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Author
Toth, Louis E.

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University of California

Ernest O. Lawrence
Radiation Laboratory

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Louis E. Toth[†]

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ABSTRACT

Two sets of equations developed for predicting activation energies
for self-diffusion in metals are generalized to describe diffusion in dilute
and concentrated alloy solid solutions. Bonding is considered as a
localized interaction and the bond strength between atoms of different
types is taken as the arithmetic mean of the bond strengths of the pure
elements. The activation energies for vacancy formation for migration
and for diffusion are shown to depend on the mole fractions of the diffusing
elements. The same empirical constants developed for self-diffusion are
used. The calculated results for alloy diffusion usually agree with the
experimental values to within the experimental error.

1. INTRODUCTION

The equations for the activation energy for self-diffusion developed
in the previous paper can be generalized to allow prediction of activation
energies for diffusion in substitutional alloys. Previous work in this area
has been largely restricted to predicting activation energies for diffusion
in dilute solutions. Lazarus and coworkers[1] found a promising correla-
tion between valence and the activation energy for solute diffusion. The

[†]Department of Mineral Technology and Lawrence Radiation
Laboratory, Inorganic Materials Research Division, University of
California, Berkeley, California.

same basic method has been applied by LeClaire[2] to the problem of movement of solute atoms in copper, silver, and gold solutions. He obtains exceptionally good results when the valence of the solute exceeds that of the solvent, but poor results when the valence of the solute is smaller than that of the solvent.

A second method that has been used is to determine the activation energy for migration, Q_m, by estimating the dilatational energy of the lattice and the compressive energy of the solute as the vacancy moves from site to site. The macroscopic shear moduli of the solvent and the compressibility of the solute are the parameters. The results, as given by Swalin,[3] agree fairly well with the experimental values when the activation energy of vacancy formation is estimated to be $0.6\ Q_D^{pure}$, the activation energy for self-diffusion for the solvent.

Turnbull and Hoffman[4] have argued that in dilute solutions the ratio of the energy of exchange of a vacancy with a solute atom to the energy of exchange of a vacancy with a solvent atom should be the same as the ratio of the solute binding energy to the solvent binding energy in the solution. The energy of formation of a vacancy adjacent to a solute atom is calculated from that for the pure solvent by correcting for the change in nearest neighbor bond energies that results from the presence of the solute atom. The energy of movement of a vacancy in the pure solvent is estimated to be $0.45\ Q_D^{pure}$.

In this paper values of the activation energies for migration and vacancy formation Q_m and Q_v are derived separately for both components of binary alloys and the sums of Q_m and Q_v are compared to experimental values of the activation energy for diffusion, Q_D, in dilute and concentrated

alloy solid solutions. The diffusion process is considered from a localized bonding approach. Only close-packed solutions will be discussed because of limitations in available data, but the method should be applicable to body-centered cubic alloys as well.

2. DEVELOPMENT OF CORRELATION

Bonds are broken to form vacancies and bonds are distorted during vacancy migration. In the preceding paper we related the energies necessary for these steps to the heat of sublimation and to the bulk modulus or melting temperature, and we adjusted the proportionality constants to give the best agreement with the known data. To extend the equations for application to alloy diffusion we consider bonding as a localized interaction between nearest neighbor atoms.

For an alloy in which X_A and X_B are the mole fractions of A and B atoms, respectively, and Z is the coordination number of any atom, the number of A-A bonds for the average A atom will be ZX_A, and the number of A-B bonds will be ZX_B. Similarly the number of B-B bonds for the average B atom will be ZX_B and the number of A-B bonds, ZX_A. The assumption is made here that the number of vacancies in the solution resulting from removing A atoms from the interior of the crystal and placing them on the surface is proportional to X_A and likewise, that the number of vacancies due to removal of B atoms is proportional to X_B. Taking the bond strengths as proportional to sublimation energy L_s, we find that the total energy for vacancy formation is proportional to

$$X_A \left(ZX_A L_s^A + ZX_B L_s^{AB} \right) + X_B \left(ZX_B L_s^B + ZX_A L_s^{AB} \right)$$

where L_s^{AB} is the arithmetic mean of L_s^A and L_s^B. Using the same proportionality constant that we used for vacancy formation in self-diffusion, 0.27, we find

$$Q_v = 0.27 \left(X_A^2 L_s^A + 2X_A X_B L_s^{AB} + X_B^2 L_s^B \right).$$

When an A atom exchanges places with a vacancy, the number of A-A bonds distorted is $X_A (Z-1)$ and the number of A-B bonds distorted is $X_B (Z-1)$. By analogy with our discussion of self-diffusion, we may correlate the distortion in the A-A bonds during movement with $(B_s V_o)_A$ or equivalently with T_m^A and the distortion of A-B bonds with $(B_s V_o)_{AB}$ or T_m^{AB}, the arithmetic mean of these quantities for the pure metals A and B. The activation energy for vacancy migration in FCC metals can then be expressed for A as

$$Q_m^A = 22.6 \left(X_A (B_s V_o)_A + X_B (B_s V_o)_{AB} \right) \tag{2a}$$

or

$$Q_m^A = 16.0 \left(X_A T_m^A + X_B T_m^{AB} \right) \tag{2b}$$

where the constants are the same as were used in the self-diffusion equations. Analogous equations, of course, describe Q_m^B. The activation energy for diffusion of A is the sum of Q_v^A and Q_m^A.

In the above equations the compressibility and the melting temperatures were used as parameters. It should be pointed out that when experimental values for Q_m^A, Q_m^B, Q_v^A, and Q_v^B in the pure metals are available, these values should be utilized in preference to the other parameters. In addition, Q_m^{AB} and Q_v^{AB} should be corrected for deviations from ideality when heats of mixing are known. Corrections for most of these

metallic systems are smaller than experimental uncertainties in the data.
The most reliable equations for diffusion would vary with composition as
follows

$$Q_D^A = X_A Q_m^A + X_B Q_m^{AB} + X_A^2 Q_v^A + 2 X_A X_B Q_v^{AB} + X_B^2 Q_v^B .$$

Since experimental values for Q_m and Q_v are generally not yet available,
we will calculate all values exclusively from compressibility and melting
temperature data.

As was first pointed out by Manning, [5] Q_m^B, the activation energy
for movement of solute atoms, should be corrected by a correlation factor
C, which is a measure of the extent to which the directions of successive
jumps of a solute atom depart from being random and is determined by
the relative rates of exchange of the vacancy with the solute atom and with
neighbor and near neighbor solvent atoms. LeClaire[2] derived the fol-
lowing equation for C:

$$C = D_2/D_0 f_0 e^{c/RT} \left(\frac{(\Delta H_2 - \Delta H_1) e^{-(\Delta H_1 + \Delta H_2)/RT} + 7/2(\Delta H_2 - \Delta H_3) e^{-(\Delta H_2 + \Delta H_3)/RT}}{\left(e^{-\Delta H_1/RT} + 7/2 e^{-\Delta H_3/RT} \right)^2} \right) .$$

Here f_0 is a purely geometric factor $= 9/11$, for cubic close-packed lat-
tices, D_0 is the frequency factor for self-diffusion, D_2 is the frequency
factor for B in A (B is the dilute solute), $\Delta H_2 = Q_m^B$, ΔH_1 is the activation
energy for the exchange of a vacancy neighboring a solute atom with any
one of the solvent atoms that are neighbors both of the vacancy and of the
solute atom. ΔH_3 is the activation energy for the exchange of the vacancy
with one of the solvent atoms which are adjacent to the vacancy but are
not neighbors of the solute atom.

In order to estimate C, an experimental determination of D_2 is necessary. We shall calculate C by estimating ΔH_1 and ΔH_3 in terms of the thermodynamic parameters already used. Since for close-packed structures a solvent atom next to both a solute atom and a vacancy is attracted to its neighbors by ten A-A bonds and one A-B bond, ΔH_1 may be estimated as $\dfrac{10Q_m^{A\,pure} + Q_m^{AB}}{11}$. Here $Q_m^{A\,pure}$ represents the exchange activation energy for pure A and Q_m^{AB} is the arithmetic mean of $Q_m^{A\,pure}$ and $Q_m^{B\,pure}$. A solvent atom next to a vacancy but not next to a solute atom is attracted to its neighbors by eleven A-A bonds so that ΔH_3 may be approximated as $Q_m^{A\,pure}$, the exchange activation energy for pure A. For the systems analyzed, RT is approximated by 2 kcal. It should be mentioned that unless $\Delta Q^B = Q_D^B - Q_D^{A\,pure}$ has a large negative value, C can be neglected.

For the activation energy of a dilute solution of B in A, with $X_A \sim 1$, $X_B \sim 0$, equations for diffusion of the solute become:

$$Q_D^B = 16.0\, T_m^{AB} + 0.27\, L_s^A - C \tag{3a}$$

and

$$Q_D^B = 22.6\, (B_s V_o)_{AB} + 0.27\, L_s^A - C. \tag{3b}$$

Further we have

$$\Delta Q^B = A_D^B - Q_D^{A\,pure} = 16.0\left(T_m^{AB} - T_m^A\right) - C \tag{4a}$$

or

$$\Delta Q^B = 22.6\left((B_s V_o)_{AB} - (B_s V_o)_A\right) - C. \tag{4b}$$

Equations 4a and 4b have been applied to dilute solutions in copper, silver, gold, nickel, and iron. The results are shown in Table I.

Table I. Comparison of theoretical and experimental values for ΔQ^B
(all energies in units kcal/mole)

The columns appropriate to calculation based on the melting temperature are
designated by M. T. The columns appropriate to calculations based
on the bulk modulus are designated by B. M.

Dilute solutes in Cu $\quad Q_D^{Cu} = 48.1 \pm 2.1$[a] $\qquad D_o = 0.62 \ cm^2/sec$[b]

Solute	D_2	$\Delta(Q_m + Q_v)$		C†		ΔQ^B Eq. 4a	ΔQ^B Eq. 4b	ΔQ exptl.
		M. T.	B. M.	M. T.	B. M.	M. T.	B. M.	
Zn	0.34	-5.1	-5.0	-2.0	-2.0	-3.1	-3.0	-2.5±1.4[c]
Cd	0.94	-6.1	-4.1	-4.1	-2.4	-2.0	-1.7	-2.3±1.0[d]
Hg	0.35	-9.0	-6.8	-5.2	-3.5	-3.8	-3.3	-4.2±1.3[e]
Ga	0.55	-8.4	-4.5	-5.5	-2.3	-2.9	-2.2	-2.3±0.9[e]
As	0.12	-2.1	-7.8	-0.1	-2.8	-2.0	-5.0	-6.1±1.3[e]
Sb	0.34	-3.6	-3.6	-1.1	-1.1	-2.5	-2.5	-4.9±1.2[f]
Ni	2.7	+3.0	+3.2	--	--	+3.0	+3.2	+8.3±1.5[g]
Co	1.93	+3.3	+2.7	--	--	+3.3	+2.7	+5.9±1.5[g]
Fe	1.40	+3.7	+2.5	--	--	+3.7	+2.5	+3.6±1.5[g]
Mn	--	+1.3	-0.2	--	--	+1.3	-0.2	-2.1 to -7.0[g]
Au	--	-0.2	+8.8	--	--	-0.2	+8.8	-2.3[h]

Dilute solute in Ag $\quad Q_D^{Ag} = 44.1 \pm 2$ $\qquad A_o = 0.44$[i]

Solute	D_2							
Zn	0.54	-4.4	-5.6	-2.3	-3.4	-2.1	-2.2	-2.4±0.4[j]
Cd	0.44	-5.1	-5.1	-2.8	-2.8	-2.3	-2.3	-2.4±0.4[k]
Hg	0.08	-8.0	-7.3	-2.4	-2.2	-5.6	-5.1	-6.0±1.2[l]
In	0.41	-6.5	-4.5	-3.8	-2.3	-2.7	-2.2	-3.5±0.4[k]
Tl	0.15	-5.3	-8.9	-1.8	-4.5	-3.5	-4.4	-6.2±1.7[m]

† RT was taken as 2 kcal

Table I. (Cont.)

Dilute solute in Ag $\qquad$ $Q_D^{Ag} = 44.1 \pm 2$ $\qquad$ $A_o = 0.44^i$

Solute	D_2	$\Delta(Q_m + Q_v)$		C		ΔQ^B Eq. 4a	ΔQ^B Eq. 4b	ΔQ exptl.
		M.T.	B.M.	M.T.	B.M.	M.T.	B.M.	
Ge	0.84	-0.2	-0.6	--	--	-0.2	-0.6	$-7.6 + 1.7^m$
Sn	0.25	-5.8	-1.9	-2.6	-0.4	-3.2	-1.5	-4.8 ± 0.4^k
Pb	0.22	-5.1	-2.9	-2.3	-0.8	-2.8	-2.1	-6.0 ± 2.2^n
Sb	0.17	-2.7	-4.0	-0.5	-1.1	-2.2	-2.9	-5.8^f
Ru	1.80	+11.7	+13.6	--	--	+11.7	+13.6	$+21.7 \pm 1.0^o$

Dilute solutes in Au $\qquad$ $Q_D^{Au} = 41.7^p$ $\qquad$ $D_o = 0.091$

Solute	D_2	M.T.	B.M.	M.T.	B.M.	M.T.	B.M.	ΔQ exptl.
Ni	0.30	+3.2	-5.6	--	-4.9	+3.2	-0.5	$+4.3^q$
Pt	7.6	+5.6	+8.6	--	--	+5.6	+8.6	$+15.7 \pm 7.0^r$

Dilute solutes in Ni $\qquad$ $Q_D^{Ni} = 66.8 \pm 1.3^s$ $\qquad$ $D_o = 1.27^s$

Solute	D_2	M.T.	B.M.	M.T.	B.M.	M.T.	B.M.	ΔQ exptl.
Mg	n.r.*	-6.4	-8.7	n.c.	n.c.**	-6.4	-8.7	-10.8 ± 2.3^t
Ti	0.86	+0.8	+0.9	--	--	+0.8	+0.9	-5.4 ± 2.3^t
Si	n.r.	-0.3	n.c.	--	--	-0.3	n.c.	-5.1^u
Al	1.87	-6.3	-5.7	-4.2	-3.7	-2.1	-2.0	-2.8 ± 2.3^t
Mn	7.50	-1.7	-3.2	-1.7	-3.2	0.0	0.0	$+0.3^u$
Mo	n.r.	+9.3	+15.3	--	--	+9.3	+15.3	$+2.1^u$
W	11.1	+15.4	+19.0	--	--	+15.4	+19.0	$+10.0 \pm 2.3^t$

* not reported = n.r.
** not calculated = n.c.

Table L. (Cont.)

Dilute solutes in Fe			Q_D^{Fe} FCC = 64.5^V			Q_D^{Fe} BCC = 59.2^V		
Solute	D_2	Phase	$\Delta(Q_m + Q_v)$		C		ΔQ^B Eq. 4a	ΔQ^B Eq. 4b	ΔQ exptl.
			M.T.	B.M.	M.T.	B.M.	M.T.	B.M.	
Ni	0.77	γ	-0.7	+0.5	--	--	-0.7	+0.5	+2.5^W
	1.3	α(paramag.)	-0.6	+0.5	--	--	-0.6	+0.5	-3.2^W
	1.4	α(ferromag.)	-0.6	+0.5	--	--	-0.6	+0.5	-0.5^W

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To calculate the activation energies for diffusion in alloys in which both components are present in comparable concentrations, C is neglected. This term contains as factors in the numerator $(\Delta H_2 - \Delta H_1)$ and $(\Delta H_2 - \Delta H_3)$, both of which become negligible in concentrated solutions. We also express the results in the form $\Delta Q^A = Q_D^A - Q_D^{A\,pure}$ where $Q_D^{A\,pure}$ refers to the calculated diffusion heat for pure A. This form is used because we are mainly interested in the effect of solution formation on the diffusion rates, and most errors in the calculation of $Q_D^{A\,pure}$ would not be reflected in ΔQ^A. In Table II we apply Eq. 2 to a large number of alloy systems in which the activation energies have been determined experimentally.

3. DISCUSSION OF RESULTS

In developing the equations of this paper, we have assumed that the energies for formation of vacancies and for movement of atoms depend only on the local bond energies of the lattice. Furthermore, we have not introduced any parameter to correct for a possible nonrandom concentration of vacancies in positions adjacent to solute atoms. Gross mismatches in the diameters of solute and solvent atoms might be expected to invalidate these assumptions. However, the predicted values of Q_D do not appear to show systematic deviations from the experimental values that can be attributed to a size effect.

For most of the substitutional alloys for which we have data, the activation energies for diffusion are predicted to within the probable errors in experimental determination of the activation energies. The satisfactory agreement between predicted and experimental activation energies lends support to the conclusions that the mechanism for diffusion

Table II. Comparison of theoretical and experimental values for ΔQ in alloy systems of varied composition (all energies in units kcal/mole)

At.% solv.	At.% solute	Ref.	Tracer	ΔQ calc. eq. 4a	ΔQ calc. eq. 4b	ΔQ exptl.
90.5 Ag	9.5 Al	a	Ag^{110}	-0.3	-0.5	-1.2
93.5 Ag	6.5 Cd	b	Ag^{110}	-1.4	-1.1	-1.5
			Cd^{115}	-6.1	-6.2	-3.6
72.0 Ag	28.0 Cd	b	Ag^{110}	-4.9	-4.6	-6.8
			Cd^{115}	-10.0	-9.7	-8.2
98.2 Ag	1.8 Cu	a	Ag^{110}	-0.3	$+0.1$	$+0.7$
98.5 Ag	1.5 Ge	a	Ag^{110}	-0.1	$+0.2$	-0.1
95.6 Ag	4.4 In	b	Ag^{110}	-1.4	-0.4	-1.5
			In^{114}	-5.1	-6.9	-3.8
83.3 Ag	16.7 In	b	Ag^{110}	-1.5	-1.2	-7.9
			In^{114}	-6.0	-8.0	-7.5
99.3 Ag	0.7 Pb	a	Ag^{110}	-0.3	0.0	$+0.6$
99.5 Ag	0.5 Pb	a	Pb^{210}	-3.3	-5.1	-5.4
90.2 Ag	9.8 Pd	c	Ag^{110}	$+1.1$	$+1.1$	-0.4
99.1 Ag	0.9 Sb	d	Ag^{110}	-0.4	0.0	-1.6
			Sb^{124}	-4.3	-4.3	-5.8
70.0 Ag	30.0 Zn	e	Ag^{110}	-4.8	-4.3	-8.1
			Zn^{65}	-10.5	-8.6	-8.9
69.0	31.0 Zn	f	Cu^{64}	-5.6	-5.8	-6.2
			Zn^{65}	-10.6	-10.0	-7.4

Table II. (Cont.)

At.% solv.	At.% solute	Ref.	Tracer	ΔQ calc. eq. 4a	ΔQ calc. eq. 4b	ΔQ exptl.
52.0 Cu	48.0 Zn	g	Cu^{64}	- 8.8	- 8.9	$\left\{ \begin{array}{l} -26.1^* \\ -11.1 \\ -12.3 \end{array} \right.$
			Zn^{65}	- 13.7	- 13.3	$\left\{ \begin{array}{l} -29.3^* \\ -3.9 \\ -11.8 \end{array} \right.$
50.0 Au	50.0 Cd	h	Au	- 14.2	- 10.5	- 13.8
			Cd	- 20.9	- 16.8	- 13.7

*The activation energy is strongly dependent upon the amount of ordering. The values 26.1 and 29.3 refer to complete disordering.

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in substitutional alloys is basically similar to the mechanism for self-diffusion and that both of these diffusion processes proceed by vacancy formation and displacement.

ACKNOWLEDGMENTS

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