

## Letters to the Editors

### A Remark on the Structure of Non-Stoichiometric $UO_2$

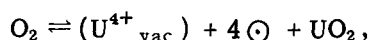
Uranium dioxide is known to exist in non-stoichiometric compositions in equilibrium with oxygen partial pressures in the surrounding atmosphere at given temperatures. The structure of over-stoichiometric  $UO_2$  was considered that of a metal-defect lattice by Kuczynski<sup>1</sup> and that of an oxygen-excess by Arrott & Goldman<sup>2</sup> and by Young *et al.*<sup>3</sup>

Kuczynski's opinion is based on the sintering behaviour of non-stoichiometric  $UO_2$  compared to that of alumina and hematite. However, we showed<sup>4</sup> that such a behavior is more compatible with the oxygen-excess structure, provided certain assumptions are made. Arrott & Goldman derived their conclusions from magnetic-susceptibility measurements interpreted according to the Weiss-Néel molecular field theory of antiferromagnetism and a spin-only model, because the  $\Theta/C$  ratio in over-stoichiometric  $UO_2$  increases with increasing oxygen content. However, they remarked that non-stoichiometric  $UO_2$  does not obey the Curie-Weiss law, while the dependence of  $C$  on the oxygen content is very erratic; clearly, some uncertainties on the electronic structure of the material remain. The deduction of Young *et al.* from the density-variation pattern of non-stoichiometric  $UO_2$  is also somewhat controversial, because the overall reduction in the lattice parameter, which takes place with increasing oxygen content, is difficult to explain if oxygen ions are to occupy interstitial sites, as postulated. In fact, in stoichiometric  $UO_2$  the uranium ion has the radius of 0.98 Å and the oxygen ion of 1.37 Å, leaving interstitial holes having radii of 0.98 Å; in over-stoichiometric  $UO_2$ , the extra attraction re-

sulting from increasing the uranium ion valence from 4+ to 5+ or 6+ should only very slightly reduce its size and increase that of the interstitial holes<sup>5</sup>.

An argument developed by Smyth for non-stoichiometric MnO and FeO and beautifully confirmed by experiments<sup>6</sup> may suggest new ground for speculation on  $UO_2$ .

As long as the thermal contribution to non-stoichiometry is negligible, the following quasi-chemical equation holds, if the metal-defect (metal-vacancy) structure is assumed:



where  $\odot$  means an electron in the conduction band. Hence the equilibrium equation is

$$K' p_{O_2} = [(U^{4+}_{vac})][\odot]^4,$$

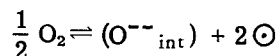
$K'$  being a temperature-dependent factor. Moreover

$$[\odot] = 4 [(U^{4+}_{vac})] = 4 v,$$

$v$  being the metal-vacancy concentration, equal to  $\frac{1}{2} x/(2+x)$  in the  $UO_{2+x}$  formula. Then

$$x/(2+x) \propto (p_{O_2})^{\frac{1}{5}}. \quad (1)$$

On the contrary, if the oxygen-excess (oxygen-interstitial) structure is assumed,



whence

$$K'' (p_{O_2})^{\frac{1}{2}} = [(O^{--}_{int})][\odot]^2$$

while

$$[\odot] = 2 [(O^{--}_{int})] = 2 i,$$

$i = \frac{1}{2} x$  being the interstitial concentration. Then

$$x \propto (p_{O_2})^{\frac{1}{6}} \quad (2)$$

Thus, either the  $\log x/(2+x)$  vs  $\log p_{O_2}$  lines should have a slope of 1/5, or the  $\log x$  vs  $\log p_{O_2}$  lines should have a slope of 1/6.

<sup>1</sup>G. C. KUCZYNSKI, in "Pulvermetallurgie in der Atomkerntechnik," p. 166. F. BENESOVSKY ed., Springer-Verlag, Wien, (1962).

<sup>2</sup>A. ARROTT and J. E. GOLDMAN, *Phys. Rev.*, **108**, 948 (1957).

<sup>3</sup>A. A. YOUNG, L. LYND, J. S. MOHL and G. G. LIBOWITZ, *Atoms International Report NAA-SR-6765* (1960).

<sup>4</sup>I. AMATO, R. L. COLOMBO and A. M. PROTTI, *J. Nucl. Mat.*, in press.

<sup>5</sup>L. PAULING, *The Nature of the Chemical Bond*, 3rd edn., p. 515. Cornell University Press, Ithaca, N. Y., (1960).

<sup>6</sup>P. M. SMYTH, *J. Phys. Chem. Solids*, **19**, 167 (1961).

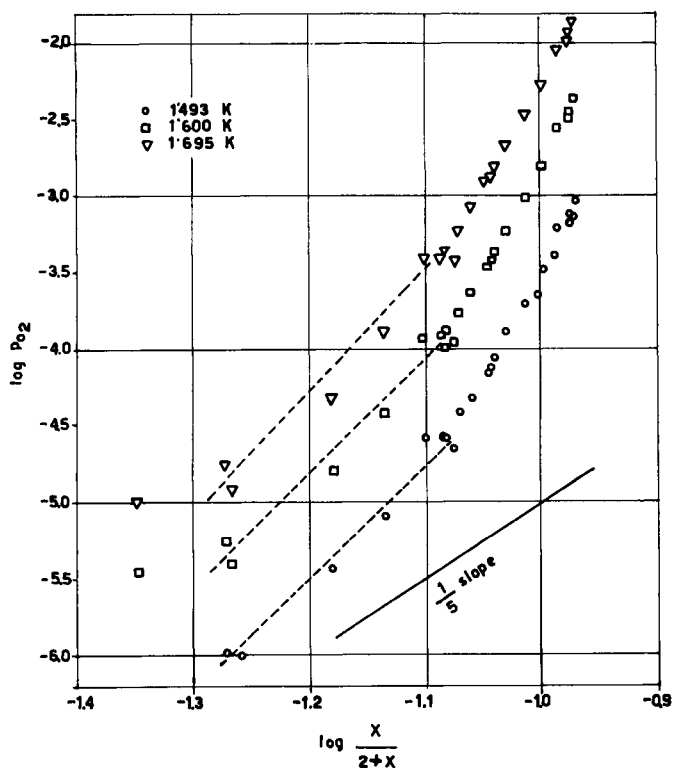


Fig. 1.  $\log x/(2+x)$  vs  $\log p_{O_2}$  plot.

Data taken from the work of Roberts & Walter<sup>7</sup> are shown in Fig. 1 and 2. One sees that eq. (1) is not likely to hold anywhere. Eq. (2) may be made to hold between, say,  $x = 0.10$  ( $\log x = -1$ ) and  $x = 0.16$  ( $\log x = \sim -0.8$ ), so that the interstitial picture would be favored. Below  $x = 0.10$ , the thermal contribution to the defect concentration might become important, and above  $x = 0.16$  the material structure might perhaps be no longer represented as that of a normal  $UO_2$  lattice containing equivalent oxygen interstitials and the electronic structure should undergo radical changes. (Young *et al.* suggest that there exist two non-stoichiometric oxides, namely  $UO_{2+x}$  and  $U_4O_{9-y}$ ; their breaking point comes also very close to  $x = 0.16$ ).

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<sup>7</sup>L. E. J. ROBERTS and A. J. WALTER, *J. Inorg. Nucl. Chem.*, **22**, 213 (1961).

## The Infinite Dilute Resonance Integral of Thorium

Previous measurements of the infinite dilute resonance integral of thorium show wide discrepancies. Values between 67 barns<sup>1</sup> and 106 barns<sup>2</sup> have been reported. Therefore, and due to the importance of the resonance integral as a check for resonance parameters, a redetermination of this quantity was performed.

In the measurements the cadmium-ratio technique was used, comparing the activation of thin circular thorium and gold foils. To eliminate self-shielding effects, foils containing only 50  $\mu\text{g}/\text{cm}^2$  thorium were prepared by alloying thorium and aluminum. The gold foils were about 700  $\mu\text{g}/\text{cm}^2$  and therefore show some self-shielding; this was, however, corrected by using previous experimental results (see below). The irradiations were performed in the pool of the Munich research reactor at a core distance of about 20 cm, where the epithermal neutrons follow a  $1/E$  spectrum. Bare and Cd-covered Au and Th foils (Cd thickness 1 mm) were irradiated simultaneously by placing them on a rotating Plexiglas turntable. Thus the average neutron flux was the same for all

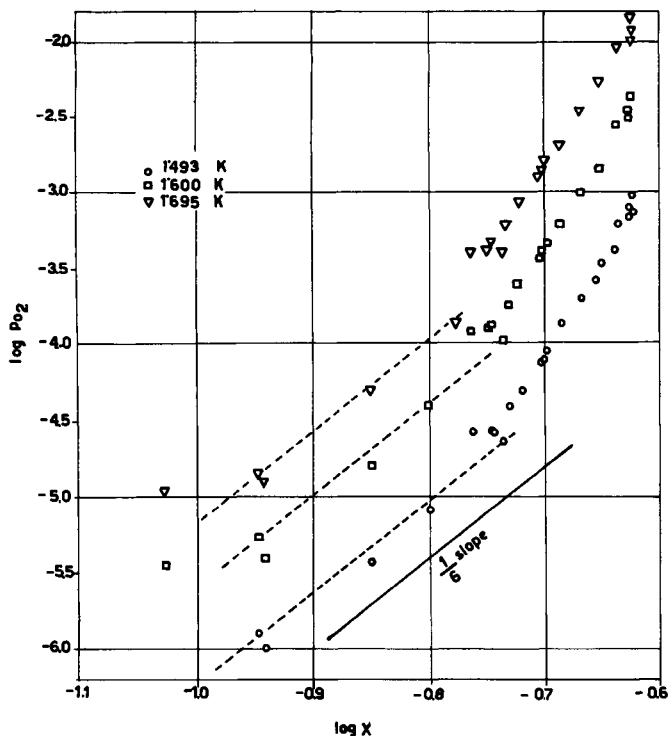


Fig. 2.  $\log x$  vs  $\log p_{O_2}$  plot.

<sup>1</sup>R. L. MACKLIN and H. S. POMERANCE, "Resonance Activation Integrals of  $U^{238}$  and  $Th^{232}$ ," *J. Nucl. Energy, Part A: Reactor Sci.* **2**, 243-246 (1956).

<sup>2</sup>R. B. TATTERSALL, TNCC (UK)-53.