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THE ALUMINUM-ALUMINUM OXIDE SYSTEM AT HIGH TEMPERATURES

Leo Brewer and Alan W. Searcy

August 31, 1949

Berkeley, California

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The Aluminum-Aluminum Oxide System at High Temperatures

Leo Brewer and Alan W. Searcy

August 31, 1949

By effusion experiments similar to those previously employed in this laboratory to determine the vapor pressure and heat of sublimation of graphite[1], we have determined vapor pressures for aluminum and for aluminum oxide. We have also investigated vaporization from aluminum-aluminum oxide mixtures. Using our data with appropriate thermodynamic data from other sources we have computed thermodynamic equations for aluminum gas and aluminum gaseous oxide species at high temperatures.

1. Aluminum.

A. Experimental

The high reactivity of liquid aluminum made the selection of a container for effusion studies difficult. Of the metals, only Ta, Mo, W, and Re seemed to offer any possibility as containers for aluminum at the temperatures we expected to employ, 1300-1500°K, and these were known to form aluminum compounds. We found experimentally that aluminum attacked Ta, W, and Mo crucibles when heated for one half hour at 1600°K. The W and Mo crucibles were swollen and cracked; the Ta crucible was not visibly attacked, but the aluminum melt showed .5-5% tantalum when analyzed spectroscopically. Rhenium was not tested.

Of possible oxide containers that could be used for molten aluminum at temperatures of 1400°K. and above, BeO was the only one which could possibly be satisfactory from consideration of thermodynamic data. If a reaction did take place with BeO, it would be the following one.

$$2Al(l) + 4BeO(s) = 3Be(l) + BeO \cdot Al_2O_3(s) \quad \ldots\ldots\ldots\ldots(1)$$

All phases would be at unit activity except the Be, which would be dissolved in the molten aluminum. There are no thermodynamic data for

$BeO \cdot Al_2O_3$, but the data of R.F. Geller, P.J. Yavorsky, B.L. Steierman and A.S. Creamer[2], indicate a congruent melting point for $BeO \cdot Al_2O_3$ just a few degrees above the eutectic temperatures.

We would estimate for the reaction

$$BeO(s) + Al_2O_3(s) = BeO \cdot Al_2O_3(s) \ , \ \Delta F^{o}_{1400} = -3 \text{ kilocalories.}$$

This together with the thermodynamic data given by L. Brewer[3] allows one, assuming $\Delta C_p = 0$, to calculate for the reaction (1), $\Delta F^{o}_{1400} = -45$ kilocals. or an activity of 10^{-2} for Be. From the Al-Be phase diagram given by M. Hansen[4], the solubility of solid Be in molten Al at 1400°K. is around a mole fraction of 0.5. Since this is near the melting point of Be, the activity of Be is about the same relative to either the liquid or solid standard state. Assuming Henry's Law for Be in Al liquid, one finally calculates that Al will reduce BeO until a mole fraction of 0.005 Be is reached in the molten Al. Since Be and Al have very closely the same boiling points, this concentration of Be would not add appreciably to the volatility nor would it be expected to reduce the Al activity appreciably. Even though increasing the temperatures a few hundred degrees would increase the Be mole fraction to 0.01 or even higher, one would expect to have an appreciable temperature range in which one could work without excessive attack on the BeO.

After eight hours heating at about 1450°K. spectroscopic examination of aluminum in a BeO crucible shows .1-1% wt. Be. This probably means either that the 147 K. cal. heat of formation chosen by Brewer[3] is slightly high or that $BeO \cdot Al_2O_3(s)$ is more stable than we have estimated. These results indicate, however, that the value of 135 K. cal. for heat of formation of BeO discarded by Brewer[3] is not correct, since that value would indicate considerable reaction

between Al and BeO at 1450°K.

Other materials which might contain aluminum without reacting are some of the carbides, silicides, and borides. Very little is known about the silicides and borides.

We heated tantalum, silicon, and .6g aluminum together in a silicide coated tantalum crucible to 1970°K and found only $TaSi_{.6}$ and $TaSi_{.20}$ from x-ray examination indicating the Ta-Al phases are not as stable as the Ta-Si phases. Thus tantalum silicides could serve as suitable containers for aluminum metal but because the silicon partial pressures over the tantalum silicide compounds are not known, and other suitable containers were found we made no effusion runs from tantalum silicide containers. Borides were tested.

Of the carbides, the most promising appeared to be TaC. It seems to be the most stable of the carbides, it is very high melting, and it is formed from a metal which appears to have relatively low reactivity toward aluminum at the temperatures of interest.

We prepared TaC containers by packing in graphite powder tantalum crucibles 38 mm high, 18 mm in diameter, about .6 mm walls and heating the crucibles and graphite for from 3-8 hours at 2550-2800°K in the induction furnace used in all the heatings reported here and described by Brewer, Bromley, Gilles, and Lofgren[5].

The Ta crucibles and graphite powder were packed tightly inside a 1" diameter graphite crucible which served as a heating element and this crucible was in turn packed in porous carbon insulation inside a zircon crucible 6" high and 2 1/2" in diameter. From the weight gains of the crucibles, their compositions after heating could be calculated as $TaC_{.92}$ to $TaC_{.98}$. The crucibles, and effusion lids similarly produced, were only slightly expanded over their original size, they were brittle and tended to split in the plane of their surfaces,

probably where carbon diffusing from opposite faces met.

Aluminum mixed with TaC powder in one of these TaC crucibles was heated to 1720°K for about twenty minutes. The TaC showed, after heating, a lattice constant of a = 4.453 ± .002Å compared to the literature value of 4.454. Only a few Al lines could be observed in the x-ray picture; these gave a constant within experimental error of the literature value. Spectroscopic examination of aluminum melts in TaC crucibles show about .01 to .1% Ta by weight dissolves in aluminum in one to two hours heating at 1400 to 1500°K. Unfortunately, though liquid aluminum and TaC do not react, the aluminum wets TaC very strongly. The TaC crucibles we prepared were soaked through by aluminum after an average of two hours heating at 1400°K. That there was no chemical reaction when this occurred was visually demonstrated by treatment of the crucibles with dilute HCl. The aluminum dissolved with evolution of hydrogen leaving the crucible intact and restored to its original gold color.

Ten effusion runs were completed for aluminum. Four in TaC and six in BeO crucibles. The TaC crucibles acted as their own heating element. The BeO crucibles, which were about 26 mm high and 18 mm in diameter, with 2 to 3 mm walls, were placed inside a snug fitting Ta crucible which served as a heating element. A series of 0.0254 mm thick molybdenum spirals surrounded the crucible and a series of molybdenum disks were set on 1.6 mm pins below the crucible. This arrangement served to decrease heat losses outward and downward. Heat losses out the top were reduced by a series of tantalum disks having regularly increasing center holes so that an unobstructed cone was available for escape of aluminum vapor. The topmost of these disks served as a collimator to determine the geometry of the beam collected

on thin platinum plates placed 18 to 25 mm above the collimator. The collector plates were supported by a water-cooled copper holder. Aluminum was allowed to escape from the crucible into the cone formed by the collimator through a knife-edged hole in the crucible lid.

The crucibles and shieldings were supported inside a zircon crucible placed inside a water-cooled pyrex tube. Pressures throughout the runs were always lower than 1×10^{-4} mm and averaged about $4\text{-}5 \times 10^{-5}$ mm. Pressures were read on both a Philips gauge and an Ionization gauge whose readings agreed to twenty percent in this range, and whose calibrations were checked several times against a McLeod gauge.

Temperatures inside the crucibles were read with an optical pyrometer sighted on the effusion hole through a 4.8 mm hole in the collector plate. Two pyrometers, one of which had been calibrated by the Bureau of Standards, were checked against each other. Their relative readings did not change during the course of this research.

The effusion holes used were of two sizes--about 3.2 mm diameter and about 1.6 mm diameter. To be certain that the holes gave black body conditions, we heated four small molybdenum crucibles in the same tubes used for our effusion experiments. One crucible was open, the other three had lids with hole sizes of 3.2, 1.6, and 1.0 mm diameter. The open crucible gave lower temperatures than the others, but the temperatures of the other three crucibles, when corrected for differences in lid surface temperatures, gave identical temperature readings at 1400, 1700 and 1950°K. Johnston and Marshall[6] observed a temperature 20 degrees lower in a 1.8 mm diameter hole at 1600° than observed in .6 and 1.2 mm holes. However the holes in their experiment corresponded to tiny open crucibles, rather than to small fractions

of the lid area as in our experiment. Their results and ours, therefore, are not discordant.

The transmission of the windows was determined. The corrections amount to 10-12° at the temperatures employed for aluminum vapor pressure measurements. The windows were protected from the effusing aluminum by the collector except for the 4.76 mm hole through the collector. They were further protected by an iron plate when temperature readings were not being made, and they were frequently cleaned.

The apparent temperatures of the upper surfaces of the crucible lids were usually about twenty degrees below that of the holes. Since the lid surfaces were not black bodies, the actual temperature differences should be smaller. One BeO lid weighed after consecutive runs showed a uniform increase in weight due to the collection of aluminum droplets on the under surface. From the increase in weight of the lid we calculate that the temperature of the inside lid surface was only 4 degrees lower than that of the aluminum melt even though the observed temperature of the upper lid surface was 22° lower.

Temperature readings were made at two or three minute intervals till equilibrium was established after which the readings were made at five to ten minute intervals for the duration of the run. The fluctuations from the mean temperature at equilibrium were only rarely over five degrees and probably averaged two to three degrees. The temperature of each run was obtained, therefore, by averaging the temperatures read, at fairly regular intervals, after equilibrium was established and applying window and pyrometer corrections to this average value. The pyrometer correction ranged from 0 to 3°.

End corrections for vaporization during the rise in temperature to the equilibrium value and during cooling after the run were applied. These corrections varied from 2 to 12 percent. Uncertainty in the

effective time at the equilibrium temperature after end corrections were made is less than 2 percent for all runs.

The aluminum employed for our experiments was 99.99% pure. Because the Al soaked through the TaC crucibles, it was necessary to make some of our runs with aluminum which had not been previously heated to drive off volatile impurities, but a spectroscopic examination of such a collection showed only .1 to 1% Mg, about .01% Fe, and less than .01% of either Bi or Si. X-ray examination showed Al as the principal phase with a very weak second phase, probably an oxide, which could not be identified. Since the amount of Al collected was determined by analysis, volatilization of impurities should not influence our results.

The analysis was done colorimetrically using the 3700Å band of the aluminum--ferron complex, a method suggested by Davenport[7]. The analysis differed from that used by Davenport only in that we used a pH of 4.7 instead of 5.0.

The platinum collection plates, which were previously heated in nitric acid and then flamed, were weighed to .1 mg before and after each run. The aluminum was then dissolved from the plates with warm 1.2 N HCl. Several of the plates were reweighed after this treatment and found to have the same weight as the cleaned plate before the run. Samples were diluted to exactly 200 ml and kept at pH 1 - 2 till 5 ml portions could be taken for analyses. The weight of aluminum in these portions was determined from a calibration curve made from solutions of known aluminum strength. The known solutions were given identical treatment to that of the unknown. Readings were made in quartz one centimeter cells in a Beckman Spectrophotometer, using identically prepared aluminum-free solutions as blanks. Since the

3700° band is dependent on pH, the pH was checked for each buffered sample solution with a Beckman pH meter.

The stock solutions required for the analysis remained stable over the two month period in which they were in use. Fresh blanks were made up daily, however, and known solutions were run each time a new series of analysis was begun to check the validity of the calibration curve. The visible spectra of both known and unknown solutions were scanned in a Cary Spectrophotometer to demonstrate that the absorption observed was in each case due to the aluminum--ferron complex. The probable error in analysis was five percent.

Shields used in the heatings were degassed several hundred degrees above the temperatures at which the effusion runs were made. The tantalum shields above the crucible were degassed after every second or third effusion run at 2300 to 2500°K. Heatings were made immediately after most of the effusion runs with empty crucibles substituted for those containing aluminum. The collections then obtained were from 10 to 20% of the weight of the collection in the preceeding runs, the higher percentages appearing when smaller holes had been used in the effusion necessitating longer runs or higher temperatures to collect a given weight of aluminum for analysis. Two blanks were analyzed. One showed 9.9% of the aluminum collected in an equivalent time in the effusion run immediately preceeding, the other 6.7%. The vapor pressures calculated were accordingly all reduced by 8% to correct for collection of aluminum from random sources.

B. Data and Thermodynamic Calculations

Table I lists the essential data and outlines the calculation of vapor pressures from our data for aluminum. The percentage of the total beam leaving a point source which strikes a concentrically

Table I

Experimental Vapor Pressures for Aluminum.

Container	Hole Area (cm^2)	Effective $\sin^2\alpha$	T°K	Time in Minutes	Wt. Aluminum collected (mg)	Vapor Pressure	Corrected Vapor Pressure
TaC	.0842	.0620	1383	80	.560	3.62×10^{-6}	3.43×10^{-6}
TaC	.0842	.0634	1391	93	.909	3.14×10^{-6}	2.89×10^{-6}
TaC	.0194	.0632	1427	125	1.120	1.98×10^{-5}	1.82×10^{-5}
TaC	.0194	.0632	1460	45	.772	3.84×10^{-5}	3.63×10^{-5}
BeO	.0814	.0650	1410	67.5	.408	3.10×10^{-6}	2.85×10^{-6}
BeO	.0814	.0647	1412	106	.648	3.16×10^{-6}	2.91×10^{-6}
BeO	.0814	.0650	1419	136	.960	3.62×10^{-6}	3.33×10^{-6}
BeO	.0228	.0650	1420	168.5	.572	6.21×10^{-6}	5.71×10^{-6}
BeO	.0228	.0648	1451	127.5	.392	5.71×10^{-6}	5.25×10^{-6}
BeO	.0228	.0647	1468	83.5	.420	9.45×10^{-6}	8.69×10^{-6}

(atmospheres)

placed collimating hole is proportional to the square of the sine of the angle α whose tangent is the radius of the collimating hole divided by the perpendicular distance from the point source to the plane of the collimator. The third line of our table lists effective $\sin^2\alpha$, that is $\sin^2\alpha$ corrected for the loss of aluminum through the 4.8 mm hole in the center of the platinum collection plate. The weights listed in column 6 are those obtained from our colorimetric analysis. These weights collected, when divided by the effective $\sin^2\alpha$ give the total weight loss to be expected through a hole of the given area. The pressures listed in the next column can then be calculated from the effusion equation

$$p = \frac{z(MT)^{1/2}}{44.38\ a.t} \qquad (2)$$

where p is the pressure in atmospheres of the species of molecular weight M and z is the number of moles effusing out of the crucible in t seconds through a hole of area a cm^2. The hole should be knife edged if the equation is to be exact. The final column of corrected vapor pressures was obtained from the preceeding column by applying an eight percent correction for aluminum collected from random sources as noted above.

Table II outlines the calculation of ΔH^o_{298} from our experimental results and calorimetric and spectroscopic data from other sources. The $\frac{\Delta F^o - \Delta H^o_{298}}{T}$ functions were obtained from combining the low temperature calorimetric results of Giauque and Meads[8], recent tables of the high temperature heat content and entropy for solid and liquid aluminum compiled by Kelley[9], and the tables of heat contents and entropies for the gaseous elements compiled by Brewer[10]. The final column of this table lists the values obtained for ΔH^o_{298} of sublimation

Table II

Calculations of ΔH_{298} for Sublimation of Aluminum.

Container	Hole Area (cm^2)	T°K	Corrected Pressures	-Log P	$\frac{\Delta F^\circ}{T}$	$\frac{\Delta F^\circ - \Delta H^\circ_{298}}{T}$	$\frac{\Delta H^\circ_{298}}{T}$	ΔH°_{298}
TaC	.0842	1383	3.43×10^{-6}	5.465	25.00	-30.53	55.53	76.80
TaC	.0842	1391	2.89×10^{-6}	5.539	25.34	-30.52	55.86	77.70
TaC	.0194	1427	1.82 x 10-5	4.740	21.69	-30.44	52.13	74.39
TaC	.0194	1460	3.63×10^{-5}	4.452	20.37	-30.36	50.73	74.07
BeO	.0814	1410	2.85×10^{-6}	5.545	25.37	-30.48	55.85	78.75
BeO	.0814	1412	2.91×10^{-6}	5.536	25.33	-30.47	55.80	78.79
BeO	.0814	1419	3.33×10^{-6}	5.478	25.06	-30.46	55.52	78.78
BeO	.0228	1420	5.71×10^{-6}	5.243	23.99	-30.45	54.44	77.30
BeO	.0228	1451	5.25×10^{-6}	5.280	24.16	-30.38	54.54	79.13
BeO	.0228	1468	8.69×10^{-6}	5.061	23.15	-30.34	53.49	78.52
							Average	77.42 ± 1.41 kcals.

(in K. cal.) by combining these data with our experimental vapor pressure determinations. All of our runs are included in the table.

The average value for ΔH^{o}_{298} for the effusions from TaC crucibles is 75.59; from BeO, 78.36. The ΔH^{o}_{298} values obtained from BeO crucibles appear to be independent of hole size; the values from TaC appear to depend on the hole size. The absolute magnitudes of our temperature determinations are probably good to ± 8 degrees, but the relative values of the temperatures determined in different runs should be consistent to ± 4 degrees, which is equivalent to .14 K. cal. deviation in the heats of sublimation. A ten percent error in the weight of sample collected, area of effusion hole used, or time of run would produce a .3 K. cal. error in the heat of sublimation. We would expect agreement of our ΔH^{o}_{298} values to within .8 K. cal. It seems possible that lower values for the heat of sublimation and higher vapor pressures were obtained from the TaC crucibles because of aluminum soaking through fine cracks in the TaC lids and vaporizing from the lid surface into the cone of the collimator. The geometry of our apparatus is such that only aluminum from a 6.36 mm diameter circle, which includes the effusion hole itself, could strike the collector plate. This source of error could not be compensated for by the blanks we ran since it was, of course, necessary to replace the effusion vessel and lid by a clean vessel and lid for the blank runs to eliminate normal effusion from the effusion hole. A small amount of aluminum could be seen to have soaked through the lids. Since the larger effusion holes left less lid surface in this critical area in the effusion cone, lower vapor pressures would be found with the larger holes. The validity of this interpretation is uncertain, however, so it seems best to give equal weight to all determinations.

Since agreement of the ΔH^{o}_{298} values was obtained when the area of the holes in BeO crucibles varied by approximately a factor of four, we can conclude that the accommodation coefficient for aluminum within the crucible is at least as large as the ratio of hole size to internal surface area of the crucibles, about 2×10^{-3}, and our results are independent of the accommodation coefficient. From comparing the weight loss of a crucible to the weight of aluminum collected on a platinum plate above the crucible we calculate an accommodation coefficient for aluminum on the plate of 1.29, within experimental error of unity.

Averaging our ten determinations and finding the mean deviation we obtain 77.42 ± 1.41 K. cal. for the heat of sublimation of aluminum at 298.16°K. Determinations by Baur and Brunner[11] using spinell containers, give a value of 74.97 K. cal. Farkas'[12] single determination at 1476°K. by effusion through a 4.2 mm hole from porcelain gives 77.83. It is difficult to estimate the probable error for either investigation.

2. Aluminum Oxide.

A. Experimental

The vapor pressure for aluminum oxide was determined by the same experimental methods as those used for aluminum. Considerably higher temperatures had to be employed, of course, in order to collect analyzable amounts of aluminum from the oxide effusions. The temperatures used ranged from 2309 to 2605°K.

A survey of available thermodynamic data indicated that the best containers for liquid Al_2O_3 would probably be molybdenum, tungsten, and rhenium, with molybdenum the poorest of the three because of its higher vapor pressure. Materials actually tested as containers for aluminum oxide were tantalum, molybdenum, tungsten, zirconium carbide, tantalum carbide, and $TaSi_x$.

As predicted by available thermodynamic data, the carbides reacted markedly with Al_2O_3 at temperatures several hundred degrees below the Al_2O_3 melting point. Alumina reacted strongly with ZrC at 2150°K. After five minutes at this temperature, X-ray analysis revealed ZrO_2 in the crucible with lesser amounts of unreacted ZrC and Al_2O_3. Completely plugging the 1/4" diameter hole through a radiation shield above the crucible was a sublimate consisting of metallic droplets and grey powder. X-ray analysis of this sublimate revealed Al, Al_2O_3 and a weaker third phase not identified. The reaction probably was $3Al_2O_3 + 2ZrC = 3Al_2O(g) + 2CO(g) + 2ZrO_2$, with the Al_2O disproportionating upon condensation. Tantalum carbide reacted similarly. The tantalum carbide is first reduced to Ta_2C and then to tantalum. When all the carbon has volatilized as CO, the tantalum metal begins to react with the Al_2O_3 to produce an unknown solid phase, probably a lower tantalum oxide or a mixed tantalum and aluminum oxide.

Al_2O_3 heated in $TaSi_x$ gave the same unknown solid phase found when tantalum metal was heated with Al_2O_3.

Al_2O_3 heated in molybdenum or tungsten for several hours from 100 to 300 degrees above its melting point shows less than .1% by weight of either metal. Accordingly these metals were used for all our effusion runs. Our earlier work was done in molybdenum because molybdenum crucibles and lids are easier to fabricate than tungsten. Spectroscopic results indicated, however, that the samples collected from effusion runs in molybdenum contained weights of molybdenum comparable to that of Al_2O_3. It would have been experimentally difficult to establish whether the alumina collected was effused independent of the molybdenum or as the result of reaction which produced volatile suboxides of both aluminum and molybdenum. Accordingly, we changed to tungsten for our later studies. Effusion from tungsten appears to be definitely established as independent of reaction with the container, so that a check of our results with a different container material is unnecessary.

As with the aluminum effusion studies, pressures were maintained lower than 10^{-4} mm throughout each effusion run, averaging about 5×10^{-5} mm. Effusion lids were made by stretching over a tungsten plate a .025 mm thick tungsten sheet through which a 1.6 to 3.2 mm diameter hole had been drilled. A concentric 6.4 mm hole was drilled through the plate. The region of the .025 mm sheet immediately around the hole which was not backed by the tungsten plate gave apparent temperature readings as much as 200 degrees below the temperature of the inside of the crucible. A noticeable amount of alumina would condense on the inside surface of the sheet in this region during the course of the higher temperature runs. The portion of the sheet

backed by the tungsten plate remained perfectly clean. The low temperature area was too small to influence our measured vapor pressures.

Window corrections amounted to 25 to 30 degrees. The windows were protected as in the aluminum runs. The effective temperature of each run was obtained as before. Uncertainty in measuring the time of the runs was less than two percent. Uncertainty in temperature measurements is about 10° on an absolute basis, but uncertainty in relative temperatures is probably only 5°.

Tungsten shielding was used at the sides and below the crucible to reduce heat loss, and tantalum shielding and collimation was again used above the crucible. To reduce contamination of the collection plates by substances vaporizing off the tantalum shields, these shields were degassed at 2500 to 2600°K and two or three runs were made at progressively lowered temperatures with a blank run after each effusion run. The shields were then degassed and a similar series repeated. The blanks averaged ten to twelve percent of the samples collected. They were not analyzed and no corrections were applied for them since weight losses from the empty tungsten crucibles as well as from the shields appear to account for most of the blanks.

Analysis of the collection plates for aluminum was complicated by the insolubility of the aluminum oxide collected and by the presence of unknown amounts of tungsten on the plates. Spectroscopic analysis by direct sparking of the plates showed 1-10% by weight of both tungsten and aluminum. This meant that on a molar basis the ratio of aluminum to tungsten might be anything between .7 and 100.

The most satisfactory way to dissolve the samples from the platinum was to fuse the collector plates in potassium pyrosulfate

for from thirty to sixty minutes in platinum dishes. The fusion product was then dissolved in concentrated HCl and evaporated to dryness. Water was then added and the dishes heated to redissolve the samples. Most of any tungsten present precipitated as WO_3 in the resulting hot dilute acid solution. The samples were next diluted to 200 ml and 5 ml samples were submitted to colorimetric analysis for aluminum.

Samples with known weights of aluminum and tungsten were run through this scheme of analysis to obtain a new calibration curve. It appeared that all but about .5 mg of tungsten was precipitated during digestion with dilute acid. A known aluminum solution containing excess tungsten gave a point falling on the calibration curve prepared using lesser amounts of tungsten. Dissolved platinum either did not interfere with the analysis or was sufficiently constant that its effect cancelled out. Each known and unknown solution was scanned across its visible spectrum by a Cary Recording Spectrophotometer. The spectra were identical in form. Readings of I_0/I were again made with a Beckman Spectrophotometer. The aluminum found averaged 45% by weight of the sample collected. Therefore the maximum possible molal ratio of tungsten collected to aluminum collected was 1/5. The true ratio must be even smaller since oxygen must represent a good portion of the remaining weight of collection. Unfortunately, sublimates often give very poor X-ray pictures and no phases were identified from the collector plates. The collections were definitely not Al or W, and they did not appear to contain α, β, or γ-Al_2O_3, WO_2, or WO_3.

Most of the analyses were made using half of a collector plate because samples were needed for other tests and because whole plates

were more difficult to handle in the fusions. Analyses made on different halves of the same plate differed by about twenty-five percent. The analysis was considerably less accurate than that for the aluminum effusions because of the foreign ions present and the necessity of fusing the samples.

B. Data and Thermodynamic Calculations.

The data and calculations employed in determining vapor pressures for Al_2O_3 are summarized in Table III. The vapor pressures listed in the final column of the table are the vapor pressures for AlO calculated on the assumption that Al_2O_3 liquid vaporizes by the reaction $Al_2O_3(l) = 2AlO(g) + O(g)$. The reasons for this assumption will be discussed later. That the accommodation coefficient inside our crucibles was at least as large as the ratio of our hole areas to interior area of the crucible is demonstrated by the agreement in position of the lines formed by the plotting vapor pressures determined with holes varied by a factor of four in area. That the accommodation coefficient on the collector plate was essentially unity, despite the fact that this plate was itself heated to at least 800°K is demonstrated by the fact that the total weight of sample collected on the plate was about 1.1 times the weight expected from weight loss by the crucible.

Treatment of the vapor pressure data by use of a sigma plot and by use of $(\Delta F-\Delta H_{298})/T$ tables gives heats agreeing within 10 kcals. or 2%, which is well within experimental uncertainty. Table IV gives the results of the ΔH_{298} calculations using $(\Delta F-\Delta H_{298})/T$ values. The necessary entropy and high temperature heat content data were obtained from Kelley[9] for Al_2O_3, from the National Bureau of Standards Tables[13] for O gas and from Ward and Hussey[14] for AlO gas. In

Table III

Experimental Vapor Pressures for Al_2O_3

Hole Area (cm^2)	Effective $\sin^2$	T°K	Time in Minutes	Wt. Aluminum Collected (mg)	Vapor Pressure (as AlO) (atm.)
.0791	.0631	2309	137.0	1.33	8.70×10^{-6}
.0791	.0575	2325	154.0	1.64	1.03×10^{-5}
.0791	.0576	2370	129.5	2.21	1.66×10^{-5}
.0791	.0631	2393	118.0	2.22	1.68×10^{-5}
.0791	.0567	2399	63.0	1.35	2.15×10^{-5}
.0791	.0631	2459	71.0	2.96	3.78×10^{-5}
.0791	.0575	2478	50.5	2.96	5.81×10^{-5}
.0198	.0564	2487	84.5	1.88	9.10×10^{-5}
.0198	.0564	2545	62.5	3.05	2.00×10^{-4}
.0198	.0631	2565	63.5	1.60	1.29×10^{-4}
.0198	.0631	2605	63.0	3.23	1.91×10^{-4}

$$P_{AlO} = \frac{\left(\frac{Wt.\ Al}{26.97}\right)(42.97\ T)^{1/2}}{44.38\ a_{cm^2} \cdot t_{sec.}}$$ See equation 2

$$P_O = \frac{\sqrt{16}}{2\sqrt{43}} \cdot P_{AlO} \text{ and } K = (P_{AlO})^2(P_O) = 0.305\ P_{AlO}^3$$

Table IV

Calculations of ΔH_{298} for $Al_2O_3(s, l) = 2AlO(g) + O(g)$

T°K	$\frac{\Delta F}{T}$	$\frac{\Delta F - \Delta H_{298}}{T}$	$\frac{\Delta H_{298}}{T}$	ΔH_{298}
2309	71.81	-124.9	196.7	454
2325	70.81	-124.7	195.5	455
2370	67.95	-124.3	192.2	456
2393	67.90	-124.1	192.0	459
2399	66.41	-124.1	190.5	457
2459	63.07	-123.7	186.8	459
2478	60.50	-123.5	184.0	456
2487	57.82	-123.4	181.2	451
2545	53.11	-123.0	176.1	448
2565	55.74	-122.9	178.6	458
2605	53.38	-122.8	176.2	459
			Ave.	456 kcals.

$Al_2O_3(s) = 2AlO(g) + O(g)$, $\Delta H_{298} = 456{,}000$ calories

$Al_2O_3(l) = 2AlO(g) + O(g)$, $\Delta F_T = 443{,}000 + 27.6\ T \log T - 212\ T$ calories

view of the difficult experimental conditions at these high temperatures, the heat obtained from the ΔF values together with ΔS or $(\Delta F^\circ - \Delta H_{298})/T$ values is considered more reliable than the value obtained from a sigma plot.

Thus we obtain for $Al_2O_3(l) = 2AlO(g) + O(g)$

$\Delta F^\circ = 443{,}000 + 12T \ln T - 212T$

The uncertainty of ΔF is about ± 4 kilocalories. The ΔH_{298} values in Table IV show an average deviation from the mean of ± 3 kilocalories even though they show some scatter as well as trend. However the scatter and trend are within experimental error.

The only recent experimental determinations of the vapor pressures and heat of vaporization for Al_2O_3 available with which our results can be compared are those of Ruff and Konschak[15]. These authors, however, made their determinations from tantalum crucibles, which we have found react with aluminum strongly to give volatile reaction products as discussed earlier in this section. Their work cannot be given any weight in deciding the volatility of pure aluminum oxide. The vapor pressures calculated from the effusion equation that we have employed are dependent on the molecular weights that we use. Since our analysis shows only the number of moles of aluminum present regardless of the phase state of that aluminum, the weight we substitute into our equation also depends on the gaseous species we think the aluminum effused as. The uncertainty of the equation due to these two causes partially cancel, so that our calculated vapor pressures vary as the square-root of the molecular weight we employ. This uncertainty is only about a factor of two in vapor pressure for any reasonable species we could choose.

The Al_2O_3 vapor pressure data will be discussed further in the next section where the aluminum oxide species are discussed.

3. Aluminum and Aluminum Oxide.

To properly evaluate the vapor pressure determinations of Al_2O_3 which were described in the last section, it is necessary to know the stable gaseous species of the aluminum-oxygen system. The possible reactions taking place during the vaporization of Al_2O_3 are the following:

$$Al_2O_3(l) = Al_2O_3(g) \quad (1)$$

$$Al_2O_3(l) = 2Al(g) + 3O(g) \quad (2)$$

$$Al_2O_3(l) = 2AlO(g) + O(g) \quad (3)$$

$$Al_2O_3(l) = Al_2O_2(g) + O(g) \quad (4)$$

$$Al_2O_3(l) = Al_2O(g) + 2O(g) \quad (5)$$

Because of the very low vapor pressure of Al_2O_3 even at very high temperatures, the conventional methods of determining species such as vapor density determinations, electron diffraction measurements, etc. are not suitable. One possible method would be the determination of the volatility of Al_2O_3 in gaseous streams of varying pressures of aluminum metal gas. If the Al_2O_3 vaporizes according to equation (1), the volatility of Al_2O_3 would be unaffected by the presence of Al. If the vaporization proceeds according to equation (2), the presence of Al would greatly diminish the volatility of Al_2O_3. If suboxides are important as indicated by equations (3) to (5), the increased reducing conditions in the presence of Al metal would increase the volatility of Al_2O_3. If increased volatility is observed indicating suboxides, the possible suboxides could be distinguished from the variation of the volatility of Al_2O_3 upon varying the Al partial pressure. This method was successfully used by Brewer and Lofgren[16] to determine the gaseous species of the

copper-chlorine system and would appear to be promising in this case. Thus if the aluminum gas were passed slowly enough over the Al_2O_3 so as to obtain equilibrium with respect to possible reactions such as

$$Al(g) + Al_2O_3(s) = 3AlO(g) \quad (6)$$

$$4Al(g) + Al_2O_3(s) = 3Al_2O(g) \quad (7)$$

$$2Al(g) + 2Al_2O_3(s) = 3Al_2O_2(g) \quad (8)$$

then the weight of Al_2O_3 required to saturate a given volume of gas would vary with $P_{Al}^{1/3}$ if reaction (6) predominates, with $P_{Al}^{4/3}$ if reaction (7) predominates, and with $P_{Al}^{2/3}$ if reaction (8) predominates.

Unfortunately a major difficulty to carrying out the proposed experiment is the lack of a suitable container for holding the aluminum vapor and Al_2O_3. No satisfactory materials could be found which would allow the experiment to be carried out in a straightforward manner as was done by Brewer and Lofgren[16] for the copper-chloride system. However the following substitute experiment was devised which it is believed gives one the desired data.

Alumina crucibles of exceptionally high purity were available. Spectroscopic analysis of these crucibles showed less than .1% Fe, Si, and Ca, and less than .01% Mg by weight. Aluminum pieces varying in weight from .02 to .7 grams were buried in Al_2O_3 powder after the powder and crucibles had been previously degassed. The crucible then was heated at temperatures from 1466°K to 1853°K. After heating at a given temperature for a period whose time was recorded, the crucible and contents were allowed to cool and the change in weight noted. The crucible and contents were then reheated to approximately the same temperature and the time of heating and weight change again noted. This process was repeated until the weight change produced by a

heating dropped down to the background level for weight change of crucible and oxide powder in the absence of aluminum metal. This background level was about ±1 mg. per hour over the temperature range investigated.

Several series of heatings in the region of 1600°K showed weight losses whose ratio to weight of aluminum present in the crucible was approximately 1.30 to 1.35 at the time that the rate of weight loss dropped to the low background rate observed in the absence of metal. Samples of the sublimate produced by these heatings were collected and submitted to X-ray and spectroscopic analysis. The spectroscopic analyses showed less than .1% by weight of Be and Fe, less than .01% by weight of Co, Cr, Mg, Mn, Ni, Si, Ta, and W, and about 1% by weight of Mo (the shielding material). X-ray analysis showed aluminum metal and a second weaker phase which could not be analyzed.

Since the vapor pressure of Al_2O_3 is far too low at the temperatures employed in these experiments to explain the weight losses observed in excess of the metal present, since the ratios of weight loss to aluminum present in the crucible was independent of the weight of metal previously effused from the crucible, and since no major impurity could be detected in the sublimates produced, we conclude that the extra volatility observed must be due to reaction of the aluminum metal with the oxide to produce a volatile gaseous sub-oxide of aluminum.

There is other evidence for formation of gaseous lower valence state aluminum compounds. Several unipositive aluminum compounds have previously been reported. AlF was reported in 1943[17], later one article reported Al_2S and Al_2Se[18] and another article[19] reported AlCl, AlBr, and AlI. All these compounds appear to be stable only in

the vapor phase. The production of AlO was claimed in patent literature in 1943 by E. Zintl, W. Krings, and W. Brauning[20]. No details of their work were available to us.

The results obtained upon heating aluminum with aluminum oxide clearly indicate the existence of an aluminum oxide gaseous species of oxidation number less than three. Now we must determine whether this species is of any importance when Al_2O_3 is vaporized alone. Equations (1) to (5) given above show the possible vaporization reactions for Al_2O_3. We can definitely exclude reaction (2) by using the heat of formation of Al_2O_3 determined by Snyder and Selz[21] together with the entropy data and heat content data given by Kelley[9], and the heat of sublimation of aluminum given here to calculate the equilibrium constant for reaction (2). The results as indicated in Fig. 1 are much lower than the observed vapor pressure of Al_2O_3 and the experimental uncertainties in the heat of formation of Al_2O_3 and the vapor pressure data are not large enough to allow possible consideration of decomposition to the atoms as the process for vaporization of Al_2O_3.

We can also exclude reaction (1) which indicates that Al_2O_3 vaporizes undecomposed. If one makes a sigma plot of the Al_2O_2 vapor pressure data on the assumption of $Al_2O_3(g)$ as the species, one obtains an abnormally high entropy of vaporization of around 67 e.u. compared to the expected value of 25 to 30 e.u. Thus $Al_2O_3(g)$ can be excluded as a possible species and Al_2O_3 must definitely vaporize by decomposition to an oxide of lower oxidation number. It is not possible from entropy considerations alone to distinguish among reactions (3) to (5) since the entropies per mole of gaseous species vaporized are too close together to be distinguished in view of the uncertainties of

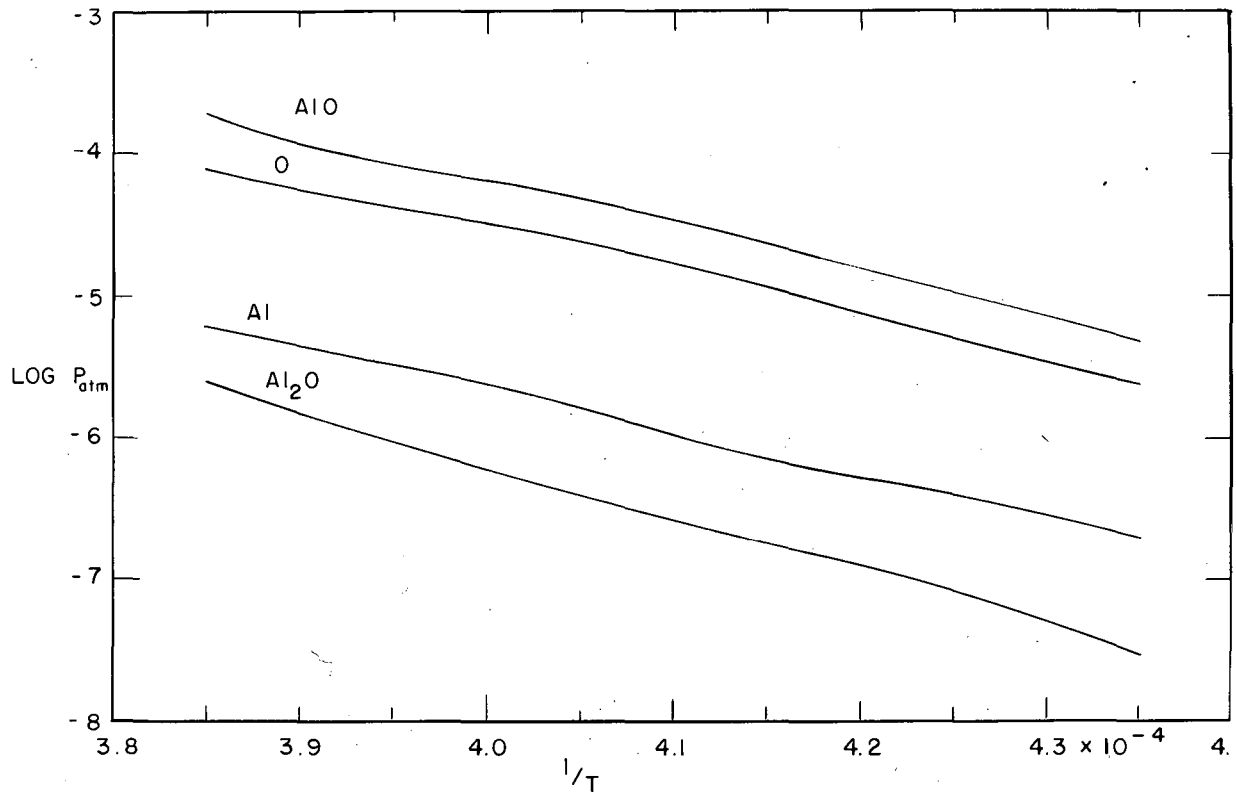

FIG. 1A

GASEOUS SPECIES OVER LIQUID Al_2O_3

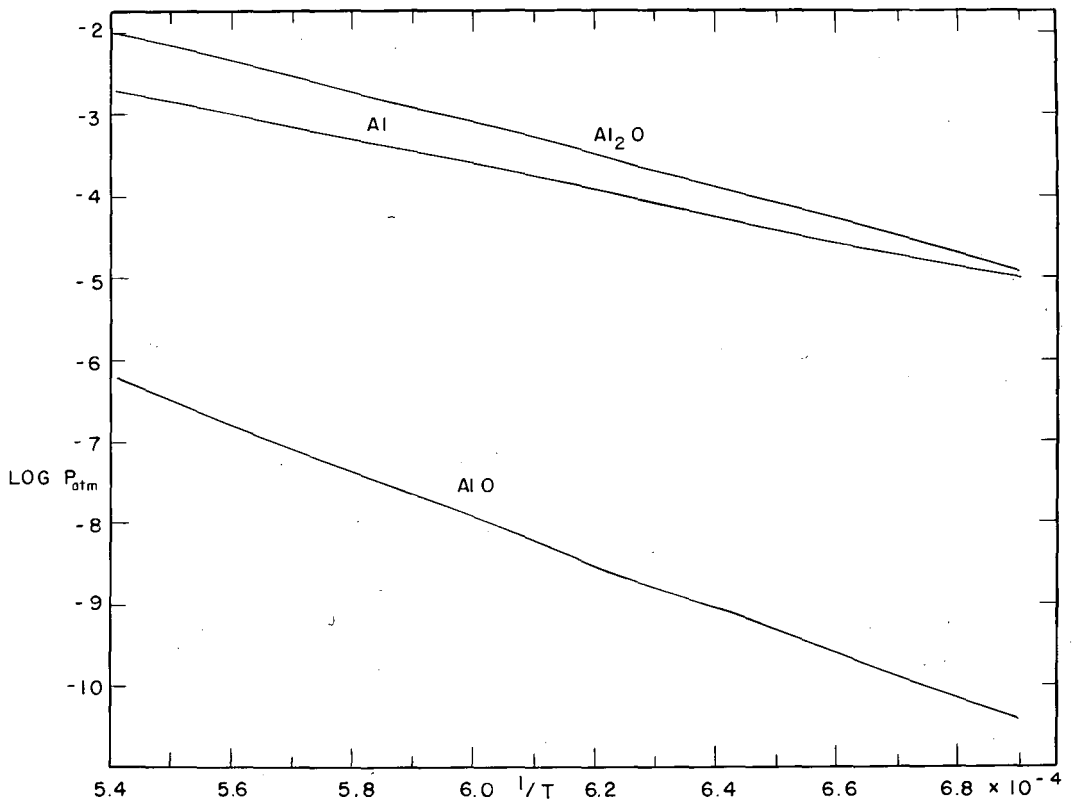

FIG. 1B

GASEOUS SPECIES OVER LIQUID Al AND SOLID Al_2O_3 MIXTURE

estimating the entropies of Al_2O and Al_2O_2, and the experimental uncertainty of the vaporization data, although we will be able to draw conclusions from the entropy effect in the Al - Al_2O_3 system as will be noted below.

However, we must check to determine if the same oxide species is of importance when Al_2O_3 vaporizes as when Al and Al_2O_3 are heated together. To determine this, we must use our data for the volatility of Al_2O_3 in the presence of Al gas to fix the thermodynamic properties of the sub-oxide species involved and then we must calculate its contribution under the conditions of vaporizing Al_2O_3 by itself.

This can be done by calculating equilibrium constants from the experimental results for the Al - Al_2O_3 heatings on the assumption of each of the possible gaseous species. Thus we can calculate the thermodynamic properties of Al_2O, AlO, and then Al_2O_2 assuming in each case a different main species. From these results, one can calculate constants for reactions (3) to (5) and compare these with the observed volatility of Al_2O_3. As will be done in detail below, it is quite easy to show that the main sub-oxide species of the Al - Al_2O_3 experiments can not be the main species when Al_2O_3 is heated alone. The change in stability upon changing the Al partial pressure would be such as to prevent explanation of both sets of data on the assumption of the same species.

The next step is to attempt to fix the main species in each case. As pointed out above, it would be possible to fix the species in the Al - Al_2O_3 experiments if it were possible to determine the dependence of Al_2O_3 volatility upon the Al partial pressure. Because of refractory limitations, it would not be possible to determine this in a straight-forward manner, but it is believed that sufficient data

have been obtained by the method used to obtain an idea of the pressure dependence.

It was observed that when aluminum metal was covered with aluminum oxide powder and heated to 1300 - 1600°K., the metal did not wet the oxide powder and soak up into the pores. Instead, the metal all remained as a liquid below the oxide covering and the vaporizing aluminum passed up through the oxide as a gas. By varying the thickness and particle size of the oxide material, one would expect to greatly reduce the aluminum partial pressure at the point of emergence from the oxide covering or the last point of contact between the vapor and the oxide. It was indeed found that the rate of escape of aluminum metal vapor could be decreased a hundred fold by several centimeters of powder. It was found that BeO and Al_2O_3 powders produced a similar reduction in the rate of escape of Al gas. From the observed rate of escape of aluminum, one could roughly calculate the aluminum partial pressure at the top of the oxide coating. Although the aluminum pressures were varied over a wide range, the ratio of oxide vaporized to aluminum vaporized at a particular temperature was relatively insensitive to the aluminum partial pressure. This was taken as evidence for the exclusion of AlO(g) as a possible species under these conditions, since one would have expected a large pressure dependence. In addition, the entropy obtained for reaction (6) by treating the data under the assumption of AlO(g) differed beyond experimental error from that expected for AlO(g). Some typical data are given in Table V where the ratio of weight of oxide vaporized to weight of aluminum vaporized are given along with the aluminum partial pressures calculated from the observed rates of escape of aluminum vapor and the assumption of unit accommodation coefficient for the vapor. It was assumed that the vapor was issuing from holes in the

Table V

Data for the Reaction $4\ Al_{(g)} + Al_2O_{3(s)} = 3\ Al_2O$.

T°K	Total wt. loss / Wt. Al present as metal	Time T(min.)	Wt. lost in Time T (g)	Wt. Al(grams) lost as $Al_{(g)}$ in time T	P_{Al_2O}/P_{Al}	P_{Al} at surface (Atm)
1466	1.18	187	.0304	.0208	.285	$2.0 \cdot 10^{-7}$
1491	1.20	196	.0236	.0154	.325	$1.39 \cdot 10^{-7}$
1501		364	.0329	.0216		$1.06 \cdot 10^{-7}$
1557	1.25	295	.0777	.0457	.436	$2.8 \cdot 10^{-7}$
1609	1.35	242	.2293	.107	.713	$8.1 \cdot 10^{-7}$
1614	1.30	30	.0377	.0198	.563	$1.22 \cdot 10^{-6}$
1614		30	.0441	.0232		$1.42 \cdot 10^{-6}$
1614		30	.0747	.0393		$2.4 \cdot 10^{-6}$
1614		30	.0884	.0464		$2.9 \cdot 10^{-6}$
1619	1.32	30	.0494	.0248	.622	$1.53 \cdot 10^{-6}$
1624		60	.1185	.0598		$1.84 \cdot 10^{-6}$
1725	1.42	(60)	.3948	.154	.970	$4.9 \cdot 10^{-6}$
1853	1.65	(<20)	.8851	.168	2.67	$>1.66 \cdot 10^{-5}$

$$\frac{P_{Al_2O}}{P_{Al}} = \frac{3(\text{Moles } Al_2O_3 \text{ vaporized})}{\left[\text{Moles Al} - 4(\text{moles } Al_2O_3)\right]} \cdot \sqrt{\frac{70}{27}}$$

top surface of the oxide covering which comprised one half of the area of the total surface. It is obvious that this is a very approximate calculation of the aluminum partial pressure at the surface, but fortunately in view of the low dependence of the equilibrium constant upon the aluminum metal partial pressure, it it not necessary to know the aluminum metal partial pressure with great accuracy. In some cases where the aluminum had completely vaporized during the experiment we have only a lower limit to the P_{Al} and only an upper limit to the equilibrium constant.

Treatment of the data on the assumption of either reactions (7) or (8) by a sigma plot treatment gives results which are consistent with estimated entropies in either case. There does not appear to be any way of distinguishing between Al_2O_2 or Al_2O from the data since they are not accurate enough to detect the difference in pressure dependence required or the difference in entropy required. It should be recognized that the treatment of the data is rather complicated, especially if a very accurate treatment is required. For, depending upon the species, one will get more or less separation of Al and the gaseous oxide species in diffusing through the holes in the oxide coating and escaping from the surface. Also the calculation of the actual Al and oxide partial pressures depends upon the species chosen. Thus if one assumes $Al_2O(g)$ as the species, much more of the Al must have been used up by reaction with Al_2O_3 as indicated by reaction (7) than would be the case if one had assumed AlO or Al_2O_2. Thus distinguishing between reactions (7) and (8) is not as clear cut in this case as distinguishing simply between a 3/4 and a 3/2 powder dependence upon the Al partial pressure. The experimental and theoretical uncertainties are too large to allow one to make a

choice. However, as will be discussed below, other considerations tend to indicate that the vaporizing oxide species is most likely Al_2O when Al and Al_2O_3 are heated together.

If one uses the data obtained upon heating Al and Al_2O_3 together to determine the thermodynamic properties of Al_2O or Al_2O_2, depending upon which one chooses, one can then calculate the importance of these species when one heats Al_2O_3 alone. If one does this, one finds that these species can not account for the observed volatility of Al_2O_3 as noted above. This is shown in Fig. 1 where the calculated partial pressure of Al_2O over Al_2O_3 is shown based on the thermodynamic data obtained for Al_2O from the mixture experiments at lower temperatures. Neither Al_2O nor Al_2O_2 can be used to explain the volatility results of both experiments. If we had only two possible gaseous species, Al_2O and AlO, we would now have fixed the species in both types of volatility experiments; since we have shown that Al_2O will explain the Al - Al_2O_3 experiments while AlO will not and we have demonstrated that the main species must be different in the two experiments. However, with Al_2O_2 as a possible species, we would have to use the following combinations to explain the data: Al_2O and AlO, Al_2O_2 and AlO, or Al_2O and Al_2O_2. However, if Al_2O_2 is assumed to be the main species in either case, one must have to assume extraordinarily strong bonding in Al_2O_2 because its complexity, and thus low entropy per atom compared to simpler molecules, tends to make it unstable at high temperatures and low pressures. Thus if Al_2O_2 is important, its heat of dissociation to AlO would have to be as high as 140 kilocals which seems unreasonable for any normal bonding. The first combination, Al_2O and AlO, is also reasonable since one would expect a lower oxidation state under the highly reducing conditions

existing in the presence of Al metal than under the more oxidizing conditions existing when one has pure Al_2O_3. However, until we know more about the type of bonding to be expected, we can not conclusively exclude Al_2O_2 as a species. Taking for the time being the reasonable assumption that Al_2O_2 is not of importance, we can now calculate our results on the basis that Al_2O gas is the main aluminum oxide gaseous species when Al and Al_2O_3 are heated together and that AlO gas is the main aluminum oxide gaseous species when Al_2O_3 is heated alone.

In Table VI, the data of Table V have been used to calculate the equilibrium constant for the reaction $4Al(g) + Al_2O_3(s) = 3Al_2O(g)$ and Σ values have been calculated using $\Delta C_p = -12$ cal/deg.

The data are not too accurate, and examination of the Σ values shows that within experimental error there is no appreciable variation of Σ with temperature, which means that ΔH_0^0 is very small. In the following equation ΔH_0^0 has been taken as zero.

$$4Al(g) + Al_2O_3(s) = 3Al_2O(g) \qquad (7)$$

$$\Delta F^\circ = 27.5T \log T - 112T \text{ from data given in Table VI.}$$

Within experimental error there is no change in Σ with temperature and ΔH_0^0 is essentially zero. The uncertainty in ΔF is ± 5 kilocalories. The uncertainty in ΔH or ΔS obtained from this equation is ± 20 kilocalories or ± 12 e.u.

$$2Al(g) + O(g) = Al_2O(g) \qquad (9)$$

$$\Delta H_{298} = -248$$

The uncertainty in ΔF is ± 2 kilocals. and in ΔH ± 7 kilocals.

$$Al_2O_3(l) = 2AlO(g) + O(g) \qquad (3)$$

$$\Delta F^\circ = 443{,}000 + 12\ T \ln T - 212T$$

Table VI

Calculation of $\Sigma = \frac{\Delta H_o}{T} + I$ for $Al_2O_3(s) + 4Al(g) = 3Al_2O(g)$

T	log T	27.6 log T	P_{Al_2O}/P_{Al}	$(P_{Al_2O}/P_{Al})^3$	P_{Al}	K	log K	4.575 log K	$-\Sigma$
1466	3.1661	87.38	.285	.0231	2.0×10^{-7}	1.15×10^5	5.061	23.15	110.5
1491	3.1735	87.59	.325	.0343	1.39×10^{-7}	2.47×10^5	5.393	24.67	112.3
1501	3.1764	87.67	.325	.0343	1.06×10^{-7}	3.24×10^5	5.511	25.21	112.9
1557	3.1923	88.11	.436	.0829	2.8×10^{-7}	2.96×10^5	5.471	25.02	113.1
1609	3.2066	88.50	.713	.362	8.1×10^{-7}	4.47×10^5	5.650	25.85	114.3
1614	3.2079	88.54	.563	.178	1.22×10^{-6}	1.46×10^5	5.164	23.63	112.2
1614	3.2079	88.54	.563	.178	1.42×10^{-6}	1.25×10^5	5.097	23.32	111.9
1614	3.2079	88.54	.563	.178	2.4×10^{-6}	7.43×10^4	4.871	22.28	110.8
1614	3.2079	88.54	.563	.178	2.9×10^{-6}	6.14×10^4	4.788	21.91	110.5
1619	3.2093	88.58	.622	.241	1.53×10^{-6}	1.57×10^5	5.196	23.77	112.3
1624	3.2106	88.61	.622	.241	1.84×10^{-6}	1.31×10^5	5.117	23.41	112.0
1725	3.2368	89.34	.970	.913	(4.9×10^{-6})	(1.86×10^5)	5.270	24.11	113.3
1853	3.2679	90.19	2.67	19.03	$(>1.66 \times 10^{-5})$	$(<1.14 \times 10^6)$	<6.057	<27.71	<117.9

Av. 112 cals.
per degree

This equation warrants a little more discussion. It is based on the data given in Table IV where ΔH_{298} = 456 kcals. was calculated for the reaction $Al_2O_3(s) = 2AlO(g) + O(g)$. The heat of fusion of Al_2O_3 is taken as 26 kcals. as given by Kelley[24], the heat capacity of $Al_2O_3(l)$ is taken as 35 cal./deg./mole, and the heat content data given by Kelley[9] are used for $Al_2O_3(s)$. The entropy calculated for the $^2\Sigma$ state of AlO by Ward and Hussey[14] was used to calculate the $(F-H_{298})/T$ values. However, there is a strong likelihood that the $^2\Sigma$ state is not the ground state and that a quartet state is the true ground state and is not observed because of the selection rules. Additional evidence that this is so is obtained by comparing the spectroscopic data for the $^2\Sigma$ state of AlO with the thermodynamic data given here. One obtains from equation (3)

$$Al(g) + O(g) = AlO(g) \qquad (10)$$

$$\Delta F^\circ = -138 + 23.3\ T$$

From spectroscopic data, the best evidence indicates that ΔH for reaction (10) is ΔH = 21 kilocalories assuming a $^2\Sigma$ ground state instead of the 127 kilocalories observed here. As pointed out by Gaydon[22], the great chemical stability of $Al_2O_3(s)$ and the readiness with which AlO bands are obtained suggested a fairly strong binding between Al and O which appears to contradict the 21 kilocalories value. There is the possibility that the observed predissociation which fixes the heat at 21 kilocalories is in error. However, even so, a linear Birge-Sponer extrapolation of the vibrational levels of the $^2\Sigma$ state of AlO would not give a heat greater than 87 kilocalories. Thus, it appears very likely that the $^2\Sigma$ state is not the ground state. If this is the case, the entropies and heat contents used for AlO are

in error due to the differing vibrational spacing and moments of inertia to be expected for the two states as well as different statistical weights for the electronic level. However, the difference to be expected is less than the experimental uncertainty of our data. A sigma plot of the Al_2O_3 vapor pressure data assuming AlO(g) gives an entropy value about 5 e.u. higher than expected from Ward and Hussey's data on AlO $(^2\Sigma)$, but this difference is well within experimental uncertainties, and the free energy equation given for reaction (10) is based on the entropy of AlO given by Ward and Hussey and the vapor pressures given here.

Baur and Brunner[23] have reported the existence of a solid sub-oxide of aluminum with a composition Al_9O_8 from melting point determinations. However, in view of possible reactions with their graphite container, their results are somewhat questionable. To test the possibility of existence of a sub-oxide, intimate mixtures of Al and Al_2O_3 were heated to temperatures ranging up to 2000°K. and in all cases, X-ray examination of the mixture showed no new phases. If a solid-sub-oxide does exist, it either disproportionates at lower temperatures or it is amorphous. Our preliminary experiments on the volatility of Al_2O_3 in the presence of Al metal appears to indicate the formation of solid sub-oxide because of the reduction of the volatility of the aluminum. However, further examination showed no evidence of reaction and only reduction of volatility because of the covering by the oxide powder. Similar reductions were obtained with Al_2O_3 or BeO powders and are due merely to the decreased pumping speed of the Al gas through the pores of the powder and the non-wetting of the powder by the liquid metal. Thus we have obtained no evidence to confirm Baur and Brunner's observation, but we can not

exclude the possibility of solid oxide with a narrow temperature range of stability near its melting point of 2300°K.

Summary

In summary, satisfactory materials have been found for containing aluminum liquid and aluminum oxide liquid separately. The vapor pressures of aluminum and aluminum oxide have been determined by an effusion method. By use of the vapor pressure data for aluminum together with the heat of formation of aluminum oxide and other thermodynamic data, one can demonstrate that aluminum oxide does not vaporize by decomposition to the atoms. By entropy considerations, one can exclude the possibility that it vaporizes undecomposed. By heating a mixture of aluminum and aluminum oxide and observing an enhancement of the aluminum oxide volatility in the presence of aluminum, one can demonstrate the existence of gaseous sub-oxides of aluminum. However, the determination of the heat of formation of the sub-oxide of aluminum by determination of the variation of the volatility of Al_2O_3 in the presence of aluminum allows one to demonstrate that the important species under these conditions can not be the main species when Al_2O_3 vaporizes by itself. Thus there must be two separate sub-oxide species of aluminum.

Of various possible species, AlO and Al_2O appear to be the most probable with Al_2O_2 also a possibility. From entropy considerations and the variation of the Al_2O_3 volatility when the Al partial pressure is varied, one can eliminate AlO as the gaseous species in the Al - Al_2O_3 mixture. The most reasonable explanation of the available data is that Al_2O gas is the main species when Al and Al_2O_3 are heated together with $Al_2O_3(s) + 4Al(g) = 3Al_2O(g)$ being the main reaction, while AlO gas is the main species when Al_2O_3 vaporizes alone as indicated by the reaction $Al_2O_3(s) = 2AlO(g) + O(g)$. It is not

possible from these data alone to definitely exclude Al_2O_2 gas as a possible species for either situation, but bond strength considerations render it less probable.

Assuming that the use of Al_2O and AlO species is correct, one obtains the following heats of formation:

$$Al(g) + O(g) = AlO(g), \quad \Delta H_{298} = -138 \text{ kilocals.}$$

$$2Al(g) + O(g) = Al_2O(g), \quad \Delta H_{298} = -248 \text{ kilocals.}$$

The AlO heat does not agree with the spectroscopic ΔH values of 21 to 87 kilocals. derived for the $^2\Sigma$ state of AlO, but it is quite likely that the ground state of AlO is a quartet state and thus data derived for the excited $^2\Sigma$ state would not apply to the species studied in a chemical system where one would have the gas mostly in the ground state.

This work was done under the auspices of the Atomic Energy Commission.