

Isoconcentration Diffusion of Zinc in GaAs at 1000° C

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A series of experiments is described in which zinc is diffused into GaAs at 1000° C using an isoconcentration technique. Standard error function complement profiles are obtained and graphs are produced showing the variation of diffusion coefficient with zinc concentration. Work carried out at two different arsenic vapour pressures is described and the effect of a variation in the stoichiometry of the semiconductor is thereby examined. The results of both sets of experiments are shown to agree with a substitutional-interstitial mechanism for the diffusion of zinc in GaAs. The solubility of zinc in GaAs is investigated as a function of ambient zinc vapour pressure and arsenic pressure. The results agree with a simple interpretation of the zinc as an almost completely ionised acceptor. A value is calculated for the maximum attainable solubility at 1000° C for GaAs in equilibrium with zinc vapour.

1. Introduction

A good deal of work has been carried out in recent years studying diffusion of zinc into GaAs [1-3] from the vapour phase. All workers agree that the diffusion coefficient, D , is a function of zinc concentration, c . Experimental work to determine the variation of D with c has fallen into two categories. In the first, a graphical method, diffusion profiles are plotted and slopes and areas under the graph are measured at a large number of points along the profile. A graph of D versus c can then be plotted using the Boltzman-Matano method of analysis. One disadvantage of the analysis is that it requires D to be a function of concentration only. For zinc diffusion in GaAs under a zinc concentration gradient, D may depend on time too, through there being a time-varying non-equilibrium vacancy concentration [3]. In this case the Boltzman-Matano analysis would not be applicable.

The second method, usually called the isoconcentration technique, involves diffusing radioactive zinc into material that is already homogeneously doped with non-radioactive zinc. The surface concentration of zinc attained during diffusion, C_0 , depends on the vapour pressure of zinc surrounding the semiconductor, and is therefore variable. If the conditions of the experiment are arranged to make C_0 equal to the homogeneous non-radioactive doping level, then

all that happens during the diffusion is that radioactive zinc diffuses into the specimen and non-radioactive zinc diffuses out. The specimen is therefore at thermal equilibrium throughout. The diffusing radioactive species is always in an atmosphere C_0 and so the diffusion profile gives a single value of D , namely that corresponding to the concentration C_0 . (The profile under these circumstances is an error function complement curve.) Carrying out a number of experiments for different values of C_0 allows the D versus c graph to be plotted.

Almost all of the published work has used the graphical technique; results have been inconsistent, however. Fig. 1 shows the D versus c curve for three different profiles with different surface concentrations. Where they overlap they disagree. The second method seems to be much more satisfactory, but the quantity of work published is much too small to give the variation of D with any accuracy. In this paper, experiments are described in which the variation of diffusion coefficient with concentration is followed over the range 10^{18} to 2×10^{20} cm⁻³, using the isoconcentration technique. The temperature of diffusion was 1000° C and experiments were carried out at two different arsenic vapour pressures. The surface concentrations indicated by the diffusion profiles were taken as values of solubility of zinc in GaAs.

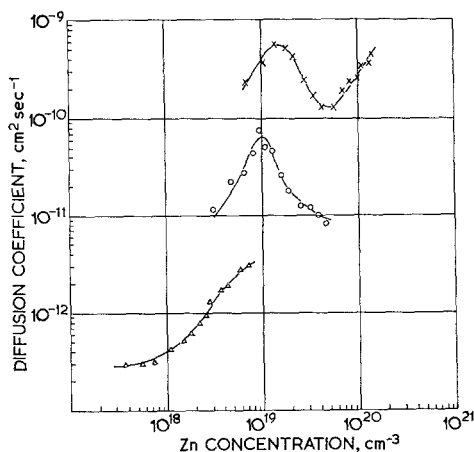


Figure 1 Boltzman-Matano analysis of three chemical diffusion curves taken at 1000°C . Data taken from [3].

2. Experimental Techniques

The experimental procedure has been described in detail elsewhere [3]. A slice of GaAs, about 1 cm^2 in area and 0.5 mm thick, and doped with non-radioactive zinc, was encapsulated in a 10 cm^3 ampoule with a piece of radioactive zinc. Some of the diffusions (table II) also had 1 mg of arsenic added to the tube. The original background doping for high concentrations was achieved by a long preliminary diffusion. This technique was used for all diffusions with added arsenic (table II) and for experiments 8 to 11 (table I) at dissociation pressure. For lower concentrations, however, the technique was impractical because the initial diffusion would have taken an unreasonably long time, and crystals which had been doped during growth were used. When the background doping was achieved by diffusion there was no difficulty in assessing the correct vapour pressure of radioactive zinc needed for the diffusion anneal; the same amount of zinc was required in the second diffusion as had been used in the first. For those cases in which the original doping was as-grown in the crystal a trial-and-error method was adopted to find the correct weight of radioactive zinc. When a good error function complement profile was obtained from the diffusion, it was assumed that the surface concentration coincided with the background doping.

The question of stoichiometry is important in these experiments. It will be shown in section 4 that the diffusion coefficient is sensitive to stoichiometry, which is effectively determined by the arsenic over-pressure. The purpose of the

preliminary diffusion is therefore not only to fix the background zinc doping but also to determine the stoichiometry, otherwise equilibrium will not exist in the second diffusion. It follows that if 1 mg of arsenic was to be used in the radioactive diffusion, then this amount of arsenic had to be included in the preliminary diffusion. Information on the length of time required by a GaAs crystal to achieve stoichiometric equilibrium is not available; the preliminary diffusions were therefore continued for several days, which seemed a reasonable time for the crystal to come to stoichiometric equilibrium in the hundred or so microns nearest the surface, which was the region to be occupied by the radioactive diffusion. The results of section 4 suggest that stoichiometric equilibrium was in fact achieved in these experiments. Any variation in stoichiometry would have shown up as a variation in zinc diffusion coefficient and error function complement profiles would not have been obtained.

Experiments 1 to 7 did not have the benefit of the preliminary anneal and so some doubt arises as to whether any necessary change in stoichiometry was achieved in a time small compared to the total diffusion time. It must be realised, however, that experiments 1 to 7 were those for which the zinc diffusion coefficient was very small and they all correspond to long diffusion times. The shortest diffusion in this group was for experiment 7 which took two days. The length of these diffusions, added to the good agreement of experiments 1 to 7 with the rest of the results suggests that stoichiometric equilibrium was achieved in the GaAs in the region in which the radiotracer profile was measured.

Diffusion took place in a three-zone furnace set to 1000°C . The slice was then removed from the ampoule and layers were removed by etching. The amount of zinc in each layer was counted and the diffusion profile plotted.

During an isoconcentration diffusion, non-radioactive zinc diffuses out of the specimen and radioactive zinc goes in to replace it. This means that the vapour phase must become increasingly diluted with non-radioactive atoms. Some proportion of the surface atoms will therefore be non-radioactive. Since only radioactive atoms are recorded in the diffusion profile, this could be a source of error. Assuming the fraction of non-radioactive zinc at the surface is the same as that in the vapour, it is clear that the amount of non-radioactive zinc in the vapour

must be kept low. It is possible that this effect was the cause of anomalously low surface concentrations measured by Chang and Pearson in their work on isoconcentration diffusion of zinc into GaAs [2]. In the present work, the fraction of non-radioactive zinc in the vapour never exceeded 8%, and it was much less than this for most experiments.

3. Phase Equilibrium

The equilibrium between phases inside the diffusion ampoule can be quite complex. In general there are three phases: the solid GaAs, a Ga;As;Zn liquid and zinc, gallium and arsenic vapours. The phase rule gives the number of degrees of freedom; $F = C - P + 2$. Since there are three components in the system, this gives two degrees of freedom. So if the temperature is set at 1000°C, there is just one degree of freedom left, i.e. either the zinc vapour pressure can be fixed by the experimenter, or the arsenic pressure. This presented a difficulty in the present work, since it was required first to carry out a number of diffusions varying the zinc vapour pressure and keeping the arsenic pressure constant and then to repeat the process for a different fixed value of arsenic pressure. It was necessary to choose both pressures to do this, i.e. to use one more degree of freedom than was available.

It was found that this problem was not serious providing only very small amounts of zinc and arsenic were added to the ampoules. The data necessary for calculating the composition of the liquid phase and the pressures of gallium, arsenic and zinc vapours has been published [4]. Table I shows the conditions for the set of experiments in which no extra arsenic was added.

TABLE I Dissociation pressure

Experiment	Surface concentration C_0 cm ⁻³	Arsenic pressure Atm	Zinc pressure Atm
1	3.5×10^{18}	1×10^{-4}	4.2×10^{-3}
2	4.4×10^{18}	1×10^{-4}	4.2×10^{-3}
3	5.0×10^{18}	1×10^{-4}	5.4×10^{-3}
4	7.5×10^{18}	1×10^{-4}	1.1×10^{-2}
5	1.1×10^{19}	1×10^{-4}	1.6×10^{-2}
6	1.1×10^{19}	1×10^{-4}	3.3×10^{-2}
7	1.3×10^{19}	1×10^{-4}	2.2×10^{-2}
8	3.0×10^{19}	1×10^{-4}	5.7×10^{-2}
9	3.5×10^{19}	1×10^{-4}	1.6×10^{-1}
10	7.4×10^{19}	3×10^{-4}	3.3×10^{-1}
11	2.0×10^{20}	2×10^{-3}	7.4×10^{-1}

The zinc and arsenic vapour pressures are calculated using the data of [4]. It may be seen that the arsenic pressure, although strictly speaking not under control, hardly varies at all from 'dissociation pressure' (1×10^{-4} atm) for experiments 1 to 9. In experiment 10 the arsenic pressure was rather larger but not large enough to make a correction worthwhile. Experiment 11 had a considerably higher arsenic pressure, however, and a correction was made as follows. It is shown in section 5.2 that the solubility C_0 varies with the arsenic pressure as $P_{As}^{\frac{1}{2}}$. Hence a corrected value of C_0 was calculated given by

$$C_0' = 2 \times 10^{20} \left(\frac{1 \times 10^{-4}}{2 \times 10^{-3}} \right)^{\frac{1}{2}}$$

This gave an estimate of the solubility under conditions of 0.74 atm for zinc pressure and 1×10^{-4} atm for arsenic pressure. The correction amounts to a factor of 1.45 and the corrected value of C_0 is used in the next section. A similar correction was made for the diffusion coefficient measured in this case, using equation 2 (see section 5.1).

TABLE II (XS arsenic)

Experiment	Surface concentration C_0 cm ⁻³	Arsenic pressure Atm	Zinc pressure Atm
12	6.0×10^{18}	4×10^{-2}	2.6×10^{-3}
13	2.0×10^{19}	4×10^{-2}	1.1×10^{-2}
14	2.2×10^{19}	4×10^{-2}	1.6×10^{-2}
15	3.5×10^{19}	4×10^{-2}	2.5×10^{-2}
16	5.6×10^{19}	4×10^{-2}	3.3×10^{-2}
17	7.4×10^{19}	4×10^{-2}	6.5×10^{-2}
18	8.8×10^{19}	4×10^{-2}	1.1×10^{-1}
19	2.0×10^{20}	4×10^{-2}	3.3×10^{-1}
20	2.5×10^{20}	1×10^{-2}	5.7×10^{-1}

For experiments with arsenic added to the ampoule a different effect becomes important. The liquid in these cases is arsenic-rich and such liquids can have very high arsenic vapour pressures [4]. If the amounts of zinc and added arsenic in the tube are small then there is insufficient material to create a high vapour pressure and the liquid cannot form. The number of phases is reduced to two and the required extra degree of freedom is gained: all of the added arsenic and zinc goes into the vapour phase. In table II are shown the calculated vapour pressures for this set of experiments. In only one of the experiments, number 20, was

sufficient zinc and arsenic added to cause a liquid to form, giving rise to a different value of arsenic vapour pressure. A similar correction to that described above was applied to give a corrected C_0 of $3.0 \times 10^{20} \text{ cm}^{-3}$. This is a "mathematical" correction only, in the sense that it would not, in fact, be possible simultaneously to achieve a zinc pressure of 0.57 atm and an arsenic pressure of 4×10^{-2} atm; equation 6 takes no account of phase equilibrium. Equation 2 is again used to correct this point on the diffusion coefficient curve.

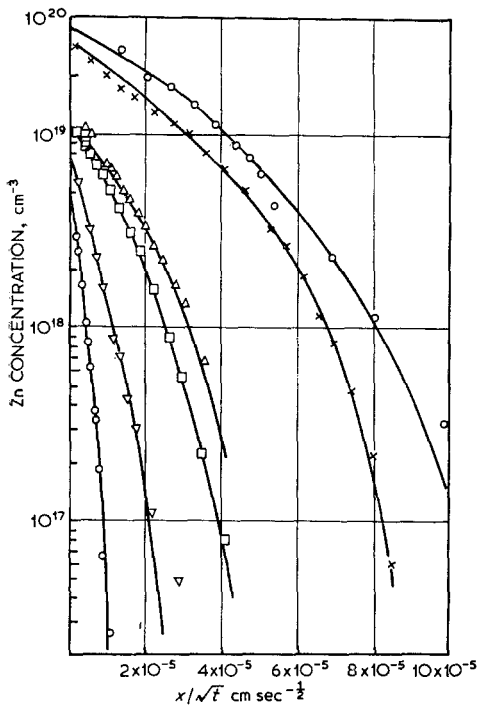


Figure 2 Diffusion profiles for zinc in GaAs at dissociation arsenic pressure. The points are experimental and the curves are error function complements. Some of the profiles have been omitted for the sake of clarity.

4. Results

Fig. 2 shows diffusion profiles for a number of different zinc vapour pressures for the set of experiments at dissociation pressure. The points are experimental and the lines are error function complement curves. Fig. 3 shows the $\log D$ versus $\log c$ plot derived from fig. 2. The point corresponding to the highest zinc concentration has been corrected as described in the previous section (the correction amounted to an increase in D by a factor of 2.1). The points fit a straight

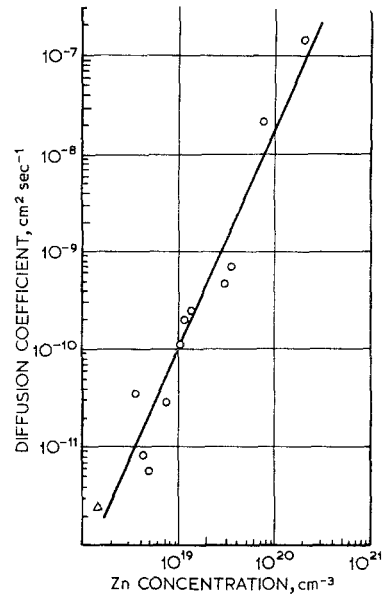


Figure 3 Variation of diffusion coefficient with zinc concentration at dissociation pressure of arsenic and 1000°C .

line of slope 2.2. A similar graph of $\log D$ versus $\log c$ at dissociation pressure of arsenic was presented in [3]. It agrees well with fig. 3 for the range of concentration over which the two sets of results overlap. The graph may be compared to the relationship predicted by Chang and Pearson [2], which varies between a cubic dependence at low concentrations and linearity at high concentrations. Fig. 4 shows profiles for the experiments with excess arsenic, and fig. 5 gives the $\log D$ versus $\log c$ plot. The latter also indicates a square-law relationship, with a slope of 2.2. The line is removed from fig. 3 by a factor varying between 2.3 and 3.0.

Solubility data taken from tables I and II is plotted in fig. 6. The upper curve refers to an arsenic vapour pressure of 4×10^{-2} atm and the highest point has been corrected, as described above. The lower curve corresponds to dissociation pressure and again the highest point has been corrected. Both curves show a square-law dependence at large concentrations, falling to approximately linear at low values. This agrees well with the results of McCaldin [5].

5. Discussion

5.1. Diffusion

Most workers now agree that zinc diffuses into

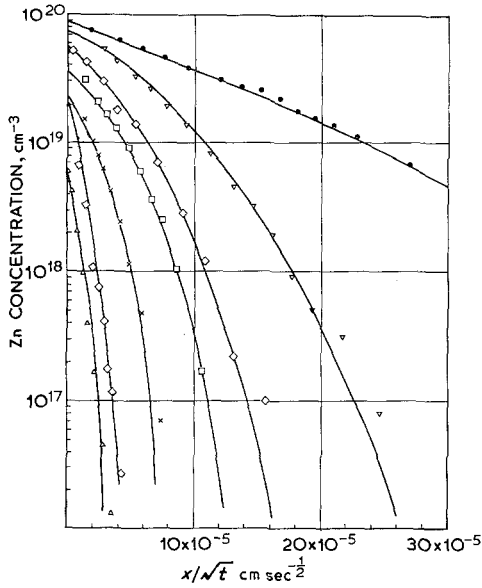


Figure 4 Diffusion profiles at excess arsenic pressure. The points are experimental and the curves are error function complements. Some of the profiles have been omitted for clarity.

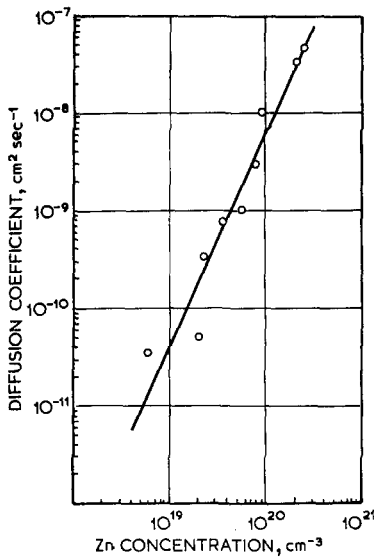


Figure 5 Variation coefficient with zinc concentration at excess pressure of arsenic and 1000°C.

GaAs by a substitutional-interstitial mechanism. A very small fraction of the diffusing zinc exists interstitially, concentration, C_i , and the diffusion coefficient for the species, D_i , is very large. Most of the zinc is substitutional, C_s , but the diffusion coefficient is assumed to be negligibly small. The

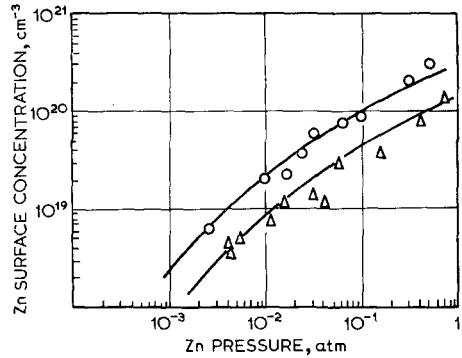
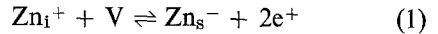


Figure 6 Solubility curves for zinc in GaAs at 1000°C.

interstitial and substitutional concentrations are related by an equation involving gallium vacancies:



where it is assumed that the interstitial species exists as a singly-ionised donor. A number of assumptions are often made:

- (i) The activity coefficient for holes is approximately unity. This is a good approximation for hole concentrations of about 10^{20} cm^{-3} and less [6].
- (ii) All of the substitutional zinc is ionised so that $C_s \approx p$, the hole concentration.
- (iii) Vacancy equilibrium is maintained. This must be true for an isoconcentration experiment, which takes place at thermal equilibrium.

Applying the law of mass action to equation 1 and employing the above assumptions, an approximate expression is found for the diffusion coefficient [3].

$$D \approx \left(\frac{3KD_i}{C_v} \right) C_s^2 \quad (2)$$

where K is an equilibrium constant, dependent on temperature only and C_v is the gallium vacancy concentration. This predicted relationship agrees well with figs. 3 and 5. The displacement of the lines in the two figures is explained by reference to equation 2. The diffusion coefficient is inversely proportional to C_v . If the arsenic species in the vapour is As_4 [4], then it can easily be shown that $C_v \propto [P_{\text{As}}]^{1/4}$ where P_{As} is the arsenic vapour pressure. The diffusion coefficients for the higher arsenic pressure should therefore be displaced below the dissociation pressure ones by a factor of about four. This agrees reasonably well with figs. 3 and 5.

At zinc concentrations less than the intrinsic carrier concentration, i.e. $C_s < n_i$, the approximation $p \simeq C_s$ is incorrect and $p = n_i$. The diffusion coefficient then becomes a constant given by

$$D_{\text{int}} \simeq \left(\frac{KD_1}{C_v} \right) n_i^2 \quad (3)$$

The quantity in brackets can be found from figs. 3 and 5. Assuming a value of 10^{18} cm^{-3} for n_i at 1000°C , values for D_{int} are obtained of $4 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$ for dissociation pressure and $2 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$ for the excess arsenic pressure. These may be compared to the values obtained from Boltzman-Matano analysis of normal diffusion profiles [3], since it seems likely that this method of analysis is valid at low concentrations. The values in [3] were $1 \times 10^{-12} \text{ cm}^2 \text{ sec}^{-1}$ and $3 \times 10^{-13} \text{ cm}^2 \text{ sec}^{-1}$ respectively.

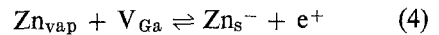
It has already been noted that these results do not agree with the theoretical prediction of Chang and Pearson [2]. This is surprising since their calculation was, in many respects, more sophisticated than the one outlined above. It seems likely that two of their assumptions were in error: (1) They assumed a doubly ionised interstitial donor, giving rise to a cubic dependence for diffusion coefficient at low C_s . (2) They did not make the assumption that all the zinc acceptors were ionised but used Fermi-Dirac statistics to calculate the ratio C_s^-/C_s over the whole range of C_s . For this calculation they used the simplification of replacing the valence band density of states function with a number of states located at the top of the valence band. They also ignored the activation energy of the zinc impurity levels. The assumptions are not valid for a heavily doped semiconductor. There is some experimental evidence that virtually all of the zinc is ionised at high concentrations [7], possibly due to the banding of zinc levels and subsequent merging of the impurity with the valence band.

It is interesting to compare figs. 1 and 5, each of which refers to zinc diffusion under conditions of an arsenic pressure of $4 \times 10^{-2} \text{ atm}$. The maxima shown in fig. 1 have been observed by several workers: two ideas have been put forward to explain the effect. It has been suggested that a maximum occurs because of a variation of hole activity, essentially due to a change in the valence band density of states function at high zinc doping [8]. The second suggestion is that maxima occur because of a breakdown in

vacancy equilibrium [3], i.e. the concentration of vacancies dropping below the thermal equilibrium value. It has been pointed out that the first explanation is unlikely because it would predict a maximum always occurring at the same value of zinc concentration, whereas in fact it varies from experiment to experiment, as shown in fig. 1. Isoconcentration tests provide a means of checking the second theory. An isoconcentration experiment, by definition, takes place under conditions of thermal equilibrium. Therefore no non-equilibrium effect should appear, and the theory would predict no maximum in the D versus C_s curve. No maximum exists either in fig. 3 or fig. 5, confirming the prediction. It seems likely that for chemical diffusion of zinc in GaAs (i.e. non-isoconcentration) it is not in general correct to assume that D is a function only of concentration, so the Boltzman-Matano type of analysis is not valid [9].

5.2. Solubility

The square law dependence of fig. 6 can be explained on a basis of assuming that a neutral zinc atom in the vapour joins the lattice as an ionised acceptor.



hence

$$[P_{\text{Zn}}] C_v = k C_s p \quad (5)$$

where $[P_{\text{Zn}}]$ is zinc vapour pressure and k is a constant. Assuming once again that $p \simeq C_s$, a square law is obtained. Using the fact that $C_v \propto [P_{\text{As}}]^{\frac{1}{2}}$, we have:

$$C_s = \{k[P_{\text{Zn}}][P_{\text{As}}]^{\frac{1}{2}}\}^{\frac{1}{2}} \quad (6)$$

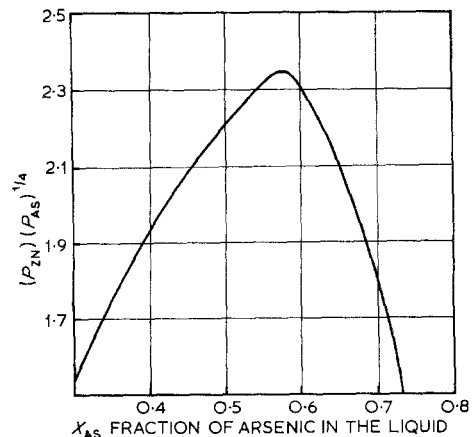


Figure 7 $[P_{\text{Zn}}][P_{\text{As}}]^{\frac{1}{2}}$ as a function of the fraction of arsenic in the liquid phase.

The two solubility lines should therefore be separated by a factor of 2.1. This agrees well with fig. 6.

It follows that the maximum attainable solubility when diffusing from the vapour phase corresponds to the maximum value of $[P_{Zn}][P_{As}]^{\frac{1}{2}}$. The maximum values for these pressures are obtained when a liquid phase is allowed to form in the ampoule. The vapour pressures have been determined by Shih *et al* [4] as functions of the composition of the liquid. Their data is used in fig. 7 to plot $[P_{Zn}][P_{As}]^{\frac{1}{2}}$ as a function of the fraction of arsenic in the liquid, X_{As} . It can be seen that a maximum occurs at $X_{As} = 0.57$. Reference to the curves of Shih *et al* show that this corresponds to a zinc pressure of 0.27 atm and an arsenic pressure of 0.70 atm. The data of fig. 6 shows that these conditions correspond to a maximum attainable solubility at 1000°C of $2.3 \times 10^{20} \text{ cm}^{-3}$. It would appear, therefore, that the highest solubility measured in

this work in diffusion 20 was a little high. However, the conditions for this particular diffusion were close to the optimum.

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