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SOLID-STATE ELECTROCHEMICAL STUDY OF Ga-Sb LIQUID ALLOYS

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### Author

Anderson, T.J.

### Publication Date

1975-09-01

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Submitted to Journal of Chemical  
Thermodynamics

LBL-4153  
Preprint c 1

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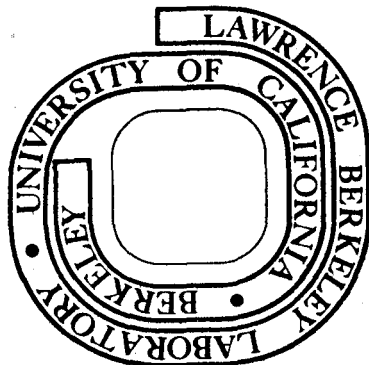
T. J. Anderson and L. F. Donaghey

September 1975

Prepared for the U. S. Energy Research and  
Development Administration under Contract W-7405-ENG-48

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Solid-State Electrochemical Study of  
Ga-Sb Liquid Alloys

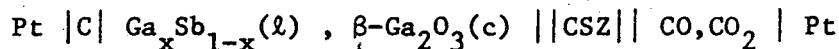
T. J. Anderson and L. F. Donaghey

Inorganic Materials Research Division,  
Lawrence Berkeley Laboratory, and  
Department of Chemical Engineering;  
University of California, Berkeley 94720

September, 1975

Abstract

Component activities in Ga-Sb liquid alloys were measured in the high temperature galvanic cell,



using calcia-stabilized zirconia (CSZ) as the solid electrolyte and a CO+CO<sub>2</sub> gaseous mixture as the reference electrode. Moderate deviations in activities from Raoult's law were found. Using the results of this study in conjunction with literature calorimetric data the degree of short range ordering in the liquid alloy was examined. Liquidus temperatures using our data were also calculated and showed excellent agreement with the experimentally measured values.

## INTRODUCTION

Gallium and antimony combine to form a single intermetallic compound, gallium antimonide (GaSb) with the sphalerite structure. This compound is of current practical interest for its semiconducting properties, especially in application to Gunn effect diodes.<sup>(1)</sup>

The thermodynamics of the gallium - antimony system at and above the melting temperature of GaSb, has received considerable attention. Much recent consideration has been given to solution models for the prediction of thermodynamic data from liquidus temperatures. Such indirect methods, however, are sensitive to errors in available liquidus data. For example, the melting point of GaSb,  $T_m$ , as determined by different studies has been reported to be 975,<sup>(11, 12)</sup> 979,<sup>(7)</sup> 982,<sup>(14)</sup> 985,<sup>(2, 6, 13)</sup> 993,<sup>(9)</sup> and 998<sup>(10)</sup> degrees Kelvin. The melting point as measured by different investigators shows marked differences though the generally accepted value is 985 K.<sup>(15, 16)</sup> Compiled in table 1 is a list of the experimentally determined enthalpy of fusion of GaSb,  $\Delta H_f^C(\text{GaSb})$ , calculated assuming the melting point is 985 K. As can be seen, the large range of  $2.0 \text{ kcal}_{\text{th}} \text{ g-atom}^{-1}$  exists for the reported  $\Delta H_f^C(\text{GaSb})$ .

The Ga-Sb phase diagram has been determined by a number of investigators<sup>(7, 14, 18)</sup> all in generally excellent agreement, though shifted somewhat below the accepted melting point.

Enthalpy of mixing data for liquid alloys have been measured by Predel and Stein<sup>(20)</sup> and Yazawa, Kawashima and Itagaki<sup>(21)</sup> who found a maximum in this quantity of  $-258$  and  $-204 \text{ cal}_{\text{th}} \text{ g-atom}^{-1}$ ,

Table 1. Comparison of enthalpy and entropy of fusion of GaSb, as reported by different investigators. ( $\text{cal}_{\text{th}} = 4.184\text{J}$ )

$\frac{\Delta H_f^C(\text{GaSb})}{\text{kcal}_{\text{th}} \text{g-atom}^{-1}}$	$\frac{\Delta S_f^C(\text{GaSb})}{\text{cal}_{\text{th}} \text{g-atom}^{-1} \text{K}^{-1}}$	Reference
7.78 ( $\pm .1$ )	7.90 ( $\pm .11$ )	2
7.9	8.0	3
6.0 ( $\pm .5$ )	6.1	4
7.3 ( $\pm .3$ )	7.4	5
7.5 ( $\pm .3$ )	7.6	8
8.0 ( $\pm .8$ )	8.1	17
7.0 ( $\pm .3$ )	7.1	19

respectively, at an equimolar composition. Activities in the liquid phase have been measured with solid state electrochemical techniques. (22-24) All of the reported results show extremely large negative deviation from ideality. Small negative deviations were found by Yazawa, Kawashima and Itagaki when they applied a strictly regular solution model to their heat of mixing data, (21) while Predel and Stein calculated moderate positive deviations near the melting point of GaSb. (20) On the other hand, vapor pressure studies (25) have shown a moderately negative derivation from ideality. Thus, the thermodynamic properties of the Ga-Sb system at and above the melting temperature of GaSb are not well defined.

In this study, component activities in the liquid phase of the Ga-Sb system were measured with a high temperature galvanic cell employing a calcia-stabilized zirconia solid electrolyte and gaseous reference electrode.

## EXPERIMENTAL

### Materials

The alloy coexistence electrodes used in this study were prepared from high purity materials. Semiconductor-grade elemental gallium and antimony were obtained from Cominco American. Powdered  $\text{Ga}_2\text{O}_3$  of 99.999% purity was obtained from Alfa Products. The materials were allowed to contact only high-purity alumina during the mixing process. High purity graphite was used in the preparation of the containers for the alloy coexistence electrode. Calcia-stabilized zirconia tubes having a nominal composition of  $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$  were obtained from Zircoa Corporation of America. The high temperature part of the experimental cell housing was constructed entirely of high

purity recrystallized alumina. The electrode assembly was contained within a split tube of 99.99 tantalum which acted as a support and as an oxygen getter.

### Apparatus

The basic experimental cell consisted of a 2 inch-diameter closed-end alumina tube 18 inch in length secured by a Viton O-ring to the brass cell head. This envelope contained the electrodes as shown in figure 1. The Ga-Sb alloy and a small amount of  $\beta\text{-Ga}_2\text{O}_3$  were placed within a graphite closed crucible in contact with a 0.250 inch diameter CSZ tube containing the  $\text{CO}+\text{CO}_2$  reference gas and a Pt-paste contact between a Pt wire and the electrolyte. Three 1/8 inch bored-through cajon connectors on the cell head for thermocouples were placed symmetrically around a 1/4 inch central cajon fitting containing a calcia-stabilized zirconia tube. The thermocouples used were type K (.020 inch Pt, Pt 10% Rh) which were calibrated in separate experiments within the cell against an NBS-traceable calibrated thermocouple.

In this investigation argon gas was used as the inert gas blanket. High purity, tank argon was further purified by passing it through a column of Linde 4A molecular sieve at the temperature of the dry ice-acetone equilibrium to remove the majority of water vapor present, then over hot Ti sponge at 1100 K.

The cell was heated with a Marshall resistance heated furnace (20 inches in length with a 2 1/2 inch bore). Excellent temperature control was furnished by an integrating, triac-controlled regulating power supply designed and built at Lawrence Berkeley Laboratory.



Cell emfs were measured with a Keithley 640 electrometer accompanied with an adaptor input head. A guarded cable connected the cell to the electrometer input head where connection was made to a triaxial connector.

Data acquisition was automated with an Intel 8008-based microcomputer. The system had the capability of setting the cell operation temperature and monitoring cell emfs and thermocouple outputs on a predetermined time base, thus allowing continuous cell operation. The precision of recorded data was 0.01%.

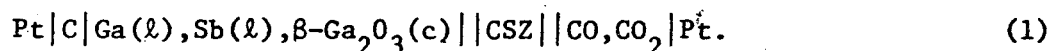
#### PROCEDURE

The general experimental procedure was to assemble the desired electrode arrangement and connect it to the peripheral apparatus. The cell was then successively evacuated (approximately  $10^{-5}$  torr) and filled with argon, and the process repeated three times. The absence of leaks was checked by sealing the cell under vacuum or under an excess pressure and monitoring the cell pressure. With the use of a ramp set-point controller, the cell temperature was then raised to the highest operating temperature at a rate of  $100 \text{ K hr}^{-1}$  in order to prevent thermal shock to the electrolyte. At this point the control was switched to the Intel 8008-based microcomputer and a control program initiated. The cell emf was monitored automatically as the microcomputer reset the temperature in increments of  $\sim 20^\circ\text{C}$  over a fixed range after complete equilibrium had been reached at each temperature. At least two cycles of the temperature range of interest were completed in order to reveal any hysteresis effects in the measurement. After completion of each run the temperature was

slowly lowered at  $100 \text{ K hr}^{-1}$  and the cell disassembled. The electrode material was then examined by x-ray diffraction analysis to confirm the absence of side reaction products.

### RESULTS

The activity of Ga in the liquid alloys of Ga-Sb was measured electrochemically in a solid-state galvanic cell which can be represented schematically as



At equilibrium, the electrochemical potential of oxygen is equal in both electrodes and is related to the cell emf by the Nernst equation,

$$E = (RT/4F) \ln \{a(\text{O}_2, \text{ref})/a(\text{O}_2, \text{Ga-Sb})\} \quad (2)$$

Here  $a(\text{O}_2, \text{ref})$  is the oxygen activity in the reference electrode while  $a(\text{O}_2, \text{Ga-Sb})$  is the oxygen activity in the alloy electrode,  $T$  is the thermodynamic temperature,  $R$  is the gas constant and  $F$  is the Faraday constant.

The reference oxygen activity was calculated for the equilibrium reaction



and therefore the oxygen activity is given by

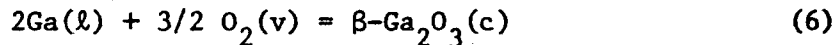
$$a(\text{O}_2, \text{ref}) = \left[ \frac{p(\text{CO}_2)}{p(\text{CO})} \right]^2 \exp\{2\Delta G(3)/RT\} \quad (4)$$

The free energy change for the reference gas reaction is

$$\Delta G(3) = -68.270 - 0.18T \ln T - 0.34 \times 10^{-3} T^2 + 0.87 \times 10^5 / T + 23.28 T, \text{ cal}_{\text{th}} \text{ mol}^{-1} \quad (5)$$

from the equations of Wicks and Block.<sup>(26)</sup> The ratio  $p(\text{CO}_2)/p(\text{CO})$  was chemically analyzed and found to be  $10.322 \pm 0.92$ .

The activity of oxygen in the measured electrode is related to the gallium activity in the same electrode through the formation of  $\beta\text{-Ga}_2\text{O}_3$  by the reaction,



from which it follows that the oxygen activity in the alloy is

$$\ln a(\text{O}_2, \text{Ga-Sb}) = 2\Delta G(6)/3RT - (4/3) \ln a(\text{Ga}). \quad (7)$$

The free energy change of reaction (6) was taken as  $\Delta G(6) = (-265309 \pm 152) + (82.47 \pm 0.16) T, \text{ cal}_{\text{th}} \text{ mol}^{-1}$ .<sup>(28)</sup> Combining equations (2), (4) and (7), one finally obtains an expression for the gallium activity in the liquid alloy,

$$RT \ln a(\text{Ga}) = 3FE - 1.5 RT \ln\{p(\text{CO}_2)/p(\text{CO})\} - 1.5 \Delta G(3) + 0.5\Delta G(6). \quad (8)$$

The measured cell emf had to be corrected for the thermal emf generated by the Pt-C couple, which has been reported by Chatterji and Smith.<sup>(27)</sup> Figure 2 shows the corrected equilibrium cell potentials as a function of temperature. A linear least squares analysis was applied to the data, the results of which are listed in table 2. Listed in table 3 is the activity of gallium calculated from equation (8). The activity of Sb was found by graphical integration of the Gibbs-Duhem equation. The relative partial molar enthalpy of Ga was then calculated from

$$\Delta\bar{H}_{\text{Ga}} = nF(T \frac{dE}{dT} - E). \quad (9)$$

Then, the relative partial molar enthalpy of Sb was obtained by graphical integration with the relation,

$$\Delta\bar{H}_{\text{Sb}} = - \int \frac{x_{\text{Ga}}}{x_{\text{Sb}}} d\Delta\bar{H}_{\text{Ga}}. \quad (10)$$

The relative partial molar entropy of Ga was determined by

$$\Delta\bar{S}_{\text{Ga}} = nF \frac{dE}{dT}, \quad (11)$$

and the relative partial molar entropy of Sb calculated from

$$\Delta\bar{S}_{\text{Sb}} = (\Delta\bar{H}_{\text{Sb}} - RT \ln a_{\text{Sb}})/T \quad (12)$$

Table 3. Summary of thermodynamic data for Ga-Sb alloys derived from emf measurements. ( $\text{cal}_{\text{th}} = 4.184\text{J}$ )

$x_{\text{Ga}}$	$a_{\text{Ga}}$	$a_{\text{Sb}}$	$\frac{\Delta\bar{H}_{\text{Ga}}}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{\Delta\bar{H}_{\text{Sb}}}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{\Delta H_{\text{mixing}}}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{\Delta\bar{S}_{\text{Ga}}}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{\Delta\bar{S}_{\text{Sb}}}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{\Delta S_{\text{mixing}}}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$	$\frac{\Delta G_{\text{mixing}}}{\text{cal}_{\text{th}} \text{ mol}^{-1}}$
0.039	0.0126	0.959	-2192	-5	-90	6.51	0.08	0.33	-420
0.293	0.166	0.632	-902	-253	-443	2.67	0.66	1.25	-1696
0.500	0.379	0.372	-433	-571	-501	1.40	1.40	1.45	-1953
0.639	0.545	0.231	-408	-940	-442	0.80	1.97	1.38	-1829
0.833	0.739	0.0982	+164	-1874	-177	0.76	2.74	1.09	-1274

Table 2. Emf of the experimental cell for different Ga-Sb system.

$E = a + b(T/K), \text{ mV}$

$x_{\text{Ga}}$	a	$-b \times 10^3$
0.0390	$413.41 \pm 2.41$	$125.16 \pm 2.36$
0.293	$432.03 \pm 0.86$	$69.57 \pm 0.83$
0.500	$438.82 \pm 1.51$	$52.64 \pm 1.45$
0.639	$439.18 \pm 1.26$	$42.60 \pm 1.22$
0.833	$447.44 \pm 0.44$	$42.03 \pm 0.41$

Also listed in table 3 are the integral values of the enthalpy, entropy and Gibbs free energy of mixing. In the above calculations, a temperature of 1003 K was used.

Figure 3 shows the gallium and antimony activities as a function of the gallium mole fraction,  $x_{\text{Ga}}$ , obtained from this study. For comparison, the emf results of Danilin and Yatsenko<sup>(23)</sup>, obtained at 988 K, and those of Gerasimenko et al.<sup>(24)</sup> at a temperature of 1023 K. Neither of these investigators reported an emf temperature derivative. Also shown are the calculated activities of Yazawa et al.<sup>(21)</sup> determined by applying a regular solution model to their heat of mixing data at a temperature of 1003 K. Not depicted are recent results by Pong,<sup>(22)</sup> determined also with a solid oxygen-conducting electrolyte but with a  $\text{Ga}_2\text{O}_3(\text{c})$  reference electrode. Pong found that the activity versus composition curve had the same general shape as that obtained in this study but shifted somewhat to more negative values. The calorimetry study at  $x_{\text{Ga}}=0.5$  by Predel and Stein<sup>(20)</sup> gave a value of  $-258 \text{ cal g-atom}^{-1}$  for  $\Delta H_{\text{mixing}}$ . The calculated activities of Predel and Stein<sup>(20)</sup> show a positive deviation from ideality while the vapor pressure studies of Hsi-Hsiung et al.,<sup>(25)</sup> agree very closely with those of this study. The large negative deviations found in the other two emf studies whose results are shown in figure 3 might have arisen from problems in the experimental galvanic cell used. Both studies used a chloride electrolyte and assumed a value of 3 for the number of equivalents in the Nernst equation whereas gallium has known

valences of both + 3 and + 1 and therefore the value of  $n$  is indeterminate. A value for  $n$  less than 3 would raise the measured activities, but the general shape of the activity curve would still differ from that found in this study.

Figure 4 shows the Gibbs free energy, enthalpy and entropy changes for mixing of the liquid elements, as determined in this study. It can be seen that gallium and antimony mix exothermically and nearly randomly (with an excess entropy of mixing of only  $0.08 \text{ cal}_{\text{th}} \text{ g-atom}^{-1}$  for the stoichiometric liquid), indicating that the liquid alloys are nearly regular in nature. Also shown in figure 3 are the entropy of mixing determined calorimetrically by Predel and Stein<sup>(20)</sup> and Yazawa, et al.<sup>(21)</sup> The latter results are more endothermic by about a factor of 2, and should be the more accurate due to their reproducibility and to the reliability of the experimental technique.

It should be noted that the temperature dependence of the activity (used to calculate  $\Delta H_{\text{mixing}}$ ) illustrated in equation (8) involves three other temperature coefficients, those in  $\Delta G(3)$ ,  $\Delta G(6)$  and the thermal emf correction. Adding the experimental errors of the above to those found from the emf fit results in sufficiently large error in the partial molar enthalpies that measured  $\Delta H_{\text{mixing}}$  here agree well with that obtained from calorimetric studies. Shown also in figure 4 is  $\Delta S_{\text{mixing}}$  obtained from the calorimetric value of  $\Delta H_{\text{mixing}}$  in conjunction with  $\Delta G_{\text{mixing}}$  measured here. This method gives a significant positive excess entropy of mixing.



A pair potential analysis was applied to these results. This analysis indicated a preference for Ga-Sb pairing which is consistent with the negative total enthalpy for the alloy. The pairing, though not extensive because of the small values of  $\Delta H_{\text{mixing}}$ , would produce a negative contribution to the excess entropy. This contribution is probably offset by a positive excess volume (as has been found for the related In-Sb<sup>(29)</sup> system and in other metallic solutions) and by possible changes in excitation of internal degrees of freedom resulting from the pairing, which contribute to the positive excess entropy observed.

In order to quantify these observations a short-range order parameter,  $\alpha$ , was calculated based on a lattice theory discussed by Averbach.<sup>(30)</sup> This parameter is defined as

$$\alpha = 1 - P_{\text{Ga-Sb}} / \{Z N_0 x_{\text{Ga}} x_{\text{Sb}}\} \quad (13)$$

where  $P_{\text{Ga-Sb}}$  is the number of Ga-Sb pairs in the liquid solution,  $Z$  is the number of nearest neighbors,  $N_0$  is the number of lattice sites and  $x$  is the mole fraction of gallium or antimony. Through statistical methods Averbach shows that the excess entropy can be approximated by

$$\Delta S_{\text{mixing}}^E \approx |\alpha| k N_0 [x_{\text{Ga}} \ln x_{\text{Ga}} + x_{\text{Sb}} \ln x_{\text{Sb}}] - \frac{\partial}{\partial T} [Z N_0 x_{\text{Ga}} x_{\text{Sb}} (1-\alpha) g(T)] \quad (14)$$

and the enthalpy of mixing by

$$H_{\text{mixing}} = Z N_0 x_{\text{Ga}} x_{\text{Sb}} (1-\alpha) [\mu + j(x)] \quad (15)$$

where  $k$  is the Boltzmann constant. The quantities  $\mu + j(x)$  and  $g(T)$  are defined in terms of the quasichemical interchange energy,  $\Omega$ , and given by

$$\Omega = Z N_0 [\mu + j(x) + g(T)]. \quad (16)$$

thus allowing the interchange energy to have a composition and temperature dependence. The authors are aware that the quasichemical solution theory is not directly applicable here because a positive excess entropy cannot be predicted, but the theory gives some insight into the relative amount of ordering in this system. Finally,  $\alpha$  can be expanded in terms of the mole fraction and the interchange energy, and truncated after the first terms to give

$$\alpha \approx \frac{2x_{\text{Ga}} x_{\text{Sb}} [\mu + j(x) + g(T)]}{kT} \quad (17)$$

If the excess entropy and enthalpy are known, then equations (14), (15) and (17) can be solved simultaneously for  $\alpha$ . The temperature dependence of  $g(T)$  was assumed to be linear and given by

$$g(T) = \bar{g}T \quad (18)$$

Figure 5 shows the calculated short-range order parameter,  $\alpha$ , as a function of the antimony mole fraction. Listed in table 4 is the calculated value of  $\alpha$ , the terms  $N_o[\mu + j(x)]$  and  $N_o\bar{g}$  and the reduced interaction energy,  $\Omega/ZRT$ , for the five compositions studied. In these calculations the heat of mixing of Predel and Stein<sup>(20)</sup> was used with the excess entropy obtained using our free energy data. A value of 6 was used for Z which is substantiated by x-ray measurements on In-Sb<sup>(30)</sup> which showed that the number of nearest neighbors was 5.7. The temperature of calculation was 1003 K.

The values of  $\alpha$  listed can be used to predict values of  $\Delta H_{\text{mixing}}$ ,  $\Delta S_{\text{mixing}}^E$  when used in equations (14) and (15). It is observed that the effect of a temperature dependent term  $g(T)$  is nearly twice that of the term  $\mu + j(x)$ , therefore the degree of Ga-Sb pairing is much greater than would be predicted by using the heat of mixing data alone.

The experimental data for the liquidus temperature of the Ga-Sb system as well as direct determinations from other sources can be checked for consistency with the following two expressions for the liquidus temperature derived elsewhere<sup>(31)</sup>

$$T = \frac{2\Delta H_f^C(\text{GaSb}) + \Delta \bar{H}_{\text{Ga}}(x) + \Delta \bar{H}_{\text{Sb}}(x)}{2\Delta S_f^C(\text{GaSb}) + R \ln\{a_{\text{Ga}}^S(T_m) a_{\text{Sb}}^S(T_m)\} + \Delta \bar{S}_{\text{Ga}}(x) + \Delta \bar{S}_{\text{Sb}}(x)} \quad (19)$$

and

Table 4. Short-range order parameter and quasichemical interchange energies. ( $\text{cal}_{\text{th}} = 4.184\text{J}$ )

$x_{\text{Ga}}$	$\alpha$	$\frac{N_o [\mu+j(x)]}{\text{cal}_{\text{th}} \cdot \text{mol}^{-1}}$	$\frac{N_o [\bar{g}]}{\text{cal}_{\text{th}} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}}$	$\Omega/ZRT$
0.039	-0.0162	-140.4	-.291	-0.216
0.293	-0.0920	-146.6	-.295	-0.222
0.500	-0.1088	-153.9	-.279	-0.218
0.639	-0.0996	-152.4	-.277	-0.215
0.833	-0.0683	-98.7	-.389	-0.245

$$T_{\ell} = \frac{2\Delta H_f^{\circ}(\text{GaSb}) - \Delta \bar{H}_{\text{Ga}}(x) - \Delta \bar{H}_{\text{Sb}}(x)}{2\Delta S_f^{\circ}(\text{GaSb}) - \Delta \bar{S}_{\text{Ga}}(x) - \Delta \bar{S}_{\text{Sb}}(x)} \quad (20)$$

where  $\Delta H_f^{\circ}(\text{GaSb})$  and  $\Delta S_f^{\circ}(\text{GaSb})$  are the standard enthalpy and entropy of forming solid GaSb from the pure liquid elements,  $T_{\ell}$  is the liquidus temperature and  $a_{\text{Ga}}^{\text{S}}(T_m)$  and  $a_{\text{Sb}}^{\text{S}}(T_m)$  are the activities of gallium and antimony in solid GaSb at the melting point. All quantities in equation (19) and (20) are expressed on a g-atom basis. In these equations GaSb(c) is considered an equimolar line compound, and the temperature dependence of the partial molar quantities and formation enthalpy and entropy is neglected. The liquidus temperature for the Sb-rich region then becomes

$$T = \frac{\Delta H_f^{\text{C}}(\text{Sb}) + H_{\text{Sb}}}{\Delta S_f^{\text{C}}(\text{Sb}) + S_{\text{Sb}}} \quad (20)$$

Tables 5 and 6 show the liquidus temperature calculated from either equation (18), (19) or (20) for the five alloy compositions studied here. In these calculations the partial molar enthalpies of Predel and Stein<sup>(20)</sup> were used while partial molar entropies were obtained from our experimental results. The fusion data listed in Table 1 was used in equation (18).

The free energy of formation of GaSb have been previously measured with emf methods by two other investigators.<sup>(32,33)</sup>

In order to use their results in equation (19), the enthalpy and entropy change for the melting of Sb had to be introduced. An

Table 5. Comparison of liquidus temperatures, (T/K) in the Ga-Sb system.

Method					Reference Source of Data for
	$x_{\text{Ga}} = 0.293$	$x_{\text{Ga}} = 0.500$	$x_{\text{Ga}} = 0.639$	$x_{\text{Ga}} = 0.833$	$\Delta H_f^{\text{C}}(\text{GaSb})/\Delta H_f^{\text{O}}(\text{GaSb})$
Equation (18)	949.3	986.0	971.4	906.2	2
"	952.5	988.8	974.4	909.8	3
"	937.6	985.1	966.1	882.9	4
"	948.6	987.8	972.2	902.7	5
"	950.0	988.2	973.0	905.2	8
"	953.1	988.9	974.7	910.9	17
"	946.4	987.3	971.0	898.8	19
Equation (19)	982.9	1019.2	1004.9	940.3	32
"	974.0	1011.5	996.6	930.0	33
Experimental	952.8	985.0	970.7	895.2	14

Table 6. Comparison of liquidus temperatures (T/K) of an antimony-rich Ga-Sb alloy.

$x_{\text{Ga}}$	$T_{\ell}$ , Equation (20)	$T_{\ell}$ , Ideal	$T_{\ell}$ , Experimental
0.039	889.8	897.2	890.7

enthalpy of fusion value of  $4750 \text{ cal}_{\text{th}} \text{ mol}^{-1}$  and a melting temperature of 904 K was selected from Hultgren et al. (15)

Listed also in table 5 for comparison is the liquidus temperature as determined by Maglione and Potier, (14) which required a small linear correction to bring their data into agreement with the accepted melting point of GaSb.

Based on the results shown in table 5, several conclusions can be made. The accepted liquidus temperature in the Ga-Sb system is very well predicted by our activity data and the enthalpy data of Predel and Stein, (20) along with accepted data for the heat of fusion. The results obtained here show that value of  $\Delta H_f^c(\text{GaSb})$  obtained by Schottley and Bewer (4) is probably too low. The results of this study are consistent with other literature data, although the measured activity for the alloy  $x_{\text{Ga}} = 0.833$  appears to be a few percent low. When the calculations of  $T_\ell$  is performed with the literature data for the GaSb formation reaction the liquidus temperatures predicted are much too high, however. Owing to the good consistency found with equation (18), the probable cause of this error is in the values assigned in previous studies to the enthalpy and entropy of the GaSb formation reaction. Table 6 shows the liquidus temperature calculated for an antimony-rich Ga-Sb liquid alloy. The accepted temperature is in excellent agreement with the derived from our experimental value, whereas an ideal solution model gives a large difference between the accepted and calculated liquidus temperature. This results also supports the consistency and accuracy of the present results.



## CONCLUSION

Previous studies on the Ga-Sb system have concluded that the liquid alloys are either ideal<sup>(4, 14)</sup> or regular<sup>(20, 21)</sup> solutions, while free energy determinations have indicated that the solutions are highly non-ideal, showing strong negative deviations from ideality. The results of this study have shown the Ga-Sb system to deviate negatively, but moderately so, from Raoult's law with a significantly positive excess entropy of mixing. Other thermodynamic data for the Ga-Sb system were examined and found to give good consistency with the experimental results obtained in this study, with the exception that the reported values for the enthalpy and entropy of the GaSb(c) formation reaction did not conform with the other data.

This work was done under the auspices of the U. S. Energy Research and Development Administration.

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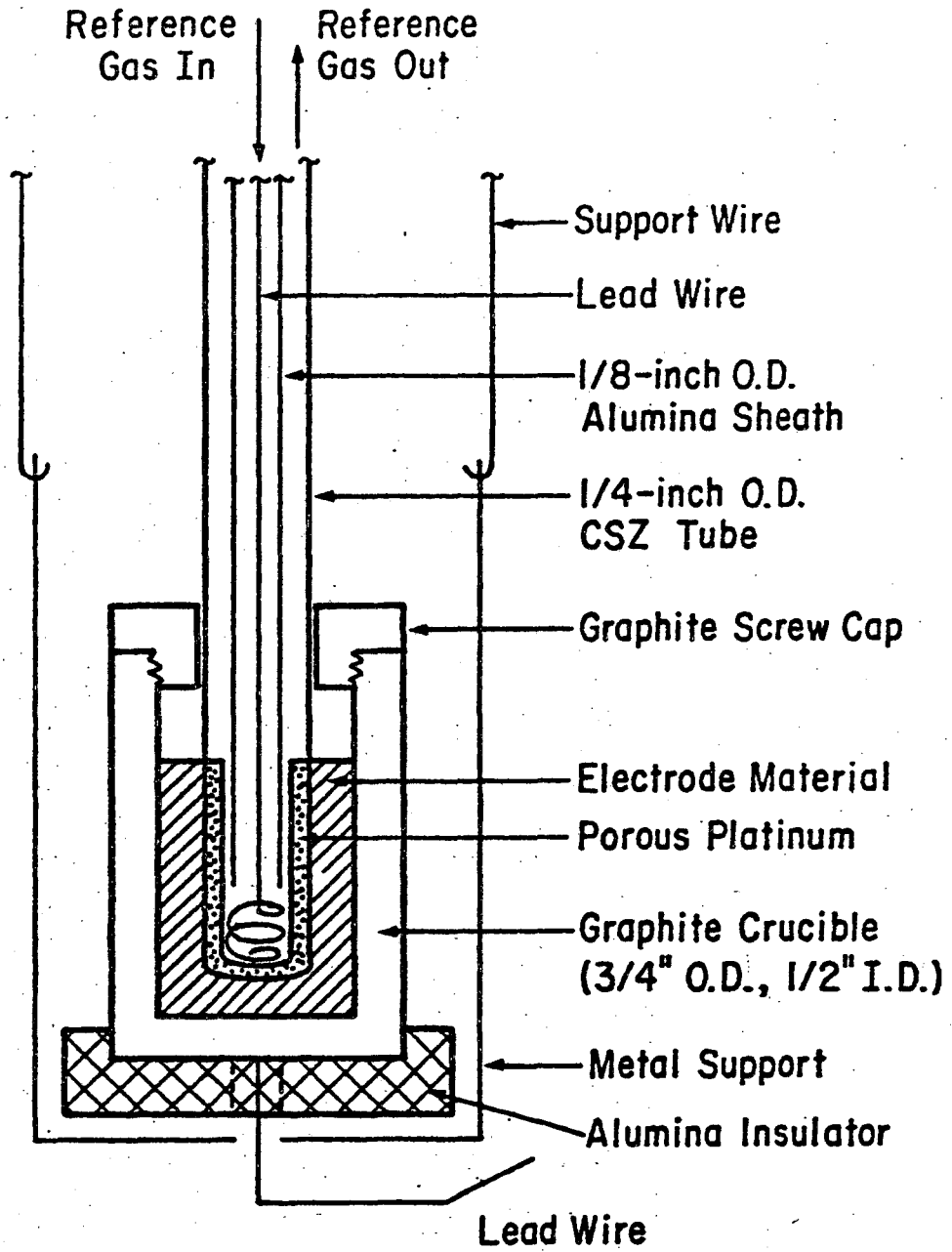
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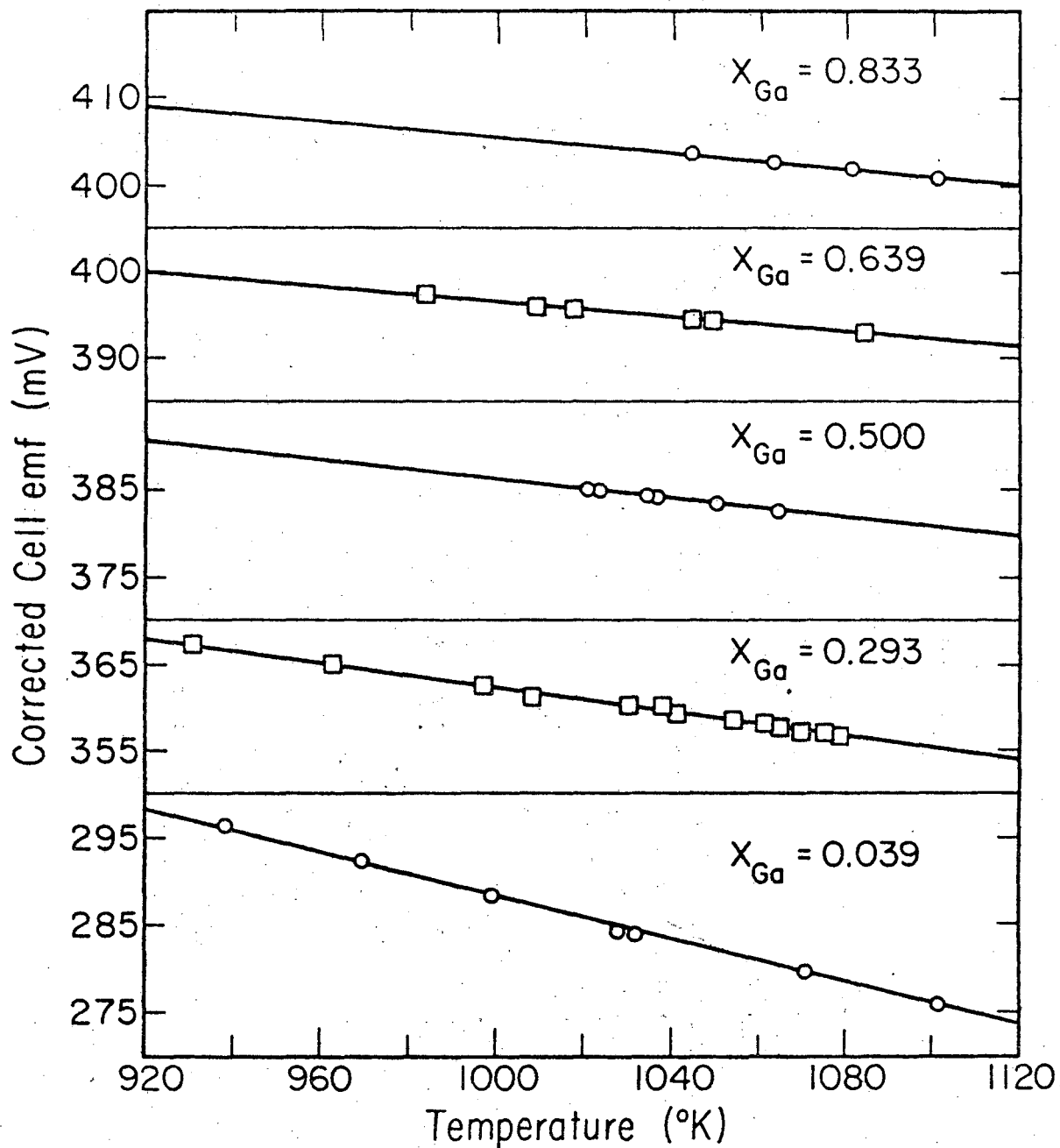
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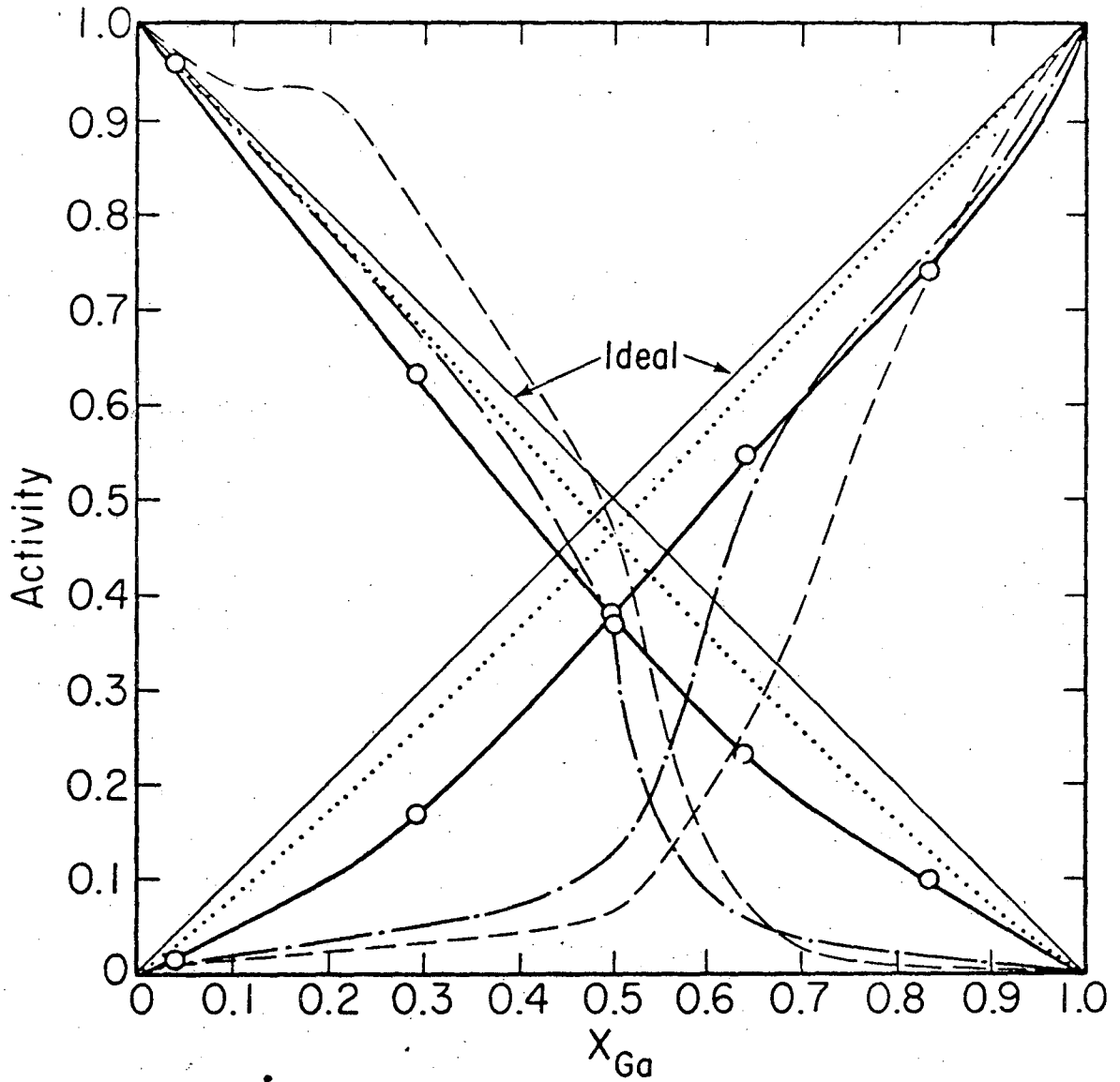
XBL 757-6782

Fig. 1



XBL 757-6794

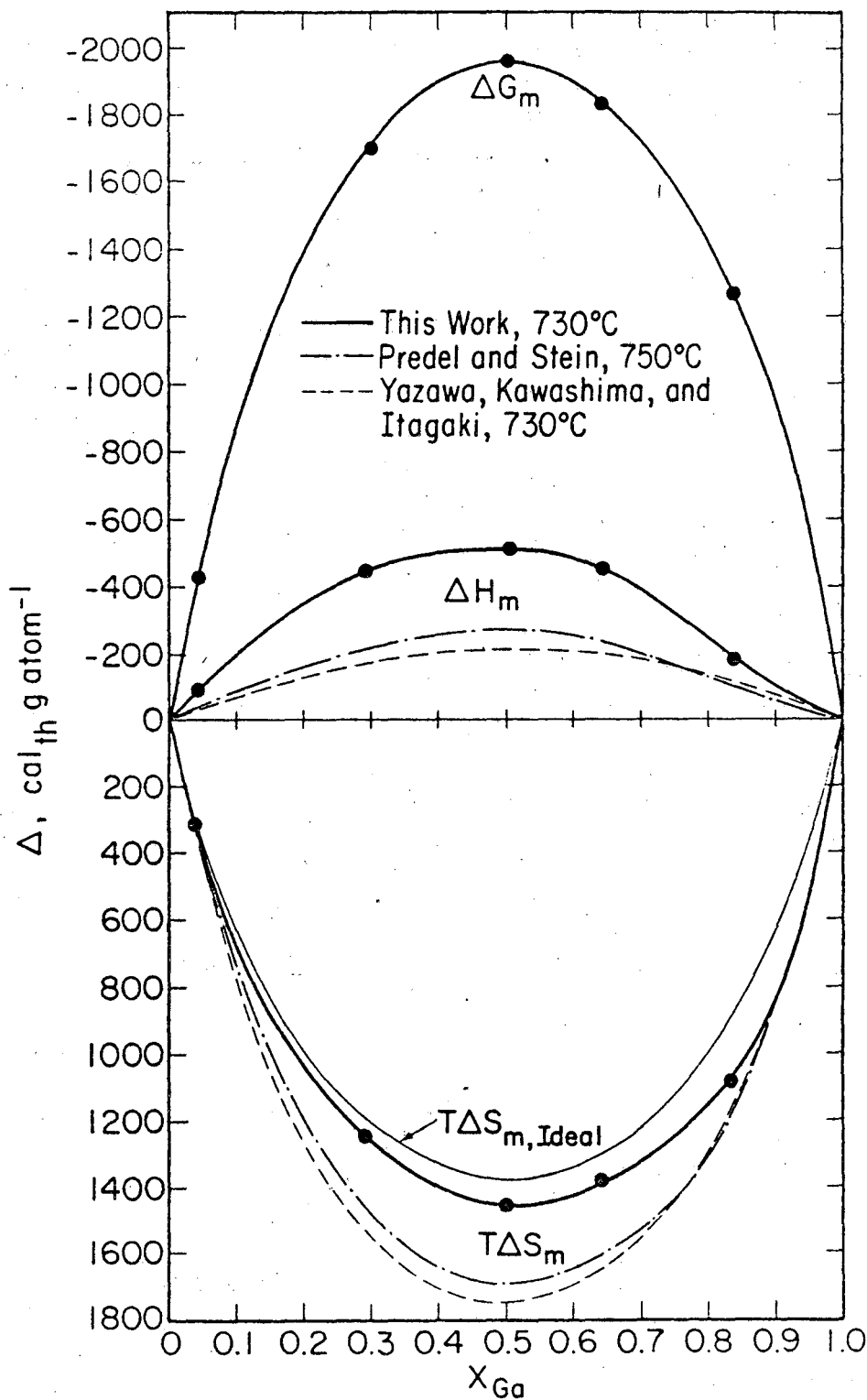
Fig. 2.



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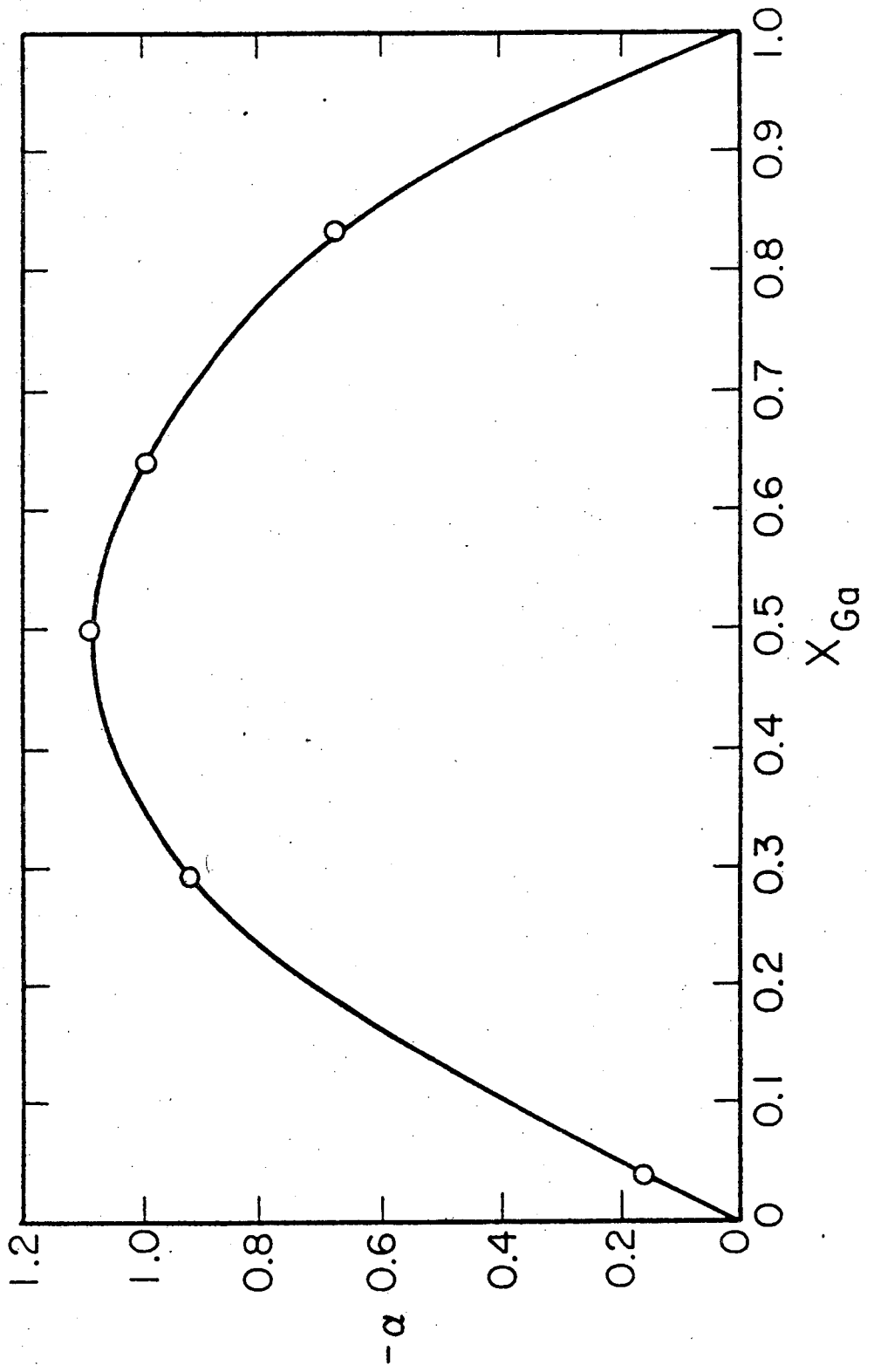
Fig. 3.





XBL 757-6767

Fig. 4.



XBL 757-6792

Fig. 5.

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