

## The evaporation coefficients of the $\text{Al}_2\text{O}_3$ vapour species

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**Abstract.** The evaporation coefficients for the vapour species from the thermal decomposition of alumina were calculated from data derived from mass spectrometric effusion and Langmuir evaporation experiments. These values for  $\alpha$  were  $\sim 0.2$  for Al, O and AlO,  $\sim 0.1$  for  $\text{Al}_2\text{O}$ ,  $\sim 0.02$  for  $\text{Al}_2\text{O}_2$ , and  $\sim 0.01$  for  $\text{AlO}_2$ .

**Keywords.** Evaporation coefficients; accommodation coefficients; dissociation energies of aluminum suboxides; thermodynamic properties; thermal decomposition.

### 1. Introduction

The thermodynamic properties of the aluminum oxide vapour species have been a source of controversy for over 20 years. Based on an evaluation of a number of spectroscopic and mass spectrometric effusion experiments, the JANAF tables and a recent review article (Srivastava and Farber 1978), fairly definitive values for the dissociation energies of the suboxides have been established. The constitution of the vapour in equilibrium with solid alumina has been determined to include Al, O, AlO,  $\text{Al}_2\text{O}$ ,  $\text{AlO}_2$  and  $\text{Al}_2\text{O}_2$  components (Farber *et al* 1972; Farber and Srivastava 1979). However, until now the accommodation, or evaporation, coefficients,  $\alpha$ , for the individual vapour species have not been reported. The average evaporation coefficients for all the species over  $\text{Al}_2\text{O}_3$  (c) have been reported to vary from 0.005 to 1.0 (Farber and Srivastava 1979).

The accommodation coefficient is generally much less than unity for solids, which decompose to lower molecular weight species and in many cases are less than  $10^{-3}$  (Yates *et al* 1964). The Langmuir theory of definite sites requires finite retention times of the vapour on the surface of the condensed species (Langmuir 1918). When polymeric species are formed in the vapour, as in the vaporization of carbon, numerous collisions are required between the vapour species and the solid to establish equilibrium (Farber *et al* 1972; Farber and Darnell 1952). The formation of polyatomic species may require collisions between the monomeric gaseous particles and the solid surface (Farber and Blauer 1962). Langmuir evaporation experiments do not usually provide sufficient surface-gas collisions to establish equilibrium, since once the gaseous particle

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leaves the surface it is lost to further reaction with the surface or with other vapour species on the surface.

Accommodation coefficients can be obtained from Knudsen effusion experiments by varying the orifice area,  $A$ , to the total solid surface area,  $A_T$ . These experiments lead to equilibrium pressures as determined from the expressions of Knudsen (1909) and Langmuir (1913)

$$G_T = \frac{\alpha p_{eq} A_T t}{(2\pi RT/M)^{1/2}}, \quad (1)$$

where  $G_T$  is the molar of vapour effusion or evaporation in a given time,  $t$ , and the relationship between the actual, pressure,  $p$ , and the equilibrium pressure,  $p_{eq}$  (Farber and Darnell 1956)

$$P = \frac{p_{eq}}{(1 + \alpha A/A_T)}. \quad (2)$$

When the orifice area is small compared to the total solid surface area the  $p$  value approaches the equilibrium partial pressure.

The mass spectrometer ion intensities are related either to the equilibrium pressures for effusion experiments, where the equilibrium has been established via eq. (2) or to  $p/\alpha$  for the mass spectrometer evaporation experiments. Thus, combining the effusion equilibrium data with those of recent mass spectrometric evaporation experiments (Cornides and Gal 1978; Fu and Burns 1976; Ho and Burns 1980) computation of  $\alpha$  values was possible for the six vapour species from the decomposition of  $Al_2O_3(c)$ .

Employing labelled oxygen isotopes,  $^{18}O$ , in a spark source mass spectrometer Cornides and Gal (1978) concluded that alumina decomposed primarily to the atomic elements and that the polyatomic species  $Al_xO_y$  were formed from combinations of the atomic elements. The formation of  $AlO_2$  and  $Al_2O_2$  would thus first require the reaction of the elements to form a diatomic molecule followed by further reaction to form the polyatomic species. Fu and Burns (1976) observed the species Al, O, AlO,  $Al_2O$  and  $Al_2O_2$  in Langmuir experiments of  $Al_2O_3(c)$ . In subsequent evaporation experiments, Ho and Burns (1980) also observed fairly weak  $AlO_2(g)$  ion intensities.

Combining the data from the evaporation experiments (Cornides and Gal 1978; Fu and Burns 1976; Ho and Burns 1980) together with the adopted equilibrium partial pressures [JANAF tables] we have computed  $\alpha$  values of  $\sim 0.2$  for Al, O, and AlO,  $\sim 0.1$  for  $Al_2O$ ,  $\sim 0.02$  for  $Al_2O_2$  and  $\sim 0.01$  for  $AlO_2$ . These values are consistent with previously reported average values for the accommodation coefficient of 0.08 (Farber and Buyers 1970) and 0.067 (Wolf and Alcock 1962) for  $Al_2O_3(c)$  vapour species, correlating the equilibrium and Langmuir results.

The values computed for  $\alpha$  for the higher suboxides support their formation as a result of recombination reactions between the atomic elements and lower suboxides,





and the reaction between the suboxides



The higher concentration of  $Al_2O_2$  may result from its formation *via* dimerization



in addition to (5) above.

Burns and coworkers calculated partial pressures for the six  $Al_2O_3(c)$  vapour species by assuming that all were in virtual equilibrium and assigned an equal  $\alpha$  value of 0.325 to them (Fu and Burns 1976; Ho and Burns 1980). Thus their equilibrium constant for reaction (6) was high by an order of magnitude and their calculated stabilities for  $Al_2O_2$  and  $AlO_2$  were therefore 8 to 20 kcal less, respectively, than the dissociation energy values obtained in the equilibrium studies and adopted by the JANAF tables (1975).

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