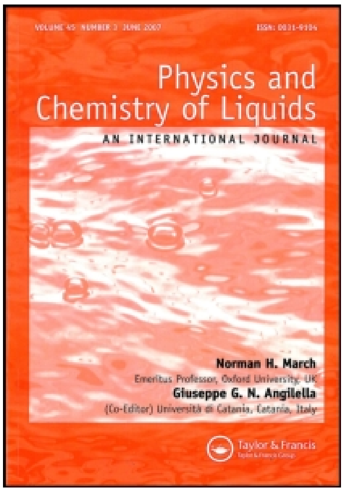

Physics and Chemistry of Liquids
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646857

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To cite this Article Bhatia, A. B. and March, N. H.(1975) 'Eutectic Type Liquidus Curves in Compound Forming Systems', Physics and Chemistry of Liquids, 4: 4, 279 — 283
To link to this Article: DOI: 10.1080/00319107508083831
URL: http://dx.doi.org/10.1080/00319107508083831

Phys. Chem. Liq., 1975, Vol. 4, pp. 279-283.
Gordon and Breach Science Publishers, Ltd.
Printed in Dordrecht, Holland

Eutectic Type Liquidus Curves in Compound Forming Systems[†]

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(*Received December 18, 1974*)

The thermodynamics of eutectic type liquidus curves in compound forming systems is developed for the case when a single compound $A_\mu B_\nu$ is formed. The liquidus curves are considered in three regions: (i) A-rich (ii) B-rich and that in which equilibrium conditions involve the compound (iii). In region (iii) the slope of the liquidus curve in the presence of the compound $A_\mu B_\nu$ has a multiplying factor $\mu-(\mu+\nu)c$ and hence changes sign at $c = \mu/\mu+\nu$, in agreement with observation.

To illustrate the formalism we have considered numerically the limiting case when there is a *strong* tendency to form compounds and results thus obtained for Mg-Bi and Mg-Sn are briefly referred to.

1. INTRODUCTION

Many of the phase diagrams for binary A B alloys listed in Hansen[3] have extremely complicated liquidus curves, with multiple eutectic points. For a simple eutectic such as Na-K, we have previously shown (Bhatia and March[1])

[†] Work supported in part by the National Research Council of Canada.

[‡] The contribution of one of us (NHM) to this work was largely carried out during a visit to the Department of Physics, University of Alberta, Edmonton in the summer of 1974.

how a simple model of the mixture can be used to construct liquidus curves displaying all the main features of the experimental results.

It is already clear from the diagrams in Hansen that the multiple eutectic points arise from compound formation. In this note we shall consider the theory for the case in which a single compound $A_\mu B_\nu$ is formed, as indicated schematically in the figure.

2. EQUILIBRIUM CONDITIONS

Let the various chemical potentials, in terms of which the equilibrium conditions are most basically expressed, be denoted by μ_i. We consider in all c gm moles of A and (1-c) gm moles of B. Though not an essential restriction, we shall also assume that volume of A $\simeq$ volume of B $\simeq 1/(\mu+\nu) \times$ volume of $A_\mu B_\nu$.

Denoting activities a for the liquid by a superscript ℓ and similarly for the solid, we can write relations between the a's and the activity coefficients γ. These are

$$a^{\ell}_{A} = \frac{n_1}{n}\,\gamma_1$$

$$a^{\ell}_{a_B} = \frac{n_2}{n}\,\gamma_2 \tag{1}$$

and for region (iii) of the figure

$$a^{\ell}_{3} = \frac{n_3}{n}\,\gamma_3\,, \tag{2}$$

where $n = n_1+n_2+n_3$. Evidently n_1 and n_2, the number of A and B atoms, are related in a straightforward way to the equilibrium number of complexes n_3. The chemical potentials are related to the activities in the usual way and we have in region (i)

$$\mu^{so}_{A} = \mu^{\ell o}_{A} + RT \ln a^{\ell}_{A} \tag{3}$$

so that

$$\ln a^{\ell}_{A} \equiv \ln \frac{n_1}{n}\,\gamma_1 = \frac{\mu^{so}_{A} - \mu^{\ell o}_{A}}{RT} = -\,\frac{F_{A}{}^{0}}{RT}\,, \tag{4}$$

the superscript zero referring to the pure component. F_{A_0} can be related to the latent heat L_{A0}, the melting temperature of A, T_{A0}, and the difference Δ in the specific heats of solid and liquid (Bhatia and March[1]). The term involving Δ generally turns out to be a small correction and we shall therefore adopt the approximate form

$$\frac{n_1}{n}\gamma_1 = \exp.\left(-\frac{F_{A0}}{RT}\right) : F_{A0} \doteqdot L_{A0}\left(1-\frac{T}{T_{A0}}\right). \qquad (5)$$

Moving along the liquidus curve from T to T+ΔT, c to c+Δc it is readily shown that

$$\frac{\Delta T}{\Delta c} = \frac{RT^2(1-c)}{S_{CC}L_A} \qquad (6)$$

where L_A is a generalized latent heat (Bhatia and March[1]). As usual

$$S_{CC} = N<(\Delta c)^2>_\ell = Nk_BT/\left(\frac{\partial^2 G_m}{\partial c^2}\right)_{T,P,N} \qquad (7)$$

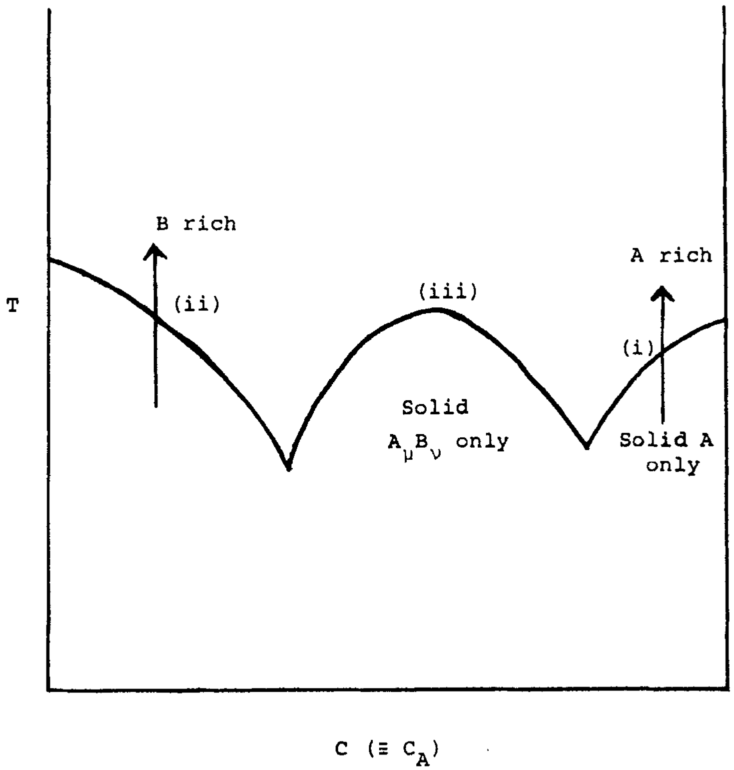

FIGURE 1 Schematic behaviour of the eutectic type liquidus curves in a system when a single compound $A_\mu B_\nu$ is formed.

G_m being the Gibbs free energy of mixing. Similar results obtain in the B-rich region.

The more interesting region (iii) is that of compound formation. Here we have

$$\frac{n_3}{n}\gamma_3 = \exp\left(-\frac{F_{30}}{RT}\right) \doteqdot \exp\left(-\frac{L_{30}}{R}\left\{\frac{1}{T}-\frac{1}{T_{30}}\right\}\right), \qquad (8)$$

where L_{30} is the latent heat of the compound and T_{30} its melting temperature. The slope of the liquidus can again be calculated, using the relation of Gibbs-Duhem type

$$\sum_{i=1}^{3} n_i \frac{\partial \ln a_i}{\partial c} = 0\,. \qquad (9)$$

Then we get from the equilibrium condition the result

$$\frac{\Delta T}{\Delta c} = \frac{RT^2}{L_3}\,\frac{[\mu-(\mu+\nu)c]}{S_{CC}}\;; \qquad (10)$$

L_3 again being a generalized latent heat as in Bhatia and March.[1] Equation (10) immediately demonstrates that the slope of the liquidus will change sign at $c = \mu/(\mu+\nu)$, in agreement with observation.

3. NUMERICAL RESULTS FOR MG-BI AND MG-SN

To illustrate the way to use these equilibrium equations, we have employed the equations of Bhatia and Hargrove[2] (see in particular their equation (25)) for the equilibrium number of complexes n_3. In the limiting case of strong compound formation, the equilibrium equation can be solved for n_3. Using their model and noting that the coefficient γ_1, for example, for this case is

$$RT\ln\gamma_1 = RT(1-n+\ln n)+(1-n_1)n_3 v_{13}, \qquad (11)$$

with v_{13} an interaction energy etc., we have carried out calculations for Mg-Bi. For Mg-Sn, v_{ij} are not available and the calculations were made by setting $v_{ij}=0$.

Because of the limiting case taken, the curves in region (iii) meet in a cusp at $\mu = (\mu+\nu)c$, and this already precludes quantitative agreement with experiment. We therefore merely summarize the conclusions:

1) Our equations generalize the ideal solution results of Reisman[4] and reduce to his when we take $\gamma_1 = \gamma_2 = \gamma_3 = 1$.

2) In regions (i) and (ii) the theoretical and experimental curves agree fairly well.

3) In region (iii) the agreement is only qualitative. The results depend a lot on the value of L_{30}, which does not seem to be very well known at present for Mg_3Bi_2 or Mg_2Sn. Also it is not clear whether the effect of the difference in specific heats Δ_3, between solid and liquid compound, a correction neglected in (8) will be quite as unimportant as the corresponding term in (5). At present no experiments seem to be available to evaluate Δ_3.

4) The curves are not sensitive to the v_{ij}'s, for the values of Bhatia and Hargrove that we have used for Mg-Bi.

In summary, we have given the basic equations determining liquidus curves with formation of a single compound $A_\mu B_\nu$. One feature in agreement with experiment comes out generally: the change in sign of the slope of the liquidus curves at $c = \mu/(\mu+\nu)$. The limiting case of strong compound formation has been examined numerically for Mg-Sn and Mg-Bi. The numerical results show that while the general features of the experimental liquidus curves follow for both systems (except for an observed discontinuity in slope at $c_{Mg} \doteq 0.68$ in Mg-Bi), quantitative agreement is lacking. Should it be thought necessary later to work out more fully the consequences of our thermodynamic equations, the most important assumption to relax it clearly that of strong compound formation. In view of the uncertainty in our knowledge of L_{30} and Δ_3, and the binding energy of the compound versus the interaction energies v_{ij}, further calculations do not seem justified at present.

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