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# Calculation of the solvent and solute enhancement factors in BCC metals assuming a hypothetical structure with fourteen first nearest neighbors

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## Abstract

In this paper the solute and solvent enhancement factors in a hypothetical body centered cubic (b.c.c) structure having fourteen first nearest neighbors are calculated by using a statistical model for diffusion in dilute alloys. Inherent to the model is the assumption of the equality of the first and second nearest neighbor jump distances, since in the b.c.c structure the difference between these distances, respectively, is only  $\sim 13.5\%$ . The number of parameters required for fitting to evaluate the enhancement factors ( $b$  and  $B$ ) is substantially reduced in comparison to existing models and therefore fewer experiments are necessary. Correlation effects are implicit in the calculated values of  $b$  and  $B$ . The results of the fitting provide values for the frequency ratios, the additional energies required to form a vacancy in the vicinity of a solute and for the binding energies between solute pairs, i.e., between the reference and tracer solute. Values of  $b$  and  $B$  in several dilute alloys were calculated at different temperatures. In general there is a good agreement between experimental and calculated values of  $b$  and  $B$  in the alloys tested. The equations for  $b$  and  $B$  can be used for temperatures where no experimental data exist.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Diffusion enhancement of solvent and solute in dilute alloys by a small impurity concentration has been observed and reported in several communications [1–4]. The solvent enhancement factor has received wide attention [5–11], but less consideration has been given to the evaluation of the solute enhancement factor. Theoretical evaluation of these factors for different structures is essential to develop an insight into the diffusion mechanism and to be able to evaluate the meaning of the experimental data. The enhancement factors are usually defined [1] by the expressions:

$$\begin{aligned} D(c) &= D(0) [1 + b_1c + b_2c^2 + \dots] \\ D_2(c) &= D_2(0) [1 + B_1c + B_2c^2 + \dots], \end{aligned} \quad (1)$$

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where  $D(c)$  and  $D_2(c)$  are the solvent and solute diffusivities in a dilute alloy,  $b_i$  and  $B_i$  are their diffusion enhancement factors, respectively, and ' $c$ ' is the solute concentration. The factors  $b$  and  $B$  may be evaluated experimentally from equations (1) if  $D(0)$  and  $D_2(0)$ , the self and the solute diffusion coefficients in pure solvent, are known and by measuring  $D(c)$  and  $D_2(c)$  at various solute concentrations. Solute concentrations in dilute alloys should not exceed  $\sim 2$  at.-%.

Various approaches were suggested to evaluate the above equations by taking into consideration the influence of the second and more remote neighbors [1, 4, 12–14]. The equations in these models contain many unknowns, which can be evaluated by least squares fitting to the experimental data [8, 10, 11, 15]. For example, the expressions for ' $b$ ' [12] and ' $B$ ' [14, 15] have 6 and 11 parameters, respectively. In order to get accurate results by least squares fitting of

equations having 6 or 11 parameters, the use of at least 7 or 12 sets of experiments, respectively, are required. It would, however, be desirable to reduce the number of experiments for the evaluation of  $b$  and  $B$ , which is the subject of this communication.

In b.c.c structures the eight first nearest neighbors (FNN) are at  $\frac{a\sqrt{3}}{2} \approx 0.866a$ , which is only  $\sim 13.5\%$  away from the six second nearest neighbors (SNN), which are at a distance ‘ $a$ ’ from a reference atom. Therefore, in any model for diffusion in b.c.c metals it is reasonable to include also the effect of the SNN. In the model suggested in this communication, the influence of the SNN is taken into account by calculating the diffusion parameters as if it would have been an FNN. Thus, in our model, a hypothetical lattice with 14 FNN is assumed. Consequently the designations of all other sites are modified accordingly (that is, the third, fourth and fifth become second, third and fourth neighbors, respectively). It will be shown, that in such a model, only 4 and 6 unknowns are required for the evaluation by least squares fitting of  $b$  and  $B$ , respectively. An appreciable reduction in the number of experiments can thus be achieved using our approach, without affecting significantly the results and our understanding of diffusion behavior in b.c.c systems.

A description of the model and the calculations are presented in section 2. Section 3 compares the experimental and calculated results obtained by the suggested approach and in section 4 the work is summarized.

## 2. Calculations

Because of the small difference in the distances between the FNN and the SNN, it will be assumed that these are equivalent from the diffusion behavior point of view. Thus, the jump distances will be considered as equal and as a consequence, altogether 14 equi-distant FNN will be assumed in the b.c.c structure. The model refers to a vacancy controlled diffusion mechanism. Correlation effects are implicitly indicated in the expression of the enhancement factor expressed as  $b_{\text{eff}}$ , but are not explicitly specified.

Cubic lattices are isotropic and all six orthogonal directions are equally likely, thus the probability for any one atomic jump in the  $x$  direction is  $p_x = 1/6$ . The selfdiffusion coefficient in a b.c.c structure is thus

$$D = \frac{1}{6}\Gamma x^2 f = \frac{1}{8}\Gamma a^2 f. \quad (2)$$

$\Gamma$ ,  $x$ ,  $f$  and  $a$  are the average number of jumps made per unit time of the solvent atom, the magnitude of its jump distance, the correlation factor and the lattice parameter, respectively.  $\Gamma$ , the average number of jumps made by a solvent atom in unit time at a rate  $\omega_0$  is given by

$$\Gamma = 14\omega_0 \exp\left(-\frac{g}{kT}\right). \quad (3)$$

In equation (3)  $g$  is the free energy change for vacancy formation in the pure solvent. Similarly, the selfdiffusion coefficient in pure solvent can be expressed as

$$D(0) = \frac{14}{8}a_0^2\omega_0 \exp\left(-\frac{g}{kT}\right) f_0. \quad (4)$$

In (4)  $a_0$  and  $f_0$  are the lattice parameter and correlation factor in pure solvent, respectively. With the above, and applying only the linear term of equation (1) we can write for diffusion in a dilute alloy

$$\begin{aligned} D(c) &= \frac{1}{8}\Gamma(c)a^2 f(c) = D(0)[1 + bc] \\ &= \frac{1}{8}14\omega_0 \exp\left(-\frac{g}{kT}\right) a_0^2 f_0 [1 + bc]. \end{aligned} \quad (5)$$

Equation (5)—under the assumption that the concentration and temperature dependence and the unit cell dimension can be neglected and taken as being equal to those in pure solvent—can be written as

$$\Gamma(c) = 14\omega_0 \exp\left(-\frac{g}{kT}\right) [1 + bc] \frac{f_0}{f(c)}. \quad (6)$$

Expanding  $f(c)$  in a series as

$$f(c) = f_0 + \left.\frac{\partial f}{\partial c}\right|_{c=0} c + \dots \quad (7)$$

neglecting the higher terms in  $c$  in equation (7), applying the approximation of  $\frac{1}{1+x} = 1 - x + x^2 + \dots$  for  $x < 1$ , multiplying equation (6) by  $(1 + bc)$  and again neglecting the higher terms, one can write for  $\Gamma(c)$

$$\Gamma(c) = 14\omega_0 \exp\left(-\frac{g}{kT}\right) \left[1 + c \left(b - \frac{A}{f_0}\right)\right]. \quad (8)$$

$A$  denotes  $\frac{\partial f}{\partial c}$  of equation (7). For details see appendix A. Let us denote  $(b - A/f_0)$  as  $b_{\text{eff}}$ , which takes into account correlation effects. Thus equation (8) can be expressed as

$$\Gamma(c) = 14\omega_0 \exp\left(-\frac{g}{kT}\right) [1 + cb_{\text{eff}}]. \quad (8a)$$

### 2.1. Calculation of $b$

We shall follow the procedure outlined by Le Claire in his classic work [12] and reproduce his equilibrium equations for solvent diffusion in dilute solid solutions:

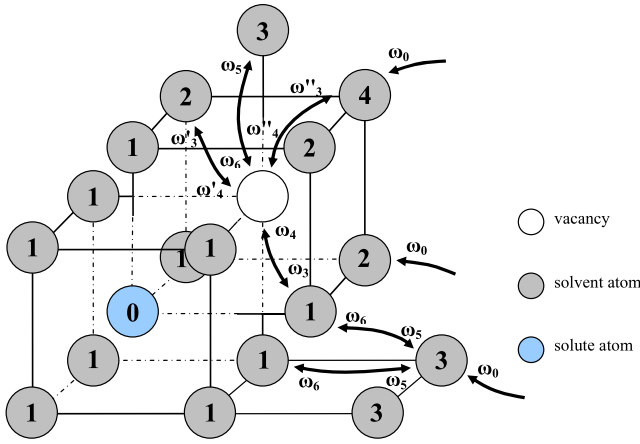
$$\omega'_4 = \omega'_3 \exp\left[\frac{-\Delta g_1}{kT}\right] \quad (9a)$$

$$\omega''_4 = \omega''_3 \exp\left[\frac{-\Delta g_1}{kT}\right] \quad (9b)$$

$$\omega_3 \exp\left[\frac{-\Delta g_1}{kT}\right] = \omega_4 \exp\left[\frac{-\Delta g_2}{kT}\right] \quad (9c)$$

$$\omega_6 = \omega_5 \exp\left[\frac{-\Delta g_2}{kT}\right] \quad (9d)$$

$\omega_i$  refer to the various solvent jump frequencies, and  $\Delta g_i$  is the additional free energy (i.e. the negative of the binding energies) to form a vacancy at FNN and SNN sites of the solute atom, respectively. Figure 1 is a schematic illustration of the hypothetical structure using the notation of our model which considers FNN and SNN as being equivalent. The reference solute (RS) in its initial position is indicated by ‘0’ and the other sites are labeled by their relative locations from the RS (i.e., being first, second, third



**Figure 1.** A schematic illustration of two unit cells in the hypothetical BCC structure showing the possible solvent jumps and their respective frequencies. The atom marked ‘0’ is the reference solute, and the numbers represent the coordination of the sites relative to the reference solute.

or fourth neighbors, respectively). All atomic sites from which a solvent jump can be made to the FNN of the RS are taken into account. Equations (9) take the following form when applying our concept regarding jump distances and considering the additional free energies for vacancy formation as  $\Delta g_1 = \Delta g_2 = \Delta g$ . The assumption that the additional free energies to form a vacancy at an FNN and an SNN site to the RS are about the same is a consequence of the fact that their distances from the RS differ by no more than  $\sim 13.4\%$ . Therefore it is considered that the influence of RS on the tendency for vacancy formation on these sites is about the same. Equations (9a)–(9d) can be written as

$$\begin{aligned} \omega_4'' &= \omega_3'' \exp\left[\frac{-\Delta g}{kT}\right] & \omega_4 &= \omega_3 \\ \omega_4' &= \omega_3' \exp\left[\frac{-\Delta g}{kT}\right] & \omega_6 &= \omega_5 \exp\left[\frac{-\Delta g}{kT}\right]. \end{aligned} \quad (10)$$

The equality of  $\omega_4$  and  $\omega_3$  is the consequence of the model which assumes that the free energy changes for vacancy formation in (9c) are equal.

Jumps remove an FNN vacancy to second, third and fourth neighbors away from the influence of the RS. Frequencies are influenced by the vacancy RS binding. But the probability of jumps to the second coordination shell from the first one is assumed to be just the same as to the third or to the fourth shell, thus the following jump frequencies are equal

$$\omega_3' = \omega_5 = \omega_3''. \quad (10a)$$

Vacancy jumps executing an exchange with a solvent atom with the frequencies indicated in (10a) are escape jumps from an FNN site. As a consequence of this assumption the jump frequencies

$$\omega_6 = \omega_4' = \omega_4'' \quad (10b)$$

are also equal. See appendix B.

Let  $N_i$  be the number of solute atoms and  $p$  the fraction of these that have vacancies at an FNN associated with them: if  $p$  is given by

$$p = 14 \exp\left(-\frac{g + \Delta g}{kT}\right) \quad (11)$$

the number of solvent jumps per unit time affected by these associated vacancies is then

$$N_i p (6\omega_3 + 3\omega_3' + \omega_3'' + 3\omega_5) \quad (11a)$$

and on the basis of equation (10a) this can be rewritten as

$$N_i p (6\omega_3 + 7\omega_5). \quad (11b)$$

Appendix C presents details of equation (11a).

Let us now consider jumps of vacancy–solvent exchanges that are outside the first coordination shell of the solute atoms. If  $N_s$  is the total number of crystal sites, the solute concentration can be expressed as  $c = \frac{N_i}{N_s}$ . The number of solvent sites which are outside the first coordination shell of the solute atoms is then

$$N_s - (z + 1) N_i = N_s(1 - 15c), \quad (12)$$

where  $z$  is the coordination number in the hypothetical structure.  $n_v$  free vacancies are randomly distributed on  $N_s(1 - 15c)$  solvent sites. The number of vacancies on SNN sites is then

$$n_v \frac{12N_i}{N_s(1 - 15c)}, \quad (13a)$$

since there are 12 such sites, and thus the number of vacancy–solvent exchanges is

$$n_v \frac{12N_i}{N_s(1 - 15c)} (4\omega_6 + 10\omega_0). \quad (13b)$$

The four  $\omega_6$  jump frequencies are actually  $\omega_4'$  type of which two have  $\frac{a\sqrt{3}}{2}$  and two ‘ $a$ ’ jump distances, respectively. According to equation (10b), however, these are equal to  $\omega_6$ . All jump distances from a site 2 to an FNN are assumed to be equal and of  $\omega_4'$  type.  $\omega_0$  is the pure solvent jump frequency.

Similarly for the 24 third and 8 fourth neighbor sites of a solute atom, the relations for the solvent–vacancy exchanges are, respectively

$$n_v \frac{24N_i}{N_s(1 - 15c)} (2\omega_6 + 12\omega_0) \quad (14)$$

and

$$n_v \frac{8N_i}{N_s(1 - 15c)} (\omega_6 + 13\omega_0). \quad (15)$$

In (14), the two  $\omega_6$  solvent vacancy exchanges from third neighbor sites both remove the solvent from the FNN of the RS. Twelve jumps of the vacancy occur by  $\omega_0$  frequencies away from the effect of the RS. In equation (15) the jump frequency is actually of  $\omega_4'$  type, but according to (10b) it is also equal to  $\omega_6$ .

The following relation is obtained by summing up equations (13b)–(15)

$$n_v \frac{8N_i}{N_s(1-15c)} (13\omega_6 + 64\omega_0). \quad (16)$$

The number of sites in the lattice where free vacancies beyond the fourth neighbors may reside is

$$n_v - n_v \frac{44N_i}{N_s(1-15c)}. \quad (17)$$

Each of these vacancies may execute fourteen  $\omega_0$  jumps resulting in the following solvent free-vacancy exchanges

$$\left[ n_v - n_v \frac{44N_i}{N_s(1-15c)} \right] 14\omega_0. \quad (18)$$

With the above expressions the total solvent jump rate per solvent atom can then be written as:

$$\begin{aligned} \Gamma(c) = & \frac{1}{N_s(1-c)} \left[ 14N_i \exp\left(-\frac{g + \Delta g}{kT}\right) (6\omega_3 + 7\omega_5) \right. \\ & + n_v \frac{8N_i}{N_s(1-15c)} (13\omega_6 + 64\omega_0) \\ & \left. + \left( n_v - \frac{n_v 44N_i}{N_s(1-15c)} \right) 14\omega_0 \right]. \end{aligned} \quad (19)$$

Following Le Claire [12],  $n_v$  can be expressed as

$$n_v = N_s(1-14c) \exp\left(\frac{-g}{kT}\right). \quad (20)$$

Substituting for  $n_v$  in equation (19), using the approximation of  $\frac{1}{1-15c} = 1 + 15c$  since  $c$  is less than 2%, retaining only the linear terms in  $c$ , expressing  $N_i$  in terms of  $c$  ( $c = \frac{N_i}{N_s}$ ) and with equation (11a) expressed as  $N_i p(6\omega_3 + 7\omega_5)$  based on relation (10a), an equation for the solvent jump rate per solvent atom can be obtained as

$$\begin{aligned} \Gamma(c) = & 14\omega_0 \exp\left(-\frac{g}{kT}\right) \left[ c \left\{ \left( 6\frac{\omega_3}{\omega_0} + 7\frac{\omega_5}{\omega_0} \right) \exp\left(-\frac{\Delta g}{kT}\right) \right. \right. \\ & \left. \left. + \frac{1}{7} \left( 52\frac{\omega_6}{\omega_0} - 143 \right) \right\} + 1 \right]. \end{aligned} \quad (21)$$

After substituting for  $\omega_5$  from relation (10) one obtains

$$\begin{aligned} \Gamma(c) = & 14\omega_0 \exp\left(-\frac{g}{kT}\right) \left[ c \left\{ 6\frac{\omega_3}{\omega_0} \exp\left(-\frac{\Delta g}{kT}\right) \right. \right. \\ & \left. \left. + \frac{1}{7} \left( 101\frac{\omega_6}{\omega_0} - 143 \right) \right\} + 1 \right]. \end{aligned} \quad (21a)$$

Equating equations (8a) and (21a) one obtains

$$c \left\{ 6\frac{\omega_3}{\omega_0} \exp\left(-\frac{\Delta g}{kT}\right) + \frac{1}{7} \left( 101\frac{\omega_6}{\omega_0} - 143 \right) \right\} + 1 = cb_{\text{eff}} + 1. \quad (22)$$

Thus  $b_{\text{eff}}$  can be expressed as

$$b_{\text{eff}} = 6\frac{\omega_3}{\omega_0} \exp\left(-\frac{\Delta g}{kT}\right) + \frac{1}{7} \left( 101\frac{\omega_6}{\omega_0} - 143 \right). \quad (23)$$

## 2.2. Calculation of $B$

In a schematic illustration of a b.c.c structure with the RS at site ‘0’ the possible jumps of a solute atom to various sites and their respective frequencies were indicated and the equilibrium equations were expressed [14, 15] as

$$\omega_{23} \exp\left(\frac{\Delta g_1}{kT}\right) = \omega_{24} \exp\left(\frac{\Delta g_{p1}}{kT}\right) \quad (24a)$$

$$\omega'_{23} \exp\left(\frac{\Delta g_2}{kT}\right) = \omega'_{24} \exp\left(\frac{\Delta g_{p2}}{kT}\right) \quad (24b)$$

$$\begin{aligned} \omega_{12} \exp\left(\frac{\Delta g_2}{kT}\right) \exp\left(\frac{\Delta g_{p1}}{kT}\right) \\ = \omega_{21} \exp\left(\frac{\Delta g_1}{kT}\right) \exp\left(\frac{\Delta g_{p2}}{kT}\right) \end{aligned} \quad (24c)$$

$\Delta g_i$  denote the free energy required to form a vacancy at the appropriate sites, as indicated earlier  $\Delta g_{p1}$  and  $\Delta g_{p2}$  are the additional free energies for breaking solute–solute bonds at first and second nearest neighbors, respectively (i.e., that of tracer solute and RS). These energies enable the respective tracer solute–vacancy exchanges. The meaning of  $\omega_{ij}$  was described earlier [14, 15]. Briefly, of these,  $\omega_{12}$  type jumps are associative to form FNN solute–solute pairs, but they are also dissociative jumps of the SNN solute–solute pair.  $\omega_{21}$  is the reverse jump of the above.  $\omega_{24}$  type jump frequencies are also associative forming FNN solute–solute pairs, whereas the  $\omega_{23}$  ones indicate their reverse jumps.  $\omega'_{23}$  type frequencies represent SNN jumps to fourth neighbors of the RS, and their reverse jumps occur with frequencies of  $\omega'_{24}$ . All other, more remote, jumps occur with frequencies  $\omega_2$ . In the above method to calculate  $B$  [14, 15], 11 unknowns are present and therefore at least 12 experimental sets are needed for their meaningful evaluation by fitting. In the suggested hypothetical b.c.c model with 14 FNN, the solute–vacancy exchanges of the respective solutes occur with the jump frequencies indicated in figure 2. The following equalities can be written:

$$\Delta g_1 = \Delta g_2 = \Delta g \quad (25a)$$

$$\Delta g_{p1} = \Delta g_{p2} = \Delta g_p. \quad (25b)$$

The rationale of equation (25b) is the same as the one that permitted the equalities in (25a), namely, the additional free energies of breaking solute–solute bonds at FNN and SNN are assumed to be the same. This also implies that equations (24a)–(24c) can be reduced to

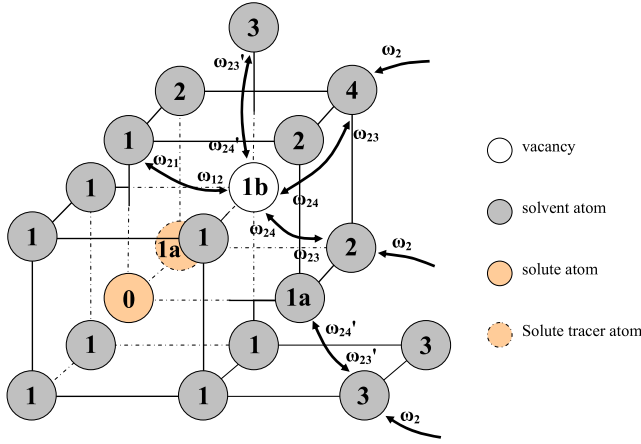
$$\frac{\omega_{24}}{\omega_{23}} = \frac{\omega'_{24}}{\omega'_{23}} \quad (26a)$$

$$\omega_{12} = \omega_{21} \quad (26b)$$

$$\omega_{23} \exp\left(\frac{\Delta g}{kT}\right) = \omega_{24} \exp\left(\frac{\Delta g_p}{kT}\right). \quad (26c)$$

Expression (25b) is a consequence of the same consideration as (25a) as indicated above in calculating ‘ $b$ ’. Expression (26b) follows from (24c) because of the assumed equalities in expressions (25a) and (25b).

The approach presented above for solvent jumps can also be used for calculating  $B$ , but the solvent atoms jump will be



**Figure 2.** A schematic illustration of two unit cells in the hypothetical BCC structure showing the possible tracer–solute jumps and their respective frequencies. The atom marked ‘0’ is the reference solute, and the numbers represent the coordination of the sites relative to the reference solute.

replaced by tracer–solute exchanges with the vacancies. Tracer atoms may occupy all the lattice sites except those already occupied by the reference solutes. In brief, let  $N_i$  be the number of solute atoms and  $p$  the fraction of these that have vacancies at an FNN associated with them: if  $p$  is given by

$$p = 14 \exp\left(-\frac{g + \Delta g}{kT}\right) \quad (27)$$

the number of such bond vacancies in the entire crystal is  $N_i p$ . The number of tracer atoms which can be FNN to bond vacancies is then  $N_i p \exp\left(-\frac{\Delta g}{kT}\right)$  (for details see appendix A in [14]). The total number of tracer jumps associated with bond vacancies is

$$N_i p \exp\left(-\frac{\Delta g}{kT}\right) \left[ 6\omega_{12} + (4\omega_{24} + 3\omega'_{24}) \exp\left(-\frac{\Delta g_p}{kT}\right) \right]. \quad (28)$$

Equation (28) is a consequence of the following considerations:

- A tracer at an SNN (site ‘2’) can execute an exchange with a bond vacancy at site ‘1b’ with a frequency of  $\omega_{24}$ . There is a probability for three such jumps. Further, the same bond vacancy can perform an exchange with a tracer at site ‘4’ with the same frequency, and thus four jumps with  $\omega_{24}$  frequencies are possible. All these jumps have a jump distance of  $a\frac{\sqrt{3}}{2}$ . Realizing these jumps does not require extra energy for breaking a bond between tracer–RS, but energy is required for pairing tracer and RS at FNN sites.
- Tracers at FNN sites may also exchange with a vacancy at site ‘1b’ with a frequency of  $\omega_{12}$ . There is a possibility for three such jumps of  $a\frac{\sqrt{3}}{2}$  length. Further tracers on the front cube at sites  $x$ ,  $-y$  and  $-z$  distant away can exchange places with a vacancy at site ‘1b’. Three such  $\omega_{12}$  jumps are possible. Tracer exchanges at sites ‘1’ with such a vacancy are assigned by a  $\omega_{12}$  frequency despite the difference in the jump distance. Altogether

then there are six jumps with  $\omega_{12}$  frequencies. These tracer–vacancy exchanges involve dissociating the tracer from the influence of the RS and pairing two solutes. Thus it is required to break bonding of the tracer from the RS to realize such exchanges and to reform a tracer solute pair. This is a consequence of the bond vacancy being an FNN of both the tracer and the RS. The energies for dissociation of the tracer from the RS and its re-association by the  $\omega_{12}$  exchange cancel (since bond forming and bond breaking of two solutes are of the same magnitude, but opposite in signs).

- There is a probability for three additional tracer jumps with  $\omega'_{24}$  frequency to a ‘1b’ vacancy. The tracers are third neighbors to RS and a distance ‘ $a$ ’ away from site ‘1b’ (i.e., at  $-x$ ,  $y$  and  $z$ ).

Now let us consider the contribution of jumps from second, third and fourth neighbors by following the approach outlined in section 2.1. There are  $n_v$  free vacancies randomly distributed on  $N_s(1 - 15c)$  sites of the crystal. The number of vacancies at SNN per crystal site outside the first coordination shell is then  $\frac{n_v 12N_i}{N_s(1-15c)}$  and the number of vacancy–tracer exchanges is:

$$\frac{n_v 12N_i}{N_s(1 - 15c)} \left( 3\omega_{23} \exp\left(\frac{\Delta g_p}{kT}\right) + 11\omega_2 \right). \quad (29)$$

In (29), a tracer at ‘1b’ can exchange place with a vacancy at an SNN site with a  $\omega_{23}$  frequency having a jump length of  $a\frac{\sqrt{3}}{2}$ . This tracer–vacancy exchange dissociates two solutes, the tracer and the RS. A vacancy in an SNN site can also perform an additional two jumps, but of length ‘ $a$ ’, to tracers at FNN sites such as ‘1a’, again involving breaking tracer–RS bonds. Vacancies at SNN sites have the option to jump away with  $\omega_2$  frequencies. Eleven such jumps are possible. Exchange jumps with  $\omega_2$  are reserved to solute diffusion in a pure solvent. Jumps of vacancies away from site ‘2’ are considered in this model to represent such diffusion.

Tracer–vacancy exchange can occur with a vacancy residing at a third neighbor site with  $\omega'_{23}$  frequency. Of the two  $\omega'_{23}$  type jumps one exchange is of length  $a\frac{\sqrt{3}}{2}$  while the second is of ‘ $a$ ’. Both involve dissociation of tracer–RS bonds. Twelve  $\omega_2$  type jumps of remote tracers to a third neighbor vacancy (escape jumps of the vacancy) can occur resulting in

$$\frac{n_v 24N_i}{N_s(1 - 15c)} \left( 2\omega'_{23} \exp\left(\frac{\Delta g_p}{kT}\right) + 12\omega_2 \right). \quad (30)$$

A tracer at an FNN site can execute a single  $\omega_{23}$  type jump exchanging with a vacancy at a fourth neighbor site. Realization of this jump requires breaking of the bond between tracer and RS. Tracers from remote sites can exchange location with such a vacancy with  $\omega_2$  frequencies. Thirteen such jumps are possible resulting in

$$\frac{n_v 8N_i}{N_s(1 - 15c)} \left( \omega_{23} \exp\left(\frac{\Delta g_p}{kT}\right) + 13\omega_2 \right). \quad (31)$$

Therefore, tracer exchanges with vacancies in second, third and fourth neighbor sites that break up the bond between

RS and tracer are given by summing up equations (29)–(31) resulting in equation (32) below:

$$\frac{n_v 4N_i}{N_s(1-15c)} \left[ \exp\left(\frac{\Delta g_p}{kT}\right) [11\omega_{23} + 12\omega'_{23}] + 131\omega_2 \right]. \quad (32)$$

In a manner similar to equation (18) the number of jumps associated with the free vacancies outside the fourth coordination shell can be expressed by replacing  $\omega_0$  with  $\omega_2$  as

$$\left( n_v - \frac{n_v 44N_i}{N_s(1-15c)} \right) 14\omega_2. \quad (33)$$

The total jump rate of the tracer–solute,  $\Gamma(c)$ , can be obtained by summing up the contributions from (28), (32) and (33)

$$\begin{aligned} \Gamma_2(c) = & \frac{1}{N_s(1-c)} \left\{ N_i p \exp\left(-\frac{\Delta g}{kT}\right) \right. \\ & \times \left[ 6\omega_{12} + (4\omega_{24} + 3\omega'_{24}) \exp\left(-\frac{\Delta g_p}{kT}\right) \right] \\ & + \frac{n_v 4N_i}{N_s(1-15c)} \left[ \exp\left(\frac{\Delta g_p}{kT}\right) [11\omega_{23} + 12\omega'_{23}] + 131\omega_2 \right] \\ & \left. + \left[ n_v - \frac{n_v 44N_i}{N_s(1-15c)} \right] 14\omega_2 \right\}. \quad (34) \end{aligned}$$

Above it was indicated [14] that

$$n_v = N_s(1-14c) \exp\left(-\frac{g + \Delta g}{kT}\right). \quad (35)$$

Substituting for  $p$  and  $n_v$ , neglecting the higher terms in  $c$  and bringing  $\omega_2$  before the bracket it is possible to write

$$\begin{aligned} \Gamma_2(c) = & 14 \exp\left(-\frac{g + \Delta g}{kT}\right) \omega_2 \left\{ c \left[ \exp\left(-\frac{\Delta g}{kT}\right) \right. \right. \\ & \times \left[ 6\frac{\omega_{12}}{\omega_2} + \left( 4\frac{\omega_{24}}{\omega_2} + 3\frac{\omega'_{24}}{\omega_2} \right) \exp\left(-\frac{\Delta g_p}{kT}\right) \right] \\ & \left. \left. + \frac{1}{7} \left[ \exp\left(\frac{\Delta g_p}{kT}\right) \left( 22\frac{\omega_{23}}{\omega_2} + 24\frac{\omega'_{23}}{\omega_2} \right) - 137 \right] \right] + 1 \right\} \quad (36) \end{aligned}$$

and with relation (26c) the following expression is obtained for  $\Gamma_2(c)$

$$\begin{aligned} \Gamma_2(c) = & 14 \exp\left(-\frac{g + \Delta g}{kT}\right) \omega_2 \left\{ c \left[ \exp\left(-\frac{\Delta g}{kT}\right) \right. \right. \\ & \times \left[ 6\frac{\omega_{12}}{\omega_2} + \left( 4\frac{\omega_{24}}{\omega_2} + 3\frac{\omega'_{24}}{\omega_2} \right) \exp\left(-\frac{\Delta g_p}{kT}\right) \right] \\ & \left. + \frac{1}{7} \left[ \left( 22\frac{\omega_{24}}{\omega_2} \exp\left(-\frac{\Delta g}{kT}\right) + 24\frac{\omega'_{23}}{\omega_2} \right) \right. \right. \\ & \left. \left. \times \exp\left(\frac{\Delta g_p}{kT}\right) - 137 \right] \right] + 1 \right\}. \quad (37) \end{aligned}$$

With equations similar to (2)–(4) but applied for solute diffusion [12, 16] it is possible to write

$$\Gamma_2(c) = 14\omega_2 \exp\left(-\frac{g + \Delta g}{kT}\right) \quad (38a)$$

$$D_2(0) = \frac{14}{8} a_0^2 \omega_2 \exp\left(-\frac{g + \Delta g}{kT}\right) f_2(0) \quad (38b)$$

$$\begin{aligned} D_2(c) = & \frac{1}{8} \Gamma_2(c) a^2 f_2(c) = D_2(0) [1 + Bc] \\ & = \frac{14}{8} a_0^2 \omega_2 \exp\left(-\frac{g + \Delta g}{kT}\right) f_2(0). \quad (38c) \end{aligned}$$

Expressing (38c) in terms of  $\Gamma_2(c)$  a relation similar to equation (6) is obtained in terms of solute enhanced diffusion i.e.

$$\Gamma_2(c) = 14\omega_2 \exp\left(-\frac{g + \Delta g}{kT}\right) [1 + Bc] \frac{f_2(0)}{f_2(c)}. \quad (39a)$$

Here  $f_2(0)$  and  $f_2(c)$  are the solute correlation factors in pure solvent and in the dilute alloy, respectively. Equation (39a) can be written following the procedure outlined for the solvent enhancement as expressed in (A.6) by

$$\Gamma(c) = 14\omega_0 \exp\left(-\frac{g + \Delta g}{kT}\right) \left[ 1 + c \left( B - \frac{F}{f_2(0)} \right) \right]. \quad (39b)$$

Let us denote  $(B - F/f_2(0))$  as  $B$  effective, then equation (39b) can be rewritten in terms of  $B_{\text{eff}}$  as

$$\Gamma(c) = 14\omega_0 \exp\left(-\frac{g + \Delta g}{kT}\right) [1 + c B_{\text{eff}}]. \quad (39c)$$

From (39c) and (37) we can get for  $B_{\text{eff}}$

$$\begin{aligned} B_{\text{eff}} = & \exp\left(-\frac{\Delta g}{kT}\right) \left[ 6\frac{\omega_{12}}{\omega_2} + \left( 4\frac{\omega_{24}}{\omega_2} + 3\frac{\omega'_{24}}{\omega_2} \right) \right. \\ & \times \exp\left(-\frac{\Delta g_p}{kT}\right) \left. + \frac{1}{7} \left[ \left( 22\frac{\omega_{24}}{\omega_2} \exp\left(-\frac{\Delta g}{kT}\right) \right. \right. \right. \\ & \left. \left. + 24\frac{\omega'_{23}}{\omega_2} \right) \exp\left(\frac{\Delta g_p}{kT}\right) - 137 \right] \right]. \quad (40) \end{aligned}$$

This equation can be reduced by one parameter by assuming that  $\omega_{24} \cong \omega'_{24}$ , resulting in

$$\begin{aligned} B_{\text{eff}} = & \exp\left(-\frac{\Delta g}{kT}\right) \left[ 6\frac{\omega_{12}}{\omega_2} + 7\frac{\omega_{24}}{\omega_2} \exp\left(-\frac{\Delta g_p}{kT}\right) \right] \\ & + \frac{1}{7} \left[ \left( 22\frac{\omega_{24}}{\omega_2} \exp\left(-\frac{\Delta g}{kT}\right) + 24\frac{\omega'_{23}}{\omega_2} \right) \right. \\ & \left. \times \exp\left(\frac{\Delta g_p}{kT}\right) - 137 \right]. \quad (41) \end{aligned}$$

### 3. Calculated and experimental enhancement factors

The equations for solvent and solute diffusion enhancement factors in dilute alloys [1–5, 14] were presented in this work by simpler relations in the form of equations (23) and (41) without sacrificing the accuracy of the calculated values compared to those of the experimental. This was achieved by the use of parameters requiring fewer experiments for their evaluation. The relations derived for the enhancement factors are applicable for dilute alloys.

#### 3.1. Evaluation of $b_{\text{eff}}$

Equation (23) allows  $b_{\text{eff}}$  to be expressed by two frequency parameters,  $\Delta g$  and  $\omega_0$ .  $\Delta g$  is the additional free energy required to form a vacancy in the presence of a solute.

It is considerably simpler than the expression for  $b$  given in the literature (see for example [12]) with only four unknowns, which must be evaluated by fitting equation (23) to experimental data. If one is interested only in the frequency ratios of equation (23), there are only three unknowns to be evaluated by fitting (thus fewer experiments for data collection are required). The value of  $b$  is obtained experimentally from diffusion measurements at various solute concentrations according to equation (1). One should note that in the experimental enhancement factor values, correlation effects are inherently already included. Thus in reality values of  $b_{\text{eff}}$  are measured. Knowledge of  $D(0)$  is also required to evaluate  $b$ . The temperature dependence of  $b$  can be obtained from experiments performed at different temperatures. Once the parameter  $\Delta g$  is evaluated equation (23) can be used to calculate new values of  $b$  at other temperatures, for which no experimental values were determined, by fitting.

$\Delta g$  can be obtained from the difference between the energy of vacancy formation,  $E_f(0)$  in pure solvent and the one in the presence of solute,  $E_f(c)$ . The values of the  $E_f$ s are assumed to be equal to  $0.6Q$  [17], where  $Q$  is the activation energy for selfdiffusion. This is a consequence of  $Q$  being equal to the sum of  $E_f$  and  $E_m$ , the energy of migration [17–19]. Contrary to  $\Delta g$  in this relation,  $E_f$  and  $E_m$  are enthalpies whereas  $\Delta g$  is a free energy term; the entropy term is often omitted from the expression relating the vacancy concentration to its formation energy. Omission of this term and taking it as  $\cong 0$  often gives an adequate approximation [20]. Some degree of approximation is always necessary if complicated expressions are to be reduced to forms that can be related to useful calculations or for comparison with experimental results. More precise expressions by refining the method of evaluating  $\Delta g$  will not necessarily bolster our understanding of the suggested model. In the present work this problem did not arise because  $\Delta g$  was obtained by fitting and was not evaluated from the difference in the activation energies as mentioned above, since the number of unknowns in equation (23) is quite small.

In equation (23) average frequency ratios are given. These are the parameters obtained by fitting. However if the jump frequencies themselves are also of explicit interest,  $\omega_0$  has to be evaluated.  $\omega_0$  is the pure solvent jump frequency. It can be easily found from diffusion measurements as follows: the jump rate,  $\omega_0$ , is related to  $E_m$  which is  $\sim 0.4Q$  [20] by

$$\omega_0 = \nu_0 \exp\left(-\frac{E_m}{kT}\right). \quad (42)$$

The frequency of vibrations,  $\nu_0$ , is related to  $D_0$ , the pre-exponential factor, by [17, 20]

$$D_0 = \nu_0 f_0 a^2 \quad (43)$$

and can be evaluated from (43). Alternatively, as indicated above,  $\omega_0$  can be obtained by fitting to equation (23) requiring additional experimental data. Required parameters can be taken from known data if available in the literature or experimentally determined. With these assumptions direct evaluation of the enhancement factor can be obtained

at temperatures for which no experimental  $b$  is available. Wherever experimental data of the energies of vacancy formation and migration are available, these could be used in preference to values obtained from their relation with  $Q$ . In table 1 the various parameters are listed which were used to calculate  $b$ . Clearly, the experimental values of  $b$  which were used for the fitting according to equation (23) are also shown. The frequency ratios are average numbers, since the fitting is within the temperature range of the experimental data of  $b$ . A test performed by iteration in one of the systems (Zr in Zr–V) at two temperatures, i.e., at 1167 and 1318 K, indicates that the average frequency ratios are very close to those calculated by equation (23). A difference of  $\sim -2.6\%$  of  $\frac{\omega_3}{\omega_0}$  from the average value listed in table 1 and almost no change in  $\frac{\omega_6}{\omega_0}$  were obtained. The relatively few experimental measurements in b.c.c. systems on which we may exercise equation (23) dictated the choice of data listed in table 1. The table lists the calculated values of  $b$  at the temperatures indicated for the following systems: V diffusion in V/Co [20], Zr diffusion in Zr/V [8], Zr diffusion in Zr/Mn [21] and V diffusion in V/Zr [9] dilute solid solutions, respectively.

One could note that the  $b_{\text{eff}}$  values can be applied to calculate a solute correlation factor using the relation of Le Claire [12] as

$$f_i = 1 - \frac{D_i}{D(0)} \frac{6f_0}{\left(b + 15 + \frac{1.53b+9.18}{b+9.06}\right)}. \quad (44)$$

The correlation was tested in the Zr/Zr–V system at two temperatures (1167 and 1318 K), using this equation. 0.71 and 0.78 are obtained respectively, which compare favorably with those listed in [7]. Thus it seems that in the tested cases solvent–vacancy exchange rate is not perturbed significantly due to the presence of the solute. To see whether, in the systems listed in the table, weak perturbation prevails or not is a matter of testing, which is out of the scope of this manuscript.

It is evident from table 1, more specifically from the frequency ratios that in the Zr systems examined vacancy–FNN solvent atom exchanges with  $\omega_3$  are higher by orders of magnitude than solvent–vacancy jumps with  $\omega_6$ . This means that the escape jump tendency of a vacancy from the influence of the RS is much less favorable than its stay at an FNN site to the RS. Contrary to this observation, in the V system this tendency is only somewhat higher in the V/V–Co case (where  $\omega_3 \sim 8\omega_6$ ) and is almost the same in the V/V–Zr one (where  $\omega_3 \sim 0.8\omega_6$ ). Further one should note that in these systems  $\Delta g$  is expressed in small negative numbers, whereas for the Zr systems a positive  $\Delta g$  was calculated.

### 3.2. Evaluation of $B$

$B$  can be expressed by equation (40) having the following parameters: four frequency ratios,  $\Delta g$  and  $\Delta g_p$ . This can be compared with the number of parameters required in the non-hypothetical b.c.c structure [14, 15]. Equation (40) can be reduced by one parameter, as indicated, to equation (41). The assumption of  $\omega_{24} \cong \omega'_{24}$  is appealing since these associative jump frequencies to an FNN site of a solute atom (RS) either from SNN, third or fourth nearest neighbor sites



**Table 1.** Comparison of calculated and experimental solvent enhancement factors  $b_{\text{eff}}$ .

$b_{\text{calc}}$ by fitting	$b_{\text{exp.}}$	$(b_{\text{cal.}} - b_{\text{exp.}})/b_{\text{exp.}}$	Temperature (K)	$\Delta g$	$\frac{\omega_3}{\omega_0}$	$\frac{\omega_6}{\omega_0}$
V in V-Co						
				-0.15	1.82	0.93
39.68	38.22 [20]	$3.82 \times 10^{-2}$	1220			
30.60	33.35	$-8.25 \times 10^{-2}$	1433			
28.69	30.03	$-4.46 \times 10^{-2}$	1496			
24.06	21.43	$1.23 \times 10^{-1}$	1694			
26.91 <sup>a</sup>	37.83 <sup>b</sup>	$-2.89 \times 10^{-1}$	1563			
25.63 <sup>a</sup>	44.99 <sup>b</sup>	$-4.30 \times 10^{-1}$	1618			
V in V-Zr						
				-0.27	1.15	0.03
29.18	28.7 [9]	$1.67 \times 10^{-2}$	1578			
26.03	26.5	$-1.77 \times 10^{-2}$	1633			
23.26	24.4	$-4.67 \times 10^{-2}$	1688			
21.03	19.9	$5.68 \times 10^{-2}$	1738			
19.29 <sup>a</sup>	15.0	0.29	1783			
16.95 <sup>a</sup>	16.9	$2.96 \times 10^{-3}$	1848			
15.65 <sup>a</sup>	17.7	-0.12	1888			
Zr in Zr-V						
				0.36	84.19	0.30
-2.39	-4.14 [8]	-0.42	1167			
0.07	0		1223			
2.79	2.80	$-3.57 \times 10^{-3}$	1281			
4.61	5.09	$-9.43 \times 10^{-2}$	1318			
7.53	8.71	$-1.35 \times 10^{-1}$	1375			
10.40 <sup>a</sup>	10.41	$-9.61 \times 10^{-4}$	1428			
13.05 <sup>a</sup>	13.60	$-4.04 \times 10^{-2}$	1476			
Zr in Zr-Mn						
				0.33	168.45	0.20
19.96	19 [21]	$5.05 \times 10^{-2}$	1173			
25.25	25	0.01	1223			
30.81	31	$-6.13 \times 10^{-3}$	1273			
36.59	37.5	$-2.43 \times 10^{-2}$	1323			
43.02 <sup>a</sup>	40.8	$5.44 \times 10^{-2}$	1373			
9.32 <sup>a</sup>	46.5	$6.06 \times 10^{-2}$	1423			

<sup>a</sup> Calculated using the parameters shown; experimental values not used for the fitting.

<sup>b</sup> Data seem to be unreliable. From extrapolated experimental curve and deleting the non-reliable points the values are  $\sim 27.04$  and  $\sim 25$ , respectively.

are not under a strong differing binding influence of the RS before executing the jump itself. Solute diffusion in pure solvent can provide experimental values of  $\Delta g$ , as indicated above, since it represents the difference between the energies of vacancy formation of self and solute diffusion in pure solvent respectively. Similarly to equation (42),  $\omega_2$ , the jump rate is related to  $E_m \sim 0.4Q_2$  by

$$\omega_2 = \nu_0 \exp\left(-\frac{E_m}{kT}\right), \quad (45)$$

where  $Q_2$  is the solute activation energy for diffusion in pure metal.

The three unknown frequencies (following the assumption of  $\omega_{24} \cong \omega'_{24}$ ) in the form of the ratios  $\frac{\omega_{12}}{\omega_2}$ ,  $\frac{\omega_{24}}{\omega_2}$  and  $\frac{\omega'_{23}}{\omega_2}$  have to be evaluated by fitting. Also  $\Delta g_p$  is evaluated during the fitting procedure.  $\Delta g$  was taken from the fitting results to equation (23). The meaning of  $\Delta g$  is the same as in the case

of solvent enhancement by solute. With the obtained data of  $\frac{\omega_i}{\omega_2}$  and  $\Delta g_p$ ,  $B_{\text{eff}}$  can be calculated at temperatures for which no experimental values exist. In table 2,  $B_{\text{eff}}$  values calculated for solute diffusion in the Zr/V [8], V/Co [22], Zr/Mn [21, 22] and V/Zr [9] systems are shown. Table 2 also lists the various parameters which were evaluated by fitting to equation (41) of the experimental  $B$  values. The agreement between calculated and experimental  $B$  values in the systems tested, except in the Co/V, is very good. The poor agreement between calculated and experimental results in this system is of an experimental nature as seen in [22], and some of the experimental  $B$  values are beyond the accepted error in diffusion work; in particular the scatter was great at 1521 K.

Suggesting this hypothetical model for b.c.c structure is quite reasonable since the SNN have almost the same distance in the unit cell as the FNN, with a difference less than 15%.

**Table 2.** Comparison of calculated and experimental solute enhancement factors  $B_{\text{eff}}$ .

V in Zr–V (fitting with four parameters equations (40))									
$B_{\text{calc}}$	$B_{\text{exp}}$ [8]	$(B_{\text{calc}} - B_{\text{exp}})/B_{\text{exp}}$	Temp. (K)	$\Delta g$	$\Delta g_p$	$\frac{\omega_{12}}{\omega_2}$	$\frac{\omega_{24}}{\omega_2}$	$\frac{\omega'_{23}}{\omega_2}$	$\frac{\omega'_{24}}{\omega_2}$
-7.49	-6.8	$1.01 \times 10^{-1}$	1166	-0.27	0.40	2.48	0.004	0.08	—
-11.53	-12.9	$-1.06 \times 10^{-1}$	1204						
-14.96	-14.8	$1.08 \times 10^{-2}$	1245						
-17.68	-17.2	$2.79 \times 10^{-2}$	1286						
-22.06	-21.7	$1.66 \times 10^{-2}$	1379						
-23.9	-23.8	$4.20 \times 10^{-3}$	1435						
-25.08	-25.5	$-1.65 \times 10^{-2}$	1480						
V in Zr–V (fitting with five parameters equation (41))									
$B_{\text{calc}}$	$B_{\text{exp}}$ [8]	$(B_{\text{calc}} - B_{\text{exp}})/B_{\text{exp}}$	Temp. (K)	$\Delta g$	$\Delta g_p$	$\frac{\omega_{12}}{\omega_2}$	$\frac{\omega_{24}}{\omega_2}$	$\frac{\omega'_{23}}{\omega_2}$	$\frac{\omega'_{24}}{\omega_2}$
-7.49	-6.8	$1.01 \times 10^{-1}$	1166	-0.27	0.40	0.55	0.005	0.08	3.86
-11.53	-12.9	$-1.06 \times 10^{-1}$	1204						
-14.96	-14.8	$1.08 \times 10^{-2}$	1245						
-17.68	-17.2	$2.79 \times 10^{-2}$	1286						
-22.06	-21.7	$1.66 \times 10^{-2}$	1379						
-23.9	-23.8	$4.20 \times 10^{-3}$	1435						
-25.08	-25.5	$-1.65 \times 10^{-2}$	1480						
Mn in Zr–Mn									
$B_{\text{calc}}$	$B_{\text{exp}}$ [21, 22]	$(B_{\text{calc}} - B_{\text{exp}})/B_{\text{exp}}$	Temp. (K)	$\Delta g$	$\Delta g_p$	$\frac{\omega_{12}}{\omega_2}$	$\frac{\omega_{24}}{\omega_2}$	$\frac{\omega'_{23}}{\omega_2}$	$\frac{\omega'_{24}}{\omega_2}$
-19.02	-19	$1.05 \times 10^{-3}$	1173	0.33	0.51	4.81	1.35	0.03	—
-23.35	-23.4	$-2.14 \times 10^{-3}$	1223						
-26.81	-26.8	$3.73 \times 10^{-4}$	1273						
-29.62	-29.6	$6.76 \times 10^{-4}$	1323						
-31.93	-31.9	$9.40 \times 10^{-4}$	1373						
-33.87	-33.9	$-8.85 \times 10^{-4}$	1423						
-35.50	-35.5	0.	1473						
Zr in V–Zr									
$B_{\text{calc}}$	$B_{\text{exp}}$ [9]	$(B_{\text{calc}} - B_{\text{exp}})/B_{\text{exp}}$	Temp. (K)	$\Delta g$	$\Delta g_p$	$\frac{\omega_{12}}{\omega_2}$	$\frac{\omega_{24}}{\omega_2}$	$\frac{\omega'_{23}}{\omega_2}$	$\frac{\omega'_{24}}{\omega_2}$
12.71	11.9	$6.81 \times 10^{-2}$	1578	0.36	-1.68	$5.38 \times 10^{-8}$	4.36	$1.23 \times 10^5$	—
13.54	13.7	$-1.17 \times 10^{-2}$	1628						
14.78	15.9	$-7.04 \times 10^{-2}$	1683						
16.5	16.8	$-1.79 \times 10^{-2}$	1738						
18.55	18.5	$2.70 \times 10^{-3}$	1788						
21.18	19.5	$8.62 \times 10^{-2}$	1838						
24.15	25.1	$-3.78 \times 10^{-2}$	1883						
Co in V–Co									
$B_{\text{calc}}$	$B_{\text{exp}}$ [22]	$(B_{\text{calc}} - B_{\text{exp}})/B_{\text{exp}}$	Temp. (K)	$\Delta g$	$\Delta g_p$	$\frac{\omega_{12}}{\omega_2}$	$\frac{\omega_{24}}{\omega_2}$	$\frac{\omega'_{23}}{\omega_2}$	$\frac{\omega'_{24}}{\omega_2}$
215	213	$9.39 \times 10^{-3}$	1337	-0.15	2.42	7.36	$1.26 \times 10^{-8}$	$1.2 \times 10^{-20}$	—
91.28	113	$-1.92 \times 10^{-1}$	1403						
64.34	64	$5.3 \times 10^{-3}$	1438						
37.40	48	$-2.21 \times 10^{-1}$	1521						

This is about the accepted error in experimental diffusivity data and the diffusion parameters. The results of the calculations are, in each system tested, considerably below this error except for the Co/V alloys at two temperatures as mentioned. For the fitting procedure the number of experimental points required is significantly reduced without sacrificing the accuracy of the results. This can be seen in tables 1 and 2 where experimental enhancement factors are compared with the calculated values.

#### 4. Summary

A model for calculating solvent and solute enhancement factors by solute in dilute b.c.c structures has been suggested. The model considers a hypothetical structure having 14 FNN. The merits of the model are:

- (a) Simpler equations for  $b$  and  $B$  with far fewer unknowns. Consequently the number of parameters for fitting is

considerably less than in the conventional approaches without sacrificing the accuracy of the calculated enhancement factors. Thus the number of experiments required to get  $b$  and  $B$  values is considerably reduced.

- (b) The enhancement factors calculated are effective values; it is believed by the author that experimental values inherently contain correlation effects. An illustration was given of how to estimate the impurity correlation factor from  $b_{\text{eff}}$ .
- (c) The small number of unknowns in the equations allows calculation of  $b$  and  $B$  values at various temperatures which have not been determined experimentally.

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### Appendix A

Let us assume that the correlation factor in a dilute alloy as influenced by concentration can be expanded in the form of

$$f(c) = f_0 + \left. \frac{\partial f}{\partial c} \right|_{c=0} c + \dots \quad (\text{A.1})$$

Denoting  $\frac{\partial f}{\partial c}$  by  $A$ , neglecting the higher terms in equation (A.1) the quotient  $\frac{f_0}{f(c)}$  of equation (6) can be written as

$$\frac{f_0}{f_0 + Ac} = \frac{1}{1 + \frac{Ac}{f_0}} \quad (\text{A.2})$$

With the approximation of  $\frac{1}{1+x} = 1 - x + x^2 - \dots$ , when  $Ac/f_0 < 1$ , (A.2) can be written as

$$\frac{1}{1 + \frac{Ac}{f_0}} = 1 - \frac{Ac}{f_0} + \left(\frac{Ac}{f_0}\right)^2 - \dots \quad (\text{A.3})$$

Again neglecting the higher terms in the quotient  $Ac/f_0$ , retaining only the two first terms, substituting into equation (6) and multiplying through with  $[1 + bc]$ , one obtains equation (8) as

$$\Gamma(c) = 14\omega_0 \exp\left(-\frac{g}{kT}\right) \left[1 + c \left(b - \frac{A}{f_0}\right)\right] \quad (\text{A.4})$$

The correlation relation of (A.1) can also be applied for solute diffusion in the form of

$$f_2(c) = f_2(0) + \left. \frac{\partial f_2}{\partial c} \right|_{c=0} c + \dots \quad (\text{A.5})$$

Again in a manner similar to the above and using the appropriate notations we can write

$$\Gamma_2(c) = 14\omega_2 \exp\left(-\frac{g + \Delta g}{kT}\right) \left[1 + c \left(B - \frac{F}{f_2(0)}\right)\right] \quad (\text{A.6})$$

In this case  $F$  represents  $\frac{\partial f_2}{\partial c}$ .

### Appendix B

The equality of (10b) is based on equation (10) and the assumption of (10a) that  $\omega'_3 = \omega''_3 = \omega_5$ . It is possible to write that

$$\omega'_4 = \omega'_3 \exp(-\Delta g/kT) = \omega_5 \exp(-\Delta g/kT), \quad (\text{B.1})$$

but also

$$\omega_6 = \omega_5(-\Delta g/kT), \quad (\text{B.2})$$

thus

$$\omega'_4 = \omega_6. \quad (\text{B.3})$$

Similarly,

$$\omega''_4 = \omega''_3 \exp(-\Delta g/kT) = \omega_5 \exp(-\Delta g/kT), \quad (\text{B.4})$$

but also as above in (B.2)  $\omega_6 = \omega_5(-\Delta g/kT)$  or

$$\omega''_4 = \omega_6, \quad (\text{B.5})$$

consequently

$$\omega'_4 = \omega''_4 = \omega_6. \quad (\text{B.6})$$

### Appendix C. Jumps of an FNN vacancy

The number of solvent jumps per unit time associated with the vacancies at FNN sites with the frequencies indicated in equation (11a) can be obtained as follows:

In the model suggested 14 sites are assumed to be equivalent. Of these eight sites are at a distance of  $a(3)^{1/2}/2$ , i.e. at the corners of a unit cell, and six are at a distance 'a' from the RS, respectively. All vacancy-FNN solvent exchanges are considered to occur with  $\omega_3$  frequencies. Six such jumps are possible of which (a) three exchanges bring the vacancy in any of the  $-x, y, z$  directions to a distance 'a' of the RS and are of length  $\frac{a\sqrt{3}}{2}$  and (b) a further three vacancy-FNN jumps of this type are possible of length 'a' in any of the  $x, -y, -z$  directions bringing the vacancy again to an FNN site at a  $\frac{a\sqrt{3}}{2}$  distance from the RS.

Further we have seven escape jumps of the vacancy from the RS as follows: three  $\omega_5$  jumps of lengths 'a' which dissociates the vacancy from the RS and brings it to a 3rd NN; three  $\omega'_3$  jumps of length  $a(3)^{1/2}/2$  to 2nd NN and one  $\omega''_3$  jump also of length  $a(3)^{1/2}/2$  but this escape jump of the vacancy brings it to a 4th NN site of the RS, respectively. However, by equation (10a) the  $\omega'_3, \omega''_3$  and  $\omega_5$  jump frequencies are equal, resulting in equation (11b). Clearly the bond vacancies, i.e., those that are at the first coordination shell are associated with equation (11a).

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