Thermodynamic modelling of phase equilibria in Al–Ga–P–As system

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Abstract. A generalized thermodynamic expression of the liquid Al–Ga–P–As alloys is used in conjunction with the solid solution model in determining the solid–liquid equilibria at 1173 K and 1273 K. The liquid solution model contains thirtyseven parameters. Twentyfour of them pertain to those of the six constituent binaries, twelve refer to the specific ternary interactions. Additionally the liquid solution model also contains a specific quaternary interaction parameter. The latter has been evaluated here based on the experimental data available in the literature. The present research shows an excellent agreement between the derived and experimental values at 1173 K and 1273 K for the system. The article also presents a comparison between the evaluated values with those based on the regular solution model for the liquid alloys.

Keywords. Excess free energy; liquid solution model; Al–Ga–P–As system; solid–liquid equilibria; solid alloys; quaternary alloy.

1. Introduction

The compounds and the solid solutions of group III–V elements are extensively used in optoelectronic and high speed electronic devices fabrication. Since the need of the electronic industries is very specific in terms of composition, reliable description of phase equilibria is considered to be extremely relevant for the purpose. The evaluation of the phase equilibria of the system is based on appropriate thermodynamic functions for the liquid alloys and the solid solutions involved in the system. It has been reported by earlier investigators that the thermodynamic behaviour of solid solution may adequately be interpreted through an extended form of regular solution model (Pollack *et al* 1975). However, the corresponding liquidus compositions of higher order systems are poorly represented using a regular solution model (Pollack *et al* 1975). In the present investigation, therefore, a multiparameter function is adopted for interpretation of thermodynamic behaviour of the liquid alloys in the system.

According to Lupis (1983), a higher order system is considered to be composed of summation of the interactions of the constituent binaries along with the specific ternary and quaternary interactions. In the present research, the integral excess free energy function of the binary alloys are analysed using four-parameter equation. Six constituent binaries in the system provide twentyfour such constants (a_1 to a_{24}). Similarly, three specific ternary interactions pertaining to four ternaries constitute twelve constants (b_1 to b_{12}) in the system. Additionally, it has been shown subsequently that appropriate quaternary interaction has also been included in the function for more reliable definition of the equilibrium properties of the system. For a binary system, the excess free energy function is represented

isothermally (Hajra and Mazumdar 1991) as

$$\frac{\Delta G^{xs}}{RT} = x_1 x_2 \{a_1 x_1 + a_2 x_2 + x_1 x_2 (a_3 x_1 + a_4 x_2)\}. \quad (1)$$

The integral excess free energy for a binary system may also be expressed by Redlich–Kister polynomial (Redlich and Kister 1948) as

$$\Delta G^{xs} = x_1 x_2 \{L_0 + L_1(x_1 - x_2) + L_2(x_1 - x_2)^2 + L_3(x_1 - x_2)^3\}. \quad (2)$$

The interrelationship between the four-parameter and Redlich–Kister polynomial may be expressed as

$$RT^* a_1 = L_0 + L_1 + L_2 + L_3,$$

$$RT^* a_2 = L_0 - L_1 + L_2 - L_3,$$

$$RT^* a_3 = -4(L_2 + L_3),$$

$$RT^* a_4 = 4(L_3 - L_2).$$

Since the literature data pertaining to the constituent binaries of the system are expressed in terms of Redlich–Kister polynomial, the latter values have been transformed to their corresponding ‘ a ’ parameters to be used in the present investigation through (1).

According to the convention as mentioned above, the present formulation for the quaternary system consists of the 1–2, 1–3, 1–4, 2–3, 2–4, 3–4 binaries and four ternaries, viz. 1–2–3, 1–2–4, 1–3–4 and 2–3–4. The components of the quaternary system, Al–Ga–P–As have been designated as 1, 2, 3 and 4, respectively. The integral excess free energy function based on this concept may be represented as

$$\begin{aligned} \frac{\Delta G^{xs}}{RT} = & x_1 x_2 \{a_1 x_1 + a_2 x_2 + x_1 x_2 (a_3 x_1 + a_4 x_2)\} + \\ & x_1 x_3 \{a_5 x_1 + a_6 x_3 + x_1 x_3 (a_7 x_1 + a_8 x_3)\} + \\ & x_1 x_4 \{a_9 x_1 + a_{10} x_4 + x_1 x_4 (a_{11} x_1 + a_{12} x_4)\} + \\ & x_2 x_3 \{a_{13} x_2 + a_{14} x_3 + x_2 x_3 (a_{15} x_2 + a_{16} x_3)\} + \end{aligned}$$

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$$\begin{aligned}
& x_2x_4\{a_{17}x_2+a_{18}x_4+x_2x_4(a_{19}x_2+a_{20}x_4)\}+ \\
& x_3x_4\{a_{21}x_3+a_{22}x_4+x_3x_4(a_{23}x_3+a_{24}x_4)\}+ \\
& x_1x_2x_3\{b_1x_1+b_2x_2+b_3x_3\}+x_1x_2x_4\{b_4x_1+b_5x_2+b_6x_4\} \\
& +x_1x_3x_4\{b_7x_1+b_8x_3+b_9x_4\}+ \\
& x_2x_3x_4\{b_{10}x_2+b_{11}x_3+b_{12}x_4\}+x_1x_2x_3x_4\{c\}, \quad (3)
\end{aligned}$$

where the mole fractions of the components Al, Ga, P and As are designated as x_1 , x_2 , x_3 and x_4 , respectively and c denotes the specific quaternary interaction in the system.

The partial excess properties of each of the components of the quaternary system are deduced based on the relations between the partials and the integral excess free energy function as expressed by the following relations

$$RT \ln g_1 = \Delta G^{xs} - x_2 \frac{\partial \Delta G^{xs}}{\partial x_2} - x_3 \frac{\partial \Delta G^{xs}}{\partial x_3} - x_4 \frac{\partial \Delta G^{xs}}{\partial x_4}, \quad (4)$$

$$RT \ln g_2 = \Delta G^{xs} + (1-x_2) \frac{\partial \Delta G^{xs}}{\partial x_2} - x_3 \frac{\partial \Delta G^{xs}}{\partial x_3} - x_4 \frac{\partial \Delta G^{xs}}{\partial x_4}, \quad (5)$$

$$RT \ln g_3 = \Delta G^{xs} - x_2 \frac{\partial \Delta G^{xs}}{\partial x_2} + (1-x_3) \frac{\partial \Delta G^{xs}}{\partial x_3} - x_4 \frac{\partial \Delta G^{xs}}{\partial x_4}, \quad (6)$$

$$RT \ln g_4 = \Delta G^{xs} - x_2 \frac{\partial \Delta G^{xs}}{\partial x_2} - x_3 \frac{\partial \Delta G^{xs}}{\partial x_3} + (1-x_4) \frac{\partial \Delta G^{xs}}{\partial x_4}. \quad (7)$$

Differentiating (3) with respect to x_2 , x_3 , x_4 respectively, we get the following three sets of relations

$$\begin{aligned}
\frac{1}{RT} \left(\frac{\partial \Delta G^{xs}}{\partial x_2} \right) = & a_1 \{ (1-3x_2-x_3-x_4)(1-x_2-x_3-x_4) \} + \\
& a_2 \{ x_2(2-3x_2-2x_3-2x_4) \} + a_3 \{ x_2(2-5x_2-2x_3-2x_4) \\
& (1-x_2-x_3-x_4)^2 \} + a_4 \{ x_2^2(3-5x_2-3x_3-3x_4) \\
& (1-x_2-x_3-x_4) \} - a_5 \{ 2x_3(1-x_2-x_3-x_4) \} - a_6 x_3^2 - a_7 \\
& \{ 3x_3^2(1-x_2-x_3-x_4)^2 \} - a_8 \{ 2x_3^3(1-x_2-x_3-x_4) \} - a_9 \\
& \{ 2x_4(1-x_2-x_3-x_4) \} - a_{10} x_4^2 - a_{11} \{ 3x_4^2(1-x_2-x_3-x_4)^2 \} - \\
& a_{12} \{ 2x_4^3(1-x_2-x_3-x_4) \} + a_{13} (2x_2x_3) + a_{14} x_3^2 + a_{15} \\
& (3x_2^2x_3^2) + a_{16} (2x_2x_3^3) + a_{17} (2x_2x_4) + a_{18} x_4^2 + a_{19} (3x_2^2x_4^2) + a_{20} \\
& (2x_2x_4^3) + b_1 \{ x_3(1-3x_2-x_3-x_4)(1-x_2-x_3-x_4) \} + \\
& b_2 \{ x_2x_3(2-3x_2-2x_3-2x_4) \} + b_3 \{ x_3^2(1-2x_2-x_3-x_4) \} \\
& + b_4 (2x_2x_3x_4) + b_5 (x_3^2x_4) + b_6 (x_3x_4^2) - b_7 (x_3^2x_4) - b_8 (x_3x_4^2) - \\
& b_9 \{ 2x_3x_4(1-x_2-x_3-x_4) \} + b_{10} \{ x_4^2(1-2x_2-x_3-x_4) \} + \\
& b_{11} \{ x_4(1-3x_2-x_3-x_4)(1-x_2-x_3-x_4) \} + \\
& b_{12} \{ x_2x_4(2-3x_2-2x_3-2x_4) \} + c \{ (1-x_2-x_3-x_4) \\
& x_3x_4 - x_2x_3x_4 \}, \quad (8)
\end{aligned}$$

$$\begin{aligned}
\frac{1}{RT} \left(\frac{\partial \Delta G^{xs}}{\partial x_3} \right) = & -a_1 \{ 2x_2(1-x_2-x_3-x_4) \} - a_2 (2x_2^2) - \\
& a_3 \{ 3x_2^2(1-x_2-x_3-x_4)^2 \} - a_4 \{ 2x_2^3(1-x_2-x_3-x_4) \} + \\
& a_5 \{ (1-x_2-3x_3-x_4)(1-x_2-x_3-x_4) \} + a_6 \\
& \{ x_3(2-2x_2-3x_3-2x_4) \} + a_7 \{ x_3(2-2x_2-5x_3-2x_4) \\
& (1-x_2-x_3-x_4)^2 \} + a_8 \{ x_3^2(3-3x_2-5x_3-3x_4) \\
& (1-x_2-x_3-x_4) \} - a_9 \{ 2x_4(1-x_2-x_3-x_4) \} - a_{10} x_4^2 - a_{11} \\
& \{ 3x_4^2(1-x_2-x_3-x_4)^2 \} - a_{12} \{ 2x_4^3(1-x_2-x_3-x_4) \} + \\
& a_{13} (x_2^2) + a_{14} (2x_2x_3) + a_{15} (2x_2^3x_3) + a_{16} (3x_2^2x_3^2) + a_{21} (2x_3x_4) + \\
& a_{22} x_4^2 + a_{23} (3x_3^2x_4^2) + a_{24} (2x_3x_4^3) + b_1 \{ x_2(1-x_2-3x_3-x_4) \\
& (1-x_2-x_3-x_4) \} + b_2 \{ x_2^2(1-x_2-2x_3-2x_4) \} + \\
& b_3 \{ x_2x_3(2-2x_2-3x_3-2x_4) \} + b_4 (x_2^2x_4) + b_5 (2x_2x_3x_4) + \\
& b_6 (x_2x_4^2) + b_7 \{ x_3x_4(2-2x_2-3x_3-2x_4) \} + \\
& b_8 \{ x_4^2(1-x_2-2x_3-x_4) \} + b_9 \{ x_4(1-x_2-3x_3-x_4) \\
& (1-x_2-x_3-x_4) \} - b_{10} (x_2x_4^2) - b_{11} \{ 2x_2x_4(1-x_2-x_3-x_4) \} - \\
& b_{12} (x_2^2x_4) + c \{ (1-x_2-x_3-x_4)x_2x_4 - x_2x_3x_4 \}, \quad (9)
\end{aligned}$$

$$\begin{aligned}
\frac{1}{RT} \left(\frac{\partial \Delta G^{xs}}{\partial x_4} \right) = & -a_1 \{ 2x_2(1-x_2-x_3-x_4) \} - a_2 (x_2^2) - \\
& a_3 \{ 3x_2^2(1-x_2-x_3-x_4)^2 \} - a_4 \{ 2x_2^3(1-x_2-x_3-x_4) \} - \\
& a_5 \{ 2x_3(1-x_2-x_3-x_4) \} - a_6 (x_3^2) - a_7 \{ 3x_3^2(1-x_2-x_3-x_4)^2 \} - \\
& a_8 \{ 2x_3^3(1-x_2-x_3-x_4) \} + a_9 \{ (1-x_2-x_3-3x_4)(1-x_2-x_3-x_4) \} + \\
& a_{10} \{ x_4(2-2x_2-2x_3-3x_4) \} + a_{11} \{ x_4(2-2x_2-2x_3-5x_4) \\
& (1-x_2-x_3-x_4) \} + a_{12} \{ x_4^2(3-3x_2-3x_3-5x_4) \\
& (1-x_2-x_3-x_4) \} + a_{17} (x_2^2) + a_{18} (2x_2x_4) + a_{19} (2x_2^3x_4) + \\
& a_{20} (3x_2^2x_4^2) + a_{21} (x_3^2) + a_{22} (2x_3x_4) + a_{23} (2x_3^3x_4) + a_{24} (3x_3^2x_4^2) - \\
& b_1 \{ 2x_2x_3(1-x_2-x_3-x_4) \} - b_2 (x_2^2x_3) - b_3 (x_2x_3^2) + \\
& b_4 (x_2^2x_3) + b_5 (x_2x_3^2) + b_6 (2x_2x_3x_4) + b_7 \{ x_3^2(1-x_2-x_3-2x_4) \} + \\
& b_8 \{ x_3x_4(2-2x_2-2x_3-3x_4) \} + b_9 \{ x_3(1-x_2-x_3-3x_4) \\
& (1-x_2-x_3-x_4) \} + b_{10} \{ x_2x_4(2-2x_2-2x_3-3x_4) \} + b_{11} \\
& \{ x_2(1-x_2-x_3-3x_4)(1-x_2-x_3-x_4) \} + \\
& b_{12} \{ x_2^2(1-x_2-x_3-2x_4) \} + c \{ (1-x_2-x_3-x_4)x_3x_4 - x_2x_3x_4 \}, \quad (10)
\end{aligned}$$

substituting (8), (9) and (10) in (4), (5), (6) and (7), the partials of the components of the Al–Ga–P–As system may be obtained.

2. Discussion

In the present investigation, the phase equilibria is evaluated by using the present generalized model, (3) for the liquid phase and a nine-parameter model developed by Onda and Ito (1987) for the solid alloys. At equilibrium,

the chemical potential of a component in solid phase equals to that of the component of the liquid phase. The latter is expressed as

$$\mathbf{m}_i^l = \mathbf{m}_i^s, \quad (11)$$

where, $i = 1$ to 4.

The chemical potential of the components are related to the corresponding activities as

$$\mathbf{m}_i^{os} + RT \ln a_i^s = \mathbf{m}_i^{ol} + RT \ln a_i^l. \quad (12)$$

The solidus composition in the system is governed by the solid solution of the compounds AlP, AlAs, GaP and GaAs. The activities of the compounds in equilibrium with the corresponding solid components of the system may be expressed as

$$(\mathbf{m}_{ij}^{(s)} - \mathbf{m}_i^{(s)} - \mathbf{m}_j^{(s)}) = 0,$$

where ij is the compound with i and j as the constituent elements. These may be expanded into the following expression

$$(\mathbf{m}_{ij}^{0(s)} - \mathbf{m}_i^{0(s)} - \mathbf{m}_j^{0(s)}) + RT \ln a_{ij}^{(s)} - RT \ln a_i^{(s)} - RT \ln a_j^{(s)} = 0.$$

By combining the above equations with (12), we obtain

$$(\mathbf{m}_{ij}^{0(s)} - \mathbf{m}_i^{0(s)} - \mathbf{m}_j^{0(s)}) + RT \ln a_{ij}^{(s)} = RT \ln a_i^{(l)} + RT \ln a_j^{(l)} - (\mathbf{m}_i^{0(s)} - \mathbf{m}_i^{0(l)}) - (\mathbf{m}_j^{0(s)} - \mathbf{m}_j^{0(l)}), \quad (13)$$

where $\mathbf{m}^{0(s)}$ and $\mathbf{m}^{0(l)}$ of the pure components and pure compounds are obtained from the literature compiled by Ansara *et al* (1994). x_i^s and x_i^l are the corresponding mole fractions pertaining to the solid and liquid alloys in the system.

For the system, under present investigation viz. $\text{Al}_x\text{Ga}_{1-x}\text{P}_y\text{As}_{1-y}$, ΔG^{ss} may be written for the solid phase in accordance with Onda and Ito (1987) as

$$\begin{aligned} \Delta G^{ss} = & xy d_1 + x(1-y) d_2 + (1-x) y d_3 + (1-x)(1-y) d_4 \\ & + x(1-x) y^2 d_5 + x(1-x)(1-y)^2 d_6 \\ & + x^2 y(1-y) d_7 + (1-x)^2 y(1-y) d_8 + x(1-x) y(1-y) d_9, \end{aligned} \quad (14)$$

where, x and y refer to the compositional parameters pertaining to the solid solutions as expressed by the formulation, $\text{Al}_x\text{Ga}_{1-x}\text{P}_y\text{As}_{1-y}$. The constants, d_1 through d_9 describe the thermodynamic behaviour of the solid phase and the choice of these parameters are based on the following pair wise interactions of the components of the system (AlAs, AlP, GaAs and GaP), $d_1 \rightarrow \text{AlP}$, $d_2 \rightarrow \text{AlAs}$, $d_3 \rightarrow \text{GaP}$, $d_4 \rightarrow \text{GaAs}$, $d_5 \rightarrow \text{AlP-GaP}$, $d_6 \rightarrow \text{AlAs-GaAs}$, $d_7 \rightarrow \text{AlP-AlAs}$, $d_8 \rightarrow \text{GaP-GaAs}$, $d_9 \rightarrow \text{AlGaPAs}$.

The corresponding partials in the solid alloys are derived based on (5) through (7) and (14) using a similar procedure

as has been adopted for the liquid alloys. The partials of the solid solution based on the above may be expressed as,

$$\begin{aligned} RT \ln g_{\text{AlP}} = & d_1(x+y-2xy) + d_2(1-x-y+2xy) + d_3 \\ & (1-x-2y+2xy) + d_4(-1+x+2y-2xy) + d_5 \\ & (2xy+y^2-2x^2y-6xy^2+5x^2y^2) + d_6 \\ & (2xy+x^2-5x^2y-2xy^2+5x^2y^2) + d_7(1-2x+5y+ \\ & x^2+5y^2+10xy-5x^2y-10xy^2+5x^2y^2) + \\ & d_8(1-4x+3x^2-2y+10xy-8x^2y-6xy^2+y^2+5x^2y^2) + \\ & d_9(x+y-6xy-x^2-y^2+5x^2y+6xy^2-5x^2y^2), \end{aligned} \quad (15)$$

$$\begin{aligned} RT \ln g_{\text{AlAs}} = & d_1(x-y) + d_2(-1+x+y) + d_3(1-x) + \\ & d_4(1-x) + d_5(2xy-2x^2y-y^2+x^2y^2) + \\ & d_6(-2xy+x^2+2x^2y-x^2y+x^2y^2) + \\ & d_7(1-2x-y+2xy+x^2+y^2-x^2y-2xy^2+x^2y^2) + \\ & d_8(-1-x^2+2x+2y-2xy-y^2+x^2y^2) + \\ & d_9(x-x^2-y+x^2y+y^2-x^2y^2), \end{aligned} \quad (16)$$

$$\begin{aligned} RT \ln g_{\text{GaP}} = & d_1(x+y) + d_2(1-x-y) + d_3(1-x) + \\ & d_4(-1+x) + d_5(2xy-2x^2y+y^2-2xy^2+x^2y^2) + \\ & d_6(x^2+2xy-3x^2y-2xy^2+x^2y^2) + \\ & d_7(1-2x+x^2-3y+6xy+y^2-3x^2y-2xy^2+x^2y^2) + \\ & d_8(1-4x-2y+y^2+6xy+3x^2-4x^2y-2xy^2+x^2y^2) + \\ & d_9(x-x^2+y-4xy-y^2+3x^2y+2xy^2-x^2y^2), \end{aligned} \quad (17)$$

$$\begin{aligned} RT \ln g_{\text{GaAs}} = & d_1(-x+y) + d_2(1+x-y) + d_3(-1+x) + \\ & d_4(1-x) + d_5(-2xy+y^2+2x^2y-2xy^2+x^2y^2) + \\ & d_6(2xy-x^2+x^2y-2xy^2+x^2y^2) + \\ & d_7(-1+2x+y-2xy-x^2+y^2+x^2y-2xy^2+x^2y^2) + \\ & d_8(1-2y+2xy-x^2+y^2-2xy^2+x^2y^2) + \\ & d_9(-x+y+x^2-y^2-x^2y+2xy^2-x^2y^2). \end{aligned} \quad (18)$$

Each of the components in the liquid phase and those of the corresponding solid alloys are substituted in (13) for the description of the solid-liquid equilibria in the system. A computer programme was developed to obtain the regression values by least squares technique using the experimental data (Llegems and Panish 1974) in the system. The binary and ternary parameters involved in (3) are used from the available literature data (Ansara *et al* 1994; Ishida *et al* 1989). Although the values of the parameters for the solid alloys, viz. d_5 to d_9 , are available at 1173 and

1273 K in the literature (Ishida *et al* 1989), d_1 , d_2 , d_3 , d_4 and d_9 along with the specific interaction parameter c have been evaluated by the above mentioned method. Incorporating these values, the phase equilibria has been calculated at 1173 K and 1273 K.

Table 1 compiles the binary and ternary interaction parameters that are available from the literature at 1173 K and 1273 K (Ansara *et al* 1994; Ishida *et al* 1989). The regression values of the solid interaction parameters for

(14) along with the specific quaternary interaction parameter at 1173 K and 1273 K are listed in table 2. For the purpose of comparison tables 3–5 list the experimental (Llegems and Panish 1974) and their corresponding calculated compositional values for the solid and liquid phases at equilibrium. The derived values of the present investigation are in closer agreement with the experimental data relative to those of the regular solution model. The use of multiparameter function of the liquid alloys is, therefore,

Table 1. Interaction parameters from Ansara *et al* (1994) and Ishida *et al* (1989) at 1173 K and 1273 K.

Binary parameter	Parameter (RT)		Ternary parameter	Parameter (RT)	
	1173 K	1273 K		1173 K	1273 K
a_1	0.00631	– 0.02289	b_1	0	0
a_2	– 0.11338	– 0.13143	b_2	0	0
a_3	– 0.13105	– 0.12075	b_3	0	0
a_4	– 0.13105	– 0.12075	b_4	– 6.79982	5.49088
a_5	– 13.69735	– 12.01003	b_5	– 6.79982	5.49088
a_6	– 13.69735	– 12.01003	b_6	– 6.79982	5.49088
a_7	0	0	b_7	0	0
a_8	0	0	b_8	0	0
a_9	– 5.71825	– 5.59184	b_9	0	0
a_{10}	– 5.71825	– 5.59184	b_{10}	– 0.52295	– 0.48187
a_{11}	0	0	b_{11}	– 0.52295	– 0.48187
a_{12}	0	0	b_{12}	– 0.52295	– 0.48187
a_{13}	– 1.01125	– 0.931808			
a_{14}	– 1.01125	– 0.931808			
a_{15}	0	0			
a_{16}	0	0			
a_{17}	– 3.66425	– 3.41714			
a_{18}	– 2.60303	– 2.44026			
a_{19}	0	0			
a_{20}	0	0			
a_{21}	0.59424	0.54756			
a_{22}	0.22904	0.21108			
a_{23}	0	0			
a_{24}	0	0			

Table 2. Regression values.

Phase	Parameter	Parameter (RT)	
		1173 K	1273 K
Solid	d_1	1.0937×10^2	0.5171
	d_2	-4.2713×10^1	15.0521
	d_3	3.5956×10^{17}	7.2455×10^{16}
	d_4	3.5956×10^{17}	7.2455×10^{16}
	d_5	0*	0*
	d_6	0.417542*	0.384742*
	d_7	0*	0*
	d_8	0*	0*
	d_9	1.1767×10^1	– 25.0920
Liquid	c	3.0614×10^4	-1.5121×10^5

*Indicates the availability of data in literature (Ishida *et al* 1989).

Table 3. Comparison of the solidus compositional data with the calculated values at 1173 K and 1273 K.

Temp. (K)	x_1^l	x_2^l	x_3^l	x_4^l	x_{expt}^s	x_{cal}^s Present study	x_{cal}^s Llegems & Panish (1974)	y_{expt}^s	y_{cal}^s Present study	y_{cal}^s Llegems & Panish (1974)
1173	0.0010	0.9576	0.0015	0.0399	0.1852	0.1789	0.2013	0.2977	0.2993	0.3143
	0.0010	0.9668	0.0023	0.0299	0.1687	0.2038	0.2290	0.5092	0.5024	0.5197
	0.0010	0.9757	0.0033	0.0200	0.1951	0.2321	0.2715	0.6307	0.6342	0.6441
	0.0010	0.9505	0.0039	0.0099	0.2376	0.2799	0.3140	0.8167	0.8385	0.8448
	0.0010	0.9945	0.0045	0.0001	0.3410	0.3352	0.3565	0.9959	0.9813	0.9713
	0.0010	0.9853	0.0039	0.0097	0.2390	0.2774	0.3167	0.8194	0.8289	0.8502
	0.0025	0.9571	0.0005	0.0399	0.3648	0.3415	0.3178	0.1588	0.1528	0.1484
	0.0025	0.9660	0.0015	0.0300	0.3816	0.3632	0.3952	0.4310	0.4143	0.4032
	0.0025	0.9755	0.0020	0.0201	0.4592	0.4626	0.4785	0.6211	0.6282	0.6388
	0.0025	0.9944	0.0030	0.0001	0.5613	0.5578	0.5777	0.9715	0.9728	0.9959
1273	0.0010	0.9846	0.0143	0.0001	0.2844	0.2731	0.2567	0.9960	0.9956	0.9940
	0.0010	0.9314	0.0078	0.0598	0.1401	0.1535	0.1725	0.5793	0.5614	0.5874
	0.0025	0.9322	0.0050	0.0603	0.2874	0.3084	0.3109	0.4864	0.4993	0.5157
	0.0025	0.9506	0.0070	0.0391	0.3495	0.3386	0.3585	0.6740	0.6810	0.7133
	0.0025	0.9693	0.0088	0.0196	0.3544	0.3652	0.4008	0.8496	0.8373	0.8684
	0.0025	0.9867	0.0106	0.0002	0.4285	0.4101	0.4539	0.9973	0.9917	0.9928

Table 4. Comparison of the liquidus compositional data with the calculated values at 1173 K.

x_1^l expt	x_1^l assume		x_2^l expt	x_2^l cal		x_3^l expt	x_3^l cal		x_4^l expt	x_4^l cal		x_{expt}^s	y_{expt}^s
	Present study	Llegems & Panish (1974)		Present study	Llegems & Panish (1974)		Present study	Llegems & Panish (1974)		Present study	Llegems & Panish (1974)		
0.0010	0.0010	0.0010	0.9576	0.9468	0.9580	0.0015	0.0014	0.0014	0.0399	0.0398	0.0401	0.1852	0.2977
0.0010	0.0010	0.0010	0.9668	0.9660	0.9710	0.0023	0.0025	0.0028	0.0299	0.0289	0.0301	0.1687	0.5092
0.0010	0.0010	0.0010	0.9757	0.9698	0.9813	0.0033	0.0032	0.0030	0.0200	0.0198	0.0196	0.1951	0.6307
0.0010	0.0010	0.0010	0.9505	0.9615	0.9855	0.0039	0.0038	0.0037	0.0099	0.0098	0.0097	0.2376	0.8167
0.0010	0.0010	0.0010	0.9945	0.9941	0.9844	0.0045	0.0044	0.0044	0.0001	0.0002	0.0001	0.3410	0.9959
0.0010	0.0010	0.0010	0.9853	0.9875	0.9849	0.0039	0.0038	0.0037	0.0097	0.0096	0.0094	0.2390	0.8194
0.0025	0.0025	0.0025	0.9571	0.9580	0.9565	0.0005	0.0006	0.0005	0.0399	0.0400	0.0404	0.3648	0.1588
0.0025	0.0025	0.0025	0.9660	0.9690	0.9664	0.0015	0.0014	0.0013	0.0300	0.0298	0.0298	0.3816	0.4310
0.0025	0.0025	0.0025	0.9755	0.9783	0.9766	0.0020	0.0021	0.0018	0.0201	0.0206	0.0199	0.4592	0.6211
0.0025	0.0025	0.0025	0.9944	0.9969	0.9927	0.0030	0.0031	0.0028	0.0001	0.0001	0.0002	0.5613	0.9715

Table 5. Comparison of the liquidus compositional data with the calculated values at 1273 K.

x_1^l expt	x_1^l assume		x_2^l expt	x_2^l calc		x_3^l expt	x_3^l calc		x_4^l expt	x_4^l calc		x_{expt}^s	y_{expt}^s
	Present study	Llegems & Panish (1974)		Present study	Llegems & Panish (1974)		Present study	Llegems & Panish (1974)		Present study	Llegems & Panish (1974)		
0.0010	0.0010	0.0010	0.9846	0.9814	0.9851	0.0143	0.0148	0.0138	0.0001	0.0001	0.0001	0.2844	0.9960
0.0010	0.0010	0.0010	0.9314	0.9416	0.9591	0.0078	0.0075	0.0072	0.0598	0.5917	0.0591	0.1401	0.5793
0.0025	0.0025	0.0025	0.9322	0.9320	0.9319	0.0050	0.0051	0.0051	0.0603	0.0601	0.0606	0.3071	0.5144
0.0025	0.0025	0.0025	0.9506	0.9530	0.9517	0.0070	0.0071	0.0069	0.0391	0.0401	0.0399	0.3630	0.7101
0.0025	0.0025	0.0025	0.9693	0.9659	0.9691	0.0088	0.0085	0.0087	0.0196	0.0201	0.0197	0.4096	0.8684
0.0025	0.0025	0.0025	0.9867	0.9815	0.9889	0.0106	0.0101	0.0106	0.0002	0.0003	0.0005	0.4481	0.9863

Figure 1. 900°C Solidus isotherms at constant, $X_{Al}^I = 0.0010$ (For x : Δ , experimental (Llegems and Panish 1974); $-O-$, present study; $\square$, Llegems and Panish's (1974) model; and for y : ∇ , experimental (Llegems and Panish 1974); $\dots\times\dots$, present study; $+$, Llegems and Panish's (1974) model).

Figure 2. 900°C Solidus isotherms at constant, $X_{Al}^I = 0.0025$ (For x : Δ , experimental (Llegems and Panish 1974); $-O-$, present study; $\square$, Llegems and Panish's (1974) model; and for y : ∇ , experimental (Llegems and Panish 1974); $\dots\times\dots$, present study; $+$, Llegems and Panish's (1974) model).

Figure 3. 1000°C Solidus isotherms at constant $X_{Al}^I = 0.0025$, (For x : Δ , experimental (Llegems and Panish 1974); $-O-$, present study; $\square$, Llegems and Panish's (1974) model; and for y : ∇ , experimental (Llegems and Panish 1974); $\dots\times\dots$, present study; O , Llegems and Panish's (1974) model).

considered to be adequate in establishing the phase equilibria in the system. Figures 1–6 exhibit the calculated values of solidus and liquidus composition based on the present research and those obtained through the simple solution model for the purpose of comparison. The figures show that the derived values of solidus composition based on the two models are in agreement with the experimental data. However, the derived values of the liquidus composition based on the present research are much closer to the experimental data for Al rich alloys at lower temperature than those derived based on the simple solution model. Since specific compositional analysis is necessary in the electronic industries in order to develop a particular electronic grade of materials for certain special applications, more exact determination of the liquidus compositions seems appropriate for the purpose. For dilute solutions, the effect of the higher order interaction bet-

Figure 4. 900°C Liquidus isotherms in the Al-Ga-P-As system at $X_{Al}^I = 0.0010$ ($\bullet$, experimental (Llegems and Panish 1974); $\dots$, present study; $\times$, Llegems and Panish's (1974) model).

Figure 5. 900°C Liquidus isotherms in the Al-Ga-P-As system at $X_{Al}^I = 0.0025$ ($\bullet$, experimental (Llegems and Panish 1974); $\dots$, present study; $+$, Llegems and Panish's (1974) model).

Figure 6. 1000°C Liquidus isotherms in the Al–Ga–P–As system at $X_{\text{Al}}^{\text{l}} = 0.0025$, (●, experimental (Llegems and Panish 1974);, present study; *, Llegems and Panish's (1974) model).

ween atoms are generally considered to be negligible. However, the role of higher order parameters are extremely necessary for appropriate description of equilibrium properties of the system without any compositional constraints.

3. Conclusions

The present research describes the isothermal section of the Al–Ga–P–As system at 1173 K and 1273 K. The proposed liquid solution model is used along with a solid

solution model by Onda and Ito (1987) to study the solid–liquid equilibria in the Al–Ga–P–As system. The parameters for which the data are not available in the literature, have been determined through the regressional analysis of the solid–liquid equilibrium data of the system. Although the derived values of simple solution model for the solid solution is adequate in representing the solidus data, it departs somewhat from those of the liquidus compositions of the alloys. The use of multi parameter function in the present research complies with the specific requirement of more exact compositional description of the liquid alloys in the system (liquidus compositions).

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