Self-diffusion in Liquid Sodium at Constant Volume and Constant Pressure

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Abstract

The self-diffusion coefficient of liquid sodium has been determined in the temperature range melting point to 300°c, under both constant pressure and constant volume conditions. The experimental technique is described in detail and current theories are reviewed in the light of the results obtained. None of the theoretical approaches is entirely correct in predicting the experimentally observed data. This is probably because there is more than one diffusion process operative in the liquid. It is, however, concluded that models of the fluctuation type most accurately describe observed conditions. The critical fluctuation concept is thought not to be applicable.

§ 1. Introduction

The present work was motivated by the need for more experimental data in order to attain a better understanding of the nature of atomic diffusion in liquid metals. Several theoretical approaches to the problem have been developed. There are, however, insufficient experimental data to provide a rigorous test of these theories. In particular, data obtained at constant volume are very sparse, and as some of the fundamental differences between the various theories involve the role of the 'free volume'‡ it is desirable to obtain diffusion data under constant volume conditions.

Liquid sodium was chosen for the initial investigation because it offers the simplest theoretical treatment. Therefore, comparison between experimentally observed and predicted data may probably be more meaningful. Also, the low melting point of sodium facilitates experimental procedures.

Diffusion data have been obtained at both constant pressure and constant volume. The former are compared with previous results by Meyer and Nachtrieb (1955). These workers used the capillary-reservoir technique in contrast to the method used in the present investigation which is described in the next section.

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‡ The difference between the liquid volume and that of all the atoms involved.

§ 2. Experimental Technique

The more familiar capillary-reservoir technique was not employed in this investigation, mainly because the presence in the high pressure cell of a reservoir and stirring mechanism would greatly increase practical difficulties. Instead, the two halves of a relatively long capillary were filled with radioactive and normal sodium, respectively. Diffusion then took place across the interface between the two halves.

Some details of the experimental procedure follow.

2.1. *High Pressure Apparatus and Capillary Filling*

A silicone-oil pressure system capable of producing pressures up to about 7 kilobars is used. The system consists essentially of a 10 000 p.s.i. single-stage pump and a complex flow circuit of valves. An intensifier magnifies the 10 000 p.s.i. by a factor of 10. Pressures are observed on a Heise gauge to the nearest 50 p.s.i.

Both fused quartz and type 316 stainless-steel capillaries were used during the investigation. The latter are required for annealing above about 230°c since at these higher temperatures quartz and liquid sodium begin to react appreciably. The internal dimensions of both types of capillary are identical, having a bore of 1 mm and length 7 cm. Outside diameters are 2 mm and 0·05 in. for quartz and stainless steel, respectively.

The capillary-filling apparatus, shown in fig. 1, is constructed entirely from fused quartz. One half of a capillary is first sealed by means of a close-fitting nickel wire. It is then held open end down in the pin-vice in the upper half of the apparatus. The lower half, containing a tube of non-radioactive sodium, is then firmly attached as shown in the sketch. The stopcock at this stage is closed so that the metal is sealed in an argon atmosphere. After flushing out the air in the upper half the stopcock is opened and the whole system is evacuated to a pressure of 10^{-4} mm of mercury, or less. At the same time the sodium is melted. The open end of the capillary is lowered into the molten metal by means of the attached steel rod. By allowing argon at atmospheric pressure to enter the apparatus liquid sodium is forced into the open half of the capillary. Next, after raising the capillary, allowing the sodium in the capillary to solidify, and closing the stopcock, the lower part of the system is removed. The capillary is reversed in the pin-vice and the nickel wire is removed under a flow of argon to prevent oxidation of the now exposed surface of the sodium. A further lower half, this time containing radioactive sodium-22, is now quickly placed in position. The upper portion is immediately evacuated and followed by a repeat of the filling procedure.

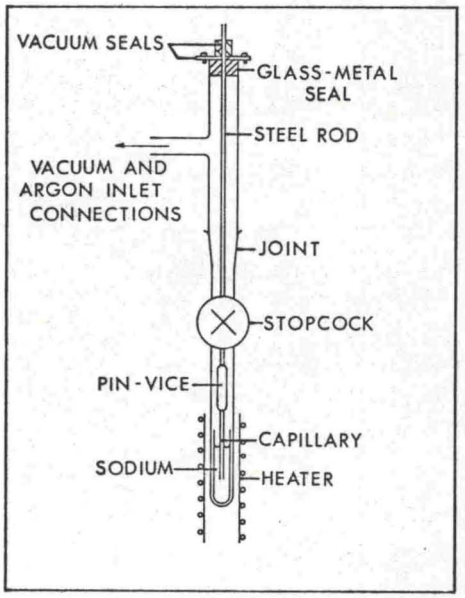
2.2. *Diffusion Annealing*

2.1.2. *Constant pressure*

Six capillaries are placed in a series of holes drilled parallel to the axis of a cylindrical copper block. A central hole houses a chromel–alumel

thermocouple, the tip of which lies adjacent to the midpoints of the capillaries. The block is sealed in a horizontal fused quartz tube which contains argon at atmospheric pressure. The tube has one end closed, the remaining end being connected to a vacuum and argon-inlet system. The block is positioned at the closed end. A resistance furnace is then slid over the tube to provide the means for heating the specimens.

Fig. 1



The capillary-filling apparatus.

A preliminary investigation showed that the temperature along the length of the capillaries does not vary by more than 1 °C at all working temperatures.

To heat the samples as rapidly as possible, the furnace is pre-heated to the desired temperature. The capillaries are annealed for a period of 10–12 hours before being cooled rapidly by removing the furnace and directing a cold air jet onto the tube.

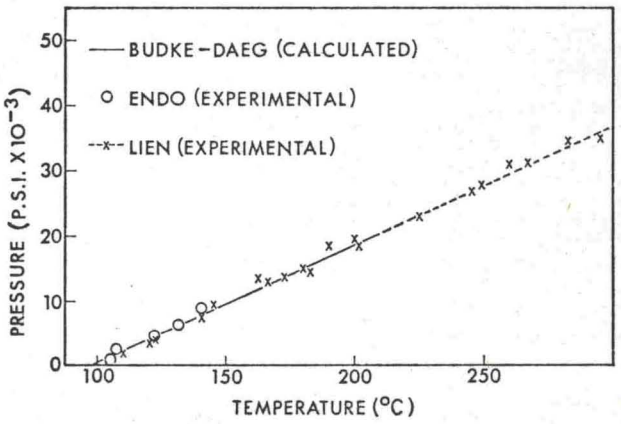
2.2.2. *Constant volume*

The pressure cell, containing six capillaries, is held in a horizontal position. As in the constant pressure case a furnace is slid over the cell. In order to heat the large mass of the cell rapidly the furnace resistance wire is wound onto an electrically insulated brass tube which fits very closely around the cell. The specimens are again annealed for a period of 10–12 hours before being quickly cooled to room temperature by means of a brass water-jacket.

The diffusion time is taken to be the interval during which the specimens are in the liquid state. This does introduce an error in the computed value of the diffusion coefficient (D) since this period includes heating and cooling times. However, the error, even at the highest temperature used, is small because the capillaries were heated and cooled rapidly. The error is, in fact, much smaller than the standard deviation of the mean of the diffusion coefficient.

The pressure required to maintain a constant volume over the temperature range was obtained from the combined P–T curves for liquid sodium determined by Lien (1967), Endo (1963) and Budke-Daeg (1966, private communication). Their data are plotted in fig. 2. The constant volume maintained is that at the melting point of liquid sodium.

Fig. 2



The pressure versus temperature plot for liquid sodium.

2.3. *Determination of Diffusion Coefficients*

After diffusion, capillaries are sectioned into lengths of about 6 mm. Each section is carefully weighed and the activity of sodium-22 is determined by standard techniques. Activity (C) versus distance plots are drawn and the diffusion coefficient is determined from Fick's second law, as described below.

The boundary conditions of diffusion samples in this experiment are as follows:

$$C = 0 \text{ for } x < 0, \quad t = 0,$$

$$C = C_0 \text{ for } x > 0, \quad t = 0,$$

where C is the activity of the radioactive isotope at x the distance from the interface, C_0 is the initial activity of the isotope and t is the diffusion time.

The solution of Fick's second law under these conditions is as follows (Jost 1960):

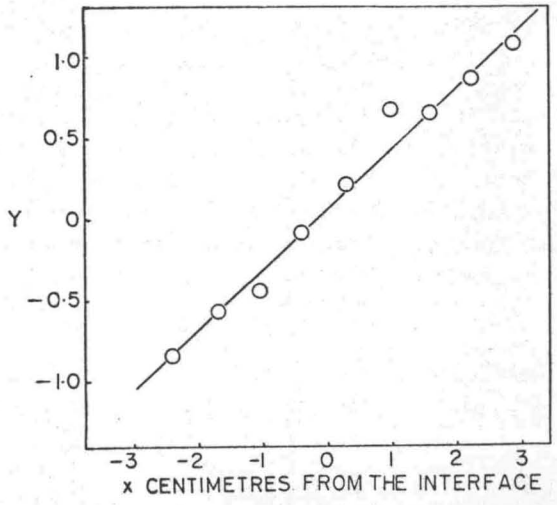
$$\left.\begin{aligned} C &= (C_0/2)\,[1-\operatorname{erf}(x/2\,[Dt]^{1/2})] \\ \text{or} \\ 2\,(C/C_0)-1 &= \operatorname{erf}(Y), \end{aligned}\right\} \qquad (1)$$

where

$$Y = x/2\,(Dt)^{1/2}.$$

From eqn. (1), the erf (Y) may be determined using values of C and C_0 obtained by experiment. A typical Y versus x plot is shown in fig. 3. The single point which does not lie close to the line is probably a result of a weighing error. The best slope is obtained by least squares analysis for each of the six specimens diffused at each temperature. The quoted D value is taken to be the mean of the values calculated from these six plots.

Fig. 3



A typical dependence of the function Y upon the distance (x) from the interface for liquid sodium at constant volume. $Y = x/2(Dt)^{1/2}$.

The value of C_0 used in these calculations is determined by filling an entire capillary with radioactive isotope at the time the six diffusion specimens are prepared. This capillary is sectioned and counted as described above so that a value of C_0 is obtained for each section. The value used in calculations is the mean of those of the sections. This is repeated with each set of six capillaries in order to allow for decay of the sodium source. However, since the half-life is about $2\frac{1}{2}$ years and the experiments were carried out over a relatively short period of time no appreciable difference between C_0 values was apparent.

§ 3. Experimental Results

The logarithm of the diffusion coefficient (D) is plotted as a function of the reciprocal of the absolute temperature in fig. 4 for both constant volume and constant pressure conditions. A summary of the constant volume results is included in the table. The quantity ΔD is the standard deviation

Experimental results for liquid sodium at constant volume. The average value of $\Delta D = \pm 0{\cdot}72 \times 10^{-5} \mathrm{cm^2\,sec^{-1}}$

$D\,(\mathrm{cm^2\,sec^{-1}}) \times 10^5$	$\pm \Delta D\,(\mathrm{cm^2\,sec^{-1}}) \times 10^5$	T (°C)
4·31	0·52	108
4·67	0·56	126
4·96	0·87	145
5·57	0·50	165
6·18	0·44	186
6·54	1·09	208
7·76	0·70	235
8·29	0·87	257
9·42	0·91	279

of the mean of the six values of D obtained at each temperature. Relatively few constant pressure data were obtained because of the close agreement between the present work and that of Meyer and Nachtrieb (1955). Further data would merely have constituted an unnecessary repeat of work. A combination of the two sets of constant pressure data shows D to be dependent upon temperature as follows:

$$D = 0{\cdot}92 \times 10^{-3} \exp(-2343/RT)\ \mathrm{cm^2/sec.}$$

RT has units of cal/g-atom.

At the time of writing no other constant volume data are known to be available for comparison with the present results.

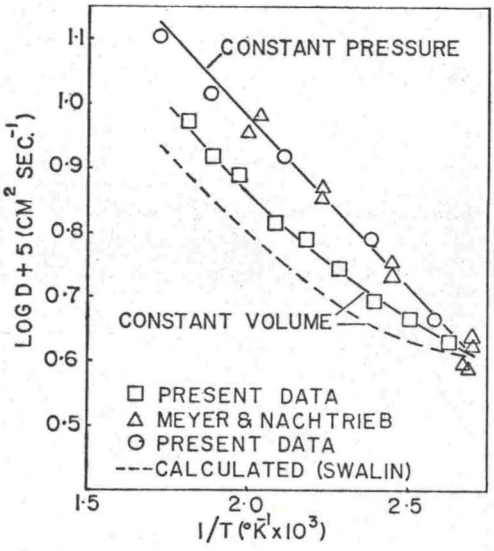
§ 4. Discussion

Of the several models concerning the diffusive motion of atoms in liquids proposed to date most have enjoyed some degree of success in forecasting experimentally observed data. However, no model has been entirely correct in its predictions. This may be due to the fact that the diffusion process cannot be described by a single mechanism. Also, it is probable that, in some cases, incorrect assumptions concerning the structure of the liquid have been made. Of these, the most common is to assume that the liquid state is either a slightly ordered gas or a disordered solid.

The essential differences between models involve, to a large extent, the part played by the free volume of the liquid. Hence, if this parameter can be controlled comparison between experiment and theory may be more meaningful. Therefore, the need for good diffusion data under constant

volume conditions is great. The present investigation has provided the first of such data for liquid metals covering a reasonable range of temperature.

Fig. 4



The dependence of log D upon $1/T$ for liquid sodium at constant pressure and constant volume.

Probably the earliest theory was the 'hole' model of Glasstone, Laidler and Eyring (1946). A distinct solid-state approach was taken whereby it was assumed that diffusion takes place by the jumping of atoms into adjacent holes in the liquid, similar to the vacancies in a solid metal. Since such holes are thermally activated an activation energy for diffusion is postulated, and is due to the surface energy of formation of the hole. This view predicts (Frenkel 1946) that the activation energy of diffusion should be proportional to the heat of vaporization. Since experiment indicates no correlation between these quantities the hole model does not appear to be adequate.

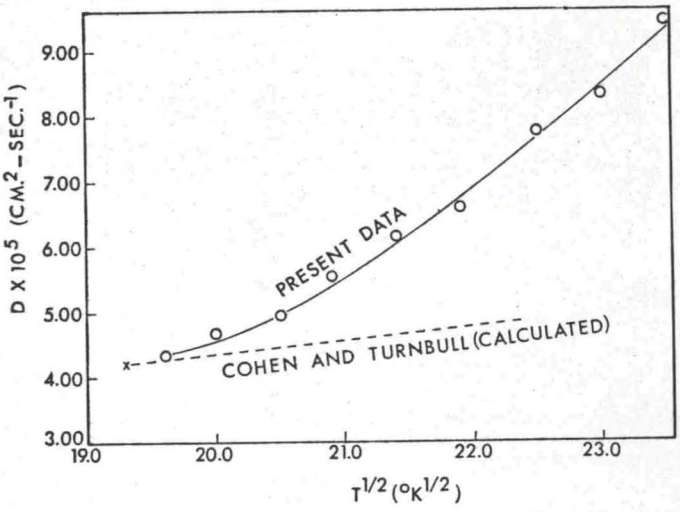
Other models assume that atoms move into voids created by density fluctuations in the liquid. Cohen and Turnbull (1959) have proposed a model of this type, suggesting that a critical fluctuation of a minimum size is necessary. The diffusion coefficient (D) is thought to be related to the free volume (V_f), defined earlier, as follows:

$$D = ga^*u \exp[-\gamma V^*/V_f], \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where g is a geometrical factor, a^* approximately equals the atomic diameter, u is the velocity of the atoms and is assumed to be equal to the gas kinetic velocity, γ is a numerical factor introduced to correct for overlap

of the free volume and V^* is the minimum critical hole volume. D is dependent upon temperature at constant volume through the variation of u, the atomic velocity. Cohen and Turnbull therefore predict that, since $u \propto T^{1/2}$ (Glasstone 1960) at constant volume, D will also show a similar temperature dependence. D, calculated from eqn. (2), using the appropriate parameters for sodium as provided by Cohen and Turnbull (1959), is plotted against $T^{1/2}$ and compared with the present experimental data in fig. 5. It is seen that considerable disagreement exists between calculation and experiment.

Fig. 5



The dependence of the diffusion coefficient (D) upon $T^{1/2}$ for liquid sodium at constant volume.

Swalin (1959) has also proposed a fluctuation model. The critical fluctuation concept is, however, not involved. Diffusion is thought to occur by the movement of atoms into voids covering the entire spectrum of diameters. The following temperature dependence is predicted:

$$D = 1{\cdot}29 \times 10^{-8} (T^2/\Delta H_v \alpha^2), \qquad (3)$$

where ΔH_v is the molar heat of vaporization in kcal. mole^{-1}, and α is a measure of the curvature of the potential energy versus distance curve of the liquid. This dependence was described by the Morse potential. Theoretical predictions have been compared satisfactorily with experimental data for liquid tin (Ma and Swalin 1962) at constant pressure covering a wide temperature range. Swalin (1968) has developed his model further, assuming the same diffusion mechanism. A close-packed group of atoms is considered, the average interatomic spacing being d_0. As a result of a

local density fluctuation this distance is increased to (d_0+j). Assuming that the diffusion energetics can be represented by the pair potential $V(d)$, and that a random walk process can be employed, it is shown by Swalin that

$$D=\frac{\bar{Z}\nu f\int_0^\infty j^2\exp\{-n\,[V(d_0+j)-V(d_0)]/kT\}\exp\left(-\Delta E_i/kT\right)dj}{6\int_0^\infty \exp\{-n[V(d_0+j)-V(d_0)]/kT\}\,dj}, \quad (4)$$

where $\bar{Z}$ is the coordination number, ν is the atomic vibrational frequency, f is the correlation function (assumed to be unity), n is the number of atoms involved in the fluctuation, and ΔE_i is either the energy change for an atom in moving from its initial position to the mid-point of its distance of travel, or from the latter to its final position, whichever is positive.

A potential for liquid sodium has been recently developed by Johnson, Hutchinson and March (1964) and Paskin and Rahman (1966) and is of the form:

$$V=V_{\mathrm{LRO}}+V_{\mathrm{R}}, \quad (5)$$

where

$$V_{\mathrm{LRO}}=-A[d_0/(d_0+j)]^3\cos\{7{\cdot}812\,[(d/d_0)+\beta]\}$$

and

$$V_{\mathrm{R}}=0{\cdot}78\exp\left(5{\cdot}0724-10{\cdot}7863\,d/d_0\right);$$

A and β are parameters which were adjusted by Paskin and Rahman so that adequate agreement with the experimental radial distribution function for liquid sodium was achieved. Values of A and β were chosen to be 0·027 ev and 0·5689 ev, respectively. If $\bar{Z}$ and ν are chosen to be 10 and $3{\cdot}35\times10^{12}\,\mathrm{sec}^{-1}$, respectively, then the value of n needed to make eqn. (4) agree with experiment is the reasonable one of 4. If this parameter is independent of T at constant V, Swalin's theory predicts the broken curve of fig. 4. The reasonable agreement between calculation and experiment could indicate that migration by means of density fluctuations forms at least part of the diffusion process. The discrepancy between the two curves may be a result of the appropriate nature of the model and/or uncertainty in the LRO part of the potential used.

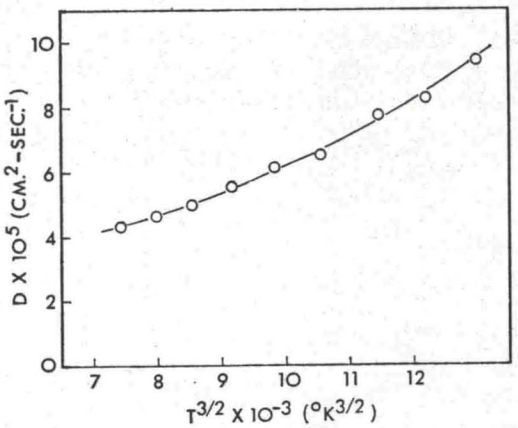
A recent approach by Rice and Nachtrieb (1967) relates the diffusion coefficient D to the friction drag imposed on an atom by its neighbours as follows:

$$D=\frac{kT}{\zeta}=\frac{kT}{\zeta_{\mathrm{S}}+\zeta_{\mathrm{H}}+\zeta_{\mathrm{SH}}}, \quad (6)$$

where ζ_{S}, ζ_{H} and ζ_{SH} are friction coefficients due, respectively, to soft interactions with the potential field of neighbouring atoms, repulsive hard-core interactions, and the cross-effect between the hard and soft forces. Relationships for these quantities have been derived by Helfand (1961), and Palyvos and Davis (1967 a, b).

Helfand (1961) assumed that ζ_{SH} is negligibly small, but Palyvos and Davis (1967 b) have shown that ζ_{SH} is of the same order as ζ_H. Rice and Nachtrieb, in the case of liquid sodium, assumed that $\zeta_{SH}+\zeta_H \ll \zeta_S$, and find that, under these conditions, D should be proportional to $T^{3/2}$ at constant volume. Rice and Nachtrieb test this relationship by plotting experimental values of D as a function of $T^{3/2}$ for liquid sodium and mercury at constant pressure. A straight line is observed. However, the $T^{3/2}$ dependence was derived using an assumption which applies only to constant *volume* data. The present results are plotted in fig. 6 and show that D at constant volume is not proportional to $T^{3/2}$.

Fig. 6



The dependence of the diffusion coefficient (D) upon $T^{3/2}$ for liquid sodium at constant volume.

§ 5. Summary and Conclusions

The self-diffusion coefficient of liquid sodium has been experimentally determined as a function of temperature under both constant volume and constant pressure conditions. Current theories of the diffusive motion of atoms in liquid metals have been briefly reviewed and predicted results have been compared with the experimental data. In no case is the agreement exact, although qualitatively Swalin's recent equation (1968) provides the most accurate temperature dependence. The use of a more accurate pair potential value may in fact reduce the quantitative discrepancy between experimental and theoretical results.

Experimental data seem, therefore, to support fluctuation theory and suggest that a critical fluctuation size is not essential. Rahman (1966) has simulated the liquid structure by means of an assembly of several hundred particles and followed atomic motions with a computer using a realistic pair potential. His results did show the presence of fluctuations of the type proposed by Swalin (1959).

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