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October 1966

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ABSTRACT

Using a Lennard-Jones 6-12 potential to represent the interactions in a fcc molecular lattice (argon) we have calculated the "activation energy", E , in the Arrhenius equation

$$\bar{D} = D_0 e^{-E/RT}$$

for self diffusion to be 3811 cal assuming that diffusion occurs via a vacancy exchange mechanism. This compares well with the experimental value of 4120 cal. The relaxation of the nearest neighbors to the vacancy-diffusing atom pair were calculated and were found to lower the barrier by 50%. We have also found that for a divacancy exchange self diffusion process the activation energy, 4742 cal, is in satisfactory agreement with experiment and the "frequency factor", D_0 , is greater than that for monovacancy diffusion.

We have calculated the activation energies for neon and krypton impurity diffusion via monovacancy exchange through an argon lattice to be 2187 and 3733 cal respectively.

INTRODUCTION

Theoretical calculations of self-diffusion coefficients have been made for copper¹⁻³ and argon.⁴ Even though the calculations for copper present a number of serious problems, rough agreement with experiment has been obtained. It would appear that more precise calculations could be made for argon than for copper since argon, for computational purposes, is reasonably well represented by a two-body potential and does not have the complications of free electrons or core polarization. Fieschi et al.⁴ have done extensive calculations on the self-diffusion coefficient in solid argon and have obtained results that are partially in agreement with experiments.⁵ Their exponential term is roughly 25% lower and the preexponential term differs by 10^4 from the experimental values.

Fieschi and coworkers estimated the barrier to diffusion by allowing the four nearest neighbors of the diffusing atom to relax while the atom and vacancy interchanged. In a recent study by the present authors,⁶ a program was developed which permits the calculation of the energy when all of the nearest neighbors of an adjacent pair of lattice sites are perturbed either by the substitution of an impurity or a vacancy, or by a combination of the two.

The expanded treatment in this paper gives a closer agreement with the observed activation energy than that of the earlier computation. Furthermore, the work done suggests that diffusion may occur equally well by the exchange of an atom with a divacancy rather than a monovacancy. It is true that the number of divacancies is low compared to the number of monovacancies, but the barrier is approximately the same, and this mechanism leads to a higher pre-exponential term when the Arrhenius equation is used to describe the diffusion process.

It is evident that these and similar computations are really only approximations, and the numerical values obtained are highly limited by the assumptions that are necessary at the present time. However, it is felt that sufficient insight into the physical process can be obtained to warrant the effort that is expended.

THEORY

It is known that most experimental diffusion coefficients⁷ can be fit by the Arrhenius equation

$$D = D_0 e^{-E/RT} \quad (1)$$

where D_0 , the "frequency factor" and E , the "activation energy" are constants. In some cases D_0 and E have been found to be temperature dependent.^{8,9}

For diffusion via some lattice defect the Arrhenius equation (Eq. 1) may be expressed as^{7,10}

$$D = \gamma a^2 \nu e^{S_D^+/R} e^{S_D/R} e^{-E_D^+/RT} e^{-E_D/RT} \quad (2)$$

γ is a numerical factor roughly equal to unity, a is the length of one diffusion jump (a is equal to the solid interatomic distance for most vacancy diffusion mechanisms), $\tilde{\nu}$ is the vibrational frequency of the diffusing atom, S_D and E_D are the entropy and energy of formation of the lattice defect, and S_D^+ and E_D^+ are the activation entropy and energy of the motion. E_D^+ is the difference in energy between states 1 and 2 in Fig. 1, the usual reaction coordinate diagram.

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MODEL

We assume that argon may be represented by a Lennard-Jones potential of the form

$$V(r) = \frac{\beta}{r^{12}} - \frac{\alpha}{r^6}$$

where r is the interatomic distance and α and β are the constants given by Kihara¹³ which yield a solid equilibrium distance of 3.79Å and an average energy of vaporization (from 0°K) of 2035 cal/mole. We assume that this potential function is pair-wise additive and that all quantum effects may be neglected. We consider only the potential energy.

Of these assumptions, two may introduce serious errors. We assume that the potential is pairwise additive. Sparnay¹⁴ has estimated that three body forces contribute 10-30% of the potential energy of the system and Jansen¹⁵ has shown that consideration of three body forces explains the observed stability of face centered cubic over hexagonal close packed structures. The neglect of the kinetic energy may also introduce a significant error in the computed activation energy; this contribution has not been evaluated at the present time.

Diffusion is assumed to occur by interchange of an atom with a vacancy at a nearest neighbor site (Fig. 2). We assume that as the diffusing atom moves, the lattice continuously relaxes to a minimum potential configuration. In this way, we consider correlation of the diffusing atom with its neighbors to obtain a potential energy diagram for use in an equilibrium calculation. We also assume that E_D^+ in Eqs. (2) and (3a) is the difference in the potential energies of states 1 and 2 in Fig. 1, where state 1 represents

now the minimum potential configuration of the lattice with a vacancy and state 2 the minimum potential configuration of the lattice with the diffusing atom displaced half the distance between its lattice site and that of the vacancy.

CALCULATIONS

Using techniques previously developed by the authors⁶ it was possible to compute the potential energy, $E_0(x)$, required to move the diffusing atom from its normal lattice site to a distance x along the "reaction coordinate", Fig. 3, in an undeformed lattice. This involved summation of the potential energy over the first through eighth nearest neighbors and use of a power series to express the contribution of the remainder of the lattice to $E_0(x)$. These computations were done with the aid of an IBM 7094 computer.

The eighteen nearest neighbors to the di-defect (diffusing atom plus vacancy) were allowed to relax to the configuration of minimum potential energy; the difference in potential energy between the unrelaxed lattice and the minimum potential configuration with the diffusing atom at (x) is designated $\Delta E(x)$. Allowing only nearest neighbors to relax and considering the symmetry of the lattice, determination of $\Delta E(x)$ is reduced to simultaneously minimizing an expression in sixteen independent variables. This minimization was carried out by an iterative half interval technique which fortunately converged. The relaxations of the nearest neighbors were found to be small throughout the diffusion process and are presented in Table 1 for states 1 and 2 for self-diffusion. Because of the great amount of machine time required to extend consideration to relaxations of more distant neighbors and the only qualitative significance of the results,

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no attempt was made to relax the more distant neighbors.

$$E(x) = E_0(x) - \Delta E(x)$$

is thus the potential energy required to move the diffusing atom from its relaxed lattice site to the position (x) in the relaxed lattice. $E(x)$ and $E_0(x)$ are shown in Fig. 3. In Fig. 3 the distance between the initial and final lattice positions is one unit. In accordance with our assumptions, we take

$$E_V^\dagger = E(.5)$$

where E_V^\dagger is the energy at the saddlepoint.

Calculations for impurity diffusion are essentially the same as for argon self-diffusion and were made for neon and krypton impurities. The potential of argon was modified as follows: Ar-Kr and Ar-Ne were related to the 6-12 potentials of Ar,¹¹ Ne,¹¹ and Kr¹⁴ in the following way. If r_{A-A} represents the gas equilibrium distance and U_{A-A} the depth of the well in the gas

$$r_{A-B} = \frac{r_{A-A} + r_{A-B}}{2}$$

$$U_{A-B} = (U_{A-A} U_{B-B})^{1/2}$$

RESULTS

In the above we have developed a method for calculating the potential energy change of the system in going from initial state 1 to intermediate state 2 (Fig. 1); this is $E(.5)$ and is equal to E_V^\ddagger in Eq. (2). For self diffusion in argon

$$E_V^\ddagger = E(.5) = 1798 \text{ cal}$$

where the units are now in cal/mole for purposes of comparison with experimental results. We have previously obtained the energy required to remove an atom from the bulk of argon, leaving an isolated vacancy;⁶ the process of physical importance involves the removal of a bulk atom to the surface of the crystal rather than to a position infinitely removed from the crystal. Assuming that the average binding energy to the surface is half the binding energy to the bulk, we obtain

$$E_V = 2013 \text{ cal}$$

In the Arrhenius Eq. (1)

$$E = E_V^\ddagger + E_V = 3811 \text{ cal}$$

which is in surprisingly good agreement with the experimental work of Boato⁵

$$D = 15 \times e^{-4120 \text{ cal}/RT} \text{ cm}^2/\text{sec.}$$

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It is interesting to note that E_V^\dagger is only slightly less than E_V for argon. Comparisons of Mukherjee's¹⁵ tables of E_V for a number of metals with the "activation energies" for diffusion tabulated by Lazarus⁷ indicates that this is generally true, assuming the diffusion mechanism is monovacancy exchange.

We have observed above that E_V^\dagger and E_V are roughly equal for monovacancy exchange. We have previously shown that the energy of formation of a divacancy, E_{V_2} ,⁶ is less than twice the energy of formation of a monovacancy, E_V ,

$$E_{V_2} = 3792 \text{ cal}$$

$$< 2E_V = 4026 \text{ cal}$$

An atom which is a nearest neighbor to both sites of the divacancy may move by exchanging position with one of the vacancies. This mechanism may be represented in a (111) plane and results in a rotation of the divacancy. For this mechanism

$$E_{V_2}^\dagger = 1280 \text{ cal}$$

without relaxation; allowing the four atoms nearest to the saddle point to relax reduces $E_{V_2}^\dagger$ to

$$E_{V_2}^\dagger = 950 \text{ cal}$$

No attempt was made to consider additional relaxations. For divacancy diffusion, the "activation energy" in the Arrhenius expression (Eq. 1) is

$$E = E_{V_2} + E_{V_2}^\dagger = 4742 \text{ cal}$$

which is also in reasonable agreement with Boato's experimental result.⁵ Diffusion may occur with a divacancy via two other mechanisms. In these the diffusing atom is a nearest neighbor with only one of the sites of the divacancy and exchanges with this site. This results in a splitting of the divacancy leaving two vacancies which are either second or third nearest neighbors depending on which neighbor of the vacancy moves. Both splitting processes have higher barriers than the totation of the divacancy.

No calculations of $S_{V_2}^\dagger$ or S_{V_2} have been made to the authors' knowledge. However, S_{V_2} must be larger than S_V and S^\dagger is certainly greater for divacancy exchange than for monovacancy.

It would thus appear that, in argon, the "frequency factor" for diffusion via divacancy exchange is greater than that for monovacancy exchange and the "activation energies" for both processes are essentially the same and in reasonable agreement with experiment.⁵ This would imply that, in fact, the preferred self-diffusion mechanism in solid argon, and perhaps in other close packed solids, is not monovacancy exchange as has been previously assumed, but rather is divacancy exchange. This conclusion is contrary to intuition, which would indicate that the concentration of divacancies is too low to be significant. However, though the concentration of divacancies is very low, the barrier for motion is much lower for divacancy exchange than for monovacancy exchange and the "frequency factor"

is higher, which leads, surprisingly, to a higher self-diffusion rate for divacancy exchange.

In order to account for Boato's⁵ experimental results, the entropy term for divacancy diffusion must be larger than that calculated by Fieschi⁴ for monovacancy diffusion by roughly 10 entropy units. It would be desirable to do extensive calculations on the divacancy exchange mechanism to find whether this very large entropy term is in fact found.

Without difficulty it was possible to compute the "activation energy" in the Arrhenius expression for both examined mechanisms in a compressed argon lattice. Under compression, a $P\Delta V$ term must be included in the "activation energy". We have previously⁶ assumed that the formation of a vacancy involves the removal of an atom from the bulk to the surface, that the "volume" of an atom on the perfect surface is equal to the average bulk "volume", and that the surface binding energy is half the bulk binding energy. With these assumptions we obtained the "activation energies" for both processes in the compressed solid; these are shown in Fig. 5 as a function of pressure. Though the "activation energy" for divacancy diffusion at low pressure is comparable to that of monovacancy exchange, at high pressures the divacancy mechanism appears to have a higher "activation energy".

In diffusion work one often studies the so-called "activation volume", writing

$$\Delta F = \Delta E + P\Delta V - T\Delta S$$

$$\left(\frac{\partial \Delta F}{\partial P}\right)_T = \Delta V$$

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The energy term used in these calculations is not a true thermodynamic state function and so we calculate the "activation volume" as

$$\Delta V^* = \frac{\Delta E(P_1) - \Delta E(P_2) + P_1 \Delta V(P_1) + P_2 \Delta V(P_2)}{P_1 - P_2}$$

Using our data for "activation energy" (Fig. 6) we have determined ΔV^* for both mono- and divacancy self-diffusion

$$\Delta V_V^* = 1.2 \text{ atomic volumes}$$

$$\Delta V_{V_2}^* = 1.8 \text{ atomic volumes}$$

No other vacancy type process can have a sufficiently low "activation energy" to agree with the experimental results. However, it would be desirable to calculate the activation energies for exchange, ring, and interstitial mechanisms in solid argon to assure that these do not give suitable "activation energies".

We have found⁶ that the energy required to produce a vacancy adjacent to an impurity atom is dependent on the nature of the impurity atom. Assuming, as before, that the binding energy of an atom to the surface is half the bulk binding energy, the energy required to form a vacancy adjacent to a neon impurity is

$$E_V = 1882 \text{ cal}$$

Using the programs developed for self diffusion we find, for monovacancy

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diffusion of neon through argon,

$$E_V^\ddagger = 305 \text{ cal}$$

The "activation energy" in the Arrhenius expression is then

$$E = E_V^\ddagger + E_V = 2187 \text{ cal}$$

Similarly for krypton diffusion through argon

$$E_V = 1658 \text{ cal}$$

$$E_V^\ddagger = 2075 \text{ cal}$$

$$E = 3733 \text{ cal.}$$

CONCLUSIONS

In this paper we have calculated the "activation energy" of self-diffusion in solid argon based on a monovacancy exchange mechanism using an equilibrium approach to the diffusional jump frequency. We have shown that monovacancy exchange gives a value in agreement with experiment⁵ for the "activation energy", E , in the Arrhenius expression

$$D = D_0 e^{-E/RT}$$

We have also shown that a divacancy exchange mechanism for self-diffusion

in solid argon leads to a "frequency factor" greater than that for monovacancy exchange and to a satisfactory value of the "activation energy", and that at high pressure the "activation energy" for divacancy diffusion is much greater than that of monovacancy diffusion.

Finally we have found that for impurity diffusion through argon via a monovacancy mechanism the "activation energy" varies greatly with the nature of the impurity.

ACKNOWLEDGMENTS

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TABLE I

The relaxing atoms are grouped into sets of points equivalent by symmetry:

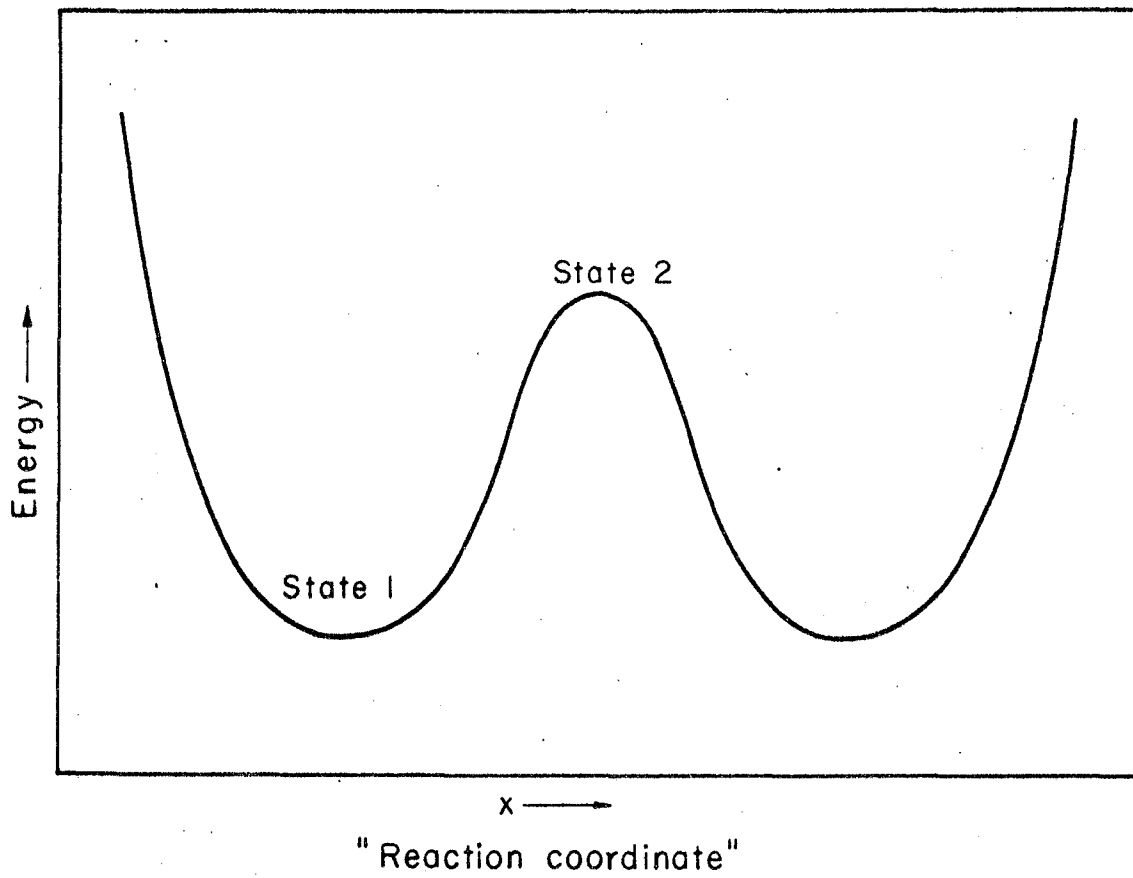
$$\begin{aligned}
 &(1,1,0) \\
 &(1,0,1) \equiv (1,0,-1) \equiv (0,1,1) \equiv (0,1,-1) \\
 &(-1,0,1) \equiv (-1,0,-1) \equiv (0,-1,1) \equiv (0,-1,-1) \\
 &(1,-1,0) \equiv (-1,1,0) \\
 &(-1,-1,0) \\
 &(2,2,0) \\
 &(1,2,1) \equiv (1,2,-1) \equiv (2,1,1) \equiv (2,1,-1) \\
 &(2,0,0) \equiv (0,2,0)
 \end{aligned}$$

$\begin{pmatrix} \delta x \\ \delta y \\ \delta z \end{pmatrix}$ is given for States 1 and 2 for one atom of each set..

x y z	State 1	State 2
$\begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$	6.42×10^{-3} 6.42×10^{-3} 0	.5 .5 0
$\begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$	6.42×10^{-3} 0 6.42×10^{-3}	-2.53×10^{-2} 2.52×10^{-2} -6.88×10^{-2}
$\begin{pmatrix} -1 \\ 0 \\ 1 \end{pmatrix}$	-6.42×10^{-3} 0 6.42×10^{-3}	-1.17×10^{-2} -1.88×10^{-3} 9.06×10^{-3}
$\begin{pmatrix} 1 \\ -1 \\ 0 \end{pmatrix}$	6.42×10^{-3} -6.42×10^{-3} 0	1.37×10^{-2} -2.63×10^{-2} 0
$\begin{pmatrix} -1 \\ -1 \\ 0 \end{pmatrix}$	-6.42×10^{-3} -6.42×10^{-3} 0	-6.25×10^{-3} -6.25×10^{-3} 0

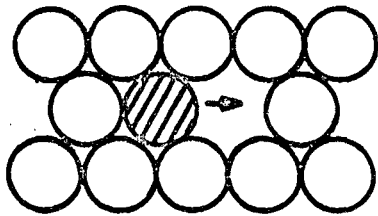
TABLE I. (Continued)

x y z	State 1	State 2
$\begin{pmatrix} 2 \\ 2 \\ 0 \end{pmatrix}$	-2.27×10^{-4} -2.27×10^{-4} 0	6.25×10^{-5} 6.25×10^{-5} 0
$\begin{pmatrix} 1 \\ 2 \\ 1 \end{pmatrix}$	5.39×10^{-4} 8.80×10^{-4} 5.39×10^{-4}	2.50×10^{-4} 1.12×10^{-2} 9.69×10^{-3}
$\begin{pmatrix} 2 \\ 0 \\ 0 \end{pmatrix}$	-3.43×10^{-3} 0 0	2.69×10^{-2} -1.46×10^{-2} 0

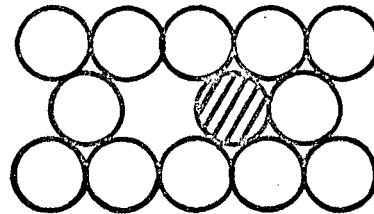


MUB-11560

Fig. 1 The reaction coordinate diagram for diffusion



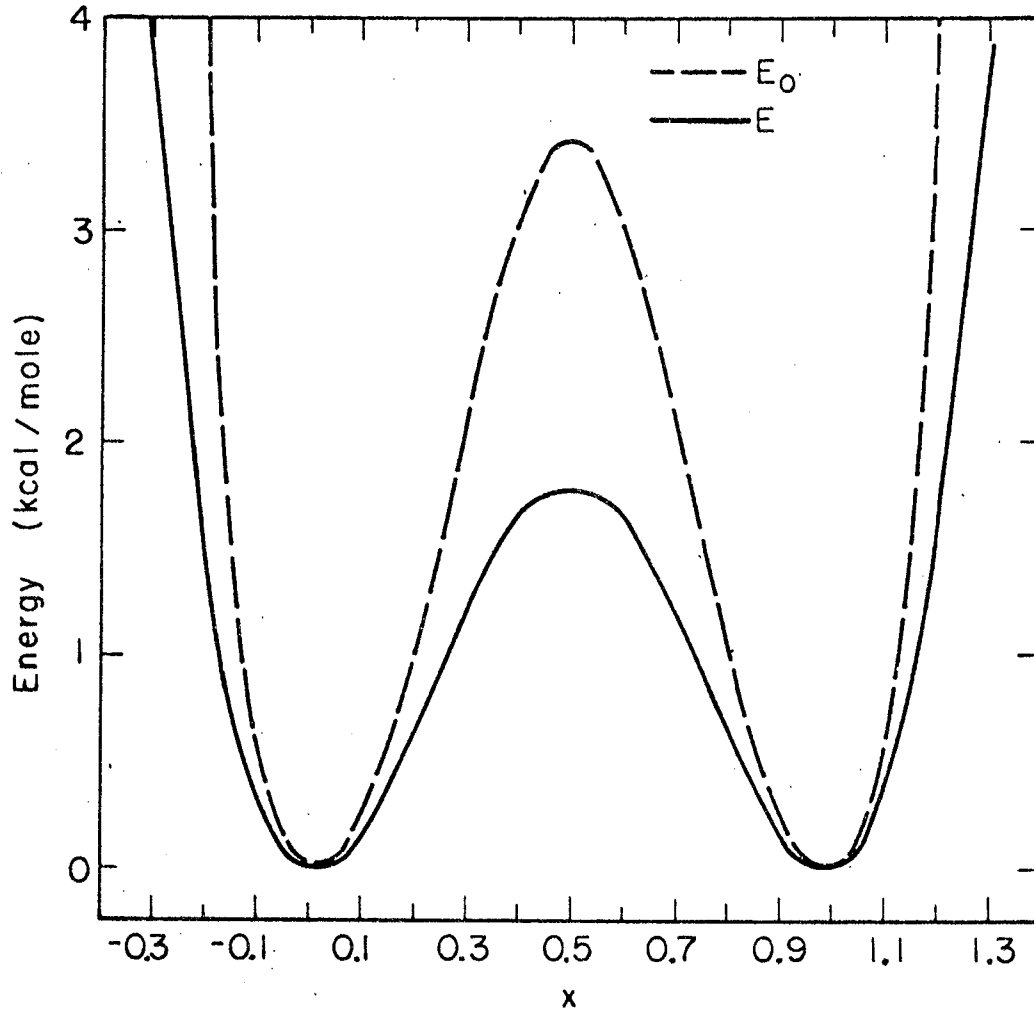
**Initial
configuration**



**Final
configuration**

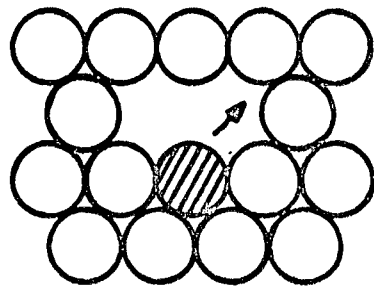
MUB-13060

Fig. 2 Exchange with a monovacancy; diffusing atom is cross hatched

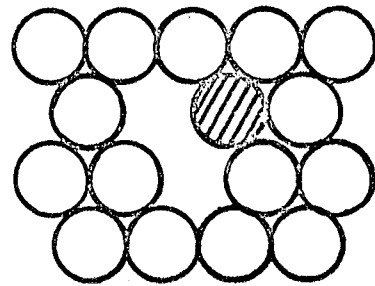


MUB-11559

Fig. 3 Energy as a function of position for diffusion via monovacancy exchange; E_0 is without relaxations, E is with relaxations.



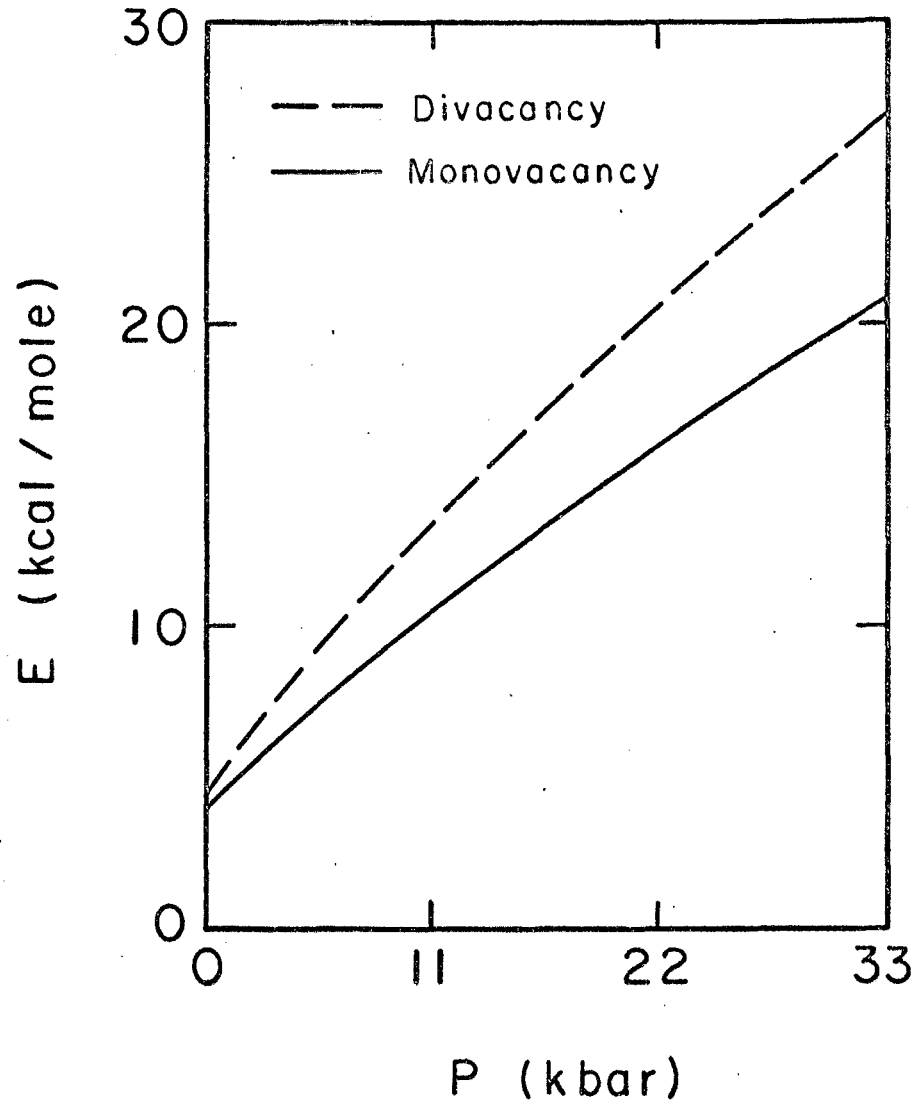
**Initial
configuration**



**Final
configuration**

MUB-13061

Fig. 4 Rotation of a divacancy; diffusing atom is cross hatched.



MUB-13062

Fig. 5 Activation energy as a function of pressure for mono- and di-vacancy diffusion

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