Fe – O (Iron – Oxygen)

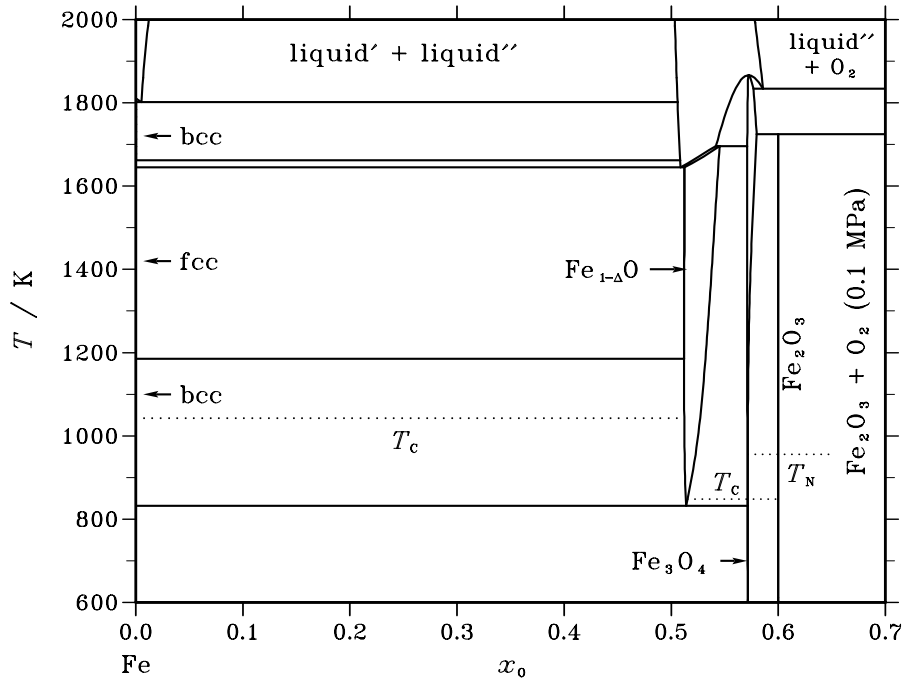

Fig. 1. Calculated phase diagram for the system Fe-O.

The solubility of oxygen in any metallic iron phase is low and there is a miscibility gap between the metallic liquid and the oxide liquid which has about equal amounts of Fe and O. There are 3 oxide phases, at low oxygen content the wüstite ($Fe_{1-\Delta}O$) has NaCl structure ($B1$) and a quite large solubility range due to the fact that iron has two valence states and there can be vacant iron sites. The spinel phase (magnetite, Fe_3O_4) has a more narrow stoichiometry range and is stabilised by its magnetic transformation at rather high temperature. At low temperature magnetite is an inverse spinel but the randomness increases with temperature. The corundum phase (hematite, Fe_2O_3) is treated as a stoichiometric oxide. This system is important in steel-making as the iron ore is normally a mixture of magnetite and hematite. The present assessment [91Sun, 96Sel] takes all important factors into account and has an ambitious modelling of the oxide phases.

Table I. Phases, structures and models.

Phase	Struktur-bericht	Prototype	Pearson symbol	Space group	SGTE name	Model
liquid					IONIC_LIQ	$Fe^{2+}_p(O^{2-},FeO_{1.5},\Box)_q$
bcc	$A2$	W	$cI2$	$Im\overline{3}m$	BCC_A2	$(Fe,O)_1$
fcc	$A1$	Cu	$cF4$	$Fm\overline{3}m$	FCC_A1	$(Fe,O)_1$
$Fe_{1-\Delta}O$	$B1$	NaCl	$cF8$	$Fm\overline{3}m$	HALITE	$(Fe^{2+},Fe^{3+},\Box)_1O^{2-}_1$
Fe_3O_4	$H1_1$	Al_2MgO_4	$cF56$	$Fd\overline{3}m$	SPINEL	$(Fe^{2+},Fe^{3+})_1(Fe^{2+},Fe^{3+},\Box)_2$ $(Fe^{2+},\Box)_2O^{2-}_4$
Fe_2O_3	$D5_1$	αAl_2O_3	$hR10$	$R\overline{3}c$	CORUNDUM	$Fe^{3+}_2O^{2-}_3$

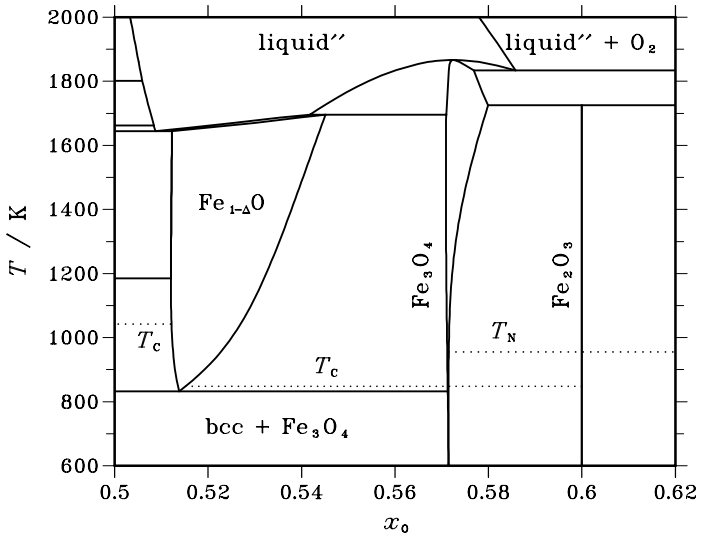

Fig. 2. Partial phase diagram for the system Fe-O.

Table II. Invariant reactions.

Reaction	Type	T / K	Compositions / x_{O}			$\Delta_{\mathrm{r}}H$ / (J/mol)
liquid″ $\rightleftharpoons$ Fe_3O_4	congruent	1866.2	0.572	0.572		−18155
liquid″ $\rightleftharpoons$ Fe_3O_4 + gas	gas-eutectic	1834.0	0.586	0.577	1.000	−12690
liquid′ $\rightleftharpoons$ bcc + liquid″	monotectic	1801.6	0.005	0.000	0.506	−14237
Fe_3O_4 + gas $\rightleftharpoons$ Fe_2O_3	gas-peritectoid	1724.9	0.580	1.000	0.600	−13385
liquid″ + Fe_3O_4 $\rightleftharpoons$ $Fe_{1-\Delta}O$	peritectic	1695.4	0.542	0.571	0.545	−12032
bcc $\rightleftharpoons$ fcc + liquid″	metatectic	1661.6	0.000	0.000	0.508	−823
liquid″ $\rightleftharpoons$ fcc + $Fe_{1-\Delta}O$	eutectic	1644.6	0.509	0.000	0.512	−16758
fcc + $Fe_{1-\Delta}O$ $\rightleftharpoons$ bcc	peritectoid	1185.0	0.000	0.512	0.000	−1010
$Fe_{1-\Delta}O$ $\rightleftharpoons$ bcc + Fe_3O_4	eutectoid	832.3	0.514	0.000	0.571	−5293

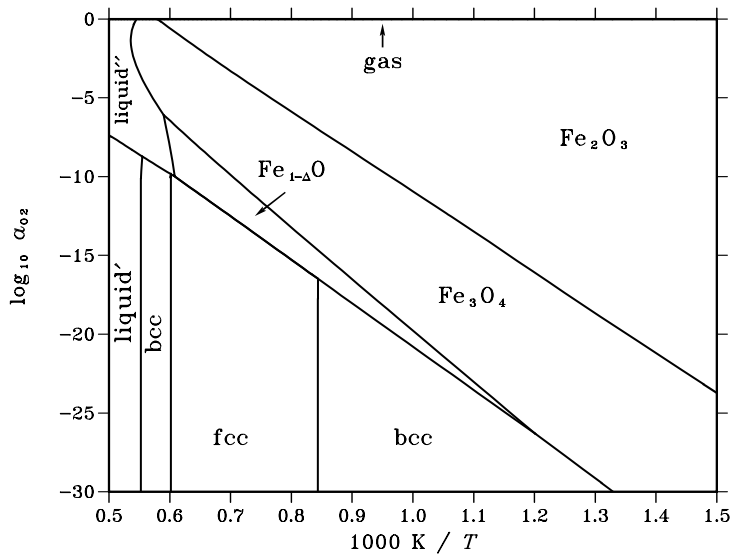

Fig. 3. Calculated temperature-activity phase diagram. Reference state: $\frac{1}{2}O_2$(gas, 0.1 MPa).

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

Compound	x_{O}	$\Delta_{\mathrm{f}}G^{\circ}$ / (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))
Fe_3O_4	0.571	−144669	−159411	−49.446	2.470
Fe_2O_3	0.600	−148302	−164657	−54.857	2.347

References

[91Sun] B. Sundman: J. Phase Equilibria **12** (1991) 127–140.
[96Sel] M. Selleby, B. Sundman: Calphad **20** (1996) 381–392.