On the Fluctuation Model of Diffusion in Liquid Metals [†]

R. A. SWALIN

School of Mineral and Metallurgical Engineering,
University of Minnesota, Minneapolis, Minnesota 55 455

(Z. Naturforsch. **23 a**, 805—813 [1968]; received 15 March 1968)

In this paper further considerations has been given to the fluctuation model of diffusion, and equations have been derived which express the self-diffusivity of liquid metals as a function of temperature and pressure. For liquid metals which are characterized by pair potentials which are relatively deep compared with $k\,T$, D is predicted to vary in a linear fashion with T at constant volume. At constant pressure, the apparent activation energy is predicted to be equal to $R\,T+R(\beta'/\beta)\,T^2$ where β is the isothermal compressibility and β' is its temperature derivative. Further, the variation in the logarithm of D with respect to pressure is predicted to be equal to $[(1/2.3)\,\beta]\ \ (\partial\beta/\partial P)_T$. A test of the equations for liquid mercury shows good correlation between theory and experiment. For liquid metals which are characterized by a shallow well in terms of the pair potential, no simple statements can be made concerning the nature of the temperature dependence, and simple approximations cannot be made. A test of the derived equations is made for liquid sodium which fits this case and for which good pair potential data exist, and good agreement is obtained at 373 °K. The temperature dependence of D as a function of T at constant volume is derived, but cannot be tested because of insufficient experimental data.

The case of thermodiffusion is discussed, and it is shown that experimental values of the heat of transport are consistent with predictions of the theory.

Introduction

A clear picture has not yet been developed concerning the mechanism and parameters important for the diffusion process in liquids. This is in part due perhaps to the fact that there probably is no single mechanism of diffusion in liquids. It is probable that many processes occur, and that the importance of various processes depends both on the temperature of the system as well as upon the nature of the system itself. Some approaches to the problem have tended to bypass the problem by ignoring the difficulty in examining the liquid structure itself and have treated the liquid as being either solid-like or gas-like in nature. In the former case, for example, it has been supposed that diffusive motions occur by discrete steps of fixed magnitude into holes of fixed dimensions. In some cases, fair agreement has been obtained between the model and experiment. Interesting as this is, this type of model appears to bypass the important aspects of real liquids and therefore appears to be highly artificial in nature, since no one really appears to believe that diffusion occurs over fixed distances into holes of standard dimensions. The problem then is to recognize the feature that are characteristic of liquids, and interpret the various properties in terms of these features. This has been done quite well for electronic transport properties in liquids, as shown by ZIMAN [1], for example.

With regard to atomic transport properties, important progres has been made in the statistical mechanical theory of liquids, as shown by RICE and co-workers [2] for example, but it will probably be a long time before something as complex as a metal system can be handled satisfactorily from first principles. Some attempts have been made, therefore, to construct models which take into account the structure of liquids, and hopefully focus on the principal mechanism of atomic transport. This writer [3] for example, suggested that diffusion may occur through local density fluctuations of variable magnitude and that a spectrum of "jump" distance may exist. Thus, the concept of a single activated process could not be invoked, and it was suggested that a $\log D$ versus $1/T$ plot is not necessarily linear. COHEN and TURNBULL [4] considered that diffusion occurs through a redistribution of free volume and

---

[†] Part of this work was performed while the author was a guest at the University of California, Lawrence Radiation Laboratory, Livermore, Calif. The research was supported in total by the U.S. Atomic Energy Commission.

[1] J. M. ZIMAN, Phil. Mag. **6,** 1013 [1961].
[2] S. A. RICE, in: Liquids; Ed. T. J. HUGHEL, Elseview 1965.
[3] R. A. SWALIN, Acta Met. **7,** 736 [1959].
[4] M. COHEN and D. TURNBULL, J. Chem. Phys. **31,** 1164 [1959].

postulated that a critically sized fluctuation is necessary in order to promote diffusion. It has also been suggested from an examination of neutron diffraction results that diffusion occurs through the rotation and translation of metastable clusters[5].

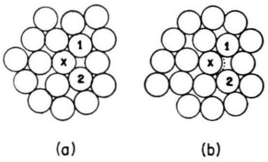
Several years have passed since our model was first proposed, and since that time more experimental data have appeared. It is the purpose of this paper then to re-examine the basic ideas proposed by this writer[3] and to redevelop the mathematical description of the models.

A principal question concerns whether or not small and variable jump distances occur or whether or not a critically sized fluctuation is needed in order to promoto a diffusive move. A contribution to the resolution of this problem has been made through the recent work of RAHMAN[6] and PASKIN and RAHMAN[7]. In both cases attempts have been made to simulate the liquid state by use of an ensemble of several hundred particles. The particles interact with one another through the use of realistic pair potentials, and the motion of particles is followed by use of a computer. Rahman, in this manner, examined in detail the displacement of simulated argon atoms on a time scale of 10^{-12} sec and found that indeed fluctuations of the type proposed[3] occur, and that further, those fluctuations result in displacive motions. Specifically, it was found that the fluctuation "makes the particle rattle in a momentarily well-defined plane of directions and allows it to 'slip' in a direction perpendicular to the plane. The rattling is a simple proces identical with the behavior of atoms in an harmonic solid. The slipping part is the process of self-diffusion ..." Paskin and Rahman have simulated liquid sodium by a similar technique, and it appears that diffusive motions result in a time period in the vicinity of 3×10^{-13} sec. An examination of the motions of particles thus simulated does not appear to reveal the existence of clusters of atoms or the necessity for critically sized voids to appear before a diffusive move results.

Development of the Model

From the computer simulated systems described in the preceding section it would appear that there is no need to invoke the concept of a critical fluctuation, and that local density fluctuations may be the principal mechanism by which diffusion occurs. It would also appear that at the instant of diffusion, the system may be treated as solid-like insofar as the vibrational spectrum is concerned.

Let us assume, therefore, that the general viewpoint expresed in Ref. [3] is valid, and that local fluctuations of the type proposed occur and are responsible for diffusion. We will assume further that the energetics insofar as diffusion is concerned may be represented adequately by the use of pair potentials $V(d)$ where $V(d)$ is a minimum at d_0 where d_0 is the mean internuclear spacing. The average number of nearest neighbors to a given atom will be $\bar{Z}$. Consider the situation shown in Fig. 1 a, and allow a local density fluctuation to occur as shown in Fig. 1 b. For a given configuration the internuclear separation between n neighbors will increase. Let it be assumed that the spacing for n neighbors increases from d_0 to $(d_0 + j)$. For a given fluctuation of magnitude j_i, the contribution toe the diffusion constant may be represented by the following equation, if it is assumed that a random walk process may be employed.



(a) (b)

Fig. 1 a. Schematic sketch of a liquid metal.
Fig. 1 b. Schematic sketch of liquid metal showing density fluctuation (from Ref. [3]).

$$dD = \tfrac{1}{6} f\, j_i^2\, \nu\, p(j_i)\, P(j_i)\, dj \qquad (1)$$

where ν is a vibrational frequency, f is the correlation coefficient (assumed to be unity in this paper), $P(j_i)\, dj$ is the probability that a fluctuation of magnitude between j_i and $(j_i + dj_i)$ will occur next to a given atom, and $p(j_i)$ is the probability that the atom will have sufficient energy to move a distance j_i once the fluctuation occurs. If ν is treated as a constant, the actual diffusion constant D will be given by

$$D = \tfrac{1}{6} \nu \int_0^\infty j^2 P(j)\, p(j)\, dj\,. \qquad (2)$$

The terms $P(j)\, dj$ and $p(j)$ will now be considered. For a given configuration, let it be assumed that

---

[5] P. A. EGELSTAFF, Phil. Mag. Suppl. **11**, 203 [1962].
[6] A. RAHMAN, J. Chem. Phys. **45**, 2585 [1966].
[7] A. PASKIN and A. RAHMAN, Phys. Rev. Letters **16**, 300 [1966].

n atoms will be involved in the fluctuation and that the separation between these n atoms from a given atom increases from d_0 to (d_0+j). The energy involved then in the fluctuation $E(j)$ is

$$E(j)=n[V(d_0+j)-V(d_0)]\,. \tag{3}$$

Let it be assumed, neglecting entropy terms, that the probability that a fluctuation of magnitude between j and $(j+\mathrm{d}j)$ will occur between two nearest neighbors is given by $P'(j)$,

$$P'(j)\,\mathrm{d}j=C\exp\{-[E(j)]/kT\}\,\mathrm{d}j\,. \tag{4}$$

The constant C may be readily evaluated, since

$$\int_0^\infty P'(j)\,\mathrm{d}j=1=C\int_0^\infty \exp\{-[E(j)]/kT\}\,\mathrm{d}j\,. \tag{5}$$

Since there are $\bar{Z}$ nearest neighbors, the probability $P(j)\,\mathrm{d}j$ that a fluctuation of magnitude between j and $(j+\mathrm{d}j)$ will occur between any nearest neighbors of the diffusing atom will be given by

$$P(j)\,\mathrm{d}j=\bar{Z}P'(j)\,\mathrm{d}j=\bar{Z}C\exp\{-[E(j)]/kT\}\,\mathrm{d}j \tag{6}$$

where C is given by Eq. (5).

The term $p(j)$ represents the probability that a given atom will have sufficient activation energy to move a distance j once a fluctuation is formed. Before moving, of the $\bar{Z}$ neighbors surrounding a given atom, n are asumed to be at a distance (d_0+j) and $(\bar{Z}-n)$ will be at the average distance d_0. At the end of the diffusive move for the particular configuration considered here, it would appear that $(\bar{Z}-n)$ atoms will be at distance d_0 and n atoms at (d_0+j). Halfway between, it will be assumed for simplicity that all $\bar{Z}$ neighbors will be at a separation $(d_0+j/2)$. Thus, the energy change for an atom in moving from its initial position to the "saddle-point" is given by

$$\varDelta E_1=\bar{Z}V(d_0+j/2)-n\,V(d_0+j)-(Z-n)\,V(d_0) \tag{7}$$

and for moving from the "saddle-point" to the final position the energy change will be

$$\varDelta E_2=n\,V(d_0+j)+(\bar{Z}-n)\,V(d_0)-\bar{Z}V(d_0+j/2)\,. \tag{8}$$

In solid systems, $\varDelta E_1$ would represent a "saddle-point" for a diffusive atom in the sense that $\varDelta E_1$ is a positive quality. It is not clear, however, for liquids where j can be very small that $\varDelta E_1$ is necessarily positive. The energy of the system might be reduced in some cases if the central atom moves a distance $j/2$ into an energy well. In that case, the atom will need an energy $\varDelta E_2$ to continue in translation. Thus, two situations might be delineated.

Case I: A true saddle point position: $\varDelta E_1$ is positive, $\varDelta E_2$ is negative,

$$p(j)=\frac{\int_{E_1}^{0}\exp[-\varDelta E_1/k\,T]\,\mathrm{d}E}{\int_0^\infty \exp[-\varDelta E_1/k\,T]\,\mathrm{d}E}=\exp(-\varDelta E_1/k\,T)\,. \tag{9}$$

Case II: $\varDelta E_1$ is negative, $\varDelta E_2$ is positive.

$$p(j)=\exp(\varDelta E_2/k\,T)\,. \tag{10}$$

Upon substitution, therefore, we find that the self-diffusion constant is given by

$$D=\frac{\bar{Z}\,\nu f\int_0^\infty j^2\exp\{-n[V(d_0+j)-V(d_0)]/k\,T\}\exp(-\varDelta E_i/k\,T)\,\mathrm{d}j}{6\int_0^\infty \exp\{-n[V(d_0+j)-V(d_0)]/k\,T\}\,\mathrm{d}j} \tag{11}$$

where $\varDelta E_i$ may be given by Eq. (7) or (8) and depends on which one yields the positive quantity. Eq. (11) may be solved in principle for D as a function of T and P if appropriate information is available about the pair potential $V(d)$. It should be pointed out here that other types of fluctuation could be considered also but it is illustrative at this point to focus on the one particular type considered here.

Equation (11) may be simplified if

$$E(j)=n[V(d_0+j)-V(d_0)]$$

can be expanded in terms of a Maclaurin's series and high-order terms neglected. It should be pointed out here that this approximation is not valid for all metals. This will be discussed later. Thus,

$$V(d_0+j)=V(d_0)+j\left(\frac{\partial V(j)}{\partial j}\right)_{j=0}+\frac{j^2}{2!}\left(\frac{\partial^2V(j)}{\partial j^2}\right)_{j=0}+\frac{j^3}{3!}\left(\frac{\partial^3V}{\partial j^3}\right)_{j=0}+\cdots, \tag{12}$$

$$E(j)=n[V(d_0+j)-V(d_0)]\,,$$

$$E(j)=n\,j\left(\frac{\partial V}{\partial j}\right)_{j=0}+n\,\frac{j^2}{2!}\left(\frac{\partial^2V(d_0)}{\partial j^2}\right)_{j=0}+\cdots\,.$$

Since at $j=0$, $(\partial V/\partial j)_{j=0}$ is zero, and high-order terms are neglected,

$$E(j) \cong \frac{n\,j^2}{2}\left(\frac{\partial^2 V}{\partial j^2}\right)_{j=0}. \qquad (13)$$

These terms can only be neglected if the principal contribution comes from very small values of j, i. e., if the potential wells are deep and narrow.

Similarly, we find the following expression for ΔE_1 and ΔE_2:

$$\Delta E_1 = \left(\frac{\bar{Z}}{4} - n\right)\frac{j^2}{2}\left(\frac{\partial^2 V}{\partial j^2}\right)_{j=0}, \qquad (14)$$

$$\Delta E_2 = \left(n - \frac{\bar{Z}}{4}\right)\frac{j^2}{2}\left(\frac{\partial^2 V}{\partial j^2}\right)_{j=0}. \qquad (15)$$

Typical values of $\bar{Z}$ would be expected to be in the range $9-11$ for metallic systems, and typical values of n might be $3-5$ for small fluctuations. Under these conditions ΔE_2 is positive and hence Eq. (8) will be employed in Eq. (11). Upon substitution of Eqs. (13) and (15) into (11), we find upon integration the following expression:

$$D = \frac{f\,\bar{Z}\,\nu\,n^{1/2}\,k\,T}{6\,(2\,n - \frac{1}{4}\,\bar{Z})^{3/2}\,(\partial^2 V/\partial j^2)_{j=0}}. \qquad (16)$$

It might be assumed that $(\partial^2 V/\partial j^2)_{j=0}$ is a function of the equilibrium inter-atomic spacing d_0, and that $\bar{Z}$ and ν are fairly independent of temperature. If this is the case, then for a material which can be represented by a deep potential well, D will be proportional to temperature at *constant volume*. If one plots $\log D$ versus $1/T$ and draws a straight line through the data points over a limited temperature range, the apparent activation energy at *constant volume* will be given by

$$\text{“}Q_V\text{”} = R\,T\,.$$

It should be emphasized again at this point that Eq. (16) is only applicable for cases where the deep potential approximation is good. In order to quantitatively apply Eq. (16), the pair potentials $V(d)$ must be known. In Ref. [3], quasichemical theory was used for this purpose, but for metals this approach yields values that are probably inaccurate by a substantial amount. Fairly reliable pair potentials, however, appear to have been derived for liquid sodium [7, 8]. Examination of these potentials shows that they are far too shallow to be adaptable to the Maclaurin series approximation used to obtain Eq. (16). Consequently, Eq. (11) must be used to obtain diffusion constants for metals such as liquid sodium. This will be done in a later section in order to examine the reliability of the model.

It will be illustrative at this point to consider, for a material which can be represented by Eq. (16), the predictions as to the effect upon D of temperature at constant pressure and the effect of pressure at constant temperature. Let us assume that the curvature $(\partial^2 V/\partial j^2)_{j=0}$ is related to the reciprocal of the compressibility of the liquid. Since the compressibility β is proportional to $(\partial^2 V/\partial v^2)$ where v is the volume of the system, $(\partial^2 V/\partial j^2)$ will be proportional to d_0/β where d_0 is the equilibrium spacing. Then we can represent Eq. (16) in the following manner:

$$D = A\,\nu\,\beta\,T/d_0 \qquad (17)$$

where β is the isothermal compressibility and A is a constant for a particular system. Eq. (17) may be used to examine the temperature dependence of a system at constant pressure. First, let us examine the apparent activation energy “Q”$_p$ for this system. Taking logarithmus of both sides and differentiating with respect to $1/T$, we find that

$$\text{“}Q\text{”}_p = R\,T + \frac{\beta'}{\beta}\,R\,T^2 \qquad (18)$$

where β' is the temperature derivative of the compressibility. Thus we find that curvature is to be expected on a $\log D$ versus $1/T$ plot as predicted in Ref. [3], although Eq. (18) has a different form than the relationship previously derived. In Ref. [3] it was predicted that “Q”$_p$ was a function only of temperature and did not involve any of the properties of the liquid directly.

In order to examine the pressure dependence of the diffusivity, it is conventional to plot $\log D$ versus pressure, P. Generally, for liquid metals, the effect of pressure is found to be small, and the results are often reported in terms of an activation volume. This interpretation in terms of activation volume is incorrect, according to the model reported here. If we neglect the pressure dependence of ν and d_0 which is small, the variation of D with pressure is given as

$$\left[\frac{\partial \log D}{\partial P}\right]_T = \frac{1}{2.3\,\beta}\left(\frac{\partial \beta}{\partial P}\right)_T. \qquad (19)$$

---

[8] M. D. Johnson, P. Hutchinson, and N. A. March, Proc. Roy. Soc. London A **282**, 283 [1964].

Application of the Model

From Eq. (17), we find that the temperature dependence of the diffusivity is different from the standard exponential form, although, as pointed out in Ref. [3], most diffusion experiments in liquids are performed over a rather limited temperature range. In view of the always present experimental error, it would be difficult in most cases to expect to detect any curvature on a $\log D$ versus $1/T$ plot. For a material that can be represented by the deep well model $(-V(d_0) \gg k\,T)$ the apparent activation energy can be found from Eq. (18) if the mean temperature of investigation is used and if (β'/β) for the particular material is known. Unfortunately, compressibility data are not available for most liquid metals nor are good values of the pair potential available, but a few metals have been examined rather extensively. Some of the data available will be discussed in this section in the context of the fluctuation model.

Mercury

Diffusion in liquid mercury has been studied rather extensively, both as a function of temperature and pressure. In addition, the pressure and temperature dependence of the compressibility of liquid mercury have been measured. As a consequence, it will be interesting to examine the experimental data in terms of the model. Early measurements of the self-diffusion in liquid mercury were made by NACHTRIEB and PETIT [9] both as a function of temperature $(273-372\ ^\circ\mathrm{K})$ and pressure $(0-8000$ kg/cm^2 at 30 °C$)$. Over the temperature range measured, the data fit a straight line on a $\log D$ versus $1/T$ plot with an aparent activation energy of 1005 cal/g atom. The pressure investigation yields a straight line when $\log D$ is plotted versus pressure with an apparent activation volume of 0.59 cm^3/g-atom. These data yield a value of $\mathrm{d} \log D/\mathrm{d}P$ of -0.98×10^{-5} cm^2/kg. MEYER [10] reinvestigated the temperature dependence of liquid mercury over a rather broad temperature range $(273-512\ ^\circ\mathrm{K})$ in order to detect curvature that might exist. Indeed, a considerable deviation was found from a straight line on the traditional $\log D$ versus $1/T$ plot. The specific deviation could not be explained precisely by assuming a linear relation between D and T or a linear relation D and T^2 as predicted in Ref. [3].

If the pair potential for liquid mercury can be represented by a narrow deep well, Eqs. (16) through (18) are applicable. An accurate self-potential is not available, but such an approximation seems reasonable. Thus, if Eq. (17) is applicable to mercury, a straight line should be obtained if D is plotted versus $\beta\,T$. Such a plot of MEYER's data is shown in Fig. 2. The values for β as a function of temperature were obtained from Ref. [11]. It is seen that the fit of data points is quite good. As another test of the model, it is instructive to plot $\log D$ versus T. The slope of the line obtained should be equal to $1/2.3\,(\beta'/\beta + 1/T)$. If this is done, a line is obtained experimentally which has a slope of 2.45×10^{-3} at 323 °K and 1.52×10^{-3} at 473 °K. From the experimental compressibility data $(\beta'/\beta = 1.40 \times 10^{-3}$ at 323 °K and $\beta'/\beta = 1.58 \times 10^{-3}$ at 473 °K$)$, the predicted slopes are 1.96×10^{-3} and 1.61×10^{-3} respectively, which is basically consistent with the experimental observations in terms of magnitude and change with temperature.

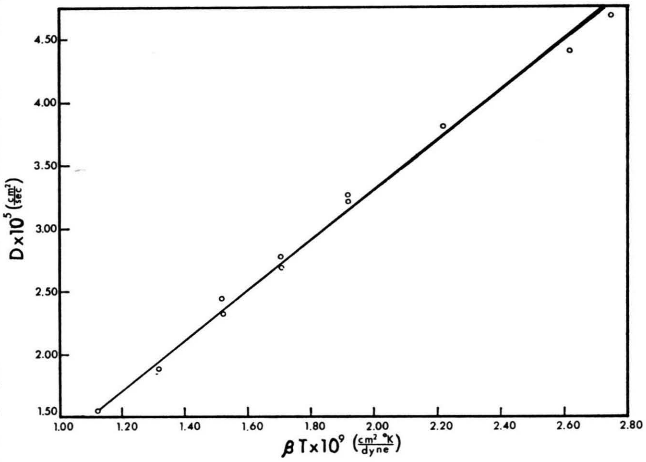


Fig. 2. Plot of experimental data from Ref. [10] as the logarithm of the diffusivity D versus $\beta\,T$, where β is the isothermal compressibility at temperature T.

In similar fashion from Eq. (19), a plot of $\log D$ versus pressure should yield a line with slope equal to $1/2.3\,\beta(\partial\beta/\partial p)_T$. The calculated values of this quantity from literature values [11] of the compressibility are -1.44×10^{-5} cm^2/kg at $P=0$ and -1.20×10^{-5} cm^2/kg at $P = 6000$ kg/cm^2. Tke ex-

---

[9] N. H. NACHTRIEB and J. PETIT, J. Chem. Phys. **24**, 746 [1956].

[10] R. E. MEYER, J. Phys. Chem. **65**, 567 [1961].

[11] American Institute of Physics Handbook, 2nd ed., D. W. Group, Ed. McGraw-Hill, New York 1963.

perimental value is -0.98×10^{-5} cm²/kg. The calculated values are consistent with experiment, although the predicted curvature of the line on the $\log D - P$ plot does not appear in the experiments reported.

It is interesting now to calculate the apparent activation energy for mercury, as compared with the measured value of 1005 ± 92 cal/g atom between 273 and 372 °K. The mean temperature of investigation was 323 °K, and β'/β at this temperature is 1.40×10^{-3} $(^\circ\mathrm{K})^{-1}$. From Eq. (18) we find that the calculated value of "Q"$_p$ is

$$\text{“}Q\text{”}_p = 640 + 290 = 930 \text{ cal/g atom}$$

which is consistent within the experimental value errors.

Sodium

The extensive experimental information which exists for mercury is not available in the case of sodium. This is compensated for by the fact that considerable work has been done on obtaining a realistic pair potential. JOHNSON and co-workers[8] derived from the radial distribution function a pair potential which has an oscillatory character and can be expressed in the form $V = V_{\mathrm{LRO}} + V_{\mathrm{R}}$, where V_{LRO} is the oscillatory attractive part of its potential and V_{R} is the repulsive part of the potential. The form for V_{LRO} is

$$V_{\mathrm{LRO}} = -A\left(\frac{d_0}{d_0+j}\right)^3 \cos\left\{7.812\left[\left(\frac{d_0+j}{d_0}\right)+\gamma\right]\right\} \text{ eV} \qquad (20)$$

and the form for V_{R} is

$$V_{\mathrm{R}} = 0.78 \exp\left[5.0724 - 10.786\left(\frac{d_0+j}{d_0}\right)\right] \text{eV}. \qquad (21)$$

PASKIN and RAHMAN[7], using a potential form of this type, reproduced the radial distribution function and diffusivity at one temperature rather well by examination of the positions of several hundred particles with the aid of a computer. By measuring the mean square displacement of the ensemble of particles as a function of time, the diffusivity was calculated to be 5.8×10^{-5} cm²/sec as compared with the experimental value of 4.2×10^{-5} cm²/sec[12]. The constants A and γ in Eq. (20) were chosen to be 0.027 and 0.5689 eV respectively.

It is interesting therefore to employ this potential to test the equations developed in this paper. Examination of the potential shows that the deep well assumption is not valid and therefore Eq. (11) must be used directly. To use Eq. (11), we must have values for $\bar{Z}$, ν and n. The quantity ν will be equated to the Debye frequency which for sodium is 3.35×10^{12} sec^{-1}. The quantity n undoubtedly varies somewhat with the magnitude of the fluctuation. There is no *a priori* way to obtain this qauntity directly. Geometrically, one might expect it to be about equal to 4.

The quantity $\bar{Z}$, the average number of nearest neighbors in liquid sodium will be assumed to be 10. The integration in Eq. (11) will be terminated at the upper limit $j = d_0$ instead of ∞ because the model is not applicable in its present form for large fluctuation of the order of the atomic volume in size. For these fluctuations, it would be expected that more than four nearest neighbors would be involved. Also it is proposed, in terms of the model presented here, that fluctuations much smaller in magnitude than the atomic volume make the principal contribution to diffusion. Substitution of the above quantities into Eq. (11) yields a value of D equal to 4.1×10^{-5} cm²/sec as contrasted to the experimental values of 4.2×10^{-5} cm²/sec at 373 °K. It would appear that the model is a realistic representation of the actual problem. Energetic considerations favor of course small fluctuations, but the presence of the j^2 term in the numerator favors large fluctuations. The net result is that most of the diffusion results from fluctuation between 0.1 and 1.2 Å. The value of $\langle j^2 \rangle^{1/2}$ in terms of the contribution to diffusion is calculated to be 0.7 Å at 373 °K. This value is probably somewhat larger for sodium than for other metals because of the "softness" of the sodium potential. By use of the same potential, values of D may be calculated as a function of temperature at *constant volume*. These calculations are shown in Fig. 3, along with the experimental data at *constant pressure*. At present, research is underway in our laboratory concerning the measurement of D at *constant volume*. These data will be published in a later paper. It is not posible to calculate D as a function of T at constant pressure for sodium from Eq. (11) since no information is available on the dependence of $V(d)$ on changing the equilibrium spacing d_0. The calculated "apparent activation energy" at constant volume is larger, however, than

---

[12] R. E. MEYER and N. H. NACHTRIEB, J. Chem. Phys. **23**, 1851 [1955].

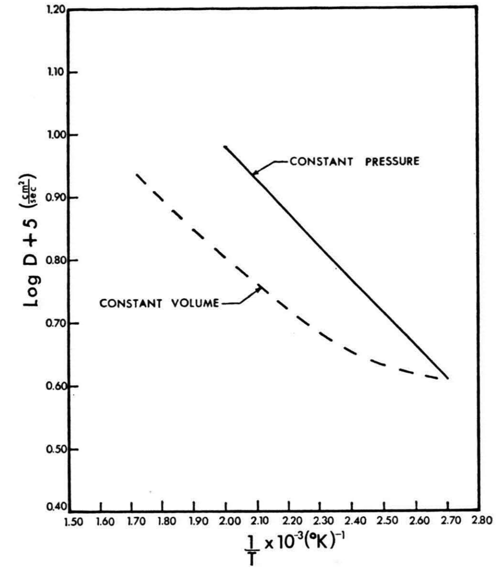


Fig. 3. Log D versus $1/T$ plot for liquid sodium. Dashed line represents calculated curve at *constant volume*. Solid line represents experimental curve at *constant pressure* from Ref. [12].

that predicted by the deep well approximation, namely RT. This occurs because the shallow potential employed for sodium shifts $\langle j^2 \rangle^{1/2}$ rather strongly with temperature. These calculated values are shown in Fig. 4.

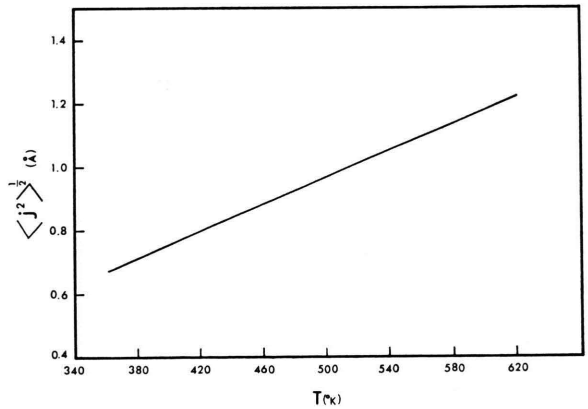


Fig. 4. Root mean square diffusion distance as a function of temperature for liquid sodium. Calculaited under *constant volume* condition.

Interpretation of Heat of Transport in Liquid Metals

A series of interesting measurements has been made of isotopic redistribution in liquid metals under the influence of temperature gradient [13, 14]. Studies on pure lithium, potassium, rubidium, and gallium show that in all cases the light isotope (for example, Li^6 in pure Li containing both Li^6 and Li^7) becomes enriched at the cold end. At steady state, the following relation is obtained [14, 15],

$$Q_{\max} - 1 = -\frac{\Delta M\, a\, Q^*}{M\, R}\left(\frac{1}{T_C} - \frac{1}{T_H}\right) \qquad (22)$$

where $Q_{\max}$ is the steady state separation factor $(C_h/C_l)_C/(C_h/C_l)_H$, C_h and C_l are the concentrations of heavy and light isotopes respectively and the subscripts C and H represent cold and hot respectively; ΔM is the mass difference between heavy and light isotopes, and a is an experimentally determined term governing the ratio of isothermal diffusion through the relation $D_h/D_l = (M_h/M_l)^a$. The quantity a is found experimentally for liquid metals to have a magnitude equal to about -0.1. From the experimental parameters, Q^* was obtained for various elements and was found to be equal to -13.6, -8.3, -10.8 and -11.9 in k gal/g-atom for the pure metals, Li, K, Rb and Ga respectively.

The principal problem then of any proposed model is to explain the magnitude and sign of Q^*. To illustrate, consider the simple hole theory of diffusion in which diffusion occurs through discrete fixed jumps of magnitude d_0. The activation energy for self-diffusion is Q, and is composed of the sum of E_m, the activation energy for jumping, and E_f, the energy of hole formation. If it assumed that all the motion energy is localized in the jumping atom and is transported a distance d_0 upon jumping, it can be shown by standard techniques [15, 16] that

$$Q^* = (E_m - E_f).$$

It is often presumed acording to this model that $E_m \sim 0$ and therefore

$$Q^* \cong -Q_D.$$

The measured values of Q^* are, however, about a factor of five to eight times more negative. Lodding [15], in attempting to explain the large negative values of Q^*, assumed that diffusion occured by means of cluster into voids. The distance between the center of the cyluster and the center of the void is of dimension Φ_l and the cluster diffuses a dis-

---

[13] A. Ott and A. Lundén, Z. Naturforsch. **19 a**, 822 [1964].

[14] A. Lodding and A. Ott, Z. Naturforsch. **21 a**, 1344 [1966].

[15] A. Lodding, Z. Naturforsch. **21 a**, 1348 [1966].

[16] S. Prager and H. Eyring, J. Chem. Phys. **21**, 1347 [1953].

tance l. By employing an analysis similar to that performed by Wirtz[17] and identifying the heat transported by the diffusing cluster as E_{m} (again close to zero), Lodding derived that

$$Q^* = \Phi(E_{\mathrm{m}} - E_{\mathrm{f}}).$$

In this analysis the center of the cluster is considered to be at temperature T and receives the activation energy at this temperature, and the center of the void is at temperature $(T + \Phi\, l \nabla T)$ and the enthalpy of void formation is provided at this temperature. This is not really satisfactory since Φ is a variable which cannot be specifically determined and as mentioned in the introduction of this paper, it is not apparent that cluster diffusion is really important as a diffusion mechanism.

It is interesting to consider, therefore, whether or not the model discussed in this paper can explain the magnitude and sign of Q^*. It is not clear at this juncture as to how Eq. (11) can be rigorously applied. Instead, let us attempt to obtain a semi-quantitative approximation. As shown for sodium at 373 °K, half of the diffusion contribution is calculated to come by means of fluctuation smaller than 0.7 Å in magnitude and half through fluctuation greater than 0.7 Å in magnitude. Let us assume, therefore, for the sake of illustration, that all fluctuations are of fixed magnitude $\langle j^2 \rangle^{1/2}$. If this is the case, the diffusion constant will be given by

$$D \cong \frac{\bar{j}^2 f \nu \bar{Z}}{6} \exp\left(-\frac{\bar{E}_{\mathrm{m}} + \bar{E}_{\mathrm{f}}}{k\,T}\right) \qquad (23)$$

where $\bar{E}_{\mathrm{f}}$ is the energy involved in creating the fluctuation of magnitude $\langle j^2 \rangle^{1/2}$ and $\bar{E}_{\mathrm{m}}$ is the activation energy for motion. By substituting the experimental value of D into Eq. (23) we find that $(\bar{E}_{\mathrm{m}} + \bar{E}_{\mathrm{f}})$ at 373° equals 1380 cal/g-atom for sodium. At a different temperature, of course, $\bar{E}_{\mathrm{m}}$, $\bar{E}_{\mathrm{f}}$ and $\langle j^2 \rangle^{1/2}$ will be different. Use of Eq. (8) for sodium for $\langle j^2 \rangle^{1/2} = 0.7$ Å yields a value for $\bar{E}_m$ of 340 cal/g-atom and thus $\bar{E}_{\mathrm{f}} = 1040$ cal/g-atom. Consider now two neighboring atoms lying parallel to the direction of a thermal gradient. The atom on the left will be considered to be at temperature T and the atom on the right will be at temperature $(T + d_0 \nabla T)$. A fluctuation of magnitudes $\langle j^2 \rangle^{1/2}$ will now be created by providing the particle on the right and its neighbors with an energy $\bar{E}_{\mathrm{f}}$. Thus it will be considered that energy $\bar{E}_{\mathrm{f}}$ is provided at temperature $(T + d_0 \nabla T)$, whereas for the particle on the left to diffuse a distance $\langle j^2 \rangle^{1/2}$, the energy $\bar{E}_{\mathrm{m}}$ is provided at temperature T. A treatment analogous to Lodding's then yields for Q^*

$$Q^* = \frac{d_0}{\langle j^2 \rangle^{1/2}} (E_{\mathrm{m}} - E_{\mathrm{f}}).$$

Substitution of appropriate quantities then yields for Q^* a value of -5500 cal/g-atom which is of the magnitude expected for sodium in terms of the experimental values for lithium, potassium and rubidium. From a physical point of view, it is easy to see why Q^* is large and negative. In the simple hole model in which diffusion occurs by jumps of magnitude d_0, the hole, which was formed at a cost of energy E_{f}, is transported in the opposite direction to the diffusing atom a distance d_0. In the picture proposed here, the atom moves a small distance $\langle j^2 \rangle^{1/2}$ but the fluctuation "void" is transported in the opposite direction a distance $(d_0 + \langle j^2 \rangle^{1/2})$. Hence, the energy of void formation $\bar{E}_{\mathrm{f}}$ is transported with a velocity much greater than the energy of motion E_{m}.

Conclusion

In this paper further consideration has been given to the fluctuation model of diffusion, and equations have been derived which express the self-diffusivity of liquid metals as a function of temperature and pressure. For liquids metals which are characterized by pair potentials which are narrow and relatively deep compared with $k\,T$, D is predicted to vary in a linear fashion with T at *constant volume*. At *constant pressure*, the apparent activation energy is predicted to be equal to $R\,T + R(\beta'/\beta)\,T^2$ where β is the isothermal compressibility and β' is its temperature derivative. Further, the variation in the logarithm of D with respect to pressure is predicted to be equal to $(1/2.3\,\beta)\,(\partial\beta/\partial P)_T$. A test of the equations for liquid mercury shows good correlation between theory and experiment. For liquid metals which are characterized by a shallow well in terms of the pair potential, no simple statements can be made concerning the nature of the temperature dependence, and simple approximations cannot be made. A test of the derived equations is made for liquid sodium which fits this case and for which good pair potential data exist and good agreement is obtained at 373 °K. The temperature dependence of D as a function of T at *constant volume* is derived,

---

[17] K. Wirtz, Z. Physik **44**, 221 [1943].

but cannot be tested because of insufficient experimental data.

The case of thermal diffusion is discussed, and it is shown that experimental values of the heat of transport are consistent with predictions of the theory.

Acknowledgement

Much of this work was done by the writer at the Lawrence Radiation Laboratory, University of California, Livermore, California, as a guest scientist. Thanks are due, in particular to D. Y. F. Lai for his assistance with the computer calculations.

Isotopenaustausch-Untersuchungen an Silicat-Ionenaustauschern

VI. Untersuchung des Ba-Isotopenaustauschs zwischen Zeolith A und wäßriger Lösung bei Temperaturen bis 180 °C mit Hilfe einer neuen experimentellen Methode

E. Hoinkis und H. W. Levi

Hahn-Meitner-Institut für Kernforschung Berlin

(Z. Naturforsch. **23 a**, 813—817 [1968]; eingegangen am 10. März 1968)

A method has been developed to measure the rate of rapid heterogeneous ion exchange reactions between powdered solids and an aqueous solution within the temperature range from 100 to 180 °C.

The principle of this method is the following: Both the preheated solid and the preheated aqueous solution are brought into contact by breaking a container. After an exchange period of $\geqq 10$ sec the process is interrupted within a time intervall of 0.2 sec by splashing cold alcohol (−115 °C) into the reaction vessel.

By means of this "temperature-jump"-method the isotopic exchange in Ba-zeolite A has been investigated.

The diffusion process was found to be not uniform at temperatures up to 100 °C just as already had been shown for Cs difussion in Zeolith A. Above 100 °C, however, it appears to become an ideal diffusion process exactly obeying the solution of the diffusion-equation for the relevant case over the entire range of the process.

Die in der V. Mitteilung[1] beschriebene Untersuchung der Kinetik des Cs- und Rb-Isotopenaustauschs in Zeolith vom Typ A (LMS A) hatte bei beiden Austauschprozessen ergeben, daß diese nicht als einheitliche Diffusionsprozesse beschrieben werden können. Es gelang jedoch mit einem dort beschriebenen Auswertungsverfahren, die gemessenen Umsatzkurven formal in zwei verschieden schnell und unabhängig voneinander verlaufende einzelne Diffusionsprozesse zu zerlegen. Als Endergebnis wurden unter Verwendung der durch das Auswerteverfahren erhaltenen Parameter Umsatzkurven maschinell berechnet, die mit den gemessenen befriedigend übereinstimmten.

Ein wesentliches Ergebnis dieser Untersuchungen war die Abnahme des Anteils des langsamen Teilprozesses am Gesamtprozeß mit steigender Temperatur. Die Frage, ob es eine Temperatur gibt, oberhalb derer der Isotopenaustausch der Umsatz-Gleichung für einen einheitlichen Diffusionsprozeß folgt, konnte durch Untersuchung des Cs- und Rb-Isotopenaustauschs nicht beantwortet werden. Die Austauschgeschwindigkeit bei höheren Temperaturen ist hier so groß, daß die Austauschkinetik nicht mehr gemessen werden konnte. Diese Frage sollte nun für den Ba-Isotopenaustausch untersucht werden, der langsamer verläuft. Hierzu war es notwendig, eine Methode zu entwickeln, die es gestattet, schnelle Austauschprozesse zwischen Festkörpern und wäßrigen Lösungen bei Temperaturen über 100° zu messen. Diese Methode wird als Temperatursprungmethode bezeichnet.

1. Die Temperatursprungmethode

Die Temperatursprungmethode dient zur Untersuchung schnell ablaufender Isotopen- oder Ionenaustauschvorgänge zwischen einem feinkörnigen Festkörper und einer wäßrigen Salzlösung bei Temperaturen zwischen 100 und 180 °C. Sie arbeitet nach folgendem Prinzip:

Der mit einem γ-strahlenden Isotop des Ions, dessen Austausch-Kinetik untersucht werden soll, markierte Festkörper wird in eine dünnwandige Glaskugel eingefüllt und die Anfangsaktivität im Bohrlochkristall gemessen.

---

[1] E. Hoinkis u. H. W. Levi, Z. Naturforsch. **22 a**, 226 [1967].