substance: Mn_3O_4
property: phase transition, crystal structure, entropy, enthalpy

phase diagram: Fig. 1. In the temperature range 860...975°C equilibrium with Mn_2O_3 has the quantitative form: 6 $Mn_2O_3 \leftrightarrow$ 4 $Mn_3O_4(\alpha)$ + O_2, whereas at 1248...1562°C the equilibrium with MnO is 2 $Mn_3O_4(\beta) \leftrightarrow$ 6 MnO + O_2.

phase boundaries

log $p_{O2} = a - b/T$ (p_{O2} in atm)

a	7.190	*T* = 860...975°C	for Mn_3O_4/Mn_2O_3 boundary	64O
b	9004 K			
a	8.05		see also [76P]	60H
b	10100 K			
a	8.2682			67S
b	10240 K			
a	13.31	*T* = 1248	for Mn_3O_4/MnO boundary	60H
b	26000 K	...1562°C		

phase transition temperature

T_{tr}	1170°C ↑	differential thermal analysis	48M
	1100°C ↓		
	1167°C ↑	differential thermal analysis	58H
	1130°C ↓		
	1150°C ↑	X-ray diffraction	67D
	1125°C ↓		
	1162°C ↑		58H
	1144°C ↓		
	1172°C		42S
	1157°C		81M

crystal structure

T < 1170°C: tetragonal distorted spinel, hausmannite (α-Mn_3O_4), space group D_{4h}^{19} – $I4_1/amd$, *Z* = 4, unit cell body centred tetragonal.

T > 1170°C: cubic spinel (β-Mn_3O_4), space group O_h^5 – Fm3m.

thermodynamic parameters

ΔH_{tr}	+ 4.96 kcal mol^{-1}	enthalpy and entropy change at	74N
	+ 4.5 kcal mol^{-1}	the transition temperature	42S
	+ 5.9(7) kcal mol^{-1}		70F
ΔS_{tr}	4.2(5) cal K^{-1} mol^{-1}		70F
	3.93 cal K^{-1} mol^{-1}		74N

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Fig. 1.

Mn_3O_4. Phase diagram for Mn_3O_4 and its interconversion to Mn_2O_3 and MnO [81M].