

# Letters

*On the approximate correlation between heats of formation of oxygen vacancies and thermochemical properties of oxides*

Kofstad [1] has shown that the heat of formation values for doubly charged oxygen vacancies,  $\Delta H_{V_{O_2}}$ , for  $TiO_2$ ,  $V_2O_5$ ,  $Nb_2O_5$ ,  $Ta_2O_5$ ,  $WO_3$  and  $Y_2O_3$  are given by the rough empirical equation

$$\Delta H_{V_{O_2}} = 2(E_a - 167) \quad (1)$$

where  $E_a$  is the heat of atomization, per oxygen atom, of the given oxide. He rationalized this correlation by suggesting that " $\Delta H_{V_{O_2}}$  is an expression for the energy needed to remove a mole of oxygen atoms from oxygen sites in the oxide and that  $E_a$  is an expression for the total average bond strength of the oxide per gram atom of oxygen". The purpose of the present note is to explore this point of view further and to suggest a possible rationalization for the number, "167" in Kofstad's rough correlation.

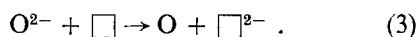
Consider the lattice of an oxide in which we are about to pull out a mole (two oxygen atoms) of oxygen, leaving behind a mole of doubly charged vacancies. This process may be followed by describing the events involved in pulling out one oxygen atom, with the subsequent doubling of the energetic quantities thus obtained in order to determine  $\Delta H_{V_{O_2}}$  per mole. To remove one oxygen atom, one breaks the equivalent of two covalent bonds (i.e., two electron-pair bonds, since oxygen is a divalent element). The energy of each of these two bonds is given by the bond energy,  $b$ , which is nothing but the heat of atomization per equivalent, except for some additional minor corrections [2]. This  $b$  value for, e.g.,  $Ta_2O_5$ , may be expressed by the equation

$$\frac{(\Delta H_{atom}/eq.)_{Ta_2O_5} = (b)_{Ta_2O_5} = -(\Delta H_f)_{Ta_2O_5} + 2(\Delta H_{Sub})_{Ta} + 5(\frac{1}{2}\Delta H_{diss})_{O_2}}{10} \quad (2)$$

Here  $\Delta H_{atom}/eq.$  denotes heat of atomization per equivalent;  $\Delta H_f$  is the heat of formation per mole;  $\Delta H_{Sub}$  is the heat of sublimation per mole;  $\Delta H_{diss}$  is the heat of dissociation; subscripts  $Ta_2O_5$ ,  $Ta$ , and  $O_2$  indicate the chemical species to which the foregoing quantities pertain; the number, 10, in the denominator converts the

$\Delta H_{atom}/mole$  of  $Ta_2O_5$  to the  $\Delta H_{atom}/eq.$ , which, of course, is the bond energy,  $b$ .

After the oxygen atom is released from the lattice, by the rupture of two metal-oxygen bonds (each with a value,  $b$ ), a neutral oxygen vacancy is created. One has thus to determine the energetic quantity involved in putting two charges on the vacancy; i.e., enthalpy of the reaction:



Here  $O^{2-}$  is an ion in the oxide adjacent to the neutral vacancy,  $\square$ ;  $\square^{2-}$  is the doubly charged oxygen vacancy and  $O$  is the oxygen atom in the oxide. Since a predominantly covalent picture of the oxide has been assumed here, which indeed is supported by the solid state properties [3] of the oxides discussed by Kofstad [1], it may be concluded that the polarization energy of the oxide may be ignored during a consideration of the energetics of reaction 4. Under this condition, the enthalpy of reaction 4 would simply be the heat evolved in extracting two electrons from the  $O^{2-}$  to form  $O$ ; i.e., negative of the sum of first and second electron affinities of oxygen to be denoted, together, by  $A_x$  here. On the basis of the foregoing discussion we note that to create one double charged oxygen vacancy, we expend an energy equal to  $2b$  but we gain energy equal to  $A_x$ ; for producing a mole of doubly charged oxygen vacancies, the energetic quantities must

TABLE I

Oxide	Exp $\Delta H_{V_{O_2}}$ (kcal mol <sup>-1</sup> )	$b$ (kcal)	$A_x$ (kcal)	$4b - 2A_x$ (kcal)
TiO <sub>2</sub>	95 to 115	113	156	140
V <sub>2</sub> O <sub>5</sub>	22 to 35	91	156	52
Nb <sub>2</sub> O <sub>5</sub>	95 to 110	111	156	132
Ta <sub>2</sub> O <sub>5</sub>	140 to 160	116	156	152
WO <sub>3</sub>	60 to 75	96	156	72
Y <sub>2</sub> O <sub>3</sub>	225 to 255	134	156	224

- Notes: 1. The experimental  $\Delta H_{V_{O_2}}$  values are taken from Fig. 2 of Kofstad's paper [1].  
 2. The  $b$  values are from Sanderson [4].  
 3. The  $A_x$  value has been taken from [3].  
 4. The  $(4b - 2A_x)$  values are the  $\Delta H_{V_{O_2}}$  values predicted by Equation 5.

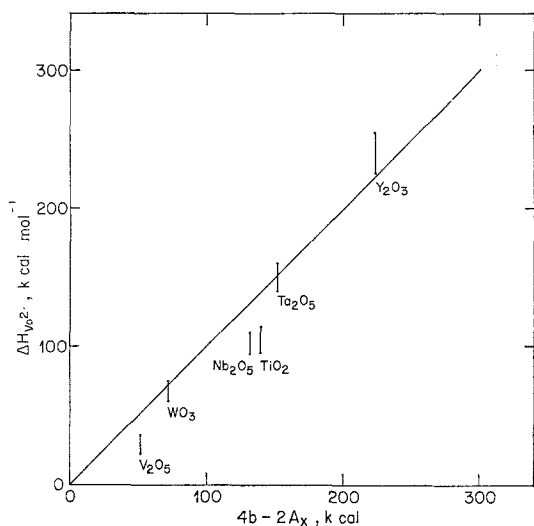


Figure 1 The experimental  $\Delta H_{V_{O_2}}$  values [1] plotted against  $(4b - 2A_x)$  values; the line represents the situation if Equation 5 (i.e.,  $\Delta H_{V_{O_2}} = 4b - 2A_x$ ) was completely successful in predicting the experimentally observed  $\Delta H_{V_{O_2}}$  values. See text for significance.

be doubled. These facts may be expressed by the equation

$$\Delta H_{V_{O_2}} = 4b - 2A_x \quad (4)$$

where  $\Delta H_{V_{O_2}}$  is, of course, per mole; the value of  $A_x$  is 156 k cal<sup>3</sup>. One may verify Equation 5 by means of the data given in Table I. It is clear that the  $\Delta H_{V_{O_2}}$  values given by Equation 5, namely,  $(4b - 2A_x)$  values, agree very well with the experimental values [1] for  $Ta_2O_5$ ,  $WO_3$  and  $Y_2O_3$ ; the agreement for  $TiO_2$ ,  $V_2O_5$  and  $Nb_2O_5$  is less than satisfactory. However, the general validity of the suggestion presented here is emphasized by Fig. 1 in which  $(4b - 2A_x)$  values have been plotted against the experimental  $\Delta H_{V_{O_2}}$  values; the line drawn represents the theoretical curve expected if Equation 5 were completely successful for predicting the experimental  $\Delta H_{V_{O_2}}$  data. It would appear that the

agreement between the experimental and the Equation 5 values of  $\Delta H_{V_{O_2}}$  is rather good, keeping in mind the scatter and uncertainties involved in the experimental determinations [1] of  $\Delta H_{V_{O_2}}$ .

It should be emphasized that the Equation 5 proposed here is not really new since it is based on the original excellent suggestion of Kofstad [1] (i.e. Equation 1). It does provide, however, a follow-up of Kofstad's reasoning, especially with regard to the present proposal that the number, "167" in Equation 1 may perhaps be identified with the  $-A_x$  value.

It should be pointed out here that in the present discussions the quantities being considered are *partial* molar heats of solution of oxygen since formation of an oxygen vacancy refers to a non-stoichiometric oxide [5, 6]. Also, since the proposed correlation (Fig. 1) has been obtained solely from the oxygen dissociation energy, it would follow that the partial heats of solution of the cations in the oxides considered have negligible values. This has indeed been observed for some oxides previously [5].

## References

1. P. KOFSTAD, *J. Phys. Chem. Solids* **28** (1967) 1842.
2. R. HOWALD, *J. Chem. Ed.* **45** (1968) 163; A. K. VIJH, "Electrochemistry of Metals and Semiconductors" (Marcel Dekker, New York, 1973).
3. A. K. VIJH, *J. Electrochem. Soc.* **116** (1969) 353.
4. R. T. SANDERSON, "Inorganic Chemistry" (Reinhold, 1967).
5. C. B. ALCOCK, S. ZADOR and B. C. H. STEELE, *Proc. Brit. Ceram. Soc.* **8** (1967) 231.
6. P. G. DICKENS, R. HECKINGBOTTOM and J. W. LINNETT, *Trans. Faraday Soc.* **64** (1968) 1489.

Received 23 May

and accepted 1 September 1973

ASHOK K. VIJH  
Hydro-Quebec Institute of Research,  
Varenes, P.Q., Canada

## Comment on "Voluminous oxidation of aluminium by continuous dissolution in a wetting mercury film"

Pinnel and Bennett [1] have used X-ray diffraction to investigate the fronds of white material which issue from the surface of aluminium wetted with mercury and exposed to moist air. Although the material had to be

heated to 750°C for 48 h to obtain an identifiable pattern, they concluded that even the "as-grown" material is  $\gamma$ -alumina in a microcrystalline form. The purpose of this letter is to question their conclusion, by recalling earlier studies and by presenting new evidence which may advance the understanding of the catastrophic oxidation of aluminium under these conditions.

In a comprehensive study of the material,