higher than the result of Clusius and Bartholomé.[6]

Table I gives the tritium results as follows: the direct measurements on liquid density minus gas density; the calculated gas densities; the liquid densities after correcting for 2.0% HT; the deviations of the final densities from a smooth curve. Table II gives smoothed tritium densities at several temperatures, from the triple point to 29°K.

Accuracy.—Error analysis shows the following possible contributions to $\rho_{\text{liq}} - \rho_{\text{gas}}$ values (first as direct units, then as error per cent.): (a) missing a liquid level mark, 0.2 mm. = 0.04%; (b) temperature of the bath, 0.003° = 0.005%; (c) temperature of the liquid tritium being above the bath temperature due to radioactive heat, 0.006° = 0.01%; (d) temperature in the gas measuring system, 0.1° = 0.03%; (e) pressure of the gas, 0.1 mm. = 0.04%; (f) volume of the gas, 0.05 cc. = 0.02%. These give a maximum error of ±0.18% if additive or a "probable" error of ±0.08% if random. The gas densities should be accurate to 0.1% in the best case (lowest temperature) and to 1% in the worst, contributing 0.000% and 0.04% errors, respectively. Finally, the HT correction should be reliable to 3%, contributing 0.01% error. Summarizing, the liquid density maximum error should be 0.23% for the worst case.

TABLE I

MOLAR DENSITIES OF LIQUID TRITIUM

T, °K.	$\rho_{\text{liq}} - \rho_{\text{gas}}$,[a] mole/liter	ρ_{gas}	ρ_{liq}[b]	Dev. from curve
20.61	45.17	0.13	45.39	0.04
22.50	43.97	.16	44.21	−.01
22.99	43.51	.29	43.88	−.04
23.59	43.11	.35	43.55	.00
24.41	42.49	.44	43.01	−.01
24.72	42.24	.48	42.81	−.02
25.66	41.53	.62	42.25	.03
26.36	40.91	.73	41.74	.00
27.09	40.17	.87	41.14	−.05
28.32	39.06	1.14	40.31	.07
29.13	38.02	1.37	39.49	−.06

[a] With 2.0% HT present. [b] Corrected to 0.0% HT.

TABLE II

SMOOTHED MOLAR DENSITIES OF LIQUID TRITIUM

T, °K.	20.62	21	22	23	24
ρ, mole/liter	45.35	45.12	44.52	43.91	43.29
T, °K.	25	26	27	28	29
ρ, mole/liter	42.65	41.98	41.26	40.48	39.66

LOS ALAMOS, NEW MEXICO RECEIVED MAY 28, 1951

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[6] K. Clusius and E. Bartholomé, *Z. physik. Chem.*, **B30**, 237 (1935).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND THE RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

The Gaseous Species of the Al–Al_2O_3 System[1,2,3]

BY LEO BREWER AND ALAN W. SEARCY

The vapor pressures of aluminum and of aluminum oxide have both been measured by the Knudsen effusion method. The results of these vapor pressure determinations and results from heatings of Al–Al_2O_3 mixtures have been used in deciding the identity of the important gaseous species of the Al–Al_2O_3 system. There are two important gaseous oxides of aluminum. Al_2O gas is evolved when Al_2O_3 is heated with aluminum or another reducing metal. AlO appears to be the principal aluminum species when Al_2O_3 is volatilized alone. No gaseous sub-hydroxides of aluminum were found. ΔH^0_{298} for sublimation of aluminum is 77.4 ± 1.4 kcal.; ΔH^0_{298} for $Al_2O_3(s) = 2AlO(g) + O(g)$ is 456 ± 10 kcal. For volatilization of liquid Al_2O_3 by decomposition to AlO and O gases $\Delta F^0 = 443{,}000 + 12T \ln T - 212T$. For the formation of AlO(g) and $Al_2O(g)$ from the gaseous atoms, $\Delta H^0_{298} = -138$ and $\Delta H^0_{298} = -248$ kcal., respectively. The boiling point of aluminum is 2750 ± 50°K. The boiling point of Al_2O_3 is 3800 ± 200°K.

Introduction

The existence of gaseous AlO has long been known from spectroscopic investigations,[4] but until recently nothing was known about what oxide species are principally obtained when Al_2O_3, alone or Al_2O_3 with aluminum is volatilized. Zintl, Krings and Brauning[5] described a process for recovering aluminum from aluminum alloys by volatilization of a suboxide which they identified as AlO; however, by analysis of sublimates from Al_2O_3–Si mixtures Grube, Schneider, Esch and Flad[6] claimed that the oxide species of Al present in the vapor under reducing conditions is Al_2O rather than AlO.

The most satisfactory means of determining the species of the Al–Al_2O_3 gaseous system might be to obtain density and electron diffraction data for the vapor above Al_2O_3 and data for the variation in volatility of Al_2O_3 with aluminum gas pressure at constant temperature. Such data have so far not been obtained because of the obstacles arising from the extremely high temperatures at which volatilization becomes appreciable in this system. Fortunately, by critical analysis of the thermodynamic data obtained for the vaporization of Al and Al_2O_3, both independently and when mixed, we can definitely limit the number of species which can be of importance in the gaseous system and identify the actual species almost unequivocally.

We will present first our determination of the vapor pressures and heats of vaporization of aluminum and of Al_2O_3 and then, using these data and data for volatilization of Al–Al_2O_3 mixtures, present the thermodynamic arguments which

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[1] Based on a thesis submitted by A. W. Searcy in partial fulfillment of requirements for the Ph.D. degree at the University of California.

[2] This research was performed under Contract No. W-7405-eng 48B for the Atomic Energy Commission.

[3] Presented at the 116th National Meeting of the American Chemical Society in Atlantic City, N. J., September, 1949.

[4] See for example G. Herzberg, "Molecular Spectra and Molecular Structure," Prentice-Hall, Inc., New York, N. Y., 1939.

[5] E. Zintl, W. Krings and W. Brauning, German Patent 742,330, Oct. 14, 1943 [*C. A.*, **39**, 2481[9] (1945)].

[6] G. Grube, A. Schneider, U. Esch and M. Flad, *Z. anorg. Chem.*, **260**, 120 (1949).

limit the number of gaseous species which can be of importance in the Al–Al_2O_3 system. Finally we we will present arguments for believing two particular oxides to be the only ones of importance in the gaseous system.

Vapor Pressure and Heat of Vaporization of Aluminum

Experimental.—The furnace and arrangement of the effusion vessels and platinum collector plates used in determining the vapor pressure of aluminum were the same as described in a previous publication from this Laboratory.[7] As before, the charge was inductively heated. Molybdenum radiation shields surrounded the sample except for a collimated path from the effusion hole to a Pt collector plate.

Molten aluminum is extremely reactive at the temperatures of our experiments; refractory materials such as carbon, tantalum, molybdenum and tungsten are unsatisfactory containers because of compound-formation with the aluminum. Both BeO and TaC crucibles proved satisfactory, however, from the standpoint of non-reactivity. After eight hours heating at 1450°K., aluminum heated in BeO showed between 0.1 and 1.0% Be by weight on spectrographic analysis. Similar examination of aluminum from a TaC crucible heated for two hours showed 0.01 to 0.1% tantalum. X-Ray diffraction examination of the aluminum gave no indication of Al_4C_3 formation or carbon dissolution. Ta_5Si was also found satisfactory but was not used.

Four runs were made using TaC, and six using highly sintered BeO crucibles. The TaC crucibles acted as their own heating elements; the BeO crucibles were heated inside snug-fitting Ta crucibles. The crucibles were about 3 cm. high and 2 cm. in diameter with lids through which circular knife-edged effusion holes had been drilled.

The TaC crucibles and lids were made by heating the tantalum packed in graphite powder at about 2600°K. for 3 to 8 hours. Compositions were determined from the increase in weight and corresponded to the one-phase region $TaC_{0.92}$ to $TaC_{0.98}$. X-Ray diffraction pictures show that the lattice constants of TaC powder were completely unchanged after heating as high as 1720°K. with aluminum. Unfortunately, however, aluminum wets TaC very strongly and within 2 hours at 1400°K. the walls of a TaC crucible were usually soaked through by aluminum.

Residual pressures throughout the runs were always lower than 10^{-4} mm. and averaged about 5×10^{-5} mm. Since our beam was wide and conical in shape, effective molecular collision cross-sections were low. Deposits on our collector plates were sharply defined at the edges indicating scattering from the beam was negligible.

Temperatures were read with optical pyrometers calibrated by the Bureau of Standards by sighting on the effusion hole through a 4.8-mm. hole in the collector plate.

The effusion holes used were of two sizes—about 3.2 mm. diameter and about 1.6 mm. diameter. To check the black body conditions, three small molybdenum crucibles were heated simultaneously. The three had lids with holes of 3.2, 1.6 and 1.0 mm. diameter. The temperatures inside the three crucibles, when corrected for slight differences in lid surface temperatures, were identical at 1400, 1700 and 1950°K. Johnston and Marshall[8] observed temperatures 20 degrees lower in a 1.8-mm. diameter hole at 1600° than observed in 0.6 and 1.2 mm. holes. However, the holes in their experiment were much larger fractions of the internal wall plus orifice areas than in our experiments and did not, therefore, approximate black body light sources as closely as our holes did.

Temperature gradients in our crucibles were small. From the small regular increase in weight of a lid due to collection of aluminum on the under surface we calculate that the temperature of the inside lid surface was only four degrees lower than that of the aluminum melt for a typical heating.

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 after equilibrium was established and applying window and pyrometer corrections to this average value. The windows were protected by an iron shutter.

Corrections were applied for vaporization during the rise in temperature to the equilibrium value and during cooling after the run. Uncertainties in the effective times at the equilibrium temperature were less than 2% for all runs.

The aluminum employed for our experiments was 99.99% pure. Because the aluminum soaked through the TaC crucibles, it was necessary to make some of our runs with aluminum which had not been further purified by heating to drive off volatile impurities, but a spectroscopic examination of a collection from such a run showed only 0.1 to 1.0% Mg, about 0.01% Fe, and less than 0.01% of either Bi or Si. X-Ray examination showed aluminum as the principal phase with a very weak second phase, probably an oxide, which could not be identified. Since the weight of aluminum collected was determined by analysis, neither volatilization of minor impurities nor oxidation of the film on the collector influenced our results. From 0.4 to 1.1 mg. of aluminum was collected for each run in from 45–170 minutes of heating.

Analyses were made colorimetrically using the 370 mμ band of the aluminum–ferron complex, a method suggested by Davenport.[9]

Aluminum was dissolved from the plates with warm 1.2 *N* HCl. Samples were diluted to exactly 200 ml. and kept at *p*H 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 known, identically treated aluminum solutions. Readings were made in one-centimeter quartz cells in a Beckman spectrophotometer, using identically prepared aluminum-free solutions as blanks. Since the 370 mμ band is dependent on *p*H, the *p*H was checked for each buffered sample solution with a Beckman *p*H meter.

The visible spectra of both known and unknown solutions were scanned in a Cary Spectrophotometer to ensure that the absorption observed was in each case due to the aluminum–ferron complex. The probable error in analysis was 5%.

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 at 2300–2600°K. after every second or third effusion run. Heatings were made after most effusion runs with empty crucibles substituted for those containing aluminum. Collections from two typical blank runs were analyzed. One showed 9.9% of the aluminum collected in an equivalent time in the effusion run immediately preceding, the other 6.7%. The vapor pressures accordingly were all reduced by 8% to correct for aluminum which reached the collector by revaporizing from hot shields.

Data and Thermodynamic Calculations.—From the known geometry of the system and the weight of aluminum found on the collector, the number of moles of aluminum that effused in the time of a run could be calculated. Pressure was then calculated from the effusion equation

$$p = \frac{z(MT)^{1/2}}{44.38\,at} \qquad (1)$$

where p is the pressure in atmospheres of the species of molecular weight M, a is hole area in cm., T is the absolute temperature and z is the number of moles effusing from the crucible in time t. This equation requires that the ratio of hole size to effective surface of the sample be smaller than the sticking coefficient. The sticking coefficient is the fraction of gas molecules which do not bounce off on striking a surface.

A summary of our results is given in Table I. The pressures in the third column of the table have been corrected for the weight of aluminum collected in the blank runs. $(\Delta F^\circ - \Delta H^0_{298})/T$

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[7] L. Brewer, P. W. Gilles and F. A. Jenkins, *J. Chem. Phys.*, **16**, 797 (1948).

[8] H. L. Johnston and A. L. Marshall, THIS JOURNAL, **62**, 1382 (1940).

[9] W. H. Davenport, Jr., Oak Ridge National Laboratory-83 (1948).

functions listed in column 5 were obtained by combining data from the low-temperature calorimetric results of Giauque and Meads,[10] recent tables of the high-temperature heat content and entropy for solid and liquid aluminum compiled by Kelley,[11] and the tables of heat contents and entropies for gaseous elements compiled by Brewer.[12] The final column lists the values of ΔH^0_{298} for sublimation of aluminum found by combining these data. All our runs are included.

TABLE I

CALCULATIONS OF ΔH_{298} FOR SUBLIMATION OF ALUMINUM[a]

Hole area, cm.^{2}	T, °K.	Corrected pressures, atm.	$\Delta F^0/T$	$(\Delta F^0 - \Delta H^0_{298})/T$	ΔH^0_{298}
0.0842	1383	3.43×10^{-6}	25.00	−30.53	76.80
.0842	1391	2.89×10^{-6}	25.34	−30.52	77.70
.0194	1427	1.82×10^{-5}	21.69	−30.44	74.39
.0194	1460	3.63×10^{-5}	20.37	−30.36	74.07
.0814	1410	2.85×10^{-6}	25.37	−30.48	78.75
.0814	1412	2.91×10^{-6}	25.33	−30.47	78.79
.0814	1419	3.33×10^{-6}	25.06	−30.46	78.78
.0228	1420	5.71×10^{-6}	23.99	−30.45	77.30
.0228	1451	5.25×10^{-6}	24.16	−30.38	79.13
.0228	1468	8.69×10^{-6}	23.15	−30.34	78.52
			Average		77.42 ± 1.41 kcal.

[a] TaC crucibles were used for the first four runs listed; BeO for the remaining six.

The average ΔH^0_{298} value from TaC vessels is 75.6 kcal.; from BeO, 78.4. The BeO results are clearly independent of hole size, the TaC values show an apparent dependence. We would predict our average deviation in results to be ±0.5 kcal. BeO container results are within these limits, regardless of hole size, and TaC results are within these limits for each of the two hole sizes considered separately.

Inspection of the TaC lids after our runs revealed that a small amount of Al had soaked through. A small amount of vaporization from the lid surface may have increased the apparent pressures in TaC containers. Since more lid surface could be "seen" by the collector when the smaller hole size was used, values obtained for apparent vapor pressure using the smaller TaC holes would be proportionately higher than when the larger holes were used.

Because good agreement in ΔH^0_{298} values were obtained when the hole areas of the BeO crucibles were varied by a factor of 4, we conclude that the sticking coefficient for aluminum within a BeO crucible at 1400°K. is at least as large as the ratio of hole area to internal surface area, about 2×10^{-3}, and our results were independent of the sticking coefficient within the crucible. A rough comparison of the weight-loss of one of our crucibles with the weight of aluminum found on the collector gives a sticking coefficient for the collector of 0.84. We have considered the sticking coefficient on the collector to be 1.0 in our calculations.

Despite some indication that determinations using BeO containers are better than those using TaC, we have given each of our 10 runs equal weight in obtaining our final value of 77.4 ± 1.4 kcal. for ΔH^0_{298}. By a dynamic method, Bauer and Brunner[13] found vapor pressures from which we calculate ΔH^0_{298} equal to 75.0 kcal. Farkas'[14] single effusion measurement at 1476°K. gives 77.8 kcal. Within their probable uncertainties, these values agree with ours. We calculate the boiling point of aluminum to be 2750 ± 50°K.

The Vapor Pressure and Heat of Vaporization of Al_2O_3

Experimental.—Molybdenum and tungsten were found to be non-reactive toward molten Al_2O_3. Al_2O_3 heated in either Mo or W for several hours at 100 to 300° above the Al_2O_3 melting point showed less than 0.1% pickup of the container metal. All the effusion runs reported here were made using tungsten crucibles. Tantalum, Ta_2C, TaC, ZrC and Ta_5Si were all found to be unsatisfactory containers for Al_2O_3. X-Ray diffraction analysis revealed that ZrO_2 was present in the residue after heating Al_2O_3 to 2100°K. with ZrC. Volatility was very high and aluminum and Al_2O_3 were identified as the principal phases of the sublimate. Later results suggest the reaction was $2ZrC(s) + 3Al_2O_3(s) = 2ZrO_2(s) + 3Al_2O(g) + 2CO(g)$ with Al_2O disproportionating at the collector surface. TaC heated with Al_2O_3 gave similar sublimates and first Ta_2C, then tantalum which, in absence of carbide, reacted with more Al_2O_3 as discussed later.

Though tungsten was shown not to dissolve in the Al_2O_3 melt, there remains the possibility that the weight of aluminum found on the collector could be high because of a reaction to form gaseous oxides of tungsten and of aluminum. For example, $W(s) + Al_2O_3(l) = WO(g) + 2AlO(g)$. Fortunately, comparison of the total weight-gain of the collector with the weight of aluminum found to be present on the collector by analysis established that a higher percentage of aluminum was present than could be explained by volatilization occurring as a result of any of the possible reactions with tungsten.

For the Al_2O_3 effusions, tungsten radiation shielding was substituted for molybdenum because Mo volatility is high at the temperatures studied. Tantalum top shields were retained. These shields were degassed frequently at 2500 to 2600°K. Weight-gains of collectors during blank runs averaged 10–12% of those for actual runs. No correction was applied for these blanks, since spectroscopic analysis indicated most of the blank collections were tungsten.

Uncertainty in temperatures were about 10°K. for these higher-temperature measurements. Uncertainty in relative temperatures for the runs were only 5°, however. Uncertainty in effective time of runs was again less than two per cent.

Analysis of the collection plates for Al was complicated by the insolubility of the aluminum oxide collected and by the presence of unknown amounts of tungsten on the plates. The most satisfactory way found for dissolving the samples from the platinum was to fuse the collector plates with potassium pyrosulfate in Pt dishes for 30 to 60 minutes. The fusion product was dissolved in concentrated HCl and evaporated to dryness. Water was then added and the dishes heated to redissolve the samples. Most of the tungsten present precipitated as WO_3. 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 identical fusions to obtain a new calibration curve for the spectrophotometric analysis. The probable error in analysis was 13%. The aluminum found averaged 45% by weight of the sample collected. The sublimates were mostly amorphous and gave very weak X-ray diffraction patterns so no phases were identified from the collector plates. The collections definitely did not contain aluminum or tungsten metals, and they did not appear to contain α, β, or γ-Al_2O_3, WO_2 or WO_3.

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(10) W. F. Giauque and P. F. Meads, THIS JOURNAL, **63**, 1897 (1941).

(11) K. K. Kelley, "High Temperature Heat-Content and Entropy Data for Inorganic Compounds," *Bur. of Mines Bull.*, 476 (1949).

(12) See L. L. Quill, "The Chemistry and Metallurgy of Miscellaneous Materials," National Nuclear Energy Series Div. IV, Vol. 19B, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, pp. 13–39.

(13) E. Bauer and R. Brunner, *Helv. Chim. Acta*, **17**, 958 (1934).

(14) L. Farkas, *Z. Physik*, **70**, 733 (1939).

Data and Thermodynamic Calculations.—The data and calculations employed in determining vapor pressures for Al_2O_3 are summarized in Table II. The vapor pressures listed in the final column of the table are the AlO pressures calculated on the assumption that Al_2O_3 liquid vaporizes by the reaction $Al_2O_3(l) = 2AlO(g) + O(g)$. Arguments favoring this assumption will be presented in the next section of the paper. That the sticking coefficient inside our crucibles was at least as large as the ratio of our hole areas to sample surface-area is demonstrated by the agreement in ΔH^0_{298} values for vaporization obtained using holes varied by a factor of four in area. That the sticking coefficient on the collector plate was essentially unity, 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. Our blanks, it should be recalled, averaged about 0.1 of the weight of sample collected.

TABLE II

EXPERIMENTAL VAPOR PRESSURES FOR Al_2O_3

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

$$p_0 = \frac{\sqrt{16}}{2\sqrt{43}} \cdot P_{AlO} \text{ and } K = (P_{AlO})^2(P_0) = 0.305\ P^3_{AlO}$$

Hole area, cm.²	Effective $\sin^2\alpha$	T, °K.	Time, min.	Wt. aluminum collected, mg.	Vapor pressure (as AlO), atm.
0.0791	0.0631	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}

Treatments of the vapor pressure data by use of a plot of $\Delta F/T + a \ln T = \Sigma = (\Delta H^0/T + I$ *vs.* $1/T$ (a sigma plot)) and by use of $(\Delta F - \Delta H_{298})/T$ tables give heats agreeing within 10 kcal., which is within experimental uncertainty. The necessary entropy and high-temperature heat-content data for calculating ΔH_{298} for the reaction $Al_2O_3(l) = 2AlO(g) + (O(g)$ were obtained from Kelley[11] for $Al_2O_3(s)$, from the National Bureau of Standards Tables[15] for monatomic oxygen, and from Ward and Hussey[16] for AlO gas. The heat of fusion for Al_2O_3 was taken as 26 kcal. as given by Kelley[17] and the heat capacity of liquid Al_2O_3 was estimated to be 35 cal. mole^{-1} deg.$^{-1}$. In view of the difficult experimental conditions at these high temperatures, the heat obtained from the ΔF values together with ΔS or $(\Delta F - \Delta H_{298})/T$ values is probably more reliable than the value obtained from a sigma plot.

We obtain for $Al_2O_3(l) = 2AlO(g) + O(g)$, $\Delta H^0_{298} =$ 456 kcal. and from this

$$\Delta F^0 = 443{,}000 + 12T \ln T - 212T \qquad (2)$$

The uncertainty of ΔF is about ±4 kilocalories. The ΔH_{298} values calculated from our pressure values show an average deviation from the mean of ±3 kcal. An atmospheric boiling point of 3770 ± 200°K. is found by extrapolating this equation.

We know of only one other paper which describes vapor pressure determinations for Al_2O_3.[18] Unfortunately, tantalum crucibles were used as containers for the Al_2O_3 in the research reported in that paper. We have found that volatilization is much greater when Al_2O_3 is heated in tantalum than when Al_2O_3 is heated in tungsten. X-Ray diffraction analysis indicates that a new phase is formed inside the tantalum crucible when the Al_2O_3 is heated. Spectroscopic analyses show the presence of considerable tantalum in the Al_2O_3 after heating. The tantalum probably reacts with $Al_2O_3(l)$ to form $Al_2O(g)$ and a mixed oxide of tantalum and aluminum.

Mixed Aluminum–Aluminum Oxide Heatings

We were unable to find a container which was inert toward reaction with both aluminum and Al_2O_3 at high temperatures, and we were unable to vary the pressure of aluminum gas over Al_2O_3 at constant temperature. By heating $Al-Al_2O_3$ mixtures together in Al_2O_3 containers, however, we were able to observe the change in volatility of Al_2O_3 in the presence of aluminum as the temperature was varied. The data so obtained are insufficient to establish independently the identity of the volatilizing species, but when these data are considered in conjunction with the other data already presented they become very useful in deciding the gaseous species of the system.

Al_2O_3 crucibles of exceptionally high purity were available. Spectroscopic analysis of these crucibles showed less than 0.1% Fe, Si and Ca, and less than 0.01% Mg by weight. Aluminum pieces varying in weight from 0.02 to 0.7 g. were buried in Al_2O_3 powder after the powder and a crucible had been previously degassed. The crucible then was heated at some fixed temperature in the range 1466 to 1853°K. After heating at the 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 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. The weight of Al_2O_3 vaporizing by reaction with aluminum could be obtained by noting the weight-loss of the crucible and contents at the time that the sudden decrease in rate of weight-loss indicated that all the aluminum had been volatilized. This weight after subtraction of the weight of aluminum initially added gave the Al_2O_3 evolved by reaction with aluminum. The rate of Al_2O_3 volatilization increased over 100-fold in the presence of aluminum

The aluminum, which was introduced as a single lump, did not soak through the Al_2O_3 powder on melting, but remained as a single pool of liquid below the powder surface. Varying the height of the powder column above the aluminum from 0.1 to 1.0 cm. produced only a small change in the ratio of Al to Al_2O_3 vaporizing under given temperature conditions, so equilibrium with respect to suboxide formation must have been rapidly established. This small variation with height and therefore with the partial pressure of aluminum at the surface indicates Al_2O to be the vaporizing species rather than AlO, but the data are not accurate enough to be used in a conclusive manner.

Data from these experiments are given in Table III where Al_2O is assumed to be the suboxide formed.

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(15) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Series III.

(16) J. J. Ward and M. A. Hussey, private communication, Batelle Memorial Institute.

(17) K. K. Kelley, *U. S. Bur. of Mines Bull.*, 393 (1936).

(18) O. Ruff and M. Konschak, *Z. Elektrochem.*, **32**, 515 (1926).

TABLE III

DATA FOR THE REACTION $4Al(g) + Al_2O_3(s) = 3Al_2O(g)$

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

T, °K.	Total wt. loss/ wt. Al present as metal	Time, t, min.	Wt. loss in time, t, g.	Wt. Al (grams) lost as Al(g) in time t	P_{Al_2O}/P_{Al}	P_{Al} at surface atm.	$-\Sigma$
1466	1.18	187	0.0304	0.0208	0.285	2.0×10^{-7}	110.5
1491	1.20	196	.0236	.0154	.325	1.39×10^{-7}	112.3
1501	1.20	364	.0329	.0216	.325	1.06×10^{-7}	112.9
1557	1.25	295	.0777	.0457	.436	2.8×10^{-7}	113.1
1609	1.35	242	.2293	.107	.713	8.1×10^{-7}	114.3
1614	1.30	30	.0377	.0198	.563	1.22×10^{-6}	112.2
1614	1.30	30	.0441	.0232	.563	1.42×10^{-6}	111.9
1614	1.30	30	.0747	.0393	.563	2.4×10^{-6}	110.8
1614	1.30	30	.0884	.0464	.563	2.9×10^{-6}	110.5
1619	1.32	30	.0494	.0248	.622	1.53×10^{-6}	112.3
1624	1.32	60	.1185	.0598	.622	1.84×10^{-6}	112.0
1725	1.42	(60)	.3948	.154	.970	(4.9×10^{-6})	(113.3)
1853	1.65	(20)	.8851	.168	2.67	$(>1.66 \times 10^{-5})$	(<117.9)

Av. 112 cal. per degree

In interpreting the data unit sticking coefficient was assumed and the area of the pores in the Al_2O_3 power through which the vapor escaped was assumed to be one-half the area of the top surface of the power. Pressures of Al and Al_2O could then be calculated from the effusion equation. The last column of the table contains values of $\Sigma = \Delta F/T + \Delta C_p \ln T$ for the reaction $4Al(g) + Al_2O_3(s) = 3Al_2O(g)$ calculated from the data and the estimated value of $\Delta C_p = -12$ cal. deg.$^{-1}$. The aluminum partial pressures found in these experiments were much below the saturated pressures. The reduced pressures could possibly be explained by solid suboxide formation, but a similar reduction in vapor pressure was observed when aluminum was heated below a layer of BeO powder. The reduced pressure of aluminum gas at the surface of the powder undoubtedly results from a pressure-drop through the pores of powder due to resistance of the powder to gas flow. Since there was no lid on the container the pressure could not build up.

Spectroscopic analyses of sublimates from these heatings showed about 1.0% by weight of Mo (the shielding material) and no other major impurities. X-Ray diffraction analysis showed aluminum metal and very weak lines of a second phase which could not be identified. Al_2O_3 diffraction lines were not found, undoubtedly due to the amorphous nature of the sublimate.

Though the fraction of the aluminum reacting to form suboxide increased with increased temperature, we were unable because of container limitations to reach a temperature where the ratio of suboxide volatilization to aluminum volatilization was high enough to establish whether the suboxide formula was $(AlO)_x$ or $(Al_2O)_x$ from the material balance alone. Further, we could not yet say whether or not the suboxide species present under reducing conditions is the species formed during volatilization of pure Al_2O_3. But we could now reach some conclusions concerning the gaseous species present from thermodynamic considerations.

Reactions by which $Al_2O_3(l)$ may volatilize are

$$Al_2O_3(l) = Al_2O_3(g) \tag{3}$$

$$Al_2O_3(l) = 2Al(g) + 3O(g) \tag{4}$$

$$Al_2O_3(l) = 2AlO(g) + O(g) \tag{5}$$

$$Al_2O_3(l) = Al_2O_2(g) + O(g) \tag{6}$$

$$Al_2O_3(l) = Al_2O(g) + 2O(g) \tag{7}$$

We can definitely exclude reaction (4), volatilization to the elements, by using the heat of formation of Al_2O_3 determined by Snyder and Seltz,[19] the entropy and heat content data given by Kelley,[11] and the heat of sublimation of aluminum reported here, to calculate the equilibrium constant for reaction (4). The calculated pressures are much lower than the observed vapor pressure of Al_2O_3.

If we assume that a particular suboxide is the gaseous species formed by reaction of Al with Al_2O_3 in our mixed heatings we can, as illustrated in Table III assuming Al_2O, determine what the thermodynamics properties of that suboxide must be. We can then calculate what the pressure of this species would be over liquid Al_2O_3 alone. When we perform these calculations we find that for any species we assume to volatilize from our Al–Al_2O_3 mixture we calculate a pressure over liquid Al_2O_3 which is less than one-hundredth of the observed pressure. This means that a different oxide species must account for the volatility of liquid Al_2O_3 than accounts for the volatility of Al–Al_2O_3 mixtures. Furthermore, since the relative concentrations of these two oxides depend on the concentrations of aluminum gas in equilibrium with them, the two oxides must contain different percentages of aluminum, and the gaseous oxide which is the major species when Al_2O_3 is heated alone must contain aluminum in a higher valence state than the aluminum in the other gaseous oxide. The hypothesis that Al_2O is the species volatilizing from liquid Al_2O_3 leaves no oxide of lower valence state which could account for the volatilization from Al–Al_2O_3 mixtures. Therefore, reaction (7), volatilization to $Al_2O + 2O$, cannot be the major path of Al_2O_3 volatilization, though Al_2O may be a major species under reducing conditions.

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(19) P. E. Snyder and H. Seltz, THIS JOURNAL, **67**, 683 (1945).

A sigma plot of the Al_2O_3 vapor pressure data on the assumption of Al_2O_3(g) as the major species reveals an abnormally high entropy of vaporization, about 67 e.u. compared to the expected value of 25 to 30 e.u. Thus reaction (3) can also be excluded and either AlO or its dimer Al_2O_2 must be the gaseous oxide produced when liquid Al_2O_3 vaporizes. It is not possible from entropy considerations alone to decide between reactions (5) and (6) since the entropies per mole of gaseous species vaporized are too close together to be distinguished in view of the uncertainties in estimating the entropy of Al_2O_2. We must decide on other grounds.

If Al_2O_2 is the principal species over Al_2O_3 liquid, then the heat of dimerization must be of the order of 140 kcal., which seems unreasonably high. On the other hand, our results would place the heat of formation of AlO from Al(g) and O(g) at −127 kcal. compared with the spectroscopic values of −21 to −87. There is, however, a strong possibility that the spectroscopic heats are in error because transitions to the true ground state have not been observed. We feel that AlO is probably the species to which Al_2O_3 volatilizes, and we have based our vaporization equations on this assumption.

The observed variation of oxide volatility with aluminum partial pressure indicates an oxide of low oxidation number, Al_2O being strongly indicated. It can be added that AlO would have been very unlikely as the main species over Al–Al_2O_3 mixtures because the entropy calculated assuming AlO to volatilize from the mixtures differs beyond probable experimental error from the entropy of AlO known from spectrosopic investigations. As noted above, Al_2O has already been demonstrated to volatilize from Si–Al_2O_3 mixtures.[6] Furthermore, gaseous monovalent aluminum halides,[20a,b] sulfides and selenides[20c] have been produced by methods entirely analogous to our preparation of Al_2O. Figure 1A which gives the logarithms of the partial pressures of the various species over a mixture of liquid aluminum and solid Al_2O_3 as a function of temperature illustrates the relative importance of Al_2O compared to the other species. Figure 1B, which gives the logarithms of the partial pressures of the various species over liquid Al_2O_3 shows how Al_2O becomes less important than AlO under less highly reducing conditions.

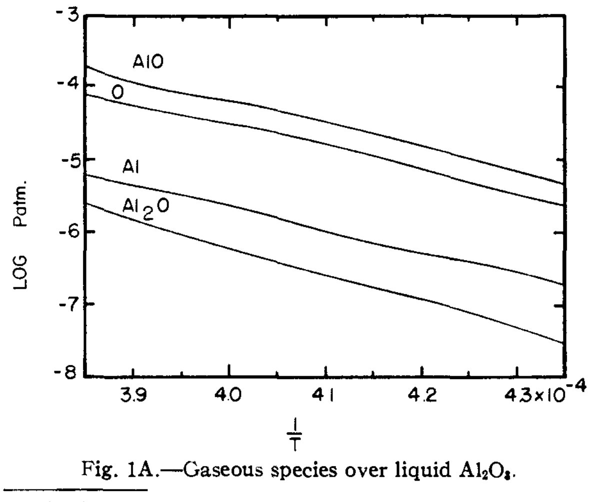

Fig. 1A.—Gaseous species over liquid Al_2O_3.

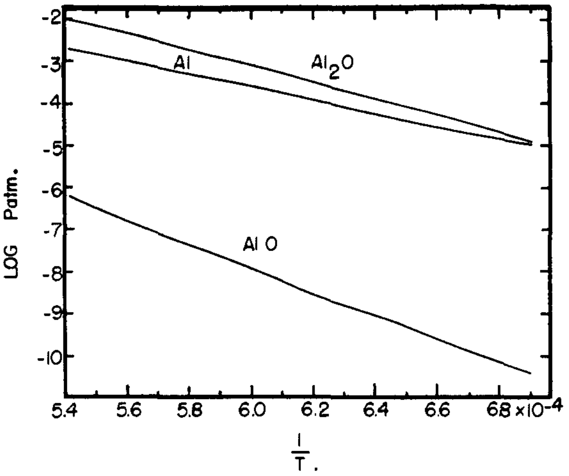

Fig. 1B.—Gaseous species over liquid Al and solid Al_2O_3 mixture.

Thermodynamic Equations.—From the Σ values of Table III we can calculate the thermodynamic functions for the reaction $4Al(g) + Al_2O_3(s) = 3Al_2O(g)$. Within experimental error there is no variation of Σ with temperature which means that ΔH_0^0 for the reaction is close to zero. We calculate for the reaction with $\Delta H_0^0 = 0$

$$\Delta F^0 = 27.5T \log T - 112\ T$$

The uncertainty in ΔF is ±5 kcal. The uncertainties in ΔH and ΔS obtained from this equation are ±20 kcal. and ±12 e.u. We can now calculate that for

$$2Al(g) + O(g) + Al_2O(g) \qquad (8)$$
$$\Delta H_{298} = -248 \text{ kcal.}$$

The uncertainty in ΔF here is ±2 cal. and in ΔH ±7 kcal. From equation (2) we find for $Al(g) + O(g) = AlO(g)$, $\Delta F^0 = -138 + 23.3T$.

To determine if any gaseous sub-hydroxide of aluminum is an important species we heated Al_2O_3 in 10^{-8} mm. of H_2. Since there was no increase in volatilization of the Al_2O_3 by reaction with H_2 there must be no very stable gaseous aluminum subhydroxide species.

One of the most significant results of this work is the large discrepancy between the heat of dissociation of AlO to the gaseous atoms of 127 kcal. found in this work and the values of 21 to 87 reported from spectroscopic studies.[21] This confirms the recent findings of Huldt and Lagerqvist[22] that spectroscopic data are indicating stabilities for many oxide molecules which are much lower than indicated by chemical data. The discrepancy appears to be due to the fact that the spectroscopic data in many cases do not involve the ground state and the spectroscopic data are only giving

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[20] (a) W. Klemm and E. Voss, *Z. anorg. allgem. Chem.*, **251**, 233 (1943); (b) W. Klemm, E. Voss and K. Geiersberger, *ibid.*, **256**, 15 (1948); (c) W. Klemm, K. Geiersberger, B. Schaeler and H. Mundt, *ibid.*, **255**, 287 (1948).

[21] A. G. Gaydon, "Dissociation Energies," John Wiley and Sons, Inc., New York, N. Y., 1947.

[22] L. Huldt and Z. Lagerqvist, *Arkiv. För Fysik*, **2**, Nr. 37, 1–4 (1950).

the stability of excited states. Thus in the case of the alkaline earths, it appears likely that the ground state is a triplet electronic state and the spectroscopic data involving singlet electronic states give misleading results. In the case of AlO, the spectroscopic data appear to indicate a $^2\Sigma$ electronic state for the ground state of gaseous AlO. The results obtained in this paper indicate either that the true ground state is a quartet electronic state or a doublet state lower in energy than those observed to date. However, there is also the possibility that Al_2O_2 is the chemical species rather than AlO as noted above.

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High-Temperature Heat Content of Nickel Chloride

BY J. P. COUGHLIN

High temperature heat content measurements of nickel chloride were conducted over the temperature range from 298.16 to 1336°K. The temperature and heat of fusion were evaluated. A table of heat content and matching entropy increments above 298.16°K. is included.

Introduction

The need for reliable high temperature heat content values for nickel chloride was made imperative by research conducted by W. F. Giauque and R. H. Busey[1] of the Chemistry Department of the University of California, who requested that the present investigation be undertaken. The only previous data are those of Krestovnikov and Karetnikov[2] (extending to 1073°K.), the average accuracy of which has been estimated by Kelley[3] as about ± 5%. The present paper reports measurements to 1336°K., which cover the entire crystalline range above 298.16°K. and a portion of the liquid range, so that the heat of fusion is obtained.

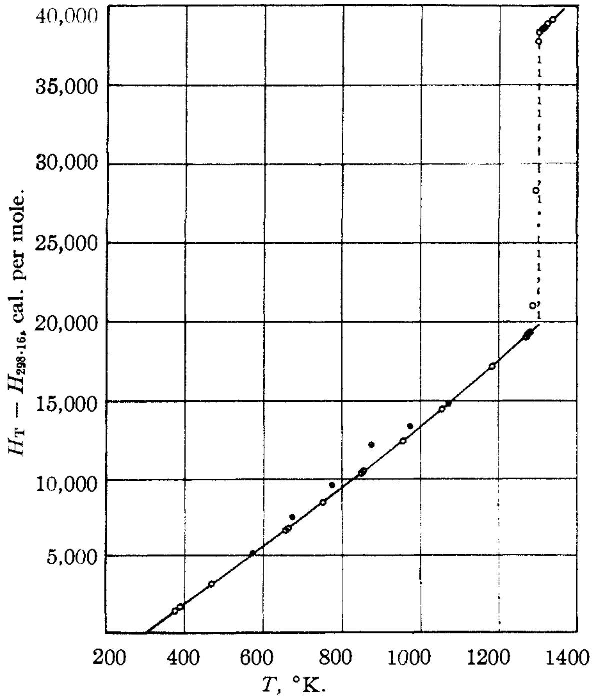

Fig. 1.—Heat content of $NiCl_2$: open circles, this research; dark circles, Krestovnikov and Karetnikov.

Material and Method

The nickel chloride was furnished by Giauque and Busey.[1] It was a portion of the material prepared, purified and used in their low temperature heat capacity and hydrogen reduction equilibrium measurements. Their analysis gave 45.29% Ni and 54.71% Cl, as compared with the theoretical 45.28 and 54.72%, respectively.

The substance was sealed in platinum-rhodium capsules preparatory to the measurements. The capsules were filled in an inert atmosphere in a dry-box, temporarily closed by tightly fitting rubber caps to permit weighing, and finally sealed gastight by pinching shut the capsule necks and welding with platinum.

The heat content measurements were made by the "dropping" method, using apparatus and techniques previously described.[4]

TABLE I

MEASURED HEAT CONTENTS OF $NiCl_2$

T, °K.	$H_T - H_{298.16}$, cal./mole	T, °K.	$H_T - H_{298.16}$, cal./mole
376.3	1,395	1183.4	17,150
389.4	1,635	1269.7	19,070
468.8	3,140	1276.1	19,210
568.3	4,940	1281.1	19.360
568.6	4,950	1286.6	20,980[a]
654.1	6,575	1295.4	28,330[a]
657.3	6,670	1300.8	37,730[a]
662.8	6,750	1303.9	38,310
752.2	8,475	1311.3	38,560
847.5	10,370	1319.1	38,610
853.2	10.420	1320.1	38,640
954.9	12,420	1324.8	38,830
1054.6	14,460	1336.0	39,120

[a] Includes premelting.

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(1) W. F. Giauque and R. H. Busey, unpublished measurements.

(2) A. N. Krestovnikov and G. A. Karetnikov, *J. Gen. Chem.* (*U. S. S. R.*), **6**, 955 (1936).

(3) K. K. Kelley, U. S. Bureau of Mines Bull., 476 (1949).

(4) K. K. Kelley, B. F. Naylor and C. H. Shomate, *Bureau of Mines Tech. Paper* 686, 1946.