JOURNAL OF MATERIALS SCIENCE 1 (1966) 399–402

Computation of Ternary Phase Diagrams from Binary Data: Immiscibility in the Ge-Bi-Si System

D. T. J. HURLE, E. R. PIKE
Ministry of Aviation, Royal Radar Establishment, Malvern, Worcs, UK

Received 29 July 1966

We describe a method for the computation of ternary phase equilibria from thermochemical data. The method is developed for the case where the binary phases show regular behaviour, and is used to construct the phase diagram of the system Ge–Si–Bi over the temperature range 960 to 1460° C. For this case, a simple approximation for the integral, molar, excess, free energy of the ternary system is used.

1. Introduction

The computation of a ternary phase diagram requires a knowledge of the functional dependence of the chemical potential of the constituents upon the state variables in the ternary phases. When the binary phases show regular behaviour, a simple approximation [1, 2] may be used which expresses the integral, molar, excess, free energy of the ternary system in terms of binary, thermochemical coefficients only. The accuracy of this approximation in any given case can, of course, be tested only by experiment; it does, however, make possible a prediction of the equilibrium surface which might provide a basis for an experimental study. The same approximation has recently been used successfully by Lehovec and Slobodskoy [3], in a calculation of isothermal sections of the liquidus surfaces in the system Ge–In–Sb.

In section 2, we outline the method, and in section 3 we apply it to systems in which the binary phases show regular behaviour, using the approximation referred to above. In section 4, we use the results of section 3 to perform a calculation of the phase diagram of the system Ge–Si–Bi, using known thermochemical data of the three binary systems.

The Si–Bi system shows liquid immiscibility, and a knowledge of the ternary diagram was required in connexion with certain experiments in our laboratory on the crystallisation of Ge–Si alloys from immiscible liquids.

2. The Equations of Ternary Phase Equilibria

The conditions for thermodynamic equilibrium between two phases, α and β, which both contain the components $i = 1$, 2, and 3 are

$$\mu_i^\alpha = \mu_i^\beta \ (i = 1, \ldots 3) \qquad (1)$$

where μ_i^γ is the chemical potential of the ith component in the ternary phase γ. This is decomposed usefully as follows

$$\mu_i = \mu_i^\theta\,(T, p) + \mathrm{R}T \log x_i + F_i{}^E{}_{(\mathrm{ter})}\,(T, x_1, \ldots x_3) \qquad (2)$$

where μ_i^θ is a reference chemical potential defined by the condition $x_i = 1$, while x_i and $F_i{}^E{}_{(\mathrm{ter})}$ are, respectively, the atom fraction and the partial, molar, excess, free energy of component i in the ternary phase.

The equilibrium surfaces in the ternary diagram are obtained by appropriate simultaneous solution of (1) for all phases present. To carry this out, we need expressions for the $F_i{}^E{}_{(\mathrm{ter})}$. We must first express the integral, molar, excess, free energy of the ternary system, $F^E{}_{123}$, in the form

$$F^E{}_{123} = F^E{}_{123}\,(x_1, x_2, x_3, T) \qquad (3)$$

The $F_i{}^E{}_{(\mathrm{ter})}$ are obtained from (3) using the relations

$$F_i{}^E{}_{(\mathrm{ter})} = F^E{}_{123} + (1 - x_i)\left(\frac{\partial F^E{}_{123}}{\partial x_i}\right)_{x_j/x_k = \mathrm{const}}$$
$$(i, j, k = 1, \ldots 3;\ i \neq j \neq k) \qquad (4)$$

These are mathematical identities which may be readily proved. To the above equations must be added the relations

$$\sum_{i=1}^{3} x_i^{\gamma} = 1 \tag{5}$$

for the problem to be fully determined.

3. The Case of Regular Binary Phases

The regular binary solution is defined to be one for which

$$F_i^E{}_{(\text{bi})} = \alpha_{ij}(T)\,(1 - x_i)^2 \tag{6}$$

where $\alpha_{ij}(T)$ is an interaction coefficient for the solution containing components i and j. (If α_{ij} is not a function of temperature, the solution is termed "strictly regular".) These interaction coefficients have the symmetry property

$$\alpha_{ij}(T) = \alpha_{ji}(T) \tag{7}$$

We introduce the approximation for $F^E{}_{123}$ [1, 2] which is consistent with (6)

$$F^E{}_{123} = \alpha_{12}\, x_1\, x_2 + \alpha_{13}\, x_1\, x_3 + \alpha_{23}\, x_2\, x_3 \tag{8}$$

Using (8), (7) and (4), a simple calculation now gives

$$F_i^E{}_{(\text{ter})} = (1 - x_i)\,(\alpha_{ij}\, x_j + \alpha_{ik}\, x_k) - \alpha_{jk}\, x_j\, x_k$$
$$(i, j, k = 1, \ldots 3;\ i \neq j \neq k) \tag{9}$$

Substitution of (9) and (2) into (1) yields the final equations

$$\mu_i^{\theta\alpha} - \mu_i^{\theta\beta} + \mathrm{R}T \log\left(\frac{x_i^{\alpha}}{x_i^{\beta}}\right) + (1 - x_i^{\alpha})$$
$$(\alpha^{\alpha}{}_{ij}\, x^{\alpha}{}_j + \alpha^{\alpha}{}_{ik}\, x^{\alpha}{}_k) - \alpha^{\alpha}{}_{jk}\, x^{\alpha}{}_j\, x^{\alpha}{}_k - (1 - x^{\beta}{}_i)$$
$$(\alpha^{\beta}{}_{ij}\, x^{\beta}{}_j + \alpha^{\beta}{}_{ik}\, x^{\beta}{}_k) + \alpha^{\beta}{}_{jk}\, x^{\beta}{}_j\, x^{\beta}{}_k = 0 \tag{10}$$

At constant pressure, the quantity

$$\mu_i^{\theta\alpha} - \mu_i^{\theta\beta} = \int_{T_i^*}^{T} \frac{h_i^{\mathrm{o}}}{\mathrm{R}T^2}\, \mathrm{d}T \tag{11}$$

where h_i^{o} = the standard, heat-content change of transfer from the first phase to the second [7]. T_i^* is the temperature at which $x_i^{\alpha} = x_i^{\beta} = 1$. If h_i^{o} is independent of T, (11) becomes

$$\mu_i^{\theta\alpha} - \mu_i^{\theta\beta} = \frac{\Delta h}{\mathrm{R}}\left(\frac{1}{T} - \frac{1}{T^*_i}\right) \tag{12}$$

where we have replaced h_i^{o} by Δh, the latent heat for the $\alpha \to \beta$ phase change.

4. The Ge–Si–Bi System

4.1. The Binary Systems

The liquidus lines of the system Si–Bi and Ge–Bi have been shown, by Thurmond and Kowalchik [4], to obey regular solution theory with an interaction parameter of the form

$$\alpha_{ij} = a_{ij} - b_{ij}T \tag{13}$$

Bi is virtually insoluble in both Si and Ge in the solid state, and hence the activities of solid Si and Ge in the system Si–Bi can be taken as unity. (The maximum solid solubility of Bi in Ge is $\sim 10^{-4}$ at. %, and in Si is $\sim 2 \times 10^{-3}$ at. % [5].)

The thermodynamics of the Ge–Si system have been studied by Thurmond [6], who has shown that Ge and Si form nearly ideal solutions in both liquid and solid states. We therefore set the interaction parameters α equal to zero for this system. The phase diagrams of the three binary systems are shown in fig. 1.

4.2. The Ternary System

Our purpose is to construct the single and two-liquid surfaces in the ternary system and to find the compositions of the solid Ge–Si alloys which are in equilibrium with the liquids.

We therefore have five equations in the form of (1), as follows:

$$\mu_{\mathrm{G}}{}^{\mathrm{L1}} = \mu_{\mathrm{G}}{}^{\mathrm{L2}} \tag{14}$$

$$\mu_{\mathrm{S}}{}^{\mathrm{L1}} = \mu_{\mathrm{S}}{}^{\mathrm{L2}} \tag{15}$$

$$\mu_{\mathrm{B}}{}^{\mathrm{L1}} = \mu_{\mathrm{B}}{}^{\mathrm{L2}} \tag{16}$$

$$\mu_{\mathrm{G}}{}^{\mathrm{L1}} = \mu_{\mathrm{G}}{}^{\mathrm{S}} \tag{17}$$

$$\mu_{\mathrm{S}}{}^{\mathrm{L1}} = \mu_{\mathrm{S}}{}^{\mathrm{S}} \tag{18}$$

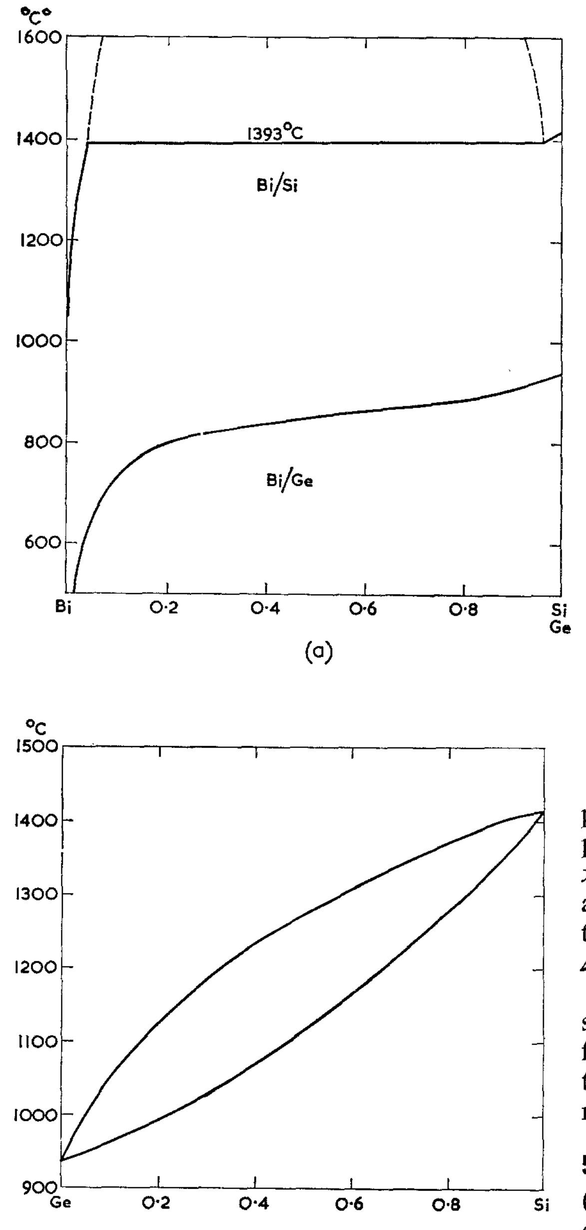
where the subscripts, G, S, and B, refer respectively to Ge, Si, and Bi, and the superscripts, L1, L2, and S, refer respectively to the two (immiscible) liquids and the solid.

Note that we do not have an equation relating the chemical potentials of Bi in the liquid and solid states. This is because we presume the concentration of Bi in solid Ge–Si alloys to be zero.

We remove the dependence between the concentrations expressed in (6) by using the independent parameters: x, the atom fraction of Bi; and r, the ratio of the atom fraction of Si to Bi, $x_{\mathrm{S}}/x_{\mathrm{G}}$.

Thus
$$x_{\mathrm{G}} = \frac{(1 - x)}{(1 + r)} \tag{19}$$

and
$$x_{\mathrm{S}} = \frac{r(1 - x)}{(1 + r)} \tag{20}$$



(a)

(b)

Figure 1 Phase diagrams of the binary systems: (a) Bi-Si and Bi-Ge; (b) Ge-Si.

Putting (14) to (18) into the form of (10), and using (19) and (20), we have:

$$\mathrm{R}T\ln\left\{\frac{r_1(1-x_1)(1+r_2)}{r_2(1-x_2)(1+r_1)}\right\}+\alpha_{\mathrm{SB}}({x^2}_1-{x^2}_2)$$
$$+(\alpha_{\mathrm{SB}}-\alpha_{\mathrm{GB}})\left\{\frac{x_1(1-x_1)}{(1+r_1)}-\frac{x_2(1-x_2)}{(1+r_2)}\right\}$$
$$=0 \qquad (21)$$

$$\mathrm{R}T\ln\frac{(1-x_1)(1+r_2)}{(1-x_2)(1+r_1)}+\alpha_{\mathrm{GB}}({x^2}_1-{x^2}_2)$$
$$-(\alpha_{\mathrm{SB}}-\alpha_{\mathrm{GB}})\left\{\frac{x_1(1-x_1)r_1}{(1+r_1)}-\right.$$
$$\left.\frac{x_2(1-x_2)r_2}{(1+r_2)}\right\}=0 \qquad (22)$$

$$\mathrm{R}T\ln\frac{x_1}{x_2}+\alpha_{\mathrm{SB}}\left\{\frac{(1-x_1)^2}{(1+r_1)}-\frac{(1-x_2)^2}{(1+r_2)}\right\}+$$
$$\alpha_{\mathrm{GB}}\left\{\frac{(1-x_1)^2}{(1+r_1)^2}-\frac{(1-x_2)^2}{(1+r_2)^2}\right\}=0 \qquad (23)$$

$$\mathrm{R}T\ln\left\{\frac{(1-x_1)(1+r_\mathrm{S})}{(1+r_1)}\right\}+$$
$$\Delta h_\mathrm{G}[1-(T/{T^*}_\mathrm{G})]-\frac{x_1}{(1+r_1)}\{\alpha_{\mathrm{SB}}\,r_1(1-x_1)$$
$$-\alpha_{\mathrm{GB}}(r_1+x_1)\}=0 \qquad (24)$$

$$\mathrm{R}T\ln\left\{\frac{(1-x_1)(1+r_\mathrm{S})r_1}{(1+r_1)r_\mathrm{S}}\right\}+$$
$$\Delta h_\mathrm{S}(1-T/{T^*}_\mathrm{S})+\frac{x_1}{(1+r_1)}$$
$$\{\alpha_{\mathrm{SB}}(1+r_1\,x_1)-\alpha_{\mathrm{GB}}(1-x_1)\}=0 \qquad (25)$$

We have dropped the phase superscript on the parameters α, since all the α's refer to the liquid phases. The phase superscripts L1, L2, and S on x and r have been changed to the subscripts 1, 2, and s for convenience. T_G* and T_S* are, respectively, the melting points of pure Ge and Si, and Δh_G and Δh_S are their latent heats of fusion.

(21) (22) and (23) together give the two-liquid surface; (24) and (25) give the solid-liquid surface; while simultaneous solution of all five gives the line of three-phase equilibrium – i.e. the monotectic line.

5. Results

(21) to (25) were solved on the RRE digital computer RREAC using the Newton-Raphson method. The values of the thermodynamic constants used were those given by Thurmond and Kowalchik [4] and Thurmond [6] and are reproduced in table I. In order to find the phase

TABLE I

			Bi alloys	
	Δh (cal/g at.)	T^* (°K)	a (cal/g at.)	b (cal/g at./°K)
Ge	8100	1210	5505	1.49
Si	12100	1683	14840	2.06

boundaries at a given temperature, it was necessary to know the range of concentrations over which there existed physically meaningful solutions, i.e. for which $0 \leqslant x \leqslant 1$ and $0 \leqslant r \leqslant \infty$. This range was delineated by first finding the monotectic line, starting from the known monotectic points of the Si–Bi system.

Isothermal sections were generated at intervals of 50° C covering the range 960 to 1460° C. Two of these sections, namely, those at 1160 and 1360° C, are reproduced in fig. 2 and fig. 3.

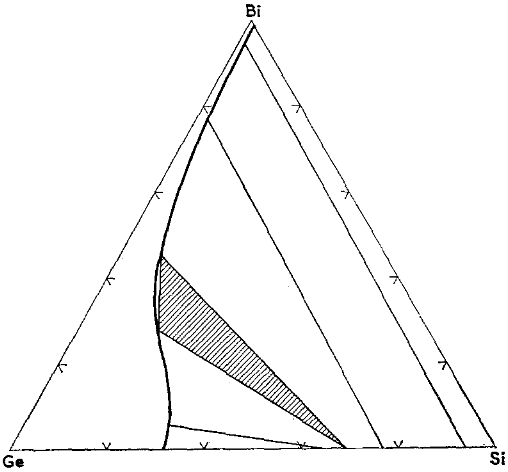


Figure 2 1160° C section of the ternary diagram showing small region of liquid immiscibility. The three-phase region is shaded.

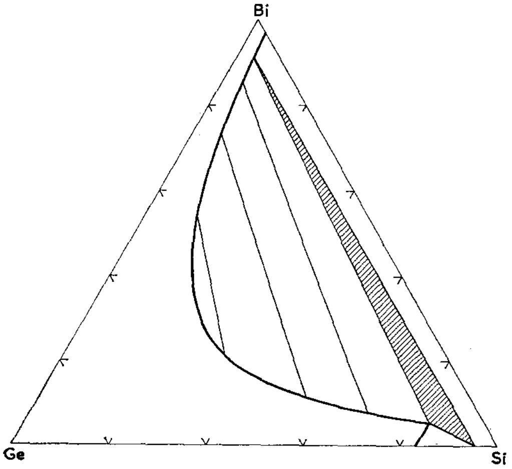


Figure 3 1360° C section of the ternary diagram. The three-phase region is shaded.

The sections were plotted automatically in triangular coordinates and used as templates for the construction of a three-dimensional model in perspex. A perspective drawing of this model is shown in fig. 4.

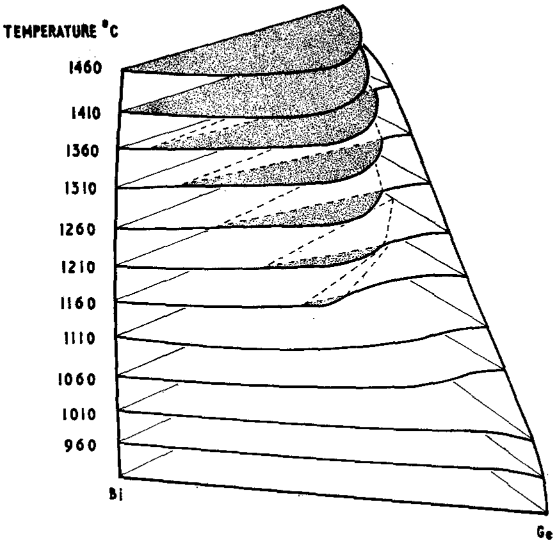


Figure 4 Perspective drawing of the ternary diagram; the shading delineates the two-liquid regions and the dotted lines define the three-phase regions.

Separate programmes were used to find the upper and lower consolute temperatures and compositions. The lower consulute temperature was found to be at 1154° C and corresponded to concentrations $x_B = 0.35$ and $x_G = 0.52$. The upper consolute temperature was approximately at 2190° C and, of course, corresponds to compositions $x_B = 0.50$ and $x_G = 0$. Solid solutions of Ge–Si which can be in equilibrium with the immiscible liquids cover the composition range 0 to 30 at. % Ge.

Acknowledgement

The authors are indebted to Dr D. P. Jenkins for advice on the numerical techniques used.

References

1. M. BENEDICT, C. A. JOHNSON, E. SOLOMON, and L. C. RUBIN, *Trans. Amer. Inst. Chem. Engrs.* **41** (1945) 371.
2. K. WOHL, *ibid*, **42** (1946) 215.
3. K. LEHOVEC and A. SLOBODSKOY, *J. Electrochem. Soc.* **111** (1964) 65.
4. C. D. THURMOND and M. KOWALCHIK, *Bell. Syst. Tech. J.* **39** (1960) 169.
5. F. A. TRUMBORE, *ibid*, **39** (1960) 205.
6. C. D. THURMOND, *J. Phys. Chem.* **57** (1953) 827.
7. I. PRIGOGINE and R. DEFAY, "Chemical Thermodynamics" (Longmans Green and Co, 1954), p. 273.