Physically this means that even when there is no divergence in the calculated κ at low temperatures due to a lack of U processes (boundary scattering will make the integrals converge) the low-frequency modes would cause extremely high conductivity at high temperature. Thus, we deduce either κ_2 does not properly take the coupling of N processes into account or the value τ_N^{-1} used in this work does not represent solely N processes for the longitudinal modes (as indicated at the end of Appendix A).

For the case of the transverse modes we have indicated $\tau_U^{-1} \gg \tau_N^{-1}$ at temperatures above the maximum, in this case κ_2, would be negligible.

These considerations lead us to use the Klemens approach in which Eq. (B1) reduces to Eq. (5) and N processes are simply an added scattering mechanism.

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Diffusion of Palladium in Copper and Silver*

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The diffusion of palladium in single crystals of copper and silver has been measured by the tracer-sectioning technique. The results are

$$D_{\mathrm{Pd}\to\mathrm{Cu}} = 1.71^{+0.23}_{-0.21} \exp[-(54\,370 \pm 300)/RT] \ \mathrm{cm}^2/\mathrm{sec},$$

and

$$D_{\mathrm{Pd}\to\mathrm{Ag}} = 9.57^{+1.63}_{-1.37} \exp[-56\,750 \pm 300)/RT] \ \mathrm{cm}^2/\mathrm{sec}.$$

The difference between the activation energies for Pd diffusion and self-diffusion in copper and silver is in only qualitative agreement with the theories of Lazarus and LeClaire. Correlation factors for palladium diffusion in silver are calculated using Lidiard's theory and the data on silver diffusion in palladium-silver alloys by Nachtrieb *et al.* From these correlation factors and Manning's theory, it is shown that palladium atoms repel vacancies in silver. This is in disagreement with the quenching studies of Hamaguchi.

INTRODUCTION

It has been shown experimentally that activation energies for the diffusion of impurities at near-zero concentration in a given solvent may be considerably different from the activation energy for self-diffusion of the solvent. In 1954, Lazarus[1] proposed a theory of impurity diffusion based on the electrostatic interactions between the impurity ion and the neighboring vacancy and solvent atoms. This model was based on the picture of an impurity of charge Z dissolved in a metal and screened by the conduction electrons. The resulting potential distribution around the impurity was assumed to be described by the linearized form of the Thomas-Fermi equation. The change in energy of vacancy formation was considered to be the change in the lattice binding energy of a nearest neighbor in the screened potential of the impurity atom. The change in the energy of motion was viewed as a corresponding change in the appropriate elastic constants. This theory predicted that the activation energy for impurity diffusion should be less than solvent self-diffusion for electropositive impurities and greater for electronegative impurities.

Although fair agreement between theory and experiment was found for electropositive impurities diffusing in copper and silver,[2] for electronegative impurities (iron, cobalt, and nickel in copper,[3] ruthenium in silver,[4] and platinum in gold[5]) only the sign of the activation energy difference was predicted correctly.

An alternative theoretical derivation of the difference, ΔQ, between the activation energies for impurity diffusion and solvent self-diffusion has recently been proposed by LeClaire.[6] The change in energy of vacancy formation was calculated in the same manner as in the Lazarus treatment, but the change in energy of motion was considered to be the difference in electrostatic energy between the configuration corresponding to the impurity atom at the saddle point and that with the impurity at the equilibrium lattice position. LeClaire used the more accurate numerical solution of the Thomas-Fermi equation as calculated by Alfred and March,[7] and also took into account the temperature dependence of the correlation factor, f, for impurity diffusion.

LeClaire's theory provided improved agreement with experiment for the electropositive impurities, although

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* This work was performed at Argonne National Laboratory under the auspices of the U. S. Atomic Energy Commission.

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the agreement was still poor for the electronegative impurities. LeClaire pointed out that much of the discrepancy between theory and experiment for electronegative impurities may be removed by selecting the proper value of Z. It has been customary to set Z equal to the difference between the atomic number of the solute and the solvent. If such values of Z actually applied, it would mean that, for example, iron, cobalt, and nickel atoms in solution in copper contained 28 localized core electrons such that the $3d$ states would be fully occupied. However, the addition of any of these solutes to copper is known to introduce a paramagnetic contribution to the susceptibility, which is inconsistent with such solute elements having filled $3d$ states in diamagnetic copper. Hence, the true values of Z are probably numerically less than the customarily ascribed values, and such changes in Z are in the proper direction to provide better agreement between theory and experiment.

In order to evaluate properly the applicability of the electrostatic theory for electronegative impurities, it is necessary to measure the diffusion in a noble metal of an impurity for which the charge is not ambiguous. Dilute Ag-Pd [8,9] and Cu-Pd [8] alloys are diamagnetic, with nearly the same value of the susceptibility as for pure silver and copper, out to 40% palladium. Therefore, the $4d$ shell of palladium is filled at low palladium concentrations and the palladium ions in solution have $Z=-1$. For the case of palladium diffusion in silver, the solute and solvent cores are electrically identical, which should give better agreement with the theory than for palladium diffusion in copper.

The measurements of palladium diffusion in silver are interesting for two other reasons: (1) from Lidiard's[10] theory on the effect of solute additions on self-diffusion, the data of Nachtrieb *et al.*[11] on the effect of palladium additions on the self-diffusion of silver, and the present values for palladium diffusion in silver, one can determine the value of the correlation factor for palladium diffusion in silver. (2) Hamaguchi,[12] on the basis of his quenching experiments on pure silver and several silver-palladium alloys, reports that palladium ions attract vacancies, in direct contrast to what one would expect from the electrostatic theories.

EXPERIMENTAL

Single crystals of copper and silver were grown from 99.999% pure material (American Smelting and Refining Company) in high-purity graphite crucibles by slowing lowering the crucible through a vacuum furnace. The 0.4-in. diam. and 6-in. long crystals were cut into 1/4-in. long cylinders, and the ends were planed flat and parallel with a Servomet spark machine. The samples were given a light etch and then annealed for 24 h in a vacuum furnace at 75°C below their melting points. After etching to be sure of monocrystallinity, the specimens were electropolished and electroplated with Pd^{103}. The plating bath consisted of 30 ml H_2O, 100 mg NH_4Cl, 0.6 ml HCl and a trace quantity of Pd^{103} in the form of $PdCl_2$. About 3 to 6 atom layers of Pd^{103} were plated on each specimen.

The 17-day half-life Pd^{103} isotope was made by neutron irradiation of 60% enriched Pd^{102}. After irradiation, the sample was allowed to decay for 5 days in order to eliminate the 13-h half-life Pd^{109} isotope. Radio-chemical-analysis showed that more than 99% of the activity was due to Pd^{103} plus its short-lived daughter, Rh^{103}.

Two specimens were placed in a tantalum cup with their active faces adjacent, but separated by a quartz disc. The cups containing the samples were sealed in evacuated quartz capsules, placed in large nickel heat sinks in the diffusion furnaces, and annealed for periods of 5 h to 1 month, depending on the temperature. The temperature of the heat sink was measured with a calibrated Pt-Pt10% Rh thermocouple throughout the diffusion anneals. The temperature differences between the heat sinks and the samples for each diffusion temperature were measured using a calibrated thermocouple embedded in a dummy sample sealed in an identical evacuated capsule. The furnace temperatures were maintained to within ± 1°C by an electronic controller. After the diffusion anneals, the specimens were quenched in ice water. Time corrections for heating and cooling were calculated using the temperature measurements on the dummy sample as it was heated and cooled.

The diffused specimens were mounted on a precision lathe, reduced in diameter to eliminate edge effects, and sectioned. Fifteen sections were taken from each sample; the total thickness removed ranged from 0.0075 to 0.040 in. The chips from each section were collected and weighed on a Mettler microbalance. The sum of the weights of the sections was within 0.1 to 0.5% of the difference in weight of the sample before and after sectioning. The thickness of each section was determined from the diameter and density of the specimen and the weight of the section.

The Pd^{103} concentration in each section was determined by counting the 40-keV gamma emitted by the 57-min half-life Rh^{103} daughter in a well-type scintillation counter. The counting was performed at least 48 h after the diffusion anneal so that the Pd^{103}–Rh^{103} equilibrium was obtained and the activity from atoms which diffused as Rh^{103} was negligible. A constant counting geometry was maintained by dissolving the chips from each section in the same amount of HNO_3 and counting the solution in standard polyethyline vials of constant size. Typically, 10^4 to 10^5 counts were taken for each section.

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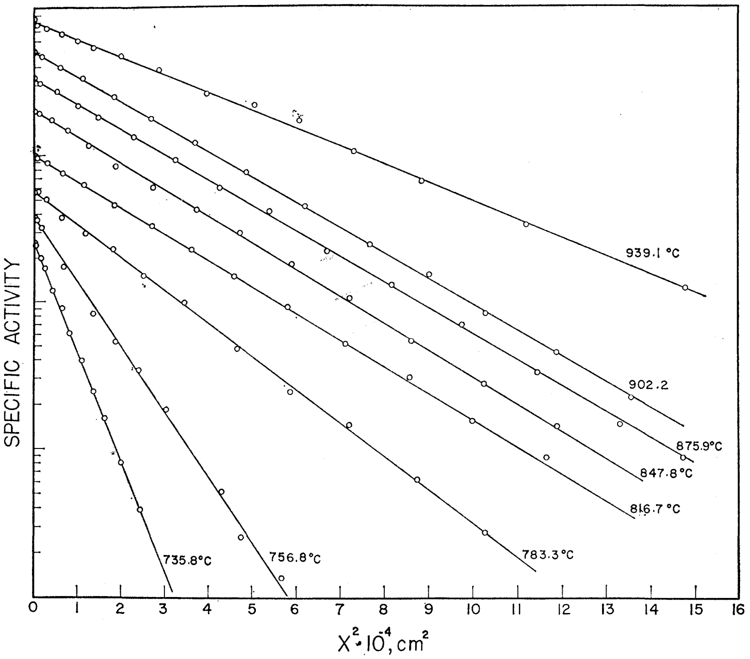

FIG. 1. Penetration curves for diffusion of Pd in Ag.

Diffusion coefficients were calculated on a computer by the method of least squares from the linearized Gaussian penetration plots. The error in the diffusion coefficients due to sectioning and counting is estimated to be ±2%. The error in the temperature measurements is 1°C, which leads to a total uncertainty in $D(T)$ of approximately 4%. The diffusion parameters D_0 and Q and their errors were determined by a least-squares fit of all the data except the two lowest temperatures for palladium diffusion in silver. The reasons for their elimination will be discussed later.

TABLE I. Diffusion of Pd^{103} in copper and silver.

Solvent material	Temperature (°C)	Time (sec)	D (cm^2/sec)
Ag	939.1	1.543×10^5	5.69×10^{-10}
Ag	939.1	1.543×10^5	5.59×10^{-10}
Ag	902.2	2.322×10^5	2.67×10^{-10}
Ag	902.2	2.322×10^5	2.77×10^{-10}
Ag	875.9	3.934×10^5	1.55×10^{-10}
Ag	875.9	3.934×10^5	1.48×10^{-10}
Ag	847.8	7.372×10^5	7.95×10^{-11}
Ag	847.8	7.372×10^5	8.06×10^{-11}
Ag	816.7	1.548×10^6	3.93×10^{-11}
Ag	816.7	1.548×10^6	4.01×10^{-11}
Ag	783.3	2.657×10^6	1.77×10^{-11}
Ag	783.3	2.657×10^6	1.76×10^{-11}
Ag	756.8	2.772×10^6	8.84×10^{-12}
Ag	756.8	2.772×10^6	9.19×10^{-12}
Ag	735.8	2.722×10^6	5.20×10^{-12}
Ag	735.8	2.722×10^6	5.32×10^{-12}
Cu	1055.6	5.802×10^4	2.00×10^{-9}
Cu	1055.6	5.802×10^4	1.99×10^{-9}
Cu	1015.2	6.678×10^5	1.01×10^{-9}
Cu	1015.2	6.678×10^5	1.01×10^{-9}
Cu	987.6	1.289×10^6	6.11×10^{-10}
Cu	987.6	1.289×10^6	6.23×10^{-10}
Cu	953.0	2.058×10^6	3.48×10^{-10}
Cu	953.0	2.058×10^6	3.42×10^{-10}
Cu	902.0	6.684×10^5	1.30×10^{-10}
Cu	902.0	6.684×10^5	1.33×10^{-10}
Cu	872.9	2.760×10^6	7.90×10^{-11}
Cu	872.9	2.760×10^6	7.64×10^{-11}
Cu	843.5	1.812×10^6	3.92×10^{-11}
Cu	843.5	1.812×10^6	3.77×10^{-11}
Cu	807.0	2.732×10^6	1.68×10^{-11}
Cu	807.0	2.732×10^6	1.66×10^{-11}

RESULTS

Two measurements of D were made at each of eight different temperatures for Pd^{103} diffusion in copper and in silver single crystals. The penetration plots for one of the two samples at each temperature are shown in Figs. 1 and 2. The diffusion coefficients and temperatures are given in Table I. Arrhenius plots of the data are given in Figs. 3 and 4 together with the data for self-diffusion in the pure solvents.[13,14] The temperature dependence of D may be represented by

$$D_{\mathrm{Pd}\to\mathrm{Ag}}=9.57\,{}^{+1.63}_{-1.37}\exp\times[-(56\,750\pm300)/RT]\,\mathrm{cm}^2/\mathrm{sec} \qquad (1)$$

$$D_{\mathrm{Pd}\to\mathrm{Cu}}=1.71\,{}^{+0.23}_{-0.21}\exp\times[-(54\,370\pm300)/RT]\,\mathrm{cm}^2/\mathrm{sec}, \qquad (2)$$

where R is the gas constant, T is the temperature in °K, and the errors are standard errors from the least-squares treatment of the data.

DISCUSSION

Dislocation Enhanced Diffusion

The enhanced diffusion evident at the two lowest temperatures for palladium diffusion in silver is similar to that generally observed for electronegative impurity

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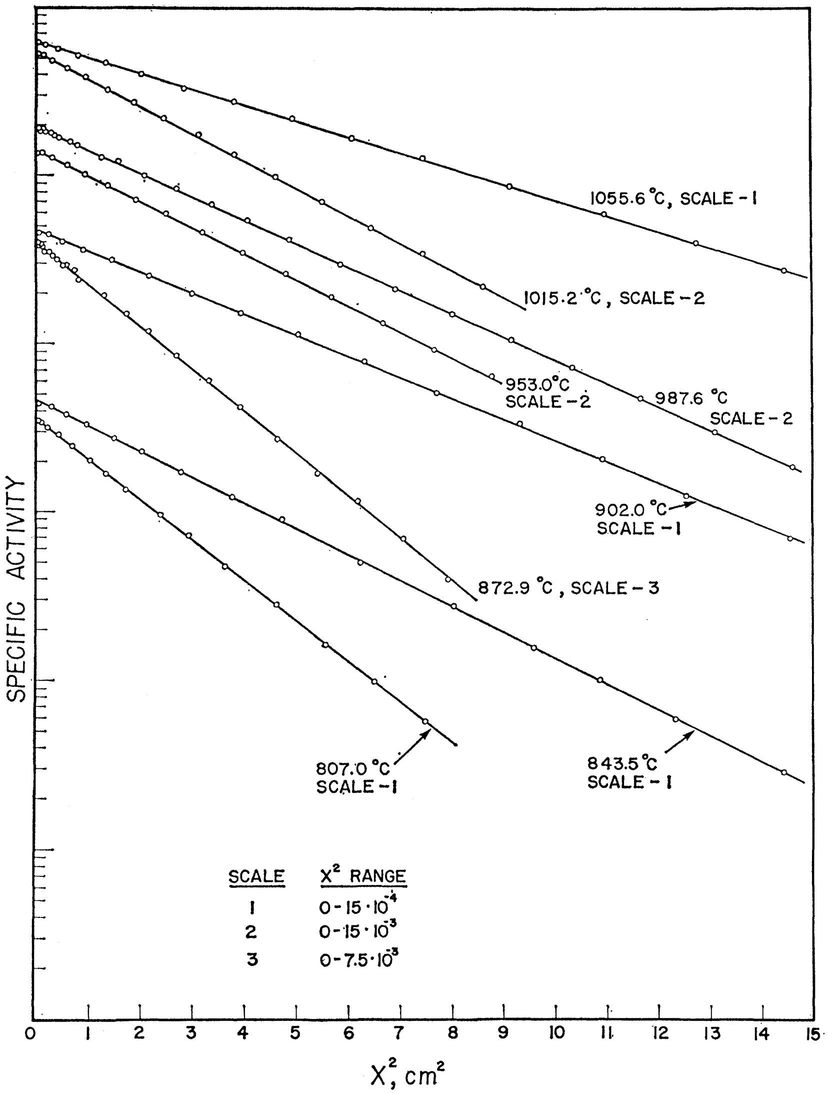

FIG. 2. Penetration curves for diffusion of Pd in Cu.

diffusion in the noble metals at $D<10^{-11}$ cm²/sec.[3,5] Hart[15] suggested that diffusion along dislocations could enhance self-diffusion at low temperatures. Later, Mortlock[16] pointed out that segregation towards the dislocations could increase this effect in the case of impurity diffusion. Mortlock showed that the enhancement in the diffusion coefficient, ΔD, may be given by

$$\Delta D/D_l = n f_0 (D_d/D_l)(C_d/C_l)\,, \tag{3}$$

where n is the number of sites that go to make up the cross-sectional area of the dislocation pipe, f_0 is the fraction of all atoms situated in the cores of the pipes, D_d/D_l is the ratio of the diffusion coefficient in the pipe to that in the lattice and C_d/C_l is the ratio of the concentration in the pipe to that in the lattice. D_d/D_l for palladium diffusion in silver at 720°C is estimated to be 10^5 from Yukawa and Sinnott's[17] work on grain boundary diffusion of nickel in copper. Taking n to be 10 and the dislocation density to be 10^6 to 10^7 lines/cm² (f_0 equals 6×10^{-10} to 6×10^{-9}), then C_d/C_l must lie in the range of 20 to 200 to account for the observed enhancement of D. This implies an impurity-dislocation binding energy of the order of 0.2 eV, which is not unreasonable.

Comparison of ΔQ with Theory

Using the published values for the activation energy for self-diffusion in silver[13] and copper[14] one obtains the difference in activation energy, ΔQ, between palladium diffusion and self-diffusion as listed in Table II. The

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[16] A. J. Mortlock, Acta Met. **8**, 132 (1960).

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TABLE II. Theoretical and experimental values of ΔQ for palladium diffusion in copper and silver (ΔQ in kcal/mole).

Solvent	ΔQ_{exp}	ΔQ_{th} (LeClaire)	ΔQ_{th} (Lazarus)	% Error
Ag	+12.6	+7.4	+2	+41
Cu	+7.3	+11.0	+3	−51

theoretical values of ΔQ obtained by the LeClaire and Lazarus theories are also listed in Table II. The LeClaire model yields the closer agreement between theory and experiment; however, the discrepancy is still large as seen in the last column of Table II.

Since the LeClaire theory gives better agreement between ΔQ_{exp} and ΔQ_{th} for electropositive impurities than for electronegative impurities (for impurity elements which immediately follow in the periodic table the noble metal in which they are diffusing, the agreement is within 6%), a closer look should be taken at the effect of the sign of the impurity charge on the degree of uncertainty of the assumptions made in the theory. The most important assumption, which may depend on this sign, is the applicability of the Thomas-Fermi approximation as an adequate description of the electrostatic potential around an impurity atom in a noble metal. According to the Thomas-Fermi model, there is a sphere of radius, r_c, surrounding an electronegative impurity, within which no electrons are allowed and on which the potential equals the Fermi energy. For an impurity with $Z=-1$, Alfred and March[7] have calculated $r_c=1.66$ Å for silver and $r_c=1.41$ Å for copper. This is inconsistent with nuclear magnetic resonance data which show appreciable s electron densities at the nucleus. No such assumption concerning the absence of electrons is required for electropositive impurities. Any further refinements in this model must produce a larger electrostatic interaction for palladium atoms in silver and a smaller interaction for palladium atoms in copper in order to produce agreement with experiment.

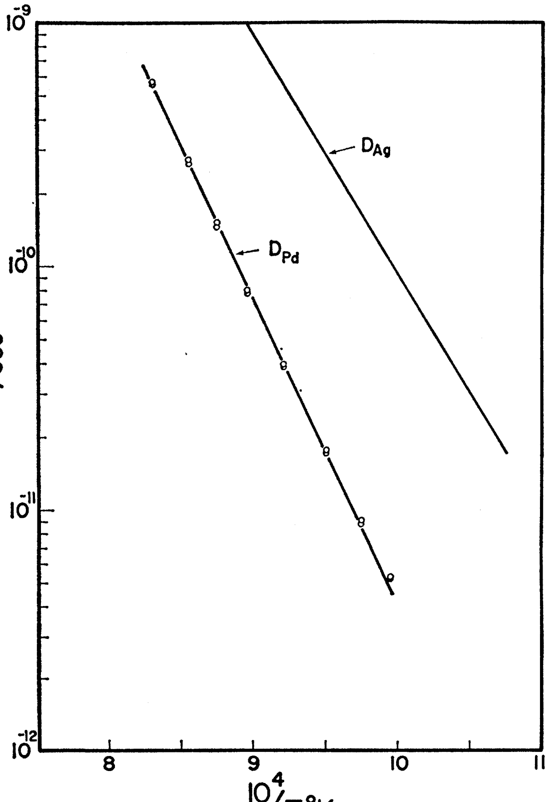

FIG. 3. Temperature-dependence of Pd diffusion in Ag. Self-diffusion in Ag is also shown. (See Ref. 13.)

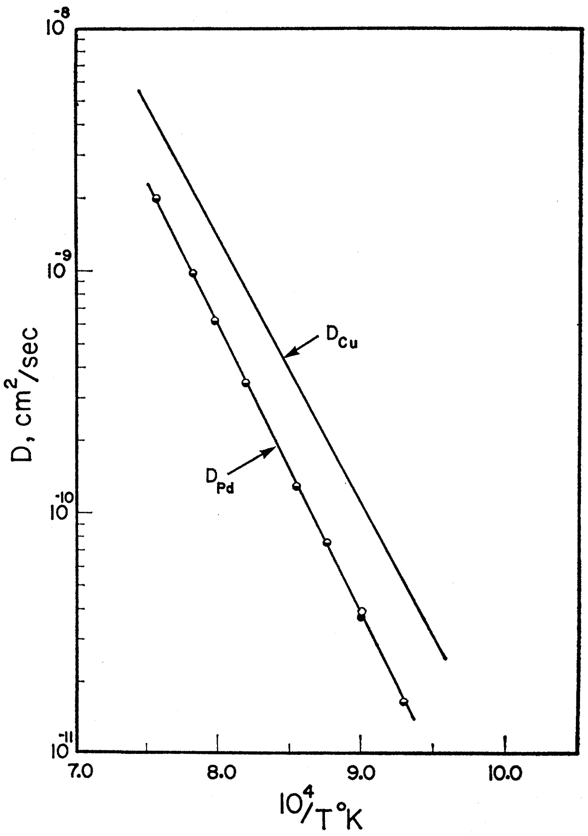

FIG. 4. Temperature dependence of Pd diffusion in Cu. Self-diffusion in Cu is also shown. (See Ref. 14.)

Recently, March and co-workers[18–20] have applied self-consistent perturbation theory in an effort to obtain a better value of the potential than that obtained by the Thomas-Fermi method. Unfortunately, for $Z=-1$, the first-order approximation gives poor agreement with experiment, and no convergent solution is obtained for the second-order approximation. They suggest that a

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third-order solution may be necessary for a convergent solution for negative values of Z.

Correlation Effects

The nonrandomness of successive jumps of an impurity is determined by the relative rates of exchange of the vacancy with the impurity atom and with neighboring solvent atoms. The correlation factor, f_i, is a measure of this nonrandomness and is given by

$$f_i=[W_1+(\tfrac{7}{2})W_3]/[W_1+W_2+(\tfrac{7}{2})W_3]. \tag{4}$$

for vacancy diffusion in a fcc lattice.[21] W_1 is the rate of exchange of a vacancy neighboring an impurity atom with any of the four solvent atoms that also are neighbors of the impurity; W_3 is the rate of exchange of a vacancy neighboring an impurity with any of the seven solvent atoms adjacent to the vacancy but not neighbors of the impurity; and W_2 is the impurity-vacancy exchange rate. The various exchange rates may be written in the form

$$W_j=\nu_j \exp(-H_j/RT), \tag{5}$$

where the ν_j's are the appropriate vibration frequencies and the H_j's are the respective activation energies. Since in general the H_j's will not be equal, f_i will vary with temperature.

From a treatment of the influence of solutes on self-diffusion in metals, Lidiard[10] has obtained the expressions:

$$D_s(C)=D_s(0)(1+bc) \tag{6}$$

and

$$f_i=1-(4f_0/(b+18))[D_i/D_s(0)],$$

where $D_s(0)$ is the self-diffusion coefficient in the pure solvent, $D_s(C)$ is the diffusion coefficient of the solvent in a dilute binary alloy of composition C, D_i is the impurity diffusion coefficient in the pure solvent, f_0 is the correlation factor for self-diffusion in the pure solvent, and b is a constant. From Nachtrieb's[11] measurements of the self-diffusion coefficient of silver in a series of silver-palladium alloys, we have $b=-8.1$. Using the available values of[22] f_0 and[13] $D_s(0)$ together with the present values of D_i, one obtains $f_i=0.96$ and 0.98 at 930° and 750°C, respectively. This may be compared to $b=-6.7$ and $f_i=0.85$ calculated from the LeClaire theory for $RT=2.0$ kcal/mole.

Mullen[23] has shown

$$f_i=1-\frac{f_0[D_i/D_s(0)](W_0/K_2)}{(W_1/W_3)+3.5F}, \tag{8}$$

where W_0 is the solvent-vacancy exchange rate when neither the vacancy nor the solvent is a nearest neighbor of an impurity, K_2 is the solvent-vacancy exchange rate when only the solvent atom is a nearest neighbor of an impurity, and F is a factor dependent only on W_0/K_2. Using Manning's[24] values of F as a function of W_0/K_2 and the data for the other terms at $RT=2$ kcal/mole, one finds that W_0/K_2 must be greater than 2.2 for palladium diffusion in silver. This corresponds to a repulsion between the impurity and a vacancy in the second coordination shell, because the K_2 jump which would bring the vacancy and impurity together is less likely than any other jump. The sign of ΔQ and the magnitude of f_i suggest a repulsive interaction between the impurity and a vacancy in the first coordination shell. These observations are in agreement with the Lazarus and LeClaire theories, but contradict the results of Hamaguchi's[12] quenching studies.

$D_s(C)$ is not known for the Cu-Pd system. From the LeClaire theory, b and f_i may be calculated to be -8.5 and 0.99, respectively, for $RT=2$ kcal/mole. Since this theory overestimates ΔQ for palladium diffusion in copper, the true values of b and f_i are probably closer to -7.0 and 0.85.

ACKNOWLEDGMENTS

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