

## Thermodynamic calculation of phase equilibria in the Al–Ge–Zn system

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### Abstract

Phase equilibria in the ternary system Al–Ge–Zn were calculated at 873, 773 and 658 K from thermodynamic data of the constituent binary systems. Quasi-regular solution and shortest distance path equations were employed to estimate the thermodynamic data of liquid Al–Ge–Zn alloys from the binary data. The thermodynamic behaviour of solid alloys was also approximated by a quasi-regular solution model. The interaction parameter for solid Al–Ge alloys was deduced from the binary phase diagram. The calculated isothermal phase diagrams are in reasonable agreement with the experimental data. Tie-lines delineating equilibria between the liquid and solid alloys were generated.

### INTRODUCTION

A knowledge of the thermodynamic behaviour and phase equilibria in the system Al–Ge–Zn is useful for a physicochemical analysis of metastable phase formation during rapid solidification processing of these alloys. Tyapkin et al. [1] have observed a metastable phase with a new type of regular (modulated) structure in the alloys 40Al–59Zn–1Ge and 20Al–70Zn–1Ge, the composition being expressed in mass percent. Experimental investigation of phase equilibria in the ternary Al–Ge–Zn system has been carried out by Tadjbakhche [2] and Storonkin et al. [3]. Tadjbakhche investigated the Al–Ge–Zn system using differential thermal analysis and microstructural observations. He studied seven isoplethal sections using about 60 alloys from which complete information on the phase equilibria has been deduced. Two invariant equilibria were reported by Tadjbakhche, i.e. a ternary eutectic reaction at 625 K at the composition 89.0 mass%Zn, 6.0 mass%Al and 5.0 mass%Ge, followed by a eutectoid reaction at 548 K. The results of Tadjbakhche show large uncertainties below the ternary eutectic temperature. Storonkin et al. [3] also studied this ternary system by

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the thermographic method to determine the liquidus at several temperatures. They also confirmed the ternary eutectic reaction at 625 K but at a composition of 6.7 mass%Al and 9.7 mass%Ge. The liquidus compositions of Storonkin et al. are not in agreement with those of Tadjbakhche. Recently, Chattopadhyay et al. [4] have carried out an evaluation of the Al–Ge–Zn system. They have deduced thermodynamically consistent isothermal sections at several temperatures above the ternary eutectic, primarily from the isopleths reported by Tadjbakhche [2].

The purpose of this study was to carry out a thermodynamic calculation of phase equilibria in the ternary Al–Ge–Zn system and compare it with the assessed data. The thermodynamic properties of ternary Al–Ge–Zn alloys are not available in the literature. Quasi-regular solution and shortest distance path equations [5] have been employed to estimate the thermodynamic data of liquid Al–Ge–Zn alloys from the binary data. The thermodynamic behaviour of solid alloys has also been approximated by a quasi-regular solution model. The shortest distance composition path model has not previously been employed for the calculation of phase diagrams.

#### ESTIMATION OF THERMODYNAMIC DATA OF TERNARY SYSTEMS

Several methods [5–11] have been proposed in the literature for the prediction of the thermodynamic properties of ternary solutions from information on the corresponding binary systems. A detailed review of the available models for the prediction of the thermodynamic properties in multicomponent systems is given by Ansara [12] and Spencer et al. [13]. The simplest of these are the regular [14] and quasi-regular solution models which lead to symmetric integral properties of mixing in binary alloys. However, only a limited number of binary solutions conform to this behaviour. For multicomponent solutions, the Gibbs energy of mixing is simply taken to be the sum of the contributions from the corresponding binaries. The basic principle underlying the other models [5–11] is that the excess thermodynamic properties of the ternary alloy are obtained from the corresponding values for the binary alloys by extrapolation along certain composition paths in the Gibbs triangle. The various models differ only in the choice of the composition paths.

##### *Regular and quasi-regular solution model*

The excess Gibbs energy of mixing of a regular ternary solution can be expressed as

$$\Delta G_{ABC}^E = X_A X_B \alpha_{AB} + X_B X_C \alpha_{BC} + X_A X_C \alpha_{AC} \quad (1)$$

where  $\alpha_{AB} = \Delta G_{AB}^E / N_A N_B$ ,  $X_i$  is the ternary mole fraction and  $N_i$  is the

binary mole fraction of component  $i$ . The interaction parameter  $\alpha$  is a constant with respect to composition and temperature for a regular solution, whereas it is a linear function of temperature for a quasi-regular solution. A ternary interaction term is sometimes incorporated in the expression for the excess Gibbs energy to represent the experimental data

$$\Delta G_{ABC}^E = X_A X_B \alpha_{AB} + X_B X_C \alpha_{BC} + X_A X_C \alpha_{AC} + X_A X_B X_C \alpha_{ABC} \quad (2)$$

The parameter  $\alpha_{ABC}$  can be derived if limited experimental information is available on the thermodynamics of the ternary system.

The expression for the partial excess Gibbs energies can be derived by means of the general thermodynamic relation at constant temperature and pressure for an  $m$ -component system:

$$G_i^E = G^E + \sum_{j=2}^m (\delta_{ij} - X_j) \frac{\partial G^E}{\partial X_j} \quad (3)$$

where  $\delta_{ij}$  is the Kronecker's delta ( $\delta_{ij} = 0$  for  $i \neq j$  and  $\delta_{ij} = 1$  for  $i = j$ ) for all values of  $i$  and  $j$ . Applying this relation to ternary regular solutions, the partial excess Gibbs energies are

$$\begin{aligned} \Delta G_{A(ABC)}^E &= X_B(X_B + X_C)\alpha_{AB} + X_C(X_B + X_C)\alpha_{AC} \\ &\quad - X_B X_C \alpha_{BC} + X_B X_C (1 - 2X_A)\alpha_{ABC} \end{aligned} \quad (4)$$

$$\begin{aligned} \Delta G_{B(ABC)}^E &= X_A(X_A + X_C)\alpha_{AB} + X_C(X_A + X_C)\alpha_{BC} \\ &\quad - X_A X_C \alpha_{AC} + X_A X_C (1 - 2X_B)\alpha_{ABC} \end{aligned} \quad (5)$$

$$\begin{aligned} \Delta G_{C(ABC)}^E &= X_B(X_A + X_B)\alpha_{BC} + X_A(X_A + X_B)\alpha_{AC} \\ &\quad - X_A X_B \alpha_{AB} + X_A X_B (1 - 2X_C)\alpha_{ABC} \end{aligned} \quad (6)$$

If ternary interactions are not considered,  $\alpha_{ABC}$  can be taken to be zero.

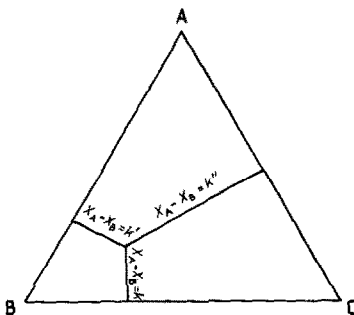


Fig. 1. Shortest distance composition path relating the ternary alloy to constituent binary alloys.

In both the regular and quasi-regular solution models, the parameter  $\alpha_{ij}$  is independent of composition. Since this assumption is not generally valid for most alloys, it has been replaced by experimentally determined binary values of  $\Delta G^E$  along certain composition paths in the proposed equations of Bonnier and Caboz [6], Toop [7], Kohler [8], Colinet [9], Muggianu et al. [10] and Jacob and co-workers [5,15]. In the expressions of Bonnier and Caboz [6] and Toop [7] the composition paths connecting the ternary point to the binary compositions are not symmetric. Therefore the values calculated using these equations for non-regular ternary alloys depend on the choice of component at the apex of the composition triangle. Thereby, different values of  $\Delta G^E$  are obtained for the same composition of the alloy. Colinet [9] employs composition paths corresponding to constant mole fractions to estimate the excess Gibbs energy of a ternary system from the constituent binaries. Kohler's equation [8] uses a constant mole fraction ratio composition path to extrapolate binary thermodynamic data to ternary systems.

The expressions for the excess Gibbs energy of a ternary system suggested independently by Muggianu et al. [10] and Jacob and co-workers

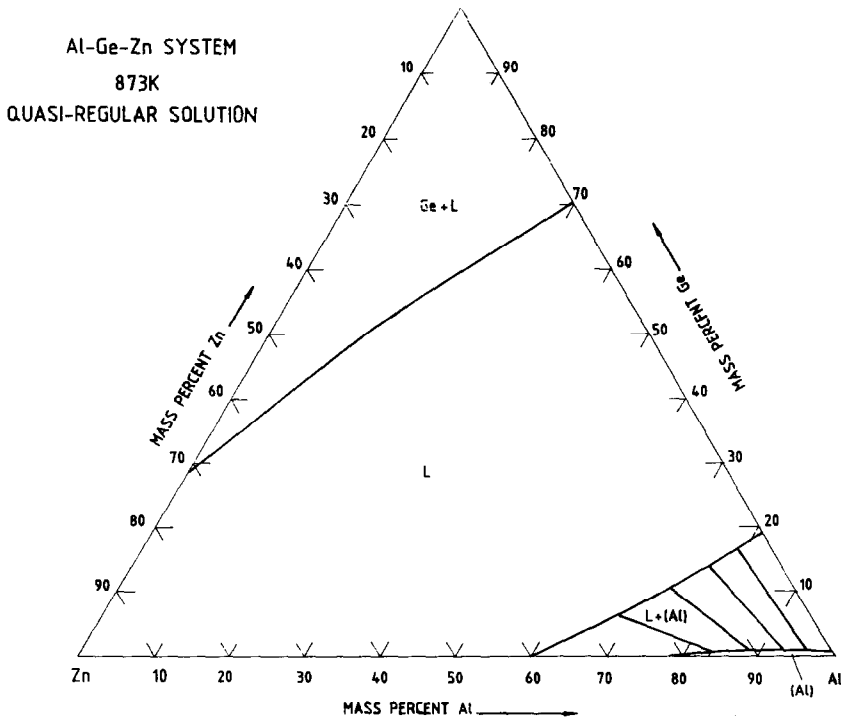


Fig. 2. Isothermal section of the Al-Ge-Zn system at 873 K computed from the quasi-regular solution equation.

TABLE 1

Quasi-regular solution parameters for liquid Al–Ge–Zn alloys

Interaction coefficient	Coefficient value ( $\text{kJ mol}^{-1}$ ) at		
	873 K	773 K	658 K
$\alpha_{\text{Al-Ge}}$	-16.7282	-16.5324	-16.3072
$\alpha_{\text{Ge-Zn}}$	-0.7195	0.5588	2.0290
$\alpha_{\text{Al-Zn}}$	7.0488	7.4286	7.8654

[5,15] are essentially the same. They employ the shortest distance composition path connecting any ternary composition to the respective binary compositions for extrapolation of thermodynamic data. Since in the shortest distance path model, the binary values incorporated correspond to binary compositions closest to the ternary point, it can be expected that the ternary property estimated along this path, and therefore the computed phase diagram, would be in better agreement with the experimental values. In the present study a quasi-regular solution model and the shortest distance path equations developed by Jacob and co-workers [5,15] were

TABLE 2

Coefficients of the shortest distance path equation for liquid Al–Ge–Zn alloys

System	Coefficient	Value of coefficient ( $\text{kJ mol}^{-1}$ ) at		
		873 K	773 K	658 K
Al–Ge	$A_1$	-17.0588	-16.8829	-16.6807
	$A_2$	-0.4161	-0.2554	-0.0706
	$A_3$	+2.3188	+2.4585	+2.6192
Ge–Zn	$B_1$	-0.9652	+0.2390	+1.6237
	$B_2$	+1.6038	+1.7745	+1.9709
	$B_3$	+1.7228	+2.2436	+2.8424
Al–Zn	$C_1$	+6.9637	+7.3434	+7.7802
	$C_2$	+0.3002	+0.2363	+0.1628
	$C_3$	+0.5971	+0.5973	+0.5975

TABLE 3

Quasi-regular solution parameters for solid Al–Ge–Zn alloys

Coefficient	Value of coefficient ( $\text{kJ mol}^{-1}$ ) at		
	873 K	773 K	658 K
$\alpha'_{\text{Al-Ge}}$	22.66	22.66	22.66
$\alpha'_{\text{Ge-Zn}}$	0	0	0
$\alpha'_{\text{Al-Zn}}$	9.4042	9.9845	10.6520

used to estimate the thermodynamic properties of the ternary Al–Ge–Zn system.

### Shortest distance composition path

Jacob and co-workers [5,15] suggested that the excess Gibbs energy of mixing in a ternary system A–B–C may be expressed by

$$\begin{aligned} \Delta G_{ABC}^E = & \frac{X_A X_B}{(X_A + X_C/2)(X_B + X_C/2)} (\Delta G_{AB}^E)_{X_A - X_B = k} \\ & + \frac{X_B X_C}{(X_B + X_A/2)(X_C + X_A/2)} (\Delta G_{BC}^E)_{X_B - X_C = k'} \\ & + \frac{X_C X_A}{(X_C + X_B/2)(X_A + X_B/2)} (\Delta G_{AC}^E)_{X_A - X_C = k''} \end{aligned} \quad (7)$$

The binary compositions at which the binary excess free energy terms are taken are shown in Fig. 1. They suggest that the binary excess Gibbs energy

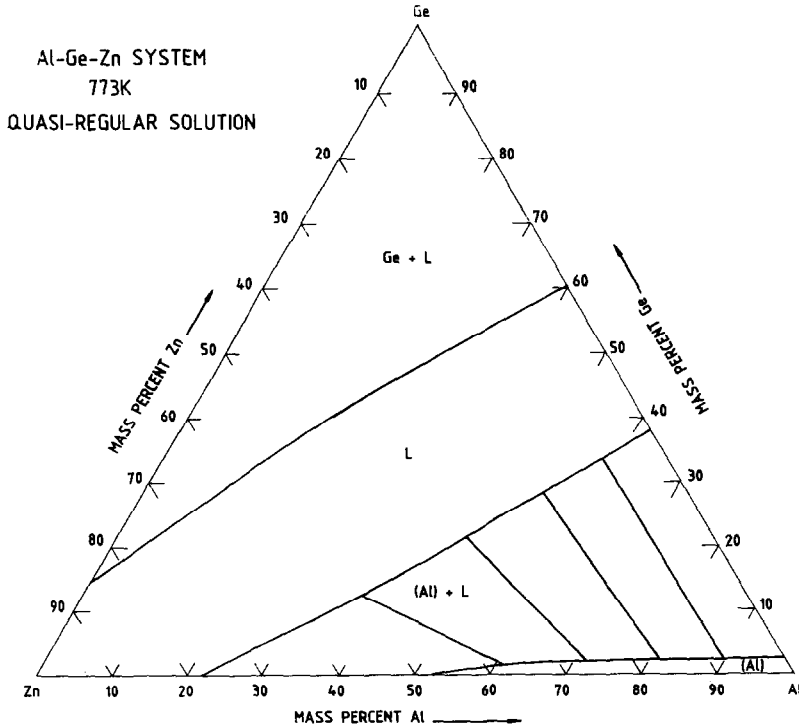


Fig. 3. Phase diagram of the Al–Ge–Zn system at 773 K computed from quasi-regular solution model.

may be expressed as a power series in  $(N_i - N_j)$  and eqn. (7) can be recast to the form

$$\begin{aligned} \Delta G_{ABC}^E = & X_A X_B \sum_{i=0} A_i (X_A - X_B)^i + X_B X_C \sum_{i=0} B_i (X_B - X_C)^i \\ & + X_A X_C \sum_{i=0} C_i (X_A - X_C)^i \end{aligned} \quad (8)$$

since along the proposed composition path,  $N_i - N_j = X_i - X_j$ . The values of coefficients  $A_i$ ,  $B_i$  and  $C_i$  can be derived from the known excess Gibbs energy of mixing of the corresponding binary systems. Equation (8) is more amenable to mathematical treatment and computer calculation of phase diagrams. The partial excess Gibbs energies corresponding to the shortest distance path equation (eqn. (8)), derived using relation (3), are

$$\begin{aligned} \Delta G_{A(ABC)}^E = & X_B (1 - X_A) \sum_{i=0} A_i (X_A - X_B)^i \\ & + X_A X_B (1 - X_A + X_B) \sum_{i=0} i \cdot A_i (X_A - X_B)^{i-1} \\ & - (X_B X_C) \sum_{i=0} B_i (X_B - X_C)^i \\ & - X_B X_C (X_B - X_C) \sum_{i=0} i \cdot B_i (X_B - X_C)^{i-1} \\ & + X_C (1 - X_A) \sum_{i=0} C_i (X_A - X_C)^i \\ & + X_A X_C (1 - X_A + X_C) \sum_{i=0} i \cdot C_i (X_A - X_C)^{i-1} \end{aligned} \quad (9)$$

$$\begin{aligned} \Delta G_{B(ABC)}^E = & X_A (1 - X_B) \sum_{i=0} A_i (X_A - X_B)^i \\ & - X_A X_B (1 + X_A - X_B) \sum_{i=0} i \cdot A_i (X_A - X_B)^{i-1} \\ & + X_C (1 - X_B) \sum_{i=0} B_i (X_B - X_C)^i \\ & + X_B X_C (1 - X_B + X_C) \sum_{i=0} i \cdot B_i (X_B - X_C)^{i-1} \\ & - (X_A X_C) \sum_{i=0} C_i (X_A - X_C)^i \\ & - X_A X_C (X_A - X_C) \sum_{i=0} i \cdot C_i (X_A - X_C)^{i-1} \end{aligned} \quad (10)$$

$$\begin{aligned}
 \Delta G_{C(ABC)}^E &= -X_A X_B \sum_{i=0} A_i (X_A - X_B)^i \\
 &\quad - X_A X_B (X_A - X_B) \sum_{i=0} i \cdot A_i (X_A - X_B)^{i-1} \\
 &\quad + X_B (1 - X_C) \sum_{i=0} B_i (X_B - X_C)^i \\
 &\quad - X_B X_C (1 + X_B - X_C) \sum_{i=0} i \cdot B_i (X_B - X_C)^{i-1} \\
 &\quad + X_A (1 - X_C) \sum_{i=0} C_i (X_A - X_C)^i \\
 &\quad - X_A X_C (1 + X_A - X_C) \sum_{i=0} i \cdot C_i (X_A - X_C)^{i-1}
 \end{aligned} \tag{11}$$

COMPUTATION OF THE Al-Ge-Zn PHASE DIAGRAM

The first attempt to calculate a ternary alloy phase diagram from thermodynamic data was made in 1957 by Meijering [11], when he calcu-

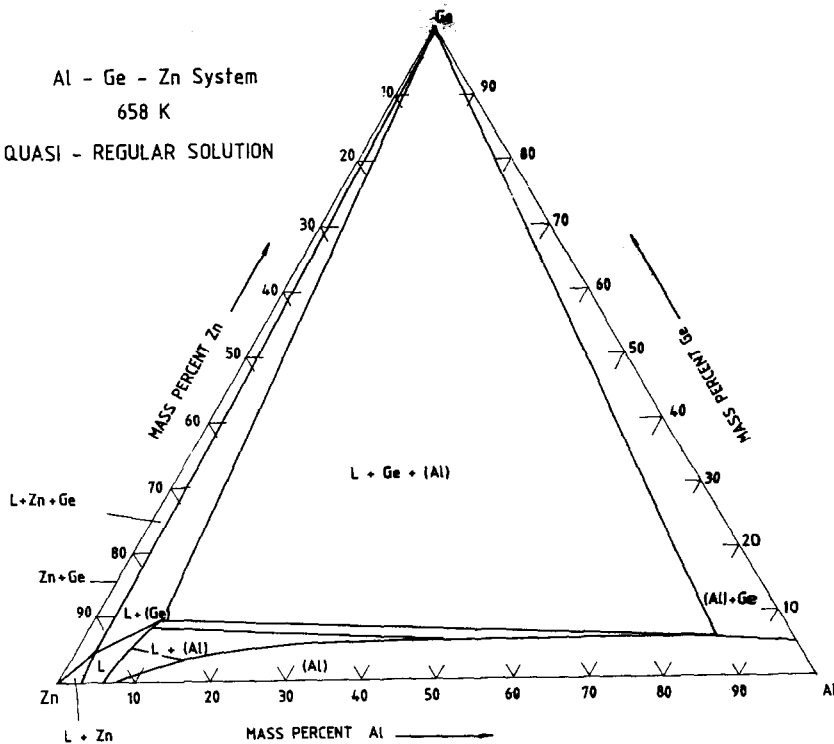


Fig. 4. Phase equilibria in the Al-Ge-Zn system at 658 K, calculated from quasi-regular solution equation.



TABLE 4

Gibbs energies ( $\text{kJ mol}^{-1}$ ) of the pure components in the Al–Ge–Zn system

$G_{\text{Al}}(\text{l})$	0
$G_{\text{Al}}(\text{s})$	$-10.792 + 11.56 \times 10^{-3}T$
$G_{\text{Ge}}(\text{l})$	0
$G_{\text{Ge}}(\text{s})$	$-36.971 + 30.54 \times 10^{-3}T$
$G_{\text{Zn}}(\text{l})$	0
$G_{\text{Zn}}(\text{s})$	$-7.322 + 10.573 \times 10^{-3}T$

lated the isothermal section of the Cr–Ni–Cu system at 1203 K. Several ternary alloy phase diagrams have been calculated from thermodynamic data since then. Ansara [16] has listed all the ternary systems for which the phase diagrams have been calculated. Thermodynamic characterisation of phase equilibria in the Al–Ge–Zn system has not been reported in the literature. Most of the investigators apply an ideal or regular solution model to approximate the thermodynamic properties of the ternary alloys. Kaufman and Nesor [17–21] and Ansara and co-workers [22–25] have

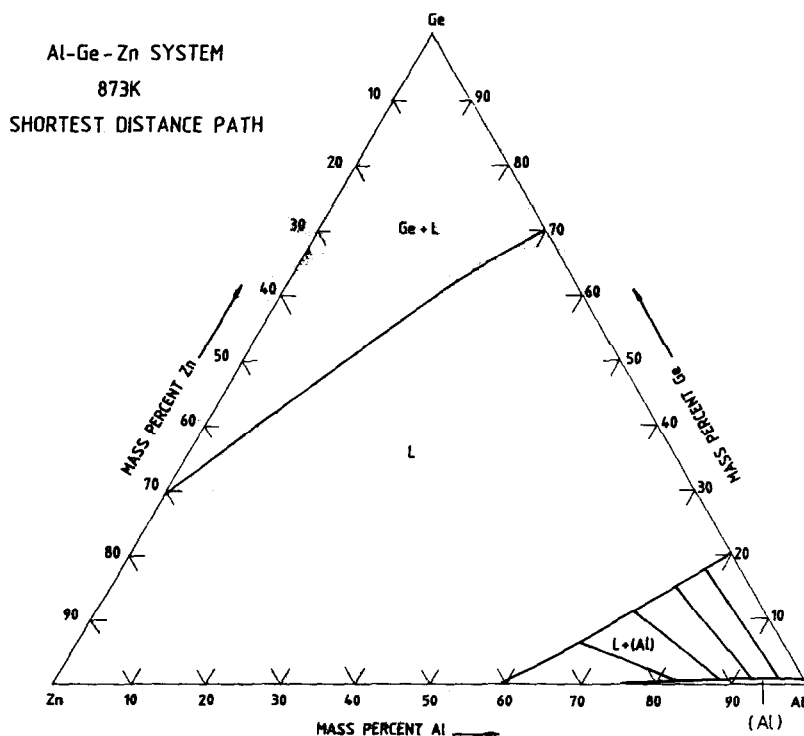


Fig. 5. Isothermal section of the Al–Ge–Zn system at 873 K calculated using shortest distance composition path equations for liquid alloys.

extensively used Kohler's equation to calculate phase diagrams of ternary alloy systems. The shortest distance composition path equation has not been used so far for the calculation of ternary phase diagrams.

The basic principle involved in the computation of an isothermal phase diagram is as follows. At a given pressure and temperature, the maximum number of coexisting phases in a system, formed by  $m$  components, is equal to  $m$  as deduced from the phase rule. If a system is formed by  $j$  phases, with  $1 < j \leq m$ , at equilibrium, the chemical potential  $\mu$  or the partial Gibbs energy of mixing of the different components ( $\Delta G_k^j$ ) is the same in each of them with respect to the same standard state. This condition can be expressed mathematically by a set of  $m$  non-linear equations

$$\mu_k^{(1)} = \mu_k^{(2)} = \dots = \mu_k^{(j)}$$

or

$$\Delta G_k^{(1)} = \Delta G_k^{(2)} = \dots = \Delta G_k^{(j)} \quad (12)$$

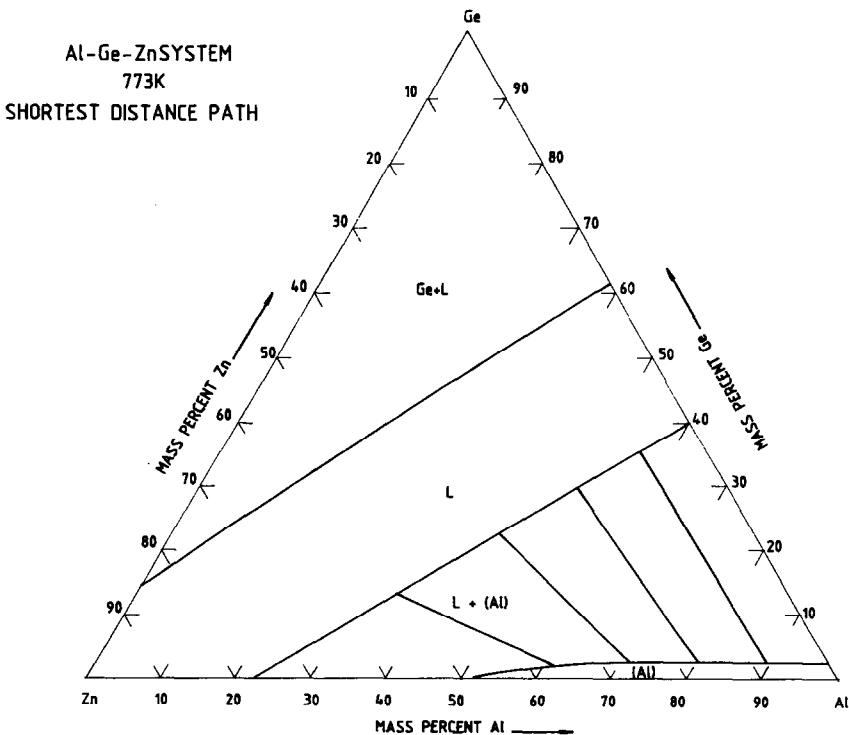


Fig. 6. Phase diagram of the Al-Ge-Zn system at 773 K computed from shortest distance composition path equations for liquid alloys.

for  $k = 1$  to  $m$ , where the superscript ( $j$ ) refers to the phase and subscript  $k$  refers to the component. This set of equations has to be solved to determine the composition of the coexisting phases at equilibrium. The basic information required for the computation of an isothermal phase diagram is as follows:

- the Gibbs energies of mixing of all the equilibrium phases present in the system;
- the Gibbs energies of formation of all the stable intermetallic compounds in the system;
- the Gibbs energies of phase transformation for all the elements constituting the system.

For the present study, the thermodynamic properties of liquid Al–Ge–Zn alloys have been estimated from binary data using the quasi-regular and shortest distance path equations. The thermodynamic properties of solid (aluminium) alloys were also approximated by a quasi-regular solution model. There are no stable intermetallic compounds in the ternary Al–Ge–Zn system and in the constituent binaries. The enthalpy and entropy of mixing in binary liquid Al–Ge and Al–Zn alloys were taken from the

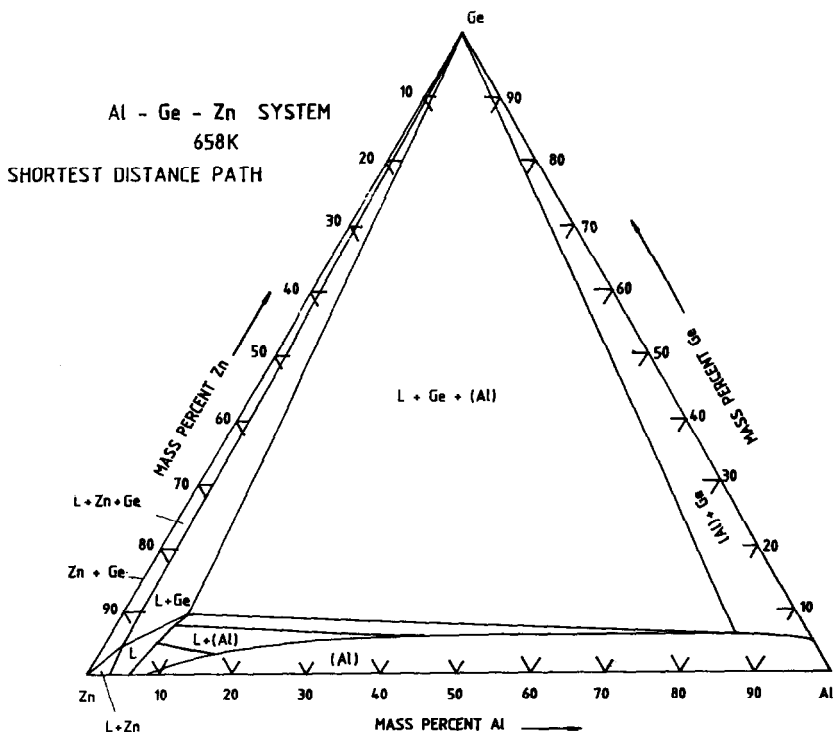


Fig. 7. Phase equilibria in the Al–Ge–Zn system at 658 K computed using shortest distance composition path equations for liquid alloys.

compilation of Hultgren et al. [26]. The thermodynamic properties of liquid Ge–Zn alloys were taken from the e.m.f. measurements of Girard et al. [27]. These measurements are in good agreement with the earlier e.m.f. measurements of Kleppa and Thalmayer [28]. The quasi-regular solution parameters,  $\alpha_{ij}$  and the values of the coefficients of the shortest distance path equation,  $A_i$ ,  $B_i$  and  $C_i$  at 873, 773 and 658 K, deduced from least-squares fitting of the binary thermodynamic data are shown in Tables 1 and 2 respectively. The mixing properties of solid Al–Zn alloys were taken from the compilation of Hultgren et al. [26] to compute the quasi-regular solution parameter  $\alpha'_{\text{Al-Zn}}$  of solid alloys. The thermodynamic behaviour of solid Al–Ge alloys over the small composition range is not available in the literature. Therefore the interaction parameter  $\alpha'_{\text{Al-Ge}}$  was deduced from the thermodynamic behaviour of liquid Al–Ge alloys [26] in combination with the binary phase diagram [29]. The suffix prime refers to solid alloys to differentiate the parameters from those of liquid alloys. The small solid solubility at the zinc-rich end of the ternary system was neglected in the present study. The quasi-regular solution parameters for solid alloys derived in the present study are given in Table 3. The enthalpy

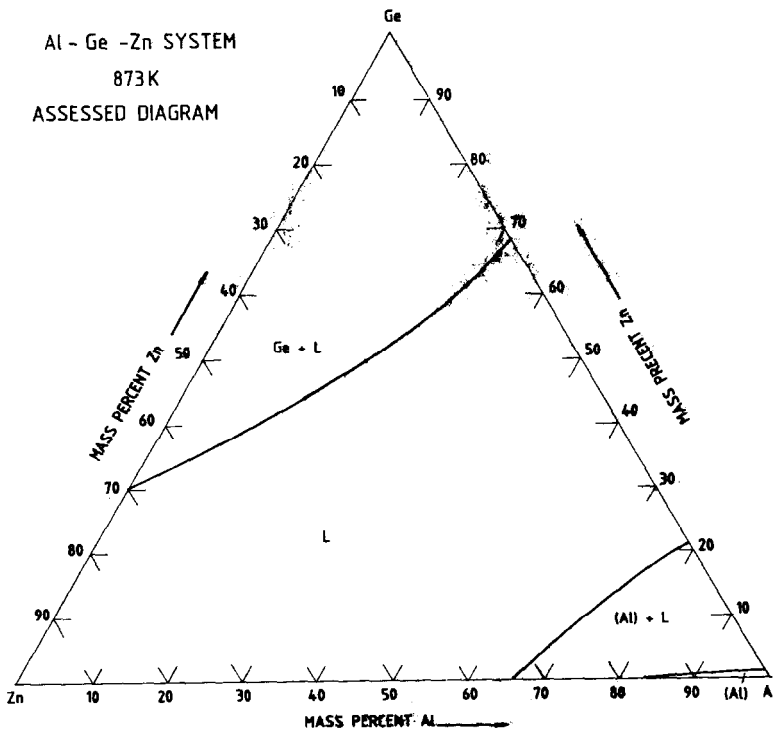


Fig. 8. Assessed isotherm of the Al–Ge–Zn system at 873 K composed from experimental data.

and entropy of fusion of aluminium, germanium and zinc were from Hultgren et al. [30] and are given in Table 4.

The experimental phase diagram of the Al–Ge–Zn system [2] is characterised by a ternary eutectic at 625 K and corresponds to a composition of 6 mass%Al and 5 mass%Ge. Above the eutectic temperature, the various two-phase equilibria occurring are L + (Al), L + (Zn), L + Ge, (Al) + Ge, (Zn) + Ge and (Zn) + (Al). The temperatures chosen for the calculation of isothermal sections were 873, 773 and 658 K. The solid solubility of germanium and aluminium in zinc has been neglected in the present calculations. The liquididi corresponding to the L + Ge and L + Zn equilibrium, the (Al) + Ge equilibrium and the tie-line compositions corresponding to the L + (Al) equilibrium were computed by equating the chemical potentials or partial Gibbs energies of mixing of the appropriate components after accounting for the change in standard states. The procedure adopted has been outlined earlier. The resultant set of non-linear equations was solved numerically using Brown's algorithm to compute the composition of the coexisting phases at equilibrium.

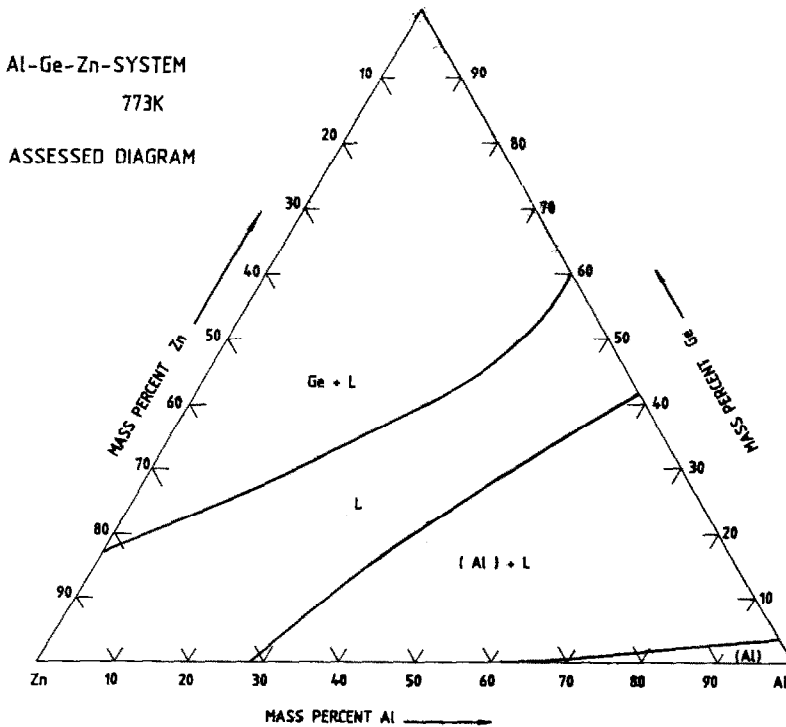


Fig. 9. Phase diagram of the Al–Ge–Zn system at 773 K composed from experimental results.

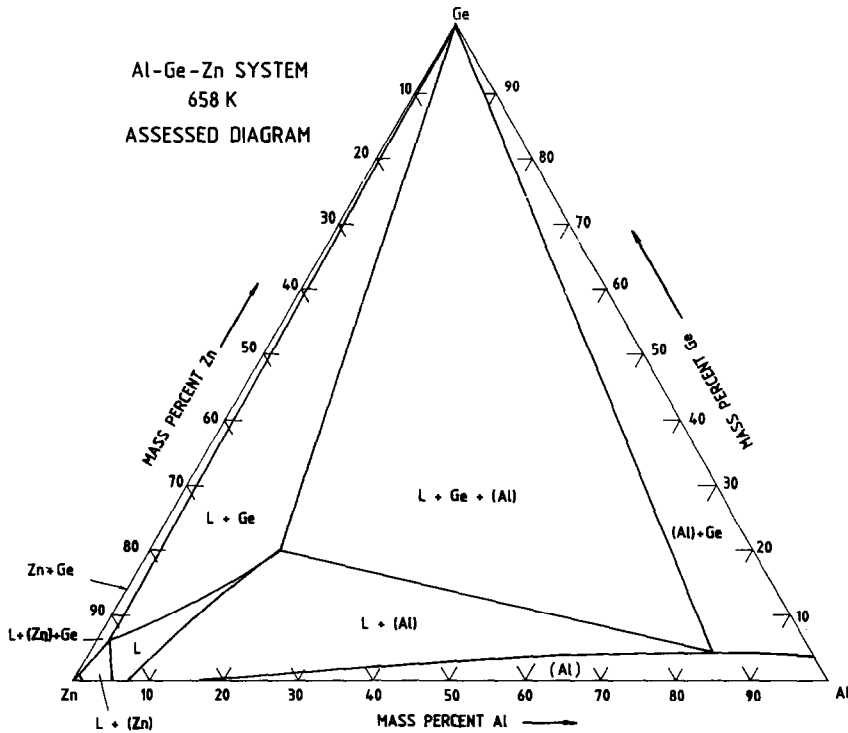


Fig. 10. Phase equilibria in the Al–Ge–Zn system at 658 K derived from experimental data.

## RESULTS AND DISCUSSION

The isothermal sections of the Al–Ge–Zn system at 873, 773 and 658 K calculated using a quasi-regular solution approximation for both liquid and solid alloys are shown in Figs. 2–4. The corresponding isotherms calculated using the shortest distance path equation for liquid alloys are shown in Figs. 5–7. The assessed isothermal sections reported by Chattopadhyay et al. [4] at these temperatures are shown in Figs. 8–10 for comparison. Tie-lines delineating equilibrium between the liquid alloy and the (Al)-rich solid solution are also shown in the computed phase diagrams. The ternary term was not incorporated in the quasi-regular solution expression for liquid alloys because of the absence of any thermodynamic data on the ternary system in the literature. The differences in the equilibrium compositions computed through the quasi-regular solution approximation and the shortest distance path equations for liquid alloys are small. This is mainly because the thermodynamic mixing properties of liquid Al–Zn, Al–Ge and Ge–Zn alloys do not deviate very significantly from a parabolic behaviour. However, there may be significant differences between the phase diagram computed from the quasi-regular solution and shortest distance path equations in strongly interacting alloys. At 873 and 773 K, the agreement

between the calculated and experimental diagrams is fair. The calculated isotherm at 658 K is not in good agreement with the experimental data. The computed diagram indicates a smaller region of stability for the liquid phase and a larger region of existence of the (Al)-rich solid alloy in comparison with the assessed diagram. An attempt was made to improve the agreement between the experimental and calculated diagram by incorporating the ternary term in the quasi-regular solution equation for liquid alloys. The presence of a ternary eutectic and the absence of any intermediate phases indicate repulsive interactions between the unlike atoms in the liquid state. This suggests positive values for the ternary interaction parameter. Phase diagram calculations were carried out using values of 5 kJ mol<sup>-1</sup>, 10 kJ mol<sup>-1</sup> and 20 kJ mol<sup>-1</sup> for  $\alpha_{ABC}$ . However, incorporation of the ternary term did not improve the general agreement between the calculated and assessed phase diagrams for the Al–Ge–Zn system.

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