Cu – O (Copper – Oxygen)

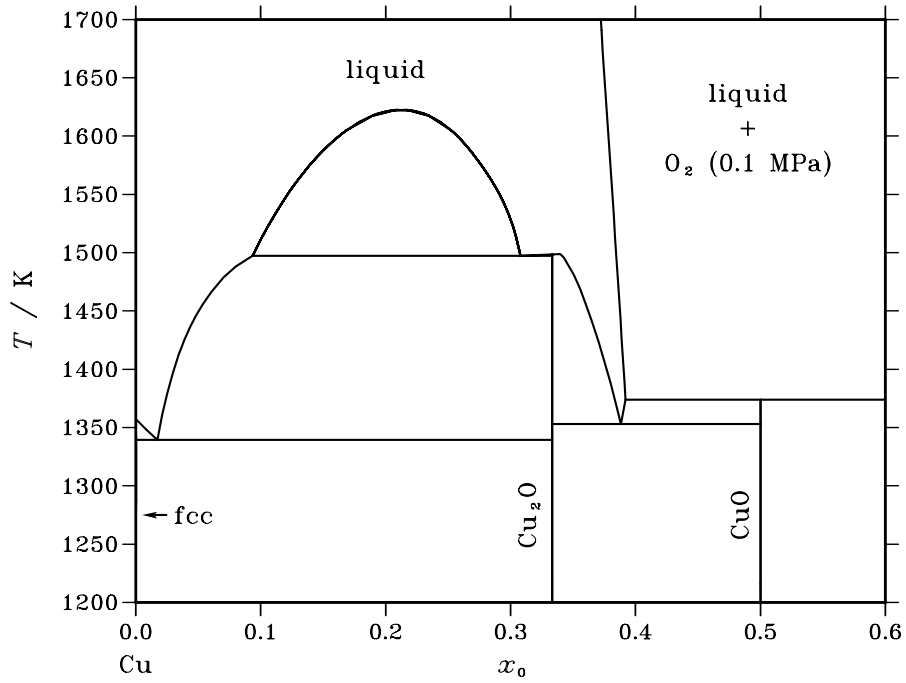

Fig. 1. Calculated phase diagram for the system Cu-O.

The Cu–O system is a basic system for copper metallurgy and high-temperature superconductors. Accordingly, it has been extensively investigated. Several thermodynamic descriptions have been presented [83Sch, 92Bou, 94Hal, 95Ran, 03Hal]. The most thorough of those is the one by [94Hal, 03Hal] and is, thus, recommended here. There are two stable oxides, Cu_2O (cuprite) and CuO (tenorite), both showing a small amount of non-stoichiometry [94Por, 99Car] (not included in the thermodynamic description). There is also a metastable oxide, Cu_4O_3 (paramelaconite). Liquid Cu dissolves appreciable amounts of O and at higher temperature there is a miscibility gap between the Cu-rich and Cu_2O-rich liquids, closing at about 1625 K. Between Cu_2O and CuO there is a deep eutectic. Solid Cu dissolves a small amount of O ($x_O \approx 2{\cdot}10^{-4}$ at the eutectic temperature). Dissolved O seriously degrades the electrical conductivity of Cu. The calculated thermodynamic quantities and the phase diagram agree very well with the experimental data. There is still some uncertainty concerning the O-rich liquid beyond the Cu_2O composition. Here, the thermodynamic description depends essentially only on the thermogravimetric data from [77Sad].

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_LIQUID	$(Cu^{1+},Cu^{2+})_p(O^{2-},\Box)_q$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$Cu_1(O,\Box)_1$
Cu_2O	$C3$	Cu_2O	$cP6$	$Pn\overline{3}m$	CU2O	Cu_2O_1
CuO	$\cdots$	CrS	$mC8$	$\cdots$	CUO	Cu_1O_1

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_O			$\Delta_r H$ / (J/mol)
liquid $\rightleftharpoons$ liquid′ + liquid″	critical	1622.5	0.213	0.213	0.213	0
liquid $\rightleftharpoons$ Cu_2O	congruent	1501.0	0.333	0.333		−19942
liquid″ $\rightleftharpoons$ liquid′ + Cu_2O	monotectic	1497.2	0.308	0.093	0.333	−19481
liquid + gas $\rightleftharpoons$ CuO	gas-peritectic	1373.9	0.392	1.000	0.500	−42085
liquid $\rightleftharpoons$ Cu_2O + CuO	eutectic	1353.2	0.388	0.333	0.500	−23386
liquid $\rightleftharpoons$ fcc + Cu_2O	eutectic	1339.4	0.017	0.000	0.333	−14553

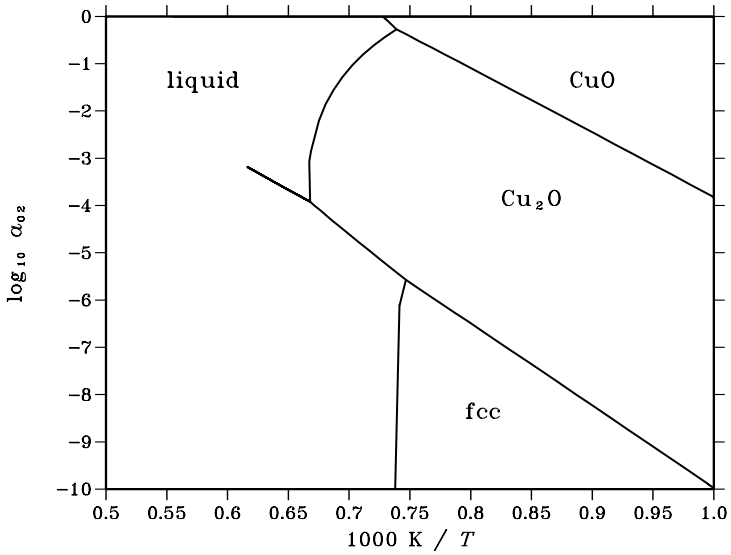

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}O_2$(gas, 0.1 MPa).

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

Compound	x_O	$\Delta_f G^\circ$ / (J/mol)	$\Delta_f H^\circ$ / (J/mol)	$\Delta_f S^\circ$ / (J/(mol·K))	$\Delta_f C_P^\circ$ / (J/(mol·K))
Cu_2O_1	0.333	−49186	−56753	−25.380	−0.330
Cu_1O_1	0.500	−63791	−77596	−46.304	1.595

References

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