1.000	1.000	−401
γCu_2S $\rightleftharpoons$ $Cu_{193}S_{100}$ + CuS	eutectoid	325.4	0.358	0.341	0.500	−1644
$Cu_{193}S_{100}$ + CuS $\rightleftharpoons$ Cu_7S_4	peritectoid	312.0	0.341	0.500	0.364	−1641

Table III. Standard reaction quantities at 298.15 K for the compounds per mole of atoms.

Compound	x_{S}	$\Delta_{\mathrm{f}}G^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}H^{\circ}$ / (J/mol)	$\Delta_{\mathrm{f}}S^{\circ}$ / (J/(mol·K))	$\Delta_{\mathrm{f}}C_P^{\circ}$ / (J/(mol·K))
$\alpha$$Cu_2S$	0.333	−27145	−23486	12.269	−3.222
$\beta$$Cu_2S$	0.333	−26973	−23072	13.083	9.000
$\gamma$$Cu_2S$	0.333	−26538	−21496	16.911	−2.724
$Cu_{193}S_{100}$	0.341	−27038	−23493	11.892	2.051
Cu_7S_4	0.364	−26421	−24534	6.330	4.195
Cu_1S_1	0.500	−22131	−19037	10.376	3.617

References

[92Sun] B. Sundman, unpublished assessment, 1992.