NASA TECHNICAL NOTE

NASA TN D-6318

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NASA TN D-6318

VAPORIZATION OF SOME GROUP IIIA METAL – METAL OXIDE SYSTEMS: MASS SPECTROMETRIC IDENTIFICATION OF INDIUM GALLIUM OXIDES ($InGaO$ AND $InGaO_2$) AND GALLIUM ALUMINUM OXIDE ($GaAlO$)

by Fred J. Kohl and Carl A. Stearns

Lewis Research Center
Cleveland, Ohio 44135

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • APRIL 1971

1. Report No. NASA TN D-6318	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle VAPORIZATION OF SOME GROUP IIIA METAL - METAL OXIDE SYSTEMS: MASS SPECTROMETRIC IDENTIFICATION OF INDIUM GALLIUM OXIDES (InGaO AND $InGaO_2$) AND GALLIUM ALUMINUM OXIDE (GaAlO)

5. Report Date
April 1971

6. Performing Organization Code

7. Author(s)
Fred J. Kohl and Carl A. Stearns

8. Performing Organization Report No.
E-6140

9. Performing Organization Name and Address
Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio 44135

10. Work Unit No.
129-03

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Technical Note

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

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17. Key Words (Suggested by Author(s))
High-temperature mass spectrometry; Knudsen effusion; Vaporization of indium, gallium, and aluminum oxides; Indium gallium oxides; Gallium aluminum oxide

18. Distribution Statement
Unclassified - unlimited

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 18	22. Price* $3.00

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*For sale by the National Technical Information Service, Springfield, Virginia 22151

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SUMMARY

The vaporization of the systems In + Ga_2O_3 and Ga + Al_2O_3 was studied by the Knudsen effusion mass spectrometric method. New gaseous molecules InGaO, $InGaO_2$, and GaAlO were positively identified. The atomization energy of InGaO was determined to be 818±17 kJ $mole^{-1}$.

The vaporization of the systems In + In_2O_3, Ga + Ga_2O_3, and Al + Al_2O_3 was reexamined. Parent molecules were identified and their relative intensities were measured. We verified that the only vaporization products significant with respect to effusive weight loss are the atomic species and M_2O-type molecules. The feasibility of studying M_2O species by the infrared matrix isolation technique was considered.

INTRODUCTION

Numerous investigators have used mass spectrometric techniques to study the mode of vaporization of the aluminum family (Al, Ga, In, and Tl) metal oxides (refs. 1 to 9). These studies have established that under neutral conditions (neither reducing nor oxidizing) the condensed-phase sesquioxide (M_2O_3) dissociates at temperatures above 1000 K to yield the gaseous species MO, O, M, and O_2. When reducing conditions prevail, for example, when the condensed-phase sample composition is M + M_2O_3, the predominant vapor components are the suboxide (M_2O) and the metal. Vapor pressure and thermodynamic data for these oxide systems have been obtained from the mass spectrometric studies and studies employing other techniques (refs. 10 to 13).

Our research has been primarily concerned with investigating metal - metal oxide systems containing a mixture of Group IIIA metals. Molecular beam mass spectrometry was used to study the vaporization of samples made up of a metal M plus a sesquioxide of a different Group IIIA metal M'. The metal - metal oxide systems studied consisted of the mixtures indium-gallium, gallium-aluminum, and indium-aluminum. Other work (ref. 14) on families of elements suggested that for such mixed metal systems the vapor components may consist of mixed species of the type $MM'O_x$. Therefore, our study was mainly concerned with identifying new molecules and obtaining thermodynamic information for them.

In the course of our investigation, the Group IIIA ($M + M_2O_3$)-type systems were also examined in some detail. These results are included here as an appendix. The objectives of this work were to confirm the vapor-phase composition and to establish the experimental Knudsen effusion conditions to be used in an infrared matrix isolation study of the Group IIIA metal suboxides (refs. 15 and 16). This part of our study was a collaborative effort with Drs. D. M. Makowiecki, D. A. Lynch, and K. D. Carlson of Case Western Reserve University, who supplied the sample materials and provided many insights through discussions.

APPARATUS

The Knudsen cell, double-focusing mass spectrometer system used in this study is basically the same as described previously (refs. 17 and 18). Both tungsten and tantalum Knudsen cells were used. The cells were fitted with yttria-stabilized zirconia (ZrO_2) liners which had an outside diameter of 1.27 centimeters and a wall thickness of 0.13 centimeter. A 0.15-centimeter-thick, flat lid was used to close the liners. A 0.25-centimeter-diameter hole in the side wall of the liners was arranged to line up concentrically with the effusion orifice in the metal cell. For the tungsten cells the orifice diameter was 0.13 centimeter and for the tantalum cells it was 0.10 centimeter.

All temperatures were measured with a Chromel-Alumel thermocouple. The 0.127-millimeter-diameter thermocouple wire was contained in a double-bore aluminum oxide sheath and the junction was made just outside the end of the sheath. The thermocouple was inserted into a vertical well located in the cell wall.

All ion species were identified by their mass-charge ratio m/e and isotopic abundance distribution. For all measurements the resolution of the spectrometer was approximately 1500 based on the 10-percent-valley definition (ref. 19). This resolution was sufficient to separate clearly the metal and metal oxide peaks from any background peaks present at the same nominal mass-charge ratio. Furthermore, there was no ambiguity in the assignment of the spectra because of the absence of overlapping peaks except in the case of the In-Al-O system. A movable shutter between the Knudsen cell and ion source was used to establish which ion species had neutral precursors originating in the Knudsen cell. The shutter effect for all ions containing aluminum (Al), gallium (Ga), or indium (In) was 100 percent. Intensities, multiplier gains, and appearance potentials were measured by previously described techniques (ref. 18).

Commercially available materials were used in all sample preparations. Table I lists the materials used, with their nominal purity and the metallic impurities that were detected by emission spectroscopy. Visual inspection, X-ray diffraction analysis, and emission spectroscopic analysis of the sample residue after each experiment showed that there was no interaction between the samples and the zirconia liners.

TABLE I. - SAMPLE MATERIALS

Material	Nominal purity, percent	Trace metallic impurities[a]
Al	---------	Fe
Al_2O_3	Ultrapure	None
Ga	99.999	In
Ga_2O_3	99.99	None
In	---------	Cr
In_2O_3	99.999	None

[a] Detected by emission spectroscopy.

PROCEDURE AND RESULTS

Vapor Species Identification

In-Ga-O system. - A 0.47-gram mixture of In and Ga_2O_3 in a mole ratio of approximately 4 to 1 was loaded into the zirconia liner in a tantalum Knudsen cell. This sample was degassed at 770 K for 18 hours before the temperature was rapidly raised to 1109 K. The Ga_2O^+ ion peak was monitored as a function of time and temperature. Although the ion current of each species listed in table II was found to increase monotonically with increasing temperature, the In^+ and Ga^+ ion currents decreased with time after the sample had reached thermal equilibrium. Consequently, the intensity of the oxide ions (Ga_2O^+, In_2O^+, and $InGaO^+$) relative to the metal ions increased for considerable times after thermal equilibrium was attained. Once the relative intensities of the major ionic species being considered became constant, the entire mass spectrum was recorded and other measurements were initiated. Table II lists the relative intensities and measured appearance potentials of all In- and Ga-containing ions observed. These appearance potentials indicated that In_2O, Ga_2O, and InGaO along with atomic In and Ga were the neutral molecules of major significance in the vapor phase. In_2O_2, Ga_2O_2, and $InGaO_2$ were low enough in abundance to be considered as minor molecular species. The high appearance-potential values obtained for the M_2^+ and MO^+ ions imply that these were

TABLE II. - GALLIUM- AND INDIUM-CONTAINING VAPOR SPECIES DETECTED AT 1320 K OVER THE MIXTURE In(l) + Ga_2O_3(s)

[30-eV electrons.]

Ion	Relative intensity	Appearance potential, eV	Parent species
Ga^+	2.7×10^{-1}	6.0±0.1	Ga, Ga_2O
GaO^+	3.6×10^{-3}	15.0±0.4	Ga_2O
GaO_2^+	9.2×10^{-4}	(a)	Ga_2O_2
In^+	1.0	[b]5.79	In, In_2O
InO^+	7.1×10^{-4}	14.8±0.5	In_2O
Ga_2^+	7.7×10^{-2}	14.5±0.4	Ga_2O
InO_2^+	2.2×10^{-5}	(a)	In_2O_2
Ga_2O^+	9.2×10^{-1}	9.1±0.2	Ga_2O
$Ga_2O_2^+$	1.5×10^{-4}	(a)	Ga_2O_2
$InGa^+$	5.6×10^{-2}	14.0±0.5	InGaO
$InGaO^+$	5.4×10^{-1}	8.7±0.2	InGaO
$InGaO_2^+$	3.0×10^{-4}	(a)	$InGaO_2$
Ga_3O^+	3.8×10^{-5}	(a)	(c)
In_2^+	6.1×10^{-3}	12.9±0.5	In_2O
In_2O^+	5.8×10^{-2}	8.3±0.3	In_2O
$In_2O_2^+$	2.0×10^{-4}	(a)	In_2O_2

[a] Intensity too low for reliable measurement.

[b] Standard for calibration of electron energy scale (ref. 19).

[c] The neutral precursor of this ion may have been Ga_3O or Ga_4O_2. Cubicciotti (ref. 8) has observed the analogous Tl_3O^+ ion over solid Tl_2O.

fragment species resulting from the electron impact fragmentation of other neutral species.

When the sample was held at temperatures above 1120 K, the relative intensities of the major species were observed to vary slightly as a function of time. These variations were probably the result of changes in the activity of the components of the condensed phase. At the conclusion of the experiment the sample residue was a mixture of light-gray powder and a large metallic drop. The X-ray diffraction analysis of the powder showed this material to be monoclinic β-Ga_2O_3. Similar analysis of the metallic drop indicated the presence of metallic In and a second phase which was not identified by

X-ray diffraction. Analysis by X-ray fluorescence and spectroscopic methods showed that In and Ga were the only metals present, demonstrating that external contamination was absent. The unidentified phase could have been an In-Ga alloy or a solid solution, possibly $In_{2-x}Ga_xO_3$ (ref. 20).

Ga-Al-O system. - Metallic Ga and powdered Ga_2O_3 were added to a previously heated Al + Al_2O_3 sample (see appendix) contained in a zirconia liner in a tantalum Knudsen cell. After preliminary heating to outgas the sample, the temperature was raised to 1608 K and the mass spectrum was recorded. Relative intensities measured for this system are listed in table III. Appearance potentials were not measured for the ions observed and it was assumed (by analogy with other M_2O systems) that GaAlO was the parent species that gave rise to the observed $GaAl^+$ ion. A careful search failed to detect $GaAlO_2{}^+$ and under the conditions of the experiment this was equivalent to this ion being less than 1×10^{-6} as intense as the Ga^+ ion. The very low intensities measured for Ga_2O^+ and other Ga-O ions indicates that little Ga_2O_3 was in the condensed-phase sample at the time the spectrum was recorded. Likewise, the very high Ga^+ intensity indicated a relatively high activity for $Ga(l)$. Apparently, the Al reduced the Ga_2O_3 to form Al_2O_3 or an Al-Ga-O mixed oxide (ref. 21). The reduction of Ga_2O_3 by Al to form Al_2O_3 is thermodynamically favored.

TABLE III. - ALUMINUM- AND GALLIUM-CONTAINING VAPOR SPECIES DETECTED AT 1608 K OVER THE MIXTURE $Ga(l) + Al_2O_3(s)$

[30-eV electrons.]

Ion	Relative intensity	Proposed parent species
Al^+	(a)	Al_2O
AlO^+	(a)	Al_2O, AlO
$Al_2{}^+$	(a)	Al_2O
Ga^+	1.0	Ga, Ga_2O
Al_2O^+	7.3×10^{-1}	Al_2O
$Al_2O_2{}^+$	1.2×10^{-4}	Al_2O_2
$GaAl^+$	2.0×10^{-4}	GaAlO
$GaAlO^+$	6.4×10^{-3}	GaAlO
Ga_2O^+	7.4×10^{-6}	Ga_2O

[a]Intensity was not measured.

The X-ray diffraction analysis of the sample residue established the presence of

α-Al_2O_3 and Al. X-ray fluorescence also indicated that Ga was present in the sample residue. No Ga_2O_3 was detected in the residue.

In-Al-O system. - Cursory attempts to identify In-Al mixed molecules were carried out using samples consisting of mixtures of In_2O_3 + Al_2O_3 or In_2O_3 + Al + Al_2O_3. Although very low intensity peaks possibly corresponding to $InAlO^+$ and $InAl^+$ ions were noted, experimental difficulties precluded positive identifications.

Atomization Energy of InGaO(g)

For these measurements the starting solid material consisted of In metal plus Ga_2O_3 powder. After outgassing and suitable preheating, the ion intensities of In_2O^+, Ga_2O^+, and $InGaO^+$ were measured at 13 temperatures in the range from 973 to 1168 K. The isomolecular gas-phase reaction

$$In_2O(g) + Ga_2O(g) = 2\ InGaO(g) \tag{1}$$

was used to obtain thermodynamic data for the InGaO molecule. It was assumed that this reaction proceeded under near-equilibrium conditions even though complications in the vaporization and condensed-state reaction processes are known to exist. In the course of several exploratory experiments with different In-Ga-O starting compositions, it was noted that while the relative intensities of In_2O^+, Ga_2O^+, and $InGaO^+$ varied considerably, the value of the equilibrium constant K_p remained essentially unchanged at a given temperature.

The equilibrium constant for reaction (1) is given by

$$K_p = \frac{\left[P_{InGaO(g)}\right]^2}{P_{In_2O(g)} \times P_{Ga_2O(g)}} \tag{2}$$

where the P represents the partial pressure of the gas designated by the respective subscripts. Measured intensities are related to pressures through the expression

$$P = \frac{kITE}{\gamma\sigma n} \tag{3}$$

where k is the pressure-relating, apparatus calibration constant; I is the measured intensity; T is the absolute temperature; E is the ionization efficiency correction term; γ is the multiplier gain; σ is the ionization cross section; and n is the isotopic abundance of the peak measured. For molecules of the same type (e.g., M_2O), it is reasonable to assume that the E, γ, and σ terms are approximately equal. Therefore, substituting the respective values of equation (3) into equation (2) yields

$$K_p = \frac{(I_{InGaO^+})^2}{I_{In_2O^+} \times I_{Ga_2O^+}} \tag{4}$$

where the intensity terms are corrected for isotopic abundance. Thus the equilibrium constant for reaction (1) can be obtained directly from measured ion intensities.

The second-law heat of reaction (1) was determined from the slope of the log K_p-against-1/T plot given in figure 1. The experimentally determined values of K_p at each temperature are listed in table IV. The line through the data points shown in the figure is a least-squares fit of the data. This line yielded a second-law heat of -22.2±2.4 kilojoules $mole^{-1}$ at the mean temperature of 1066 K. The uncertainty of 2.4 kilojoules $mole^{-1}$ is the standard deviation of the slope. Using $H_T^o - H_0^o$ values for the respective constituents, the second-law heat corrected to 0 K is -22.2±6.7 kilojoules $mole^{-1}$. The overall estimated error associated with this value was obtained by combining twice the standard deviation with the uncertainty resulting from an estimated maximum temperature error of ±10 K. The estimated error in the sum of the $H_T^o - H_0^o$ values was taken as 4.2 kilojoules $mole^{-1}$.

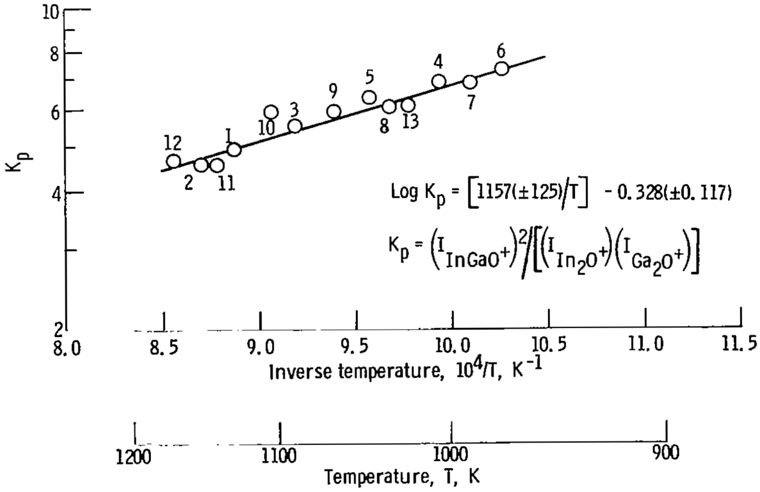

Figure 1. - Second-law plot, log K_p against 1/T for reaction $In_2O(g) + Ga_2O(g) = 2\ InGaO(g)$. Points are numbered in chronological order.

TABLE IV. - EQUILIBRIUM CONSTANTS AND THIRD-LAW HEATS

FOR REACTION $Ga_2O(g) + In_2O(g) = 2InGaO(g)$

Temperature, T, K	Equilibrium constant, K_p	Change of Gibbs free-energy function, $-\Delta\left[\left(G_T^o - H_0^o\right)/T\right]$, J $mole^{-1}$ deg^{-1}	Third-law enthalpy, ΔH_0^o, kJ $mole^{-1}$
1125	4.92	10.57	-3.0
1150	4.51	10.57	-2.3
1087	5.45	10.57	-3.8
1006	6.92	10.58	-5.5
1045	6.51	│	-5.2
973	7.23	│	-5.7
990	6.69	│	-5.2
1031	5.99	↓	-4.4
1066	5.90	10.57	-4.5
1103	5.98	10.57	-4.8
1137	4.57	10.57	-2.4
1168	4.68	10.56	-2.7
1017	6.04	10.58	-4.5
Third-law average ΔH_0^o			-4.1±6.3
Second-law ΔH_0^o			-22.2±6.7

The third-law heat of reaction (1) was calculated from the relation

$$\Delta H_0^o = -2.303\ RT \log K_p - T\left[\Delta\left(\frac{G_T^o - H_0^o}{T}\right)\right] \tag{5}$$

where R is the gas constant and $\Delta\left[\left(G_T^o - H_0^o\right)/T\right]$ is the change of the Gibbs free-energy function for the reaction. The free-energy functions for $In_2O(g)$, $Ga_2O(g)$, and $InGaO(g)$ were taken from reference 15. The calculated third-law heats for each data point are listed in table IV. The estimated error associated with the listed average value of ΔH_0^o was obtained by combining twice the standard deviation from the mean of all data points with the following estimated uncertainties for the other quantities: K_p, ±50 percent; T, ±10 K; and $\Delta\left[\left(G_T^o - H_0^o\right)/T\right]$, ±4 kilojoules $mole^{-1}$ $degree^{-1}$.

Although the agreement between the second- and third-law heats is acceptable, the second-law value is preferable because the individual third-law values showed a slight temperature dependence.

The second-law heat of reaction (1) was combined with the atomization energies (ref. 3) of $In_2O(g)$ (748.9±17 kJ $mole^{-1}$) and $Ga_2O(g)$ (865.3±29 kJ $mole^{-1}$) to obtain the atomization energy $D^{o}_{0,atom}$ of InGaO:

$$InGaO(g) = In(g) + Ga(g) + O(g) \qquad D^{o}_{0,atom} = 818.2\pm17\ kJ\ mole^{-1}$$

SUMMARY AND DISCUSSION

An interesting aspect of chemical bonding is related to the atomization energy of the InGaO molecule. Hastie, Hauge, and Margrave (ref. 22) have recently pointed out that a useful thermodynamic empirical rule is apparent from studies of families of molecules having the same types of bonds. The rule states that bond energies can be transferred from one molecular species to another if there is no obvious formal change of valence. Previous investigations (refs. 14, and 23 to 25) on various binary and ternary systems have provided the basis for this rule. The bonding in the InGaO molecule seems to follow the rule quite satisfactorily. If we assume that in the series Ga_2O-InGaO-In_2O the molecule consists of only two metal-oxygen bonds (disregarding any metal-metal bonding), the predicted atomization energy of InGaO would be equal to the sum of one Ga-O bond from Ga_2O and one In-O bond from In_2O; that is,

$$\frac{1}{2} D_{0,atom}(Ga_2O) + \frac{1}{2} D_{0,atom}(In_2O) = 807.1\pm34\ kJ\ mole^{-1}$$

This predicted value is in good agreement with the experimental atomization of InGaO of 818.2±17 kilojoules $mole^{-1}$. Using this rule, the atomization energies of GaAlO and InAlO may be estimated as 940 and 880 kilojoules $mole^{-1}$, respectively.

On the basis of the existence of InGaO and GaAlO, we may speculate that the other possible heterometallic Group IIIA M_2O-type molecules exist as stable species. Furthermore, in addition to $InGaO_2$, other $MM'O_2$-type molecules should be stable species. All these are rather interesting from a theoretical standpoint because they form complete classes of molecules having similar bond types with systematically varying bond energies. Their atomization energies may be predicted by use of the empirical correlation previously discussed. The measurements of their dissociation energies and other molecular parameters should be of considerable value to bonding theories.

Results of infrared matrix isolation and electron diffraction studies have shown that the M_2O molecules of the Group IIIA elements are symmetrical structures with the oxygen atom separating the two metals with bond angles of approximately 130° to 150° (ref. 15 and refs. cited therein). Thus, the M_2O molecule could be viewed as a combination of two metal-oxygen bonds. The occurrence of the ν_2 fundamental bending mode for these molecules at relatively high energies has been interpreted by Makowiecki et al.

(refs. 15 and 16) as suggesting the existence of an additional metal-metal bond which yields a ring-type bonding structure which is more rigid than one involving only metal-oxygen bonds. The existence of possible metal-metal bonds has added support from arguments regarding an empirical addition of bond energies (ref. 15). For example, the sum of the dissociation energies of two GaO molecules plus the dissociation energy of Ga_2, that is,

$$2D_0(Ga-O) + D_0(Ga-Ga) = 888.7 \pm 29 \text{ kJ mole}^{-1}$$

is very close to the atomization energy of Ga_2O (865.3±29 kJ mole^{-1}). The mere addition of $2D_0(Ga-O)$ is some 134 kilojoules less. The significant feature of the mass spectra in this regard is the presence of the dimer metal ion M_2^+ as a fragment and the absence of larger concentrations of the diatomic fragment ion MO^+, except for the Al-O system. Cubicciotti (ref. 7) was the first to point out the structural significance of the M_2^+ species. This evidence, however, may be misleading because very little is known about the dynamics of electron impact fragmentation processes. Nevertheless, if metal-oxygen bonds were the only important ones involved in the structure of the M_2O molecules, one would expect to see primarily MO^+ and M^+ fragments.

The investigation of the vaporization of the simple metal oxide systems has confirmed the results of the previous studies. The mass spectra of the vapors over the various aluminum family metal - metal oxide condensed phases (see appendix) indicate that the only vaporization products significant with respect to effusive weight loss or matrix isolation experiments are the M_2O molecules and the atomic species. The identification of the parent molecules and measurements of their relative intensities establishes the feasibility and provides the data for studying these species by the infrared matrix isolation technique. The relative intensities of the minor molecular species can be used to prescribe the experimental conditions required for future structural investigations.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 17, 1971,
129-03.

APPENDIX - VAPORIZATION OF THE INDIUM, GALLIUM, AND ALUMINUM METAL - METAL OXIDE SYSTEMS

The mass spectrometric experiments reported in this appendix were used to supplement some vacuum balance measurements made in conjunction with an infrared matrix isolation study of the Group IIIA metal suboxides (ref. 15). The purpose of the mass spectrometric work was to establish the composition of the vapor under a given set of conditions. These conditions included sample composition, sample size, orifice size, Knudsen cell size, and temperature. Parent molecular vapor species were identified, relative intensities were measured, and approximate vapor pressures were determined.

In-In_2O_3 System

Species identification. - Indium metal and In_2O_3 powder were mixed in a mole ratio of 4 to 1 to prepare a 0.60-gram sample. This sample was loaded into a zirconia liner in a tantalum Knudsen cell with a 0.10-centimeter effusion orifice. After degassing for several hours at approximately 970 K, the sample temperature was raised to 1170 K. The mass spectrum of the effusing vapors was recorded at 1170 K and ionization efficiency curves were recorded for most In-containing species. These results are listed in table V. The relative intensities noted are in good agreement with the values reported

TABLE V. - INDIUM-CONTAINING VAPOR SPECIES DETECTED AT 1173 K OVER THE MIXTURE $In(l) + In_2O_3(s)$

[22-eV electrons.]

Ion[a]	Relative intensity	Appearance potential, eV	Parent species
In^+	7.5×10^{-1}	[b]5.79	In, In_2O
InO^+	1.6×10^{-3}	14.8±0.5	In_2O
InO_2^+	1.4×10^{-5}	(c)	In_2O_2
In_2^+	9.2×10^{-2}	12.9±0.5	In_2O
In_2O^+	1.0	8.3±0.3	In_2O
$In_2O_2^+$	3.2×10^{-4}	(c)	In_2O_2

[a] No other In-containing ions were detected up to m/e ≅ 350.
[b] Standard for calibration of electron energy scale (ref. 19).
[c] Intensity too low for reliable measurements.

by Shchukarev, Semenov, and Rat'kovskii (ref. 4). The measured appearance potential of In_2O^+ (8.3±0.3 eV) agrees with the value of 8.0±0.5 electron volts reported by Burns, DeMaria, Drowart, and Inghram (ref. 6) and indicates that this species is a parent ion formed by the direct ionization of In_2O. The high appearance potentials found for In_2^+ and InO^+ indicate that these species are formed by dissociative ionization (fragmentation) of In_2O. Although ionization efficiency curves could not be measured for InO_2^+ and $In_2O_2^+$, these are probably fragments and parents, respectively. The ionization efficiency curve for In^+ showed no sharp break which might be attributed to the onset of fragmentation. Nevertheless, at high electron energies (>15 eV), some of the In^+ is believed to be formed by fragmentation of In_2O.

In these and other experiments with $In + In_2O_3$ it was observed that when a fresh sample was first heated the intensity of the In_2O^+ peak varied with time. A constant value of the relative intensity of In_2O^+ to In^+ was only obtained after heating to 1120 K. Once the steady value was achieved the relative intensity was found to be a monotonic function of temperature. These observations were taken to indicate that some kinetic barrier had to be overcome before reaction between $In(l)$ and $In_2O_3(s)$ was complete and steady-state vaporization of $In_2O(g)$ could be attained.

Vapor pressure measurements. - Measured ion currents are converted to pressures by the use of equation (3). The calibration constant k is determined experimentally by measuring the ion intensity of a species of known vapor pressure. In this study, pure indium was used to determine k for a fixed Knudsen cell - mass spectrometer geometry, orifice, and set of instrumental parameters.

A sample of In metal was loaded into the zirconia liner in a tungsten Knudsen cell. This sample was degassed overnight at 1130 K. Intensity measurements were begun by locating the In^+ peak in the mass spectrum. All instrumental controls were adjusted to produce the maximum In^+ ion current. Intensities of In^+ were then measured at five temperatures in the range from 937 to 1150 K. Ionization efficiency and multiplier gain were also measured for In^+. Equation (3) was then used to determine a value of k for each temperature at which the intensity of In^+ was measured. The equilibrium vapor pressure of $In(l)$ was taken from Hultgren, Orr, Anderson, and Kelley (ref. 26); the ionization efficiency factor E_{In^+} for 30-electron-volt electrons was found to be equal to unity; the relative cross section $\sigma_{In} = 6.74$ was taken from Mann (ref. 27); the measured multiplier gain γ_{In^+} was determined to be 7.0×10^6. An average of the five measured values of k was used as the calibration constant.

At the conclusion of the calibration measurements a 1.50-gram sample of $In + In_2O_3$ was added to the Knudsen cell. After degassing at 1180 K, the In_2O^+ intensity was measured at four temperatures and $E_{In_2O^+}$ and $\gamma_{In_2O^+}$ were determined to be 1.0 (30-eV electrons) and 6.0×10^6, respectively. The pressures of In_2O calculated are listed in

TABLE VI. - VAPOR PRESSURE

OF $In_2O(g)$ OVER THE MIXTURE

$In(l) + In_2O_3(s)$

[The measurements were made on a 1.50-g sample in a ZrO_2-lined tungsten Knudsen cell with 0.13-cm-diam orifice.]

Temperature, T, K	Pressure, N/m^2
1073	3.85×10^{-1}
1126	1.34
1011	6.21×10^{-2}
923	3.51×10^{-3}

table VI. For the calculation of these pressures, σ_{In_2O} was taken as 0.75 $(2\sigma_{In} + \sigma_O)$ = 11.09, where σ_{In} and σ_O were taken from Mann (ref. 27).

$Ga-Ga_2O_3$ System

The vapor species for this system were identified and discussed in the main text in the section on the In-Ga-O system.

For calibration purposes a sample of pure Ga was loaded into the zirconia liner in a tungsten Knudsen cell with a 0.13-centimeter-diameter effusion orifice. Similar to the In^+ case, intensities were measured at four temperatures in the range from 1073 to 1263 K and E_{Ga^+} and γ_{Ga^+} were measured. The constant k was calculated using vapor pressures for $Ga(l)$ taken from reference 26. The relative cross section $\sigma_{Ga} = 5.12$ was taken from Mann (ref. 27) and it was found that $E_{Ga^+} = 1.0$ (30-eV electrons) and $\gamma_{Ga^+} = 6.0\times10^6$. An average k was calculated and used in the pressure calculations.

A 0.89-gram Ga + Ga_2O_3 sample was added to the Knudsen cell and this was outgassed overnight at temperatures ranging to 1160 K. Ga_2O^+ intensities were then measured at four temperatures and the pressures listed in table VII were calculated. For the calculations, measured values of $\gamma_{Ga_2O^+} = 5.7\times10^6$ and $E_{Ga_2O^+} = 1.0$ were used. The relative cross section σ_{Ga_2O} was taken as 0.75 $(2G_{Ga} + G_O) = 8.66$, where σ_{Ga} and σ_O were obtained from Mann (ref. 27).

TABLE VII. - VAPOR PRESSURE OF $Ga_2O(g)$ OVER THE MIXTURE

$Ga(l) + Ga_2O_3(s)$

[The measurements were made on a 0.89-g sample in a ZrO_2-lined tungsten Knudsen cell with 0.13-cm-diam orifice.]

Temperature, T, K	Pressure, N/m^2
1175	1.10
1230	2.33
1140	4.11×10^{-1}
1076	7.80×10^{-2}

Al-Al_2O_3 System

A 0.19-gram sample was prepared by mixing powdered Al and α-Al_2O_3 in a mole ratio of approximately 4 to 1. This sample was contained in a zirconia liner in a tantalum Knudsen cell. The effusion orifice was 0.10 centimeter in diameter. The sample was outgassed at 1120 K for several hours before the temperature was raised to 1531 K and the mass spectrum was recorded. Relative intensities and measured appearance potentials for the various Al-containing species are given in table VIII. Except for the low-intensity AlO_2^+ species, the detected ions are the same as those reported in the literature (refs. 1 and 2).

The appearance potentials of Al^+ and Al_2O^+ indicate that these were parent species formed at low electron energies by the ionization of Al and Al_2O. In general, the recorded ionization efficiency curves for each ion species had a normal shape characterized by a linear threshold region, a region of maximum intensity between 20 and 40 electron volts, and a region of slowly decreasing intensity at higher electron energies. One exception was the curve for AlO^+ which had a break at 16.1±0.5 electron volts. This break is believed to be due to the onset of the formation of AlO^+ by the fragmentation of Al_2O. The appearance potential value of 10.0±0.5 electron volts corresponds to simple ionization of AlO. Although appearance potentials could not be measured for AlO_2^+ and $Al_2O_2^+$ because of their extremely low intensity, Al_2O_2 is probably the parent molecule for both these ions.

This experiment confirms previous studies and shows that Al_2O and Al are indeed the only high-intensity species in the vapor phase over the mixture $Al + Al_2O_3$ at the temperature of this investigation.

TABLE VIII. - ALUMINUM-CONTAINING VAPOR SPECIES DETECTED AT 1531 K OVER THE MIXTURE $Al(l) + Al_2O_3(s)$

[30-eV electrons.]

Ion[a]	Relative intensity	Appearance potential, eV	Parent species
Al^+	7.3×10^{-1}	[b]5.98	Al, Al_2O
AlO^+	1.2×10^{-2}	10.0±0.5	AlO[c]
		16.1±0.5	Al_2O
Al_2^+	7.3×10^{-3}	16.5±0.5	Al_2O
AlO_2^+	7.0×10^{-6}	(d)	Al_2O_2
Al_2O^+	1.0	8.0±0.1	Al_2O
$Al_2O_2^+$	2.8 ± 10^{-4}	(d)	Al_2O_2

[a] No other Al-containing ions were observed up to m/e ≅ 150.
[b] Standard for calibration of electron energy scale (ref. 19).
[c] The AlO^+ ion fraction which had an appearance potential of 10.0±0.5 eV was less than 2 percent of the total AlO^+ ion current.
[d] Intensity was too low for reliable measurements.

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NASA-Langley, 1971 —— 6 E-6140