

TABLE I. Comparison of values of aT for various solids.

Solid	Temperature, T (°K)	a	aT
Sodium	363	27.9	10 130
Zinc (⊥)	580	86.6	50 230
Zinc (∥)	580	34.7	20 130
Mercury (liquid)	303	6.5	1970
Gallium (liquid)	303	6.5	1970
Silver in silver chloride	573	91.9	52 660
Silver in silver bromide	573	128.0	73 340
Lead	526	139.9	73 590
Lead	574	121.5	69 740

where P is the pressure and ΔG refers to the Gibbs free-energy changes for vacancy formation and for the formation of the activated state configuration. This free-energy change is calculated from the measured diffusion coefficient as a function of pressure. It follows from Eq. (58) that (60) may be written

$$\Delta V^\ddagger = -kT \left[\frac{(M/kT)\partial(\Delta V/V_0)}{\partial P} \right]_T$$

$$= -akT \left[\frac{\partial(\Delta V/V_0)}{\partial P} \right]_T. \quad (61)$$

Since

$$\left[\frac{\partial(\Delta V/V_0)}{\partial P} \right]_T = -\beta,$$

where β is the compressibility, the activation volume defined by (61) can be calculated from the simple formula

$$\Delta V^\ddagger = a\beta kT. \quad (62)$$

Table II presents values of the activation volume calculated from Eq. (62) at atmospheric pressure for those systems for which data are available.

CONCLUSIONS

A statistical mechanical theory was developed that relates the diffusion coefficient to strain in terms of the

TABLE II. Activation volumes for self-diffusion of various solids at 1 atmosphere calculated from Eq. (62).

Solid	Temperature, T (°K)	Activation volume, ΔV^\ddagger (cc/g-atom)
Sodium	363	12.3
Phosphorous (white)	314	71.7
Zinc (⊥)	580	3.0
Zinc (∥)	580	8.3
Mercury (liquid)	303	0.62
Gallium (liquid)	303	0.62
Silver in silver chloride	573	10.3
Silver in silver bromide	573	13.7
Lead	526	13.9
Lead	574	12.0

atomic properties of the system. The theory makes the following statements:

1. For diffusion as a function of hydrostatic pressure, the diffusion coefficient is an exponential function of the volume strain.

2. The rate of change of the diffusion coefficient with strain is related to the interatomic forces. The relation is explicit enough that the variation of the diffusion coefficient with pressure can be interpreted in terms of the interatomic potential-energy functions of the material.

3. For diffusion under hydrostatic pressure, the activation volume can be calculated from the compressibility and the rate of change of the diffusion coefficient with volume strain.

In every case for which data are available, these conclusions are in agreement with experiment.

The general framework of the theory provides a basis for understanding the effect of strain on diffusion in terms of the atomic properties of the system and should provide a valuable tool for comparing diffusion rates for different states of strain, as well as for investigating the mechanism of diffusion.

APPENDIX

The Vacancy Concentration Formula

Consider a canonical ensemble containing X member systems, each system being a crystal containing N atoms and l vacancies. Let E_j^l be the j th energy level of a system containing l vacancies and let Ω_j^l be the corresponding degeneracy. Then the number of systems containing l vacancies is

$$N_l = X \frac{\sum_j \Omega_j^l \exp(-E_j^l/kT)}{Z}, \quad (A1)$$

where Z is the total partition function for the ensemble.

The number of vacancies in the ensemble is

$$N_v = \sum_l l N_l, \quad (A2)$$

and the number of atoms in the ensemble is

$$N_A = N \sum_l N_l. \quad (A3)$$

The atomic fraction of vacancies is given by $n_v = N_v / (N_A + N_v)$. Since $N_v \ll N_A$, n_v is given by the ratio of Eqs. (A2) to (A3) to an excellent approximation, and therefore

$$n_v = \frac{\sum_l l Q_l}{N \sum_l Q_l}, \quad (A4)$$

where Q_l is defined by

$$Q_l = \sum_j \Omega_j^l \exp(-E_j^l/kT). \quad (A5)$$

Q_l is the partition function of a system containing l vacancies.

Carrying out the division in (A4) and retaining only the leading term give

$$n_v = (1/N)Q_1/Q_0, \tag{A6}$$

which is an excellent approximation, since the energy of formation of a vacancy is of the order of 1 ev, and therefore the higher terms in the series are very small. Q_0 is the partition function of a perfect crystal and Q_1 is the partition function of a crystal containing a vacancy.

In the semiclassical approximation,

$$\frac{Q_1}{Q_0} = (N+1) \int \dots \int e^{-\psi_v/kT} \prod_i dp_j dq_j / \int \dots \int e^{-\psi_0/kT} \prod_i dp_j dq_j, \tag{A7}$$

where $\psi_v = \psi_v(p, q)$ is the energy of a crystal containing

a vacancy and $\psi_0 = \psi_0(p, q)$ is the energy of a perfect crystal. The integrations are carried out over all values of the momenta and coordinates p_j and q_j . The factor $(N+1)$ arises from the fact that N indistinguishable atoms can be placed in $(N+1)$ numbered lattice sites in $(N+1)$ ways so that Q_1 is proportional to $(N+1)$.

Combining Eqs. (A6) and (A7) gives

$$n_v = \int \dots \int e^{-\psi_v(p_j, q_j)/kT} \prod_i dp_j dq_j / \int \dots \int e^{-\psi_0(p_j, q_j)/kT} \prod_i dp_j dq_j, \tag{A8}$$

where unity has been neglected relative to N .

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