Correlation Effects and Activation Energies for Diffusion in Alloys *

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The problems involved in calculating correlation factors for diffusion in dilute alloys can be contrasted to those arising in concentrated solid solutions. As one moves from the pure element to the dilute alloy to the concentrated alloy, the calculation becomes progressively more difficult. Because of the complex atom configurations which can occur in concentrated alloys, it usually is not possible to calculate correlation factors in these alloys exactly.

Several important simplifications are available in non-dilute random alloys. A large reduction in complexity can be secured by using a random alloy model where each atom is treated as diffusing in a uniform matrix, with the matrix properties being determined by the composition and jump frequencies in the alloy. Resulting equations in this random alloy model can be expressed directly in terms of the experimentally measurable tracer diffusion coefficients with no unknown vacancy jump frequencies appearing. Also these equations have the advantage of being in simple analytic form and not requiring numerical methods to evaluate the correlation factors. These two features make possible the direct expression of the temperature dependence of the correlation factor in terms of the experimental activation energies.

Equations are found for $\Delta H/\Delta Q$ in random binary cubic alloys, where ΔH is the difference between the activation enthalpies for diffusion of the two species and ΔQ is the difference between the experimentally measured activation energies of the two species. This ratio is never less than unity and can be much larger than unity. Values are plotted for diamond, body-centered cubic and face-centered cubic structures. From the magnitude and composition dependence of $\Delta H/\Delta Q$, it is concluded that the temperature dependence of the correlation factor cannot by itself explain the difference between the activation energies measured from tracer diffusion and from internal friction in the non-dilute range.

Introduction

In any crystal containing sufficient symmetry, the correlation factor f_i for the diffusion of atom i by a single vacancy mechanism is given by [1]

$$f_i = h_i/(2\,w_i + h_i)\,. \tag{1}$$

Here w_i is the jump frequency for exchange of i with a neighboring vacancy and h_i is the randomization frequency for such a vacancy to move away from i and randomize its position with respect to i. Because of its simplicity, Eq. (1) is a useful equation to apply in calculating correlation factors in alloys. Difficulties arise in concentrated alloys both in satisfying the condition of "sufficient" symmetry and in the evaluation of h_i. In the following section, the situation in concentrated alloys is compared to that in pure crystals and dilute alloy, and applications of Eq. (1) in these materials are discussed. This discussion leads naturally to a method of treating non-dilute alloys in terms of a random alloy model.

Comparison of Pure Crystals, Dilute Alloys and Concentrated Alloys

If one wishes to use Eq. (1) to calculate the atom correlation factor, it is necessary first to obtain expressions for the randomization frequency h_i. This frequency depends on the jump frequency of the vacancy for exchange with atoms other than the particular atom i whose correlation factor is being calculated. For simplicity, it is assumed in the present paper that diffusion in the crystals being discussed occurs only by a nearest-neighbor single-vacancy mechanism and that the crystals have cubic structures with one atom per primitive cell. Then, in a pure crystal, where there is only one type of atom, there is only one vacancy jump frequency. As a result, h_i quals w_i multiplied by a numerical geometric constant M_0,

$$h_i = M_0\,w_i\,. \tag{2}$$

It follows that the correlation factor in these pure cubic crystals will always be a simple numerical

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[1] J. R. MANNING, Diffusion Kinetics for Atoms in Crystals, D. van Nostrand, Princeton 1968, p. 115.

constant. Values of M_0 in several cubic crystals are given in Table I.

Crystal Structure	M_0
Diamond	2
Simple cubic	3.77
Body-centered cubic	5.33
Face-centered cubic	7.15

Table 1. Values of geometric constant M_0.

In a dilute alloy, the vacancy jump frequencies near the dilute impurity atoms will be altered because of the presence of the impurity. Also, the impurity jump frequency w_i can differ from the various solvent jump frequencies w_s. Since h_i depends on the vacancy jump frequencies other than w_i, one finds

$$h_i = \Sigma_s F_s w_s \tag{3}$$

where the summation is over all possible jumps by a vacancy from a site neighboring on i except for a vacancy exchange with i itself. The F_s depend on all jump frequencies in the crystal except those originated by a vacancy neighboring on i. Thus, for a dilute impurity, f_i is no longer a pure number but instead depends on the ratios of all the various w_s's and w_i.

For an isolated impurity in an infinite lattice, an exact analytic equation for f_i can be obtained by substituting Eq. (3) into Eq. (1). This is true even though vacancy motion is altered near the impurity and the vacancy no longer follows a random walk in this region. The resulting equation, which is rigorously correct for an isolated impurity, also is valid to a very good approximation for the impurity atoms i in a dilute alloy if the impurities are well separated. In such a dilute alloy, it often is possible to make the further approximation that only those vacancy jump frequencies very near the impurity are affected by the impurity. Then h_i will depend on only a small number of vacancy jump frequencies, and the F_s and h_i can be calculated explicitly in terms of these frequencies. This approach has been applied to a number of cubic crystals to yield simple expressions for the impurity correlation factor [2, 2a].

In moving from dilute alloys to concentrated alloys, one finds that the crystal becomes more complex. As a convenient summary, some differences between pure crystals, dilute alloys and concentrated alloys are outlined in Table II. Because of the many possible local configurations of atoms and vacancies in a concentrated alloy, one expects many different atom-vacancy exchange frequencies. This large number of jump frequencies by itself would greatly complicate the calculation of h_i. In addition, however, the vacancy in a concentrated alloy cannot be treated anywhere as following a random walk. Thus, a correction for the vacancy correlation factor must be made. Finally, there is a question whether it is proper to apply Eq. (1) to non-dilute alloys at all. Symmetry around the jump direction or across a set of planes normal to the diffusion direction is required in order for Eq. (1) rigorously to be valid. Non-symmetric local configurations in a concentrated alloy can lead to violations of these symmetry rules. Because of these problems, a rigorous exact calculation of f_i in concentrated alloys is really not possible. Reasonable approximate calculations are possible, however, especially in random alloys as is discussed below.

Random Alloy Model

When a single impurity atom i diffuses in an infinite, otherwise-pure cubic crystal, h_i can be ex-

Table 2. Influences on correlation factor for diffusion by single vacancy mechanism in cubic crystals.

Alloy Type	Vacancy Motion	Number of Vacancy Jump Frequencies	Atom Correlation Factor
Pure Crystal	Random walk	One	Pure number
Dilute Alloy	Non-random near an impurity but random elsewhere	Several	For an isolated impurity, analytic equation in terms of jump frequency ratios
Concentrated Alloy	No random walk	Many	No exact analytic equation — approximation required

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[2] See e. g., J. R. Manning, Phys. Rev. **136**, A 1758 [1964]. Treatise, ed. by H. Eyring, D. Henderson, and W. Jost, Chap. 5.

[2a] A. D. LeClaire, Physical Chemistry, An Advanced Vol. X, Solid State, Academic Press, New York 1970.

pressed in terms of exact analytic equations. This is true even if the influence of the impurity on neighboring vacancy jump frequencies is very long range, since all that is required is the introduction of additional jump frequencies in the appropriate infinite matrices or determinants[3]. If the impurities are in very dilute concentration so that the spheres of influence of the different impurity atoms do not overlap, the expression for the isolated impurity applies to a very good approximation to each atom of dilute species i. This provides a reliable analytic equation for f_{i} for a dilute impurity.

One reason why this approach to the calculation of f_{i} for dilute impurities proceeds so smoothly is that each impurity in this approach is assumed to be in identical surroundings, in particular to be an isolated impurity in an otherwise uniform matrix. This approximation should be quite good at very low concentrations of impurity since in the absence of clustering the other impurity atoms usually will be rather far away from the particular impurity atom being studied. The local surroundings for each such impurity therefore can be treated as being identical.

It is tempting to see if a similar approximation cannot be applied to the calculation of correlation factors in concentrated alloys. Since one wishes a situation where the surroundings of each atom can be assumed to be identical to the surroundings of each other atom, one is drawn to a model based on a random alloy. In such an alloy, the desired uniform surroundings might be approximated by treating each matric lattice site as if it were occupied by N_{A} atoms of species A, N_{B} atoms of species B and so on, where N_m is the mole fraction of species m in the crystal. The vacancy jump frequency to any given neighboring site in this uniform matrix then would be

$$W = N_{\mathrm{A}}\, w_{\mathrm{A}} + N_{\mathrm{B}}\, w_{\mathrm{B}} + \ldots = \Sigma_m N_m w_m \qquad (4)$$

where w_m is the jump frequency for jump of a vacancy to a neighboring site in this uniform matrix if the site is occupied by an m atom.

In an actual alloy, there will be many possible jump frequencies for exchange of vacancies with the various m atoms, since the jump frequency will depend on the surrounding atom configuration. The actual alloy can be related to the uniform matrix by defining w_m in Eq. (4) as equal to the average jump frequency in the actual alloy for exchange of an m atom with a neighboring vacancy. Thus, W by definition also equals the average vacancy jump frequency to a neighboring site in a random alloy.

A specific i atom whose motions are to be followed can be introduced into the uniform matrix. Since any i atom which is introduced is treated as having uniform surroundings, possible influences of local atom configurations on its jump frequency w_{i} are eliminated and there is only one possible jump frequency for each species. As a result, the many possible different jump frequencies in a concentrated alloy are drastically reduced. For example, in a binary A – B alloy, there then are only three vacancy frequencies to consider, w_{A}, w_{B}, and an average random vacancy jump frequency.

Because of correlation effects for diffusion of vacancies in alloys, the frequency W does not equal the random vacancy jump frequency. Nevertheless, it is shown later that this random frequency $f_{\mathrm{v}}\, W$ can be expressed in terms of the individual jump frequencies w_{m}. Thus, in a binary alloy, one finally is concerned with only two jump frequencies, w_{A} and w_{B}; and, in a multicomponent alloy, the number of independent jump frequencies equals simply the number of species.

The present model of vacancy jump frequencies implies that there are no binding energies which bind the vacancy to any particular atom or bind the various atoms in preferred configurations. This result is consistent with the idea of a random alloy model.

Vacancy Correlation Factors

A vacancy diffusing in a uniform matrix will diffuse by a random walk with correlation factor equal to unity. In an actual concentrated alloy, however, the vacancy motion will not be random. For consistency and completeness, the effect of correlated vacancy motion should be included in the present equations. This can be done by including the vacancy correlation factor f_{v}.

To find the average correlation factor f_{v} for diffusion of vacancies, one first defines partial vacancy correlation factors $f_{\mathrm{v}}{}^m$ for diffusion of vacancies by exchange with the various species m. These $f_{\mathrm{v}}{}^m$ then are weighted according to the number of jumps per unit time for each species to obtain the average,

$$f_{\mathrm{v}} = \Sigma_m N_m w_m f_{\mathrm{v}}{}^m / \Sigma_m N_m w_m \,. \qquad (5)$$

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[3] J. R. MANNING, Phys. Rev. **139**, A 2027 [1965].

In the random alloy model, f_v is always less than or equal to unity. Thus, the effect of vacancy correlation is to decrease the effective frequency of random vacancy jumps.

It is of interest to note that individual $f_v{}^m$ often will be greater than unity. In a random alloy, a vacancy which has just exchanged with a slow diffusing atom B will have a smaller than random probability of retracing its jump by re-exchanging with B. This leads to a partial correlation factor $f_v{}^B$ which is greater than unity. However, after a vacancy has exchanged with a fast diffusing atom A, the probability of a re-exchange will be greater than the random probability. Thus, the correlation factor $f_v{}^A$ would be smaller than unity. Nevertheless, since w_m appears in Eq. (5), exchanges with fast diffusing atoms having $f_v{}^i$ less than unity are favored in the weighting process, making f_v in the random alloy model always less than or equal to unity.

If the average vacancy jump frequency in an alloy is W, equal to the denominator in Eq. (5), then the effective frequency of random jumps equals $W f_v$, equal to the numerator in Eq. (5). To make the rate of vacancy diffusion in the random alloy model where a uniform matrix is assumed correspond to that in an actual random alloy, it is necessary to replace the actual vacancy jump frequency W with the effective frequency of random vacancy jumps, equal to $W f_v$. With this final correction, one arrives at a self-consistent model in a random concentrated alloy where the individual atom whose diffusion is being followed retains its identity and has jump frequency w_i but other atoms in the crystal are replaced by average matrix atoms all having a jump frequency $W f_v$ for exchange with a neighboring vacancy. This picture corresponds to that of an isolated impurity in an infinite uniform medium, so the correlation factor can be calculated by much the same methods as have been extensively applied to calculate correlation factors for dilute alloys.

Random Alloy Equations

In the random alloy model, vacancy binding energies will all be zero. Therefore, the probability of an vacancy being at any given site equals N_v, the mole fraction of vacancies in the crystal; and the tracer diffusion coefficient $D_i{}^*$ for species i in a cubic crystal is given by

$$D_i{}^* = \tfrac{1}{6} \lambda^2 z N_v w_i f_i \tag{6}$$

where λ is the jump distance and z is the number of nearest neighbor sites to which jumps can occur. Since each atom is treated as being in identical surroundings, the randomization frequency h_i is the same for a vacancy neighboring on any atom regardless of its species. This frequency is equal to that in a pure crystal having an effective vacancy jump frequency $W f_v$. Thus, from Eq. (2),

$$h_i = M_0 W f_v . \tag{7}$$

Combining Eqs. (4) and (5) yields

$$W f_v = \Sigma_m N_m w_m f_v{}^m . \tag{8}$$

Also, in the random alloy model, it can be shown that the atom correlation factor f_m and the partial vacancy correlation factor $f_v{}^m$ for exchanges with atoms of species m are related by the equation [4]

$$f_m = f_v{}^m f_0 \tag{9}$$

where f_0 is the atom correlation factor in a pure crystal, given by

$$f_0 = M_0 / (M_0 + 2) \tag{10}$$

Equations (6) – (10) can be substituted into Eq. (1) to yield

$$f_i = \frac{-2 D_i{}^* + (M_0+2) \sum N_m D_m{}^*}{(M_0+2) \sum N_m D_m{}^*} . \tag{11}$$

The summation over m is over all atoms species in the crystal. Here, the right hand side of Eq. (11) can be expressed directly in terms of the $D_m{}^*$ rather than $w_m f_m$ since in Eq. (6) λ and z are geometric constants and N_v does not depend on m.

In a binary alloy, Eq. (11) reduces to

$$f_A = \frac{(M_0+2)(N_A D_A{}^* + N_B D_B{}^*) - 2 D_A{}^*}{(M_0+2)(N_A D_A{}^* + N_B D_B{}^*)} , \tag{12}$$

$$f_B = \frac{(M_0+2)(N_A D_A{}^* + N_B D_B{}^*) - 2 D_B{}^*}{(M_0+2)(N_A D_A{}^* + N_B D_B{}^*)} . \tag{13}$$

Also, in a binary alloy, substituting Eqs. (9) – (11) into Eq. (5) yields

$$f_v = 1 - \frac{2}{M_0} \left[\frac{(M_0+2) N_A N_B (D_A{}^* - D_B{}^*)^2}{(M_0+2)(\bar{D})^2 - 2 D_A{}^* D_B{}^*} \right] \tag{14}$$

where

$$\bar{D} = N_A D_A{}^* + N_B D_B{}^* . \tag{15}$$

Graphs showing values of f_A, f_B and f_v can be found elsewhere [5], as can more detailed discussions of the general dependence of these correlation factors on composition and diffusion coefficient ratios.

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[4] J. R. Manning, Acta Met. **15**, 817 [1967]; Metall. Trans. **1**, 499 [1970].

[5] J. R. Manning, Phys. Rev., to be published.

If D_A^* equals D_B^* in a binary alloy, it follows that $f_A = f_B = f_0$. For ratios of D_A^*/D_B^* which differ from unity, the correlation factor for the faster diffusing species will be less than f_0, whereas the correlation factor for the slower diffusing species will be greater than f_0. These values can range as high as unity and as low as zero. The deviation of f_i from f_0 tends to be largest when $D_i^*/\overline{D}$ differs from unity by a maximum amount. Thus, for constant diffusion coefficient ratios, the deviation from f_0 increases as N_i becomes smaller. Though it is not obvious from Eq. (14), the restrictions on the D_i^* are such that f_v also must lie in the range from zero to unity.

Evaluation of Random Alloy Model

The present treatment results in an averaging of the many possible jump frequencies which can occur in concentrated alloys. This allows the results to be expressed in terms of a limited number of independent jump frequencies, equal to the number of atom species in the crystal. The assumption that the net effect from the various atom configurations which might surround the various atoms is equivalent to the effect from a suitable uniform matrix does involve an approximation. However, this approximation should not be large if one is dealing with a reasonably random non-dilute alloy.

By contrast, the present equations may not apply well to ordered alloys or those with appreciable clustering. Also the random alloy model should apply best to the more concentrated alloys and be less accurate for dilute alloys. In particular, the assumption of zero vacancy binding energy, implying that a vacancy is not preferentially attracted to any particular atom or site, is reasonable in concentrated alloys, where a vacancy regardless of its position always can expect to neighbor on one or two atoms of a given species, but becomes doubtful in dilute alloys where strong impurity-vacancy binding involving isolated impurities can occur. Nevertheless, despite limitations on its range of applicability, the present random alloy model presents a reasonable picture for a large number of alloys. For many alloys, this model should be very useful, providing acceptable accuracy and illustrating major effects concerning correlation factors in concentrated alloys.

The present equations also have two positive advantages. (1) They are simple in form and thus are easy to manipulate mathematically, and (2) they contain no unknown jump frequencies since they are expressed directly in terms of measureable diffusion coefficients. This latter point is especially important in allowing direct comparison with experiment.

The value of having a simple analytic expression for the correlation factor becomes particularly evident when one wishes to obtain the derivative of the correlation factor, as in necessary in the following section on activation energies. In methods which require a numerical solution of complex equations, the evaluation of the correlation factor itself at a given point is a major task, with the accurate calculation of its derivative being even more difficult. By contrast, evaluating the derivative of Eq. (11) is a simple analytic operation.

Activation Energies

Experimentally, it is observed that the tracer diffusion coefficient D_i^* depends exponentially on the temperature. Thus,

$$D_i^* = D_{i0} \cdot \exp\{-Q_i/k\,T\} \qquad (16)$$

where Q_i is the measured activation energy for diffusion, k is Boltzmann's constant, T is the absolute temperature and D_{i0} is the measured pre-exponential.

According to theory, the tracer diffusion coefficient can be expressed in terms of atomic quantities as

$$D_i^* = \tfrac{1}{6}\,\lambda^2\,\nu_i\,f_i \qquad (17)$$

where the atom jump frequency, ν_i, equal to $z\,N_v\,w_i$ in Eq. (6), also depends exponentially on the temperature.

$$\nu_i = \nu_0 \cdot \exp\{-H_i/k\,T\} \qquad (18)$$

where H_i is the activation enthalpy.

It has been pointed out previously [6, 7] that, because of the temperature dependence of the correlation factor, H_i can differ appreciably from Q_i. Specific calculations of this difference were made for dilute alloys based on particular assumptions about the temperature dependence of the vacancy jump frequencies. In the present paper, this analysis is extended to non-dilute alloys. No further assumptions about the temperature dependence of the

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[6] J. R. MANNING, Phys. Rev. Letters **1**, 365 [1958].

[7] A. D. LECLAIRE, Phil. Mag. **7**, 141 [1962].

various jump frequencies are necessary here since the random alloy equations already are expressed in terms of the experimental tracer diffusion coefficients.

From the experimental relation, Eq. (16), one obtains

$$Q_i = -k[\partial \ln D_i^*/\partial(1/T)] . \tag{19}$$

From the theoretical expression, Eq. (18),

$$H_i = -k[\partial \ln \nu_i/\partial(1/T)] \tag{20}$$

and from the theoretical expression, Eq. (17),

$$-k\frac{\partial \ln D_i^*}{\partial(1/T)} = -k\frac{\partial \ln \nu_i}{\partial(1/T)} - k\frac{\partial \ln f_i}{\partial(1/T)} . \tag{21}$$

The term arising from the temperature dependence of the correlation factor may be designated as C_i,

$$C_i = k\frac{\partial \ln f_i}{\partial(1/T)} , \tag{22}$$

so Eq. (21) can be written as

$$Q_i = H_i - C_i . \tag{23}$$

To find the difference between the enthalpy H_i and the experimental activation energy Q_i, one must calculate the derivative of the correlation factor f_i with respect to T^{-1}. This can be done very easily by use of the analytic expression Eq. (11). For a binary alloy, one obtains

$$k\frac{\partial \ln f_A}{\partial(1/T)} = \frac{2N_B D_A^* D_B^*\{[k\,\partial \ln D_B^*/\partial(1/T)] - [k\,\partial \ln D_A^*/\partial(1/T)]\}}{\bar{D}[(M_0+2)\bar{D} - 2D_A^*]} . \tag{24}$$

Similarly, by merely interchanging the subscripts A and B,

$$k\frac{\partial \ln f_B}{\partial(1/T)} = \frac{2N_A D_A^* D_B^*\{[k\,\partial \ln D_A^*/\partial(1/T)] - [k\,\partial \ln D_B^*/\partial(1/T)]\}}{\bar{D}[(M_0+2)\bar{D} - 2D_B^*]} \tag{25}$$

where $\bar{D}$ is the average diffusion coefficient defined by Eq. (15). The derivatives on the right hand side can be expressed in terms of the experimental activation energies Q_A and Q_B, as in Eq. (19). Thus,

$$C_A = \frac{2N_B D_A^* D_B^*(Q_A - Q_B)}{\bar{D}[(M_0+2)\bar{D} - 2D_A^*]} , \tag{26}$$

$$C_B = \frac{-2N_A D_A^* D_B^*(Q_A - Q_B)}{\bar{D}[(M_0+2)\bar{D} - 2D_B^*]} . \tag{27}$$

Because of restrictions on the ratio D_A^*/D_B^* for a binary alloy in the random alloy model, the denominators in Eqs. (24) – (27) can never be negative. This "forbidden region" is discussed in detail elsewhere[5]. If Q_B is larger than Q_A, it follows from Eq. (27) that C_B will be positive and H_B will be larger than Q_B. Similarly, C_A will then be negative, so H_A will be smaller than Q_A. The difference between H_B and H_A therefore is necessarily larger than the difference between the experimental quantities Q_B and Q_A. This relationship is illustrated in Figure 1. The absolute magnitudes of C_A and C_B can be appreciably different from one another if either N_A/N_B or D_A^*/D_B^* differs appreciably from unity. The separations shown in Figure 1 for example are those in a diamond structure alloy with $N_A = 1/6$ and $D_A^*/D_B^* = 1$.

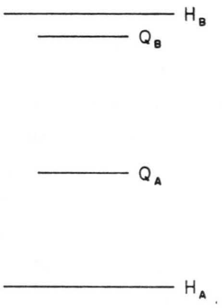

Fig. 1. Relative values of the activation energies Q and enthalpies H for constituents A and B in a binary alloy. Energy is plotted vertically. The separations shown are those in a diamond structure alloy with $N_A = 1/6$ and $D_A^*/D_B^* = 1$ in the random alloy model.

All binary alloys can be represented as having one constituent B whose activation energy is larger than or equal to the activation energy of the other constituent A. There is no necessary connection between the sign of $(D_A^*/D_B^*) - 1$ and $Q_B - Q_A$ unless the pre-exponentials are equal. However, in random alloys, the pre-exponentials normally do not differ greatly, so the component with the lower activation energy usually has the higher diffusion coefficient. To maintain best consistency with examples where D_A^*/D_B^* was conventionally taken to be unity or larger, $Q_B - Q_A$ in Figure 1 is shown as being positive.

One of course could equally well represent all binary alloys, while at the same time avoiding redundancy, by using the convention that $Q_A \geqq Q_B$ or by allowing all values of Q_A/Q_B but with letter subscripts designating the species being chosen to satisfy a restriction such as $N_A \leqq 0.5$ or an alternative restriction such as $D_A^*/D_B^* \geqq 1$. In the present paper, this last-mentioned alternative is found convenient and used in several figures. In any case, the sign of $(Q_B - Q_A)/(H_B - H_A)$ is not affected by the choice of conventions since $Q_B - Q_A$ and $H_B - H_A$ necessarily both have the same sign.

Since C_A and C_B are both proportional to the experimental $Q_B - Q_A$, it is possible to express the relation between $\Delta H = H_B - H_A$ and $\Delta Q = Q_B - Q_A$ in a particularly simple form. From Eq. (23),

$$H_B - H_A = Q_B - Q_A + C_B - C_A, \tag{28}$$

so with C_A and C_B given by Eqs. (26) and (27),

$$\Delta H = \Delta Q + \frac{2 D_A^* D_B^* \Delta Q}{\bar{D}} \left[\frac{N_A}{(M_0+2)\bar{D} - 2 D_B^*} + \frac{N_B}{(M_0+2)\bar{D} - 2 D_A^*} \right] \tag{29}$$

or

$$\frac{\Delta H}{\Delta Q} = 1 + \frac{2 M_0 D_A^* D_B^*}{[(M_0+2)\bar{D} - 2 D_A^*][(M_0+2)\bar{D} - 2 D_B^*]}\,. \tag{30}$$

This simple equation for $\Delta H/\Delta Q$ is a consequence of the previously obtained result that both C_A and C_B are expressable in simple analytic form and depend linearly on ΔQ. Again there are only geometric constants and measureable experimental quantities on the right.

The ratio $\Delta H/\Delta Q$ according to Eq. (30) will always be greater than unity. It will be largest for those values of composition and D_A^*/D_B^* for which one of the bracketed factors in the denominator on the right approaches zero. Then the ratio $\Delta H/\Delta Q$ will go to infinity. As discussed below Eq. (27) the bracketed factors in Eq. (30) can never become negative in the random alloy model. The dependence of $\Delta Q/\Delta H$ on composition and on the ratio D_A^*/D_B^* is shown in Figures 2, 3, and 4 for diamond, body-centered cubic, and face-centered cubic structures. These figures all show similar features but differ in detail since the value of the geometric constant M_0, quoted in Table I, depends on crystal structure.

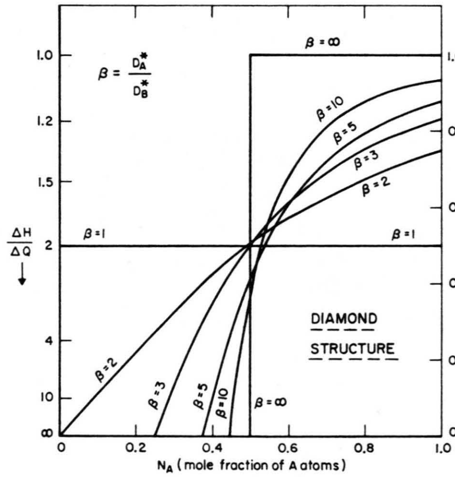

Fig. 2. Diamond structure, dependence of $\Delta H/\Delta Q$ on composition and the ratio $\beta = D_A^*/D_B^*$ for binary alloy in random alloy model. Here, $\Delta H = H_B - H_A$ and $\Delta Q = Q_B - Q_A$ where H is enthalpy and Q is experimental activation energy.

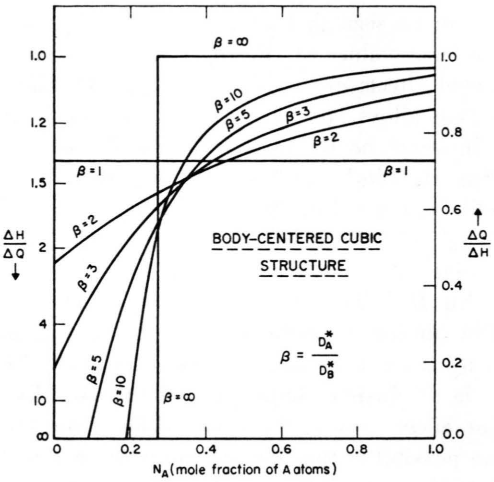

Fig. 3. Body-centered cubic structure, dependence of $\Delta H/\Delta Q$ on composition and the ratio $\beta = D_A^*/D_B^*$ for binary alloy in random alloy model. Here, $\Delta H = H_B - H_A$ and $\Delta Q = Q_B - Q_A$ where H is enthalpy and Q is experimental activation energy.

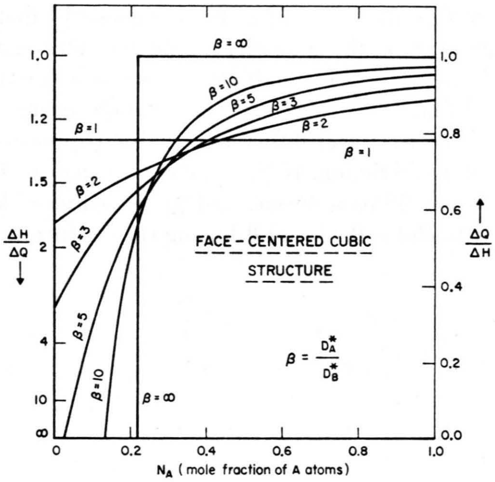

Fig. 4. Face-centered cubic structure, dependence of $\Delta H/\Delta Q$ on composition and the ratio $\beta = D_A^*/D_B^*$ for binary alloy in random alloy model. Here $\Delta H = H_B - H_A$ and $\Delta Q = Q_B - Q_A$ where H is enthalpy and Q is experimental activation energy.

It can be seen that small values of $\Delta Q/\Delta H$ and hence large values of $\Delta H/\Delta Q$ can often occur. The expected effects are particularly large for diamond structure alloys. In these figures, the positions of the limiting horizontal and vertical lines representing D_A^*/D_B^* equal to unity and to infinity, respectively, depend on M_0. The value of $\Delta Q/\Delta H$ for $D_A^*/D_B^* = 1$ always equals $M_0/(M_0+2)$; whereas the value of N_A at which $\Delta Q/\Delta H$ goes from one to zero for $D_A^*/D_B^* = \infty$ equals $2/(M_0+2)$.

The major contribution to the deviation of $\Delta H/\Delta Q$ from unity usually comes from $H_i - Q_i$ for the fast-diffusing impurity. Mathematically the major effect causing the H's to differ from the Q's is the possibility that the denominator in Eqs. (26) and (27) or Eq. (30) can become small.

For $D_A^*/D_B^* > 2$, the curves of $\Delta H/\Delta Q$ in Figure 4 are roughly similar to those one would obtain for $1 + |C_i/\Delta Q|$ for the faster diffusing species, where $C_i = H_i - Q_i$. It has been suggested [7] that the magnitude of this quantity might be large enough in dilute, or even non-dilute, alloys to account for the difference between the activation energy Q_D measured by tracer diffusion and that Q_{IF} measured by internal friction. If Q_D is taken as equal to Q_i for the faster diffusing species and Q_{IF} is assumed identical with H_i for the faster diffusing species (presuming that internal friction measures an uncorrelated jump frequency such as that in Eq. (18) and the measurement is dominated by the fast-diffusing species), one indeed would expect that $Q_D - Q_{IF}$ would equal $Q_i - H_i$ for the fast diffusing species. Experimentally, however, as one moves into a more concentrated alloy, the measured differences $Q_D - Q_{IF}$ and ΔQ usually do not change greatly. By contrast, the quantity $C_i/\Delta Q$ from the present equations does show a large composition dependence. Also for $N_i = 0.5$, the ratio $|C_i/\Delta Q|$ is small in face-centered cubic crystals, while $Q_D - Q_{IF}$ can be of approximately the same magnitude as ΔQ. Thus, both in magnitude and in composition dependence the correlation term C_i does not have the proper properties in the non-dilute range to explain the measured differences between Q_D and Q_{IF}. The full explanation of the difference between Q_D and Q_{IF} very likely will take into account not only C_i but also other influences on Q_{IF}, as suggested for example by WELCH [8]. However, the specific additional effects calculated by Welch, even when added to C_i, still do not provide agreement with experiment. Thus, it appears that further explanation of the difference between Q_F and Q_{ID} is required.

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[8] D. O. WELCH, Mat. Sci. Eng. **4**, 9 [1969].