Co – O (Cobalt – Oxygen)

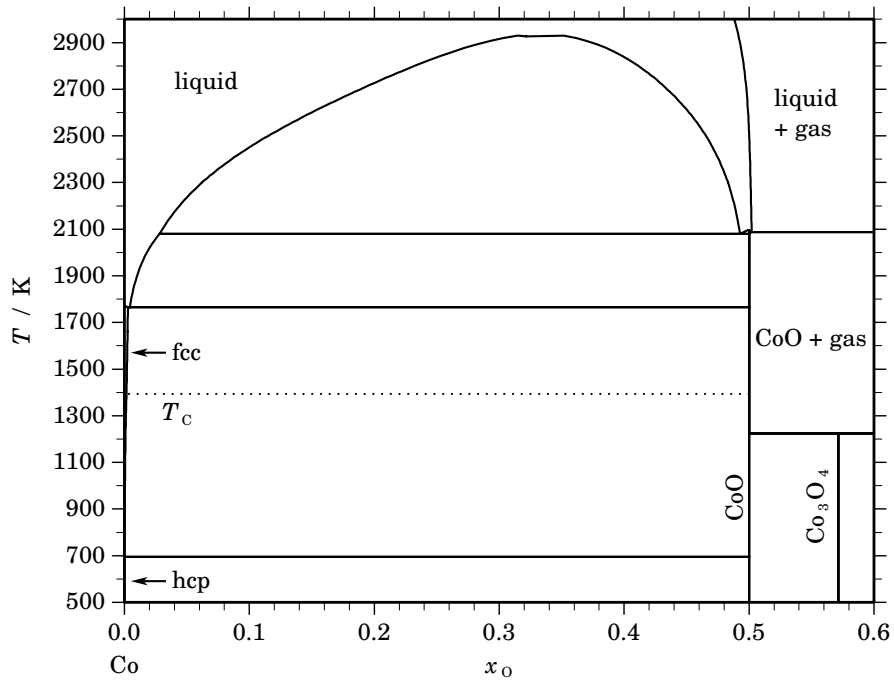

Fig. 1. Calculated phase diagram for the system Co-O.

A thorough review on the cobalt-oxygen system and a thermodynamic assessment has been given by [2003Che]. The stable phases in the system are the liquid, metallic cobalt (hcp and fcc) with limited solubility for oxygen and two oxides, CoO and Co_3O_4, which are described as stoichiometric compounds. The optimisation of the dataset is based on the evaluation of a large amount of experimental data from the literature. It includes the solubility and the activities of oxygen in the liquid phase, the solubility of oxygen in Co metal, the oxygen activities in the 2-phase equilibria of the condensed phases, data for the heat capacity and the heat content of both oxides as well as the enthalpies of formation and the entropy of these oxides at 298.15 K.

Table I. Phases, structures and models.

Phase	Strukturbericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_L	$(Co^{2+},Co^{3+})_p(O^{2-},\square)_q$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$Co_1(O,\square)_1$
hcp	$A3$	Mg	$hP2$	$P6_3/mmc$	HCP_A3	$Co_2(O,\square)_1$
CoO	$B1$	NaCl	$cF8$	$Fm\overline{3}m$	CO1O1	Co_1O_1
Co_3O_4	$H1_1$	$MgAl_2O_4$	$cF56$	$Fd\overline{3}m$	CO3O4	$(Co^{2+},Co^{3+})_1(Co^{2+},Co^{3+})_2O_4$

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_O			$\Delta_r H$ / (J/mol)
liquid ⇌ liquid′ + liquid″	critical	2935.5	0.334	0.334	0.334	0
liquid″ ⇌ CoO	congruent	2096.6	0.500	0.500		−21226
liquid″ ⇌ CoO + gas	gas-eutectic	2087.3	0.502	0.500	1.000	−20259
liquid″ ⇌ liquid′ + CoO	monotectic	2079.9	0.493	0.028	0.500	−22325
liquid′ ⇌ fcc + CoO	eutectic	1765.6	0.004	0.003	0.500	−16693
CoO + gas ⇌ Co_3O_4	gas-peritectoid	1223.7	0.500	1.000	0.571	−23383
fcc ⇌ hcp + CoO	degenerate	694.9	0.000	0.000	0.500	−429

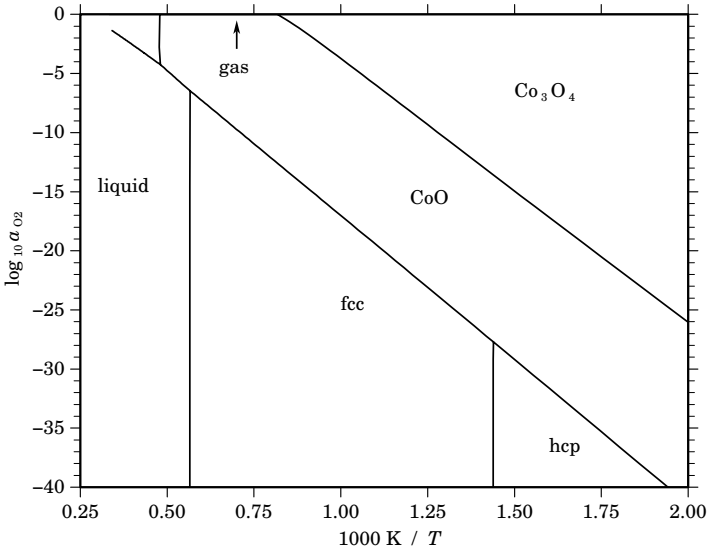

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}O_2$(gas, 0.1 MPa).

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))
Co_1O_1	0.500	−106765	−118430	−39.123	7.567
Co_3O_4	0.571	−114126	−130769	−55.822	−1.712

References

[2003Che] M. Chen, B. Hallstedt, L.J. Gauckler: J. Phase Equilibria **24** (2003) 212–227.