

Vapour Pressures in the System Al-Al₂O₃ Investigated by the Effusion Method

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The vapour pressures of Al and Al₂O over alumina plus aluminium metal have been investigated at the temperature 1556°K employing the Knudsen effusion method. The observed vapour pressures yield values of -31.8 kcal.mole⁻¹ for the heat of formation of Al₂O(g) and 79.5 kcal.mole⁻¹ for the heat of sublimation of aluminium at 298°K.

The first reliable investigation of the vaporization behaviour of the aluminium-oxygen system was done by Brewer and Searcy¹ using a weight-loss effusion method. These authors established that Al₂O and Al are the predominant gaseous species in equilibrium with the condensed phases Al₂O₃(s) plus Al(l), and also derived tentative thermodynamic data for these species. Subsequent investigations by mass spectrometry²⁻⁴ as well as by classical weight-loss effusion techniques⁵⁻⁷ agreed as to the main conclusions but showed considerable differences in the quantitative data derived for Al₂O(g).

In an attempt to resolve the discrepancies, Herstad and Motzfeldt⁸ studied this system by the weight-loss effusion method using a thermobalance. Chemical analysis of the remainder in the cell after a run allowed calculation of the Al₂O and Al pressures separately. They also studied the vapour pressures at somewhat higher temperatures and pressures (10-100 torr range) by means of the "twist method",⁹ this method giving only the sum of the partial pressures. The two sets of measurements, when combined with the known entropies of the gaseous species, showed good internal consistency, and the standard heat of formation of Al₂O(g) derived from these experiments compared favourably with the value obtained from mass spectrometric work.⁴ There were several difficulties, however, in the effusion experiments of Herstad and Motzfeldt. The size of the effusion orifice (and hence the rate of weight loss) was observed to decrease with time due to condensation of alumina in the orifice. Even more serious, the ratio Al₂O/Al in the gas phase (evaluated from the chemical analysis) appeared to increase very strongly with increasing orifice size. The authors determined the composition of the equilibrium gas by an extrapolation which cannot be considered very reliable.

In an added note in their publication, Herstad and Motzfeldt⁸ point out that the observed strong increase in the ratio Al₂O/Al with increasing orifice size was probably due to interaction between the effusing Al₂O gas and the inside of the graphite heating element used in their experiments. The present work was undertaken to perform similar effusion experiments in an environment devoid of carbon, in order to test the given explanation and to obtain more reliable data for the composition of the equilibrium gas.

EXPERIMENTAL

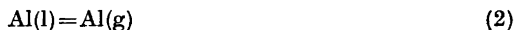
The apparatus was similar to that used by Herstad and Motzfeldt,⁸ with the difference that the furnace heating element in the present case consisted of a molybdenum tube made from 0.2 mm Mo foil. Several layers of foil were used in the middle section of the tube to obtain a zone of uniform temperature. A tube of dense-sintered alumina fitted snugly inside this heating element. The effusion cell, also of alumina, was thus suspended in an environment of its own material.

The temperature was measured by a disappearing-filament optical pyrometer (Leeds & Northrup, Cat. No. 8622C) sighted through a silica glass prism on to the orifice of the cell. The pyrometer was calibrated against a tungsten strip lamp and also by determining the melting points of silver and copper. All runs were done at the same temperature, 1556 ± 4°K. It was attempted to keep the top of the cell about 3° hotter than the bottom to prevent condensation of the vapour around the orifice. The weight change was continuously recorded by an electronic balance connected to a potentiometric recorder.

As in the previous work,⁸ the effusion cells were made from alumina crucibles (about 2 cm diameter) with ground-on lids. The center part of the lid was ground down to a thickness of about 1 mm, in which the desired orifice was drilled. The effective orifice size was determined from the diameter and length of the orifice using the appropriate Clausing factor.¹⁰

The charges were made from weighed amounts of 99.97 % aluminium turnings (British Aluminium Ltd.), loosely mixed with a weighed excess of 99.9 % alumina powder (Linde Division of Union Carbide, U.S.A.). After the effusion run, of sufficient duration to give a total weight loss equal to about two-thirds the initial weight of aluminium, the cell with contents was immersed in hydrochloric acid and the remaining amount of metal was determined from the volume of hydrogen evolved.

The two evaporation processes are represented by the equations



The total weight loss, minus the loss of metal, gives the loss of alumina. From eqn. (1), for each mole of alumina vaporized, four moles of metal have been used, giving three moles of Al₂O(g). Metal loss in excess of this must have occurred by simple evaporation according to eqn. (2). With n_i for moles evaporated, and M_i for the corresponding molecular weight, and P_i for pressures, it is seen from the effusion equation that we will have the ratio of the pressures

$$F = P_{\text{Al}_2\text{O}}/P_{\text{Al}} = (n_{\text{Al}_2\text{O}}/n_{\text{Al}})(M_{\text{Al}_2\text{O}}/M_{\text{Al}})^{\frac{1}{2}} \quad (3)$$

RESULTS

It was found also in these experiments that clogging of the hole, and hence a decrease in the rate of weight loss as time passed, could not be completely avoided. The clogging was more pronounced for the smallest orifice sizes, with a length to diameter ratio exceeding unity. As a consequence, the runs with

the smaller orifices had to be interrupted and the orifice re-drilled several times in order to obtain sufficient weight change for the subsequent analysis. The ratio $\text{Al}_2\text{O}/\text{Al}$ in the gas as evaluated from the analysis was found to increase somewhat with increasing orifice size, although not nearly as much as in the carbon-furnace.⁸ Fig. 1 shows the weight loss as a function of time for

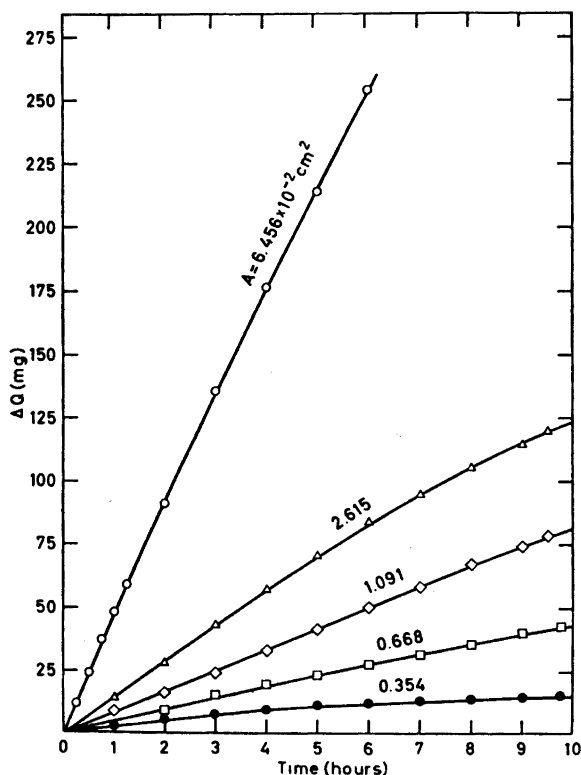


Fig. 1. Weight loss versus time for five different effective orifice areas. Number on curves represent effective orifice area in $\text{cm}^2 \times 10^{-2}$.

five different hole sizes. The effective orifice size as measured is strictly valid only for the start of any run, hence the rate of weight loss, dQ/dt , is evaluated from the slopes of the curves (Fig. 1) for $t=0$. In Fig. 2, these values are plotted against the corresponding orifice sizes.

It was mentioned above that the value of the ratio $F = P_{\text{Al}_2\text{O}}/P_{\text{Al}}$ determined from the chemical analyses appeared to increase with increasing orifice size. It was also mentioned that the effective orifice size decreased during any one run. Hence the F value determined after a run will be smaller than that corresponding to the initial size of the orifice. To circumvent this problem, the following procedure was adopted. For any of the runs, at any time, a linear

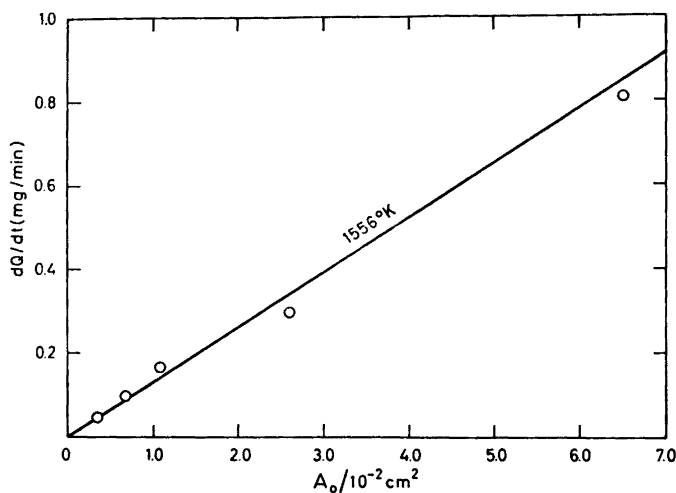


Fig. 2. Rate of weight loss (dQ/dt), at the start of runs ($t \rightarrow 0$), versus effective initial area A_0 of the orifice.

The heavy straight line corresponds to the average slope of lines from the origin through each individual point.

relation is assumed for the dependence of the rate of weight loss upon the effective area of the orifice:

$$dQ/dt = k \times A \quad (4)$$

We also know the total duration t and the total weight loss Q during an experiment, these must be related by the equation

$$Q = k \int_0^t A dt = k A_{\text{ave}} t$$

or

$$A_{\text{ave}} = Q/kt \quad (5)$$

The area A_{ave} as determined from this equation is the average effective orifice area during an experiment, and presumably it is also the orifice area which corresponds to the \bar{F} value determined by analysis after that experiment. The value of the coefficient k could be taken as the average k for all experiments (corresponding to the heavy straight line in Fig. 2); it was decided, however, that more correct results would be obtained by using for each experiment the k value obtained as the slope of a straight line drawn from the origin through the individual experimental point in Fig. 2.

According to Rosenblatts¹¹ treatment of evaporation processes with evaporation coefficients less than unity, one would expect a linear relationship between the inverse of the measured pressure and the two-thirds power of the effective orifice area. Assuming that the increase in the \bar{F} value is caused by a decrease in P_{Al} (with $P_{\text{Al}_2\text{O}_3}$ remaining essentially independent of orifice

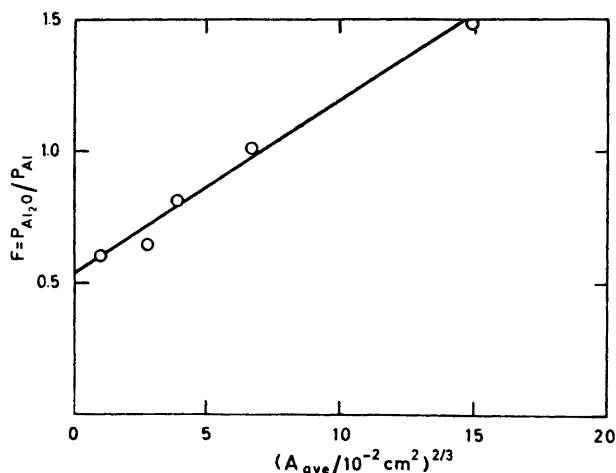


Fig. 3. The ratio $F = P_{Al_2O}/P_{Al}$ in the effusing gas, as determined from chemical analysis of the remainder after a run, versus two-thirds power of the average effective orifice area A_{ave} calculated from eqn. (4).

size) one would expect this relationship to hold true also for the F' value. This is borne out by Fig. 3, where the abscissa represents the average orifice area as calculated by eqn. (5). A least squares fit to the points give the equation

$$F' = 0.54 + 6.36 A^{2/3} \quad (6)$$

Thus knowing the value of $F = P_{Al_2O}/P_{Al}$ for any given orifice area and the rate of weight loss dQ/dt at the start of the run where the effective orifice area is known, one is able to calculate the individual pressures of Al_2O and Al for each of the runs by means of the effusion equation. The results are given in Table 1. In Fig. 4, the inverse values of the pressure are plotted as functions of the two-thirds power of the orifice area, in accordance with the Rosenblatt

Table 1. Effusion data and derived pressures for the $Al-Al_2O_3$ system at $1556 \pm 4^\circ K$.

Initial effective orifice area A_0 $cm^2 \times 10^{-2}$	dQ/dt at start of first run mg/min	No. of runs	Total duration of runs min	P_{Al_2O}/P_{Al} from chemical analyses	P_{Al_2O}/P_{Al} calculated for area A_0	P_{Al_2O} atm. $\times 10^{-6}$	P_{Al} atm. $\times 10^{-6}$
0.354	0.049	7	7504	0.60	0.68	1.37	1.99
0.668	0.096	2	2168	0.64	0.77	1.41	1.83
1.091	0.167	2	1560	0.81	0.84	1.56	1.86
2.615	0.297	2	1290	1.01	1.10	1.29	1.17
6.456	0.808	1	375	1.48	1.56	1.57	1.01
Equilibrium pressure						1.44	2.50

equation.¹¹ The equilibrium value of the Al₂O pressure is taken as the average of the individual values, while that for the Al pressure is obtained by extrapolation to zero orifice of the straight line fitted through the points on Fig. 4.

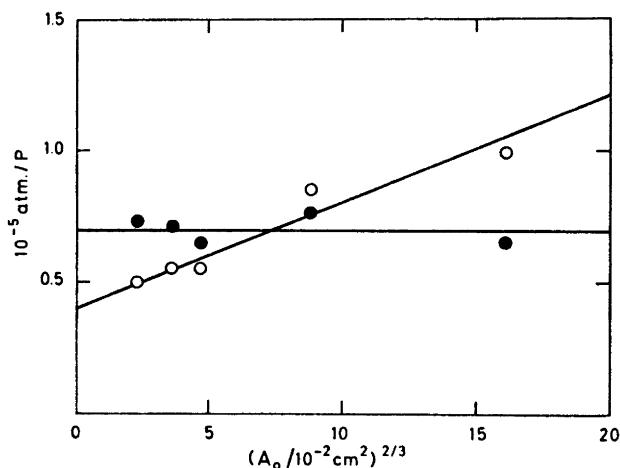
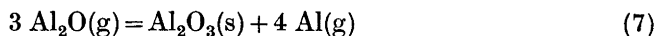


Fig. 4. Inverse experimental values of the pressures of Al₂O and Al, versus two-thirds power of the effective initial orifice area A_0 . Filled circles: Al₂O. Open circles: Al.

DISCUSSION

The results indicate that the pressures of Al₂O are independent of orifice size within experimental error while the pressures of Al decrease with increasing orifice. A physical interpretation of this would have to take into account that the Al gas has to pass through a layer of alumina powder where the reaction (1) may take place, so that the gas leaving the cell will be somewhat depleted in aluminium. This may also explain the un-avoidable clogging of the orifice: with diminishing Al pressure, the equilibrium of the disproportionation reaction



will be shifted towards the right, with deposition of alumina at the outlet.

It should be noted that the treatment used here cannot be strictly correct, since the rate of weight loss (Fig. 2) should not be a strictly linear function of orifice when the Al pressure is diminishing. This is one reason why it was preferred to use the individual values of k in eqn. (4) rather than the average of all k values.

Knowing the partial pressures of Al₂O and Al at one temperature, the heat of formation of Al₂O(g) and the heat of evaporation of aluminium have been calculated by the third-law method,¹² with free-energy functions for all the components taken from the JANAF Tables.¹³ The third law heat obtained for reaction (1) at 298°K is 296.9 kcal. When combined with the heat of formation of Al₂O₃ and the heat of melting of Al,¹³ this yields the heat of formation of

$\text{Al}_2\text{O}(\text{g})$ at 298°K, $\Delta H_{(298)}^0 = -31.8$ kcal mole⁻¹, which is in good agreement with the most recent JANAF¹³ value, -31.4 ± 7 kcal mole⁻¹. The value of the Al pressure obtained here is only about 60 % of the JANAF value at the same temperature corresponding to a heat of evaporation higher by 1.5 kcal. It is interesting to note that the heat of sublimation of aluminium at 298°K evaluated from the present experiments, 79.5 kcal, is identical with the value obtained from the extensive investigation by Potter, as quoted in the JANAF Tables.¹³

Comparing finally with the previous investigation of Herstad and Motzfeldt,⁸ it is seen that the pressure values obtained by them were roughly 50 % higher than the present values. The agreement between their value for the ratio $F = P_{\text{Al}_2\text{O}}/P_{\text{Al}}$ at equilibrium 0.55 (at 1600°K) and the present value of 0.54 (at 1556°K) must be considered partly accidental, the latter value being obtained by a more reliable method of calculation.

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