ON THE INFLUENCE OF IMPURITIES ON THE RATE OF SELF-DIFFUSION

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ON THE INFLUENCE OF IMPURITIES ON THE RATE OF SELF-DIFFUSION

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The question of the influence of small concentrations of alloying elements on the diffusion mobility of the solvent atoms of a solid alloy is of substantial practical importance in connection with the task of obtaining alloys with preassigned properties, in particular heat-resistant ones. The action of impurities on volume and boundary diffusion should be distinguished.

The concept that explains the influence of impurities on the rate of volume diffusion and self-diffusion by their effect on the thermodynamic properties of an alloy (for example, on the heat of sublimation) is unsuitable for explaining the action of small concentrations. Indeed, impurities substantially increase the coefficient of self-diffusion of the solvent at such small concentrations that the heat of evaporation of the solvent and its other partial thermodynamic properties are practically unchanged.

For illustration of this point we determined the parameters of self-diffusion and the thermodynamic characteristics of the solvent in two systems, one of which (Ag–Cu) has positive deviations from Raoult' s law, and the other (Ag–Sn) negative deviations.

Table 1

Parameters of self-diffusion of silver in silver–copper alloys

Alloy No.	Cu, at. %	D_0, cm^2/sec	E, cal/mol	Temperature interval, °C
1	0.00	0.62	45200	690–906
2	0.17	0.65	45200	780–906
2	0.17	1.06	41000	690–780
3	0.84	0.68	45200	780–906
3	0.84	0.08	39000	690–906
4	1.68	0.07	40600	725–906
5	5.00	0.06	39900	725–880
6	8.15	0.04	38300	725–830

Self-diffusion was studied by the thin-layer method (^{1}). The values found for the self-diffusion parameters are given in Tables 1 and 2.

As can be seen from Tables 1 and 2, a small percentage of copper and tin impurity significantly lowers the activation energy of silver.

Impurities in amounts of 0.17; 0.84% Cu and 0.18% Sn affect the activation energy only at relatively low temperatures.

The thermodynamic characteristics of silver in the systems under consideration were determined by us experimentally by the isotope-exchange method (^{2}). In addition, for the silver—copper system the heat of dilution was calculated from the semiempirical formulas proposed by Krupkowski (^{3}).

Table 2

Parameters of self-diffusion of silver in silver–tin alloys

Alloy No.	Sn, at. %	D_0, cm^2/sec	E, cal/mol	Temperature interval, °C
7	0.18	0.622	45200	830—900
7	0.18	0.132	41700	700—830
8	0.48	0.128	40900	700—850
9	0.91	0.170	40500	700—850
10	2.80	0.200	40250	700—850
11	4.56	0.225	39700	700—830

The heats of dilution of silver obtained in solutions containing up to 1.68 at. % copper and up to 2.8 at. % tin are practically equal to zero. The magni-

values pertaining to alloys of more substantial concentrations are presented in Table 3. It can be seen from them that the diffusion characteristics of alloys are more sensitive to impurities than the thermodynamic ones.

Obviously, small additions cannot substantially change the heat of vaporization, which is an average quantity. The energy of the transition state of self-diffusion near impurity atoms may be sharply lowered, which affects the rate of self-diffusion, especially at relatively low temperatures. Let us note that small impurities cannot give a significant decrease in the diffusion rate, since experiments cannot be carried out in which the conductivity of the main mass of the crystal would not be manifested.

Table 3

Heats of dilution of silver

System	Second component, at. %	Heat of dilution of silver, cal/mole (experimental data)	Heat of dilution of silver, cal/mole (calculated data)
Ag—Cu	5	−40	−16
Ag—Cu	8.15	−100	−46
Ag—Sn	4.56	+130	–

The reason for the change in the diffusion characteristics of dilute solutions is the appearance around the atoms of the dissolved substance of regions with increased mobility, or so-called "short diffusion paths" (^{4}). Independently of the concrete reasons for the appearance of "short diffusion paths," the problem arises of describing their influence on the average mobility of atoms in the alloy.

Let us consider the following simple model. Let the impurities create, in a part of the volume ρ, an increased self-diffusion coefficient D_1, while the self-diffusion coefficient of the pure solvent is D_0, and the effective self-diffusion coefficient is D.

The diffusion resistance of the medium when its sections are connected in series is approximately equal to the sum of their diffusion resistances (for the stationary regime this is exact), i.e., equal to the sum of quantities reciprocal to the diffusion coefficient $\left(\frac{1}{D_i}\right)$.

This approximation, suitable for describing diffusion along linear trajectories, is applicable, as will be shown below, to boundary diffusion and does not at all describe volume diffusion.

Indeed, equality to zero of the diffusion coefficient in one of the sections stops the whole process ($D = 0$), which, of course, should not occur in volume diffusion. It will also be incorrect to sum conductivities (D_i), which corresponds to the idea of parallel flow of fluxes. This is easily verified by taking one of the partial diffusion coefficients equal to infinity.

It is obvious that the presence in the volume of regions with altered mobility corresponds neither to parallel nor to series connections.

For a stationary diffusion process this question can be considered in general form. The action of such a region is completely analogous to the effect on the electric field of spheres inside a dielectric with a different value of the dielectric constant, since Poisson' s equation in the absence of charges is equivalent to the stationary diffusion problem.

For the case of spherical regions these problems are considered in connection with the derivation of the Clausius—Mossotti, Lorentz—Lorenz equations, the theory of magnetic permeability, etc. For ellipsoidal regions a solution was given by Fricke (^{5}), when considering the electrical conductivity of suspensions.

For the case of spherical regions and small concentrations, this solution may be written in the following form:

$$\frac{D - D_0}{D_0} = 3\rho \frac{D_1 - D_0}{D_1 + 2D_0}. \tag{1}$$

For the case $\dfrac{D_0}{D_1} \ll 1$, the equation becomes the following:

$$\frac{D - D_0}{D_0} = 3\rho \left(1 - \frac{3D_0}{D_1}\right). \tag{2}$$

Thus, if $D \to \infty$, then:

$$\frac{D - D_0}{D_0} = 3\rho. \tag{3}$$

This means that it is not the ρ-part of the volume that is excluded, as would be the case for a series connection, but a value three times larger.

From equation (2), using the expression that defines the activation energy,

$$\frac{\partial \ln D}{\partial T} = \frac{E}{RT^2},$$

it is not difficult to derive the effective value of the activation energy and the pre-exponential factor:

$$E = E_0 - 9\rho \frac{D_0}{D_1}(E_0 - E_1), \tag{4}$$

$$A = A_0 \left\{1 + 3\rho - 9\rho \frac{D_0}{D_1} \left(1 - \frac{E_0 - E_1}{RT}\right)\right\}, \tag{5}$$

where E_0 and D_0 are the activation energy and diffusion coefficient of the pure solvent, and E_1 and D_1 are the same quantities referring to the region with enhanced mobility.

We see that, for $D_1 \to \infty$, $E = E_0$, which is natural, since under these conditions diffusion proceeds outside the regions with enhanced mobility. Since for $E_1 = E_0$ the equality $E = E_0$ again arises, E must pass through a maximum.

Fig. 1. Concentration dependence of the change in the self-diffusion coefficient of silver at 1000°K:
1 –Ag–Sn,
2 –Ag–Cu

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Figure 1: Fig. 1. Concentration dependence of the change in the self-diffusion coefficient of silver at 1000°K: 1 —Ag—Sn, 2 —Ag—Cu

A linear dependence between the change in the self-diffusion coefficient and the concentration is obtained for the alloy of silver with copper at concentrations not exceeding 2 at. %, and with tin—1 at. %.

The slope coefficient of the straight lines in Fig. 1 is connected with two characteristics, ρ and D_1, which cannot be determined from a single experiment. There are, however, possibilities for the following two estimates.

1. Taking $D_1 = \infty$, we obtain from the value of ρ the radius of the perturbed region. This value, equal in the Ag—Cu system to $4 \cdot 10^{-8}$ cm and in the Ag—Sn system to $7 \cdot 10^{-8}$ cm, will be the lower limit of the radius, as is evident from equation (2).
2. From the temperature dependence of $\dfrac{D - D_0}{D_0}$, assuming that ρ does not depend on temperature and taking an exponential dependence for D_1, one can obtain the value of D_1. The calculation shows that in the systems studied its value is expressed by the equations:

$$D_1 = 1.1 \cdot 10^{-5} \exp\left(\frac{17000}{RT}\right) \qquad \text{(Ag—Cu)},$$

$$D_1 = 1.6 \cdot 10^{-5} \exp\left(\frac{18000}{RT}\right) \qquad \text{(Ag—Sn)}.$$

The question arises of the applicability of relation (1) for describing processes involving the superposition of volume diffusion and diffusion along grain and block boundaries. Apparently, because here the "short" paths are connected with one another, a closer approximation for large diffusion paths is the representation of a parallel connection of resistances.

Let us consider, from an analogous point of view, the influence of impurities on boundary diffusion. Since boundary diffusion may be regarded as a series connection of resistances, small impurities can sharply reduce the effective diffusion coefficient. From equation (1) for volume diffusion it follows that if $D_1 = 0$, i.e., if diffusion ceases in some sphere, then

$$\frac{D - D_0}{D_0} = -\frac{3}{2}\rho.$$

Thus, the effect of the action of a region with zero mobility is 1.5 times greater than the effect that would occur for a parallel connection. Meanwhile, it has been shown[6] that 0.1% boron reduces the diffusion coefficient of tin along nickel grain boundaries almost tenfold. This effect is apparently connected not only with the presence of an increased concentration of boron at the grain boundary, but also with the enhanced influence of retarding additions in a scheme of resistances connected in series. The accelerating action of short diffusion paths in boundary diffusion should be less than in volume diffusion.

Thus, for the same intensity of action, a retarding effect will act more strongly at the boundary than in the bulk, while an accelerating effect will act less strongly.

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Note: Figure translations are in progress. See original paper for figures.