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DISSOCIATION ENERGIES OF SOME  
HIGH TEMPERATURE MOLECULES  
CONTAINING ALUMINUM

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| 16. Abstract<br>The Knudsen cell mass spectrometric method has been used to investigate the gaseous molecules $Al_2$ , $AlSi$ , $AlSiO$ , $AlC_2$ , $Al_2C_2$ , and $AlAuC_2$ . Special attention was given to the experimental considerations and techniques needed to identify and to measure ion intensities for very low abundance molecular species. Second- and third-law procedures were used to obtain reaction enthalpies for pressure calibration independent and isomolecular exchange reactions. Dissociation energies (in $kJ\ mol^{-1}$ ) for the molecules were derived from the measured ion intensities, free-energy functions obtained from estimated molecular constants, and auxiliary thermodynamic data: $Al_2$ , $D_0^0 = 149.8 \pm 14$ ; $AlSi$ , $D_0^0 = 225.5 \pm 30$ ; $AlSiO$ , $D_{0,atoms}^0 = 996.3 \pm 20$ ; $Al_2C_2$ , $D_{0,atoms}^0 = 1507 \pm 25$ ; $AlC_2$ , $D_{0,atoms}^0 = 1104 \pm 21$ ; and $AlAuC_2$ , $D_{0,atoms}^0 = 1418 \pm 21$ . The bonding and stability of these aluminum-containing molecules are compared with other similar species. |  |   |                      |
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# DISSOCIATION ENERGIES OF SOME HIGH TEMPERATURE

## MOLECULES CONTAINING ALUMINUM\*

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### SUMMARY

The Knudsen cell mass spectrometric method has been used to investigate the gaseous molecules  $\text{Al}_2$ ,  $\text{AlSi}$ ,  $\text{AlSiO}$ ,  $\text{AlC}_2$ ,  $\text{Al}_2\text{C}_2$ , and  $\text{AlAuC}_2$ . Parent molecular species were established on the basis of measured appearance potentials. Special attention was given to the experimental considerations and techniques needed to identify and to measure ion intensities for very low abundance molecular species. Second- and third-law procedures were used to obtain reaction enthalpies for pressure calibration independent and isomolecular exchange reactions. Dissociation energies for the molecules were derived from the measured ion intensities, free-energy functions obtained from estimated molecular constants, and auxiliary thermodynamic data:

| Reaction  | Third-law<br>$\Delta H_0^\circ$ ,<br>$\text{kJ mol}^{-1}$ | $D_0^\circ$ , atoms,<br>$\text{kJ mol}^{-1}$ |
|---|---|--|
| $\text{AlAu(g)} + \text{Al(g)} = \text{Al}_2\text{(g)} + \text{Au(g)}$                          | 171.5±18  | } $\text{Al}_2$ , 149.8±14                   |
| $2\text{AlAu(g)} = \text{Al}_2\text{(g)} + \text{Au}_2\text{(g)}$                               | 273.7±18  |  |
| $\text{Al(g)} + \text{Si}_2\text{C(g)} + \text{C(s)} = \text{AlSi(g)} + \text{SiC}_2\text{(g)}$ | 296.1±19  | $\text{AlSi}$ , 225.5±30                     |
| $\text{Al}_2\text{O(g)} + \text{Si(g)} = \text{AlSiO(g)} + \text{Al(g)}$                        | 47.2±16   | $\text{AlSiO}$ , 996.3±20                    |
| $\text{Al(g)} + 2\text{C(s)} = \text{AlC}_2\text{(g)}$  | 315.1±21  | $\text{AlC}_2$ , 1104±21                     |
| $\text{Al}_2\text{(g)} + 2\text{C(s)} = \text{Al}_2\text{C}_2\text{(g)}$                        | 61.4±20   | $\text{Al}_2\text{C}_2$ , 1507±25            |
| $\text{AlAu(g)} + 2\text{C(s)} = \text{AlAuC}_2\text{(g)}$                                      | 323.4±20  | $\text{AlAuC}_2$ , 1418±21                   |

The dissociation energies and bonding of these molecules are compared with previously reported literature values and with other similar molecules.

\*An abbreviated account of this work was presented as a technical paper at the twentieth Annual Conference on Mass Spectrometry and Allied Topics, sponsored by The American Society of Mass Spectrometry and the American Society for Testing and Materials Committee E-14, Dallas, Texas, June 4-9, 1972.

## INTRODUCTION

Aluminum-containing alloys, coatings, and ceramics are being used widely in high temperature materials applications. The continued interest in the vaporization thermodynamics and structures of high temperature molecules containing aluminum (and other Group IIIA elements) is evident from the number of recent papers on this topic. The thermodynamic properties of the aluminum chalcogenides (refs. 1 and 2) are fairly well established although there is still controversy concerning the structural parameters (refs. 2 to 5) of some of the molecular species. Recently, the dissociation energies of a number of other aluminum containing molecules (i. e. ,  $\text{Al}_2$  (refs. 2 and 6),  $\text{AlAg}$  (ref. 6),  $\text{AlCu}$  (refs. 2 and 6),  $\text{AlAu}$  (refs. 6 and 7),  $\text{Al}_2\text{N}$  (ref. 8),  $\text{AlOCN}$  (ref. 9),  $\text{AlCN}$  (ref. 10),  $\text{AlP}$  (ref. 11),  $\text{AlP}_2$  (ref. 12),  $\text{Al}_2\text{C}_2$  (ref. 13),  $\text{AlGaO}$  (ref. 14), and  $\text{AlBO}$  (ref. 15)) have been determined.

In the present study, the Knudsen cell mass spectrometric method has been used to investigate the stability of the gaseous molecules  $\text{Al}_2$ ,  $\text{AlSi}$ ,  $\text{AlSiO}$ ,  $\text{AlC}_2$ ,  $\text{Al}_2\text{C}_2$ , and  $\text{AlAuC}_2$ . The primary objective of this work has been to establish the nature of high temperature chemical reactions for some aluminum-containing molecules and to obtain experimental thermochemical data which can be used to elucidate certain basic thermodynamic properties of simple gaseous molecules.

The authors would like to thank Dr. Kenneth R. Thompson of the Dupont Experimental Station for providing some of the sample materials.

## EXPERIMENTAL CONSIDERATIONS AND PROCEDURE

### Mass Spectrometer

For the experimental program an original design Knudsen cell inlet has been coupled to a commercial double focusing mass spectrometer as described previously (ref. 16). A short summary of the apparatus and general technique is given here. The physical arrangement is such that the neutral molecular beam emanating from the Knudsen cell is coaxial with the ion beam produced by electron impact (see fig. 1).

Located between the Knudsen cell and the ion source chamber is a movable shutter slit which is used to intercept or maximize the transmission of the condensable molecular beam.

The Knudsen cell, ion source, and mass analyzer are each contained in separate vacuum chambers which are interconnected but differentially pumped. The mass analyzer is of the Mattuch-Herzog type and is operated at a resolution of approximately 2000 based on the 10-percent valley definition. Ion intensities are measured with an electron multiplier and vibrating reed electrometer. The 17-stage focused Allen type multiplier is operated

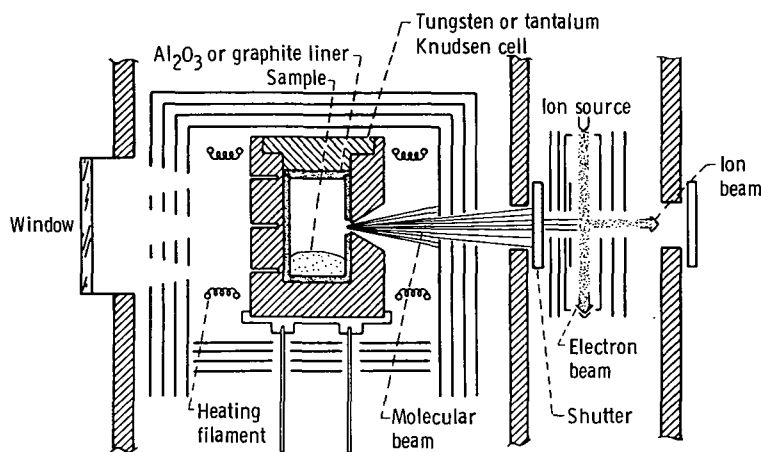


Figure 1. - Knudsen cell assembly and ion source.

at up to 256 volts per stage with a maximum gain of approximately  $10^7$ . The sensitivity and dynamic range of the apparatus provide the ability to measure partial pressures in the Knudsen cell from  $10^{-3}$  to  $10^{-10}$  atmosphere.

The mass spectrometer design requires a somewhat unconventional Knudsen cell with the effusion orifice ( $\sim 1$  mm diameter) in the side wall rather than in the top. In the present investigation the sample materials are contained in graphite or alumina liners in either tungsten or tantalum cells. The cell is heated by radiation and electron bombardment from two independently powered tungsten ribbon filaments circumscribing the cell at locations near its top and bottom. Tantalum heat shields completely surround the cell. The cell and shield assembly can be remotely moved in two orthogonal directions relative to the shutter slit and ion source entrance slit. Cell temperatures are measured by sighting a calibrated optical pyrometer into the three blackbody holes located at different heights on the side of the cell opposite the orifice. The depth to diameter ratio of each hole is at least 9 to 1. The necessary window transmission corrections are made (ref. 17). By appropriate adjustment of the power to each heating filament, the temperature read at each blackbody hole can be made identical within the precision of the pyrometer. The location of the effusion orifice in the side of the massive cell wall effectively prevents the orifice from being cooler than other parts of the cell.

## Measurement of Low Concentration Molecular Species

Because all of the aluminum-containing molecules studied here exist in low concentration in their equilibrium vapors, special attention is paid to the experimental considerations and techniques needed to measure accurately the concentration of these molecules.

The basic procedures for determining thermodynamic properties of high temperature gaseous species by the techniques of molecular beam mass spectrometry are well established (refs. 18 and 19). The fundamental relationship used to derive thermodynamic data from mass spectral measurements is the equation relating partial pressure  $P$  of a species to its measured ion intensity  $I$ :

$$P = \frac{kIT}{\sigma \gamma n} \quad (1)$$

where  $k$  is the pressure relating sensitivity constant,  $T$  the temperature of the sample in the Knudsen cell,  $\sigma$  the electron impact ionization cross section,  $\gamma$  the multiplier gain, and  $n$  the isotopic abundance for the ion measured. The calibration constant  $k$  can be determined by established procedures (refs. 18 and 19). Alternately, if use is made of pressure calibration independent reactions or isomolecular exchange reactions, the  $k$  factors cancel one another in expressions for equilibrium constants and need not be determined experimentally. In general, cross sections are normally taken from the work of Mann (ref. 20) or others while the multiplier gain can be determined experimentally or estimated by empirical relations.

Normally, for the major vapor phase components of any system, ion intensity measurements are made without difficulty by conventional techniques, and the resultant thermodynamic quantities are both accurate and precise. However, several special considerations are required when reliable ion intensity measurements are to be carried out on very low abundance molecular species. The most common type of error is the recording of an apparent ion intensity which is higher than the true value. Possible contributions to such an erroneously high value are:

- (1) The recording of background organic ions whose precursors originate in the neighborhood of the heated cell and exhibit a partial shutter effect
- (2) Isotopes of metallic ions which arise from metallic impurities on the ppm level in the samples
- (3) Isotopes of metallic ions of a different composition which arise from other molecular species in the system
- (4) Fragment metal ions formed by electron impact bombardment of larger molecular species

If any of these interferences are unrecognized in the measurement of an ion intensity, the molecular species under consideration will appear to have a higher intensity, resulting in a high value for its (third-law) dissociation energy.

In the present study we have recognized these four sources of interference and have tried to eliminate them:

- (1) All ion species were identified by their mass to charge ( $m/e$ ) ratio and isotopic abundance. For all measurements the resolution of the spectrometer was approximately

2000 which was sufficient to separate clearly the metal-containing peaks from any organic background peaks present at the same nominal  $m/e$  ratio. This feature of high resolution operation is imperative for the positive identification of low flux molecular species emanating from the Knudsen cell.

(2) and (3) In addition to the resolution of metal-containing ions from organic ions, it is necessary to separate metallic isotopes at the same nominal  $m/e$  from other inorganic ions at the same nominal  $m/e$  (high resolution inorganic mass spectrometry). An example of this is the measurements on  $Al_2^+$  which will be discussed subsequently. However, if the attainable resolution is insufficient to provide usable separation, the contribution to a low ion intensity by a nonresolvable isotope can be subtracted out by proper interpretation of the spectra. This procedure is employed in the measurements on  $AlSi^+$ . An alternate method of bypassing isotopic interference is to substitute an isotope in the ion being studied. This method is illustrated in the measurements on  $AlSiO^+$ .

(4) Normally the method used to avoid the problem of metallic fragmentation contributions is to employ ionizing electrons of sufficiently low energy (i. e. , several volts above the appearance potential) so that fragmentation reaction cross sections are negligible or zero. In some instances this procedure may lead to difficulty because the resultant parent ion intensities are also proportionally smaller due to smaller ionization cross sections at low energies. In addition, because the variation of cross section with electron energy is not well defined (Mann's cross sections (ref. 20) represent the maximum of the ionization efficiency curve), the approximations needed to correct the ion intensity recorded at a reduced energy to the maximum may introduce significant errors in the final values. This problem can be eliminated in some cases by the selection of sample composition and stoichiometry so that no parent molecules exist in sufficient concentration to yield fragment ion intensities of importance. This concept is discussed in regard to the measurements on the  $Al_2(g)$  molecule.

Other sources of error common to mass spectrometric measurements in general are the improper determination of relative multiplier gains and ionization cross sections at the ion source electron bombardment energy. The multiplier gain problem can be eliminated by the use of an ion counting system. (This technique was not used in the present study.) The cross section problem can only be handled at present for most systems by making reasonable estimates of atomic and molecular cross sections.

## Samples and Measurements

A list of the starting materials used in the vaporization experiments is given in table I along with the source and analysis of the samples.

$Al_2$ . - The diatomic molecule  $Al_2(g)$  was studied by vaporizing a mixture of aluminum

TABLE I. - SOURCE AND PURITY OF SAMPLES

| Material                                      | Source                        | Nominal purity, percent | Analysis  |   |
|---|-------------------------------|-------------------------|---|---|
|   |                               |                         | Supplied by manufacturer  | In-house emission spectroscopy                              |
| Al  | Spex Industries, Inc.         | 99.99+                  | Pb (10-20 ppm);<br>Mg, Si, Cu (5-10 ppm)  | Cu, Fe (weak); Ag, Mg, Si (very weak);<br>Pb (faint trace)  |
| Au  | Sigmund Cohn Corp.            | 99.9999                 | -----   | Ag, Cu (trace); Mg, Pb, Si (faint trace)                    |
| C (graphite)                                  | Ultra Carbon Co.              | Grade UF4S              | Al, Fe, Mg, Si (trace)  | B, Ca, Cu, Fe, Mg, Si (faint trace)                         |
| Si  | Spex Industries, Inc.         | 99.9999                 | Mg, Cu (0.1-0.5 ppm)  | Fe, Ag (trace); Mg, Pb (faint trace)                        |
| SiO <sub>2</sub>                              | Spex Industries, Inc.         | 99.9999                 | Mg (0.5-1.0 ppm);<br>Al, Fe, Cu (0.1-0.5 ppm)                                       | Ag (trace); Mg (faint trace)                                |
| Al <sub>2</sub> O <sub>3</sub>                | Spex Industries, Inc.         | 99.9999                 | Ag, Si (0.5-1.0 ppm);<br>Mg, Fe, Cu, Ca (0.1-0.5 ppm)                               | Ag, Fe, Mg (very weak); Cu, Si (trace);<br>Ni (faint trace) |
| SiO <sub>2</sub> ( <sup>30</sup> Si enriched) | Oak Ridge National Laboratory | -----                   | Zn (<0.2 percent); Na (0.1 percent); W (~0.1 percent); other metals (<0.05 percent) | Fe (trace); Ca, Cu, Mg, Ni (faint trace)                    |

TABLE II. - IONS OBSERVED IN THE Al-Au SYSTEM

| Ion                            | Relative intensity (1940 K, 30 eV) | Appearance potential, eV |                   | Parent species    |
|--------------------------------|------------------------------------|--------------------------|-------------------|-------------------|
|                                |                                    | Present work             | Literature (ref.) |                   |
| Al <sup>+</sup>                | 1.00                               | Standard                 | 5.984(21)         | Al                |
| Al <sub>2</sub> <sup>+</sup>   | 2.9×10 <sup>-5</sup>               | 5.4±1.0                  | -----             | Al <sub>2</sub>   |
| Al <sub>2</sub> O <sup>+</sup> | 7.2×10 <sup>-4</sup>               | (a)                      | -----             | Al <sub>2</sub> O |
| Au <sup>+</sup>                | 2.4×10 <sup>-1</sup>               | Standard                 | 9.22(21)          | Au                |
| AlAu <sup>+</sup>              | 1.5×10 <sup>-1</sup>               | 7.6±0.3                  | -----             | AlAu              |
| Au <sub>2</sub> <sup>+</sup>   | 8.7×10 <sup>-5</sup>               | 9.5±0.3                  | 9.2(22)           | Au <sub>2</sub>   |
|                                |                                    |                          | 9.7(23, 24)       |                   |

<sup>a</sup>Not measured.

(0.300 g) and gold (1.143 g) from a graphite liner in a tantalum Knudsen cell. The gold was used as a source of AlAu molecules and to reduce the activity of aluminum. Table II lists the relative intensities of the ions observed at a cell temperature of 1940 K along with the measured appearance potentials and probable parent species. The low appearance potentials measured for Al<sub>2</sub><sup>+</sup>, AlAu<sup>+</sup>, and Au<sub>2</sub><sup>+</sup> indicated that these ions had the diatomic molecules as their parents.

The mass spectrum peak at nominal  $m/e = 54$  corresponding to the <sup>54</sup>Al<sub>2</sub><sup>+</sup> ion (mass = 53.9631 amu) was resolved from the organic background ions (mass = 54.0+ amu) and also sufficiently resolved from the <sup>54</sup>Fe<sup>+</sup> impurity peak (mass = 53.9396 amu) to allow reliable measurements. The identification of the <sup>54</sup>Fe<sup>+</sup> was confirmed by measurement of



the  $^{56}\text{Fe}^+$  and  $^{57}\text{Fe}^+$  ions. Another possible interfering metallic impurity ion which could show up at  $m/e$  54 is  $\text{Cr}^+$ . The absence of chromium was shown by the absence of the  $^{52}\text{Cr}^+$  and  $^{53}\text{Cr}^+$  ions. The only other interference expected at  $m/e$  54 would be the  $\text{Al}_2^+$  fragment contributions from the  $\text{Al}_2\text{O}$  species which is normally present in the vapor over a condensed phase containing aluminum in a reducing system (i. e. ,  $\text{Al}-\text{Al}_2\text{O}_3$ ) (ref. 25). The containment of the sample in the graphite liner served to reduce the aluminum oxide present. Nevertheless, a low intensity  $\text{Al}_2\text{O}^+$  parent ion was still observed. Based on previous data which gave the ratio of fragment  $\text{Al}_2^+$  to parent  $\text{Al}_2\text{O}^+$  at an ionizing energy of 30 electron volts ( $\sim 7 \times 10^{-3}$ ) (ref. 14), the fragment  $^{54}\text{Al}_2^+$  contribution to the total  $^{54}\text{Al}_2^+$  intensity could be determined. Thus, the  $\text{Al}_2\text{O}^+$  intensity was measured at each experimental temperature and the correction applied. The correction generally amounted to about 30 percent of the total  $^{54}\text{Al}_2^+$  intensity.

Measurements of ion intensities for  $\text{Al}^+$ ,  $\text{Al}_2^+$ ,  $\text{Al}_2\text{O}^+$ ,  $\text{Au}^+$ ,  $\text{AlAu}^+$ , and  $\text{Au}_2^+$  were made at eight temperatures in the 1921 to 2032 K range.

AlSi. - The molecule  $\text{AlSi}(\text{g})$  was investigated by vaporizing a mixture of aluminum (0.032 g) and silicon (0.103 g) from a graphite liner in a tantalum Knudsen cell. Table III lists the relative intensities of the ions observed at a cell temperature of 2039 K along with the measured appearance potentials and parent species. The appearance potentials measured for the well established  $\text{SiC}_2^+$  and  $\text{Si}_2\text{C}^+$  ions agree with the literature values (ref. 26) and establish  $\text{SiC}_2^+$  and  $\text{Si}_2\text{C}^+$  as parent ions along with  $\text{Al}^+$ ,  $\text{Si}^+$ , and  $\text{AlSi}^+$ .

The  $\text{AlSi}^+$  was identified by shutter measurements and isotopic distribution. The major  $\text{AlSi}$  isotope is at nominal  $m/e$  55 and the only interfering ion was the  $^{55}\text{SiC}_2^+$  ( $^{30}\text{Si}^{12}\text{C}^{13}\text{C}^+$ ). The resolution was insufficient to separate clearly  $^{27}\text{Al}^{28}\text{Si}^+$  (mass = 54.9585 amu) from  $^{28}\text{Si}^{12}\text{C}^{13}\text{C}^+$  (mass = 54.9771 amu). Thus, the contribution of  $^{55}\text{SiC}_2^+$  was calculated from the intensity of the major  $^{28}\text{Si}^{12}\text{C}_2^+$  peak at  $m/e$  52 and subtracted from the measured  $m/e$  55 intensity. In general, the  $^{55}\text{SiC}_2^+$  contribution amounted to

TABLE III. - IONS OBSERVED IN THE Al-Si-C SYSTEM

| Ion                       | Relative intensity<br>(2039 K, 30 eV) | Appearance potential, eV |                    | Parent species  |
|---------------------------|---------------------------------------|--------------------------|--------------------|---|
|                           |                                       | Present work             | Literature (ref. ) |   |
| $\text{Al}^+$             | 1.00                                  | Standard                 | 5.984(21)          | Al  |
| $\text{Si}^+$             | $\sim 6 \times 10^{-2}$               | Standard                 | 8.149(21)          | Si  |
| $\text{SiC}^+$            | $\sim 6 \times 10^{-4}$               | (a)                      | 9.0(26)            | $\text{SiC}$ , $\text{SiC}_2$ , $\text{Si}_2\text{C}$ |
| $\text{SiC}_2^+$          | $9.3 \times 10^{-3}$                  | 10.1 $\pm$ 0.5           | 10.2(26)           | $\text{SiC}_2$  |
| $\text{Si}_2^+$           | $\sim 4 \times 10^{-4}$               | (a)                      | 7.3(26)            | $\text{Si}_2$ , $\text{Si}_2\text{C}$                 |
| $\text{AlSi}^+$           | $5.7 \times 10^{-5}$                  | 6.5 $\pm$ 1.0            | -----              | AlSi  |
| $\text{Si}_2\text{C}^+$   | $1.7 \times 10^{-2}$                  | 9.0 $\pm$ 0.5            | 9.1(26)            | $\text{Si}_2\text{C}$                                 |
| $\text{Si}_2\text{C}_2^+$ | $\sim 1 \times 10^{-6}$               | (a)                      | -----              | $\text{Si}_2\text{C}_2$                               |

<sup>a</sup>Not measured.

less than 5 percent of the  $m/e$  55 peak intensity. The only other interference expected at  $m/e$  55 would be  $^{55}\text{Mn}^+$ . Spectroscopic analysis of the sample and crucible materials indicated that manganese was not present and no evidence of it was seen in the mass spectrum.

Measurement of ion intensities for  $\text{Al}^+$ ,  $\text{SiC}_2^+$ ,  $\text{AlSi}^+$ , and  $\text{Si}_2\text{C}^+$  were made at twelve temperatures in the 1988 to 2080 K range.

AlSiO. - The molecule  $\text{AlSiO}(\text{g})$  was investigated by vaporizing mixtures of Al,  $\text{Al}_2\text{O}_3$ , Si, and  $\text{SiO}_2$  or Al,  $\text{Al}_2\text{O}_3$ , and  $\text{SiO}_2$ . In the initial experiments mixtures of Al,  $\text{Al}_2\text{O}_3$ , Si, and  $\text{SiO}_2$  were heated in a Morganite  $\Delta\text{RR}$  alumina liner in a tungsten Knudsen cell.

The nominal mass to charge ratio for the major isotope of the normal abundance  $\text{AlSiO}^+$  ion is 71. The mass spectrum recorded for a sample temperature of about 1700 K showed a shutterable peak at  $m/e$  71 plus peaks at 69, 70, 72, and 73 in addition to other ions. The relative intensities of these peaks were  $I_{69} = 4 \times 10^{-4}$ ,  $I_{70} = 1.0$ ,  $I_{71} = 1.5 \times 10^{-3}$ ,  $I_{72} = 2 \times 10^{-3}$ , and  $I_{73} = 2 \times 10^{-5}$ . Direct positive identification of  $^{71}\text{AlSiO}^+$  could not be made for several reasons. First, the  $^{70}\text{Al}_2\text{O}^+$  concentration was sufficiently large to produce a significant contribution from its  $^{27}\text{Al}_2^{17}\text{O}^+$  isotope to the 71 peak ( $^{70}\text{Al}_2\text{O}/^{71}\text{Al}_2\text{O} = 2.67 \times 10^3$ ). Secondly, the peak at  $m/e$  69 could only be attributed to  $^{69}\text{Ga}^+$  with a corresponding  $^{71}\text{Ga}^+$  isotope arising from residual gallium in the system from previous runs. By subtracting the relatively large  $^{71}\text{Ga}^+$  and  $^{71}\text{Al}_2\text{O}^+$  contributions from the recorded intensity of  $m/e$  71 a difference was obtained which could only be assigned to  $^{71}\text{AlSiO}^+$ . However, this difference was too small for unequivocal identification or reliable quantitative measurements.

To circumvent the ion interference problem a  $^{30}\text{Si}$  isotopically enriched sample of  $\text{SiO}_2$  was obtained from the Oak Ridge National Laboratory with an isotopic abundance in atomic percent of  $^{28}\text{Si} = 4.71 \pm 0.10$ ,  $^{29}\text{Si} = 0.64 \pm 0.05$ , and  $^{30}\text{Si} = 94.65 \pm 0.10$  (natural isotopic abundance is  $^{28}\text{Si} = 92.21$ ,  $^{29}\text{Si} = 4.70$ , and  $^{30}\text{Si} = 3.09$  (ref. 27)). A sample was prepared by mixing the enriched  $\text{SiO}_2$  (0.023 g) with  $\text{Al}_2\text{O}_3$  (0.052 g) and Al (0.042 g). The mass spectrum (table IV) showed a peak at nominal  $m/e$  73 which could only be attributed to  $^{27}\text{Al}^{30}\text{Si}^{16}\text{O}^+$ . The relative intensities of ions recorded at 1694 K (corrected for isotopic abundance) and their appearance potentials are also given in table IV. Other possible interferences to the  $^{73}\text{AlSiO}^+$  intensity such as  $\text{Ge}^+$ ,  $\text{Si}_2\text{O}^+$ , or other combinations of atoms were examined and shown to be absent.

Measurements of the ion intensities for  $\text{Al}^+$ ,  $\text{Si}^+$ ,  $\text{Al}_2\text{O}^+$ , and  $\text{AlSiO}^+$  were made at nine temperatures in the 1647 to 1769 K range.

$\text{AlC}_2$ ,  $\text{Al}_2\text{C}_2$ , and  $\text{AlAuC}_2$ . - The molecules  $\text{AlC}_2(\text{g})$ ,  $\text{Al}_2\text{C}_2(\text{g})$ , and  $\text{AlAuC}_2(\text{g})$  were studied by vaporizing a mixture of aluminum and gold in a graphite liner in a tantalum crucible. The ions reported in table V were observed when the sample used for the measurements on  $\text{Al}_2(\text{g})$  was heated to higher temperatures (above 2000 K). The same consid-

TABLE IV. - IONS OBSERVED IN THE Al-Si-O SYSTEM

| Ion   | Relative intensity<br>(1694 K, 20 eV) | Appearance potential, eV |  | Parent species                                    |
|---|---------------------------------------|--------------------------|--|---|
|   |                                       | Present work             | Literature (ref.)                              |   |
| Al <sup>+</sup>                             | 1.00                                  | Standard                 | 5.984(21)                                      | Al  |
| Si <sup>+</sup>                             | 1.9×10 <sup>-2</sup>                  | Standard                 | 8.149(21)                                      | Si  |
| AlO <sup>+</sup>                            | 6.8×10 <sup>-3</sup>                  | 15.1±0.3                 | 9.5, parent (1, 28, 29)<br>16.1, fragment (14) | Al <sub>2</sub> O                                 |
| SiO <sup>+</sup>                            | 1.15                                  | 11.3±0.3                 | 11.6(30)                                       | SiO   |
| Al <sub>2</sub> <sup>+</sup>                | 5.2×10 <sup>-3</sup>                  | 15.2±0.5                 | 16.5, fragment (14)                            | Al <sub>2</sub> O                                 |
| AlSi <sup>+</sup>                           | 1.6×10 <sup>-3</sup>                  | 6.9±1.0                  | -----  | AlSi  |
| AlO <sub>2</sub> <sup>+</sup>               | 1.1×10 <sup>-5</sup>                  | (a)                      | 10(1)  | Al <sub>2</sub> O <sub>2</sub> , AlO <sub>2</sub> |
| Al <sub>2</sub> O <sub>2</sub> <sup>+</sup> | 3.7×10 <sup>-1</sup>                  | 7.7±0.2                  | 8.5(1); 8.0(14); 7.7(25, 28, 29)               | Al <sub>2</sub> O                                 |
| AlSiO <sup>+</sup>                          | 4.0×10 <sup>-4</sup>                  | 6.3±1.0                  | -----  | AlSiO   |
| Al <sub>2</sub> O <sub>2</sub> <sup>+</sup> | (a)                                   | (a)                      | 10(1)  | Al <sub>2</sub> O <sub>2</sub>                    |

<sup>a</sup>Not measured.

TABLE V. - IONS OBSERVED IN THE Al-Au-C SYSTEM

| Ion   | Relative intensity<br>(2147 K, 30 eV) | Appearance potential, eV |                        | Parent species                                     |
|---|---------------------------------------|--------------------------|------------------------|--|
|   |                                       | Present work             | Literature (ref.)      |  |
| Al <sup>+</sup>                             | 1.00                                  | Standard                 | 5.984(21)              | Al   |
| AlC <sup>+</sup>                            | 1.7×10 <sup>-6</sup>                  | 14.0±1.0                 | -----                  | AlC <sub>2</sub> , (AlC?)                          |
| AlC <sub>2</sub> <sup>+</sup>               | 2.4×10 <sup>-5</sup>                  | 9.3±1.0                  | -----                  | AlC <sub>2</sub>                                   |
| Al <sub>2</sub> <sup>+</sup>                | 2.5×10 <sup>-5</sup>                  | 5.4±1.0                  | -----                  | Al <sub>2</sub>                                    |
| Al <sub>2</sub> C <sup>+</sup>              | 1.3×10 <sup>-6</sup>                  | (a)                      | -----                  | Al <sub>2</sub> C?, Al <sub>2</sub> C <sub>2</sub> |
| Al <sub>2</sub> C <sub>2</sub> <sup>+</sup> | 6.4×10 <sup>-5</sup>                  | 8.0±0.5                  | -----                  | Al <sub>2</sub> C <sub>2</sub>                     |
| Au <sup>+</sup>                             | ~7×10 <sup>-2</sup>                   | Standard                 | 9.22(21)               | Au   |
| AlAu <sup>+</sup>                           | 3.4×10 <sup>-1</sup>                  | 7.6±0.3                  | -----                  | AlAu   |
| AlAuC <sup>+</sup>                          | ~10 <sup>-6</sup>                     | (a)                      | -----                  | AlAuC?, AlAuC <sub>2</sub>                         |
| AlAuC <sub>2</sub> <sup>+</sup>             | 2.0×10 <sup>-6</sup>                  | (a)                      | -----                  | AlAuC <sub>2</sub>                                 |
| Au <sub>2</sub> <sup>+</sup>                | (a)                                   | 9.5±0.3                  | 9.2(22)<br>9.7(23, 24) | Au <sub>2</sub>                                    |

<sup>a</sup>Not measured.

erations of resolution and ion interference were made for the ions listed as discussed previously. The appearance potentials (A. P.) measured for AlC<sub>2</sub><sup>+</sup>, Al<sub>2</sub><sup>+</sup>, Al<sub>2</sub>C<sub>2</sub><sup>+</sup>, AlAu<sup>+</sup>, and Au<sub>2</sub><sup>+</sup> indicated that these were parent molecular ions. AlC<sup>+</sup> is probably a fragment ion from AlC<sub>2</sub> because of its high appearance potential of 14 electron volts. The estimation of A. P. of the AlC<sup>+</sup> fragment is A. P. (AlC<sub>2</sub><sup>+</sup>) + D<sub>0</sub>(C<sub>2</sub>) = 9.3 + 6.2 = 15.5 electron volts, which is in reasonable agreement with the measured value. Appearance potentials were not measured for Al<sub>2</sub>C<sup>+</sup>, AlAuC<sup>+</sup>, or AlAuC<sub>2</sub><sup>+</sup> because of their low intensities. We

assume that  $\text{AlAuC}_2^+$  is a parent molecular ion while no judgment is made for  $\text{Al}_2\text{C}^+$  or  $\text{AlAuC}^+$ .

Ion intensities were measured for  $\text{Al}^+$ ,  $\text{AlC}_2^+$ ,  $\text{Al}_2^+$ ,  $\text{Al}_2\text{C}_2^+$ ,  $\text{AlAu}^+$ , and  $\text{AlAuC}_2^+$  over the temperature range of 2051 to 2171 K.

## CALCULATIONS AND RESULTS

### Thermodynamic Functions

Free-energy and enthalpy functions for the molecules considered are needed for the second- and third-law treatments of the ion intensity data. Whenever possible the free-energy functions and enthalpies for the various molecular species were taken from either the JANAF tables (ref. 31) or Hultgren's compilation (ref. 32) (see our table VI for sources of thermal data). The experimental and estimated molecular constants used to calculate thermodynamic functions for the diatomic molecule  $\text{Al}_2$ ,  $\text{AlAu}$ ,  $\text{Au}_2$ , and  $\text{AlSi}$  are listed in table VII(a). For the polyatomic molecules the estimated molecular constants are listed in table VII(b).

TABLE VI. - SOURCES OF THERMODYNAMIC FUNCTIONS  
AND AUXILIARY THERMODYNAMIC DATA

| Species                  | Quantity   | Reference |
|--------------------------|--|-----------|
| $\text{Al(g)}$           | $H_T^0 - H_0^0$ and $- [(G_T^0 - H_0^0)/T]$  | 31        |
| $\text{Au(g)}$           | $H_T^0 - H_0^0$ and $- [(G_T^0 - H_0^0)/T]$  | 32        |
| $\text{Si}_2\text{C(g)}$ | $H_T^0 - H_0^0$ and $- [(G_T^0 - H_0^0)/T]$  | 31        |
| $\text{SiC}_2\text{(g)}$ | $D_{0, \text{atoms}}^0 = 1070.2 \pm 17 \text{ kJ mol}^{-1}$  | 33        |
|                          | $H_T^0 - H_0^0$ and $- [(G_T^0 - H_0^0)/T]$  | 31        |
| $\text{C(s)}$            | $D_{0, \text{atoms}}^0 = 1258.1 \pm 17 \text{ kJ mol}^{-1}$  | 33        |
|                          | $H_T^0 - H_0^0$ and $- [(G_T^0 - H_0^0)/T]$ , $\Delta H_{0, \text{vap}}^0 = 709.5 \pm 1.9 \text{ kJ mol}^{-1}$ | 31        |
| $\text{Si(g)}$           | $H_T^0 - H_0^0$ and $- [(G_T^0 - H_0^0)/T]$  | 31        |
| $\text{Al}_2\text{O(g)}$ | $D_{0, \text{atoms}}^0 = 1043.5 \pm 17 \text{ kJ mol}^{-1}$  | 34        |
| $\text{C}_2\text{(g)}$   | $\Delta H_{0, \text{formation}}^0 = 829.3 \pm 3.8 \text{ kJ mol}^{-1}$   | 31        |
| $\text{AlAu(g)}$         | $D_0^0 = 322.2 \pm 6 \text{ kJ mol}^{-1}$  | 35        |
| $\text{Au}_2\text{(g)}$  | $D_0^0 = 221.8 \pm 6.3 \text{ kJ mol}^{-1}$  | 35        |

TABLE VII. - MOLECULAR CONSTANTS

## (a) Diatomic molecules

|  | Molecule                           |                                    |                                    |                                    |
|--|------------------------------------|------------------------------------|------------------------------------|------------------------------------|
|  | Al <sub>2</sub><br>(a)             | AlAu<br>(b)                        | Au<br>(c)                          | AlSi<br>(d)                        |
| Vibrational frequency,<br>$\omega$ , cm <sup>-1</sup>        | 350.0                              | 333.0                              | 190.9                              | 500                                |
| Anharmonicity constant,<br>$\omega_e x_e$ , cm <sup>-1</sup> | 2.02                               | 1.16                               | -----                              | -----                              |
| Interatomic distance,<br>$r_{mx}$ , Å                        | 2.4668                             | 2.338                              | 2.472                              | 2.36                               |
| Rotational constant,<br>$B_e$ , cm <sup>-1</sup>             | 0.2053                             | 0.1299                             | 0.0280                             | 0.2199                             |
| Symmetry number, $\sigma$                                    | 2                                  | 1                                  | 2                                  | 1                                  |
| Electronic ground state                                      | <sup>3</sup> Σ, g <sub>0</sub> = 3 | <sup>1</sup> Σ, g <sub>0</sub> = 1 | <sup>1</sup> Σ, g <sub>0</sub> = 1 | <sup>2</sup> Π, g <sub>0</sub> = 4 |

## (b) Polyatomic molecules

|  | Molecule  |  |  |  |  |
|--|---|--|--|--|--|
|  | Al <sub>2</sub> O   | AlSiO  | AlCC   | AlCCAl   | AlCCAu   |
| Point group  | <sup>e</sup> C <sub>2v</sub>  | C <sub>s</sub>   | C <sub>∞v</sub>  | D <sub>∞h</sub>  | C <sub>∞v</sub>  |
| Symmetry number, $\sigma$  | 2   | 1  | 1  | 2  | 1  |
| Angle, $\alpha$ , deg  | <sup>e</sup> 145  | 145  | 180  | 180  | 180  |
| Interatomic distances,<br>Å  | AlO, <sup>e</sup> 1.66  | AlO, 1.66<br>SiO, <sup>f</sup> 1.60  | AlC, <sup>g</sup> 1.61<br>CC, <sup>h</sup> 1.31  | AlC, 1.61<br>CC, 1.31  | AlC, 1.61<br>CC, 1.31<br>CAu, <sup>i</sup> 1.86  |
| Moment of inertia,<br>(g)(cm <sup>2</sup> )  | -----   | -----  | 12.54×10 <sup>-39</sup>  | 47.68×10 <sup>-39</sup>  | 105.3×10 <sup>-39</sup>  |
| I <sub>A</sub> ·I <sub>B</sub> ·I <sub>C</sub> ,<br>(gm <sup>3</sup> )(cm <sup>6</sup> ) | 263.4×10 <sup>-117</sup>  | 246.5×10 <sup>-117</sup>   | -----  | -----  | -----  |
| Force constants,<br>N/m  | k <sub>AlO</sub> , 3.86×10 <sup>2</sup><br>k <sub>δ</sub> /l <sup>2</sup> , 0.386×10 <sup>2</sup> | k <sub>AlO</sub> , 3.86×10 <sup>2</sup><br>k <sub>SiO</sub> , 6.30×10 <sup>2</sup><br>k <sub>δ</sub> /l <sup>2</sup> , 0.508×10 <sup>2</sup> | k <sub>AlC</sub> , 5.0×10 <sup>2</sup><br>k <sub>CC</sub> , 9.25×10 <sup>2</sup><br>k <sub>δ</sub> , 0.67×10 <sup>-18</sup> N/m<br>rad | k <sub>AlC</sub> , 5.0×10 <sup>2</sup><br>k <sub>CC</sub> , 9.25×10 <sup>2</sup><br>k <sub>δ</sub> , 1.50×10 <sup>-19</sup> N/m<br>rad | k <sub>AlC</sub> , 5.0×10 <sup>2</sup><br>k <sub>AuC</sub> , 5.0×10 <sup>2</sup><br>k <sub>CC</sub> , 9.25×10 <sup>2</sup><br>k <sub>δ</sub> , 1.50×10 <sup>-19</sup> N/m<br>rad |
| Vibrational frequencies<br>(degeneracy), cm <sup>-1</sup>                                |   |  |  |  |  |
| $\nu_1$  | 615(1)  | 679(1)   | 755(1)   | 1842(1)  | 1834(1)  |
| $\nu_2$  | 369(1)  | 417(1)   | 503(2)   | 492(1)   | 347(1)   |
| $\nu_3$  | <sup>e</sup> 994(1)   | 1151(1)  | 1751(1)  | 1011(1)  | 950(1)   |
| $\nu_4$  | -----   | -----  | -----  | 321(2)   | 310(2)   |
| $\nu_5$  | -----   | -----  | -----  | 109(2)   | 95(2)  |
| Ground electronic state  | <sup>1</sup> A <sub>1</sub> , g <sub>0</sub> = 1  | g <sub>0</sub> = 2   | g <sub>0</sub> = 2   | g <sub>0</sub> = 1   | g <sub>0</sub> = 1   |

<sup>a</sup>Ref. 2.<sup>b</sup>Ref. 7.<sup>c</sup>Ref. 36.<sup>d</sup>By comparison with FeSi, CoSi, NiSi (ref. 33), Al<sub>2</sub> (ref. 2), and Si<sub>2</sub> (ref. 31).<sup>e</sup>Ref. 37.<sup>f</sup>Estimated by comparison to the Si-O bond length in SiO (ref. 31) and (SiO)<sub>x</sub> (ref. 38).<sup>g</sup>The Al-C bond length was taken to be the same as that used by Chupka et al. (ref. 13).<sup>h</sup>From C<sub>2</sub> (ref. 39).<sup>i</sup>The Au-C bond length was estimated by comparison of the values for AuSi (ref. 36) and AuB (ref. 36) with the Pt-, Rh-, Ru-, and Ir - carbides, silicides, and borides (refs. 36, 40, and 41).

Although much experimental work has been devoted to the determination of the fundamental vibrational frequencies for  $\text{Al}_2\text{O}$  (refs. 3, 4, 37, and 42) (and other  $\text{M}_2\text{O}$  type molecules), only the  $\nu_3$  frequency is well established. The recent experimental work of Lynch (ref. 3) indicates that various assignments of  $\nu_1$  and  $\nu_2$  for  $\text{Al}_2\text{O}$  (refs. 4, 37, and 42) are in error. Therefore, for the present study,  $\nu_1$  and  $\nu_2$  for  $\text{Al}_2\text{O}$  were calculated by the valence force formulation given by Herzberg (ref. 43) based on a force constant  $k_1$  calculated from the experimental value of  $\nu_3$  (ref. 37). The bending force constant was taken as 10 percent of  $k_1$ . For  $\text{AlSiO}$ , a bent structure similar to that for  $\text{Al}_2\text{O}$  was chosen. The force constant for the Al-O stretching mode was taken from  $\text{Al}_2\text{O}$ . The Si-O stretching force constant was estimated by multiplying the force constant ratio for the Al-O bond in  $\text{Al}_2\text{O}(\text{g})$  and  $\text{AlO}(\text{g})$  times that for the Si-O bond in  $\text{SiO}(\text{g})$  (ref. 39):  $[k_{\text{Al-O}}(\text{Al}_2\text{O}(\text{g}))/k_{\text{Al-O}}(\text{AlO}(\text{g}))][k_{\text{Si-O}}(\text{SiO}(\text{g}))] = [(3.86 \times 10^2)/(5.67 \times 10^2)][9.25 \times 10^2] = 6.30 \times 10^2$  newtons per meter. The bending force constants for  $\text{AlSiO}$  was taken as 0.1 times the average of  $k_{\text{Al-O}}$  and  $k_{\text{Si-O}}$ .

For the dicarbide molecules  $\text{AlC}_2$  and  $\text{Al}_2\text{C}_2$ , a linear asymmetric Al-C-C and a lin-

TABLE VIII. - FREE-ENERGY FUNCTIONS AND ENTHALPIES FOR MOLECULES

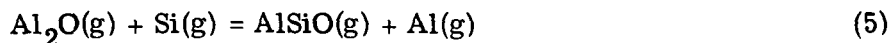
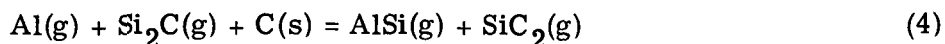
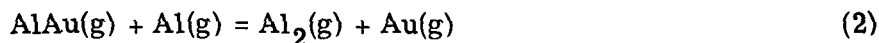
| Temperature,<br>K                                      | Molecule      |               |               |               |                       |                |                |                         |                  |
|--|---------------|---------------|---------------|---------------|-----------------------|----------------|----------------|-------------------------|------------------|
|  | $\text{Al}_2$ | $\text{AlAu}$ | $\text{Au}_2$ | $\text{AlSi}$ | $\text{Al}_2\text{O}$ | $\text{AlSiO}$ | $\text{AlC}_2$ | $\text{Al}_2\text{C}_2$ | $\text{AlAuC}_2$ |
| $-[(G_T^0 - H_0^0)/T], \text{JK}^{-1} \text{mol}^{-1}$ |               |               |               |               |                       |                |                |                         |                  |
| 298.15   | 200.35        | 218.67        | 235.02        | 207.19        | 218.83                | 229.78         | 201.33         | 224.16                  | 253.89           |
| 1500   | 256.43        | 274.82        | 292.68        | 261.45        | 291.35                | 300.66         | 269.79         | 325.61                  | 357.74           |
| 1600   | 258.78        | 277.18        | 295.05        | 263.75        | 294.67                | 303.93         | 273.09         | 330.37                  | 362.57           |
| 1700   | 261.01        | 279.39        | 297.28        | 265.92        | 297.81                | 307.03         | 276.23         | 334.89                  | 367.14           |
| 1800   | 263.11        | 281.49        | 299.38        | 267.97        | 300.79                | 309.97         | 279.21         | 339.18                  | 371.47           |
| 1900   | 265.11        | 283.47        | 301.37        | 269.91        | 303.62                | 312.77         | 282.06         | 343.28                  | 375.61           |
| 2000   | 267.00        | 285.36        | 303.26        | 271.75        | 306.33                | 315.44         | 284.79         | 347.19                  | 379.55           |
| 2100   | 268.80        | 287.16        | 305.06        | 273.51        | 308.91                | 317.99         | 287.40         | 350.93                  | 383.32           |
| 2200   | 270.53        | 288.87        | 306.77        | 275.19        | 311.38                | 320.43         | 289.90         | 354.52                  | 386.94           |
| $H_T^0 - H_0^0, \text{kJ mol}^{-1}$                    |               |               |               |               |                       |                |                |                         |                  |
| 298.15   | 9.651         | 9.692         | 10.186        | 9.265         | 11.308                | 11.058         | 10.088         | 15.215                  | 15.803           |
| 1500   | 54.759        | 54.634        | 55.015        | 53.369        | 76.889                | 75.706         | 76.355         | 110.30                  | 111.61           |
| 1600   | 58.577        | 58.424        | 58.754        | 57.096        | 82.623                | 81.413         | 82.366         | 118.77                  | 120.09           |
| 1700   | 62.401        | 62.218        | 62.494        | 60.824        | 88.366                | 87.134         | 88.402         | 127.26                  | 128.60           |
| 1800   | 66.232        | 66.016        | 66.233        | 64.554        | 94.117                | 92.865         | 94.458         | 135.78                  | 137.13           |
| 1900   | 70.069        | 69.818        | 69.973        | 68.285        | 99.875                | 98.605         | 100.53         | 144.32                  | 145.68           |
| 2000   | 73.911        | 73.624        | 73.713        | 72.017        | 105.64                | 104.35         | 106.62         | 152.88                  | 154.25           |
| 2100   | 77.760        | 77.434        | 77.453        | 75.750        | 111.41                | 110.11         | 112.72         | 161.45                  | 162.84           |
| 2200   | 81.614        | 81.247        | 81.194        | 79.484        | 117.18                | 115.87         | 118.84         | 170.04                  | 171.43           |

ear symmetric Al-C-C-Al structure were chosen by analogy to other metal dicarbides (refs. 13, 44, 45, and 46). The fundamental frequencies again were calculated according to the valence force formulation (refs. 43 and 47). The stretching force constant for Al-C was assumed to be  $5.0 \times 10^2$  newtons per meter to be consistent with the work of Chupka et al. (ref. 13). The C-C force constant was taken from  $C_2$  (ref. 39). By analogy to  $Al_2C_2$  a linear structure was assumed for Al-C-C-Au and the Au-C force constant was assumed to be equal to the Al-C force constant.

Thermodynamic functions were calculated with a NASA computer program (ref. 48) using the rigid-rotator harmonic oscillator approximation except for  $Al_2$  and  $AlAu$ . For the latter two molecules, a correction was included for anharmonicity (ref. 48). Free-energy functions and enthalpies for the various molecules are listed in table VIII. The free-energy functions for  $Al_2O(g)$  based on the molecular constants listed in table VII(b) differ from the JANAF values (ref. 31 dated Sept. 30, 1965) by about 2.5 joules per kelvin per mole at 1500 K.

## Enthalpies for Reactions

The following reactions were used to characterize the molecules  $Al_2$ ,  $AlSi$ ,  $AlSiO$ ,  $AlC_2$ ,  $Al_2C_2$ , and  $AlAuC_2$ :



These reactions are also given in tables IX to XII along with the logarithms of the equilibrium constants  $K_p$  at each experimental temperature. For the isomolecular exchange reactions (2) to (5) involving  $Al_2$ ,  $AlSi$ , and  $AlSiO$ , the equilibrium constants were calculated directly from the ratios of ion intensities (corrected for isotopic abundance) with the

TABLE IX. - LOGARITHMS OF EQUILIBRIUM CONSTANTS AND THIRD-LAW ENTHALPIES FOR REACTIONS INVOLVING Al<sub>2</sub>(g)

[Sample consisted of a mixture of Al and Au in a graphite liner in a tantalum cell. Ion intensity measurements were made using 30 eV electrons at 150 μA anode current.]

| Point number   | Temperature, T, K | Logarithm equilibrium constant, log <sub>10</sub> K <sub>p</sub> | Change of Gibbs free-energy function, -Δ[(G <sub>T</sub> <sup>0</sup> -H <sub>0</sub> <sup>0</sup> )/T], JK <sup>-1</sup> mol <sup>-1</sup> | Third-law enthalpy, ΔH <sub>0</sub> <sup>0</sup> (III), kJ mol <sup>-1</sup> |
|--|-------------------|--|---|--|
| AlAu(g) + Al(g) = Al <sub>2</sub> (g) + Au(g)        |                   |  |   |  |
| 1  | 1940              | <sup>a</sup> -4.790  | -2.23   | 173.6  |
| 2  | 1968              | -4.688   | -2.23   | 172.2  |
| 3  | 2003              | -4.593   | -2.24   | 171.6  |
| 4  | 2032              | -4.528   | -2.24   | 171.6  |
| 5  | 1990              | -4.580   | -2.24   | 170.0  |
| 6  | 1956              | -4.691   | -2.23   | 171.3  |
| 7  | 1936              | -4.690   | -2.23   | 169.5  |
| 8  | 1921              | -4.794   | -2.22   | 172.1  |
|  |                   |  |   | Average 171.5±1.2 <sup>b</sup>   |
| 2AlAu(g) = Al <sub>2</sub> (g) + Au <sub>2</sub> (g) |                   |  |   |  |
| 1  | 1940              | <sup>c</sup> -7.404  | -0.46   | 274.1  |
| 2  | 1968              | -7.353   | -0.46   | 276.1  |
| 3  | 2003              | -7.134   | -0.46   | 272.6  |
| 4  | 2032              | -7.065   | -0.46   | 273.9  |
| 5  | 1990              | -7.154   | -0.46   | 271.6  |
| 6  | 1956              | -7.331   | -0.46   | 273.6  |
| 7  | 1936              | -7.418   | -0.46   | 274.0  |
| 8  | 1921              | -7.465   | -0.46   | 273.6  |
|  |                   |  |   | Average 273.7±1.2 <sup>b</sup>   |

$${}^a K_p = \left( \frac{I_{Al_2^+} \times I_{Au^+}}{I_{AlAu^+} \times I_{Al^+}} \right) \left( \frac{\sigma_{AlAu} \times \sigma_{Al}}{\sigma_{Al_2} \times \sigma_{Au}} \right)_{30 \text{ eV}} \left( \frac{\gamma_{AlAu^+} \times \gamma_{Al^+}}{\gamma_{Al_2^+} \times \gamma_{Au^+}} \right). \text{ The } \sigma \text{ factor and}$$

$\gamma$  factor were assumed to equal 1.00 for the isomolecular reaction. Typical relative ion intensity at 1940 K:  $I_{54Al_2^+} = 2.60 \times 10^1$ ;  $I_{197Au^+} = 6.50 \times 10^5$ ,

$I_{224AlAu^+} = 3.90 \times 10^5$ , and  $I_{27Al^+} = 2.67 \times 10^6$ .

<sup>b</sup>Error is the standard deviation of the points. See text and table XIII for overall estimated uncertainty.

$${}^c K_p = \left( \frac{I_{Al_2^+} \times I_{Au_2^+}}{I_{AlAu^+}^2} \right) \left( \frac{\sigma_{AlAu_2}}{\sigma_{Al_2} \times \sigma_{Au_2}} \right)_{30 \text{ eV}} \left( \frac{\gamma_{AlAu^+}^2}{\gamma_{Al_2^+} \times \gamma_{Au_2^+}} \right). \text{ The } \sigma \text{ factor and}$$

$\gamma$  factor were assumed to equal 1.00 for the isomolecular reaction. Typical relative ion intensity at 1940 K:  $I_{54Al_2^+} = 2.60 \times 10^1$ ,  $I_{224AlAu^+} = 3.90 \times 10^5$ , and  $I_{384Au_2^+} = 2.31 \times 10^2$ .



TABLE X. - LOGARITHMS OF EQUILIBRIUM CONSTANTS AND THIRD-LAW

ENTHALPIES FOR REACTION INVOLVING AlSi(g)

[Sample consisted of a mixture of Al and Si in a graphite liner in a tantalum cell. Ion intensity measurements were made using 30 eV electrons at 150  $\mu$ A anode current. ]

| Point number  | Temperature, T, K | Logarithm equilibrium constant, $\log_{10} K_p^a$ | Change of Gibbs free-energy function, $-\Delta[(G_T^0 - H_0^0)/T]$ , $\text{JK}^{-1} \text{mol}^{-1}$ | Third-law enthalpy, $\Delta H_0^0$ (III), $\text{kJ mol}^{-1}$ |
|---|-------------------|---|---|--|
| $\text{Al(g)} + \text{Si}_2\text{C(g)} + \text{C(s)} = \text{AlSi(g)} + \text{SiC}_2\text{(g)}$ |                   |   |   |  |
| 1   | 2030              | -4.620  | 59.41   | 300.2  |
| 2   | 2033              | -4.493  | 59.41   | 295.6  |
| 3   | 2050              | -4.446  | 59.37   | 296.2  |
| 4   | 2069              | -4.402  | 59.33   | 297.1  |
| 5   | 2060              | -4.475  | 59.35   | 298.7  |
| 6   | 2039              | -4.495  | 59.39   | 296.6  |
| 7   | 2020              | -4.440  | 59.44   | 291.7  |
| 8   | 2010              | -4.546  | 59.46   | 294.4  |
| 9   | 1999              | -4.697  | 59.48   | 298.7  |
| 10  | 1988              | -4.669  | 59.51   | 296.0  |
| 11  | 2039              | -4.414  | 59.39   | 293.4  |
| 12  | 2080              | -4.305  | 59.30   | 294.8  |
|   |                   |   |   | Average $296.1 \pm 2.3^b$                                      |

$$a_{K_p} = \left( \frac{I_{\text{AlSi}^+} \times I_{\text{SiC}_2^+}}{I_{\text{Al}^+} \times I_{\text{Si}_2\text{C}^+}} \right) \left( \frac{\sigma_{\text{Al}} \times \sigma_{\text{Si}_2\text{C}}}{\sigma_{\text{AlSi}} \times \sigma_{\text{SiC}_2}} \right)_{30 \text{ eV}} \left( \frac{\gamma_{\text{Al}^+} \times \gamma_{\text{Si}_2\text{C}^+}}{\gamma_{\text{AlSi}^+} \times \gamma_{\text{SiC}_2^+}} \right) \left( \frac{1}{a_C} \right). \text{ The } \sigma$$

factor and  $\gamma$  factor were assumed to equal 1.00 for the exchange reaction and the activity of graphite was assumed to be 1. Typical relative ion intensity at 2039 K:  $I_{27\text{Al}^+} = 8.6 \times 10^5$ ,  $I_{52\text{SiC}_2^+} = 8.0 \times 10^3$ ,  $I_{55\text{AlSi}^+} = 4.9 \times 10^1$ , and  $I_{68\text{Si}_2\text{C}^+} = 1.44 \times 10^4$ .

<sup>b</sup>Error is the standard deviation of the points. See text and table XIII for overall estimated uncertainty.

TABLE XI. - LOGARITHM OF EQUILIBRIUM CONSTANTS AND THIRD-LAW ENTHALPIES FOR REACTION INVOLVING AlSiO(g)

[Sample consisted of a mixture of Al<sub>2</sub>O<sub>3</sub>, Al, and <sup>30</sup>Si-enriched (94.65 percent) SiO<sub>2</sub> in an alumina liner in a tungsten cell. Ion intensity measurements were made using 20 eV electrons at 100 μA anode current.]

| Point number                                    | Temperature, T, K | Logarithm equilibrium constant, log <sub>10</sub> K <sub>p</sub> <sup>a</sup> | Change of Gibbs free-energy function, -Δ[(G <sub>T</sub> <sup>0</sup> - H <sub>0</sub> <sup>0</sup> )/T], JK <sup>-1</sup> mol <sup>-1</sup> | Third-law enthalpy, ΔH <sub>0</sub> <sup>0</sup> (III), kJ mol <sup>-1</sup> |
|---|-------------------|---|--|--|
| Al <sub>2</sub> O(g) + Si(g) = AlSiO(g) + Al(g) |                   |   |  |  |
| 1   | 1687              | -1.199  | 5.85   | 48.6   |
| 2   | 1740              | -1.164  | 5.81   | 48.9   |
| 3   | 1684              | -1.143  | 5.85   | 46.7   |
| 4   | 1754              | -1.136  | 5.80   | 48.3   |
| 5   | 1647              | -1.193  | 5.88   | 47.3   |
| 6   | 1679              | -1.123  | 5.86   | 45.9   |
| 7   | 1714              | -1.138  | 5.83   | 47.3   |
| 8   | 1740              | -1.076  | 5.81   | 46.0   |
| 9   | 1769              | -1.035  | 5.79   | 45.3   |
|   |                   |   |  | Average 47.2 ± 1.2 <sup>b</sup>  |

$${}^a K_p = \left( \frac{I_{\text{AlSiO}^+} \times I_{\text{Al}^+}}{I_{\text{Al}_2\text{O}^+} \times I_{\text{Si}^+}} \right) \left( \frac{\sigma_{\text{Al}_2\text{O}} \times \sigma_{\text{Si}}}{\sigma_{\text{AlSiO}} \times \sigma_{\text{Al}}} \right)_{20 \text{ eV}} \left( \frac{\gamma_{\text{Al}_2\text{O}^+} \times \gamma_{\text{Si}^+}}{\gamma_{\text{AlSiO}^+} \times \gamma_{\text{Al}^+}} \right).$$

The σ factor and γ factor were assumed to equal 1.00 for the isomolecular reaction. Typical relative ion intensity at 1684 K: I<sub>27</sub>Al<sup>+</sup> = 3.7 × 10<sup>5</sup>, I<sub>30</sub>Si<sup>+</sup> = 6.5 × 10<sup>2</sup>, I<sub>70</sub>Al<sub>2</sub>O<sup>+</sup> = 4.75 × 10<sup>5</sup>, and I<sub>73</sub>AlSiO<sup>+</sup> = 6.0 × 10<sup>1</sup>.

<sup>b</sup>Error is the standard deviation of the points. See text and table XIII for overall estimated uncertainty.

TABLE XII. - LOGARITHM OF EQUILIBRIUM CONSTANTS AND THIRD-LAW ENTHALPIES FOR REACTIONS INVOLVING  $\text{AlC}_2(\text{g})$ ,  $\text{Al}_2\text{C}_2(\text{g})$  AND  $\text{AlAuC}_2(\text{g})$

[Sample consisted of a mixture of Al and Au in a graphite liner in a tantalum cell. Ion intensity measurements were made using 30 eV electrons at 150  $\mu\text{A}$  anode current.]

| Point number  | Temperature, T, K | Logarithm equilibrium constant, $\log_{10} K_p$ | Charge of Gibbs free-energy function, $-\Delta[(G_T^0 - H_0^0)/T]$ , $\text{JK}^{-1} \text{mol}^{-1}$ | Third-law enthalpy, $\Delta H_0^0$ (III) $\text{kJ mol}^{-1}$ |
|---|-------------------|---|---|---|
| $\text{Al}(\text{g}) + 2\text{C}(\text{s}) = \text{AlC}_2(\text{g})$            |                   |   |   |   |
| 1   | 2082              | <sup>a</sup> -4.858                             | 56.65   | 311.6   |
| 2   | 2113              | -4.505  | 56.58   | 301.8   |
| 3   | 2147              | -4.818  | 56.51   | 319.4   |
| 4   | 2171              | -4.784  | 56.46   | 321.4   |
| 5   | 2162              | -4.818  | 56.48   | 321.5   |
|   |                   |   |   | Average 315.1 $\pm$ 7.6 <sup>b</sup>                          |
| $\text{Al}_2(\text{g}) + 2\text{C}(\text{s}) = \text{Al}_2\text{C}_2(\text{g})$ |                   |   |   |   |
| 1   | 2051              | <sup>c</sup> 0.218                              | 35.38   | 64.0  |
| 2   | 2074              | .386  | 35.41   | 58.1  |
| 3   | 2085              | .423  | 35.43   | 57.0  |
| 4   | 2059              | .537  | 35.39   | 51.7  |
| 5   | 2082              | .333  | 35.42   | 60.5  |
| 6   | 2113              | .492  | 35.47   | 55.1  |
| 7   | 2147              | .346  | 35.52   | 62.1  |
| 8   | 2171              | .106  | 35.55   | 72.8  |
| 9   | 2162              | .126  | 35.54   | 71.6  |
|   |                   |   |   | Average 61.4 $\pm$ 6.7 <sup>b</sup>                           |
| $\text{AlAu}(\text{g}) + 2\text{C}(\text{s}) = \text{AlAuC}_2(\text{g})$        |                   |   |   |   |
| 1   | 2113              | <sup>d</sup> -5.325                             | 49.50   | 320.0   |
| 2   | 2147              | -5.332  | 49.57   | 325.6   |
| 3   | 2171              | -5.191  | 49.61   | 323.5   |
| 4   | 2162              | -5.247  | 49.60   | 324.4   |
|   |                   |   |   | Average 323.4 $\pm$ 2.1 <sup>b</sup>                          |

$${}^a K_p = \left( \frac{I_{\text{AlC}_2^+}}{I_{\text{Al}^+}} \right) \left( \frac{\sigma_{\text{Al}}}{\sigma_{\text{AlC}_2}/30 \text{ eV}} \right) \left( \frac{\gamma_{\text{Al}^+}}{\gamma_{\text{AlC}_2^+}} \right) \left( \frac{1}{a_{\text{C}}} \right)^2. \text{ The cross sections for Al and C}$$

were taken from Mann (ref. 20),  $\left( \frac{\sigma_{\text{Al}}}{\sigma_{\text{AlC}_2}} \right) = 0.6246$ ; the  $\gamma$  terms were assumed to cancel and the activity of graphite was assumed to be 1. Typical relative ion intensity at 2147 K:  $I_{27\text{Al}^+} = 9.00 \times 10^6$  and  $I_{51\text{AlC}_2^+} = 2.19 \times 10^2$ .

<sup>b</sup>Error in the standard deviation of the points. See text and table XIII for overall estimated uncertainty.

$${}^c K_p = \left( \frac{I_{\text{Al}_2\text{C}_2^+}}{I_{\text{Al}_2^+}} \right) \left( \frac{\sigma_{\text{Al}_2}}{\sigma_{\text{Al}_2\text{C}_2}/30 \text{ eV}} \right) \left( \frac{\gamma_{\text{Al}_2^+}}{\gamma_{\text{Al}_2\text{C}_2^+}} \right) \left( \frac{1}{a_{\text{C}}} \right)^2. \text{ The cross sections for Al}$$

and C were taken from Mann (ref. 20),  $\left( \frac{\sigma_{\text{Al}_2}}{\sigma_{\text{Al}_2\text{C}_2}} \right) = 0.7755$ ; the  $\gamma$  terms were assumed to cancel and the activity of graphite was assumed to be 1. Typical relative ion intensity at 2147 K:  $I_{54\text{Al}_2^+} = 2.03 \times 10^2$  and  $I_{78\text{Al}_2\text{C}_2^+} = 5.80 \times 10^2$ .

$${}^d K_p = \left( \frac{I_{\text{AlAuC}_2^+}}{I_{\text{AlAu}^+}} \right) \left( \frac{\sigma_{\text{AlAu}}}{\sigma_{\text{AlAuC}_2}/30 \text{ eV}} \right) \left( \frac{\gamma_{\text{AlAu}^+}}{\gamma_{\text{AlAuC}_2^+}} \right) \left( \frac{1}{a_{\text{C}}} \right)^2. \text{ The cross sections for}$$

Al, Au, and C were taken from Mann (ref. 20),  $\left( \frac{\sigma_{\text{AlAu}}}{\sigma_{\text{AlAuC}_2}} \right) = 0.7921$ ; the  $\gamma$  terms were assumed to cancel and the activity of graphite was assumed to be 1. Typical relative ion intensity at 2147 K:  $I_{224\text{AlAu}^+} = 3.06 \times 10^6$  and  $I_{248\text{AlAuC}_2^+} = 1.80 \times 10^1$ .

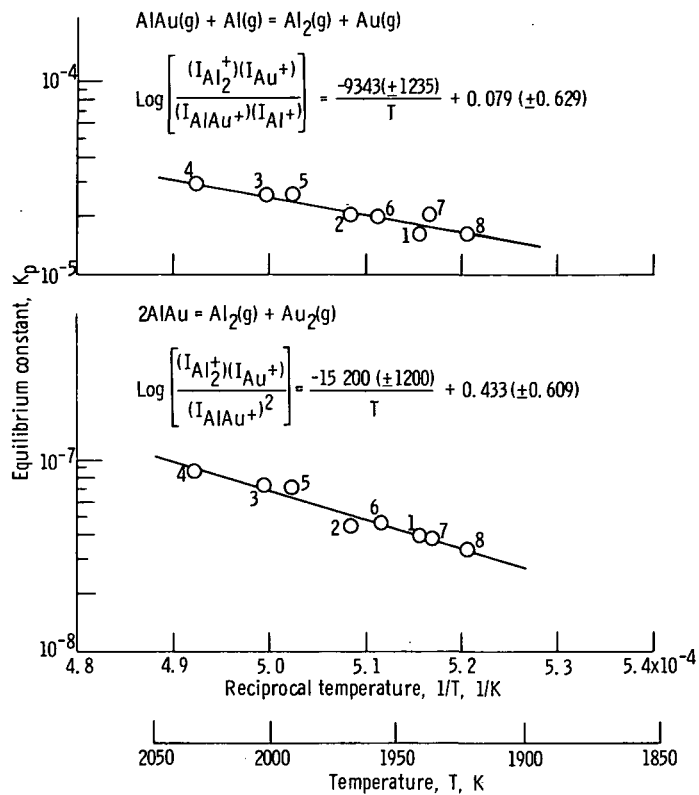


Figure 2. - Equilibrium constant as function of reciprocal temperature for reactions involving  $\text{Al}_2\text{(g)}$ . Points are numbered chronologically.

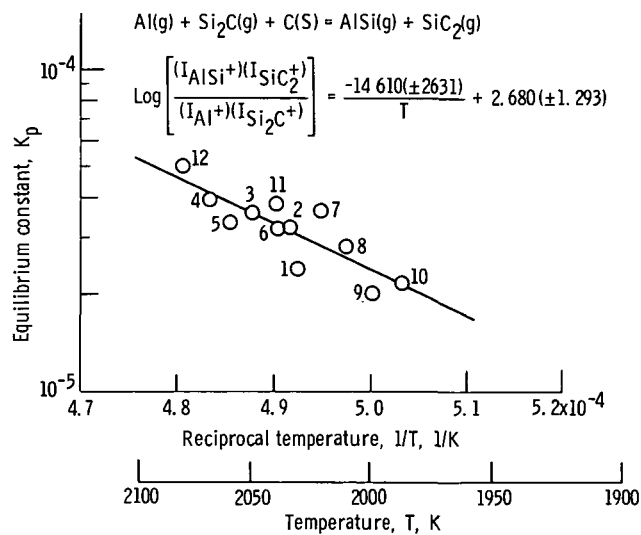


Figure 3. - Equilibrium constant as function of reciprocal temperature for reactions involving  $\text{AlSi(g)}$ . Points are numbered chronologically.

well founded assumption that the ratios of ionization cross sections at the experimental electron energy and the ratios of multiplier gains are unity.

For the pressure calibration independent reactions (6) to (8) involving the three Al-C molecules, estimates of molecular cross sections were needed. The cross sections were taken from Mann (ref. 20) for the atoms and those for molecules were obtained by summing the values for the constituent atoms. The logarithms of the equilibrium constants expressed as ion intensity ratios are plotted against  $1/T$  in figures 2 to 4 for reactions (2) to (5) involving  $\text{Al}_2$ ,  $\text{AlSi}$ , and  $\text{AlSiO}$ . The lines drawn through the data points shown in the figures are the least squares fits of the data to an equation of the form  $\log K_p = A/T + B$ .

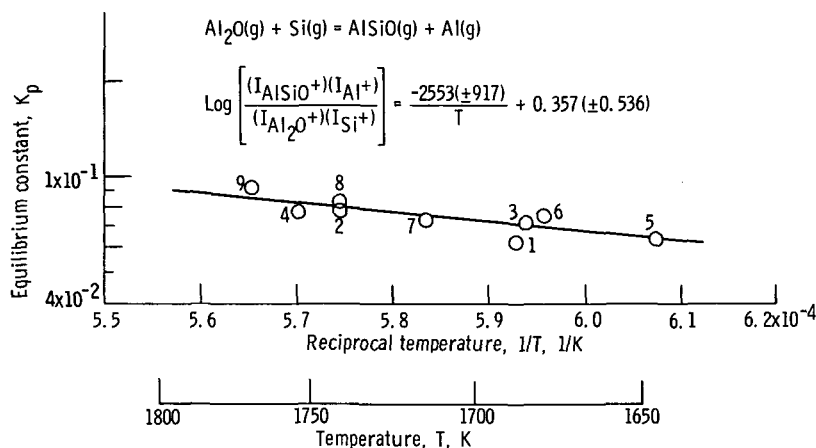


Figure 4. - Equilibrium constant as function of reciprocal temperature for reactions involving  $\text{AlSiO}(\text{g})$ . Points are numbered chronologically.

Second-law enthalpies for reactions (2) to (5) were calculated by use of the Clausius-Clapeyron equation

$$\Delta H_T^0 = -R \, d \ln K_p / d (1/T) \quad (9)$$

and are listed in table XIII. The  $\Delta H_T^0$  values were corrected to 0 K to obtain second-law heats  $\Delta H_0^0$ . The errors associated with the  $\Delta H_0^0$  values are overall estimated errors and were obtained by combining standard deviations with the uncertainty produced by a temperature uncertainty of  $\pm 5$  K and an uncertainty in the sum of the heat content functions of  $\pm 1$  kilojoule per mol. Second-law heats were not calculated for reactions (6) to (8) involving the Al-C molecules because of the scatter of the data points and the relatively short temperature range covered.

TABLE XIII. - SUMMARY AND COMPARISON OF SECOND- AND THIRD-LAW ENTHALPIES FOR REACTIONS

| Molecule                           | Reaction   | Temperature range, K | Enthalpy, kJ mol <sup>-1</sup> |                                |                                | Third-law atomization energy, <sup>b</sup> D <sub>0</sub> <sup>o</sup> , atoms', kJ mol <sup>-1</sup> | Third-law heat of formation, ΔH <sub>298</sub> <sup>o</sup> , formation', kJ mol <sup>-1</sup> |
|------------------------------------|--|----------------------|--------------------------------|--------------------------------|--------------------------------|---|--|
|                                    |  |                      | Second law                     |                                | Third law                      |   |  |
|                                    |  |                      | ΔH <sub>T</sub> <sup>o a</sup> | ΔH <sub>0</sub> <sup>o b</sup> | ΔH <sub>0</sub> <sup>o b</sup> |   |  |
| Al <sub>2</sub> (g)                | AlAu(g) + Al(g) = Al <sub>2</sub> (g) + Au(g)                        | 1921-2032            | 178.9±24<br>(1968 K)           | 179.1±27                       | 171.5±18                       | 150.7±19  |  |
|                                    | 2AlAu(g) = Al <sub>2</sub> (g) + Au <sub>2</sub> (g)                 | 1921-2032            | 290.9±23<br>(1968 K)           | 290.5±30                       | 273.7±18                       |   |  |
| AlSi(g)                            | Al(g) + Si <sub>2</sub> C(g) + C(s) = AlSi(g) + SiC <sub>2</sub> (g) | 1988-2080            | 279.7±50<br>(2034 K)           | 288.5±55                       | 296.1±19                       | Average 149.8±14  | 498.7±15   |
| AlSiO(g)                           | Al <sub>2</sub> O(g) + Si(g) = AlSiO(g) + Al(g)                      | 1647-1769            | 48.9±18<br>(1712 K)            | 51.2±18                        | 47.2±16                        | 225.5±30  | 546.3±31   |
| AlC <sub>2</sub> (g)               | Al(g) + 2C(s) = AlC <sub>2</sub> (g)                                 | 2051-2171            | -----                          | -----                          | 315.1±21                       | 996.3±20  | 19.8±21  |
| Al <sub>2</sub> C <sub>2</sub> (g) | Al <sub>2</sub> (g) + 2C(s) = Al <sub>2</sub> C <sub>2</sub> (g)     | 2082-2171            | -----                          | -----                          | 61.4±20                        | 1104±21   | 642.6±22   |
| AlAuC <sub>2</sub> (g)             | AlAu(g) + 2C(s) = AlAuC <sub>2</sub> (g)                             | 2113-2171            | -----                          | -----                          | 323.4±20                       | 1507±25   | 563.6±26   |
|                                    |  |                      |                                |                                |                                | 1418±21   | 696.4±22   |

<sup>a</sup>Errors are standard deviations of the slopes.

<sup>b</sup>Errors are the overall estimated uncertainties (see text).

Third-law enthalpies were calculated at each experimental temperature for all reactions by use of the equation

$$\Delta H_0^o = -RT \ln K_p - T\Delta \left[ \frac{(G_T^o - H_0^o)}{T} \right] \quad (10)$$

and are listed in tables IV to XII. The third-law ΔH<sub>0</sub><sup>o</sup> values summarized in table XIII are the average of all data points. The estimated errors listed with these values were obtained by combining the standard deviations of the mean of all respective data points with estimated uncertainties in the values of K<sub>p</sub> (±50 percent), T (±5 K), and Δ[(G<sub>T</sub><sup>o</sup> - H<sub>0</sub><sup>o</sup>)/T] (±8.2 JK<sup>-1</sup> mol<sup>-1</sup>).

The good agreement between the second- and third-law enthalpies for reactions involving Al<sub>2</sub>, AlSi, and AlSiO indicate that the results are reliable and that significant systematic errors were absent. For the Al-C molecules the dashed lines in figure 5 were drawn using the third-law heats converted to ΔH<sub>T</sub><sup>o</sup>.

## Dissociation Energies and Heats of Formation

The third-law enthalpies for the reactions (2) to (8) were combined with auxiliary thermodynamic data listed in table VI to obtain dissociation or atomization energies and standard heats of formation for the molecules of interest. These values are listed in table XIII.

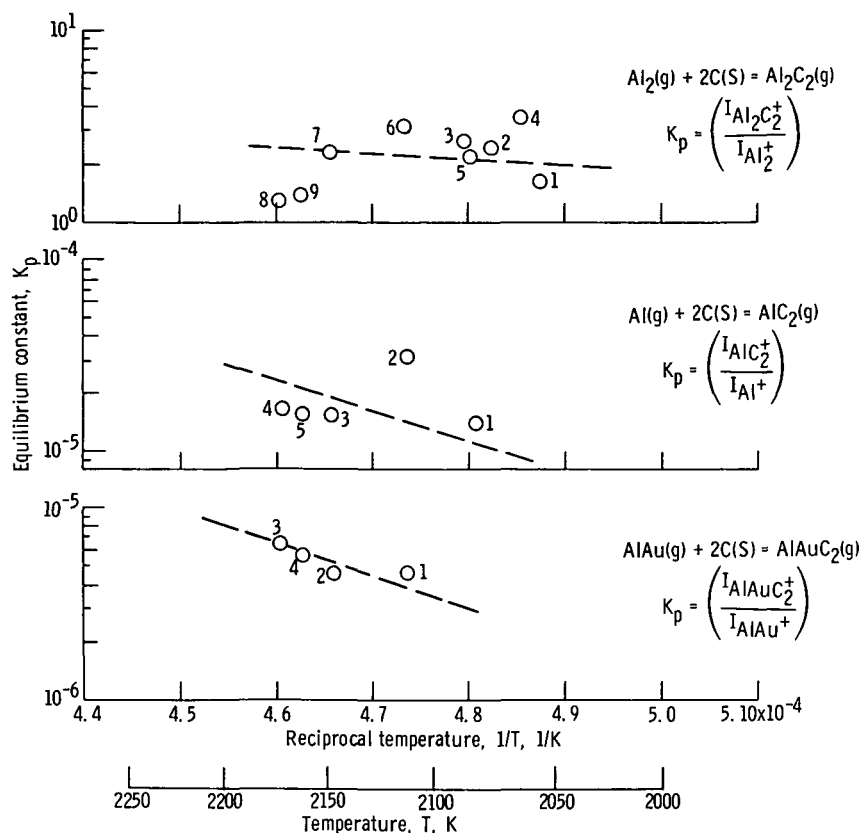


Figure 5. - Equilibrium constant as function of reciprocal temperature for reactions involving Al-C molecules. Points are numbered chronologically.

## DISCUSSION

### $Al_2(g)$

The dissociation energies derived for  $Al_2(g)$  from reactions (2) and (3) of 150.7 and 148.9 kilojoules per mole were averaged to give the selected value of  $149.8 \pm 14$  kilojoules per mol. This value is somewhat lower than all of the previous determinations by others which are compared in table XIV. We believe that our value is correct. It is likely that all of the previous mass spectrometric determinations resulted in an upper limit or a slightly high value for  $D_0^0$  because of the interferences due to the measurement of the  $Al_2^+$  ion intensities from extraneous molecules as discussed previously. In each earlier investigation the possibility of fragmentation of an  $Al_2X$  species or the presence of some other metallic or organic ion would result in a high value for  $D_0^0$ . Moreover, all of the previous mass spectrometric determinations of  $D_0^0$  were obtained only by the third-law method with no second-law verification.

TABLE XIV. - DISSOCIATION ENERGY OF Al<sub>2</sub>(g)

| Investigator (ref.)    | Method (system)                                  | Reactions   | Dissociation energy, D <sub>0</sub> <sup>o</sup> , kJ mol <sup>-1</sup> |
|------------------------|--|---|---|
| Present work           | Mass spectroscopy (Al-Au-C)                      | AlAu(g) + Al(g) = Al <sub>2</sub> (g) + Au(g)<br>2AlAu(g) = Al <sub>2</sub> (g) + Au <sub>2</sub> (g) | 149.8±14  |
| Uy and Drowart (2)     | Mass spectroscopy (Al-Cu-S)                      | Al <sub>2</sub> (g) + S(g) = Al(g) + AlS(g)   | 172±18  |
| Blue and Gingerich (6) | Mass spectroscopy (Al-Au)<br>(Al-Ag)<br>(Al-Au?) | Al <sub>2</sub> (g) = 2Al(g)  | <sup>a</sup> ≤174   |
|                        |  | Al <sub>2</sub> (g) = 2Al(g)  | ~174  |
|                        |  | AlAu(g) + Al(g) = Al <sub>2</sub> (g) + Au <sub>2</sub> (g)   | 161   |
| Chupka et al. (13)     | Mass spectroscopy (Al-C)                         | Al <sub>2</sub> (g) = 2Al(g)  | <sup>b</sup> ≤189.5±42  |
| Ginter et al. (49)     | Spectroscopy                                     | Linear Birge-Sponer extrapolation   | 181   |

<sup>a</sup>No error limits or molecular constants given in ref. 6.

<sup>b</sup>Value recalculated from the data of Chupka et al. (ref. 13) by Uy and Drowart (ref. 2). Error is as quoted in ref. 13.

### AlSi(g)

Gingerich (ref. 35 and references cited therein) has demonstrated that the Pauling concept of a polar bond (ref. 50) may be used quite successfully to estimate values for dissociation energies of mixed metal molecules if the dissociation energies of the homonuclear diatomics are known. With the use of the geometric mean method and electronegatives of Al and Si from Pauling (ref. 50), the dissociation energy of Al<sub>2</sub>(g) determined here, and the dissociation energy of Si<sub>2</sub>(g) from the literature (ref. 19), the value of the dissociation energy of Al-Si is calculated as

$$\begin{aligned}
 D(\text{Al-Si})(\text{kJ mol}^{-1}) &= [D(\text{Al-Al}) \cdot D(\text{Si-Si})]^{1/2} + 125.5(X_{\text{Al}} - X_{\text{Si}})^2 \\
 &= [(149.8)(310)]^{1/2} + 125.5(1.5 - 1.8)^2 = 227 \text{ kJ mol}^{-1}
 \end{aligned}$$

This value is in excellent agreement with the experimentally determined value of 225.5±30 kilojoules per mol. Vander Auwera-Mahieu, McIntyre, and Drowart (ref. 33) have recently determined the dissociation energies of the iron, cobalt, and nickel silicides to be 293.0, 270.7, and 314.8 kilojoules per mol, respectively, while the noble metal silicides (ref. 36) (Ru, Rh, Pd, Ir, Pt, and Au) have dissociation energies in the range of 308 to 497 kilojoules per mol. The decreased stability of the Al-Si bond is due probably to the lack of d-orbital bonding in this molecule.



## AlSiO(g)

Stable gaseous heteronuclear metallic suboxide molecules have been reported recently for the Group IIIA metals aluminum, gallium, and indium (ref. 14). While the observed mixed metal suboxides involved metals within the same group, the possible existence of species with metal atoms from the different groups of the periodic table was suggested. AlSiO(g) is an example of such a molecule. Thompson (ref. 34) has also recently observed the AlSiO(g) molecule in a mass spectrometric study of the vaporization of mixtures of aluminum and silicon oxides. He studied the reaction  $\text{Al(g)} + \text{SiO(g)} = \text{AlSiO(g)}$  and determined an upper limit to the atomization energy of AlSiO of  $D_{0,\text{atoms}}^{\circ} \leq 1050 \pm 42$  kilojoules per mol based on a  $D_0^{\circ}(\text{SiO})$  of 796.6 kilojoules per mol (ref. 51) and the free-energy functions calculated by us (table VIII). This upper limit for  $D_{0,\text{atoms}}^{\circ}$  agrees with the present value of  $996.3 \pm 14$  kilojoules per mol.

In the present study a number of preliminary experiments yielded rough data which indicated that the equilibrium constant for reaction (5) was in the  $10^0$  to  $10^{-2}$  range at  $\sim 1700$  K. Accurate data (see fig. 4) were obtained only when the enriched  $^{30}\text{Si}$  sample was used and interfering ions eliminated.

It is interesting to note that the atomization energy ( $1043.5 \text{ kJ mol}^{-1}$ ) of  $\text{Al}_2\text{O}$  consisting of two Al-O bonds can be approximated by the mere addition of two single Al-O bond energies from  $\text{AlO(g)}$  (ref. 1):  $2D_0^{\circ}(\text{AlO}) = 1004$  kilojoules per mol. One is thus tempted to estimate the AlSiO atomization energy based on the logical Al-O-Si structure by the addition of  $D_0^{\circ}(\text{AlO}) + D_0^{\circ}(\text{SiO})$  which equals 1299 kilojoules per mol, a value obviously in very poor agreement with the experimental value of 996 kilojoules per mol. The estimated value would certainly be an upper limit because the Si-O bond order in Al-O-Si is expected to be less than that in  $\text{SiO(g)}$ . An alternate scheme based on the same simple premise is to add the dissociation energies of AlSi and SiO,  $D_0^{\circ}(\text{AlSi}) + D_0^{\circ}(\text{SiO}) = 1022$  kilojoules per mol, a value which is reasonably close to the experimental value. This agreement may indicate that the structure for AlSiO is really Al-Si-O and not Al-O-Si as assumed by analogy to  $\text{Al}_2\text{O}$ . Indeed, the structure Al-B-O has been proposed (ref. 15) for the molecule of this composition. The sum of  $D_0^{\circ}(\text{AlO})$  and  $D_0^{\circ}(\text{AlSi})$  is 728 kilojoules per mol. This is a low value for the dissociation energy of AlSiO and probably rules out the Si-Al-O structure.

Another speculation which can be derived from the relatively high value for  $D_{0,\text{atom}}^{\circ}(\text{AlSiO})$  is that the unobserved  $\text{Si}_2\text{O(g)}$  molecule (Si-O-Si or Si-Si-O) would be a stable species.

## $\text{AlC}_2(\text{g})$ , $\text{Al}_2\text{C}_2(\text{g})$ , and $\text{AlAuC}_2(\text{g})$

The measurement of the dissociation energies of  $\text{AlC}_2$  and  $\text{Al}_2\text{C}_2$  is an extension of previous work in this laboratory on the determination of the stabilities of the transition metal dicarbides (ref. 44). Again we see that dicarbide molecules are formed which are analogous to the stable monoxides  $\text{AlO}$  and  $\text{Al}_2\text{O}$ . For most metal dicarbide molecules it is found that the dissociation energy of the  $\text{M}-\text{C}_2$  bond is 40 to 130 kilojoules per mol less than that of the corresponding  $\text{M}-\text{O}$  bond. The  $\text{Al}-\text{C}_2$  bond in  $\text{AlC}_2$  is an apparent exception to this empirical rule because  $\bar{E}(\text{Al}-\text{C}_2)$  of  $514.2 \pm 21$  kilojoules per mol is slightly higher than  $D_0^0(\text{AlO})$  of  $502 \pm 15$  kilojoules per mol. On the other hand, each  $\text{Al}-\text{C}$  bond in  $\text{Al}_2\text{C}_2$  of 459 kilojoules per mole is 63 kilojoules per mol lower in energy than the  $\text{Al}-\text{O}$  bonds in  $\text{Al}_2\text{O}(\text{g})$  of 522 kilojoules per mol and follows the trend for most metal dicarbides.

Assuming that all of the observed  $\text{AlC}^+$  ion is fragment, a maximum value of  $D_0^0$  for the unobserved  $\text{AlC}(\text{g})$  ( $^2\Pi$  ground state) molecule of 390 kilojoules per mol is calculated. This value is consistent with the JANAF estimate (ref. 31) of  $D_0^0(\text{AlC}) = 347$  kilojoules per mol.

The atomization energy of  $\text{Al}_2\text{C}_2(\text{g})$  of  $1507 \pm 25$  kilojoules per mol is in good agreement with the value calculated from the experimental results of Chupka et al. (ref. 13) of  $1556 \pm 42$  kilojoules per mol.

For the  $\text{AlAuC}_2$  molecule we have assumed the structure  $\text{Al}-\text{C}-\text{C}-\text{Au}$ . If the energies of the  $\text{Al}-\text{C}$  ( $459 \text{ kJ mol}^{-1}$ ) and  $\text{C}-\text{C}$  ( $594 \text{ kJ mol}^{-1}$  (ref. 31)) bonds are subtracted from the experimentally determined atomization energy, the balance ( $365 \text{ kJ mol}^{-1}$ ) may represent the energy for an  $\text{Au}-\text{C}$  bond. This value is consistent with an upper limit ( $375 \text{ kJ mol}^{-1}$ ) determined for the unobserved (ref. 40)  $\text{AuC}$  diatomic molecule.

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Cleveland, Ohio, September 26, 1972,  
502-01.

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