

THERMODYNAMIC STUDY OF GASEOUS Cu_2Sn AND CuSn_2
BY KNUDSEN CELL MASS SPECTROMETRY

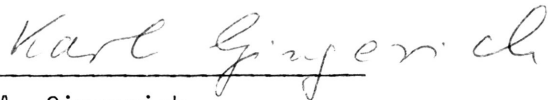
by

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ABSTRACT

The equilibria involving gaseous species above the condensed Cu-Sn system have been experimentally investigated at elevated temperatures by the high temperature mass spectrometric technique. The molecules Cu_2 , CuSn , Sn_2 , Cu_2Sn , CuSn_2 , and Sn_3 were found to exist in the vapor phase above the liquid Cu-Sn alloy which is predominantly atomic in composition. Third-law enthalpy changes have been determined from the experimental data for the following gaseous reactions: $\text{Cu}_2 = 2\text{Cu}$, $\text{Sn}_2 = 2\text{Sn}$, $\text{Sn}_3 = 3\text{Sn}$, $\text{CuSn} = \text{Cu} + \text{Sn}$, $\text{Cu}_2\text{Sn} = 2\text{Cu} + \text{Sn}$, $\text{Cu}_2\text{Sn} = \text{Cu}_2 + \text{Sn}$, $\text{Cu}_2\text{Sn} + \text{Sn} = 2\text{CuSn}$, $\text{CuSn}_2 = \text{Cu} + 2\text{Sn}$, $\text{CuSn}_2 = \text{Cu}_2 + \text{Sn}$, $\text{CuSn}_2 + \text{Cu} = 2\text{CuSn}$. The values of the reaction enthalpies have been combined to give the bond dissociation energies, D_0° , of the diatomic molecules, and the atomization energies, $\Delta H_{\text{ATM},0}$, of the various triatomic molecules assuming different molecular structures for the latter.

The previously known molecules Cu_2 , Sn_2 , Sn_3 , and CuSn , have been evaluated, yielding atomization energies of 48.1 ± 2.0 , 44.2 ± 1.0 , 103.2 ± 0.4 , and 39.8 ± 2.0 kcal mole⁻¹, respectively. These values agree within the quoted error limits with the reported literature values. The atomization energies, $\Delta H_{\text{ATM},0}$, (in kcal mole⁻¹) are presented for the previously unreported molecules: Cu_2Sn (linear symmetric, 107.9 ± 5.3 ; bent symmetric, 103.6 ± 5.2 ; linear asymmetric, 106.7 ± 5.3 ; bent asymmetric, 102.7 ± 5.2) and CuSn_2 (linear symmetric, 95.8 ± 2.6 ; bent symmetric, 95.3 ± 2.6 ; linear asymmetric, 97.4 ± 2.6 ; bent asymmetric, 87.9 ± 2.6).

The values of the heats of atomization for Cu_2Sn and CuSn_2 were averaged to be 106.0 ± 2.5 and 93.8 ± 4.2 kcal mole⁻¹, respectively. The heats of formation, $\Delta H_{\text{f},0}^\circ$, of Cu_2Sn and CuSn_2 were 127.0 ± 2.5 and 130.7 ± 4.2 kcal mole⁻¹, respectively.

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INTRODUCTION

Alloys of various metals have been widely used in many scientific and industrial applications. The properties of many of these alloys have been measured on a macroscopic scale, such as melting points, hardness, composition, and other physical properties. A knowledge of binding energies and structures of the free polyatomic molecules is of value in the study of these physical properties and the understanding of heterogeneous catalysis and nucleation. In this case, the polyatomic molecules may be considered as molecular analogues of condensed metals, alloys, and polymers, which bridge the behavior of molecular and crystalline solids.

The thermodynamic study of polyatomic molecules at high temperatures was introduced twenty years ago by Chupka and Inghram,¹ when the Knudsen cell-mass spectrometric method was used to find the heats of vaporization and sublimation of graphite. Since then, the use of this technique has contributed to the knowledge of the thermodynamics of numerous high temperature inorganic gaseous molecules. With this method, many diatomic metallic and intermetallic molecules have been studied.²

To date, there has not been much thermodynamic data on higher polyatomic intermetallic molecules, especially those with transition elements and containing three or more atoms. Thus, a general paucity in the knowledge of polyatomic intermetallic molecules exists. Recently, the values for the atomization energies of

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gaseous polyatomic intermetallic molecules and metals have been reported for TbAu_2 , HoAu_2 ,³ EuAu_2 ,⁴ SnAu , Sn_2Au , SnAu_2 , Sn_2Au_2 , Sn_3Au ,⁵ Pb_2 , Pb_3 , Pb_4 ,⁶ and $\text{Sn}_2\text{-Sn}_7$.⁷

The primary intent of the following reported experimental investigation was the identification and thermodynamic characterization of gaseous polyatomic intermetallic molecules containing copper and tin. Presently, only the Cu-Sn molecule has been studied, and the dissociation energy was calculated to be 41.4 ± 4 kcal/mole.⁸ In this report, thermodynamic data of gaseous Cu_2Sn and CuSn_2 molecules were determined by the Knudsen cell-mass spectrometric method.

The Knudsen cell-mass spectrometric method, on which a complete summary can be found in a number of reports,⁹⁻¹⁴ was used in identifying the gaseous species and in determining the equilibrium partial pressures. From the experimentally determined data, the enthalpy of reaction, ΔH° , was obtained from the third law of thermodynamics. This method of calculation relies on the knowledge of the thermal functions of the molecules investigated. Since most of the molecules, including Cu_2Sn and CuSn_2 , were unknown, the thermal functions of these molecules had to be calculated on the basis of molecular parameters, which were either obtained from literature or estimated. A portion of this report has been appropriated to the discussion of the calculation of the free energy functions.

If a large enough temperature range could be measured, the reaction enthalpy at temperature T was obtained from the second

law of thermodynamics. The advantage of this method lies in that only the temperature and variations of equilibrium constants are needed. Thus the calculated enthalpies of reactions are not affected by the choice of structure. As a consequence, if both methods are used in the calculation of reaction enthalpies, one may be able to obtain information concerning the structure of an unknown molecule by comparing the enthalpy values calculated by different methods.

The calculated reaction enthalpies were used to determine the atomization energies and heats of formation of the new molecules. These experimental results may then be used in the testing of existing cluster theories, such as homogeneous nucleation and dispersed metal catalysis.

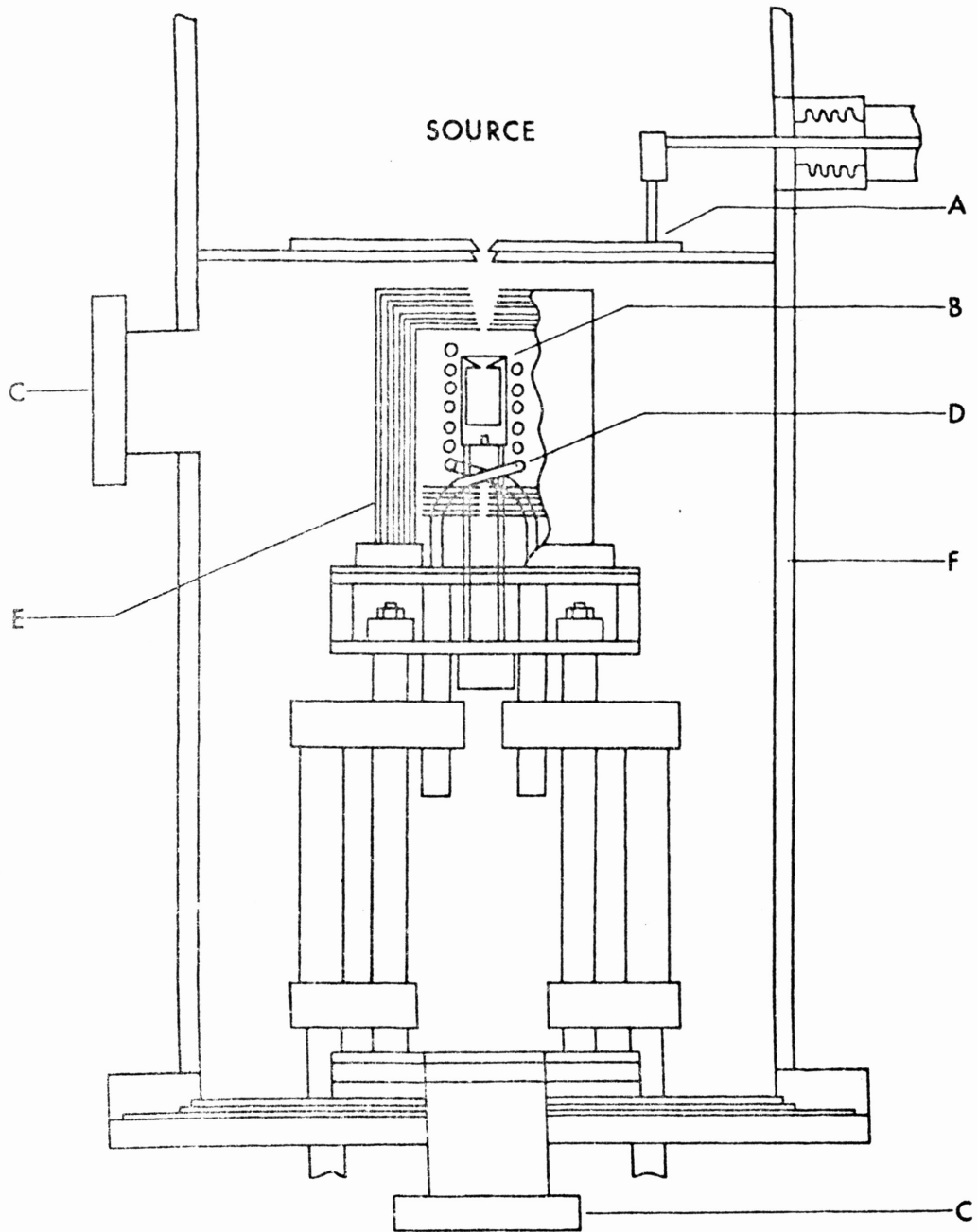
EXPERIMENTAL

In recent years, Knudsen cell effusion and mass spectrometry together has become a powerful combination in analyzing inorganic gas-solid or gas-liquid equilibria at high temperatures.⁹⁻¹⁶ This technique enables one to analyze, both qualitatively and quantitatively, equilibrium vapors above a condensed system. The method consists of four basic processes: 1) isolation of neutral gas phase and formation of ions from the species present in the form of a molecular beam;¹⁴ 2) mass analyzing and identification of neutral species from the ions; 3) measuring changes in ion intensities with temperature; and 4) calculating thermodynamic quantities from the measured ion intensities, by correlating them with the absolute pressures of the gaseous species (if the sensitivity of the instrument is known). The basic principles behind Knudsen cell-mass spectrometry have been fully discussed by other researchers.^{9-13,16} Books by Margrave¹⁷ and Hastie¹⁸ contain articles on high temperature molecules. General treatises on mass spectrometry are by Kiser¹⁹ and Beynon.²⁰

In this section, the description of the instrument used, calibration of the instrument for the Cu-Sn run, and calculation of the free energy functions for the individual molecules, will be discussed.

Knudsen Cell Mass Spectrometer

The instrument used for this research is a single focusing, magnetic deflection, 12-inch radius, 90-degree sector, Nuclide Corporation (State College, Pennsylvania), Knudsen cell, high temperature mass spectrometer. Like all mass spectrometers, this instrument has a vapor source, an ion source, and a mass analyzer and detector. The distinguishing characteristic of this instrument is the vapor source or the Knudsen cell region which allows solids to be vaporized at high temperatures under equilibrium conditions and mass analyzed. A diagram²¹ of the Knudsen cell assembly is given in Figure 1 and is referred to in the following discussion. To obtain the thermodynamic data about the gas phase, the vapor must be contained in a Knudsen cell so as to approximate the equilibrium between the vapor and the condensed phase within the cell. The Knudsen cell (B) is a closed, cylindrical container with a small single orifice at the top. The Knudsen cell is made of some refractory material, such as tantalum, tungsten, molybdenum or graphite, that will not react with the sample that is being studied at high temperatures. The orifice diameter is chosen so as to attain the highest gas pressures within the cell, and the mean free path of the gaseous species is still long compared to the orifice diameter. Under these conditions, the thermodynamic equilibrium is assumed to exist within the cell, but there is a continuous loss of vapor through the orifice. The vapor stream of the Knudsen cell makes up a molecular beam and is directed



KNUDSEN CELL ASSEMBLY

Fig. 1. Schematic diagram of the high temperature
Knudsen cell assembly

into the ionizing region of the ion source. In this region, an ionizing electron beam interacts with the molecular beam so that the composition of the gaseous species within the cell could be determined. The Knudsen cell (B) is heated by radiation from a noninductively wound tungsten spiral resistance heater (D). For maximum sensitivity, the effusion orifice is situated as close to the entrance of the ion source as possible. Since the ion source is close to the high temperatures of the Knudsen cell region, efficient refractory metal radiation shields (E) are needed to surround the Knudsen cell region. Because of the high temperatures involved, the entire jacket (F) of the assembly is water-cooled.

The entire Knudsen cell assembly region is closed from the ion source (SOURCE) except for a small circular hole that can be partially or completely closed by a moveable shutter (A). The shutter is operated externally by means of a bellowed micrometer. This allows the molecular beam effusing out of the Knudsen cell to be partially or completely blocked before its ionization in the ion source. The shutter is an important feature, because it allows ions originating from background gases to be differentiated from the ions formed from the molecular beam effusing from the Knudsen cell.

Temperatures on the Knudsen cell were measured with an NBS calibrated Leeds and Northrup optical pyrometer by sighting on a cylindrical "black body hole" located in the bottom of the Knudsen cell. This measurement was made possible by use of the magnetically shuttered viewing window (C) and a quartz deflecting

prism. The temperatures were corrected for the effective emissivity of the "black body radiation" used. An additional correction was applied for the interposed viewing window and deflecting prism from previous calibrations.

The entire Knudsen cell assembly is mounted on a flange to facilitate changing of samples. The assembly, ion source, and mass analyzer regions are pumped by 50-liter sec^{-1} ion pumps, so that pressures in the 10^{-7} - 10^{-8} torr range can be maintained. The Knudsen cell assembly region is differentially pumped by a six-inch silicon oil diffusion pump to allow pressures in the 10^{-7} torr range to be maintained under high rates of effusion.

The ion source consists of a conventional electron bombardment ion source. The ion source was used to ionize the effusing molecular beam by electron impact from electrons emitted from a heated tungsten ribbon filament. The electron energy was variable between 0 and 100 eV, and the emission current was variable between $50\mu\text{A}$ and 5mA. Ionization efficiency curves (plots of the variation of ion intensity with electron energy) and appearance potentials for the individual ions were obtained by varying the electron energy. The electron energy was kept below 20eV (18eV used in this experiment) to minimize fragmentation, and the ion source pressures were low enough to eliminate the possibility of ion-molecule reactions.

The ions were mass analyzed in the analyzer portion of the mass spectrometer according to the mass to charge ratios by varying the magnetic field strength. The magnetic field strengths

were measured by a differential magnetometer. All ions were accelerated into the analyzer tube by 4.5 kV energy.

Ion detection was done by a 20 stage Pi-type electron multiplier, and the resulting ion currents were amplified by a vibrating reed electrometer. Multiplier gains γ_i for the ions i were measured by interposing a Faraday cup collector just before the entrance shield to the electron multiplier. A similar description of a nearly identical mass spectrometer is given in the literature.²²

Experimental Procedure

The experiment consisted of one run which the sample contained a 0.5-0.5 molar ratio of Cu-Sn alloy. Tin, 99.99+% pure, was purchased from Alfa Inorganics, Danvers, Massachusetts. The copper sample was 99.999% pure and was obtained from Research Organic/Inorganic Chemical Corporation, Sun Valley, California.

A major problem exists in the selection of the Knudsen cell material. The selection is usually difficult, because in some cases, phase diagrams of the equilibrium between the cell material and the sample are not available. In this run, a graphite cell seemed adequate and was chosen.

The instrument was standardized at an emission current of 1.1 mA, which was sustained throughout the run. The ions were produced with an ionizing energy of 18eV. The ionic species were identified by mass-to-charge ratio, shutterability, ionization efficiency curves (where possible) and isotopic distribution.

The parent ions identified in the present investigation are listed in Table 1.

The gas phase above the condensed system Cu-Sn was analyzed in the temperature range 1243 to 1597 degrees Kelvin. The observed principal ion current intensities relevant to the evaluation of enthalpy changes for the various reactions are listed in Table 2 in the sequence they were recorded. The ion currents were corrected for isotopic abundance. This experiment warrants discussion, because of the first observation of $\text{Cu}_2\text{Sn}(\text{g})$ and $\text{CuSn}_2(\text{g})$. These molecules were identified before the termination of the run due to the evaporation of the sample. Due to the low ion intensities, no meaningful appearance potentials could be measured for CuSn_2 .

Absolute pressures were derived at any given temperature $T(\text{K})$ for a particular specie (i) from the intensity data according to the relationship

$$P_i = k_i I_i^+ T$$

where P_i is the pressure in atmospheres, k_i the reference calibration constant for specie i in $\text{ATM A}^{-1}\text{K}^{-1}$, I_i^+ the ion intensity in amps, and T the temperature in K. The reference calibration constant k_i is defined by the relationship

$$k_i = k_j \left[\frac{G_j N_j E_i}{G_i} \left(\frac{\gamma_i}{\gamma_j} \right) N_i E_j \right]$$

where k_j is the reference calibration constant for a standard, G is the ionization cross section, γ the multiplier gain, N the isotopic abundance, and E is the intensity correction factor.

TABLE I - OBSERVED PARENT IONS

Cu - Sn SYSTEM

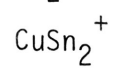
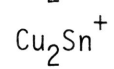


TABLE 2 - OBSERVED ION INTENSITIES OF PARENT
IONS ABOVE THE CONDENSED SYSTEM Cu-Sn

DATA SET #	T, °K	Cu ⁺	Sn ⁺	Cu ₂ ⁺	Sn ₂ ⁺
1.	1243	1.09x10 ⁻¹¹	1.00x10 ⁻¹⁰	--	--
2.	1296	3.14x10 ⁻¹¹	2.64x10 ⁻¹⁰	--	--
3.	1348	8.46x10 ⁻¹¹	6.28x10 ⁻¹⁰	--	--
4.	1454	4.52x10 ⁻¹⁰	3.58x10 ⁻⁹	--	--
5.	1507	2.09x10 ⁻⁹	1.35x10 ⁻⁸	7.33x10 ⁻¹³	2.14x10 ⁻¹¹
6.	1483	1.42x10 ⁻⁹	9.55x10 ⁻⁹	--	1.40x10 ⁻¹¹
7.	1383	2.55x10 ⁻¹⁰	2.39x10 ⁻⁹	2.14x10 ⁻¹³	4.91x10 ⁻¹²
8.	1410	3.50x10 ⁻¹⁰	3.11x10 ⁻⁹	1.88x10 ⁻¹³	7.49x10 ⁻¹²
9.	1429	3.86x10 ⁻¹⁰	3.34x10 ⁻⁹	6.28x10 ⁻¹⁴	4.17x10 ⁻¹²
10.	1442	5.37x10 ⁻¹⁰	4.70x10 ⁻⁹	1.19x10 ⁻¹³	1.60x10 ⁻¹¹
11.	1545	2.95x10 ⁻⁹	2.40x10 ⁻⁸	--	5.24x10 ⁻¹¹
12.	1543	2.73x10 ⁻⁹	2.87x10 ⁻⁸	9.61x10 ⁻¹³	6.71x10 ⁻¹¹
13.	1575	4.69x10 ⁻⁹	4.88x10 ⁻⁸	9.36x10 ⁻¹³	1.40x10 ⁻¹⁰
14.	1580	2.50x10 ⁻⁹	5.49x10 ⁻⁸	2.45x10 ⁻¹³	1.58x10 ⁻¹⁰
15.	1562	1.66x10 ⁻⁹	4.15x10 ⁻⁸	1.95x10 ⁻¹³	1.12x10 ⁻¹⁰
16.	1597	1.35x10 ⁻⁹	5.71x10 ⁻⁸	1.57x10 ⁻¹³	1.53x10 ⁻¹²

TABLE 2 - CONTINUED

DATA SET #	CuSn^+	Cu_2Sn^+	CuSn_2^+	Sn_3^+
1.	--	--	--	--
2.	--	--	--	--
3.	--	--	--	--
4.	1.82×10^{-12}	--	--	--
5.	2.95×10^{-12}	8.96×10^{-13}	--	--
6.	1.97×10^{-12}	2.74×10^{-14}	--	--
7.	2.98×10^{-13}	--	--	--
8.	--	--	--	--
9.	1.19×10^{-13}	--	--	--
10.	1.79×10^{-13}	--	--	--
11.	7.16×10^{-12}	--	--	--
12.	8.05×10^{-12}	3.1×10^{-13}	7.58×10^{-13}	2.64×10^{-12}
13.	1.47×10^{-11}	5.65×10^{-12}	4.67×10^{-13}	8.69×10^{-12}
14.	7.98×10^{-12}	6.85×10^{-12}	1.71×10^{-13}	--
15.	3.87×10^{-12}	1.01×10^{-12}	2.22×10^{-13}	6.12×10^{-12}
16.	5.07×10^{-12}	5.99×10^{-13}	2.56×10^{-13}	8.70×10^{-12}

In the Cu-Sn run, the pressure calibration done with a standard, such as silver or gold, was not possible, because the melting point of tin (525°K) is lower than that of silver or gold. Because of this difference, the vapor pressure of tin would interfere with the calibration measurements. However, the reference calibration constant was based on vapor pressure data and activities of copper and tin taken from the compilations by Hultgren.^{23,24} The relationships

$$k_i = P_i a_i / I_i^{+T}$$

$$k_i = k_j [G_j N_j E_i / G_i (\frac{\gamma_i}{\gamma_j}) N_i E_j]$$

where a_i is the activity of specie i based on a 0.5-0.5 molar ratio of the binary alloy, were used to calculate the pressure constants. The values of the activities used were $a_{Cu} = 0.220 \pm 0.025$ and $a_{Sn} = 0.467 \pm 0.05$.²⁴ The calculated average values of the reference calibration constants were $k_{Cu} = 0.636 \pm 0.13$ and $k_{Sn} = 0.344 \pm 0.07$.

The determination of the remaining parameters used in the second relationship in the previous paragraph was done as follows. Relative multiplier gains γ_i were measured for Cu^+ and Sn^+ . Values for the multiplier gains of the polyatomic metal molecules were assumed equal to that of the atoms. The γ_i values for the mixed species were obtained by taking the arithmetic means of the γ_i value of the composite atoms. The relative maximum ionization cross sections for singly ionized atomic species were taken from Mann.²⁵ Ionization cross sections of diatomic

and higher polyatomic molecules were estimated as 0.75 times that of the sum of the cross sections of the composite elements.¹³ Experimental ionization efficiency curves (where applicable) provided an empirical correction factor, $E_i = I_i^+ (\text{max.}) / I_i^+ (18\text{eV})$. Where no ionization efficiency curves are available, the E_i values were taken as equal to the E_i value of the most abundant atom in the molecule. The various instrument parameters employed for the Cu-Sn run are listed in Table 3.

Calculation of Thermal Functions

The thermodynamic functions of molecules in the gas phase can be calculated from computer programs based on statistical thermodynamic relations, particularly the free-energy function, $-(G_T^\circ - H_{298}^\circ)/T$, and the enthalpy function, H_{298}° . When molecular constants or spectroscopic data are known, the results are very accurate and reliable. However, experimentally determined molecular constants are limited or nonexistent for many molecules, so they have to be estimated. The following is a discussion of the known or estimated molecular parameters of the molecules studied in this investigation.

The thermal functions for Cu and Sn were taken from the compilation by Hultgren,²³ and for Cu_2 , the functions were taken from JANAF tables.²⁶ The free energy and heat content functions are listed in Table 4.

TABLE 3 - EXPERIMENTAL AND ESTIMATED PARAMETERS FOR CALCULATING ABSOLUTE PRESSURES

ION	APPEARANCE POTENTIAL (eV)	IONIZATION CROSS SECTION σ_i (\AA^2)	MULTIPLIER GAIN $\gamma_i \times 10^{-4}$	INTENSITY CORRECTION FACTOR, E_i	PRESSURE CONSTANT k_i (ATM/ \AA °K)
Cu^+	7.72*	3.80	7.86	1.015	0.636
Sn^+	7.34*	7.70	7.44	1.053	0.344
Cu_2^+	-	5.70	7.86	1.015	0.424
CuSn^+	7.2 \pm 1.0	8.63	7.65	1.005	0.285
Sn_2^+	6.81 \pm 1.0	11.60	7.44	1.020	0.221
Cu_2Sn^+	7.72 \pm 1.0	11.50	7.72	1.019	0.215
CuSn_2^+	-	14.40	7.58	1.053	0.181
Sn_3^+	6.35 \pm 1.0	17.30	7.44	1.053	0.153

* TAKEN AS REFERENCE FROM: R. W. KISER, INTRODUCTION TO MASS SPECTROMETRY (ENGLEWOOD CLIFFS, N.J., PRENTICE-HALL, INCORPORATED, 1965).

TABLE 4 - FREE ENERGY FUNCTIONS, $-(G_1^{\circ}-H_{298}^{\circ})/T$, IN CAL MOLE⁻¹K⁻¹ AND HEAT CONTENT FUNCTIONS, $(H_1^{\circ}-H_{298}^{\circ})$, IN KCAL MOLE⁻¹ FOR THE GASEOUS SPECIES Cu, Sn, Cu₂, CuSn, Sn₂, AND Sn₃

MOLECULE	TEMPERATURE (°K)									
	298	1100	1200	1300	1400	1500	1600	1700		
Cu	FEF	39.74	42.61	42.93	43.23	43.52	43.77	44.05	44.29	
	HCF	1.481	3.983	4.480	4.977	5.475	5.973	6.472	6.973	
Sn	FEF	40.24	43.75	44.19	44.62	45.03	45.42	45.80	46.15	
	HCF	1.481	5.506	6.316	7.039	7.866	8.573	9.362	10.11	
Cu ₂	FEF	57.75	62.88	63.46	64.01	64.53	64.03	65.50	65.95	
	HCF	2.373	7.211	8.123	9.038	9.954	10.87	11.79	12.71	
CuSn	FEF	64.40	69.51	70.08	70.62	71.14	71.62	72.09	72.53	
	HCF	2.411	7.132	8.026	8.919	9.812	10.71	11.60	12.49	
Sn ₂	FEF	64.27	69.34	69.91	70.45	70.96	71.45	71.91	72.35	
	HCF	2.337	7.098	7.990	8.882	9.775	10.67	11.56	12.54	
Sn ₃ (L)	FEF	81.50	90.00	90.96	91.86	92.72	93.53	94.30	95.04	
	HCF	3.843	11.87	13.36	14.85	16.34	17.83	19.32	20.81	
Sn ₃ (B)	FEF	85.95	93.87	94.77	95.61	96.41	97.16	97.89	98.57	
	HCF	3.599	11.08	12.47	13.86	15.25	16.64	18.03	19.42	

Sn₂ and Sn₃:

A valence force-field calculation utilizing a modification of the Schachtshneider computer program, which employs the Wilson FG matrix method,²⁷ was made to evaluate the vibrational frequencies of the Sn₃ molecule, as well as for the Cu₂Sn and CuSn₂ molecules. The vibrational frequency and bond length of Sn₂ was estimated by Ackerman *et al.*⁸ as 300 cm⁻¹ and 2.80 Å, respectively. The vibrational frequency corresponds to a force constant of 1.582 mdyne/Å. For the Sn₃ molecule, both the linear and bent structures were assumed. In addition to the stretching force constant, a linear bending force constant and angle bending force constant of 0.158 mdyne/Å was used. This value was taken as 1/10 of the arithmetic mean of the stretching force constants. One then assumes that the interaction between bond stretching and bond stretching-angle bends to be zero. The calculated vibrational frequencies for the linear Sn₃ molecule were $\omega_1 = 260.5 \text{ cm}^{-1}$, $\omega_2 = 150.4 \text{ cm}^{-1}$, and $\omega_3 = 41.6 \text{ cm}^{-1}$ (d.d.), and for the bent Sn₃ molecule, assuming a bond angle of 95° from the bond angle of SnCl₂,²⁸ the frequencies were $\omega_1 = 217.3 \text{ cm}^{-1}$, $\omega_2 = 208.8 \text{ cm}^{-1}$, and $\omega_3 = 29.9 \text{ cm}^{-1}$. The electronic ground state for each molecule was assumed to have a statistical weight, $g_i = 4$. The free-energy and heat content functions obtained from the calculated frequencies and the assumed molecular constants are summarized in Table 4.

Cu-Sn:

The vibrational frequency and bond length of the Cu-Sn molecule was estimated by Ackerman *et al.*⁸ as 215 cm^{-1} and a 2.58 \AA , respectively. The corresponding force constant was calculated to be 0.566 mdyne/\AA . In the calculation of the thermal functions, the electronic ground state assumed to have $g_i = 4$. The values of the free energy and heat content functions for the Cu-Sn molecule are summarized in Table 4.

Cu₂Sn and CuSn₂:

Since the molecules Cu₂Sn and CuSn₂ have not been studied previously, spectroscopic determination of the molecules is needed to obtain a more accurate determination of their molecular structures. Because of this lack of information, one must consider various structures in context with the available information. Assuming the possible monovalent and divalent states of copper, the symmetric and asymmetric structures of both Cu₂Sn and CuSn₂ were chosen.

The linear and bent symmetric Cu-Sn-Cu and asymmetric Sn-Cu-Cu molecules were considered for the Cu₂Sn molecule. In the linear and bent Cu-Sn-Cu molecules, the bond distances and bond stretching frequencies were taken to be the same as for the Cu-Sn molecule, namely 2.58 \AA and 0.566 mdyne/\AA , respectively. For the bent molecule, a bond angle of 95° was taken from a SnCl₂ analog,²⁸ and the bending force constant of 0.0566 mdyne/\AA was used. The

bond distances and stretching frequencies of the linear and bent asymmetric Sn-Cu-Cu molecules were assumed similar to that of the Cu-Sn and Cu₂ molecules. The bond distance of 2.22 $\overset{\circ}{\text{A}}$ and a stretching frequency of 266.1 cm⁻¹ for Cu₂ were taken from Rosen.²⁹ The stretching frequency of Cu₂ corresponds to a force constant of 0.666 mdyne/ $\overset{\circ}{\text{A}}$. The bond angle of the bent asymmetric molecule was assumed to be 87°, based on the CuBr₂ molecule,³⁰ and the bending force constant of 0.0616 mdyne/ $\overset{\circ}{\text{A}}$ was used. Again, the bending force constants were estimated to be 1/10 of the arithmetic mean of the stretching force constants. The calculated vibrational frequencies (in cm⁻¹) of the Cu₂Sn molecule are listed below:

	ω_1	ω_2	ω_3
a) Linear Cu-Sn-Cu	177.1	123.1	30.7 (d.d.)
b) Bent Cu-Sn-Cu	154.8	150.4	25.1
c) Linear Sn-Cu-Cu	152.5	133.5	40.3 (d.d.)
d) Bent Sn-Cu-Cu	189.3	152.9	26.1

The values of the free-energy and heat content functions of the Cu₂Sn molecule calculated from the above frequencies and estimated molecular parameters are listed in Table 5.

The linear and bent structures of the symmetric Sn-Cu-Sn and asymmetric Cu-Sn-Sn molecules were also considered. The molecular parameters for CuSn₂ were assumed similar to those of the Cu₂Sn molecule. The Sn-Sn bond in the asymmetric Cu-Sn-Sn molecule was taken to have the same parameters as Sn₂ molecule,

TABLE 5 - FREE ENERGY FUNCTIONS, $-(G_T^{\circ}-H_{298}^{\circ})/T$, IN CAL MOLE⁻¹K⁻¹ AND HEAT CONTENT FUNCTIONS, $(H_T^{\circ}-H_{298}^{\circ})$, IN KCAL MOLE⁻¹ FOR GASEOUS Cu₂Sn MOLECULE

MOLECULE AND STRUCTURE	298	1100	1200	1300	1400	1500	1600	1700
Cu-Sn-Cu (LINEAR)	FEF	81.12	89.66	90.62	91.52	93.19	93.97	94.71
	HCF	3.982	11.91	13.40	14.89	16.38	17.87	20.85
Cu-Sn-Cu (BENT)	FEF	84.55	92.52	93.41	94.25	95.06	96.54	97.23
	HCF	3.729	11.12	12.50	13.89	15.28	16.68	19.46
Cu-Cu-Sn (LINEAR)	FEF	81.86	90.40	91.36	92.27	93.12	94.72	95.45
	HCF	3.970	11.91	13.40	14.89	16.38	17.87	20.85
Cu-Cu-Sn (BENT)	FEF	85.10	93.06	93.96	94.80	95.60	97.08	97.77
	HCF	3.689	11.10	12.49	13.88	15.27	16.66	19.44

namely a bond distance of 2.80 \AA and a stretching force constant of 1.582 mdyne/\AA . For the bent Sn-Cu-Sn and Cu-Sn-Sn molecules, the bond angles were taken the same as for the Cu_2Sn molecule, namely 87° and 95° , respectively. The corresponding bending force constants, taken to be 1/10 of the arithmetic mean of the stretching force constants, were 0.0566 mdyne/\AA for Sn-Cu-Sn and 0.107 mdyne/\AA for Cu-Sn-Sn. The calculated vibrational frequencies (in cm^{-1}) of the CuSn_2 molecule are listed below:

	ω_1	ω_2	ω_3
a) Linear Sn-Cu-Sn	152.5	90.0	33.9 (d.d.)
b) Bent Sn-Cu-Sn	156.0	149.9	19.6
c) Linear Cu-Sn-Sn	227.4	129.6	38.5 (d.d.)
d) Bent Cu-Sn-Sn	123.4	151.2	25.1

In both Cu_2Sn and CuSn_2 , the electronic ground state was assumed to have a statistical weight of $g_j = 4$. The values of the free-energy and heat content functions of the CuSn_2 molecule calculated from the above frequencies and estimated molecular parameters are listed in Table 6.

TABLE 6 - FREE ENERGY FUNCTIONS, $-(G_T^0 - H_{298}^0)/T$, IN CAL MOLE⁻¹K⁻¹ AND HEAT CONTENT FUNCTIONS, $(H_T^0 - H_{298}^0)$ IN KCAL MOLE⁻¹ FOR GASEOUS CuSn₂ MOLECULE

MOLECULE AND STRUCTURE	TEMPERATURE (°K)										
	298	1100	1200	1300	1400	1500	1600	1700			
Sn-Cu-Sn (LINEAR)	FEF	83.46	92.02	92.98	93.88	94.74	95.56	96.33	97.07		
	HCF	4.038	11.92	13.41	14.90	16.39	17.88	19.37	20.86		
Sn-Cu-Sn (BENT)	FEF	86.42	94.39	95.28	96.13	96.93	97.69	98.41	99.10		
	HCF	3.736	11.12	12.51	13.90	15.29	16.68	18.07	19.46		
Sn-Sn-Cu (LINEAR)	FEF	82.43	90.95	91.91	92.81	93.67	94.48	95.26	96.00		
	HCF	3.904	11.89	13.38	14.87	16.36	17.85	19.34	20.83		
Sn-Sn-Cu (BENT)	FEF	89.17	97.15	98.04	98.89	99.69	100.4	101.2	101.9		
	HCF	3.763	11.12	12.51	13.90	15.29	16.68	18.07	19.46		

RESULTS AND DISCUSSION

As in the previously outlined procedures, the measured ion intensities have been converted to partial pressures, which in turn, yielded valuable thermodynamic data. There are two standard procedures by which thermodynamic values, such as reaction enthalpies and entropies, can be obtained from the measured partial pressures. These procedures are known as the second- and third-law methods. Both methods yield the same type of thermodynamic values, but each one has distinct advantages depending on the temperature range, the number of data points, and the availability of absolute entropy data. These two methods are briefly discussed in the following section.

Evaluation of Thermodynamic Properties

In the evaluation of the thermodynamic data, the third-law method is utilized more than the second-law method. This method is based on the knowledge of the absolute entropies of the reactants and products. One may use the expression for the changes in free energy (ΔG_T°) of a reaction,

$$\Delta G_T^\circ = - RT \ln K_p = \Delta H_T^\circ - T\Delta S_T^\circ$$

to derive the following relationship,

$$\Delta H_{298}^\circ = - RT \ln K_p - T\Delta[(G_T^\circ - H_{298}^\circ)/T]$$

where K_p is the pressure equilibrium constant of the reaction, T is the absolute temperature, R is the ideal gas constant, ΔH_{298}° is

the standard enthalpy change with reference to 298°K, G_T° is the standard molar free energy of a substance at temperature T, and H_{298}° is the standard molar enthalpy at 298°K. The change in the free energy function, $-\Delta[(G_T^\circ - H_{298}^\circ)/T]$, of a reaction can be determined for a specified reaction by taking the sum of the free energy functions for the reaction products and subtracting the sum of the free energy functions of the reactants. The change in the free energy function can be calculated at any given temperature T, and the latter equation is commonly employed in third-law evaluations.

The analysis of the data by the third-law method is generally superior to the second-law method. The third-law allows for independent calculation of an enthalpy value for the reaction from individual data sets at each temperature. This analysis will reveal trends in the equilibrium constants which indicate non-equilibrium or errors in the free-energy functions. The biggest disadvantage of this method is that in the calculation of the free energy functions, the structural and spectroscopic information are required, much of which are often not available. Another disadvantage is that absolute values of K_p are necessary, which involves the knowledge of relative multiplier gains and ionization cross sections.

The relationship between the variation of the equilibrium constant (K_p) with the temperature and the ΔH_T° for the given reaction is given by the Van't Hoff equation,

$$\frac{d(\ln K_p)}{d(1/T)} = \frac{-\Delta H_T^\circ}{R}$$

where ΔH_T° is the enthalpy change for the reaction involving gaseous species, and the values K_p , R , and T are as previously defined. The value of the enthalpy change for a reaction may be obtained from the slope of the $\ln K_p$ versus $1/T$ plot. The variation of ΔH_T° with temperature is assumed to be sufficiently small for the plot to be linear. The values of ΔH_T° are determined by least-squares procedure. The entropy change (ΔS_T°) is given by the intercept with the $\ln K_p$ axis, provided that absolute values of K_p are used.

There are some advantages and disadvantages of the second-law method. The significant advantage is that the absolute entropy data is not necessary if only the ΔH_T° is to be obtained. Another advantage is that the pressure calibration of the instrument and the knowledge of the relative multiplier gains and ionization cross sections are not necessary for either the pressure independent or pressure dependent reactions. In this case, the pressure calibration would not affect the slope of the second-law plot. The disadvantages, however, include the calculation of one ΔH_T° value at the mid-temperature of the plot for the entire data set. Also, the measurement of the slope is subject to large uncertainties due to a small number of data points or a narrow temperature range.

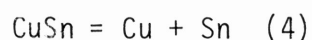
When conditions permit, a combination of the two methods is desirable. The second-law determination permits a check on the values of the free energy functions. However, in this Cu-Sn experiment, the calculated second-law values are not reliable enough for comparison with the corresponding third-law values. The reason for the poor second-law values is due to the experimental scattering

of four to twelve data points within approximately 200°K range. As brought up previously, the utilization of four to twelve temperature points resulted in large uncertainties in the second-law ΔH_T° values. Thus, as in this experiment, the comparison between the second- and third-law values will not be possible for structure considerations.

In this experiment, the results are based on the third-law enthalpies of reactions. The reactions and treatment used in determining the thermodynamic values are described in the following discussion.

Molecules Cu_2 , Sn_2 , Sn_3 , and CuSn

The enthalpy changes for the following gaseous reactions,



were determined by the third- and second-law methods. Due to the large uncertainties in the second-law values, only the third law will be reported throughout this discussion.

The third-law enthalpy changes (ΔH_0°) for reactions 1, 2, 3, and 4 were 48.1 ± 2.0 , 44.2 ± 1.0 , 103.2 ± 0.4 , and 39.8 ± 2.0 kcal mole⁻¹, respectively. The enthalpy change for reaction 3 is for the case of a linear Sn_3 molecule. For the bent Sn_3 molecule, the enthalpy value is 97.3 ± 0.3 kcal mole⁻¹. The uncertainties associated with the above values are standard deviations.

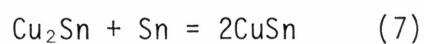
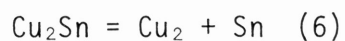
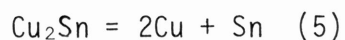
The enthalpy changes involving the diatomic molecules (reactions 1, 2, and 4) also correspond to the bond dissociation energies, D_0° . The calculated bond dissociation energies compare reasonably well with the literature values. The literature values of the bond dissociation energies are for Cu_2 , $47.3 \pm 2.2 \text{ kcal mole}^{-1}$;²⁹ for Sn_2 , $45.8 \pm 4 \text{ kcal mole}^{-1}$;²⁹ and for CuSn , $41.4 \pm 4 \text{ kcal mole}^{-1}$.⁸

The heat of atomization, $\Delta H_{\text{ATM},0}^\circ$, for Sn_3 was calculated by Gingerich, Desderi, and Cocke,⁷ to be $114.9 \pm 4.1 \text{ kcal mole}^{-1}$. The experimental values are slightly lower than the literature value, but from the standpoint of the lower standard deviation, the linear structure of Sn_3 seems to be favored. Gingerich *et al.*⁷ suggested double-bonded linear chains, but the formation of a triangle in Sn_3 is also possible. Spectroscopic data concerning molecular and electronic structures will be needed to probe into the nature of bonding in Sn_3 .

The reasonableness of the calculated values with the literature values suggests that the pressure calibration constants, k_i , used in the evaluations are fairly good. The bond dissociation energies of Cu_2 , Sn_2 , and CuSn measured in this investigation will be used to calculate the heats of atomization of Cu_2Sn and CuSn_2 .

Molecules Cu_2Sn and CuSn_2

The heats of atomization of Cu_2Sn and CuSn_2 were calculated from the enthalpy values of three different reactions, as in the case of Cu_2Sn ,



Reactions 5 and 6 are pressure dependent reactions, while reaction 7 is pressure independent. A pressure dependent reaction is defined as a reaction for which the total number of moles of gaseous products and gaseous reactants are different and are dependent on the pressure calibration of the mass spectrometer. As the difference in the number of moles of reactant decreases compared to the number of moles of product, a small uncertainty in the pressure constant of the constituents may produce a larger uncertainty in the evaluated enthalpies of reactions. Therefore, the addition of the pressure independent reaction 7 would provide a check on the reliability of the pressure calibration.

The third-law enthalpies of reaction and heats of atomization of Cu_2Sn are listed in Table 7. The $\Delta H_{\text{O}}^{\circ}$ values are the third-law enthalpies for the reactions 5, 6, and 7, and the $\Delta H_{\text{ATM}, \text{O}}^{\circ}$ values are the heats of atomization of Cu_2Sn calculated from the respective reactions. The heats of atomization of Cu_2Sn are calculated for all possible structures of Cu_2Sn . The bond dissociation energies of Cu_2 , $48.1 \pm 2.0 \text{ kcal mole}^{-1}$, and CuSn , $39.8 \pm 2.0 \text{ kcal mole}^{-1}$, were used in conjunction with the enthalpies of reactions 6 and 7, respectively, to calculate the heats of atomization.

Since a comparison between the second- and third-law enthalpy values is not possible, the bond additivity rule and the magnitude

TABLE 7 - THIRD LAW ENTHALPIES AND HEATS OF ATOMIZATION (IN KCAL MOL⁻¹) OF THE GASEOUS Cu₂Sn MOLECULE

REACTION	Cu-Sn-Cu(L)		Cu-Sn-Cu(B)		Cu-Cu-Sn(L)		Cu-Cu-Sn(B)	
	$\Delta H^\circ_{\text{ATM},0}$	ΔH°	$\Delta H^\circ_{\text{ATM},0}$	ΔH°	$\Delta H^\circ_{\text{ATM},0}$	ΔH°	$\Delta H^\circ_{\text{ATM},0}$	ΔH°
Cu ₂ Sn = 2Cu + Sn	107.6±	107.6±	103.5±	103.5±	106.5±	106.5±	102.4±	102.4±
	4.6	4.6	4.6	4.6	4.6	4.6	4.5	4.5
Cu ₂ Sn = Cu ₂ + Sn ^(a)	62.4±	110.5±	58.2±	106.2±	61.2±	109.3±	57.2±	105.±
	4.0	4.5	4.0	4.4	4.0	4.5	4.0	4.4
Cu ₂ Sn + Sn = 2CuSn ^(b)	28.2±	107.8±	23.9±	103.6±	27.1±	106.7±	23.1±	102.7±
	4.9	5.3	4.8	5.200	4.9	5.3	4.8	5.2

(a) USING D₀(Cu₂) = 48.0 ± 1.9 KCAL MOL⁻¹ (THIS INVESTIGATION).

(b) USING D₀(CuSn) = 39.8 ± 1.9 KCAL MOL⁻¹ (THIS INVESTIGATION).

of statistical errors provide two additional arguments for structure consideration. The bond additivity rule is that the atomization energy of a molecule is roughly equal to the sum of the bond dissociation energies of the constituent bonds in the molecule. Using the previously defined bond dissociation energies, the atomization energy for the symmetric Cu-Sn-Cu molecule is approximately $39.8 + 39.8$ or $79.6 \text{ kcal mole}^{-1}$, and for the asymmetric Cu-Cu-Sn molecule, the value is $87.9 \text{ kcal mole}^{-1}$. By referring to the atomization energy values in Table 7, the value for the asymmetric Cu-Cu-Sn molecule is closer to the corresponding atomization energies of the asymmetric molecule than that of the symmetric Cu-Sn-Cu molecule in relation to its corresponding atomization energies. Thus the asymmetric Cu-Cu-Sn structure seems to be a likely choice of structure.

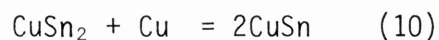
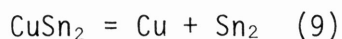
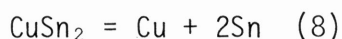
The atomization energies of the asymmetric Cu_2Sn measured from Reaction 7 are $106.7 \pm 5.3 \text{ kcal mole}^{-1}$ for the linear molecule and $102.7 \pm 5.2 \text{ kcal mole}^{-1}$ for the bent molecule. Application of the bond additivity rule may be taken as an indication that the bent structure is preferred, because of the smaller difference between the atomization energies. The lower statistical error for the enthalpy of the bent structure as compared to the linear case also suggests that the bent structure is preferred.

Further examination of Table 7 shows that the bent asymmetric structure is not the only possible choice of structure. Due to the similarities in the atomization energies, the bent symmetric molecule is also another possibility. Since there are no clear-cut

differences in the atomization energies, the application of the bond additivity rule should not be relied upon.

It appears that the bent structure, either symmetric or asymmetric, is preferred over the linear one. In analogy to MAu_2 molecules, where M represents a Group IIIA or IVA metal, it had been found^{4, 5, 31, 32} that the symmetric structures are the preferred ones. One may suggest the same as in the case for Cu_2Sn . However, in the case of MAu_2 the monovalency of Au makes the asymmetric structure unlikely. This restriction does not apply to copper compounds, because Cu can readily be in both the monovalent or divalent states. Thus either the bent symmetric or asymmetric structures are possible for Cu_2Sn . It would be interesting to decide the question through further experimentation, such as matrix isolation infrared studies.

The heats of atomization of CuSn_2 were calculated from the following reactions,



These reactions are analogous to those of reactions 5 - 7. The third-law enthalpies for reactions 8 - 10 and the heats of atomization of all possible structures of CuSn_2 are listed in Table 8. The bond dissociation energies of Sn_2 , $44.2 \pm 1.0 \text{ kcal mole}^{-1}$, and CuSn , $39.8 \pm 2.0 \text{ kcal mole}^{-1}$, measured in this investigation, were used in conjunction with reactions 9 and 10, respectively, to calculate the atomization energies of CuSn_2 .

TABLE 8 - THIRD LAW ENTHALPIES AND HEATS OF ATOMIZATION (IN KCAL MOLE⁻¹) OF GASEOUS CuSn₂ MOLECULE

REACTION	Sn-Cu-Sn(L)		Sn-Cu-Sn(B)		Sn-Sn-Cu(L)		Sn-Sn-Cu(B)	
	ΔH°	$\Delta H^\circ_{\text{ATM},0}$	ΔH°	$\Delta H^\circ_{\text{ATM},0}$	ΔH°	$\Delta H^\circ_{\text{ATM},0}$	ΔH°	$\Delta H^\circ_{\text{ATM},0}$
CuSn ₂ = Cu + 2Sn	95.7± 2.1	95.7± 2.1	92.2± 2.1	92.2± 2.1	97.2± 2.1	97.2± 2.1	87.8± 2.1	87.8± 2.1
CuSn ₂ = Cu + Sn ₂ ^(c)	52.5± 2.0	96.7± 2.3	48.8± 2.0	93.1± 2.3	54.0± 2.0	98.3± 2.3	44.5± 2.0	88.7± 2.3
CuSn ₂ + Cu = 2CuSn ^(d)	16.2± 1.7	95.8± 2.6	12.6± 1.7	95.2± 2.6	17.8± 1.6	97.4± 2.6	8.3± 1.7	87.9± 2.6

(c) USING D₈(Sn₂) = 44.2 ± 1.0 KCAL/MOLE (THIS INVESTIGATION).

(d) USING D₈(CuSn) = 39.8 ± 1.9 KCAL/MOLE (THIS INVESTIGATION).

Examination of the results in Table 8 again shows a similarity of the atomization energy values for all possible structures of CuSn_2 . The experimental analogies of CuSn_2 are $\text{Ge}_2\text{Au}^{31}$ and $\text{Al}_2\text{Au}^{32}$, where the asymmetric bent structures were determined to be the preferred structures. This could be the case for CuSn_2 , but due to the two possible valence states of Cu, the symmetric structure must be included as another possibility. The problem of structure is similar to that of Cu_2Sn , and further experimentation is necessary to determine the exact structure of CuSn_2 .

Summary and Conclusion

The atomization energies of Cu_2 , Sn_2 , Sn_3 , and CuSn , as determined in this study, are 48.1 ± 2.0 , 44.2 ± 1.0 , 103.2 ± 0.4 , and $39.8 \pm 2.0 \text{ kcal mole}^{-1}$, respectively. The error terms are standard deviations. These values were within the error limits of the reported literature values.

The atomization energies of Cu_2Sn and CuSn_2 are listed in Tables 7 and 8, respectively. The error terms used are the square roots of the sum of the squares of the respective standard deviations. The selected atomization energies of Cu_2Sn and CuSn_2 were taken as the averages of the atomization energies for all structures as 106.0 ± 2.5 and $93.8 \pm 4.2 \text{ kcal mole}^{-1}$, respectively.

Due to the similarities in the values of the atomization energies, it is not possible to assign exact structures for Cu_2Sn and CuSn_2 . The bent structures of GeAu_2^{31} and AlAu_2^{32} imply that the bent structure is possible for Cu_2Sn . From the

previous studies of Ge_2Au ,³¹ Al_2Au ,³² and CuGe_2 ,³³ the bent structures of the M_2Au molecules were indicated as the preferred ones, which also suggests a bent structure for CuSn_2 . The existence of either the symmetric or asymmetric Cu_2Sn and CuSn_2 molecules is possible due to the monovalent and divalent states of copper. The possibility of a triatomic ring may also be considered since the triatomic molecules investigated have a somewhat larger atomization energy as would be calculated from the bond additivity concept. In such a ring they could have three instead of two bonds. The resolution of these structures can be enhanced by matrix isolation infrared studies.

The heats of formation, $\Delta H_{f,0}^\circ$, for the gaseous Cu_2Sn and CuSn_2 molecules were derived as 127.0 ± 2.5 and 130.7 ± 4.2 kcal mole⁻¹, respectively. In the calculation of the heats of formation, the heat of vaporization for copper (80.5 ± 0.3 kcal mole⁻¹) and the heat of vaporization for tin (72.0 ± 0.4 kcal mole⁻¹) were taken from Hultgren *et al.*²³

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