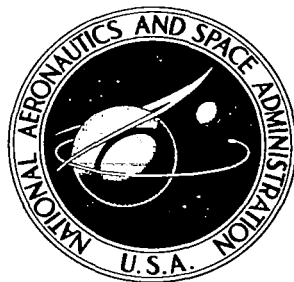


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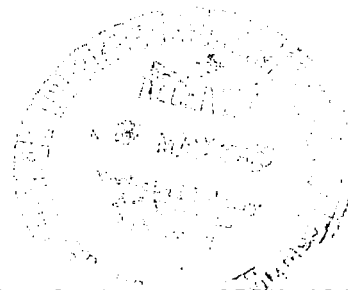
**TERNARY PHASE DIAGRAMS FOR THE  
Ga-P-Zn and Ga-As-Zn SYSTEMS WITH  
APPLICATIONS TO DIFFUSION PROBLEMS**

*by J. W. Allen and G. L. Pearson*

Prepared under Grant No. NsG-555 by  
STANFORD UNIVERSITY  
Stanford, Calif.

*for*

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## ABSTRACT

A number of aspects of the diffusion of zinc into gallium phosphide or arsenide can be usefully discussed in terms of the ternary phase diagrams. In the absence of sufficient experimental data an approximate theory has to be used to calculate the relevant parts of the phase diagram. Using the activity coefficients in the binary system Ga-As deduced by Thurmond and assuming that these coefficients are insensitive to temperature change and to the replacement of gallium by zinc, it is possible to calculate the position of the liquidus surface in the Ga-As-Zn ternary. This is in reasonable agreement with the experimental data of Köster and Ulrich. Using the same approach it is then possible to calculate the position of the liquidus surface on the Ga-P-Zn ternary, and also to estimate arsenic or phosphorus pressures over the liquidus surface. Using these results it is then possible to calculate thermodynamic parameters such as the pressures of the components over the system in terms of experimental quantities such as the weights of the components and the volume of the system. The Phase Rule is applied to each region of the ternary phase diagram to determine the number of degrees of freedom, i.e., the number of experimental parameters which are independently variable. A variety of published experiments on diffusion and crystal growth are described in terms of the phase diagram and in this way their results can be correlated. Some practical applications are indicated. For instance, the Phase Rule may be used to choose regions of the phase diagram which have advantages in manufacturing processes. The numerical data allow one to choose experimental parameters so that the system will lie in the required region.



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## LIST OF SYMBOLS

|                       |   |
|-----------------------|---|
| C                     | number of components in a system                      |
| F                     | number of degrees of freedom of a system              |
| $K_1(T), K_2(T)$ etc. | mass action equilibrium constants                     |
| P                     | number of phases present in a system                  |
| $P_\alpha$            | the partial pressure of substance $\alpha$            |
| $P_\alpha^\circ$      | the pressure of substance $\alpha$ over pure $\alpha$ |
| T                     | temperature in $^\circ\text{K}$                       |
| $X_\alpha$            | atomic concentration of substance $\alpha$            |
| $\gamma_\alpha$       | activity coefficient of substance $\alpha$            |



### ACKNOWLEDGMENT

It was during consideration of Mr. Kwang Shih's experimental results that the idea of writing this report originated, and we are grateful to him for discussion of the many points involved. We should also like to thank Dr. C. D. Thurmond of Bell Telephone Laboratories who kindly allowed us to use his thermodynamic analysis of the Ga-P and Ga-As systems before publication, and who has led us to clarify our thoughts during conversations with him.

## I. INTRODUCTION

A binary semiconducting compound doped with a single impurity constitutes a three-component thermodynamic system and as such displays considerably more complex behavior than an elemental semiconductor with a single dopant. In many cases this complexity may not be immediately apparent since the compound may exhibit departures from stoichiometry which are small compared with the doping level used, and in some circumstances it may therefore be possible to treat the system as being quasi-binary. However, this approach is often inadequate. This report shows how the thermodynamic description of ternary systems can provide a conceptual framework within which to order experimental results. Although the ideas presented are general to any doped binary compound, we will restrict ourselves to a discussion of the Ga-P-Zn and Ga-As-Zn systems since these are important in the semiconductor field and there are some experimental data to hand. Moreover, these are good illustrative systems since they display a number of different types of behavior of interest.

To be concrete, suppose we want to diffuse zinc into gallium phosphide, or to grow zinc-doped gallium phosphide crystals by dissolving phosphorus and zinc in gallium and then cooling the solution, or to perform any similar experiment in which gallium, phosphorus (or arsenic), and zinc are brought together in a closed tube. The readily accessible experimental parameters are the weights of the various components and the volume of the tube, and these are the parameters with which a device manufacturer would prefer to characterize a process. Unfortunately there are no simple relations between these quantities and such quantities of interest as the solubility of zinc in gallium phosphide under the conditions of the experiment, or the lattice defect concentrations, or the amount of surface attack in a diffusion experiment. This is because the zinc, for example, may be partly in the vapor phase and partly in a liquid phase, and without further information it is not possible to calculate its ratio in the two phases. It is necessary to introduce as intermediates the thermodynamic variables, namely the partial pressures of the components, the concentrations of the components in the various phases, and so on, and to describe the experimental results as functions of these variables.

In this report some results of the theory of equilibrium thermodynamics will be used, but many of the applications considered will be diffusion processes which are not equilibrium situations. However, in a typical diffusion experiment there are a rather large number of experimental parameters available, and to simplify the system one tries to select conditions such that many parts of the system are in equilibrium with each other and that the changes brought about by the diffusion have a negligible effect on this equilibrium state. For instance, if zinc is diffused into gallium phosphide in a closed ampoule under conditions in which a liquid phase is present, then the times and quantities involved are usually such that zinc vapor is in equilibrium with the liquid phase, the amount of zinc diffusing into the solid gallium phosphide is so small that it has a negligible effect on the zinc vapor pressure, and the surface of the gallium phosphide is approximately in equilibrium with the vapor and liquid phases so that the surface concentration of zinc in gallium phosphide can be taken to be the solubility under the conditions of the experiment. Moreover, it often happens that lattice defects diffuse much more rapidly than the impurity so that they can also be taken to be in the equilibrium state, or conversely it may happen that the impurity diffuses so rapidly that the lattice defects can be regarded as being fixed.

An investigation of a system of the type to be considered will therefore consist of three stages:

1. Finding which parts of the system can be treated as being in equilibrium, and which parts can be treated as being unchanged during an experiment.
2. Determining the relations between the experimentally available parameters and the thermodynamic parameters.
3. Determining the relations between the thermodynamic parameters and the final quantities of interest (solubilities, etc.).

Stage 3 has been investigated by Prof. Pearson and his students, notably Chang [Ref. 1], and by Longini [Ref. 2], McCaldin [Ref. 3], and others. Stage 2 is the subject of this report. Stage 1 has not received the attention it deserves.

The approach adopted here will be that of establishing the main features of the ternary phase diagram and making this quantitative in so far

as presently available data allow. Since there are several thermodynamic variables, there are a large number of relationships which can be explored experimentally: the phase diagram is a convenient method of demonstrating the connection between various types of experiments which have been performed. In addition, a quantitative knowledge of the phase diagram allows us to calculate several quantities of practical importance.

## II. THE TERNARY PHASE DIAGRAM

### A. INTRODUCTION

In a ternary system the relative concentrations of the components can be represented on a triangular diagram. We adopt the convention that the concentrations refer to the condensed phases only. The vapor compositions are then represented by the partial pressures of the components, which are to be specified at each point on the diagram. In principle the complete diagram can be represented in a space of six dimensions, two for the condensed phase compositions, one for temperature, and three for the partial pressures (neglecting reactions in the vapor phase). In many experiments the variation of one parameter with another is investigated and if this variation is represented by a curve, then the curve will map a cross-section of this multidimensional space. Obviously there are many different types of cross-section, but by considering them within the framework of the phase diagram it is easy to see the connection between different experiments.

Of course, in practice, one uses a diagram on a sheet of paper, and the diagram is then either a two-dimensional cross-section of the multidimensional space or a projection of the space onto one of its planes as in a geographical map.

### B. THE Ga-As-Zn LIQUIDUS - EXPERIMENT

Köster and Ulrich [Ref. 4] have determined the liquidus surface for the Ga-As-Zn system. They did this by putting weighted amounts of Ga, As, and Zn into closed ampoules which were then heated to a high temperature. The ampoules were cooled and the temperature at which a solid phase first formed was found by differential thermal analysis. They used quantities of the components which were nearly sufficient to fill the ampoule so the amounts of the components in the liquid phase were approximately equal to the amounts put into the ampoule. An estimate was made of the amounts of the components in the vapor phase and a correction was made for this, but under their conditions the correction was small. This procedure is hazardous since high pressures occur in some regions of the diagram but

despite the difficulties the scatter in the experimental data is small. With this approach it would be tedious to cover many points in the composition diagram so Köster and Ulrich explored the GaAs-Zn, GaAs-Zn<sub>3</sub>As<sub>2</sub> and GaAs-ZnAs<sub>2</sub> pseudo-binary lines, used the published Ga-As and Zn-As phase diagrams, and then interpolated over the composition field. Their diagram is reproduced in Fig. 1. If we consider a prism with the composition triangle as its base and with temperature as the vertical scale, the liquidus will be a surface within the prism: Fig. 1 is a contour map of this surface. Over the temperature range 750 °C - 1238 °C it consists of two intersecting half-cones, one centered on GaAs and the other on Zn<sub>3</sub>As<sub>2</sub>.

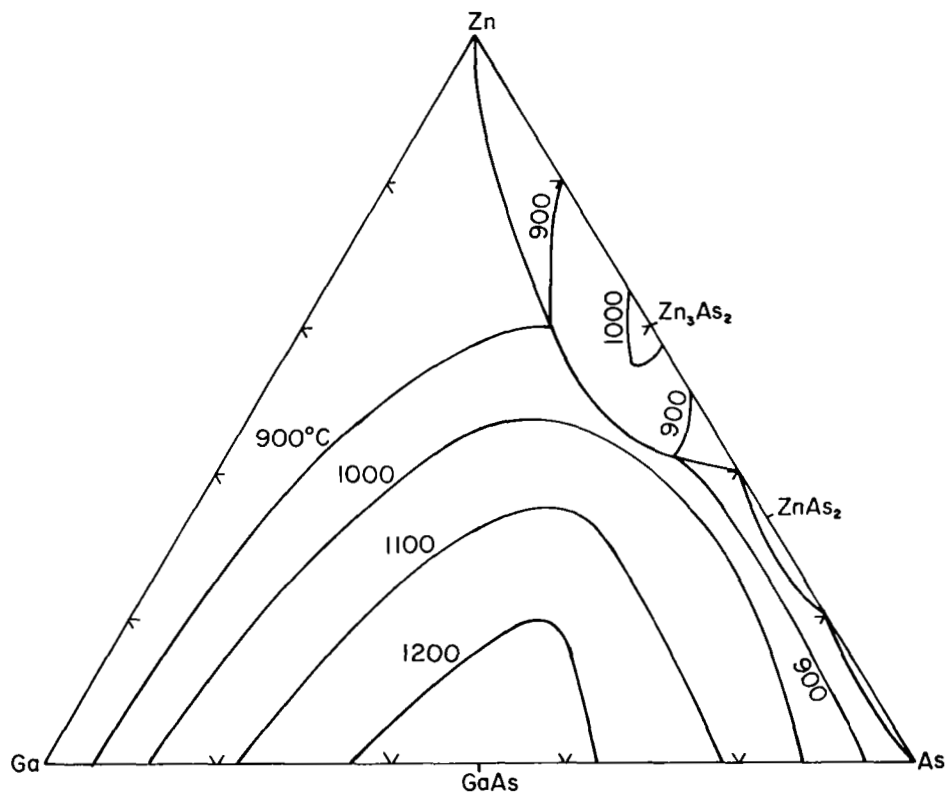


FIG. 1. LIQUIDUS ISOTHERMS IN THE Ga-As-Zn SYSTEM FROM THE EXPERIMENTS OF KÖSTER AND ULRICH.

C. THE Ga-As-Zn LIQUIDUS - THEORY

Since there is no generally applicable theory by which ternary phase boundaries can be calculated, we must proceed on an ad hoc basis.

Consider the binary Ga-As system. When solid GaAs, a vapor phase, and a liquid phase are in equilibrium, as they are on the liquidus surface, the following equation may be written down for the formation of solid GaAs from the gaseous components:



Since the departure from stoichiometry is small for GaAs, the mass action equation can be written:

$$P_{\text{Ga}} P_{\text{As}_4}^{1/4} = K_1(T) \quad (2)$$

where  $P_\alpha$  is the partial pressure of  $\alpha$  and  $K_1$  is the equilibrium constant. We define activity coefficients  $\gamma_\alpha$  by the equations:

$$\gamma_{\text{As}} \equiv \frac{1}{X_{\text{As}}} \left( \frac{P_{\text{As}_4}}{P_{\text{As}_4}^0} \right)^{1/4} \quad (3)$$

and

$$\gamma_{\text{Ga}} \equiv \frac{1}{X_{\text{Ga}}} \left( \frac{P_{\text{Ga}}}{P_{\text{Ga}}^0} \right) \quad (4)$$

where  $X_\alpha$  is the atomic fraction of  $\alpha$  in the liquid phase and  $P_\alpha^0$  is the vapor pressure of pure liquid  $\alpha$ . Then,

$$\gamma_{\text{Ga}} X_{\text{Ga}} \gamma_{\text{As}} X_{\text{As}} = \frac{P_{\text{Ga}} P_{\text{As}_4}^{1/4}}{P_{\text{Ga}}^0 P_{\text{As}_4}^{1/4}} = K_2(T) \quad (5)$$

Equation (5) is a mass action law for formation of solid GaAs from the liquid phase.

Thurmond [Ref. 5] has examined the thermodynamic data available for GaAs (the liquidus curve, decomposition pressure, specific heats, etc.) and has deduced values for  $K_1(T)$  and the activity coefficients  $\gamma$ .

The coefficients  $\gamma$  are functions of the concentrations  $X$  and of temperature, i.e.,  $\gamma_\alpha = \gamma_\alpha(X_\alpha, T)$ , but in a binary system there is a relation between composition and temperature which is expressed by the liquidus line, so there is only one independent variable. Also by definition  $X_{Ga} + X_{As} = 1$ .

In the ternary system, the mass action Eq. (5) can still be written down. However, the conservation condition is now  $X_{Ga} + X_{As} + X_{Zn} = 1$ . In addition the liquidus is a surface so that in  $\gamma_\alpha = \gamma_\alpha(X_\alpha, T)$  the variables  $X_\alpha$  and  $T$  are independent.

We now make the approximation that the activity coefficients of gallium and of arsenic in the ternary liquid are functions of the arsenic content only. This approximation is based on two assumptions:

1. For a given arsenic concentration the activity coefficients are nearly independent of temperature. Since in the Ga-As-Zn and Ga-P-Zn systems we are usually concerned with a temperature range of 300 °K, while the absolute temperature is around 1200 °K, this assumption is not too extreme.
2. Zinc and gallium atoms have similar behavior in the liquid. This assumption is more difficult to justify, although it may be noted that Zn-Ga liquid alloys do not show gross departures from regularity, except at high zinc concentrations [Ref. 6].

The procedure is now simple. Figure 2 shows the activity coefficients  $\gamma$  deduced by Thurmond. From the binary liquidus and Fig. 2 it is possible to find the equilibrium constant  $K_2$  of Eq. (5) as a function of temperature. At a given temperature for any value of  $X_{As}$ , we can take  $\gamma_{Ga}$  and  $\gamma_{As}$  from Fig. 2 and thus find  $X_{Ga}$  from Eq. (5). Knowing  $X_{Ga}$  and  $X_{As}$  we find  $X_{Zn}$  from the conservation condition. In this way, by varying  $X_{As}$  we can trace out the ternary liquidus line and by repeating the process at different temperatures we can trace out that part of the liquidus surface which corresponds to the presence of solid GaAs.



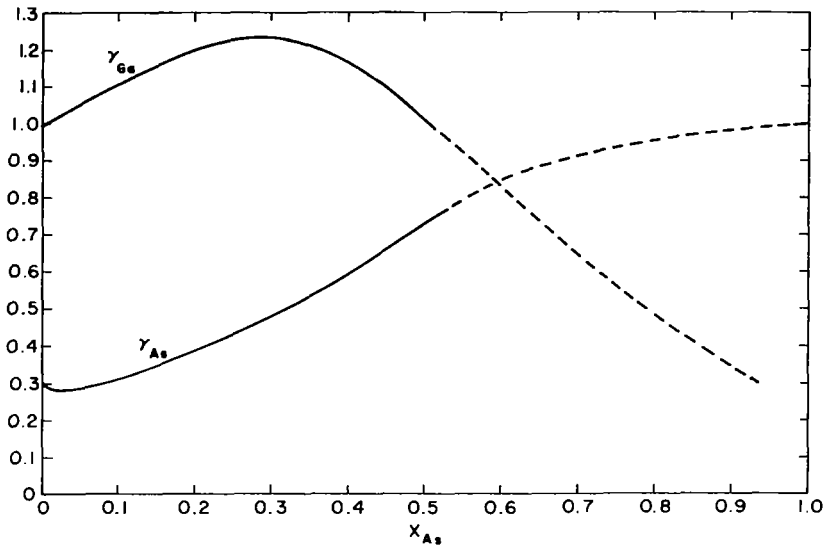
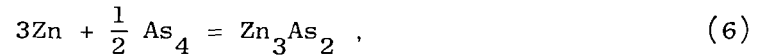


FIG. 2. ACTIVITY COEFFICIENTS OF GALLIUM AND ARSENIC ALONG THE Ga-As BINARY LIQUIDUS, ACCORDING TO THURMOND.

Below 1015 °C the  $Zn_3As_2$  phase appears over part of the constitution diagram. For that part of the liquidus corresponding to the presence of this phase, a similar procedure has been adopted. The reaction of formation from the gas phase is:



with a mass action equation:

$$P_{Zn}^3 P_{As_4}^{1/2} = K_3 \quad (7)$$

Since we have no information concerning activities and since the composition range is short at temperatures of interest here, we assume that, for the zinc-rich side of the liquidus, zinc obeys Raoult's law ( $P_{Zn} \propto X_{Zn}$ ) and arsenic obeys Henry's law ( $P_{As_4}^{1/4} \propto X_{As}$ ), so one has

$$x_{\text{Zn}}^3 x_{\text{As}}^2 = K_4(T) \quad (8)$$

for the liquidus.

Below 771 °C a  $\text{ZnAs}_2$  phase appears but experimental information is scarce in this part of the phase diagram. Since in diffusion and crystal growth experiments one normally works at higher temperatures, this phase will not be considered.

The results of the calculations are shown in Fig. 3 together with points obtained from Köster and Ulrich's pseudo-binary data. It will be seen that agreement between experiment and theory is good over most of the region considered. An exception is the 1200 °C isotherm. However, an examination of Köster and Ulrich's data shows that the experimental point which is furthest from the curve is the one which is most sensitive to a small error in the thermal arrest temperature.

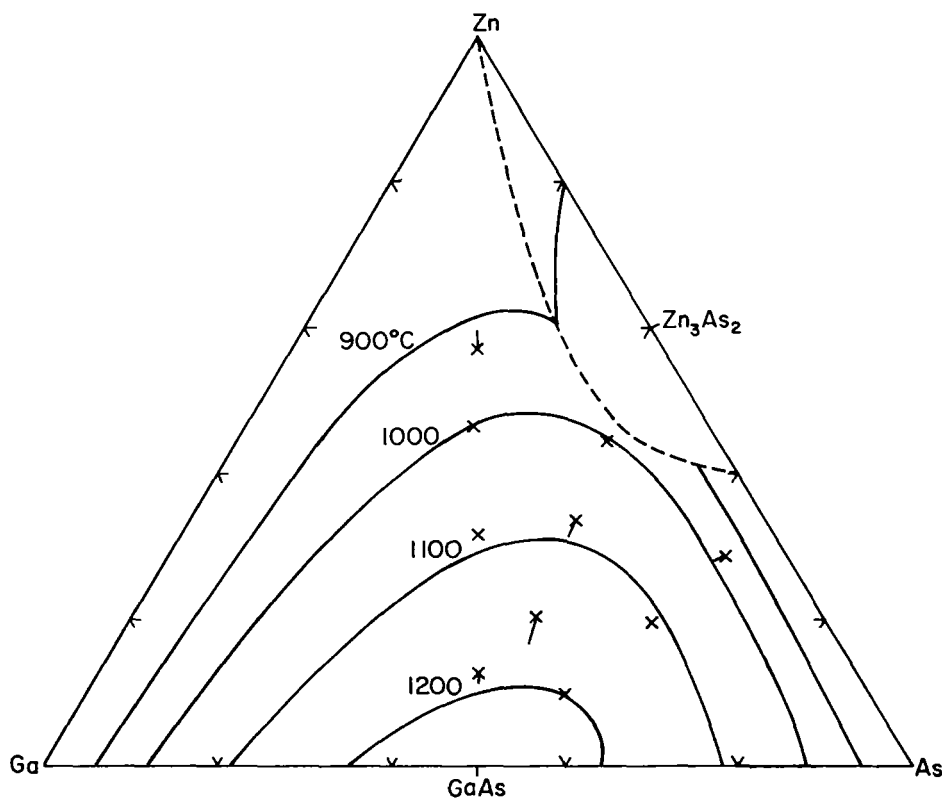


FIG. 3. THEORETICAL LIQUIDUS ISOTHERMS IN THE Ga-As-Zn SYSTEM. Crosses are interpolated points from the experimental data of Köster and Ulrich.

#### D. THE Ga-P-Zn LIQUIDUS - THEORY

Since our simple approximate theory gives a reasonably good description of the ternary liquidus of Ga-As-Zn, starting out from information concerning only the binary systems, we can apply the same method to the Ga-P-Zn system with some confidence. The binary Ga-P system has been extensively studied by Thurmond [Ref. 5]. As before, we use the Ga-P binary liquidus, the activity coefficients determined from the binary system (Fig. 4), and the approximation that the activity coefficients are functions of  $X_p$  only. The results of the calculation are shown in Fig. 5. As yet we have no experimental data for comparison. The temperatures considered here are above the melting points of  $Zn_3P_2$  and  $ZnP_2$ , so the phase diagram is simpler than in the Ga-As-Zn system.

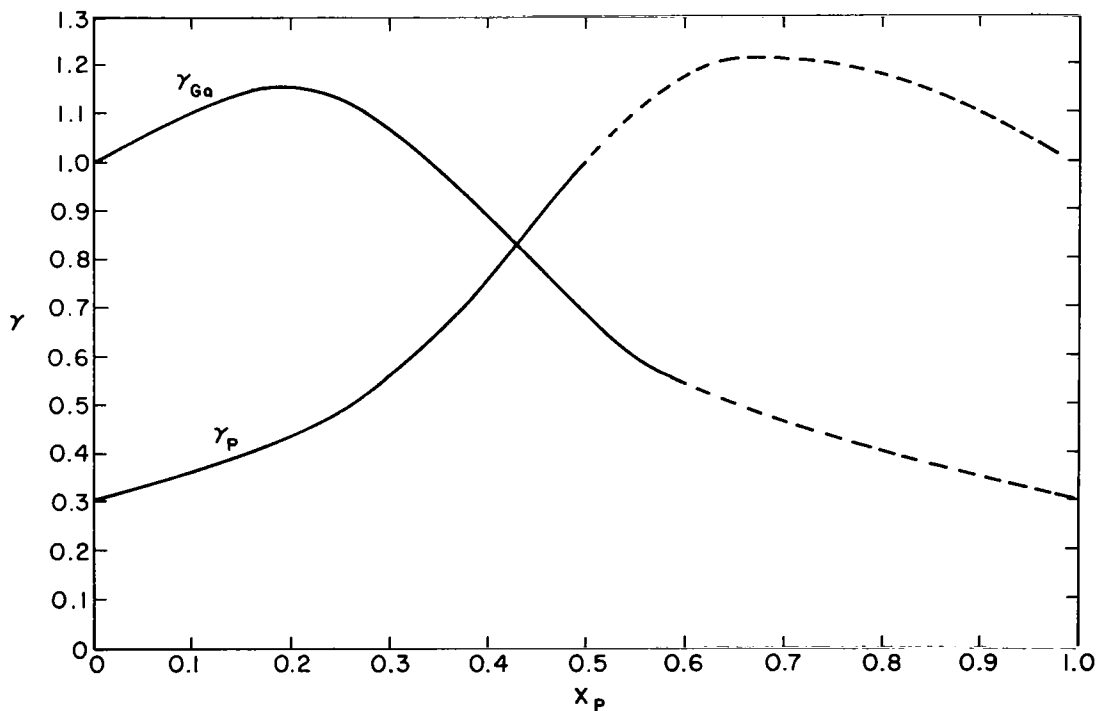


FIG. 4. ACTIVITY COEFFICIENTS OF GALLIUM AND PHOSPHORUS ALONG THE Ga-P BINARY LIQUIDUS, ACCORDING TO THURMOND.

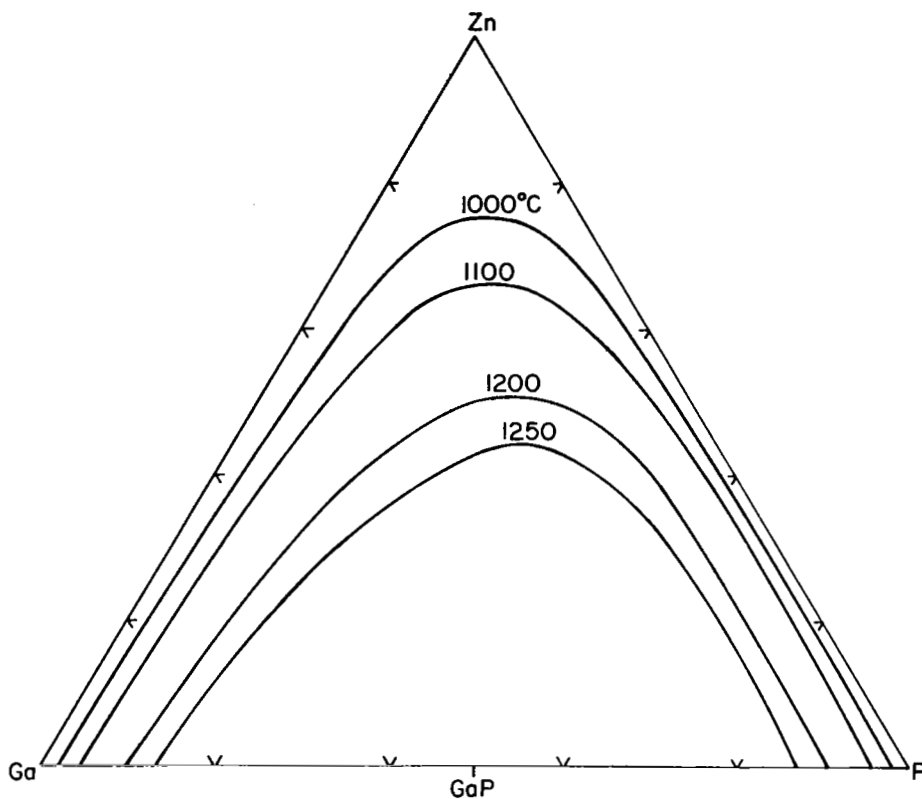


FIG. 5. THEORETICAL LIQUIDUS ISOTHERMS IN THE Ga-P-Zn SYSTEM.

E. PRESSURE OF PHOSPHORUS OR ARSENIC ON THE LIQUIDUS SURFACE - THEORY

Using our basic approximation concerning activity coefficients, it is possible to estimate the phosphorus or arsenic pressures over the liquidus by using the set of equations:

$$\left. \begin{aligned}
 P_{As_4} &= (\gamma_{As} X_{As})^4 P_{As_4}^o \\
 P_{As_2} &= (\gamma_{As} X_{As})^2 P_{As_2}^o \\
 P_{P_4} &= (\gamma_P X_P)^4 P_{P_4}^o \\
 P_{P_2} &= (\gamma_P X_P)^2 P_{P_2}^o
 \end{aligned} \right\} \quad (9)$$

These equations follow from the definition of the activity coefficients exemplified by Eq. (3). Values of the pressure of arsenic over pure liquid arsenic were taken from Thurmond's paper [Ref. 5], while values of the pressure of phosphorus over pure liquid phosphorus were taken from the JANAF tables [Ref. 7]. Calculated curves of the partial pressure variations along some liquidus isotherms are given in Figs. 6 and 7. Over most of the range the tetramer is the important species at the temperatures considered, but for low zinc concentrations the dimer becomes dominant in the phosphorus system.

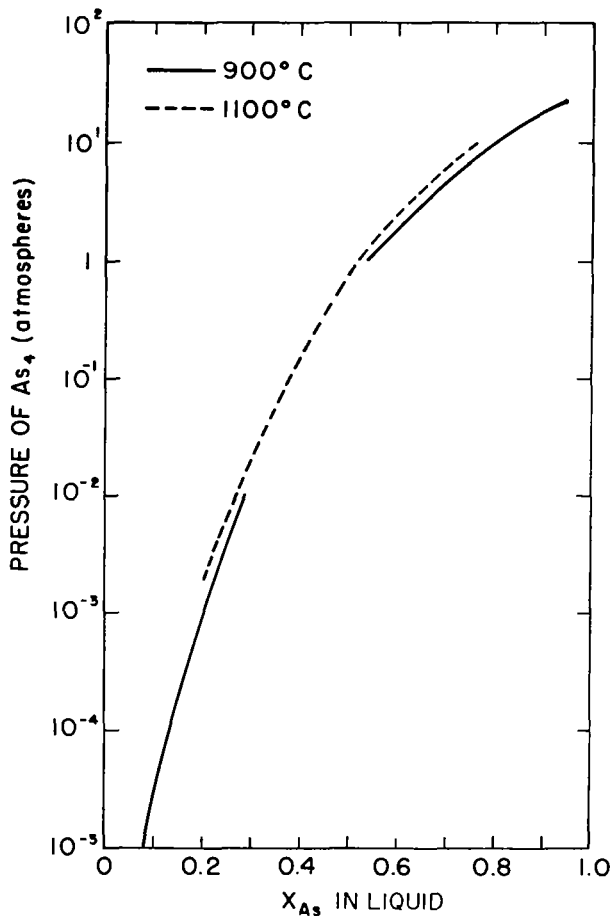


FIG. 6. VARIATION OF THE PRESSURE OF  $As_4$  ALONG THE LIQUIDUS IN THE Ga-As-Zn SYSTEM AT 900 °C AND 1100 °C. The pressure of  $As_2$  is negligible except at the lowest pressures.

The calculated pressures are subject to much greater errors than the calculated liquidus curves since in order to use Eq. (9) we have had to use an approximate theory to obtain  $\gamma$  and  $X$ , and since, in addition,

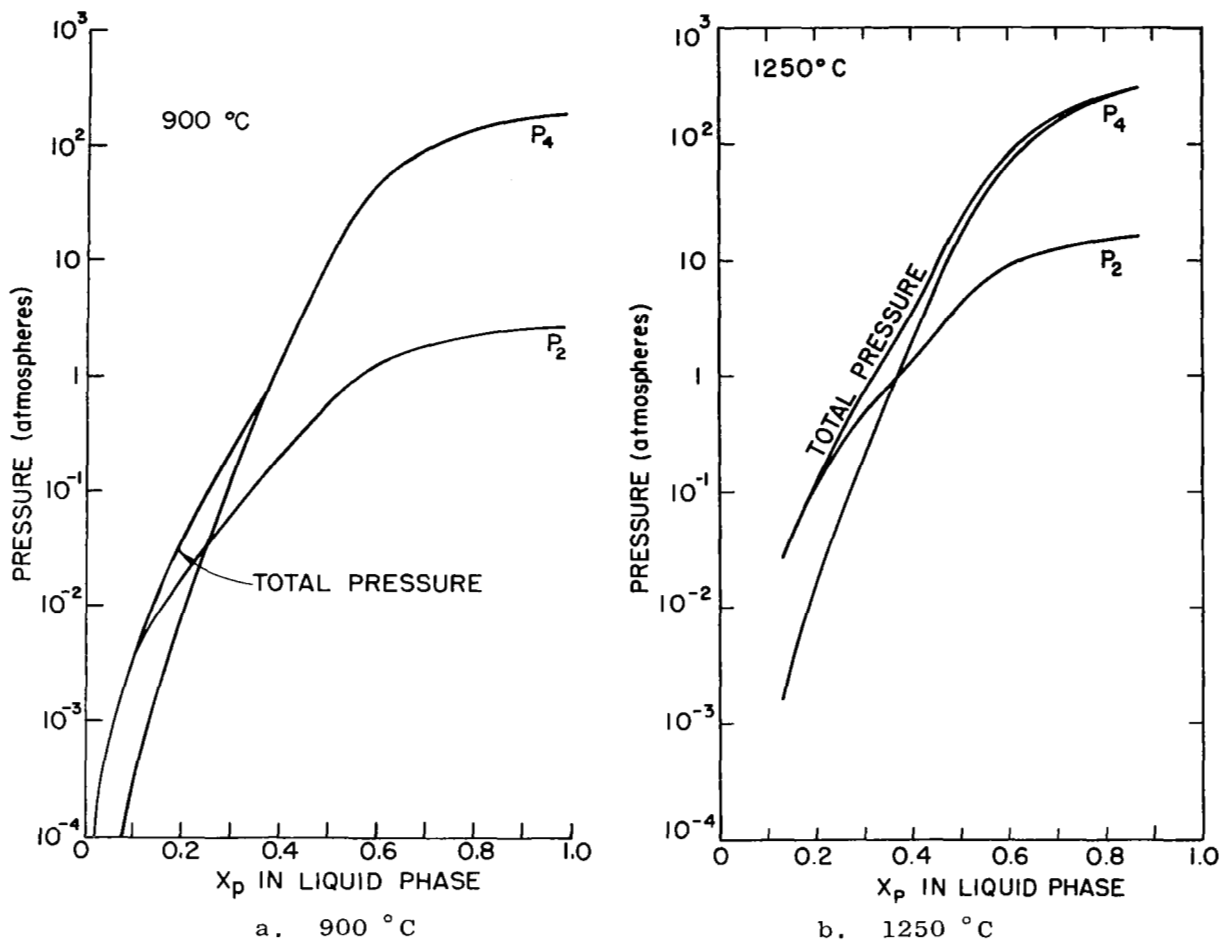


FIG. 7. VARIATION OF THE PRESSURE OF  $P_4$  AND  $P_2$  AND OF THE TOTAL PHOSPHORUS PRESSURE ALONG THE LIQUIDUS IN THE Ga-P-Zn SYSTEM.

over most of the range these approximate values are raised to the fourth power. The errors are likely to be most serious at high phosphorus or arsenic concentrations, for which the behavior of the binary system is less well known. However, the data of Figs. 6 and 7 should be correct as to order of magnitude, and in many cases this is sufficient to permit reasonably accurate predictions concerning the behavior of the condensed phases.

#### F. OTHER PHASE DOMAINS

As yet there is only scanty evidence concerning other regions of the phase diagram. Some of the relevant experiments will be discussed in the next section. However, it is known that when GaAs is doped with Zn the

Zn atoms replace Ga atoms, and that departures from stoichiometry are small compared with the zinc content. This implies that the region of stability of solid Zn-doped GaAs is a long, narrow region extending along the 50 atomic percent As isoconcentration line, as shown in schematic form in Fig. 8. Exactly the same considerations apply to GaP-Zn.

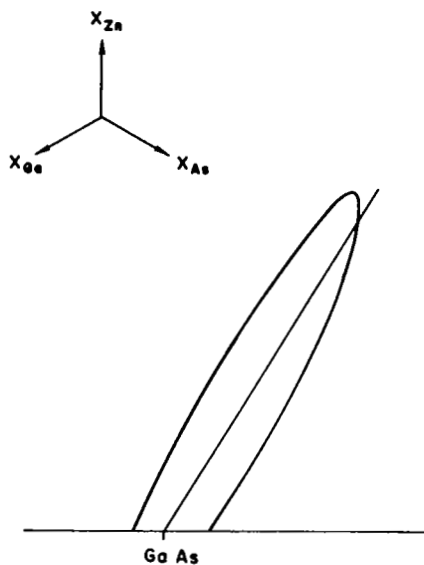


FIG. 8. A SCHEMATIC REPRESENTATION OF A SOLIDUS ISOTHERM IN THE Ga-As-Zn SYSTEM.

### III. PHASE RULE CONSIDERATIONS

The phase rule gives the number of independent parameters required to specify the state of a system unambiguously. The rule is:

$$F = C - P + 2 , \quad (10)$$

where  $F$  is the number of degrees of freedom,  $C$  the number of components, and  $P$  the number of phases. In the ternary systems there are three components so Eq. (10) becomes  $F = 5 - P$ . It is instructive to catalogue the various phase domains and to apply the phase rule in each. For this purpose we consider the 900 °C isothermal section of the Ga-As-Zn phase diagram since this demonstrates several types of behavior. This section is shown schematically in Fig. 9, in which the regions of existence

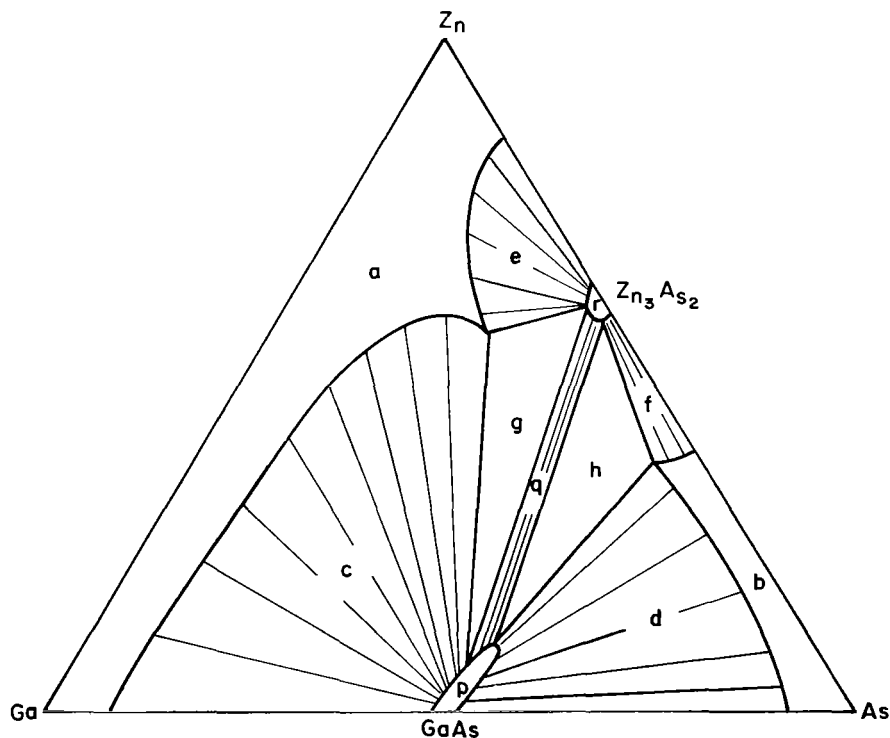


FIG. 9. SCHEMATIC TERNARY PHASE DIAGRAM OF Ga-As-Zn AT 900 °C. For purpose of illustration the regions of existence of the solid phases have been grossly enlarged.



of the solid phases in contact with only a vapor are grossly distorted, and in which schematic tie-lines have been drawn.

1. Regions a, b - liquid in equilibrium with a vapor;  $P = 2$ ,  $F = 3$ .  
For fixed temperature two parameters specify the system, which can be for instance the concentration of Ga and of Zn in the liquid, or the partial pressures of  $As_4$  and Zn in the vapor
2. Region c - liquid with a composition on the liquidus in equilibrium with a solid (namely Zn-doped GaAs) with a composition on the solidus, and with a vapor;  $P = 3$ ,  $F = 2$ . For fixed  $T$  one parameter is required. For instance if the concentration of Ga in the liquid is specified this fixes a point on the liquidus, and the tie-line from here fixes a point on the solidus, so the state of the system is determined. Most published work on diffusion of Zn in GaAs or the growth of Zn-doped crystals of GaAs is concerned with region c at a variety of temperatures.
3. Regions d, e, f - these are similar to region c.
4. Region p - solid (Zn-doped GaAs) in equilibrium with a vapor;  $P = 2$ ,  $F = 3$ . At fixed  $T$  two parameters are required, which could be for instance the partial pressures of Zn and  $As_4$  over the solid.
5. Region r - as in region p there is a solid ( $Ga$ -doped  $Zn_3As_2$ ) in equilibrium with a vapor, and at fixed  $T$  two parameters will specify the system.
6. Region q - two solids with variable compositions connected by tie-lines, in equilibrium with a vapor;  $P = 3$ ,  $F = 2$ . At fixed  $T$  one parameter, such as the partial pressure of  $As_4$ , specifies the state of the system.
7. Region g, h - two solids (Zn-doped GaAs and  $Ga$ -doped  $Zn_3As_2$ ) in equilibrium with a liquid and a vapor;  $P = 4$ ,  $F = 1$ . At fixed  $T$  there are no remaining available degrees of freedom, so the state of the system is completely specified. This means that independent of whereabouts in region g the constitution of the system lies, such parameters as the amount of Zn dissolved in solid GaAs, the amount of Ga dissolved in  $Zn_3As_2$ , the partial pressure of  $As_4$ , the defect concentrations in GaAs and  $Zn_3As_2$ , and so on will be fixed quantities.

At higher temperatures in the Ga-As-Zn system, and at all temperatures considered here (900 °C - 1465 °C) in the Ga-P-Zn system, the phase diagram becomes simpler, having only three regions; namely solid + vapor, liquid + vapor, and solid + liquid + vapor, with behaviors corresponding to regions p, a, and c above respectively.

#### IV. A REVIEW OF SOME EXPERIMENTAL RESULTS

In this section some of the published experimental results will be discussed in relation to the ternary phase diagram. In many cases the results are expressed in terms of the solubility of Zn in GaP or GaAs. Note that if only condensed phases are of importance the solubility is usually defined as a concentration on a phase boundary (e.g., the solubility of salt in water is the concentration of salt in water in equilibrium with solid salt), while if a gaseous phase is important one usually works within a phase domain rather than on its boundary and a pressure variable is specified (e.g., one refers to the solubility of oxygen in water at a given pressure).

In the ternary systems the region of stability of Zn-doped GaP or Zn-doped GaAs is a volume in the three-dimensional phase space bounded by the constitution triangle and the temperature axis. For points within this volume three parameters are required to specify the system while for points on the boundary two parameters are required in general, although when solid  $\text{Zn}_3\text{As}_2$  is present together with a liquid only one parameter suffices. One frequently sees in the literature statements concerning the solubility of impurity Y in a binary compound MX at a given temperature or as a function of temperature. Clearly these statements have no precise meaning unless the other phases in equilibrium with the doped solid are specified, together with as many independent variables as are required by the Phase Rule. Ideally one would like these variables to be the thermodynamic ones, but for practical purposes it may be sufficient to state such things as the volume of the enclosure and the amounts of the reactants.

McCaldin [Ref. 3] has investigated the relation between zinc concentrations in solid GaAs and in the gas phase at 1000 °C for three conditions of arsenic pressure, namely 1 ats, 0.17 ats, and the pressure produced when only GaAs and Zn are added to the system. This last condition probably corresponds to working on the solidus boundary, although insufficient experimental details are given to make this certain. We can map region p of Fig. 9 by taking as logarithmic co-ordinates the arsenic pressure and the zinc concentration in atoms per unit volume. On an

isothermal section we can draw contour lines of constant arsenic pressure and of constant zinc pressure. Restated in these terms, McCaldin's experiments provide information on the positions of these contours. In Fig. 10 a schematic plot of this type is shown.

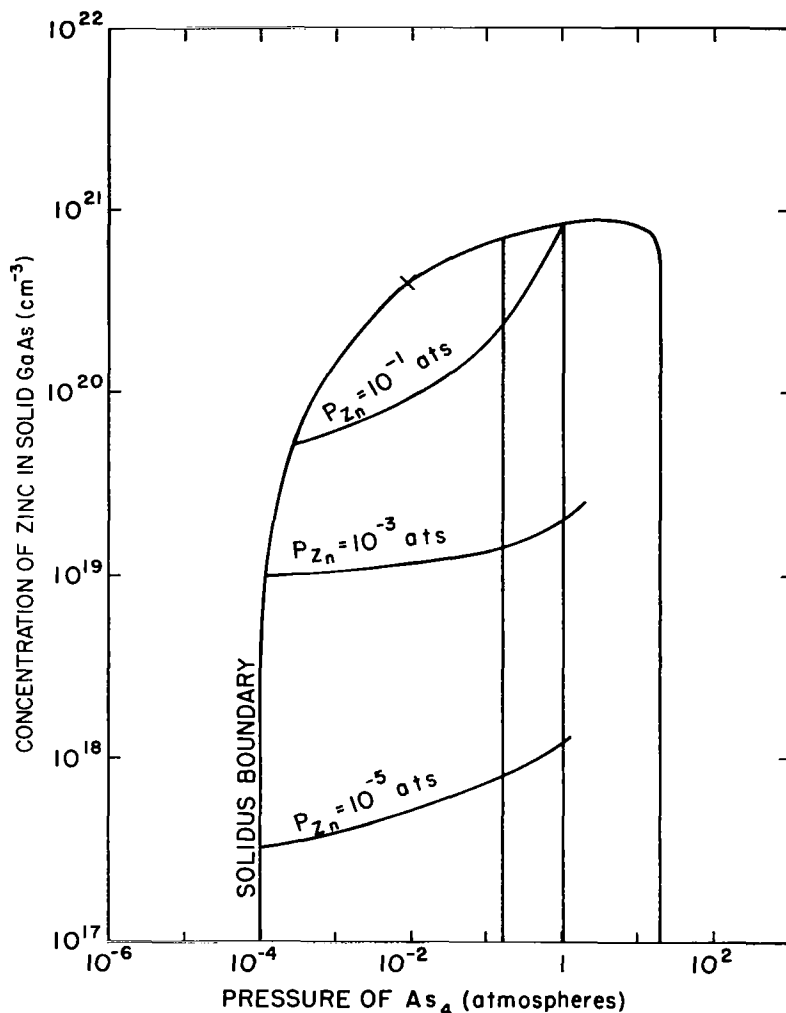


FIG. 10. A SCHEMATIC DIAGRAM OF THE REGION OF EXISTENCE OF SOLID GaAs IN THE Ga-As-Zn SYSTEM AT 1000 °C. Zinc isobars from McCaldin's experiments and a point on the solidus from Chang and Pearson's experiments are indicated.

Chang and Pearson [Ref. 8] diffused Zn into GaP and GaAs at several temperatures and measured the surface concentration of Zn, which they took to be the solubility. Using the composition and pressure variations along the liquidus as calculated above, it is possible to show that under their conditions the liquid phase had a composition close to the pseudo-binary line (i.e., GaP-Zn or GaAs-Zn lines), as they assumed. However, their assumption that the solid phase also had the pseudo-binary composition is less likely to be correct since this implies that a neutral arsenic vacancy is produced for each Zn atom entering the lattice.

Since in Chang and Pearson's experiments the composition of the liquid phase can be found, it is possible to estimate the arsenic pressure over their system by using Fig. 6. At a given temperature their results therefore give a point on the solidus curve defined in terms of the concentration of Zn in solid GaAs and of the arsenic pressure, i.e., in terms of Fig. 10. This gives the connection between McCaldin's and Chang and Pearson's experiments: McCaldin worked within the solidus volume, Chang and Pearson worked on its boundary.

Trumbore et al [Ref. 9] measured the distribution coefficient of Zn between a gallium-rich melt in the Ga-P-Zn system and solid GaP. In terms of the ternary phase diagram their results determine the positions of the tie-lines between the liquidus and solidus curves at the temperature of their experiments (1040 °C). Although in this particular case the exercise is less useful, it is possible to restate these results as defining a portion of the solidus curve on a plot of phosphorus pressure against zinc concentration, analogous to the GaAs-Zn case discussed above. To do this one uses the liquidus of Fig. 5 to determine the liquid compositions and then Fig. 7 can be used to find the phosphorus pressure over the system. Chang and Pearson's results on the GaP-Zn system can be displayed in the same way, thus showing the connection between the two experiments.

A number of other experiments on the Ga-P-Zn and Ga-As-Zn systems have been performed, but those mentioned above are the ones which give the most exact information. From the discussion two points emerge. Firstly, by the use of the liquidus and pressure curves it is possible to relate a number of experiments of different types to each other by way of the ternary phase diagram. Unfortunately, experimental data concerning these

curves are lacking except in the case of the Ga-As-Zn liquidus surface, and we have had to rely on a theoretical approximation. Clearly it would be an advantage to have more experimental data. Secondly, solubility in the ternaries must be stated in terms of a variable additional to the temperature. Experimental convenience suggests that a good choice of variable is the arsenic or phosphorus pressure. Within the solidus boundary yet another variable must be specified to define the solubility, and a good choice might be the zinc pressure.

## V. APPLICATION TO DIFFUSION

### A. DYNAMIC EQUILIBRIUM

The point was made in the Introduction that in studying diffusion processes it is necessary to determine which are the rate-limiting steps, either by experience or by direct experiment. It may then be possible to treat some parts of the system as being in dynamic equilibrium and therefore describable by the methods of equilibrium thermodynamics. In manufacturing processes it can be advantageous to have as many parts of the system as possible in dynamic equilibrium since this will minimize the effects of past history of the materials and thereby lead to greater manufacturing uniformity.

Suppose for example that Zn and GaP are heated together to say 1000 °C in a silica ampoule. If the zinc and gallium phosphide are initially separate, then some zinc will vaporize, and since the equilibrium pressure of Zn over pure GaP is less than that over pure Zn, the vapor will condense and dissolve some GaP. The solution will lose a little phosphorus and a negligible amount of gallium to the vapor phase. The processes of evaporation from a liquid and transport in the gas phase are likely to be rapid compared with diffusion processes, so it may be possible to take the vapor, the liquid, and a small volume of the solid in contact with the liquid as having compositions close to the equilibrium values represented by a point on the phase diagram. On the other hand, suppose that a crystal of GaAs and a dilute solution of Zn in Ga are placed at the opposite ends of a closed tube heated to say 850 °C. Zinc will rapidly evaporate and distribute itself between the surface of the GaAs and the liquid Ga. There will be some decomposition at the surface of the GaAs and arsenic will go into the vapor phase, travel down the tube and dissolve in the liquid Ga. At 850 °C this transfer of arsenic will be slow, since the pressure differences involved are small, so during the course of a typical diffusion experiment the liquid phase may be a long way away from equilibrium, and the geometry of the equipment can be an important factor in determining the diffusion parameters.

## B. RELATION BETWEEN EXPERIMENTAL AND THERMODYNAMIC QUANTITIES

Once one has decided which parts of the system are in dynamic equilibrium, the next step is to relate the masses of the components and the container volume to the thermodynamic parameters, in particular the quantities and compositions of the various phases present.

In Section II the compositions of the condensed phases were discussed and a method was presented for estimating the phosphorus or arsenic vapor pressure over the liquidus surface. The gallium vapor pressure is everywhere negligible for the temperatures under consideration. To complete the description of the system it is necessary to know the zinc vapor pressure over the composition diagram. Until experimental data become available this has to be estimated. We shall assume that a reasonable approximation is obtained by using Raoult's law.

In principle the activities of gallium and arsenic estimated in Section II can be used together with a Gibbs-Duhem equation to estimate the zinc activity in the ternary, and hence the zinc vapor pressure over the liquidus. This approach gives a calculated value which is removed from firm experimental data by too many steps of approximation, and this is why we choose the Raoult's law approach. However, it is necessary to demonstrate that this is reasonable. It is easily shown that the Gibbs-Duhem equation reduces to the form:

$$\frac{d \ln \gamma_{Zn}}{dX_{As}} = \frac{d \ln \gamma_{Ga}}{dX_{As}}, \quad (11)$$

when the approximation concerning activity coefficients discussed in Section II is used. The activity coefficients given by Thurmond deviate less than 30 percent from unity for  $X_P < 0.5$  in the Ga-P-Zn system and  $X_{As} < 0.7$  in the Ga-As-Zn system, while in the Ga-Zn system the activity coefficient of Zn changes only from 1.0 to 1.3 as  $X_{Zn}$  varies from 1.0 to 0.35. Since zinc vapor is monatomic, the departure from Raoult's law is directly proportional to the deviation of the activity coefficient from unity, so over most of the composition and temperature ranges of interest Raoult's law will be a useful approximation. (The vapor is much lighter



than the liquid, so a 30 percent error in the weight of the vapor will make very little change in the weight of the condensed components, in which we are chiefly interested.)

Because the phase boundaries in the ternary phase diagram are not represented by simple analytic expressions, it is not possible to proceed directly from the weights of the components to a point on the phase diagram. Rather, one has to guess approximately where on the diagram the system lies, calculate the amounts of the components, and then repeat the process for neighboring points until the calculated amounts agree with those used in an actual experiment. The following example will illustrate this procedure.

A closed ampoule, volume  $2 \text{ cm}^3$ , contains 0.3 gms GaAs and 2.6 mgm Zn. It is heated to  $900^\circ \text{C}$  for a diffusion experiment. We expect that there will be a vapor phase containing Zn and  $\text{As}_4$  and a negligible amount of Ga, a liquid phase containing Ga, As, and Zn, and a solid phase of GaAs containing negligible weight of Zn. We also expect the liquid to have a composition somewhere near the GaAs-Zn line, but since some  $\text{As}_4$  is lost to the vapor the liquid composition will be slightly to the Ga side of this line.

At  $900^\circ \text{C}$   $X_{\text{Zn}} \sim 0.6$  and the vapor pressure of pure Zn is 0.92 ats, so by Raoult's law the pressure of Zn in the system is 0.55 ats. The weight of  $2 \text{ cm}^3$  of Zn vapor at 0.55 ats at  $900^\circ \text{C}$  is 0.63 mgm. The weight of Zn in the liquid phase is therefore about 2 mgm. From the phase diagram we can find values of  $X_{\text{Ga}}$ ,  $X_{\text{As}}$ , and  $X_{\text{Zn}}$  for points on the liquidus near the GaAs-Zn line, and knowing the weight of Zn we can convert these concentrations to weights. Since the source of Ga and As is GaAs, the difference  $X_{\text{Ga}} - X_{\text{As}}$  tells us how much arsenic has gone into the vapor phase. From this we can calculate the arsenic pressure and compare this with the pressure found from the pressure-composition curve of the phase diagram. For some point on the liquidus these two pressures will agree

and this will be the point describing the system. The following quantitative values apply:

| $X_{As}$ | $X_{Ga}$ | $X_{Zn}$ | $X_{Ga} - X_{As}$ | weight<br>$As_4$ in vapor | $P_{As_4}$<br>calculated | $P_{As_4}$ from<br>phase diagram |
|----------|----------|----------|-------------------|---------------------------|--------------------------|----------------------------------|
| 0.195    | 0.195    | 0.61     | 0                 | 0                         | 0                        | $8 \cdot 10^{-4}$ ats            |
| 0.18     | 0.22     | 0.60     | 0.04              | 0.13 mgm                  | $2.1 \cdot 10^{-2}$ ats  | $6 \cdot 10^{-4}$ ats            |
| 0.16     | 0.26     | 0.58     | 0.10              | 0.33 mgm                  | $5.4 \cdot 10^{-2}$ ats  | $3 \cdot 10^{-4}$ ats            |

It will be seen that in this example the point at which the calculated  $As_4$  pressure equals that determined from the phase diagram will lie very close to the GaAs-Zn line along which  $X_{As} = X_{Ga}$ .

As another example suppose that a crystal of GaP is heated to  $1000^\circ C$  in an ampoule of  $2 \text{ cm}^3$  volume together with 2.5 mgm of zinc and that in order to reduce surface deterioration extra phosphorus is added. From the liquidus and pressure curves it is possible to calculate the weight of gallium in the liquid and the amount of phosphorus in excess of that provided by the gallium phosphide, this being simply the weight of phosphorus added. Since the gallium in the liquid phase comes from dissolution of GaP, its weight is a measure of surface attack. Figure 11 shows the result of the calculation and it will be seen that in this case the addition of a small amount of phosphorus will give a better surface, but too much will make matters worse.

### C. SOME CONSEQUENCES

The complete ternary phase diagram contains a wealth of information. Just a few important points will be noted here, as being representative of the possible applications.

Surface deterioration has been treated above as a solution effect, rather than a decomposition effect, except when a dilute zinc source is used. This has been emphasized by Loescher [Ref. 10]. If surface deterioration were due to decomposition then addition of arsenic or phosphorus would always result in better surfaces, but Fig. 11 shows that although

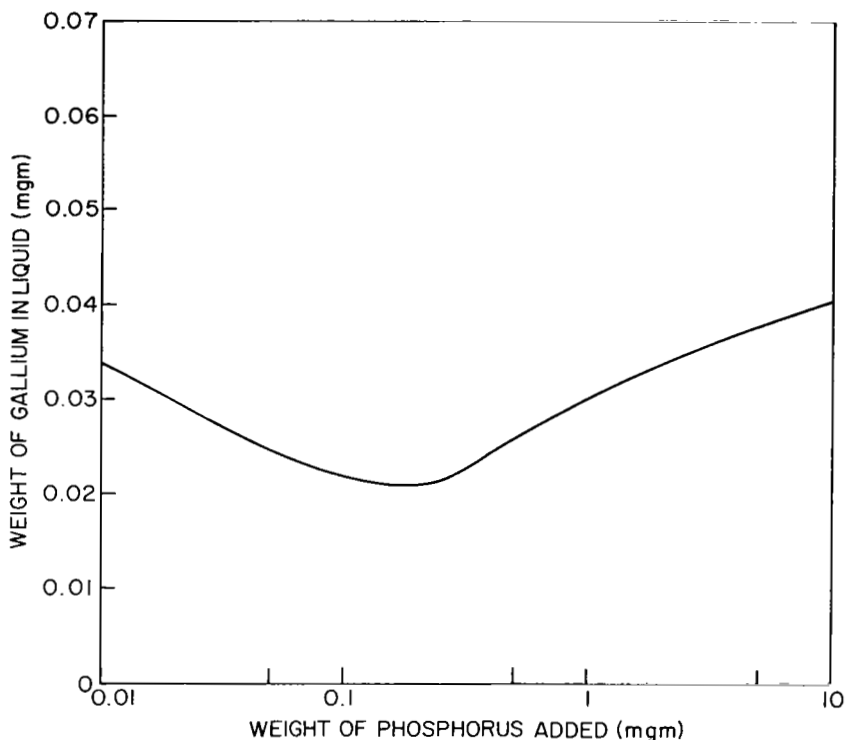


FIG. 11. THE VARIATION OF SURFACE DISSOLUTION OF GaP BY ZINC AS A FUNCTION OF EXCESS PHOSPHORUS ADDED, CALCULATED FROM THE THEORETICAL PHASE DIAGRAM. Conditions are ampoule volume 2 cm<sup>3</sup>, weight of zinc 2.5 mgm, temperature 1000 °C.

the addition of a little phosphorus will improve the surface, addition of too much can make it worse. Moreover, the optimum amount will depend on the amount of zinc present and the temperature.

In the Ga-As-Zn system the existence of a Zn<sub>3</sub>As<sub>2</sub> phase produces some interesting possibilities. (Below 771 °C ZnAs<sub>2</sub> may occur. Diffusion experiments are normally carried out above this temperature and if ZnAs<sub>2</sub> is added to the system, it will decompose into other phases.) If one works in region q of Fig. 9 there is no liquid phase, so surface deterioration of the GaAs will be at a minimum. Note that in order to reach this region it will not be sufficient simply to place solid Zn<sub>3</sub>As<sub>2</sub> and GaAs in an ampoule unless their amounts are large enough in relation to the volume: otherwise in order to establish the equilibrium vapor composition enough decomposition may occur to move the system over a phase boundary. Again,

in order to achieve reproducibility it may be advantageous to work in the four-phase region g of Fig. 9 since then at a given temperature the system is invariant, i.e., small changes in the amounts of material placed in the ampoule will have no effect on the zinc and arsenic pressures and so on. On the other hand although the compositions of the phases do not vary in region g the relative amounts do, and technically it may be useful to perform a diffusion with the system being in region g but close to the boundary of region q since this will give a diffusion process which is insensitive to small changes in the conditions and which simultaneously produces little surface deterioration.

If zinc is diffused into GaAs at 1000 °C and extra arsenic is added to the system, then the arsenic pressure will vary smoothly with the amount of arsenic added. At 900 °C this will no longer be true since the rate of change of pressure with weight of added arsenic will vary greatly between the different regions of the phase diagram. It is essential to bear this in mind when calculating say the variation of vacancy concentration with arsenic pressure and its effect on diffusion.

Finally, the obvious point can be made that diffusion into elemental semiconductors is often carried out in an open-tube flow system as this is rather convenient, but for compound semiconductors this type of system will only be useful when the desired vapor composition has been found from the phase diagram and the composition of the gas flow adjusted accordingly.

## VI. CONCLUSIONS

1) Although diffusion is a kinetic process, in a typical diffusion experiment several parts of the system may be in quasi-equilibrium and therefore amenable to study by the techniques of thermodynamics.

2) The liquidus compositions and the pressure of phosphorus or arsenic over the liquidus in the Ga-P-Zn and Ga-As-Zn systems can be calculated from the Ga-P and Ga-As binary systems by making a simple approximation concerning activity coefficients.

3) Several apparently different types of experiment can be correlated by considering them as describing various cross-sections of the ternary phase diagram.

4) When giving the results of an experiment in which a binary compound is doped with an impurity, it is advisable to use the Phase Rule to check that the experimental conditions are completely specified.

5) Knowledge of the phase diagram is a necessary intermediate when deriving thermodynamic parameters such as pressures of the components from initial weights of the components.

6) Surface deterioration during diffusion of zinc into gallium phosphide or arsenide is generally due to dissolution rather than decomposition. In minimizing deterioration a knowledge of the phase diagram is useful.

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