

with $a = 5.42 \text{ \AA}$, $b = 8.03 \text{ \AA}$, $c = 11.30 \text{ \AA}$, $\alpha = 103\frac{1}{2}^\circ$, $\beta = 97^\circ$, $\gamma = 72^\circ$. There is one formula unit per unit cell; density, calc. 1.85, found 1.88 g/cm³. The space group $C_2^1 - P\bar{1}$ indicated by the morphology would require centrosymmetry for the cation also here. The intensity distribution along the reciprocal c axis is very similar to that of the triclinic hydrogenfluoride dimorph (c spacings 10.97 and 11.08 \AA respectively).

Trithiourea-tellurium(II) di(hydrogenfluoride), $\text{Te}(\text{tu})_2(\text{HF}_2)_2$. This salt was obtained as prisms growing on top of a layer of the monoclinic tetrathiourea-tellurium(II) salt, as recounted above, and was the only product when a tellurium dioxide: thiourea molar ratio of 1 : 3 was employed (4.5 g thiourea in 15 ml of water in the above procedure). Yield, 2.7 g (52 %). (Found: F 17.36; S 22.23; Te 29.57. Calc. for $\text{C}_3\text{H}_{14}\text{F}_2\text{N}_6\text{S}_2\text{Te}$: F 17.51; S 22.17; Te 29.40.)

The salt forms monoclinic prisms {011} with $a = 5.91 \text{ \AA}$, $b = 20.68 \text{ \AA}$, $c = 11.47 \text{ \AA}$, $\beta = 95^\circ$. The space group, from systematic absences, is $C_{2h}^2 - P2_1/c$. There are four formula units per unit cell; density, calc. 2.06, found 2.05 g/cm³. The crystal structure has been solved, and will be published later.

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The Equilibrium Between Molten FeO—Fe₂O₃ Mixtures and O₂ Gas

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From simple energetic assumptions it is possible to calculate the equilibrium between O₂ gas, Fe(II) and Fe(III) in solid solutions of Fe₃O₄ — Fe₂O₃, Fe₃O₄ — MgFe₂O₄ and Fe₃O₄ — FeCr₂O₄ based on spinel models with a defect cation lattice (cation vacancies and interstitial cations)¹⁻³. These and similar models are also applicable^{1,2} for the calculation of the equilibrium between oxygen gas and molten oxide mixtures, including a larger part of the range of composition from FeO—Fe₃O₄.

In the following a more plausible model will be suggested for the molten oxide mixtures based on a spinel like structure where instead of interstitial cations a corresponding number of oxygen ion vacancies are assumed.

The structure model is thus characterized by a Schottky disorder which can be expressed by

$$\frac{n_{\square}}{n_c} \times \frac{n_{\square}}{n_a} = N_{\square} \times N_{\square} = \text{const.} \quad (1)$$

where

$$\begin{aligned} n_{\square} &= \text{number of cation vacancies} \\ n_{\square} &= \text{number of anion vacancies} \\ n_c &= \text{number of cation positions} \\ n_a &= \text{number of anion positions} \end{aligned}$$

(The cation and anion vacancies are simultaneously present only in a composition range very close to stoichiometric Fe₃O₄).

The requirement for the model is that

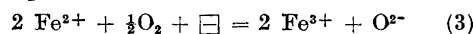
$$\frac{n_c}{n_a} = \frac{3}{4} \quad (2)$$

where

$$\begin{aligned} n_a &= n_{\text{Fe(II)}} + n_{\text{Fe(III)}} + n_{\square} \\ n_c &= n_{\text{O}^{2-}} + n_{\square} \end{aligned}$$

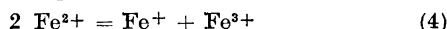
A liquid of stoichiometric FeO thus corresponds to the structural formula $\text{Fe}_2\text{O}_3\Box$.

Fe(II) and Fe(III) ions are assumed to be statistically distributed over two kinds of positions, formally octahedral and tetrahedral with respect to the anion positions. The equilibrium between Fe(II), Fe(III) and O_2 gas can then be expressed by the equation



(for $\text{Fe(III)/Fe(II)} < 2$. When $\text{Fe(III)/Fe(II)} > 2$ the corresponding equilibrium equation with cation vacancies can be applied¹).

An additional assumption is necessary to make $p_{\text{O}_2} \neq 0$ for stoichiometric FeO. This can be accounted for by a disproportionation equilibrium



(or alternatively $3 \text{Fe}^{2+} = \text{Fe} + 2 \text{Fe}^{3+}$)

This equilibrium equation becomes important at compositions close to stoichiometric FeO only.

These assumptions lead to the following expression for $\log p_{\text{O}_2}$ as a function of the ratio O/Fe, (applicable in the composition range FeO– Fe_3O_4):

$$\log p_{\text{O}_2} = \text{const.} + 4 \log \left[\frac{x-1}{3-2x} \left(1 + \sqrt{1 + \frac{(2x-1)(3-2x)}{(x-1)^2} K_2} \right) \left(\frac{x}{\frac{1}{2}(4+y)-x} \right)^{\frac{1}{2}} \right] \quad (5)$$

where

$x = \text{O/Fe}$ in the melt

$K_2 =$ the equilibrium constant of (4)

$y = 4 \cdot \frac{n_{\Box}}{n_{\text{Fe}}} (\approx 0 \text{ when } x < \frac{4}{3})$

A calculation based on a randomly distributed cationic mixture only, without structural defects (Temkin model) leads to the following equation:

$$\log p_{\text{O}_2} = \text{const.} + 4 \log \frac{x-1}{3-2x} \quad (6)$$

The two models are compared with the experimental values of Darken and Gurry⁴

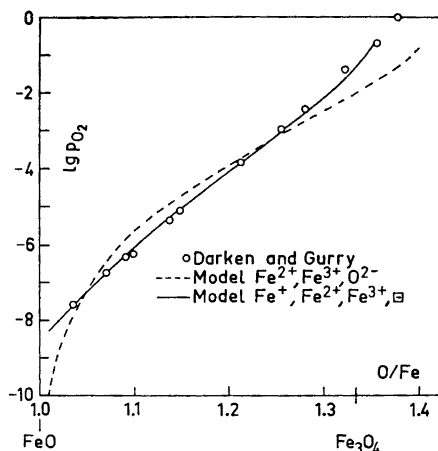


Fig. 1. $\lg p_{\text{O}_2}$ as a function of O/Fe in the melt ($\lg = \log_{10}$).

at 1 600°C as shown in Fig. 1. The superiority of the defect spinel model is evident.

A structural model of molten ionic compounds based on randomly distributed

vacancies, mainly of the type which occupies the positions of the larger ion present, may possibly be of a more general applicability. This will be shown in a subsequent communication.

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