

Thermodynamics of Aluminum-Barium Alloys

S. SRIKANTH and K.T. JACOB

The activity of barium in liquid Al-Ba alloys ($X_{\text{Ba}} \leq 0.261$) at 1373 K has been determined using the Knudsen effusion-mass loss technique. At higher concentrations ($X_{\text{Ba}} \geq 0.38$), the activity of barium has been determined by the pseudo-isopiestic technique. Activity of aluminum has been derived by Gibbs-Duhem integration. The concentration-concentration structure factor of Bhatia and Thornton^[22] at zero wave vector has been computed from the thermodynamic data. The behavior of the mean-square thermal fluctuation in composition indicates a tendency for association in the liquid state. The associated solution model with Al_5Ba_4 as the predominant complex has been used for the description of the thermodynamic behavior of liquid Al-Ba alloys. Thermodynamic data for the intermetallic compounds in the Al-Ba system and the enthalpy of mixing in liquid alloys have been derived using the phase diagram and the Gibbs' energy of mixing of liquid alloys.

I. INTRODUCTION

A knowledge of activities in liquid Al-Ba alloys is useful for the analysis of the physical chemistry of the reduction of barium oxide by aluminum in vacuum. During this process, an Al-Ba alloy is formed, which decreases the efficiency of utilization of aluminum and recovery of barium. The intermetallic compound Al_4Ba was widely used in thermionic valves as the main component of evaporated barium getters. Notin *et al.*^[1] have measured the partial enthalpy of mixing of barium in Al-Ba alloys by drop calorimetry at 1215 K. Their measurements spanned over the composition range $0.013 < X_{\text{Ba}} < 0.466$. Measurements in the concentration range $0.061 < X_{\text{Ba}} < 0.320$ lie in the two-phase region comprising liquid and Al_4Ba . Notin *et al.*^[1] have subsequently derived the integral enthalpy of mixing by successive summation. For liquid alloys between $0.34 < X_{\text{Ba}} < 0.47$, the enthalpy of mixing is $-31.6 (\pm 0.2)$ kJ/g·atom with respect to pure liquid aluminum and barium as standard states, almost independent of composition. The values for integral enthalpy derived by this procedure are subject to uncertainties, especially at higher concentrations of barium, because of the accumulation of the errors associated with each measurement of the partial property. Burylev *et al.*^[2] have measured the vapor pressure of barium over liquid Al-Ba alloys by Knudsen effusion-mass loss analysis between 1223 and 1373 K for three compositions. The values for the activity of barium at 1373 K are 9.504×10^{-4} at 10 at. pct Ba, 3.455×10^{-3} at 20 at. pct Ba, and 0.0355 at 33.3 at. pct Ba with respect to liquid barium as the standard state. Vigdorovich *et al.*^[3] have also measured the vapor pressure of barium over Al-Ba alloys using the Knudsen effusion-mass loss technique in the temperature range of 870 to 1370 K for $0.1 < X_{\text{Ba}} < 0.75$. Most of the measurements lie in the two-phase regions. The results suggest strong negative

deviations from ideal behavior for Al-rich alloys. Activity data for liquid alloys are not available over the entire concentration range.

The phase diagram of the Al-Ba system given in the assessments of Elliott and Shunk^[4] and Massalski *et al.*^[5] is based on early thermal and microscopic studies of Alberti,^[6] Flanigen,^[7] and Iida.^[8] It shows the presence of three intermetallic compounds— Al_4Ba melting congruently at 1370 K and the compounds Al_2Ba and AlBa melting incongruently at 1018 and 991 K, respectively. The Ba-rich eutectic occurs at 72.0 at. pct Ba and 801 K. More recent phase diagram studies by Bruzzone and Merlo^[9] show that the compound Al_2Ba decomposes peritectically at 1187 K, rather than at 1118 K, as in Elliott and Shunk's diagram.^[4,5] Further, Bruzzone and Merlo^[9] do not indicate any solid solubility of Al in Ba, in contrast to the assessed diagram.^[4,5] No attempt was made by Bruzzone and Merlo^[9] to determine terminal solubilities. They report the melting point of barium as 983 K, in contrast to the accepted value of 1002 K.^[10] This discrepancy may be caused by impurities present in their sample. The impurities are also likely to alter the liquidus for barium-rich compositions. There exists some discrepancy over the stoichiometry of the compounds Al_2Ba and AlBa . Even though the studies of Bruzzone and Merlo^[9] concur with the previously accepted formulae,^[4] an immediate reinvestigation by Fornasini and Bruzzone^[11] reveals that the formula $\text{Al}_{13}\text{Ba}_7$ better describes the phase previously reported as Al_2Ba .^[9] Similarly, a reexamination by Fornasini^[12] of a single-crystal sample used in the study of Bruzzone and Merlo^[9] using an advanced experimental technique suggests that the formula Al_5Ba_4 more appropriately describes the phase close to the equiatomic composition.

Measurements of the enthalpy and free energy of formation of solid Al-Ba alloys have been reported in the literature. Notin *et al.*^[1] have measured the enthalpy of formation of the solid compound Al_4Ba by precipitating the intermetallic from a liquid Al-Ba bath. They report a value of $-37.1 (\pm 1.5)$ kJ/g·atom at 1215 K for the enthalpy of formation of Al_4Ba from pure solid components. Nepochatov *et al.*^[13] have measured the enthalpies of formation of the intermetallic compounds

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Al₄Ba, Al₂Ba, and AlBa by dissolving these alloys in 20 pct HCl at 323 K. They determined the enthalpies of solution of aluminum and barium under identical conditions and have calculated the enthalpy of formation for the compounds using Hess's law. Their measurements yield: $\Delta H_f(\text{Al}_4\text{Ba}) = -50.6 \text{ kJ/g} \cdot \text{atom}$; $\Delta H_f(\text{Al}_2\text{Ba}) = -54.8 \text{ kJ/g} \cdot \text{atom}$; and $\Delta H_f(\text{AlBa}) = -86.6 \text{ kJ/g} \cdot \text{atom}$ with respect to pure solid components as standard states. This method of determination of the enthalpy of formation involves three separate measurements under precisely identical conditions. The final result is a small difference between the large heat effects produced by the dissolution of the compound and the reactants and is therefore prone to large uncertainties. Kulichikina and Nikonov^[14] have measured the free energy of formation of Al₄Ba from solid Al and gaseous Ba in the temperature range of 933 to 1023 K using a vapor pressure method. The equilibrium pressure of barium over Al₄Ba is described by the relation, $\log P_{\text{Ba}}(\text{Pa}) = 10.645 - 14,800/T$ in the measured temperature range. Their calculated enthalpy of formation from vapor pressure data is $\Delta H_{298}^\circ(\text{Al}_4\text{Ba}) = -22.7 \pm 0.4 \text{ kJ/g} \cdot \text{atom}$ with respect to pure solid components. Values for enthalpy derived from the temperature dependence of vapor pressure are not very accurate. Recently, Kharif *et al.*^[15] have estimated the Gibbs' energies of formation as a function of temperature for the intermetallic compounds Al₄Ba, Al₂Ba, and AlBa from the phase diagram assuming an ideally associated liquid solution. These estimates have large uncertainties, because the information used in their study is incomplete. Accurate information on activities in liquid Al-Ba alloys over the complete composition range will permit a more rigorous assessment of the Al-Ba system. In this study, activities of barium in liquid Al-Ba alloys have been measured at 1373 K over the entire range of composition using a combination of Knudsen effusion-mass loss analysis and pseudo-isopiestic measurements. The data for intermetallic compounds have been derived using information for the liquid alloys and the phase diagram.

II. EXPERIMENTAL

A. Materials

Barium metal of 99.4+ purity was supplied by Dominion Magnesium Ltd., Haley, ON, Canada, and aluminum of 99.99 pct purity was obtained from Johnson Matthey Chemicals, Royston, Hertz, U.K. The alumina crucibles for containing the alloy were obtained from Leico Industries, Inc., New York, NY. For the pseudo-isopiestic measurements, pure aluminum or Al-Ba alloys were held in alumina crucibles lined with barium oxide. The alumina crucibles were lined with barium oxide under an argon atmosphere inside a dry box. The barium oxide was prepared by thermal decomposition of BaCO₃ in vacuum (1 Pa) at 1173 K. Barium carbonate of 99.8 pct purity was obtained from Aldrich Chemicals, Gillingham, Dorset, U.K. The barium oxide was compacted along the inside surface of the alumina crucible. The crucible was then loaded with pure Al or Al-Ba alloy and placed inside the isopiestic apparatus. Care is taken

to avoid the exposure of BaO to air and possible formation of BaCO₃ and BaO₂.

B. Knudsen Effusion Studies

Knudsen effusion studies on liquid Al-Ba alloys ($X_{\text{Ba}} \leq 0.261$) at 1373 K were conducted using cells made of steel. The alloys were prepared by *in situ* melting in an alumina crucible ~1.5 cm in diameter placed inside the Knudsen cell. A schematic diagram of the Knudsen cell is shown in Figure 1. A thin foil of iron, 0.05 mm in thickness, was clamped between the lid and the barrel sections of the Knudsen cell. Knudsen orifices ranging in diameter from 0.01 to 0.1 mm were made by laser drilling. The iron foil near the orifice was thinned to give a knife edge. The diameters were measured under an optical microscope provided with a sensitive internal scale that could be superimposed on the orifice image. The orifice diameter at the experimental temperature was calculated from that at room temperature using the thermal expansion coefficient for iron.

The experimental arrangement was similar to that used in earlier studies.^[16,17,18] The Knudsen cell was suspended from a Cahn microbalance inside a vacuum furnace provided with tungsten resistance heater and molybdenum shields. The temperature of the furnace was controlled to $\pm 1 \text{ K}$ and measured by a Pt/Pt-13 pct Rh thermocouple calibrated against the melting point of gold. The vacuum was generated by a diffusion pump backed by a mechanical rotary pump. A typical pressure inside the furnace during most of the measurements was 10^{-3} Pa . Effusion measurements were carried out on three Al-Ba alloys at 1373 K. There was some superficial reaction between the alloy and the alumina crucible. Once the equilibrium ternary oxide formed at the alloy-crucible interface, further reaction was sluggish. The rate of mass loss becomes constant after ~2 hours. The composition of the alloy was determined by chemical analysis after each experiment.

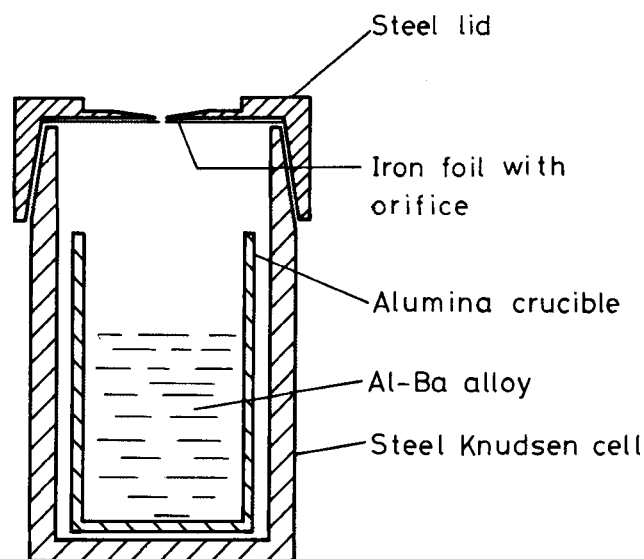


Fig. 1—Schematic diagram of the Knudsen cell.

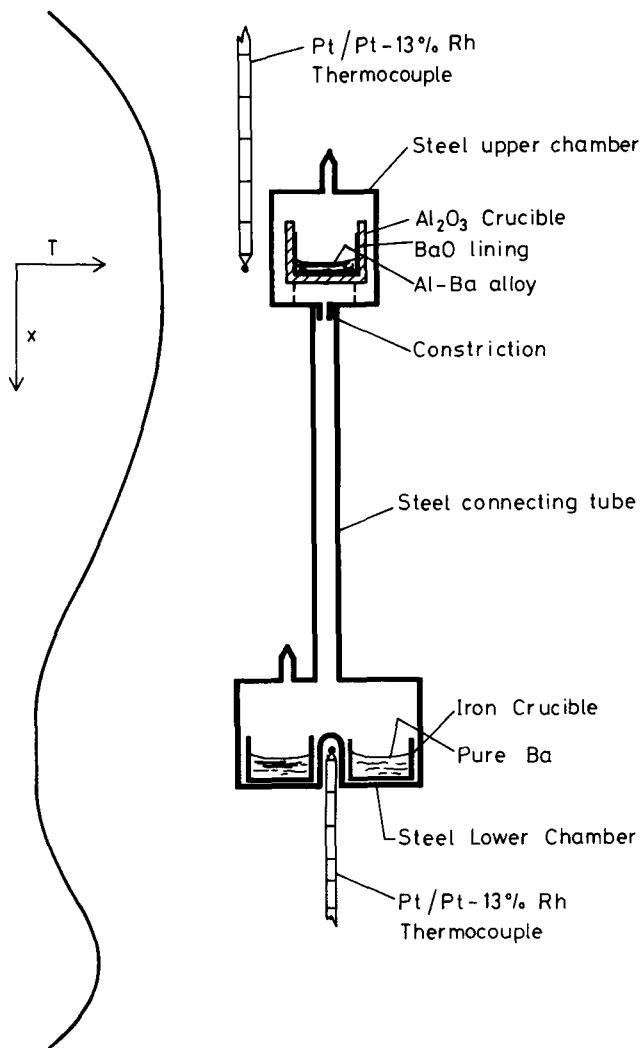


Fig. 2—Schematic section of the pseudo-isopiestic apparatus.

C. Pseudo-Isopiestic Measurements

The apparatus used for pseudo-isopiestic measurements was similar to the one used earlier.^[18] It was made of steel and consisted of upper and lower chambers connected by a long tube, as shown in Figure 2. The lower chamber contained pure barium in iron crucibles. Liquid barium was found to wet iron and exhibited a tendency to creep out of the crucible and along the walls of the chamber. The creep was minimized by sharpening the edge of the crucibles. The lower chamber was also provided with a thin steel baffle to prevent the creep of barium into the connecting tube by capillary action. A thermocouple well was provided in the lower chamber for accurate measurement of the temperature of pure barium. The upper chamber contained either pure aluminum or Al-Ba alloy in an alumina crucible lined with BaO. The upper end of the connecting tube had a constriction ~0.25 mm in diameter. The upper and lower chambers were provided with openings for feeding the metal and the alloy into the crucibles and subsequent evacuation. The iron crucible in the lower chamber was half filled with pure barium, and the opening was closed by crimping and flame sealing. Pure Al or Al-Ba alloy was then

charged into the upper crucible. The entire assembly was evacuated by a diffusion pump backed by a mechanical rotary pump to a pressure of 10^{-2} Pa. After evacuating for 3 hours, the opening on the upper chamber was sealed.

The evacuated steel assembly was placed in a two-zone split furnace. Pure barium was held in the lower temperature zone, and Al or Al-Ba alloy was held in the higher temperature zone, as indicated in Figure 2. The temperature of each zone was controlled independently to ± 0.5 K using thyristor power controllers. The temperatures were measured by Pt/Pt-13 pct Rh thermocouples. The pressure of barium in the steel apparatus was determined by the temperature of the lower chamber. After rising through the steel tube, the vapor entered the upper chamber and was absorbed by liquid Al or Al-Ba alloy. This process proceeded until the alloy was saturated with respect to the vapor. At the end of the specified period, the furnace was opened, and the pseudo-isopiestic apparatus was removed. High-pressure jets of air were directed on the apparatus for rapid cooling. The upper and lower chambers were cut open. The crucibles and the inner surface of the steel apparatus were examined. Preliminary experiments indicated that depending on the temperature of the lower chamber, periods ranging from 8 to 26 hours were required for the alloy composition to reach a steady-state value.

During quenching, the steel container cooled faster than the alloy. This led to distillation of some barium from the alloy and its condensation on the inside walls of the steel container. To obtain the correct composition of the alloy at temperature, it was necessary to dissolve the barium condensed on the inner surface of the upper chamber and add this to the solution of the alloy solidified in the alumina crucible lined with barium oxide. The function of the constriction at the end of the connecting steel tube was to restrict the outflow of vapor from the upper chamber during quenching. The correction for composition of the alloy varied from 0.6 at. pct for low concentration of Ba to 2.5 at. pct for barium-rich alloys. There was no evidence of reaction between the alloy and barium oxide lining in the alumina crucible for Ba-rich compositions.

III. RESULTS

A. Knudsen Effusion Measurements

The vapor pressure of barium was calculated from the rate of mass loss of the Knudsen cell using the equation

$$P = 2286 \frac{m'}{f \cdot A} \sqrt{\frac{T}{M}} \quad [1]$$

where P is the pressure in pascals, m' is the rate of mass loss in grams per second, A is the area of the Knudsen orifice in square centimeters, T is the temperature in Kelvin, M is the molecular weight of the effusing species, and f is the Clausing factor for nonideal orifice. The equilibrium vapor pressure of barium for $X_{\text{Ba}} = 0.092$ calculated from the observed mass loss using Eq. [1] is 0.2964 Pa. The vapor pressures for $X_{\text{Ba}} = 0.181$ and 0.261 are 2.1328 and 7.656 Pa, respectively. Clausing factors used in this study were taken from Iczkowski

et al.^[19] The measured vapor pressure was found to be independent of orifice diameter for all of the alloys. This suggests the absence of surface depletion of alloys due to preferential vaporization of Ba. Alloys containing $X_{Ba} > 0.261$ were not used, because the partial pressure of barium over these alloys would lie in a range where the Knudsen results would be unreliable. To compute the activity of Ba in the alloy, the vapor pressure of pure liquid barium at 1373 was taken as 547 Pa from a recent study by Jacob and Waseda.^[20] The calculated activities from Knudsen effusion measurements for $X_{Ba} = 0.092, 0.181, \text{ and } 0.261$ are 0.00054, 0.0039, and 0.014, respectively, with respect to liquid barium as the standard state.

B. Pseudo-Isopiestic Studies

The results of the pseudo-isopiestic measurements are summarized in Table I. The pressure inside a nonisothermal enclosure is not strictly uniform.^[21] Since in the present study, the correction for pressure differential is negligible in comparison to the total pressure inside the cell, it has not been incorporated. The pressure of barium in the apparatus was calculated from the temperature of the lower chamber containing pure barium, using the recent vapor pressure data of Jacob and Waseda.^[20] For pure liquid barium,

$$\log P_{Ba}(\text{Pa}) = \frac{-8867}{T} + 9.196 \quad [2]$$

There is a printing error in the expression for the vapor pressure of solid Ba in Reference 20. The correct expression is

$$\log P_{Ba}(\text{Pa}) = \frac{-9304}{T} + 9.633 \quad [3]$$

The activity of barium calculated from the vapor pressure over the alloy is plotted as a function of composition in Figure 3 and is summarized in Table I.

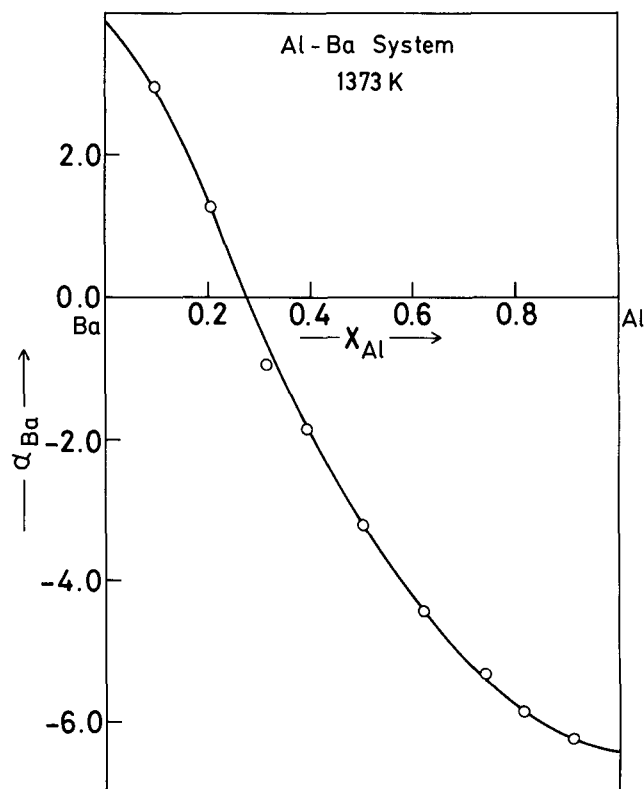


Fig. 3—Variation of α -function for barium with X_{Al} for liquid Al-Ba alloys at 1373 K.

C. Gibbs Energy of Mixing and Concentration-Concentration Structure Factor

The activity coefficient of aluminum ($\gamma_{Al} = a_{Al}/X_{Al}$) for the entire composition range at 1373 K was derived by Gibbs-Duhem integration employing the α -function:

$$\ln \gamma_{Al} = -\alpha_{Ba} X_{Ba} X_{Al} - \int_{X_{Al}=1}^{X_{Al}} \alpha_{Ba} dX_{Al} \quad [4]$$

Table I. Summary of Results of Pseudo-Isopiestic Measurements

Temperature of Alloy, K (± 0.5)	Temperature of Pure Ba, K (± 0.5)	Equilibration Time, ks	At. Pct Ba in Alloy (± 0.6)	a_{Ba}
1373.1	1365.7	32	90.6	0.929
1327.9	1365.8	40	90.2	
1373.0	1356.7	32	79.3	0.837
1373.2	1356.8	43	79.1	
1373.2	1331.3	43	68.6	0.627
1373.3	1331.2	61	68.8	
1372.8	1304.6	61	60.7	0.459
1373.1	1304.7	79	61.1	
1372.9	1247.3	79	50.0	0.223
1373.1	1247.2	108	49.6	
1372.8	1164.0	94	38.2	0.0691
1373.3	1163.8	120	37.8	

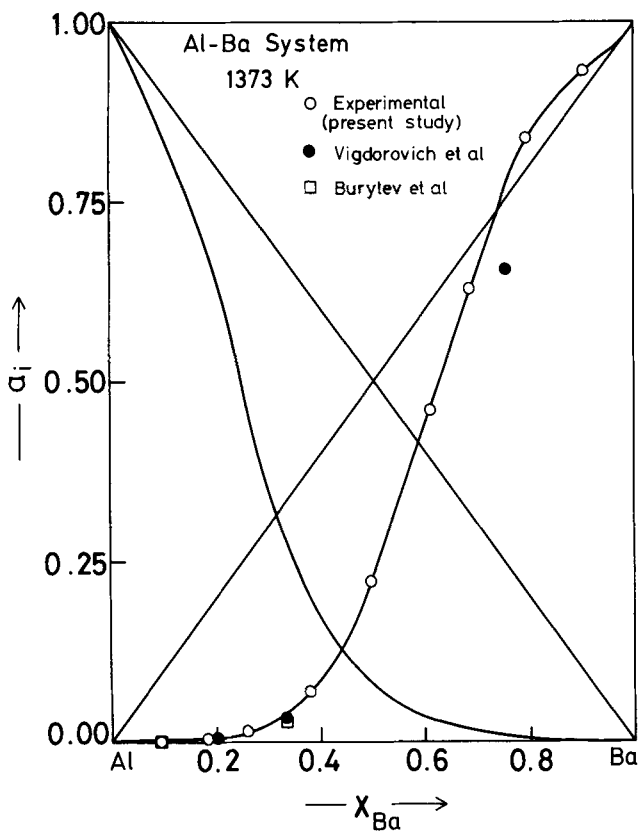


Fig. 4—Composition dependence of activities in liquid Al-Ba alloys at 1373 K.

where $\alpha_{Ba} = \ln \gamma_{Ba}/(1 - X_{Ba})^2$. The activity of aluminum obtained from the Gibbs-Duhem relation is shown in Figure 4 as a function of composition. The activity of aluminum exhibits a strong negative deviation from Raoult's law. The activity of barium shows a negative deviation from Raoult's law for $0.74 < X_{Ba} < 1$ and a mild positive deviation at higher concentrations. The activities and activity coefficients for both components at 1373 K are given in Table II. The Gibbs' energy of mixing computed from the activities using the relation

$$\Delta G = RT(X_{Al} \ln a_{Al} + X_{Ba} \ln a_{Ba}) \quad [5]$$

is shown by points in Figure 5 with respect to liquid barium and aluminum as standard states. The free energy of mixing shows a minimum at $X_{Ba} \sim 0.41$. The

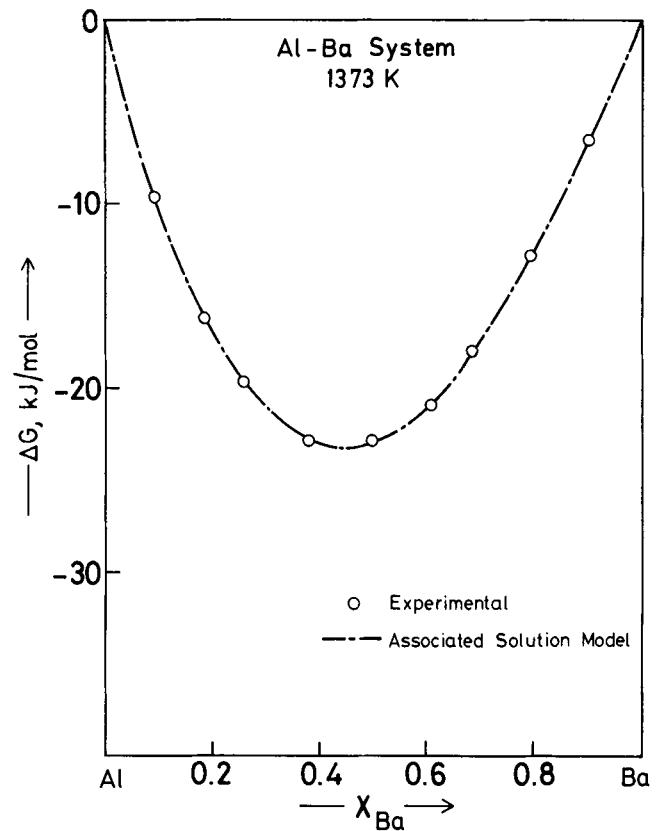


Fig. 5—Comparison of the experimental values for the Gibbs' energy of mixing with those given by the associated solution model for liquid Al-Ba alloys at 1373 K.

concentration-concentration structure factor of Bhatia and Thornton^[22] at zero wave vector [$S_{cc}(0)$] can be evaluated from the activity data:

$$S_{cc}(0) = (1 - X_{Ba}) \left[\frac{\partial \ln a_{Ba}}{\partial X_{Ba}} \right]^{-1} \quad [6]$$

The variation of $S_{cc}(0)$ as a function of composition determined from the experimental activity data is shown in Figure 6. It is seen that the concentration-concentration structure factor is significantly below the value for ideal solution, indicating a tendency to form associated species in the liquid state. The difference between $S_{cc}(0)$ for an ideal solution and that for liquid Al-Ba alloys is plotted in Figure 7. The maximum occurs at 0.47. This

Table II. Activities of Ba and Al in Liquid Al-Ba Alloys at 1373 K Relative to Pure Liquid Al and Ba as Standard States

X_{Ba}	a_{Ba}	$\ln \gamma_{Ba}$	$\ln \gamma_{Al}$	a_{Al}	Technique
0.092	5.42×10^{-4}	-5.134	-0.0705	0.846	Knudsen effusion
0.187	3.90×10^{-3}	-3.868	-0.265	0.624	Knudsen effusion
0.261	0.014	-2.949	-0.525	0.437	Knudsen effusion
0.380	0.069	-1.705	-1.113	0.204	pseudo-isopiestic
0.498	0.223	-0.803	-1.820	0.0814	pseudo-isopiestic
0.609	0.459	-0.283	-2.446	0.0339	pseudo-isopiestic
0.687	0.627	-0.059	-2.855	0.0180	pseudo-isopiestic
0.792	0.837	0.0553	-3.161	8.82×10^{-3}	pseudo-isopiestic
0.904	0.929	0.0273	-2.967	4.94×10^{-3}	pseudo-isopiestic

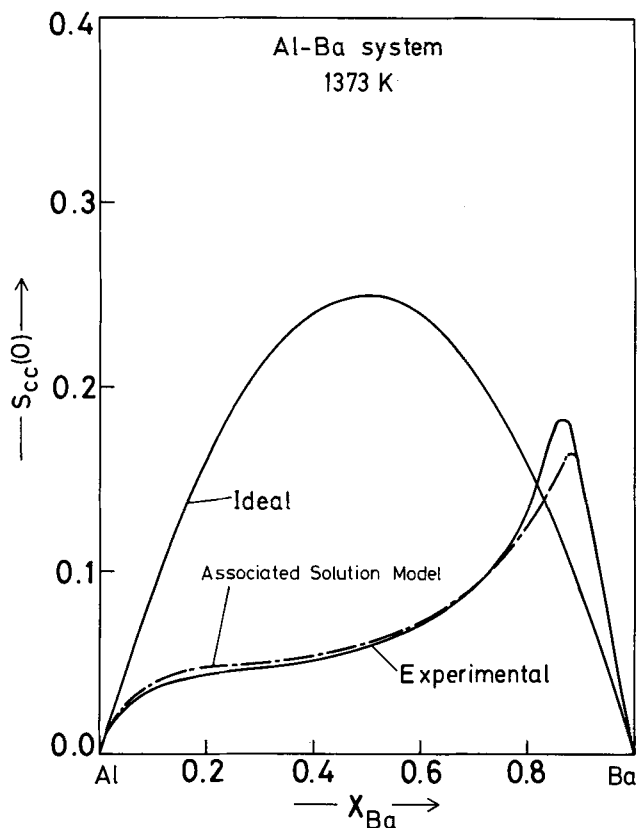


Fig. 6—Concentration-concentration structure factor at zero wave vector, $S_{cc}(0)$, for liquid Al-Ba alloys at 1373 K.

composition is close to that of the intermetallic compound Al_5Ba_4 . It therefore appears that a complex of the type Al_5Ba_4 may be present in liquid alloys. This is in contrast to the behavior of Al-Ca and Al-Sr systems, where

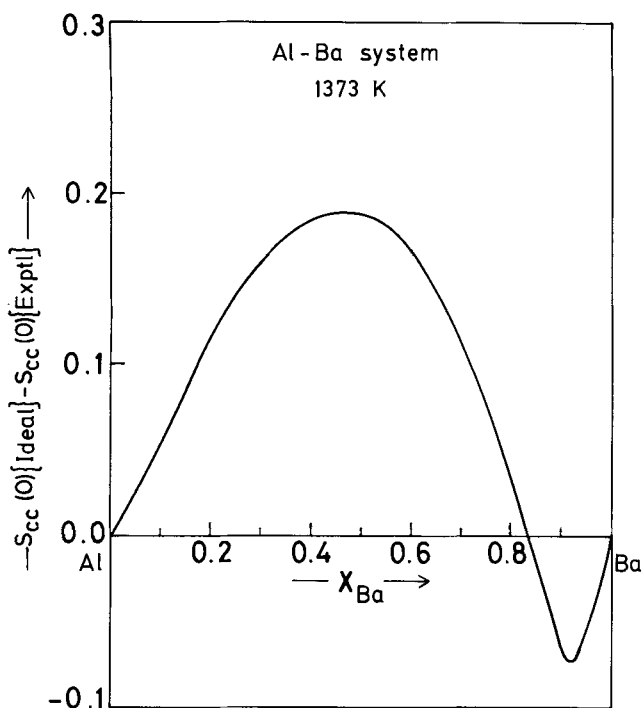


Fig. 7—Variation of $S_{cc}(0)\{\text{Ideal}\} - S_{cc}(0)\{\text{Experimental}\}$ with X_{Ba} .

Al_2X -type species are more probable.^[17,18] The structure factor is related to the mean square thermal fluctuation in composition:

$$S_{cc}(0) = \bar{N} \langle (\Delta c)^2 \rangle \quad [7]$$

where \bar{N} is the average number of particles in a fixed volume and $(\Delta c)^2$ is the mean-square thermal fluctuation in concentration.

IV. DISCUSSION

A. Application of the Associated Solution Model

The thermodynamics of liquid Al-Ba alloys can be described by an associated solution model.^[23] The associated solution model postulates the existence of complexes in the liquid due to chemical interactions. The complexes will be in equilibrium among themselves and with the monomers of the pure components. The complexes and the monomers termed species, to differentiate them from the components, exhibit a regular solution behavior. The components can exhibit a nonregular behavior. In the regular associated solution model, the interaction energies are independent of temperature. Srikanth and Jacob have modified the associated solution model to include volume effects and excess entropy.^[24,25] In the present study, the modified associated solution model incorporating volume effects^[25] is used to model thermodynamic properties of liquid Al-Ba solution in which the two monomers Al and Ba are in equilibrium with the associated species Al_5Ba_4 . However, the temperature dependences of interaction energies were not assessed, since reliable values for the enthalpy of mixing in liquid Al-Ba alloys are not available over the entire composition range. Hence, a regular associated solution approximation has been adopted wherein the interactions among the species conform to a strictly regular solution behavior. The free energy of mixing and $S_{cc}(0)$ have been computed using the model parameters^[25] and compared with the experimental results.

The Gibbs' energy of mixing of the three species is given by^[26,27]

$$\begin{aligned} \Delta G = & -n_3 g + RT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3] \\ & + n_1 \phi_2 v_{12} + n_2 \phi_3 v_{23} + n_1 \phi_3 v_{13} \end{aligned} \quad [8]$$

where n_1 , n_2 , and n_3 are the number of moles of species Al, Ba, and Al_5Ba_4 per mole of the binary liquid alloy, respectively. The species concentrations are related to the absolute mole fraction of components by mass balance restrictions:

$$\begin{aligned} n_1 = X_{Al} - 5n_3; \quad n_2 = X_{Ba} - 4n_3 \\ n = 1 - 8n_3 \end{aligned} \quad [9]$$

The term $(-n_3 g)$ represents the decrease of the free energy due to the formation of the chemical complex. The symbol g represents the free energy of dissociation of the complex given by

$$g = -RT \ln K \quad [10]$$

where K is the equilibrium constant for the dissociation

reaction $\text{Al}_5\text{Ba}_4 \rightleftharpoons 5\text{Al} + 4\text{Ba}$. The term ϕ_i is the concentration by volume of the i th species in the pseudo-ternary mixture, and v_{ij} is the free energy interaction term. If the volumes of Al and Ba atoms in the liquid solution are denoted by V_1 and V_2 and the volume of the Al_5Ba_4 complex by V_3 , then

$$\phi_1 = \frac{n_1 V_1}{V} \quad \phi_2 = \frac{n_2 V_2}{V} \quad \text{and} \quad \phi_3 = \frac{n_3 V_3}{V} \quad [11]$$

where

$$V = n_1 V_1 + n_2 V_2 + n_3 V_3$$

The equilibrium number of chemical complexes at a given temperature and pressure is given by the condition of minimization of the free energy of mixing

$$\left[\frac{\partial \Delta G}{\partial n_3} \right]_{T,P} = 0 \quad [12]$$

Srikanth and Jacob^[25] have developed an analytical expression for the equilibrium constant in terms of the model parameters:

$$K = \frac{\phi_1^5 \cdot \phi_2^4}{\phi_3 \cdot V_f} \cdot \exp(z - 8) \quad [13]$$

where

$$V_f = \exp(\delta n/V)$$

$$\delta = 5V_1 + 4V_2 - V_3$$

and

$$z = \frac{1}{VRT} [(\delta n_1 \phi_2 - 4n_1 V_2 - 5n_2 V_2)v_{12}$$

$$+ (\delta n_2 \phi_3 + n_2 V_3 - 4n_3 V_3)v_{23}$$

$$+ (\delta n_1 \phi_3 + n_1 V_3 - 5n_3 V_3)v_{13}]$$

The concentration of the complex at any temperature and pressure can be determined from the known interaction energies using an iteration procedure.

The pairwise free energy interaction coefficients (v_{ij}), the free energy of dissociation, and the volume of the complex can be evaluated from the experimental Gibbs' energy of mixing using an optimization procedure developed by Srikanth and Jacob.^[25] An object function (s), is defined as the sum of the square of the deviations for the experimental data points;

$$s = \sum_i [(\Delta G_1 - \Delta G)_i^2] \quad [14]$$

where ΔG_1 is the measured free energy of mixing and ΔG is the corresponding value derived from the associated solution model. Clearly, the best values of the model parameters are those that minimize s . The minimization was accomplished using Powell's algorithm.^[28] Values for the free energy of mixing were taken from the present study. Volumes of the free atoms were computed from experimental density.^[29] The model parameters for the Al-Ba system derived from the optimization procedure are shown in Table III. All three interaction energies are negative. There is significant reduction in volume associated with the formation of the complex. The integral Gibbs' energy of mixing for the Al-Ba system at 1373 K as a function of composition, estimated from the associated solution model using Eq. [8], is shown in Figure 5 in comparison with the experimental results. It is seen that the values computed from the model agree well with the experimental Gibbs' energy.

Srikanth and Jacob^[25] have deduced an expression for the concentration-concentration structure factor in terms of the parameters of the associated solution model:

$$S_{cc}(0) = (1 - X_{\text{Al}}) \left[\left\{ \left(\frac{n'_1}{n_1} - \frac{V'}{V} \right) - \frac{V_1}{V} \left(n' - \frac{nV'}{V} \right) \right\} \right.$$

$$+ \frac{1}{RT} \cdot (\phi'_2 v_{12} + \phi'_3 v_{13})$$

$$- \frac{V_1}{V \cdot R \cdot T} \sum_{i < j}^3 (n_i \phi'_j + n'_i \phi_j) v_{ij}$$

$$\left. + \frac{V_1 V'}{V^2 \cdot R \cdot T} \sum_{i < j}^3 n_i \phi_j v_{ij} \right]^{-1} \quad [15]$$

Here, the prime denotes differentiation with respect to X_{Al} . The values for n'_1 , n' , V' , and ϕ'_i can be expressed in terms of a single variable n'_3 using Eqs. [9] and [11]. The parameter n'_3 can be solved for by differentiating Eq. [13] and using a numerical iteration procedure when values for the model parameters are known. From the known values of the model parameters (Table III), $S_{cc}(0)$ was calculated as a function of concentration for the Al-Ba system at 1373 K. The results are shown in Figure 6 in comparison to the values obtained from experimental data on activity. The computed values are in good agreement with those obtained directly from experimental data. The complex Al_5Ba_4 can be visualized as a tetrahedron with barium atoms at the corners and the smaller aluminum atoms at the face centers and the center of the tetrahedron.

Table III. Interaction Energies, Free Energy of Dissociation, and Volume of the Complex in the Al-Ba System at 1373 K ($V_{\text{Al}} = 18.7 \text{ \AA}^3$, $V_{\text{Ba}} = 69 \text{ \AA}^3$)

Object Function	Interaction Energies (kJ/mol)			Free Energy of Dissociation (kJ/mol)	Volume of Complex (\AA^3)
	v_{12}	v_{13}	v_{23}	g	$V_{\text{Al}_5\text{Ba}_4}$
s					
0.06	-16.06	-11.05	-39.98	143.14	235.62

B. Thermodynamic Evaluation and Assessment

Activity data for liquid Al-Ba alloys have been reported by Burylev *et al.*^[2] for $X_{Ba} = 0.1, 0.2,$ and 0.33 between 1223 and 1373 K and by Vigdorovich *et al.*^[3] for $X_{Ba} = 0.1$ to 0.75 in the temperature range of 870 to 1370 K. Both of them have employed Knudsen effusion-mass loss analysis to determine the vapor pressure of barium over the alloy. The activity of barium at 1373 K reported in the studies of Burylev *et al.*^[2] is shown in Figure 4 in comparison with the results obtained in the present study. Most of the measurements of Vigdorovich *et al.*^[3] lie in the two-phase region. Activities of barium at 1373 K derived from their recommended vapor pressure equation extended up to 1373 K for selected single-phase compositions are also shown in Figure 4. Both Burylev *et al.*^[2] and Vigdorovich *et al.*^[3] have not employed the Clausius correction factor for nonideal orifice. Since the present activity measurements cover the entire concentration range for single-phase liquid alloy and the results from both Knudsen effusion and pseudo-isopiestic measurements are consistent, they have been adopted for thermodynamic and phase diagram assessment of the Al-Ba system. At 1373 K, the excess Gibbs' energy for liquid Al-Ba alloys can be represented by an equation of the form

$$\begin{aligned} G^E = X_{Al}(1 - X_{Al}) [-59,730 + 23,185(1 - 2X_{Al}) \\ + 9880(1 - 2X_{Al})^2 \\ + 1140(1 - 2X_{Al})^3] \text{ J/mol} \end{aligned} \quad [16]$$

with respect to pure liquid components as standard states. Notin *et al.*^[1] have calculated the integral enthalpy of mixing of Al-Ba alloys at 1215 K from the partial enthalpy of barium determined by drop calorimetry by successive summation. Their results for single-phase liquid alloys are available only over a very narrow composition range $0.0129 < X_{Ba} < 0.0450$ and $0.3439 < X_{Ba} < 0.4664$ and are shown by points in Figure 8. As mentioned earlier, this method of deriving the integral property from the partials by successive summation is prone to uncertainties, especially at higher concentrations of barium. However, in the absence of better information, the calorimetric data of Notin *et al.*^[1] have been used in the assessment.

The phase diagram of the Al-Ba system chosen in the present assessment is based on the studies of Bruzzone and Merlo^[9] up to the eutectic point ($X_{Ba} < 0.72$) and the assessed data of Elliott and Shunk^[4,5] for $X_{Ba} > 0.72$. In the present assessment, preference was given to the formula $Al_{13}Ba_7$ and Al_5Ba_4 on the basis of crystallographic data of Fornasini and Bruzzone^[11] and Fornasini.^[12] The barium-rich end of the diagram was not taken from the studies of Bruzzone and Merlo^[9] because of the discrepancy in the melting point of barium reported in their study and the fact that they did not explore the solid solubility of Al in Ba. The phase diagram chosen for the present evaluation is shown in Figure 9.

The free energy of formation of the compound Al_4Ba was obtained by combining the calorimetric results of Notin *et al.*^[1] with the Gibbs' energy of mixing of the

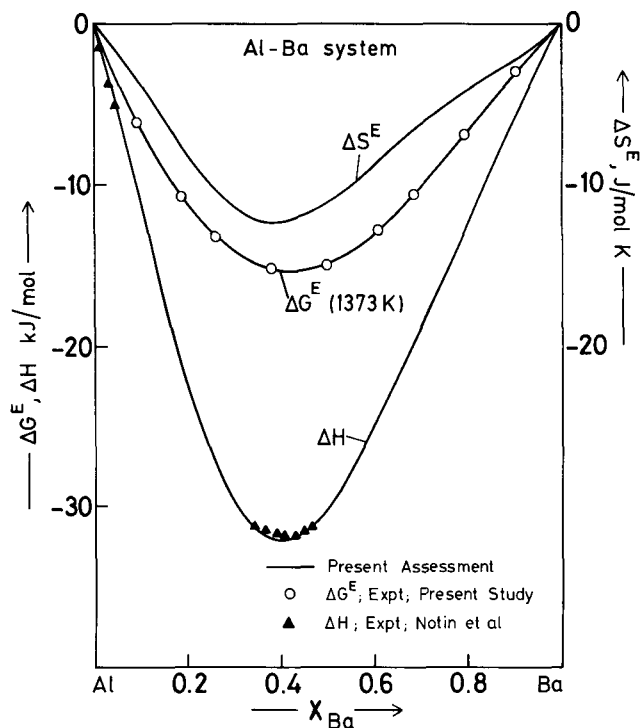


Fig. 8—Variation of assessed excess integral molar Gibbs' energy (ΔG^E), enthalpy (ΔH), and excess entropy (ΔS^E) with concentration for liquid Al-Ba alloys.

liquid alloy at the stoichiometric composition ($X_{Ba} = 0.2$) and the melting point of the compound (1377 K). It is given by

$$\Delta G_f^\circ(Al_4Ba) = -47,250 + 21.98T \text{ J/g} \cdot \text{atom} \quad [17]$$

with respect to pure liquid components as standard states. It was assumed that the Gibbs' energy of mixing of liquid alloy at the stoichiometric composition of the compound does not vary significantly with temperature between 1373 K, the temperature in the present measurements, and 1377 K, the melting point of the compound. Input data for the elemental transformations were from standard sources as follows:

$$\text{Ba: } \Delta_{\text{fus}}G(\text{bcc} \rightarrow \text{L}) = 7900 - 7.880T \text{ J/mol} \quad [18]$$

$$\text{Al: } \Delta_{\text{fus}}G(\text{fcc} \rightarrow \text{L}) = 10,710 - 11.473T \text{ J/mol} \quad [19]$$

With this information on Al-Ba alloys and the pure elements, an attempt was made to estimate the enthalpy of mixing of liquid Al-Ba alloys over the entire concentration range and the Gibbs' energy of formation of the intermetallic compounds $Al_{13}Ba_7$ and Al_5Ba_4 from the phase diagram using an optimization procedure. It was found that the resultant enthalpy of mixing of liquid alloys obtained from the optimization procedure conforms to the expression

$$\begin{aligned} \Delta H = (1 - X_{Al}) [-121,020 + 74,390(1 - 2X_{Al}) \\ + 33,630(1 - 2X_{Al})^2 \\ - 58,900(1 - 2X_{Al})^3] \end{aligned} \quad \text{J/mol} \quad [20]$$

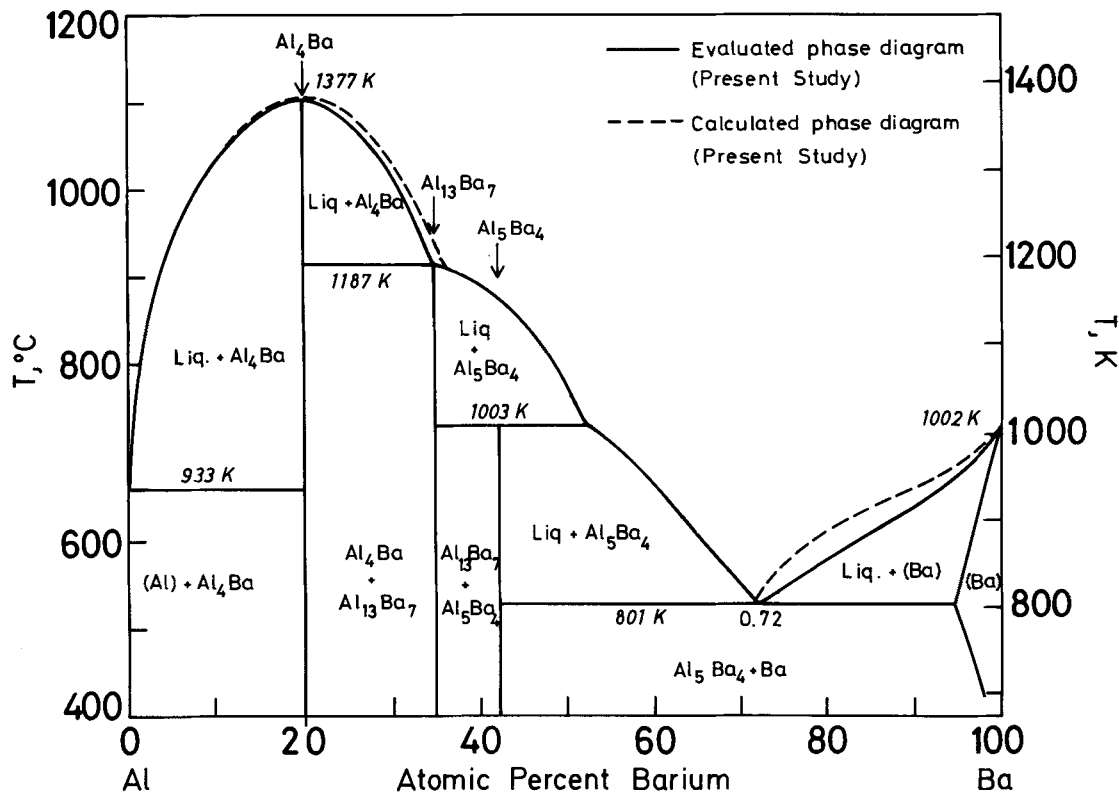


Fig. 9—Calculated and assessed phase diagram for the Al-Ba system.

and the excess entropy of mixing can be represented by the expression

$$\begin{aligned} \Delta S^E = X_{Al}(1 - X_{Al}) [-45 + 37(1 - 2X_{Al}) \\ + 17(1 - 2X_{Al})^2 \\ - 44(1 - 2X_{Al})^3] \text{ J/mol K} \end{aligned} \quad [21]$$

The calorimetric data of Notin *et al.*^[1] were used to normalize the enthalpy of mixing in the liquid state. The integral enthalpy, excess free energy, and entropy of liquid Al-Ba alloys obtained in the present evaluation are shown in Figure 8 in comparison with the experimental results. The estimated free energy of formation of the solid compounds from pure liquid components can be expressed as

$$\Delta G_f^\circ(\text{Al}_{13}\text{Ba}_7) = -55,660 + 27.0T \text{ J/g} \cdot \text{atom} \quad [22]$$

$$\Delta G_f^\circ(\text{Al}_5\text{Ba}_4) = -53,930 + 27.5T \text{ J/g} \cdot \text{atom} \quad [23]$$

They are compared with the other reported data in Table IV.

Using the optimized data for liquid Al-Ba alloys (Eqs. [20] and [21]) and the estimated thermodynamic data for solid alloys (Eqs. [17], [22], and [23]), the phase diagram of the Al-Ba system was recalculated. Barium was assumed to obey Raoult's law in the solid solution. The calculated diagram is shown in Figure 9 in comparison with the assessed diagram. It is seen that there is good agreement between the calculated and experimental liquidus. Small differences between the calculated and experimental liquidus are seen in the range of

$0.2 < X_{Ba} < 0.35$ and near the barium-rich end of the phase diagram.

V. SUMMARY

The activity of barium in liquid Al-Ba alloys has been measured at 1373 K using a combination of Knudsen effusion-mass loss analysis for $X_{Ba} \leq 0.261$ and pseudo-isopiestic measurements for $X_{Ba} \geq 0.380$. The activity of barium shows a negative deviation from Raoult's law for $0 < X_{Ba} < 0.74$ and mild positive departures at higher concentrations. The activity of aluminum exhibits a negative deviation over the entire composition range. The Bhatia-Thornton^[22] concentration-concentration structure factor at zero wave vector calculated from the activity data indicates the presence of a complex with a composition close to Al_5Ba_4 in the liquid state. The thermodynamic properties of liquid Al-Ba alloys have

Table IV. Comparison of the Enthalpy of Formation of the Intermetallic Compounds in the Al-Ba System with Respect to Pure Solid Components as Standard States

Compound	ΔH_f° (kJ/g · atom)		
	Notin <i>et al.</i>	Nepochatov <i>et al.</i>	Present Study
Al_4Ba	-37.1	-50.63	-37.1
Al_2Ba	—	-54.81	—
AlBa	—	-86.61	—
$\text{Al}_{13}\text{Ba}_7$	—	—	-45.93
Al_5Ba_4	—	—	-44.47

been described by an associated solution model based on Al_5Ba_4 -type complex. The phase diagram information available in the literature is critically evaluated. The enthalpy of mixing of liquid alloys and the Gibbs' energies of formation of the intermetallic compounds $\text{Al}_{13}\text{Ba}_7$ and Al_5Ba_4 have been estimated using the phase diagram, calorimetric information on the enthalpy of formation of solid Al_4Ba and enthalpy of mixing of liquid alloys,^[1] and the results on the Gibbs' energy of mixing at 1373 K obtained in the present study.

REFERENCES

1. M. Notin, B. Djamshidi, J.Cl. Gachon, and J. Hertz: *Thermochim. Acta*, 1982, vol. 57, pp. 57-66.
2. B.P. Burylev, A.V. Vakhobov, and T.D. Dzhuraev: *Russ. J. Phys. Chem.*, 1974, vol. 48 (6), pp. 809-11.
3. V.N. Vigdorovich, A.V. Vakhobov, and Yu.V. Plotnikov: *Russ. J. Phys. Chem.*, 1972, vol. 46 (6), pp. 822-24.
4. R.P. Elliott and F.A. Shunk: *Bull. Alloy Phase Diagrams*, 1981, vol. 2 (3), pp. 351-53.
5. T.B. Massalski, J.L. Murray, L.H. Bennet, and H. Baker: *Binary Alloy Phase Diagrams*, ASM, Metals Park, OH, 1986, p. 92.
6. E. Alberti: *Z. Metallkd.*, 1934, vol. 26, pp. 6-9.
7. E.M. Flanigen: unpublished Master's Thesis, Syracuse University, Syracuse, NY, 1952.
8. M. Iida: *Nippon Kinzoku Gakkaishi*, 1953, vol. 17, pp. 632-34.
9. G. Bruzzone and F. Merlo: *J. Less-Common Met.*, 1975, vol. 39, pp. 1-6.
10. R. Hultgren, P.D. Desai, D.T. Hawkins, M. Gleiser, and K.K. Kelley: *Selected Values of the Thermodynamic Properties of the Elements*, ASM, Metals Park, OH, 1973, p. 59.
11. M.L. Fornasini and G. Bruzzone: *J. Less-Common Met.*, 1975, vol. 40, pp. 335-40.
12. M.L. Fornasini: *Acta Crystallogr.*, 1975, vol. B31, pp. 2551-52.
13. V.M. Nepochatov, E.V. Kiseleva, and A.A. Bundel: *Russ. J. Phys. Chem.*, 1979, vol. 53 (4), pp. 588-89.
14. S.T. Kulichikina and B.P. Nikonov: *Russ. J. Phys. Chem.*, 1967, vol. 41 (9), pp. 1167-69.
15. Ya. L. Kharif, P.V. Kovtunencko, A.A. Maier, I.Kh. Avetisov, and M.M. Bebakin: *Inorg. Mater.*, 1984, vol. 20, pp. 1182-86.
16. K.T. Jacob: *Z. Metallkd.*, 1985, vol. 76, pp. 415-19.
17. K.T. Jacob, S. Srikanth, and Y. Waseda: *Trans. Jpn. Inst. Met.*, 1988, vol. 29, pp. 50-59.
18. S. Srikanth and K.T. Jacob: *Z. Metallkd.*, 1991, in press.
19. R.P. Iczkowski, J.L. Margrave, and S.M. Robinson: *J. Phys. Chem.*, 1963, vol. 67, pp. 229-33.
20. K.T. Jacob and Y. Waseda: *J. Less-Common Met.*, 1988, vol. 139, pp. 249-59.
21. J.H. Norman and P. Winchell: in *Physico-Chemical Measurements in Metals Research*, R.A. Rapp, ed., Interscience Publishers, New York, NY, 1970, vol. IV.
22. A.B. Bhatia and D.E. Thornton: *Phys. Rev.*, 1970, vol. 2B, pp. 3004-12.
23. A.S. Jordan: *Metall. Trans.*, 1970, vol. 1, pp. 239-49.
24. S. Srikanth and K.T. Jacob: *Metall. Trans. B*, 1988, vol. 19B, pp. 465-70.
25. S. Srikanth and K.T. Jacob: *CALPHAD*, 1989, vol. 13, pp. 149-58.
26. P.J. Flory: *J. Chem. Phys.*, 1942, vol. 10, pp. 51-61.
27. P.J. Flory: *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
28. M.J.D. Powell: *Comput. J.*, 1964, vol. 7, pp. 155-62.
29. E.A. Brandes: *Smithell's Metals Reference Book*, 6th ed., Butterworth's, London, 1983, p. 14-7.