

Determination of vacancy jump frequency ratios and correlation factors of impurity diffusion and estimation of vacancy-impurity binding Gibbs free energies in dilute silver-antimony alloys

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1989 J. Phys.: Condens. Matter 1 3601

(<http://iopscience.iop.org/0953-8984/1/23/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.93

The article was downloaded on 10/05/2010 at 18:16

Please note that [terms and conditions apply](#).

Determination of vacancy jump frequency ratios and correlation factors of impurity diffusion and estimation of vacancy–impurity binding Gibbs free energies in dilute silver–antimony alloys

H Hagenschulte and Th Heumann

Institut für Metallforschung, Universität Münster, Wilhelm-Klemm-Strasse 10, D 4400 Münster, Federal Republic of Germany

Received 14 July 1988

Abstract. The dependences of intrinsic diffusion coefficients (D_{Sb} , D_{Ag}) and interdiffusion coefficients (\bar{D}) upon temperature and composition in dilute AgSb alloys have been measured. The interdiffusion coefficients $\bar{D}(0)$ obtained with infinitely dilute solutions agree well with tracer data for $D_{\text{Sb}}^*(0)$ from the literature. The ratio of the intrinsic diffusion coefficients was determined by applying the thin plate method. Within the error margins the ratio $D_{\text{Sb}}/D_{\text{Ag}}$ can be regarded as independent of concentration up to 3 at. % Sb. The values of $D_{\text{Sb}}/D_{\text{Ag}}(0)$ with infinitely dilute solutions decrease linearly with increasing temperature.

The jump frequency ratios w_4/w_0 , w_2/w_1 and w_3/w_1 were calculated according to the five-frequency model on the basis of the vacancy flow factor $L_{\text{AB}}/L_{\text{BB}}(0)$, the ratio of tracer diffusion coefficients $D_{\text{Sb}}^*/D_{\text{Ag}}^*(0)$ and the linear enhancement factor b_1 . From these the correlation factor f_{Sb} of impurity diffusion is obtained, which increases with temperature from 0.30 at 890 K to 0.49 at 1048 K, as expected.

The binding Gibbs free energy δg_1 of a vacancy–antimony pair has been estimated using four different methods of evaluation using the values measured in the present paper and diffusion data from the literature. The temperature dependence of δg_1 is critically discussed.

1. Introduction

The five-frequency model, which serves as the basis for the theory of Howard and Manning (1967), provides a detailed description of atomic jump behaviour in very dilute binary alloys with FCC structure. Assuming that only single vacancies interact with isolated impurity atoms, the jump frequency ratios w_2/w_1 , w_3/w_1 and w_4/w_0 (with w_i defined in the usual way) may be related to four experimentally obtainable diffusion quantities. These are the ratio of the tracer diffusion coefficients of the solute and the solvent $D_{\text{B}}^*/D_{\text{A}}^*$, the linear enhancement factor of solvent diffusion b_1 , the vacancy flow factor $L_{\text{AB}}/L_{\text{BB}}$ and the correlation factor f_{B} of impurity diffusion. However, only three of these quantities are required for the determination of the jump frequency ratios.

For the system AgSb only two of these quantities are known, namely $D_{\text{B}}^*/D_{\text{A}}^*$ and b_1 . Since a suitable second Sb radio-isotope is not available the correlation factor f_{B} cannot be determined by employing the usual isotope effect measurements (Rockosch and Herzig 1984). However, it is possible to calculate this quantity from the otherwise known jump frequency ratios.

The first aim of this work is to determine the jump frequency ratios at different temperatures. For this purpose previous diffusion investigations in the α -solid solution range (Sonder 1955, Schmidt 1978) of the system **AgSb** have been enlarged by precise measurements of the intrinsic diffusion coefficients D_B and D_A . These quantities yield the vacancy flow factor via the relation (Heumann 1979):

$$\frac{L_{AB}}{L_{BB}}(0) = \frac{D_A^*}{D_B^*}(0) \frac{1}{f_0} - \frac{D_A}{D_B}(0) \frac{\bar{V}_B}{\bar{V}_A} \quad (1)$$

where $\bar{V}_{A,B}$ is the partial molar volume of components A and B, and f_0 is the correlation factor of the pure host metal A. A further intention of this work is to provide a reasonable estimation of the binding Gibbs free energy δg_1 of a vacancy–impurity pair, i.e., the difference between Gibbs free energy of formation of a vacancy at a nearest-neighbour site of an impurity and at a site in the pure host metal. All available diffusion data should be employed for this purpose. The diffusion behaviour of an impurity in a host metal depends sensitively on the vacancy–impurity binding Gibbs free energy.

2. Experimental procedure

For the measurements of the intrinsic diffusion coefficients the thin plate method (Heumann 1977) was applied. **AgSb** alloys were prepared from materials with a nominal purity of 99.999%. Rods were first melted in quartz capsules under an argon atmosphere using a resistance furnace. In order to achieve a good mixing of the components they were melted a second time by RF heating in a graphite crucible of spectral purity. A remaining small porosity was eliminated by hammering, which reduced the rods from 9 mm to 6.4 mm in diameter. During the subsequent homogenisation anneal at $T = 1030$ K for one week, the alloys recrystallised to a mean grain size of about 1 mm. By means of the Bridgman method single crystals of pure silver were grown with the same diameter of 6.4 mm.

The rods were cut into thin plates of 1, 2 and 4 mm thickness by means of spark erosion. The front surfaces of the plates were precisely ground parallel to each other by using a special grinding and buffing attachment. Subsequent to the polishing of the front surfaces the plates were welded in a resistance furnace. The time of the welding treatment was 15 min at 1030 K under a pressure of 1 N cm^{-2} .

The arrangement of several thin plates, welded together to a complete diffusion couple, is shown in figure 1. The sample dimensions and the sandwich-like construction of single-crystalline **Ag** and coarse-grained **AgSb** plates are clearly seen. The grain structure appears after etching for one minute with a solution of 100 ml H_2O and 11 ml H_2SO_4 . A small CrO_3 crystal of about 1 mg was dissolved in this solution. In order to demonstrate the welding interfaces the same etching technique was applied.

Before the diffusion anneal the distances between the welding interfaces were measured with a microscope in dark field illumination at a magnification of 120. The individual measurement was performed at two plane-parallel ground surfaces. Each reading was repeated along three lines perpendicular to the welding interfaces. Subsequently the samples were annealed in quartz capsules in an argon atmosphere until the concentration was uniform; this yields the maximum possible Kirkendall migration for the given sample dimensions. The annealing times at the temperatures $T = 1048$ K, 1014 K and 971 K were 3, 4 and 5 months, respectively.

To avoid influences of surface diffusion and diffusion via the vapour phase plane-parallel layers at least 1 mm thick were removed from the existing ground surfaces and

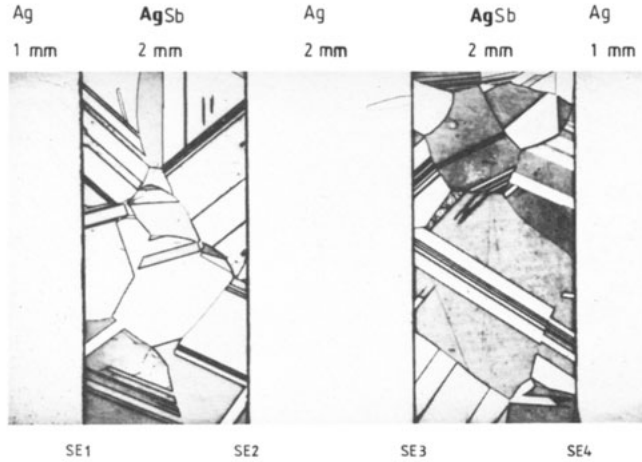


Figure 1. Thin plate sample; 14×.

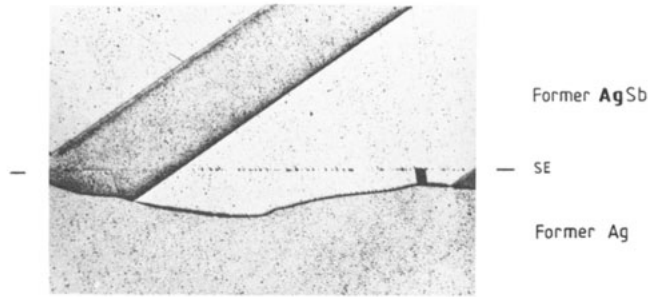


Figure 2. Welding interface SE after diffusion annealing, etched; 200×.

the distances between the welding interfaces were remeasured. Because of the specific sandwich-like arrangement (figure 1), which causes adjacent welding planes to move in opposite directions, the double welding interface displacement is determined in this way. After diffusion annealing a typical welding interface shows up as a thin dotted line (figure 2). The grain on the right top of the picture is—as well as the sloped twin—grown across the welding interface without producing any kink or curvature in the welding interface. This indicates perfect welding and an undisturbed diffusion.

In the case of annealing the samples to a complete homogenisation in concentration the ratio of the intrinsic diffusion coefficients for an arrangement of two plates is given by (Heumann 1977)

$$\frac{D_{Sb}}{D_{Ag}} = \frac{\bar{V}_{Sb} (c_{Sb}^- - c_{Sb}^+)(d^- - \delta) + c_{Sb}^- \delta}{\bar{V}_{Ag} (c_{Ag}^+ - c_{Ag}^-)(d^+ + \delta) - c_{Ag}^+ \delta} = \frac{\bar{V}_{Sb} (c_{Sb} - c_{Sb}^+)(d^+ + \delta) + c_{Sb}^+ \delta}{\bar{V}_{Ag} (c_{Ag}^+ - c_{Ag}^-)(d^+ + \delta) - c_{Ag}^+ \delta} \quad (2)$$

where $c_i^{-(+)}$ is the initial concentration in Sb-rich (Sb-deficient) plates (in mol cm⁻³); c_i is the final concentration of component i ($i = Ag, Sb$); $d^{-(+)}$ is the thickness of Sb-rich (Sb-deficient) plates; and δ is the welding interface displacement.

3. Results

3.1. Samples with finite thickness

The temperatures, concentrations and results for samples with finite thickness are listed in table 1. Initial concentrations as well as final homogeneous concentrations were

Table 1. Results from samples with finite thickness. Δl change of the sample length; \bar{d} mean plate thickness; 2δ mean double welding interface displacement; c_{Sb} final antimony concentration.

| Initial concentrations (at. %) | \bar{d} (μm) | Δl (μm) | 2δ (μm) | $D_{\text{Sb}}/D_{\text{Ag}}$ | c_{Sb} (at. %) |
|-----------------------------------|-----------------------------|------------------------------|-----------------------------|-------------------------------|-------------------------|
| $T = 1048 \text{ K}$ | | | mean value: | 1.51 ± 0.08 | |
| 0–1.87 | 1052 | +1.7 | 10.4 ± 2 | 1.57 ± 0.19 | 0.94 |
| 0–2.80 | 1056 | –1.2 | 14.4 ± 2 | 1.51 ± 0.11 | 1.40 |
| 0–3.96 | 1057 | +0.7 | 20.3 ± 2 | 1.51 ± 0.09 | 1.98 |
| 1.82–3.87 | 1082 | –0.1 | 9.6 ± 3 | 1.43 ± 0.23 | 2.85 |
| $T = 1014 \text{ K}$ | | | mean value: | 1.62 ± 0.09 | |
| 0–1.95 | 1002 | +1.3 | 10.3 ± 3 | 1.58 ± 0.25 | 0.98 |
| 0–2.94 | 1020 | +1.2 | 16.9 ± 2 | 1.63 ± 0.13 | 1.47 |
| 0–3.92 | 1016 | –0.8 | 24.2 ± 3 | 1.72 ± 0.17 | 1.96 |
| 1.91–3.78 | 1059 | +0.5 | 10.0 ± 2 | 1.54 ± 0.18 | 2.85 |
| $T = 971 \text{ K}$ | | | mean value: | 1.71 ± 0.09 | |
| 0–1.91 | 1092 | +0.3 | 12.0 ± 2 | 1.66 ± 0.19 | 0.96 |
| 0–2.89 | 1049 | +1.6 | 18.6 ± 2 | 1.74 ± 0.14 | 1.45 |
| 0–4.10 | 1073 | –0.9 | 26.8 ± 4 | 1.73 ± 0.22 | 2.05 |
| 1.95–3.74 | 1016 | –1.0 | 11.0 ± 2 | 1.72 ± 0.18 | 2.85 |

measured by electron microprobe analysis. The plate thicknesses of each sample differed by only a few $10 \mu\text{m}$, which allows the mean value $\bar{d} = (d^- + d^+)/2$ to be used in the evaluation. The error in the determination of the welding interface displacements is $\pm 1 \mu\text{m}$ and therefore an error of $\pm 2 \mu\text{m}$ results for the double displacement. In some cases, where greater corrections were necessary or where only less precise measurements were possible, an additional uncertainty of $\pm 1 \mu\text{m}$ is indicated. All other errors affecting the determination of $D_{\text{Sb}}/D_{\text{Ag}}$ are assumed to be negligible. The increase in sample length Δl , given in table 1, is obtained from changes in distance between the interfaces SE1 and SE3 or SE2 and SE4 (figure 1), because they moved in the same direction. Within the error margins mentioned above no lengthening of the sample was detectable. Due to the Kirkendall effect the formation of voids is in principle possible in originally Sb-rich plates. With very few exceptions no Kirkendall voids could be detected by microscopic inspection (figure 2), which allows us to assume that the measured welding interface displacements correspond to the real Kirkendall effect.

Within the error margins no concentration dependence can be derived from the values of the ratios of the intrinsic diffusion coefficients listed in table 1. Therefore the ratios $D_{\text{Sb}}/D_{\text{Ag}}(0)$ at infinitely dilute solution are given as mean values of the four data points at each temperature. The resulting linear temperature dependence is shown in figure 3.

3.2. Samples with infinite thickness

The samples with infinite thickness were prepared in a similar way to those with finite thickness with only minor differences in the arrangement of the plates (2 mm Sb-deficient, 4 mm Sb-rich, 2 mm Sb-deficient). For samples with double infinite thickness the boundary conditions were fulfilled by employing annealing times of 40 h at $T = 971 \text{ K}$ and 35 h at $T = 1014 \text{ K}$, 1048 K. Penetration curves of about 1 mm in length were produced in this way.

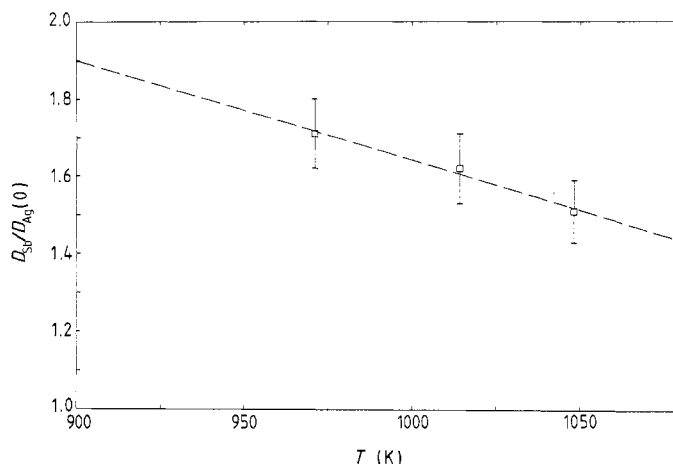


Figure 3. Ratio of the intrinsic diffusion coefficients $D_{Sb}/D_{Ag}(0)$ at infinitely dilute solution as function of temperature T .

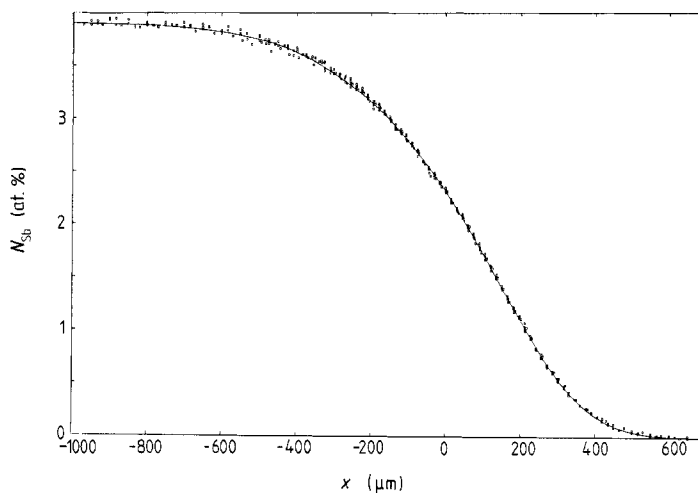


Figure 4. Diffusion profile (3.92 at. % Sb, pure Ag); $T = 1048$ K; $t = 35$ h.

A total of six concentration profiles were analysed for each sample by means of an electron microprobe. Following the semi-empirical method of Ziebold and Ogilvie (1963) the determination of the concentrations was accurate to 1.5%. As described by Heumann and Rottwinkel (1975), a fit was made to the superposition of the six individual sample profiles. A typical profile with the corresponding fitted curve is shown in figure 4. In order to calculate the chemical diffusion coefficients we employed the appropriate equation given by Sauer and Freise (1962) or Wagner (1969), where the general case of a concentration-dependent molar volume is taken into account. Because of a higher uncertainty in concentration in the peripheral zones of the profiles several samples with overlapping concentration ranges were used for the evaluation at each temperature. The chemical diffusion coefficients determined by this method are plotted against concentration in figure 5. There is good agreement in the range up to 3.5 at. % Sb between the data and the second-order polynomials

$$T = 1048 \text{ K} \quad \bar{D}(N_{Sb}) = 1.67 \times 10^{-13} (1 + 12.6 N_{Sb} + 1185 N_{Sb}^2) \text{ m}^2 \text{ s}^{-1} \quad (3a)$$

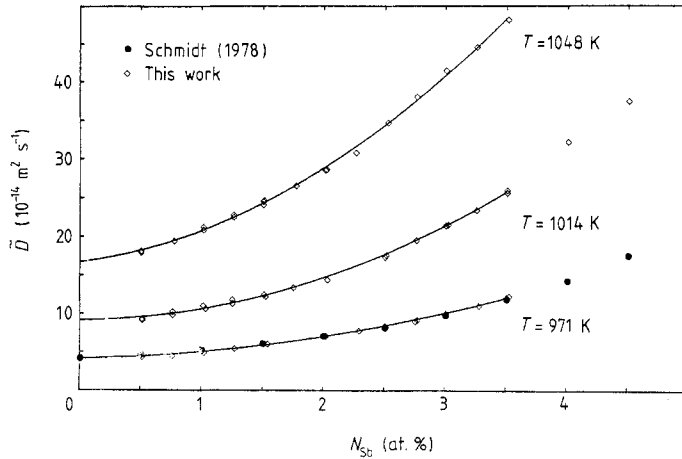


Figure 5. Interdiffusion coefficient \tilde{D} versus Sb concentration N_{Sb} .

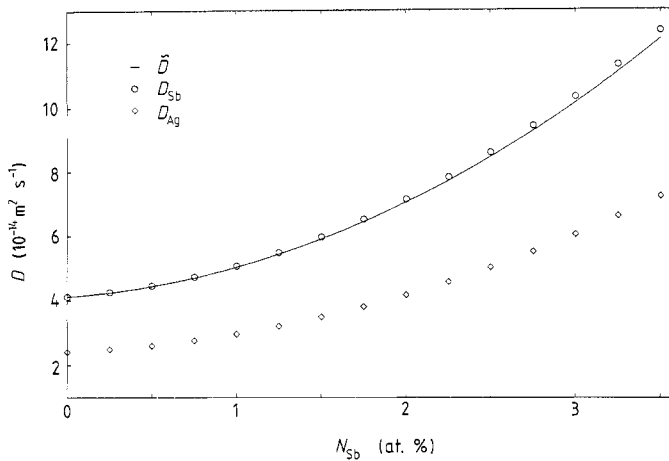


Figure 6. Interdiffusion coefficient \tilde{D} and intrinsic diffusion coefficients D_{Sb} , D_{Ag} as functions of Sb concentration at $T = 971$ K.

$$T = 1014 \text{ K} \quad \tilde{D}(N_{Sb}) = 9.13 \times 10^{-14} (1 + 2.2 N_{Sb} + 1425 N_{Sb}^2) \text{ m}^2 \text{ s}^{-1} \quad (3b)$$

$$T = 971 \text{ K} \quad \tilde{D}(N_{Sb}) = 4.12 \times 10^{-14} (1 + 9.1 N_{Sb} + 1318 N_{Sb}^2) \text{ m}^2 \text{ s}^{-1}. \quad (3c)$$

In all three cases the values $\tilde{D}(N_B \rightarrow 0)$ for infinitely dilute solution obtained from equations (3) agree well with tracer diffusion data of $D_B^*(0)$ (Sonder *et al* 1954, Schmidt 1978). Within the error margins of $\pm 5\%$ there is also agreement with the chemical diffusion coefficients measured by Schmidt (1978) at $T = 971$ K.

By means of the generalised Darken equation

$$\tilde{D} = c_A \bar{V}_A D_B + c_B \bar{V}_B D_A \quad (4)$$

the intrinsic diffusion coefficients D_{Sb} and D_{Ag} can be calculated using the ratios D_{Sb}/D_{Ag} determined in this work. For $T = 971$ K typical curves are shown in figure 6. In the investigated concentration range the difference between the D_{Sb} values and the chemical diffusion coefficients \tilde{D} is only very small.

Table 2. Values of D_{Sb}^*/D_{Ag}^* , D_{Sb}/D_{Ag} , L_{AB}/L_{BB} at infinitely dilute solution and enhancement factors b_1, b_2 at four temperatures.

| T (K) | D_{Sb}^*/D_{Ag}^* | D_{Sb}/D_{Ag} | L_{AB}/L_{BB} | b_1 | b_2 |
|---------|---------------------|-----------------|-----------------|-------|-------|
| 1048 | 6.24 | 1.51 | -0.76 | 27 | 1055 |
| 952 | 8.69 | 1.77 | -0.67 | 43 | 1523 |
| 926 | 9.60 | 1.84 | -0.66 | 47 | 1591 |
| 890 | 10.85 | 1.92 | -0.64 | 51 | 2237 |

Table 3. Jump frequency ratios $w_4/w_0, w_3/w_1, w_2/w_1$ and correlation factors f_{Sb} of antimony diffusion in silver at four temperatures.

| T (K) | w_4/w_0 | w_3/w_1 | w_2/w_1 | f_{Sb} |
|---------|-----------|-----------|-----------|----------|
| 1048 | 2.02 | 0.38 | 1.85 | 0.49 |
| 952 | 3.50 | 0.70 | 3.36 | 0.40 |
| 926 | 3.96 | 0.84 | 4.35 | 0.36 |
| 890 | 4.40 | 0.99 | 6.44 | 0.30 |

4. Jump frequency ratios and correlation factors

The data used to calculate the jump frequency ratios are summarised for four temperatures in table 2. Mean values from diffusion coefficients measured by Schmidt (1978), Sonder (1955) and Sonder *et al* (1954) were calculated for the ratio D_{Sb}^*/D_{Ag}^* . The ratios of the intrinsic diffusion coefficients were taken from figure 3 and the vacancy flow factors were determined according to equation (1). The enhancement factors are obtainable from the well known equation

$$D_A^*(N_B) = D_A^*(0)(1 + b_1N_B + b_2N_B^2 + b_3N_B^3 + \dots) \tag{5}$$

Since the enhancement factors are fitting parameters of this polynomial, where the order of the fitted polynomial depends on the considered concentration range, the accuracy of b_1 is sensitively related to the quality and the number of the data points used in the fitting procedure.

Measurements of the silver diffusion coefficient in dependence on the antimony concentration are available from Schmidt (1978) and Sonder (1955). Faupel and Hehenkamp (1986) obtained enhancement factors by fitting a third-order polynomial to the data of Schmidt (1978) in the concentration range $N_{Sb} < 0.05$. Sonder (1955) investigated the concentration dependence of the activation enthalpy Q and the frequency factor D_0 in the range up to 1.5 at. % Sb. By fitting a second-order polynomial with respect to the smaller concentration range, to the diffusion coefficients calculated from the Arrhenius equations given by Sonder (1955), we estimated another set of b_1 and b_2 values. In comparison with the b_1 values of Faupel and Hehenkamp (1986) considerably higher linear enhancement factors were obtained. Hence a recalculation of the enhancement factors was made on the basis of the diffusion data of both these authors. The values obtained for b_1 and b_2 are given in table 2.

The jump frequency ratios calculated by means of a computer program are listed in table 3. According to the following equation (Howard and Manning 1967)

$$f_B = (1 + 3.5Fw_3/w_1)/(1 + w_2/w_1 + 3.5 Fw_3/w_1) \tag{6}$$

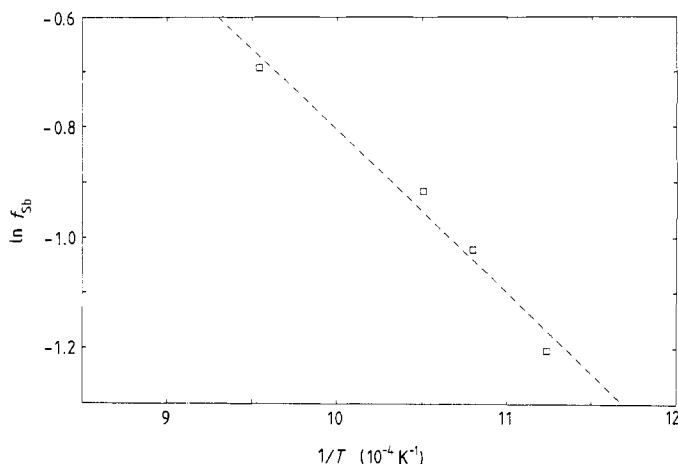


Figure 7. Correlation factor f_{sb} plotted logarithmically as function of the reciprocal temperature $1/T$.

where F is a function of w_4/w_0 , the correlation factor of impurity diffusion is calculated. Increasing values of f_B are obtained with increasing temperature (table 3), as is to be expected in the case of single vacancies.

The difference ΔQ of the activation enthalpies between solute and solvent diffusion has been calculated by Le Claire (1962) in terms of an electrostatic model. In ΔQ the quantity C is included, which takes into account the temperature dependence of the correlation factor f_B . According to the definition $C = k\{[d(\ln f_B/T)](1/T)\}$ Le Claire (1962) determined the value $C = -0.27$ eV for the AgSb system at $T \approx 1000$ K. A logarithmic plot (figure 7) of the f_B values from table 3 versus $1/T$, yields $C = -0.25$ eV, which is in good agreement with the value from the literature.

5. Estimation of binding Gibbs free energies

According to the definition of the binding Gibbs free energy δg_1 can be calculated straightforwardly, if the dependence of the vacancy concentration upon temperature and composition can be determined exactly. Since measurements of absolute vacancy concentrations are experimentally difficult to perform and since the exact evaluation also gives rise to many problems, several investigators have tried to estimate the binding Gibbs free energy using diffusion data only. In the following four of these methods will be briefly explained, which are applicable to the system AgSb.

(i) The basis of the first method is the well known relation between δg_1 and the jump frequencies w_3 and w_4 .

$$w_4/w_3 = \exp(-\delta g_1/kT). \quad (7)$$

Apart from theoretical considerations, the ratio w_4/w_3 cannot be calculated in a straightforward manner from the three other jump frequency ratios. An additional assumption is therefore required. For this purpose it was suggested (Arnhold *et al* 1981), that the mean jump frequency of a vacancy in a vacancy-impurity complex is approximately the same as in the pure solvent, i.e., $12w_0 \approx 4w_1 + 7w_3 + w_2$. Combined with equation (7), this assumption yields

$$\delta g_1 = -kT \ln \{(w_4/w_0)/[7 + 4(w_1/w_3) + (w_2/w_1)(w_1/w_3)]/12\}. \quad (8)$$

Although this assumption seems to be plausible in the case of weak binding, it is not expected to apply in general. Hence values of δg_1 calculated by equation (8) have to be examined carefully.

(ii) The ratio D_B/D_A serves as an important quantity when applying the second method. We employ previously derived equations (Heumann 1979), which relate the phenomenological coefficients L_{ik} to the intrinsic and tracer diffusion coefficients:

$$D_A = \left(\frac{N_B + 1}{2N_B} \frac{L_{AA}RT}{c_A} - \frac{N_A}{2N_B} D_A^*(N_B) \frac{1}{\bar{f}_A} + \frac{L_{BB}RT}{2c_B} - \frac{D_B^*(N_B)}{2\bar{f}_B} \right) \frac{V}{\bar{V}_B} \varphi \quad (9)$$

$$D_B = \left(\frac{N_A + 1}{2N_A} \frac{L_{BB}RT}{c_B} - \frac{N_B}{2N_A} D_B^*(N_B) \frac{1}{\bar{f}_B} + \frac{L_{AA}RT}{2c_A} - \frac{D_A^*(N_B)}{2\bar{f}_A} \right) \frac{V}{\bar{V}_A} \varphi \quad (10)$$

where N_i is the molar fraction of component i ($i = A, B$); and c_i is the concentration of component i (in mol cm⁻³). These equations, which may be regarded as an extension of the so-called random alloy model (Manning 1967), are useful in the case of very dilute solutions. The concentration-dependent molar volume V and the thermodynamic factor φ cancel out when the ratio D_B/D_A is formed. For dilute binary substitutional alloys ($N_B < 0.005$) with FCC structure the expression $L_{AA}RT/c_A$ is given according to Bocquet (1974) by

$$L_{AA}RT/c_A = (D_A^*(0)/f_0 N_A) (1 + bN_B). \quad (11)$$

The factor b is a function of the jump frequency ratios, which should however not be mistaken for the enhancement factor b_1 of solvent diffusion. In the case of small impurity concentrations one may apply an equation for $L_{BB}RT/c_B$ given by Manning (1967):

$$L_{BB}RT/c_B = D_B^* \{ 1 + [(1/f_0) - 1] N_B D_B^* / (N_A D_A^* + N_B D_B^*) \}. \quad (12)$$

The second term in parentheses is rather insensitive to small impurity concentrations. The quantities $1/\bar{f}_i$ ($i = A, B$) are defined as

$$1/\bar{f}_A = f^{\wedge}/f_A \quad 1/\bar{f}_B = f^{\vee}/f_B \quad (13)$$

where f_i is a correlation factor of atoms of components i , and f^{\vee} is a correlation factor of vacancies with respect to jumps with atoms of component i .

According to equation (6) the correlation factor f_B can be obtained from the jump frequency ratios. The quantity f^{\vee} is also calculable if the jump frequency ratios are known (Dirkes 1985). Since this estimation of δg_1 should be restricted to a concentration range where no contributions of higher-order complexes with two or more impurity atoms bound to a vacancy have to be taken into account, both these correlation factors and also $1/\bar{f}_B$ may be regarded as independent of concentration, while on the contrary $1/\bar{f}_A$ has a strong dependence on concentration. When distinguishing between vacancies bound to an impurity and free vacancies this different behaviour has to be taken into consideration. For free vacancies, just like in the pure metal A, $1/\bar{f}_A = 1/f_0$ is valid. For vacancies bound to impurities the quantity $1/\bar{f}_A^c$ is introduced which, analogous to $1/\bar{f}_B$, can be regarded as independent of concentration. Assuming that the number of free and bound vacancies is given by the Lomer equation (Lomer 1958) one obtains:

$$\frac{1}{\bar{f}_A} = \frac{(1 - 12N_B)(1/f_0) + 12 N_B \exp[-(\delta g_1/kT)](1/\bar{f}_A^c)}{1 - 12 N_B + 12 N_B \exp[-(\delta g_1/kT)]}. \quad (14)$$

$1/\bar{f}_A$ is to be calculated by employing equations (9) and (10), using the known ratio D_B/D_A from § 3.1. The application of equation (14) for two different concentrations,

e.g., $N_B = 0.001$ and $N_B = 0.005$, yields the vacancy–impurity binding Gibbs free energy δg_1 and the quantity $1/\bar{f}_A^c$. The estimation of δg_1 with equation (14) is restricted to vacancy–impurity pairs only. With respect to the extremely small concentrations chosen here it seems justified to neglect influences of higher-order complexes as indicated above. Finally, one should bear in mind that this is only an estimation.

(iii) In a paper (Heumann 1986) dealing with the theoretical background of a linear relation between normalised diffusion coefficients $D_A^*(N_B)/D_A^*(0)$ and normalised vacancy concentrations $N_V(N_B)/N_V(0)$, which was empirically found (Hehenkamp *et al* 1980, Hehenkamp and Faupel 1983, Hehenkamp 1983), another possibility for an estimation of the binding Gibbs free energy was derived. With A constant the relation

$$D_A^*(N_B)/D_A^*(0) - 1 = A (N_V(N_B)/N_V(0) - 1) \quad (15)$$

should hold (Hehenkamp and Faupel 1983).

For a reasonable estimation of binding Gibbs free energies it is necessary that the linear relation of equation (15) can be applied also in the range of second-order complexes, i.e., when two impurities are bound to a vacancy. For a single-vacancy mechanism the macroscopically observable diffusion of the solvent atoms is also influenced by the vacancy concentration and the mean effective jump frequencies $\bar{w}_i \bar{f}_i$, $i = 0, \dots, 12$ (Hehenkamp *et al* 1980). The mean jump frequency of solvent atoms in a complex with i impurities is denoted by \bar{w}_i , the mean correlation factor by \bar{f}_i . By using the additional assumption that the mean effective jump frequency in first-order complexes is approximately the same as in second-order complexes, we obtain after a transformation of the equations from the previous paper (Heumann 1986)

$$\delta g_1 = -kT \ln \left(\frac{(D_A^{2c}/D_A^*(0)) - 0.9 (D_A^{1c}/D_A^*(0)) - 0.1}{1.1(D_A^{2c}/D_A^{1c}) - 0.1 (D_A^{2c}/D_A^*(0)) + 0.2 (D_A^{1c}/D_A^*(0)) - 1.2} \right) \quad (16)$$

where D_A^{1c} is the mean diffusion coefficient of the 11 A atoms in a first-order complex and D_A^{2c} is the diffusion coefficient related to the 10 A atoms in a second-order complex. These diffusion coefficients are related to the enhancement factors b_1 and b_2 of solvent diffusion.

$$D_A^{1c}/D_A^*(0) = b_1/11 + 1 \quad (17a)$$

$$D_A^{2c}/D_A^*(0) = b_2/55 + 2(D_A^{1c}/D_A^*(0)) - 1. \quad (17b)$$

The enhancement factors can be obtained according to equation (5). Inserting the equations (17) into equation (16) the following relation between the enhancement factors b_1 and b_2 and the binding Gibbs free energy δg_1 is obtained.

$$\delta g_1 = -kT \ln \left[\frac{(11 + b_1)}{\{11 - [(0.1 b_1)/(1 + 5.5 b_1/b_2)]\}} \right]. \quad (18)$$

Obviously there is only a very small influence of the enhancement factor b_2 on the value of δg_1 obtained from equation (18).

(iv) In the framework of the complex model (Dorn and Mitchell 1966) and regarding a random solute distribution around vacancies according to Bérces and Kovács (1983) the binding Gibbs free energies of first-, second- and third-order complexes can be calculated using terms derived by Faupel and Hehenkamp (1986), if the enhancement factors b_1, b_2, b_3 of solvent diffusion and B_1, B_2 of solute diffusion are known. The enhancement factors of solute diffusion correspond to a polynomial of the form $D_B^*(N_B) = D_B^*(0) (1 + B_1 N_B + B_2 N_B^2 + \dots)$. In the temperature range $870 \text{ K} \leq T \leq 1048 \text{ K}$ the binding Gibbs free energy of first-order complexes in dilute AgSb alloys was

Table 4. Vacancy–antimony binding Gibbs free energies δg_1 (eV) calculated according to equations (8), (14), (18) and (19).

| T (K) | Equation (8) | Equation (14) | Equation (18) | Equation (19) |
|---------|--------------------|--------------------|--------------------|--------------------|
| 1048 | -0.12 ₀ | -0.11 ₃ | -0.13 ₄ | -0.19 ₇ |
| 952 | -0.13 ₄ | -0.12 ₅ | -0.16 ₄ | -0.18 ₁ |
| 926 | -0.13 ₇ | -0.13 ₀ | -0.16 ₆ | -0.17 ₅ |
| 890 | -0.14 ₂ | -0.12 ₈ | -0.17 ₃ | -0.18 ₄ |

estimated from experimental values of these five enhancement factors to be $\delta g_1 = -0.20$ eV (Faupel and Hehenkamp 1986).

In the case of short-range impurity–impurity repulsion Faupel and Hehenkamp (1987a) have derived an approximate relation for the estimation of the binding Gibbs free energy. D_A^{1c} and D_A^{2c} are again the diffusion coefficients of the A atoms in first- and second-order complexes, respectively, which are calculable from the enhancement factors b_1 and b_2 of solvent diffusion according to equations (17).

$$\delta g_1 = -kT \ln[(D_A^{2c}/D_A^{1c})/0.818]. \quad (19)$$

By applying this equation, Faupel and Hehenkamp (1987a) obtained the same value of δg_1 for the system AgSb as mentioned above. From this result it is concluded that without knowledge of the other enhancement factors a suitable estimation of δg_1 is possible. For our present estimates equation (19) is also used.

6. Results and discussion

The binding Gibbs free energies estimated when employing the four different methods for evaluating δg_1 are summarised in table 4. As explained in § 5, different assumptions were required for each of the four evaluation methods. In the discussion of the results obtained these assumptions have to be taken into consideration. The estimation of δg_1 by employing equation (8) is directly and that by employing equation (14) indirectly related to the three jump frequency ratios of table 3. These jump frequency ratios were calculated on the basis of several experimental findings. In the case of AgSb they yield meaningful results for the correlation factor of impurity diffusion. The good agreement of the values of these in principle very different estimations via equations (8) and (14) may be regarded as an indication that the introduced assumptions are in no way unreasonable.

The two other estimates via equations (18) and (19) yield somewhat larger absolute values of the binding Gibbs free energy. These evaluation methods are solely based on enhancement factors of solvent diffusion. The principal difficulties in determining these quantities by a polynomial fitting, even if reliable measurements of the solvent diffusion coefficient in dependence on concentration are available, have been explained in § 5. From this it has to be concluded, that the values obtained by means of equations (18) and (19) are afflicted with larger experimental uncertainties. It seems reasonable to assume that the enhancement factors for the system AgSb are not sufficiently accurate; in particular, the b_2 values of table 2 are apparently too large. The following argument may be regarded as an additional indication of this assumption.

From the ratio of the diffusion coefficients D_A^{2c}/D_A^{1c} , which is required for the calculation of δg_1 from equation (18) as well as from equation (19), additional information is obtained on the binding Gibbs free energy δg_2 of a vacancy in second-order

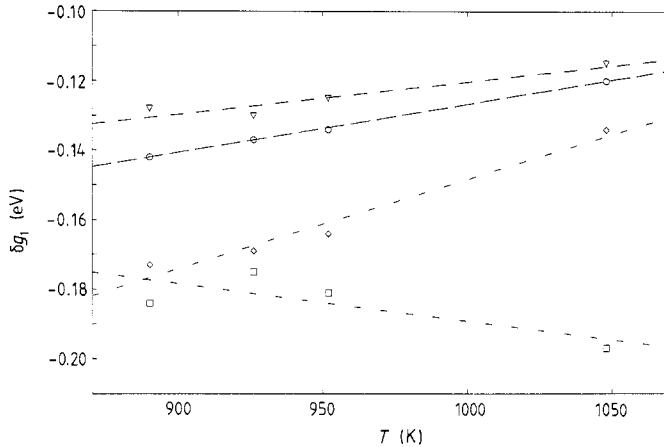


Figure 8. Binding Gibbs free energies δg_1 calculated by different methods applying equation (8) \circ , equation (14) ∇ , equation (18) \diamond or equation (19) \square , plotted versus temperature T .

complexes (Heumann 1986). For noble metals alloyed with excess valent impurities the relation $|\delta g_2| \leq 2|\delta g_1|$ is expected from the repulsive interaction of neighbouring impurities. In the present case of the system **AgSb** this relation is not fulfilled for all temperatures when using the b_1 and b_2 data listed in table 2. Such a result is physically unreasonable. The relation mentioned above would, however, be satisfied with somewhat smaller values of b_2 .

It was the purpose of the previous discussion to reveal that the differences of δg_1 obtained from the four independent evaluation methods are most likely to result from the uncertainties in the determination of the enhancement factors b_1 and b_2 . Hence we prefer the results which were calculated by applying equations (8) and (14).

In the following the temperature dependence of the binding Gibbs free energy δg_1 will be examined as a further criterion for assessing the quality of the results obtained. The values of δg_1 calculated with equation (19) seem to increase in absolute value with increasing temperatures, while there is a decrease in $|\delta g_1|$ when the other three methods are applied. This difference is clearly shown in figure 8, where all values of δg_1 of table 4 are plotted against temperature.

Recently binding Gibbs free energies calculated from enhancement factors according to equation (19) were also reported for the system **AgSn** in dependence on temperature (Faupel and Hehenkamp 1987b). The cited absolute δg_1 values increase drastically with temperature from $\delta g_1 = -0.15$ eV at $T = 629$ K to $\delta g_1 = -0.21$ eV at $T = 1127$ K. According to the Gibbs–Helmholtz relation

$$\delta g_1 = \delta h_1 - T\delta s_1 \quad (20)$$

where δh_1 is the binding enthalpy of a vacancy–impurity pair, and δs_1 is the binding entropy of a vacancy–impurity pair. A positive binding entropy δs_1 is needed for such a temperature dependence. But this requirement seems to be in contradiction with the entropy difference ΔS calculated from diffusion data:

$$\Delta S = S_B - S_A = (S_B^m + S_B^f) - (S_A^m + S_A^f). \quad (21)$$

Entropy contributions related to migration are labelled m and those related to formation f. The entropy difference ΔS is given by the general equation

$$D_B^*(0)/D_A^*(0) = (\nu_B/\nu_A) (f_B/f_0) \exp [(\Delta S/k) \exp (-H_B^f + H_B^m - H_A^f - H_A^m)/kT] \quad (22)$$

with the activation enthalpy of solvent diffusion $H_A = H_A^i + H_A^m$ and that of solute diffusion $H_B = H_B^i + H_B^m - C$ and $C = k (d \ln f_B / d 1/T)$. To a good approximation the ratio of the vibrational frequencies ν_B and ν_A is given by

$$[\nu_B / \nu_A = [(H_B + C) / H_A] (M_A / M_B)^{1/2} \quad (23)$$

where M_A and M_B are the atomic weights. Using diffusion data (Sonder *et al* 1954, Sonder 1955, Hehenkamp and Faupel 1983, Tomizuka and Slifkin 1954), clearly negative values of ΔS are obtained for AgSn as well as for AgSb. According to equation (21) ΔS consists of the migration entropy term $S_B^m - S_A^m$ and the formation entropy term $\delta s_1 = S_B^f - S_A^f$. When ΔS is split up into identical parts of migration and formation entropy contributions as a rough approximation, we obtain $\Delta S/2 = -1.61 k$ in the case of AgSn and $\Delta S/2 = -1.86 k$ for AgSb. In accordance with these results we expect a decrease in $|\delta g_1|$ with increasing temperature in both systems. Three of the four independent methods of estimating δg_1 (figure 8) fulfil this requirement.

The binding enthalpy δh_1 and the binding entropy δs_1 may be regarded as temperature independent in the considered temperature range. Therefore the binding Gibbs free energy should depend linearly on temperature. The δg_1 values obtained by employing equation (8) fulfil this expectation excellently (figure 8). It therefore seems reasonable to evaluate the binding entropy from the slope of the straight line, although the investigated temperature range is relatively small. The value $\delta s_1 = -1.61 k$ is obtained, which is in adequate agreement to $\Delta S/2 = -1.86 k$ with respect to the somewhat arbitrary choice of the factor 1/2 when characterising δs_1 .

The corresponding binding enthalpy δh_1 is given by the intersection with the δg_1 axis for $T = 0$ K and is found to be $\delta h_1 = -0.26$ eV. Within the error margins this result is in good agreement with the value of $\delta h_1 = -0.23_5$ eV calculated by Flynn (1962).

It was the purpose of these comments to demonstrate that estimates of binding Gibbs free energies, which rely on enhancement factors only, have to be examined critically. As shown in the present calculation for the system AgSb these fitted parameters may be afflicted with larger errors. In contrast to the estimations with equation (18) and equation (19) the two other methods of estimating δg_1 via equations (8) and (14) are based on additional reliable experimental information like D_B^*/D_A^* , the correlation factor f_B , the vacancy flow factor L_{AB}/L_{BB} , the intrinsic diffusion coefficients and finally the three jump frequency ratios, which describe the relationships with respect to the five-frequency model.

Acknowledgments

The authors wish to thank Professor Dr Chr Herzig and Professor Dr V Ruth for the critical reading of the manuscript. The financial support of Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

- Arnhold V, Dayananda M A and Heumann T 1981 *Verhandlungen DPG (VI)* **16** 365
 Bérces G and Kovács I 1983 *Phil. Mag. A* **48** 1883
 Bocquet J L 1974 *Acta Metall.* **22** 1

- Dirkes H 1985 *PhD Thesis* Münster University
Dorn J E and Mitchell J B 1966 *Acta Metall.* **14** 170
Faupel F and Hehenkamp T 1986 *Phys. Rev. B* **34** 2116
—— 1987a *Acta Metall.* **35** 771
—— 1987b *Mater. Sci. Forum* **15–18** 1207
Flynn C P 1962 *Phys. Rev.* **125** 881
Hehenkamp T 1983 *DIMETA 82, Diffusion in Metals and Alloys, Diffusion and Defect Monograph Series* vol 7, p 100
Hehenkamp T and Faupel F 1983 *Acta Metall.* **31** 691
Hehenkamp T, Schmidt W and Schlett V 1980 *Acta Metall.* **28** 1715
Heumann T 1977 *Z. Naturf. a* **32** 54
—— 1979 *J. Phys. F: Met. Phys.* **9** 1997
—— 1986 *Z. Metallkunde* **77** 274
Heumann T and Rottwinkel T 1975 *Z. Naturf. a* **30** 1282
Howard R E and Manning J R 1967 *Phys. Rev.* **154** 561
Le Claire A D 1962 *Phil. Mag.* **7** 141
Lomer W A 1958 *Vacancies and Other Point Defects in Metals* vol 23 (London: Institute of Metals) p 85
Manning J R 1967 *Acta Metall.* **15** 1817
Rockosch H J and Herzig C 1984 *Phil. Mag. A* **49** 717
Sauer E and Freise V 1962 *Z. Elektrochem.* **66** 353
Schmidt W 1978 *Diploma Thesis* Göttingen University
Sonder E 1955 *Phys. Rev.* **100** 1662
Sonder E, Slifkin L and Tomizuka C T 1954 *Phys. Rev.* **93** 970
Tomizuka C T and Slifkin L 1954 *Phys. Rev.* **96** 1610
Wagner C 1969 *Acta Metall.* **17** 99
Ziebold T O and Ogilvie R E 1963 *Anal. Chem.* **35** 322