Letters

On the Stoichiometry Limits in NiO and Fe_2O_3

(Comment on the note by R. W. Drakeford and C. M. Quinn)
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I read with interest the communication by Drakeford and Quinn on the stoichiometry limits in NiO and Fe_2O_3 and concur entirely with their result that the oxygen content of these oxides does not exceed the expected stoichiometric amount under their experimental conditions (500 and 700°C at 1 kbar oxygen pressure). This confirms my own unpublished results obtained with only 0.1 kbar oxygen pressure. However, it is the main purpose of this communication to draw attention to the systematic study by LcBlanc and Sachse [1], which once and for all excluded the existence of the nickel oxides Ni_2O_3 and NiO_2 (still quoted in the literature as shown by Drakeford and Quinn's note) by exact determination of the excess O-content and by X-ray studies; at the same time it was pointed out that wrong assumptions have often been made by neglecting, in the analysis, other constituents such as H_2O. These results were confirmed by Müller [2].

References

1. M. LEBLANC and H. SACHSE, *Z. Elektrochem.* **32** (1926) 58-62, 204-10.
2. RICHARD MÜLLER, Thesis, Leipzig, 1931, ("The system NiO-O-H_2O") *Chem. Abstr.* **27** (1933) 1267.

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Precision Lattice Parameters and Thermal Expansion of Calcium Tungstate

Calcium tungstate, mineralogically known as scheelite, crystallises in the space group I $4_1/a$. Many reports are available in literature on the determination of the room temperature lattice parameters of this crystal. Nassau and Broyer [1] have studied its thermal expansion using a quartz dilatometer from liquid nitrogen temperature to 1030°C. However, no X-ray studies of the temperature variation of the lattice parameters and thermal expansion appear to have been made. The present note reports such studies on $CaWO_4$ over the range of temperature 28 to 347°C. We have already reported similar results on potassium metaperiodate [2], sodium metaperiodate [3], strontium tungstate [4], barium tungstate [5], calcium molybdate [6] and cadmium molybdate [7]. All these crystals belong to the same space group and are isotypes of scheelite.

The X-ray powder photographs at six different temperatures were taken employing a high temperature symmetrical focusing camera [8] and CuK radiation. The reflections from $(620)_{\alpha_1\alpha_2}$, $(536)_{\alpha_1\alpha_2}$, $(543)_{\alpha_1}$, $(624)_{\alpha_1\alpha_2}$, $(3.0.13)_{\alpha_1}$ $(631)_{\alpha_1\alpha_2}$ and $(448)_{\alpha_1\alpha_2}$ planes, recorded in the Bragg angle region between 68 and 84°, were used to evaluate the lattice parameters. Cohen's [9] method, in combination with an error function $\phi \tan \phi$, was employed. The values of the lattice parameters, at different temperatures along with the corresponding errors calculated by the method of Jette and Foote [10], are listed in table I.

TABLE I Values of the lattice parameters of calcium tungstate at different temperatures.

Temperature °C	a (Å)	c (Å)
30	5.2437 ± 0.0003	11.3754 ± 0.0012
75	5.2443 ± 0.0005	11.3863 ± 0.0035
138	5.2483 ± 0.0002	11.3935 ± 0.0013
225	5.2533 ± 0.0001	11.4128 ± 0.0023
263	5.2540 ± 0.0006	11.4211 ± 0.0035
347	5.2588 ± 0.0006	11.4336 ± 0.0032

The room temperature values of the lattice parameters obtained in the present study are in good agreement with those from recently published literature, as shown in table II.

The values of the principal coefficients of thermal expansion α_a and α_c at different temperatures were evaluated by the procedure suggested by Deshpande and Mudholkar [11]. These data can be represented by the following equations: