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# Dissociation energies of the intermetallic molecules CuIn, AgIn, and AuIn

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The gaseous diatomic intermetallic molecules of the IA-IIIB groups, elements CuIn, AgIn, and AuIn, were investigated in a Knudsen cell-mass spectrometric study of the vapors over the respective alloys. From a number of all-gas equilibria their dissociation energies have been derived:  $D_0^\circ(\text{CuIn}) = 183.7 \pm 7.9$ ,  $D_0^\circ(\text{AgIn}) = 162.8 \pm 4.9$ ,  $D_0^\circ(\text{AuIn}) = 282.3 \pm 5.7$  kJ/mol. These values were compared to the values calculated from empirical models of bond. Of particular interest is the strikingly high dissociation energy of AuIn which was interpreted in terms of relativistic effects rather than due to multiple bond. The implications in the indium electronegativity value and the mode of formation of AuIn(g) are also discussed.

## I. INTRODUCTION

The study both experimentally and theoretically of small metal clusters has become a topic of fast increasing interest in recent years because of its relevance to surface chemistry and, in particular, heterogeneous catalysis.

The understanding of chemical bonding in homonuclear and heteronuclear dimers and, possibly, polymers, is of basic importance for developing and testing empirical or semiempirical models of bond in such units. Recent publications include a large number of articles and references in this area.<sup>1-3</sup> Several reviews have appeared which more specifically report experimental and calculated thermochemical dissociation energies of diatomic and, in few cases, triatomic and higher polyatomic molecules.<sup>4-8</sup>

The study object of this paper constitutes a contribution to the knowledge of the nature of the metal-metal bond in gaseous intermetallic compounds between IB group and IIIA group elements. Specifically, we report here the results concerning the thermochemistry of the IB metals-Indium gaseous species CuIn, AgIn, AuIn. Of these, only for AgIn, a preliminary thermochemical characterization has been reported previously.<sup>9</sup> For the other species, Bondybey *et al.*<sup>10</sup> in their laser induced vaporization-laser induced fluorescence (LIV-LIF) study of Cu-Ga and Cu-In alloys observed a LIF spectrum indicating the formation of a gaseous CuIn species, but no structural data have been reported. Barrow *et al.*<sup>11</sup> in a spectroscopic study of many gold-containing intermetallic systems observed a bands system in the region 15 600–17 900 cm<sup>-1</sup> which has been attributed to a AuIn molecular species without performing analyses of their bands.

In the present study the bond energies obtained from the study of several gas-phase reactions are compared with those derived from the application of various semiempirical models of bond.

## II. EXPERIMENTAL

The experiments were carried out with a single-focusing, 60° magnetic sector, 30.5 cm radius of curvature HT

mass spectrometer (built by Nuclide Associates, USA) equipped with a Knudsen cell molecular source. The Knudsen cell (with cylindrical orifice and clausius factor of 0.23) used throughout the experiments was made of high density, high purity graphite to ensure reducing conditions and to avoid as far as possible interactions of cell material with the metal systems under study at the operating temperatures. The cell was heated by radiation from a tungsten spiral resistance element. The temperature measurement was accomplished with a disappearing filament optical pyrometer. The vapors effusing from the cell were ionized with 70 eV energy electrons.

Various vaporization experiments were carried out using different sample systems and the same cell. The alloy samples used were, in sequence: Cu(83)-In(17), Cu(71)-Au(14)-In(15), Ag(81)-In(19) where the numbers in brackets are the respective molar percentages. The intensities measured for the various ions were converted into pressures by the usual relation:  $P = K \cdot f_s \cdot I \cdot T$ . The instrument sensitivity constant  $K$  was evaluated by quantitative silver calibration vaporizations and the values found ranged from 3.3 to 1.2 atm A<sup>-1</sup> K<sup>-1</sup>. As for the coefficients  $f_s$ , which are specific of the ion considered, the values adopted were as follows: <sup>63</sup>Cu<sup>+</sup> (3.15), <sup>115</sup>In<sup>+</sup> (1.65), <sup>126</sup>Cu<sub>2</sub><sup>+</sup> (4.65), <sup>178</sup>CuIn<sup>+</sup> (2.29), <sup>197</sup>Ag<sup>+</sup> (2.66), <sup>312</sup>AuIn<sup>+</sup> (1.81), <sup>394</sup>Au<sub>2</sub><sup>+</sup> (2.26), <sup>107</sup>Ag<sup>+</sup> (4.24), <sup>216</sup>Ag<sub>2</sub><sup>+</sup> (3.88), <sup>222</sup>AgIn<sup>+</sup> (3.01). The necessary ionization cross sections for the atoms were taken from Mann<sup>12</sup> while those for the diatomic species were assumed to be 0.75 times the sum of the cross sections of the constituents atoms. Finally, the multiplier gains were assumed to be proportional to the inverse square roots of the relevant ionic masses.

## III. RESULTS

### A. Identification of ions

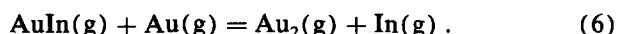
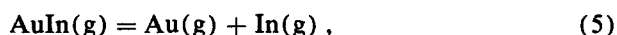
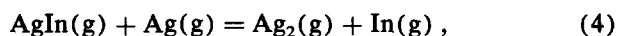
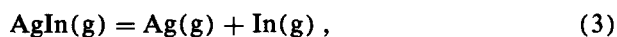
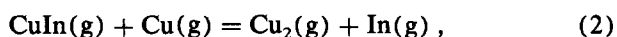
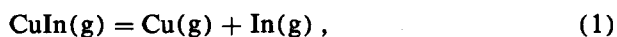
The following singly ionized species were observed and identified by computer-simulated isotopic distributions: Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, In<sup>+</sup>, Cu<sub>2</sub><sup>+</sup>, Ag<sub>2</sub><sup>+</sup>, Au<sub>2</sub><sup>+</sup>, In<sub>2</sub><sup>+</sup>, CuIn<sup>+</sup>, AgIn<sup>+</sup>, and AuIn<sup>+</sup>. The heteronuclear species CuIn<sup>+</sup> and

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$\text{AuIn}^+$  were here identified for the first time. The measured values of the appearance potentials (AP) for  $\text{CuIn}^+$ ,  $\text{AgIn}^+$ , and  $\text{AuIn}^+$  were 5.7, 6.1, and 7.3 eV, all within an uncertainty of  $\pm 0.5$  eV. For the elements monomers and dimers the AP values were in substantial agreement with literature data (see Moore<sup>13</sup> for Cu, Ag, Au; Powers *et al.*<sup>14</sup> for  $\text{Cu}_2$ ; Cocke and Gingerich<sup>15</sup> for  $\text{Ag}_2$ ; Kingcade and Gingerich<sup>16</sup> for  $\text{Au}_2$ ). The shape of the ionization efficiency curves (IEC) indicated that, under the actual experimental conditions, fragmentation processes were unimportant. Only in the case of  $\text{AuIn(g)}$  some features in IEC measured in one experiment at relatively low temperature might suggest the setup of the fragmentation process with threshold energy at about 12 eV, the extent of which could not be established. However, in the subsequent thermochemical analysis of reactions involving  $\text{AuIn(g)}$  and  $\text{Au(g)}$  the effects of different fragmentation values up to 30% on the equilibrium constant were considered.

## B. Reaction enthalpies and atomization energies

The following gaseous dissociation and exchange reactions were studied:



Possible equilibria involving  $\text{In}_2\text{(g)}$  were not studied because the  $\text{In}_2^+$  ion intensity measured in the course of various experiments showed much less reproducibility than that for other ion species.

The temperature dependences of the equilibrium constants of the reactions (1) to (6) are reported in Figs. 1 to 3, while in Tables I to III are reported the second-law and third-law analyses of the equilibrium data.

As concerns the aforementioned fragmentation of

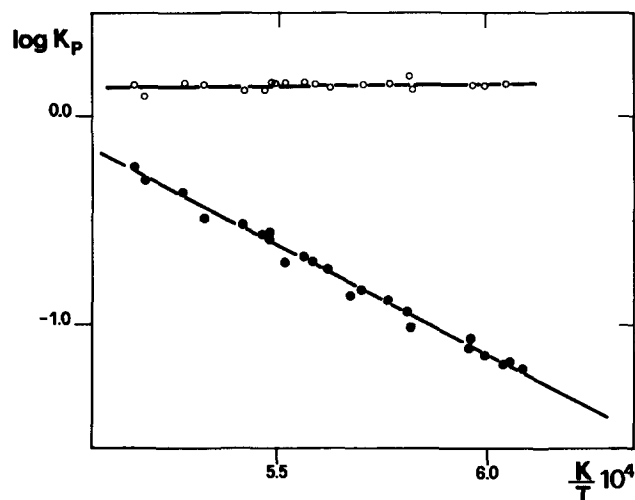


FIG. 1. Second-law plots for reactions (1)  $\text{CuIn(g)} = \text{Cu(g)} + \text{In(g)}$  (●) and (2)  $\text{CuIn(g)} + \text{Cu(g)} = \text{Cu}_2\text{(g)} + \text{In(g)}$  (○).

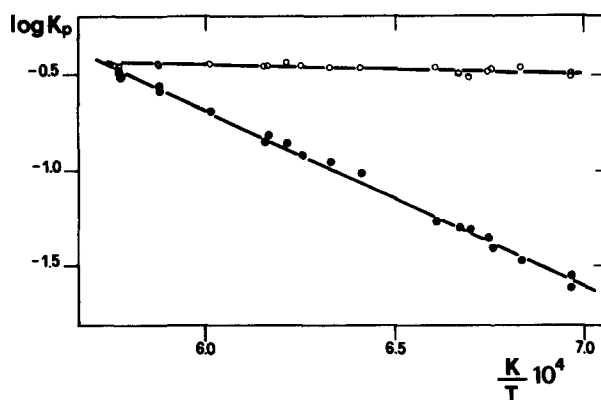


FIG. 2. Second-law plots for reactions (3)  $\text{AgIn(g)} = \text{Ag(g)} + \text{In(g)}$  (●) and (4)  $\text{AgIn(g)} + \text{Ag(g)} = \text{Ag}_2\text{(g)} + \text{In(g)}$  (○).

$\text{AuIn(g)}$  to  $\text{Au}^+$ , an analysis of equilibrium (5) made by assuming a fragmentation extent ranging from zero to the estimated upper limit of 0.3, showed that inclusion of the fragmentation contribution in the evaluation of the ion intensities and, hence, of the equilibrium constant resulted in a slight dependence from the temperature of the individual third-law enthalpy values. Moreover, a better overall agreement between second-law and third-law values was obtained when no fragmentation contribution was included. Consequently, we preferred to give reliance to the thermodynamic analysis and, therefore, to evaluate the data without accounting for fragmentation contribution to the measured ion intensities.

A summary of the equilibria studied and of the hence derived dissociation energies of  $\text{AgIn(g)}$  and of the newly identified molecules  $\text{CuIn(g)}$  and  $\text{AuIn(g)}$  is reported in Table IV.

The following dissociation energies of the reference diatomic molecules were selected and used:  $D_0^\circ(\text{Cu}_2) = 198.9 \pm 2.4$  kJ/mol,<sup>17</sup>  $D_0^\circ(\text{Ag}_2) = 160.2 \pm 8.7$  kJ/mol,<sup>18</sup>  $D_0^\circ(\text{Au}_2) = 221.9 \pm 8.7$  kJ/mol.<sup>18</sup>

## C. Thermodynamic functions

The thermodynamic functions for the monoatomic elements were taken from Hultgren *et al.*,<sup>19</sup> for the dimers they

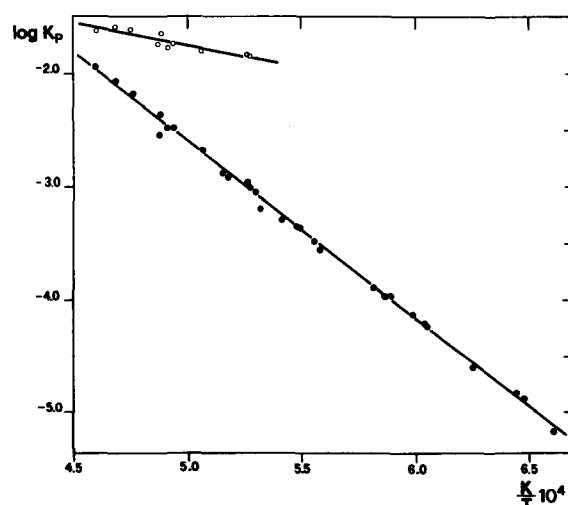


FIG. 3. Second-law plots for reactions (5)  $\text{AuIn(g)} = \text{Au(g)} + \text{In(g)}$  (●) and (6)  $\text{AuIn(g)} + \text{Au(g)} = \text{Au}_2\text{(g)} + \text{In(g)}$  (○).

TABLE I. Equilibrium data and third-law enthalpies (in kJ/mol) for reactions:  $\text{CuIn(g)} = \text{Cu(g)} + \text{In(g)}$  (1) and  $\text{CuIn(g)} + \text{Cu(g)} = \text{Cu}_2\text{(g)} + \text{In(g)}$  (2).

Run	<i>T</i> /K	$\ln K_{p,1}$	$\Delta H_{0,1}^\circ$	$\ln K_{p,2}$	$\Delta H_{0,2}^\circ$
1,1	1677	-2.51	179.6	0.34	-17.3
	1763	-1.99	182.0		
	1680	-2.48	180.9		
	1735	-2.01	179.3	0.36	-18.0
	1644	-2.81	179.9		
1,2	1652	-2.72	179.7		
	1754	-1.92	180.1	0.34	-17.8
	1722	-2.15	179.7	0.44	-19.1
	1779	-1.68	179.2	0.32	-17.7
	1813	-1.62	182.0	0.37	-18.8
	1830	-1.28	178.6	0.29	-17.7
2,1	1799	-1.55	179.4	0.38	-18.8
	1846	-1.19	179.0	0.30	-17.8
	1941	-0.54	178.6	0.35	-19.2
	1932	-0.70	180.2	0.23	-17.2
	1880	-1.13	181.7	0.36	-19.0
2,2	1655	-2.73	180.1	0.34	-17.1
	1669	-2.64	180.5	0.32	-17.0
	1719	-2.33	181.9	0.30	-17.0
	1791	-1.60	179.3	0.35	-18.3
2,3	1824	-1.34	178.9	0.38	-18.9
	1821	-1.30	178.1	0.37	-18.8
	1896	-0.82	178.5	0.38	-19.3
Avg	<i>T</i> /K = 1771				
Third law		$\Delta H_0^\circ = 179.9 \pm 1.2$	$\Delta H_0^\circ = -18.1 \pm 0.8$		
Second law		$\Delta H_0^\circ = 200.9 \pm 4.7$	$\Delta H_0^\circ = -2.2 \pm 3.4$		
Second law		$\Delta H_0^\circ = 185.8 \pm 4.7$	$\Delta H_0^\circ = -8.5 \pm 3.4$		

were recalculated on the basis of molecular parameters taken from Huber and Herzberg,<sup>18</sup> except for the equilibrium interatomic distance of  $\text{Ag}_2^{20}$ ; for the heteronuclear species thermodynamic functions evaluations were based almost en-

TABLE II. Equilibrium data and third-law enthalpies (in kJ/mol) for reactions:  $\text{AgIn(g)} = \text{Ag(g)} + \text{In(g)}$  (3) and  $\text{AgIn(g)} + \text{Ag(g)} = \text{Ag}_2\text{(g)} + \text{In(g)}$  (4).

Run	<i>T</i> /K	$\ln K_{p,3}$	$\Delta H_{0,3}^\circ$	$\ln K_{p,4}$	$\Delta H_{0,4}^\circ$
3,1	1480	-3.26	163.8	-1.08	2.6
	1622	-1.88	162.3	-1.04	2.6
	1702	-1.31	162.9	-1.04	3.0
	1735	-1.13	163.9	-1.05	3.4
3,2	1499	-3.01	163.0	-1.13	3.3
	1609	-1.98	162.2	-1.01	2.1
3,3	1436	-3.72	164.2	-1.17	3.3
	1560	-2.35	161.6	-1.07	2.7
	1580	-2.21	162.1	-1.07	2.8
	1599	-2.13	163.1	-1.05	2.6
	1624	-1.96	163.7	-1.06	2.9
	1663	-1.60	162.9	-1.02	2.5
	1702	-1.36	163.7	-1.04	3.0
	1513	-2.92	163.6	-1.06	2.4
	1482	-3.14	162.6	-1.12	3.0
	1436	-3.58	162.4	-1.12	2.8
	1463	-3.40	163.6	-1.06	2.2
	1493	-3.02	162.5	-1.18	3.9
	1733	-1.19	164.5	-1.07	3.6
Avg	<i>T</i> /K = 1569				
Third law		$\Delta H_0^\circ = 163.1 \pm 0.8$	$\Delta H_0^\circ = 2.9 \pm 0.5$		
Second law		$\Delta H_0^\circ = 175.6 \pm 2.9$	$\Delta H_0^\circ = 6.7 \pm 1.7$		
Second law		$\Delta H_0^\circ = 162.6 \pm 2.9$	$\Delta H_0^\circ = 1.4 \pm 1.7$		

tirely on estimated molecular parameters. The calculated thermodynamic functions and the molecular constants adopted for  $\text{CuIn(g)}$ ,  $\text{AgIn(g)}$ , and  $\text{AuIn(g)}$  are reported in Tables V and VI, respectively.

The only experimental value available refers to the vibrational frequency of  $\text{AgIn(g)}$  reported in Ref. 18. As concerns the  $\text{CuIn}$  molecule, to which the laser excitation spectrum observed upon laser vaporization of a  $\text{CuIn}$  alloy has been attributed,<sup>10</sup> the reported  $75\text{ cm}^{-1}$  spacing of a single progression of bands appears to us definitely too low, if compared with the known vibrational frequencies of the intermetallic molecules of the groups IB–IIIA, to be assumed in the ground state frequency estimate. Therefore, as for  $\text{AuIn(g)}$  the frequency of  $\text{CuIn(g)}$  was evaluated from the estimated value of the force constant by analyzing the known data for the IB–IIIA groups molecules. The force constants for these molecules appear to be fairly constant on varying the IIIA group element so that it has been possible to estimate with reasonable confidence the following force constants:  $\text{CuIn}$  ( $K_f = 9.01 \times 10^4\text{ dyn cm}$ ),  $\text{AuIn}$  ( $K_f = 1.46 \times 10^5\text{ dyn cm}$ ). The soundness of these estimates can be checked by plotting the known vibrational frequencies of many diatomics of copper, silver, and gold with heteroatoms of the periods II to V as a function of the period itself. From such a

TABLE III. Equilibrium data and third-law enthalpies (in kJ/mol) for reactions:  $\text{AuIn(g)} = \text{Au(g)} + \text{In(g)}$  (5) and  $\text{AuIn(g)} + \text{Au(g)} = \text{Au}_2\text{(g)} + \text{In(g)}$  (6).

Run	<i>T</i> /K	$\ln K_{p,5}$	$\Delta H_{0,5}^\circ$	$\ln K_{p,6}$	$\Delta H_{0,6}^\circ$
2,1	1799	-8.10	280.7		
	1848	-7.67	281.9		
	1888	-7.12	280.0		
	1941	-6.74	282.3		
	1932	-6.82	282.1		
	1880	-7.45	284.0		
	1552	-11.19	280.2		
2,2	1599	-10.68	282.3		
	1655	-9.77	280.1		
	1669	-9.59	280.1		
	1719	-9.06	281.2		
	1791	-8.29	282.3		
	1824	-7.80	280.4		
	1513	-11.99	283.0		
2,3	1703	-9.22	280.9		
	1697	-9.21	279.6		
	1821	-7.82	280.2		
	1896	-7.02	279.8	-4.23	55.9
	1974	-6.25	279.4	-4.14	57.0
	2052	-5.89	284.9	-4.03	57.7
	1544	-11.30	280.1		
2,4	1652	-9.73	280.2		
	1899	-6.91	278.5	-4.23	56.0
	2037	-5.80	281.1	-4.10	58.5
	2024	-5.79	279.2	-3.98	55.9
	2048	-5.51	277.8	-3.79	53.6
	2102	-5.10	278.4	-3.71	53.7
	2135	-4.83	278.6	-3.66	53.9
	2175	-4.56	279.1	-3.74	56.4
Avg	<i>T</i> /K = 1822				
Third law		$\Delta H_0^\circ = 280.6 \pm 1.7$	$\Delta H_0^\circ = 55.9 \pm 1.7$		
Second law		$\Delta H_0^\circ = 299.7 \pm 2.9$	$\Delta H_0^\circ = 72.3 \pm 12.5$		
Second law		$\Delta H_0^\circ = 284.0 \pm 2.9$	$\Delta H_0^\circ = 65.0 \pm 12.5$		

TABLE IV. Summary of the all-gas equilibria studies and dissociation energies derived for CuIn(g), AgIn(g), and AuIn(g) (all values in kJ/mol).

Molecule	Reaction	No. Points	Temp. range	$\Delta H_{0,3rd\ law}^\circ$	$\Delta H_{0,2nd\ law}^\circ$	$\Delta H_{0,selected}^\circ$	$D_0^\circ(\text{MeIn})$	$D_0^\circ(\text{MeIn})^a$ Proposed
CuIn	CuIn = Cu + In	22	1644–1941	$179.9 \pm 1.2^b$	$185.8 \pm 4.7^c$	$182.9 \pm 9.4^d$	$182.9 \pm 9.4^e$	$183.7 \pm 7.9$
	CuIn + Cu = Cu <sub>2</sub> + In	19	1677–1941	$-18.1 \pm 0.8$	$-8.5 \pm 3.4$	$-13.3 \pm 14.4$	$185.6 \pm 14.6$	
AgIn	AgIn = Ag + In	19	1436–1735	$163.1 \pm 0.8$	$162.6 \pm 2.9$	$162.9 \pm 5.8$	$162.9 \pm 5.8$	$162.8 \pm 4.9$
	AgIn + Ag = Ag <sub>2</sub> + In	19	1436–1735	$2.9 \pm 0.5$	$1.4 \pm 1.7$	$2.2 \pm 3.4$	$162.4 \pm 9.3$	
AuIn	AuIn = Au + In	29	1544–2175	$280.6 \pm 1.7$	$284.0 \pm 2.9$	$282.3 \pm 5.8$	$282.3 \pm 5.8$	$282.3 \pm 5.7$
	AuIn + Au = Au <sub>2</sub> + In	10	1896–2175	$55.9 \pm 1.7$	$65.0 \pm 12.5$	$60.5 \pm 25.0$	$282.4 \pm 26.4$	

<sup>a</sup> Obtained as the mean of the values originated from the different reactions by assigning weights proportional to the inverse squares of the reported standard deviations.

<sup>b</sup> Uncertainties are as follows: standard deviation on the points.

<sup>c</sup> Standard deviation on the slope.

<sup>d</sup> Estimated standard deviation.

<sup>e</sup> As evaluated by the propagation rules.

plot it is apparent that the estimated frequency values for AuIn and CuIn appear *in linea* with the known trends. The interatomic distances  $r_e$  were evaluated through a procedure similar to that used by Pauling<sup>21</sup> utilizing the available experimental values for the IB–IIIA groups diatomics AgAl and AuAl. For all three molecules under study a  $\Sigma^1$  ground state has been assumed.

#### IV. DISCUSSION

##### A. Dissociation energies

From the equilibrium data summarized in Table IV the selected values for the dissociation energies at 0 K of CuIn, AgIn, and AuIn are  $183.7 \pm 7.9$  kJ/mol,  $162.8 \pm 4.9$  kJ/mol, and  $282.3 \pm 5.7$  kJ/mol, respectively. The value here found for  $D_0^\circ(\text{AgIn})$ , obtained with extensive measurements in a large temperature interval and second- and third-law evaluation of the data, confirms the value 163.2 kJ/mol reported by Gingerich and Blue.<sup>9</sup>

Among the various empirical models of bond that have been used in order to rationalize bond energies of diatomic intermetallic molecules, those of Pauling<sup>21</sup> and Miedema and Gingerich<sup>4,5,7</sup> have been most widely adopted. In Table VII we report the dissociation energies calculated with the

models together with the experimental values now available for the diatomics between IB–IIIA groups elements. Inspection of this table clearly shows that, while the values calculated with the Miedema and Gingerich model result, overall, slightly better, both the models fail in reproducing the experimental values.

The most striking feature of the values here determined for the dissociation energies of the diatomics between indium and copper, silver and gold can be appreciated in Fig. 4 where it is apparent the large increase of the dissociation energy in going from silver to gold which follows a decrease on going from copper to silver. This behavior parallels that found for the Cu<sub>2</sub>, Ag<sub>2</sub>, Au<sub>2</sub> sequence. In the case of the homonuclear diatomics the tempting hypothesis<sup>22</sup> of a role which could be played in the bonding by the configuration  $d^9 s^2$  or  $d^9 sp$  (with promotion energies showing a trend along the IB group complementary to that of the bond energies) seems to have been abandoned. Indeed, a detailed orbital occupation analysis for the Cu<sub>2</sub> molecule<sup>23</sup> confirms the single-bond interpretation of Bauschlicher *et al.*<sup>24</sup> contrary to the triple-bond hypothesis advanced by Pauling.<sup>25</sup> At present, the relativistic contribution along the IB group elements, which peaks at 1 eV for Au<sub>2</sub><sup>26</sup> appears to be the accepted explanation for the anomalous trend observed.

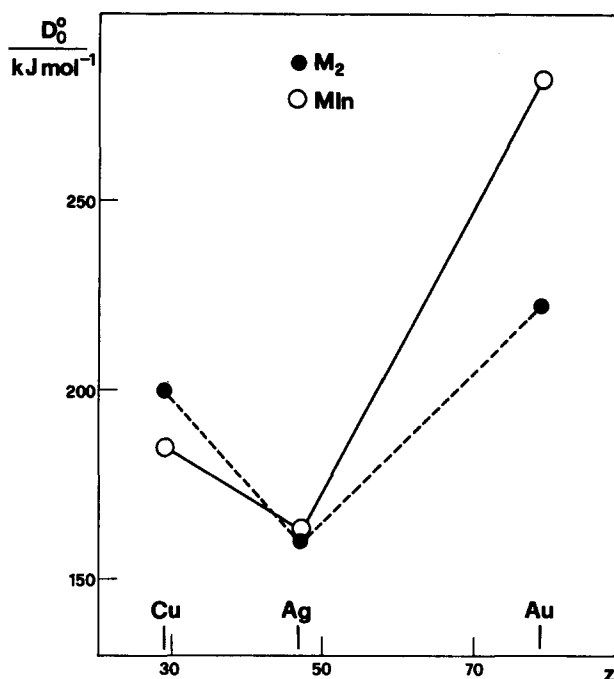
TABLE V. Gibbs functions, in J/K mol, and heat content functions, in kJ/mol, for CuIn(g), AgIn(g), and AuIn(g).

T/K	CuIn (g)		AgIn (g)		AuIn (g)	
	$-(G_T^\circ - H_0^\circ)/T$	$(H_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$	$(H_T^\circ - H_0^\circ)$	$-(G_T^\circ - H_0^\circ)/T$	$(H_T^\circ - H_0^\circ)$
298.15	224.450	10.178	231.999	10.344	236.583	10.211
1300	276.844	47.527	284.884	47.742	289.078	47.572
1400	279.556	51.266	287.608	51.482	291.793	51.311
1500	282.084	55.005	290.147	55.222	294.323	55.050
1600	284.452	58.745	292.524	58.962	296.693	58.790
1700	286.679	62.484	294.759	62.702	298.922	62.529
1800	288.781	66.244	296.878	66.443	301.025	66.270
1900	290.771	69.964	298.864	70.183	303.017	70.010
2000	292.661	73.704	300.759	73.294	304.907	73.750
2100	294.460	77.445	302.563	77.665	306.707	77.491
2200	296.175	81.185	304.284	81.406	308.424	81.231

TABLE VI. Molecular constants adopted for thermodynamic functions evaluation of gaseous CuIn, AgIn, AuIn.

Molecule	Frequency $\omega/\text{cm}^{-1}$	Bond distance $r/\text{\AA}$	Ground state
CuIn	$193 \pm 20$	$2.61 \pm 0.1$	$^1\Sigma$
AgIn	154.7	$2.78 \pm 0.1$	$^1\Sigma$
AuIn	$185 \pm 20$	$2.64 \pm 0.1$	$^1\Sigma$

Turning now to the heteronuclear molecules here studied CuIn, AgIn, AuIn, and on inspection of Fig. 4 two questions arise: (a) Why the decrease of the dissociation energy on going from CuIn to AgIn is smaller than in the case of the corresponding homonuclear molecules  $\text{Cu}_2$  and  $\text{Ag}_2$ , and (b) Why the increase of the dissociation energy for AuIn is substantially larger than for  $\text{Au}_2$ . An answer to the first question could be rather expectable and is most probably related to the different sizes of the atoms involved in the bonding. Indeed, on going from  $\text{Cu}_2$  to  $\text{Ag}_2$  the influence of the increase in the atom diameter is twice as that which occurs in the CuIn to AgIn sequence. Consequently, the overlap of the  $s$  orbitals is less reduced in AgIn than in  $\text{Ag}_2$  as compared with CuIn and  $\text{Cu}_2$ , respectively. An answer to the second question can be given, at least in a qualitative manner, by arguing on the entity of the relativistic effects. We are here reversing the reasoning advanced by Ziegler *et al.*<sup>27</sup> on the smallness of the relativistic effects in AuCl as compared to  $\text{Au}_2$  and AuH. They argued that in AuCl, being the ionicity larger, the valence orbitals could be concentrated on the chlorine side where the relativistic effects are smaller. In the case of AuIn it comes out that the opposite is true as the electronegativity of gold is substantially larger than that of indium (2.4 against 1.7 or 1.2 if our revised value for indium is considered to be significant, as discussed in the subsequent section). As a matter of fact here the ionicity is even larger than in AuCl. Following this reasoning the orbitals should be concentrated on the Au center where the relativistic effects are originated so providing a particularly large dissociation energy. Accordingly, the increase observed for the dissociation energy of the corresponding IB group hydrides should be intermediate between those for the dimers and for the diatomic intermetallics with

FIG. 4. Behavior of dissociation energy of homonuclear  $M_2$  and heteronuclear  $M\text{In}$  diatomic molecules along the IB group elements.

indium as it is actually found.<sup>18</sup> Finally, it must be mentioned here that while the overall picture for the other IB–IIIA molecules (see Table VII) is more or less similar, a merely empirical plot of the dissociation energies of these molecules as a function of the IIIA group atoms would suggest that as concerns the values reported for CuGa and AuGa ( $212 \pm 15$  and  $290 \pm 15$  kJ/mol)<sup>28</sup> more credit should be given to values at the lower end of the range delimited by the given errors.

## B. Indium electronegativity

As already discussed, the Pauling model does not reproduce the measured dissociation energies. However, the results of this model ultimately depend on the adopted values of the electronegativity of the atoms involved in the bond. As for not many diatomic molecules data exist in which indium

TABLE VII. Comparison of experimental bond energies and model predictions (values in kJ/mol).

Molecule	Experimental $D_E^0$	Pauling $D_P^0$	Miedema and Gingerich $D_{MG}^0$	$D_E^0 - D_P^0$	$D_E^0 - D_{MG}^0$
				$D_E^0$	$D_E^0$
CuIn	184	145	147	0.21	0.20
AgIn	163	126	134	0.23	0.18
AuIn	282	199	233	0.29	0.17
CuAl	213	179	178	0.16	0.16
AgAl	188	160	166	0.15	0.12
AuAl	322	253	256	0.21	0.20
CuGa	215	175	166	0.19	0.23
AgGa	179	156	155	0.13	0.13
AuGa	293	239	249	0.18	0.15

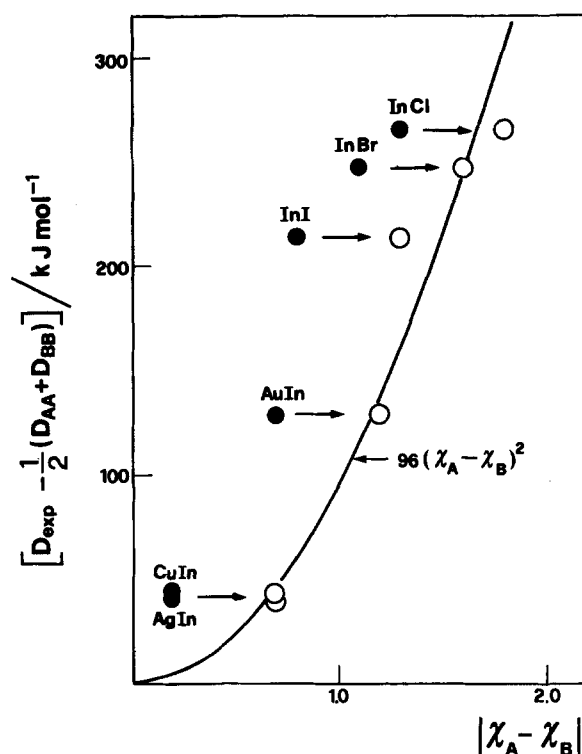


FIG. 5. Plot of the fraction of the dissociation energy explained with the electronegativity concept in the Pauling's model against the absolute differences in electronegativities for the indium-containing diatomics with monovalent bond.

can be reasonably considered as single-bonded, it seems to us that having here determined the bond energies for three indium-containing diatomics, we are in a position to inquire into the reliability of the quoted electronegativity value for monovalent indium. To this end we can trace back from the Pauling's formula,  $D_{AB}^\circ = 1/2 (D_{AA}^\circ + D_{BB}^\circ) + 96 (\chi_A - \chi_B)^2$ , the value of the indium electronegativity which could provide the best overall agreement with the available experimental data. In Fig. 5 the quantity  $D_{\text{exp}}^\circ - 1/2 (D_{AA}^\circ + D_{BB}^\circ)$  is reported as a function of the differences in the values of the electronegativity of the atoms for six indium containing molecules. The electronegativity differences considered have been evaluated by reducing the Pauling's electronegativity values to a common monovalent state as proposed by Barbe.<sup>29</sup> The resulting values, reported in brackets, are as follows: Cu(1.8), Ag(1.9), Au(2.3), In(1.7). Now, assuming as more reliable the metal and halogen electronegativities for which a larger number of diatomics are known, it can be seen from the plot that a lowering of indium electronegativity of 0.5 units brings into a reasonable agreement calculated and experimental values. Consequently, we would propose to use the value  $\chi_{\text{In}} = 1.2$  for the electronegativity of monovalent Indium, in particular, for estimation of the dissociation energies of indium-containing intermetallic molecules.

### C. Mechanism of formation of molecular products

Some interesting comments on the mechanism of formation of gaseous CuGa have been reported by Bondybey *et*

*al.*<sup>10</sup> in their laser induced fluorescence study of laser vaporized molecules. Indeed, these authors present three convincing pieces of evidence in favor of gas-phase recombination processes. Briefly, their observations are: (a) comparable CuGa signals were observed in vaporizing alloys or pure metals simultaneously, (b) CuGa signals increased with carrier gas pressure in a manner consistent with a collisional stabilization of the molecule, (c) a time lag was observed between atomic Gallium and molecular CuGa signals. Apparently, as it is reasonable, these results for the CuGa molecule are considered to be representative also for the Cu–In system.

In the course of the present study we carried out vaporization runs on the Au–In system in order to ascertain whether the molecular species would be formed from equilibrium established within the Knudsen cell or could also be detected as originating directly from the surface of the melted sample. In experiments made using an indium–gold mixture with approximately 20% at. concentration in indium in free evaporation conditions at 1300 K, the following approximate intensity ratios were measured:  $I(\text{AuIn}^+)/I(\text{Au}^+) \simeq 1.5$ ,  $I(\text{In}^+)/I(\text{AuIn}^+) \simeq 40$ . This result clearly indicates that heteronuclear molecules of this kind of intermetallic system are also formed directly in the evaporation step. Actually, different chemical systems were employed by Bondybey *et al.* and by us, also it would be reasonable at first to assume, as Bondybey and co-workers did, that a similar behavior should be found for the IB–IIIA groups intermetallic systems.

Two further comments seem to be appropriate here: Our results for the Au–In system could be due to the exceptionally high stability of the AuIn molecule caused by the large relativistic effect at work in this species. Another possible reason, which could be of much more relevance in connection with current interest in metal clusters formation, could be a different behavior in the thermal-activated and laser-activated evaporation of materials.

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