

# A Vacancy-Flux Effect in Diffusion in Metallic Systems

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Serious disagreements are often found between experimentally determined intrinsic diffusion coefficients and those calculated employing the usual form of the vacancy theory. In the new theory it is proposed that the total intrinsic flux,  $J_i$ , of component  $i$ , is the sum of a part,  $J_i^r$ , due to the usual random exchanges of component  $i$  with the vacancies, and a second part,  $J_i^f$ , due to exchanges with the vacancies composing the net vacancy flux. The present treatment, while less powerful than that of Manning, has the advantage of easy visualization and of facilitating the application of the vacancy-flux effect to complex systems.

IT is becoming increasingly evident that there are serious deficiencies in the version of the vacancy theory of diffusion that has been widely used for the past 20 years. One type of evidence is the frequent lack of agreement between intrinsic diffusion coefficients and tracer diffusion coefficients, even taking account of the thermodynamic factor. A second kind of evidence is the observation of a Kirkendall shift larger than theoretically possible, that is, larger than can be accounted for without assigning a negative value to one of the two intrinsic diffusion coefficients.<sup>1-3</sup> The thermodynamic factor could conceivably make both coefficients negative, but not just one.

It is clear that a cause of these anomalies, apart from any inadequacy of the usual vacancy theory, might lie in an oversimplified treatment of the data. Adequate experimental techniques, including the use of moderate pressure during the diffusion anneal, are now available to insure that porosity, lateral expansion, and so forth, can be kept negligibly small in most cases. The effect of differences in atomic volume can be of major importance, and it is essential that one of the available methods<sup>4</sup> be used to account for this factor. In the present treatment this is accomplished by the consistent use of moles per cubic centimeter as the unit of concentration.

Of the various possible inadequacies of the vacancy theory, attention will be given here only to effects of the net vacancy flux. Manning<sup>5</sup> has previously considered this question, beginning with an analysis of atomic jumping of tracer atoms. When he added the effect of a concentration gradient, new terms arose that could be associated with the flow of vacancies. The present treatment uses quite a different approach. The usual vacancy flux,  $J_v$ , is introduced explicitly, and a simple analysis predicts major changes in the intrinsic diffusion coefficients from this cause.

The usual assumptions are made that only a vacancy mechanism is operative, that the formation of voids can be neglected, and that changes in the partial molal volumes,  $\bar{V}_1$  and  $\bar{V}_2$ , are negligible. The significant

diffusion coefficients for the present topic are  $D_1$  and  $D_2$ , the intrinsic coefficients, which enter in the equations,

$$J_1 = -D_1 \frac{\partial c_1}{\partial x} \quad [1]$$

and

$$J_2 = -D_2 \frac{\partial c_2}{\partial x} = +D_2 \frac{\bar{V}_1}{\bar{V}_2} \frac{\partial c_1}{\partial x} \quad [2]$$

where the flux  $J_i$ , moles per sq cm per sec, is that crossing the Kirkendall interface. The concentration,  $c_i$ , is in units of moles per cu cm, and the concentration gradient,  $\partial c_i / \partial x$ , is evaluated at the Kirkendall interface. It will be recalled<sup>1</sup> that the calculation of  $D_1$  and  $D_2$  involves the measurement of areas on the diffusion curve with respect to the positions of the Kirkendall and Matano interfaces. In the case of the anomalies mentioned earlier, the Kirkendall shift is too large to be accounted for by the difference in fluxes ( $J_2 - J_1$ ), given by Eqs. [1] and [2]. The logical inference is that the flux of the solvent atoms,  $J_1$ , is actually in the same direction as the flux of the solute atoms,  $J_2$ . In terms of Eq. [1] this requires that  $D_1$  have a negative value. However, it would be somewhat misleading to state that the solvent atoms are diffusing up their own concentration gradient. The explanation that will be advanced here pictures competing processes producing the net flux of solvent atoms: 1) diffusion of the solvent atoms down their own gradient by random exchanges with vacancies; and 2) diffusion of solvent atoms in the opposite direction by exchanges with the net vacancy flux.

## ACTION OF THE NET VACANCY FLUX

Theories of vacancy diffusion can be formulated with varying degrees of refinement, and the present theory has purposely been kept as simple as appeared adequate to explain the phenomenon in question. In particular the following aspects have been neglected:

- 1) the gradient of vacancy concentration in comparison to the gradient of the atomic species;
- 2) departure of vacancy concentration from the local equilibrium value;
- 3) variation of the jump frequency,  $w$ , with the specific surroundings of the atom-vacancy pair being considered;
- 4) correlation effects.

These and other refinements can be considered once the essential mechanism has been established.

The essential idea of the present analysis is to calculate the total intrinsic flux,  $J_i$ , of component  $i$  as the sum,

$$J_i = J_i^r + J_i^f \quad [3]$$

where  $J_i^r$  is attributable to the usual random atomic jumping, and  $J_i^f$  is a contribution arising from the net vacancy flux,  $J_v$ . The latter quantity, of course,

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is known to be  $-(J_1 + J_2)$ . Each of the two terms on the right-hand side of Eq. [3] will now be discussed.

A simple expression for the rate of random jumping of component  $i$  from a given atomic plane to the adjacent plane a distance  $\lambda$  to the right is,

$$(J_i^r)_{\text{forward}} = c_i \lambda N_v w_i \quad [4]$$

where  $J_i^r$  will have units of moles per sq cm sec if  $c_i$  is the concentration of component  $i$  in moles per cm<sup>3</sup>,  $N_v$  is the mole fraction of vacancies, and  $w_i$  is the jump frequency for the exchange of a vacancy with a neighboring atom of component  $i$ . When the reverse jumping is taken into account, the net flux of component  $i$  is found to be

$$J_i^r = -\lambda^2 N_v \frac{\partial c_i}{\partial x} w_i \quad [5]$$

Of the astronomical number of vacancy jumps that are involved in the random diffusion process across 1 sq cm of a given atomic plane for 1 sec, only about one jump in  $10^5$  contributes to the net vacancy flux,  $J_v$ . Consequently, one can treat this small fraction of jumps separately from the rest without significantly biasing the random process already discussed. For the purpose of obtaining a numerical analysis of the effect of the net vacancy flux, a specific orientation of the fcc lattice has been chosen for the present treatment. A more quantitative treatment could be employed, but it seems preferable to postpone this refinement until the effect of correlation is also taken into account.

If one considers the orientation in which a (111) plane is perpendicular to the direction of diffusion, then a given vacancy has three nearest neighbors in each of the planes (to the left and to the right) in the direction of diffusion. Since the flux  $J_v$  is composed of those (net) vacancies that have crossed a given plane in the crystal from left to right, these vacancies can either: 1) exchange laterally with one of six neighbors or 2) exchange with one of three neighbors in the next plane to the right. Neglecting any biasing in the direction of diffusion, one third of the flux  $J_v$  can be expected to continue on to the next plane. It should be noted that this flux is in addition to the random flux characteristic of the plane in question. For generality the quantity  $\alpha \approx \frac{1}{3}$  will be used in the following analysis.

The terms  $J_1^f$  and  $J_2^f$  in Eq. [3], produced as a result of the vacancy flow, are in the same ratio as the numbers of exchanges of each species with vacancies,

$$J_1^f = -\alpha J_v \frac{N_1 w_1}{N_1 w_1 + N_2 w_2} \quad [6]$$

$$J_2^f = -\alpha J_v \frac{N_2 w_2}{N_1 w_1 + N_2 w_2} \quad [7]$$

where the minus sign takes account of the fact that these atomic fluxes are in the direction opposite to the net vacancy flux. When Eq. [3] is written for each component using Eqs. [5] and [6] or [7], and these equations are then solved simultaneously, the resulting expressions are:

$$J_1 = -\lambda^2 N_v \frac{\partial c_1}{\partial x} \left\{ \frac{w_1 [N_1 w_1 + (1 - \alpha) N_2 w_2] - w_2 \frac{\bar{V}_1}{\bar{V}_2} \alpha N_1 w_1}{(1 - \alpha)(N_1 w_1 + N_2 w_2)} \right\} \quad [8]$$

$$J_2 = +\lambda^2 N_v \frac{\partial c_1}{\partial x} \left\{ \frac{w_2 \frac{\bar{V}_1}{\bar{V}_2} [N_2 w_2 + (1 - \alpha) N_1 w_1] - w_1 N_2 w_2}{(1 - \alpha)(N_1 w_1 + N_2 w_2)} \right\} \quad [9]$$

The ratio of the fluxes can then be determined as a function of the ratio  $w_1/w_2$ ,

$$\frac{J_1}{J_2} = -\frac{w_1 \left[ N_1 \frac{w_1}{w_2} + (1 - \alpha) N_2 \right] - \frac{w_1}{w_2} \frac{\bar{V}_1}{\bar{V}_2} \alpha N_1}{\frac{\bar{V}_1}{\bar{V}_2} \left[ N_2 + (1 - \alpha) N_1 \frac{w_1}{w_2} \right] - \frac{w_1}{w_2} N_2} \quad [10]$$

The conditions under which  $D_1$  becomes negative can most easily be determined with reference to those that make  $D_1 = 0$ , that is, make  $J_1 = 0$ . These are the conditions for which the numerator of Eq. [10] is zero. One of these,  $w_1/w_2 = 0$ , is not of interest. Others can be deduced from the equation,

$$N_1 \frac{w_1}{w_2} + (1 - \alpha) N_2 = \alpha N_1 \frac{\bar{V}_1}{\bar{V}_2} \quad [11]$$

which has the solution,

$$\frac{w_1}{w_2} = \alpha \frac{\bar{V}_1}{\bar{V}_2} - (1 - \alpha) \frac{N_2}{N_1} \quad [12]$$

For the case when  $\bar{V}_1 = \bar{V}_2$  and  $\alpha = \frac{1}{3}$ , Eq. [12] predicts that the largest ratio of  $w_1/w_2$  at which a negative  $D_1$  should be observed is  $w_1/w_2 < \frac{1}{3}$  (i.e.,  $w_2/w_1 > 3$ ), when the concentration at the Kirkendall interface is almost  $N_1 = 1$ . With decreasing concentration of component 1 at the Kirkendall interface, the limiting value of  $w_1/w_2$  decreases still further and reaches 0 at  $N_1 = \frac{2}{3}$ . In terms of the solute atom, this means that, even if the vacancies exchange preferentially with the solute atoms, negative values for  $D_1$  should not occur at solute concentrations above  $N_2 = \frac{1}{3}$  at the Kirkendall interface.

Although the above predictions can only be considered semiquantitative, it is significant that they are in qualitative agreement with the available information on the occurrence of negative  $D_1$  values. The most conclusive case studied by Correa da Silva and Mehl<sup>1</sup> was diffusion of tin in a copper matrix with the Kirkendall interface at 3 at. pct Sn. The Kirkendall shift was found to be three times greater than could be accounted for by assuming that  $D_{Cu} = 0$ . It is reasonable to assume<sup>6</sup> that  $w_{Sn}$  is much greater than  $w_{Cu}$  in the concentration range studied, thus fulfilling the conditions necessary for obtaining a negative value for  $D_{Cu}$  according to the present theory. Hartley *et al.*<sup>2</sup> summarized their results as follows: "Studies of interdiffusion in the Cb-V, Cb-Ti, and Mo-Ti systems indicate that under certain conditions, that is, an incremental couple of an equiatomic alloy with the pure slower-moving component, negative intrinsic diffusion coefficients for the slower-moving species are obtained from the observed marker shift by applying the Darken analysis."

The question of the interpretation of negative diffusion coefficients has taken on new importance with the growing interest in three-component systems, where negative values have been found for both interdiffusion coefficients and intrinsic diffusion coeffi-

cients.<sup>7,8</sup> In fact, the present theoretical treatment grew out of an experimental verification on the binary Ni-Cr and Co-Cr systems of data previously obtained on the Ni-Co-Cr ternary systems. This research is still in progress.

## DISCUSSION

The principal contribution of this paper is a simple picture for visualizing the effect of the net vacancy flux on the intrinsic diffusion of the components of a solid solution. It clearly reveals that diffusion in a concentration gradient is determined not only by random atomic jumping but also by the net vacancy flux (which is absent in an ordinary tracer-diffusion experiment). This second term is especially significant for a slow-diffusing solvent since it has the opposite sign to the first term. Using the present picture, it is possible to visualize the relation that would be expected between intrinsic and tracer diffusion coefficients even in multicomponent or other complex systems.

Future developments of this topic may be expected in two main directions. The same qualitative picture should be applicable to other aspects of vacancy interactions and may offer further useful insights. Refinement of the quantitative features is likely to come through the more elegant theory of Manning<sup>5</sup> and its extensions. It appears<sup>9</sup> that the two approaches give the same result in the approximation neglecting cor-

relation effects. An important advance over the present treatment would be the inclusion of correlation, a result that can perhaps be achieved best by combining the directness of this approach with the more powerful methods employed by Manning.

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# The Equilibrium Phase Diagram, Niobium (Columbium)-Aluminum

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*The phase equilibria of the binary system, Nb-Al, were established by metallographic, X-ray diffraction, hardness, and thermal-analysis techniques. Three intermediate phases were identified, Nb<sub>3</sub>Al, Nb<sub>2</sub>Al, and NbAl<sub>3</sub>. The Nb<sub>3</sub>Al and Nb<sub>2</sub>Al phases have extensive ranges of solubility. The maximum solubility of aluminum in niobium is 23.0 ± 0.5 at. pct (8.0 wt pct) Al at 1960° ± 10°C. The maximum solubility of niobium in aluminum is less than 0.3 ± 0.1 at. pct (1.0 wt pct) Nb. The Nb<sub>3</sub>Al and Nb<sub>2</sub>Al intermediate phases form peritectically at 1960° ± 10°C and 1870° ± 10°C, respectively, whereas the NbAl<sub>3</sub> phase forms congruently from the melt at 1605° ± 10°C. A eutectic reaction oc-*

*curs at 57.8 ± 0.5 at. pct (28.5 wt pct) Al and 1500° ± 10°C between Nb<sub>3</sub>Al and NbAl<sub>3</sub>. The aluminum-rich region of the system has a peritectic reaction where liquid reacts with NbAl<sub>3</sub> to form aluminum solid solution. Structural and lattice-parameter data for the intermediate phases were determined by X-ray diffraction analyses. An unusual transformation having characteristics of nucleation-growth and martensitic mechanisms occurs on cooling the niobium solid solution in the region from 18 at. pct (6 wt pct) Al to 23 at. pct (8 wt pct) Al. The transformed product on rapid quenching is an acicular Nb<sub>3</sub>Al.*

THE intent of an over-all research program was to develop niobium-aluminide-base coatings for refractory metals since these coatings exhibit useful high-

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temperature resistance to oxidation. As a prerequisite, the phase equilibria of the system, Nb-Al, were necessary. A literature survey revealed that the phase-equilibria data reported by various investigators were rather incomplete and conflicting. Therefore a complete determination of the system was undertaken by the authors from 0 to 100 pct of solute addition.<sup>1</sup> In 1959 Savitskiy<sup>2</sup> presented a tentative diagram which