Mn – O (Manganese – Oxygen)

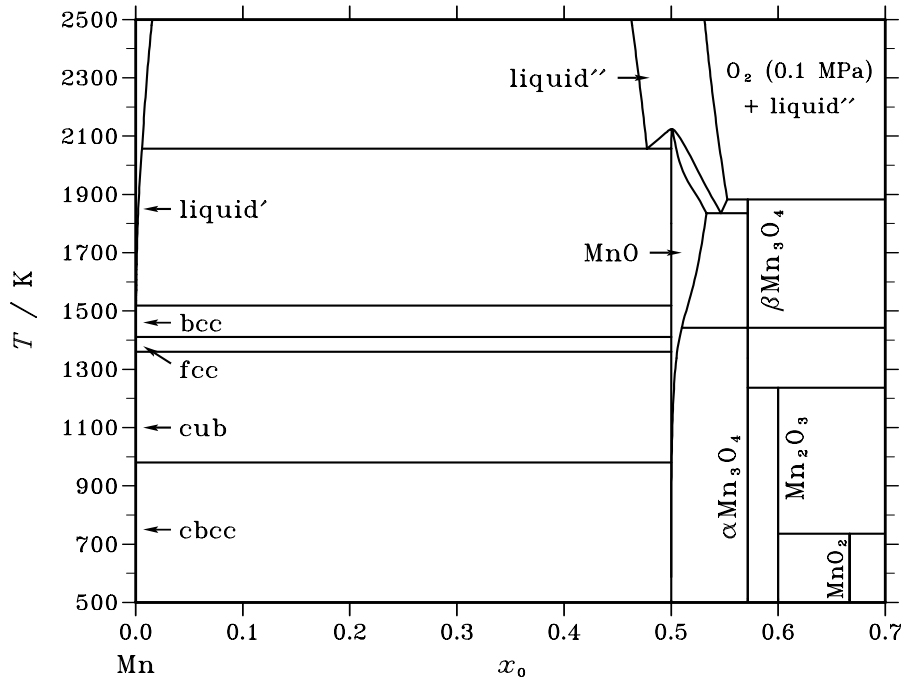

Fig. 1. Calculated phase diagram for the system Mn-O.

Thermodynamic assessments and literature reviews of the Mn-O system have been provided by [92Wan] and [03Gru]. The optimisation by [03Gru] is recommended here, because it provides a consistent set of data and a thorough evaluation of the literature. The optimisation is based on data for the phase equilibria, EMF investigations on the oxides, heat capacity data and enthalpy increments for the oxides. Manganosite (MnO) is described as a non-stoichiometric compound whereas all other oxides are treated as stoichiometric compounds.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_LIQ	$(Mn^{2+},Mn^{3+})_p(O^{2-},\square)_q$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	Mn_1
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	Mn_1
cbcc	$A12$	αMn	$cI58$	$I\overline{4}3m$	CBCC_A12	Mn_1
cub	$A13$	βMn	$cP20$	$P4_132$	CUB_A13	Mn_1
MnO	$B1$	NaCl	$cF8$	$Fm\overline{3}m$	HALITE	$(Mn^{2+},Mn^{3+},\square)_1O_1^{2-}$
αMn_3O_4	$\cdots$	$\cdots$	$tI28$	$I4_1/amd$	MN3O4	Mn_3O_4
βMn_3O_4	$H1_1$	Al_2MgO_4	$cF56$	$Fd\overline{3}m$	SPINEL	Mn_3O_4
Mn_2O_3	$\cdots$	$\cdots$	$cI80$	$Ia3$	MN2O3	Mn_2O_3
MnO_2	$C4$	TiO_2	$tP6$	$P4_2/mnm$	MnO2	Mn_1O_2

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_O			$\Delta_r H$ / (J/mol)
liquid″ ⇌ MnO	congruent	2124.1	0.501	0.501		−22127
liquid″ ⇌ liquid′ + MnO	monotectic	2057.0	0.477	0.006	0.500	−22800
liquid″ + gas ⇌ βMn_3O_4	gas-peritectic	1882.1	0.552	1.000	0.571	−28556
liquid″ ⇌ MnO + βMn_3O_4	eutectic	1835.5	0.547	0.533	0.571	−17681
liquid′ ⇌ bcc + MnO	eutectic	1518.5	0.000	0.000	0.500	−12946
βMn_3O_4 ⇌ αMn_3O_4	polymorphic	1443.0	0.571	0.571		−2978
bcc + MnO ⇌ fcc	degenerate	1411.0	0.000	0.500	0.000	−1908
fcc ⇌ cub + MnO	degenerate	1360.0	0.000	0.000	0.500	−2166
αMn_3O_4 + gas ⇌ Mn_2O_3	gas-peritectoid	1236.5	0.571	1.000	0.571	−7262
cub ⇌ cbcc + MnO	degenerate	980.0	0.000	0.000	0.500	−2254
Mn_2O_3 + gas ⇌ MnO_2	gas-peritectoid	736.6	0.600	1.000	0.667	−12850

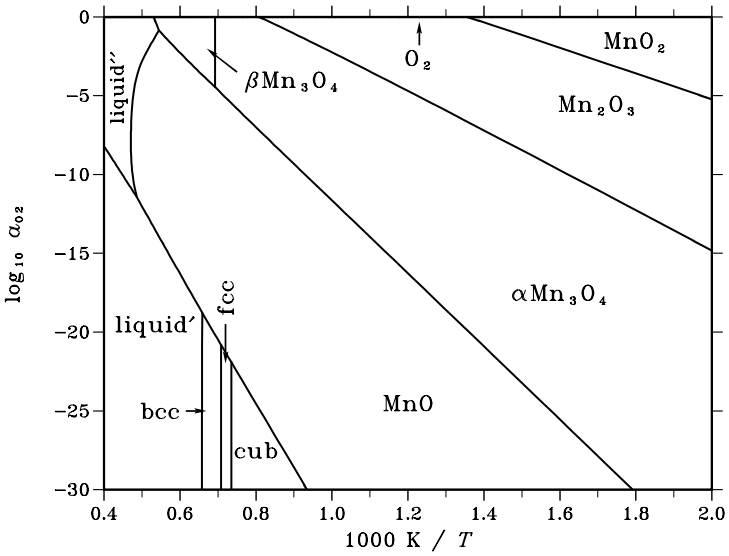

Fig. 2. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}O_2$(gas, 0.1 MPa).

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))
MnO	0.500	−182083	−193372	−37.862	1.690
αMn_3O_4	0.571	−183121	−197534	−48.342	0.768
βMn_3O_4	0.571	−180758	−194556	−46.278	0.768
Mn_2O_3	0.600	−177021	−192519	−51.979	0.667
MnO_2	0.667	−155274	−173492	−61.102	0.226

References

[92Wan] M. Wang, B. Sundman: Metall. Trans. B **23B** (1992) 821–831.
[03Gru] A.N. Grundy, B. Hallstedt, L. Gauckler: J. Phase Equilibria **24** (2003) 21–39.