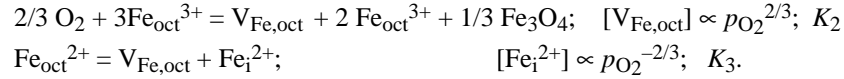


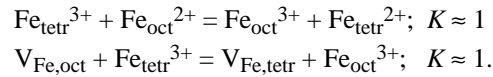
substance: Fe₃O₄

property: defect equilibria

Fe₃O₄ is commonly cation deficient and the deviation from stoichiometry can be very large (Figs. 1(a) and 1(b)). Tracer diffusion experiments [77D1] show that $(d \log D_{\text{Fe}}^*/d \log p_{\text{O}_2})$ is $\approx 2/3$ at high oxygen pressures and $-2/3$ at low pressures. The equilibria involved are



At low oxygen pressures, diffusion is therefore by interstitials, and at high oxygen pressures by cation vacancies. A more detailed analysis at high temperature (1300°C) [77D2] indicates that a better fit to the data can be obtained if the following equilibria hold



From an analysis of the data of [77D2, 68S, 35G, 46D, 57S, 41S] values of $K_2 = 24$ and $K_3 = 10^{-8}$ at 1200°C are obtained; plot of $\ln K_2$ vs. $1/T$: Fig. 1(b). This random distribution of Fe²⁺ on octahedral and tetrahedral sites is also supported by thermopower measurements [70G] and by structural investigations [69K, 71W]. Originally, only vacancies on the 16(d) sites of cation deficient Fe₃O₄ were considered, since heating Fe₃O₄ in air at 400°C for long periods led to γ -Fe₂O₃ (maghemite), which contains only such vacancies ordered in a rather complex way [58F, 61U]. By heating for very long periods [69K], or by heating in sulfur [69K, 71W] tetrahedral vacancies were also found, cation vacancies being randomly distributed between tetrahedral and octahedral sites according to Moessbauer evidence [71W].

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Fig. 1.

$\text{Fe}_{3-x}\text{O}_4$. Composition parameter x vs. oxygen partial pressure at various temperatures (a) results from [72K] (b) results from several authors of $\ln K_2$ (defined in text) vs. $1/T$ collected by [77D2].

