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MASTER

DIFFUSION STUDIES IN LIQUID METALS

United States Atomic Energy Commission

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I. BRIEF SUMMARY OF ACTIVITIES

During the past year, substantial accomplishments have been made. This was due to the fact that years of earlier preparatory work on different aspects of our liquids program came to fruition at the same time.

Thus in connection with the diffusion program we succeeded in measuring the self diffusivity in liquid sodium as a function of temperature under conditions of constant molar volume. Our isothermal solute diffusion program is being terminated with the completion of the measurement of the diffusivity of nickel in liquid silver. A series of eight solutes in silver has now been methodically investigated. Work is now underway on a study of the Soret effect in liquids. To date a general procedure has been developed, equipment has been designed and partially constructed. The first system to be studied will be dilute silver-antimony alloys.

Additional calculations pertaining to the fluctuation model of diffusion in liquids have been carried out in the past year. These calculations have been applied to liquid mercury and sodium and yield quite good results with experiment.

The X-ray diffraction program for liquid sodium has been basically completed and the radial distribution function (RDF) has been obtained as a function of temperature and pressure. It is found that under isothermal conditions the interference function $I(K)$ is insensitive to pressure up to 20,000 psi. At constant pressure, however, the height of the first maximum in $I(K)$ decreases linearly as the temperature increases. Under constant volume conditions, the

position of the first maximum remains constant with changes in temperature.

Electrical resistivity measurements under constant volume conditions have now been completed for sodium ($97.5^{\circ} - 350^{\circ}\text{C}$), potassium ($63.7^{\circ} - 250^{\circ}\text{C}$) and rubidium ($39.0^{\circ} - 197^{\circ}\text{C}$). The values for the resistivity at the melting point, ρ_0 and the coefficients $(\partial \rho / \partial T)_V$ are listed below

<u>Material</u>	<u>ρ_0 ($\mu\text{-ohm-cm}$)</u>	<u>$(\partial \rho / \partial T)_V$ ($\mu\text{-ohm-cm}/^{\circ}\text{C}$)</u>
Na	9.60	0.021
K	13.1	0.030
Rb	22.0	0.046

The temperature dependences obtained agree quite well with those predicted for classical correlated density fluctuations in conjunction with the Born Approximation.

II. RESEARCH PROGRESS

Work has been accomplished along the following avenues during the past year:

A. Diffusion Program

1. Measurement of D , the diffusivity in liquid Na as a function of T at constant volume.
2. Calculations of the self diffusivity in liquid metals as a function of T and P based on fluctuation concepts.
3. Measurement of the diffusivity of Ni in liquid Ag.
4. Initiation of experimental program to measure Soret Effect in liquid metals.

B. X-Ray measurements of the RDF of Sodium.

C. Resistivity Measurements for Liquid Metals.

A. Diffusion Program

1. Self-diffusion in Liquid Sodium

Successful results were finally obtained for the self-diffusivity of liquid Na under conditions of constant volume. The results, we believe, are significant and offer substantial challenge to anyone who constructs a theoretical model of the liquid state. Constant volume data are significant since it is easier to construct a theoretical model of a liquid at constant volume than for constant pressure. Only by performing constant volume experiments, then, can theory be confronted directly by experimental work.

The experimental details and the results obtained were described in full in Technical Information Document No. COO-841-14. This material is in press in Philosophical Magazine. As one would expect the diffusivity of liquid sodium at constant volume is substantially different from results at constant pressure. The data obtained are shown in Fig. 1. The constant volume results are incompatible with some models of liquid state diffusion. The model of Cohen and Turnbull which is based on critically sized voids predicts a temperature dependence at constant volume which disagrees substantially with experiment. Similarly a recent calculation by Nachtrieb and Rice shows considerable disagreement. Prediction based on the concept of fluctuations as observed by Swalin are in quite good agreement with the data. Experimental information on more systems is needed, however, before general deductions can be drawn.

2. Diffusion calculations based on fluctuation concepts.

During the past year, the fluctuation concept was re-examined and modifications of our previous calculations (1959) were made. These results are put forth in detail in Technical Information Document No. COO-841-13 and are in press in Zeitschrift für Naturforschung. In these calculations many of the basic premises of our earlier work were used and others were modified in view of basic advances in our knowledge of liquids since 1959. Two metals (Hg and Na) are examined in some detail in terms of the model and quite good agreement is obtained between experiment and the model. In addition the heat of transport as obtained experimentally from isotopic redistribution measurements in a temperature gradient was examined in terms of the model in a semi-quantitative

fashion. It appears that, what seems to be experimentally anomalous results can be adequately interpreted by use of fluctuation concepts.

3. Diffusion of Ni in liquid Ag.

As part of our general program to examine the influence of solute valence on solute diffusion coefficients in liquids, the diffusion of Ni in liquid Ag has been measured during the past year. This solute is one addition to the several others that have been measured in our laboratory in past years. These other solutes include In, Sn, Sb, Au, Ru, Fe and Co. The most recent results for Ni represents the completion of this part of our liquids program and the results are reported in detail in Technical Information Document No. COO-841-12. Enclosed with this report is a reprint of this work which was published in Scripta Metallurgica. (Also included are reprints of the material previously submitted as Technical Information Documents Nos. COO-841-9 and COO-841-11 which have been published in Advances in Physics and Acta Metallurgica respectively.)

The technique used for studying the diffusion of nickel in liquid silver was basically the same as that used for the previous solutes studied in our laboratory. Over the range of temperature investigated the diffusivity of trace concentrations of nickel in liquid silver followed the equation

$$D = (7.4 \pm 1.6) \times 10^{-4} \exp \left[- \frac{8120 \pm 620}{RT} \right] \text{ cm}^2 \text{ sec}^{-1}$$

At 1200°C, for example, the ratio of the diffusivity of nickel in silver to that of silver in silver is 1.11. In the technical report describing this work, an interpretation of the results is given in terms of valence theory and quasi-chemical theory. The experimental data for nickel are consistent with a solute

valence of about -0.3 . This valence is consistent with experimental diffusion data for solid Ag-Ni alloys and with general magnetic measurements on dilute solid Cu-Ni alloys.

In the last renewal proposal we mentioned an intention to measure the diffusion of Zn, Ga and Ge before terminating the solute diffusion program but for the present, at least, these will not be investigated.

4. Soret Effect in Liquid Silver

In this work we propose to measure the redistribution of solute in liquid silver capillaries placed in a temperature gradient. The rationale behind this work was described in the last renewal proposal. Suffice it to say, at this point, that information concerning the heat of transport associated with the diffusive process in liquids can be obtained from the proposed measurements. These results can be compared with theory and with the seemingly anomalous results obtained from isotopic redistribution measurements⁽¹⁾⁽²⁾. To date equipment has been designed and is being constructed. A description of the planned procedure follows below.

The experiment consists essentially of (1) holding a capillary containing the liquid alloy of silver and trace concentrations of radioactive solute in a temperature gradient until the steady state has been reached and then (2) quenching the sample and get the concentration profile of the solute.

(1) A. Lodding and A. Ott, Z. Naturf. 21, 1344 (1966).

(2) A. Lodding, Z. Naturf. 21, 1348 (1966).

An apparatus has been designed to conduct the thermal diffusion experiment. Most of the parts are assembled except the radiation shields. The technique is described with reference to the Fig. 2.

The apparatus consists essentially of a brass vacuum fitting, a quartz tube, a capillary tube and the dual furnace assembly. The brass vacuum fitting is water cooled and comprises a double o-ring seal to prevent lateral movement of the tube. The capillary and the furnaces are attached to the top plate of the vacuum fitting so that they can be easily removed and installed.

Capillaries and furnaces are machined from boron nitride because of its excellent heat conduction, machinability and stability at high temperatures. Kanthal A-1 wire is used for furnace winding and can be maintained continuously at temperatures below a maximum of 1350°C .

Capillaries are threaded at either end and are screwed into the two furnace blocks. Also, the capillaries may be split along the axis into two halves so that the solidified specimen may easily be removed for counting after annealing. The capillaries may then be reused. Filling is done by (1) placing the required amount of solid in the cup (2) evacuate the furnace chamber, (3) melting the sample and then (4) applying the argon pressure. Because the capillary is split, one can easily check if it is properly filled.

The furnaces have alumina linings. Radiation shields are provided to reduce heat losses. After the steady state is reached the sample is quickly cooled to the room temperature by jet of argon positioned such that there is a directional solidification from bottom of the capillary to the top. This procedure will reduce

FIG.2. APPARATUS FOR THERMAL DIFFUSION EXPERIMENT

the possible mixing due to convection currents produced during solidification. The use of a positive gradient upwards eliminates the possibility of thermal convection in liquid silver while running the experiment.

Temperatures are controlled by two West proportional controllers in conjunction with two Pt-1% Rh/Pt-13% - Rh. Thermocouples located in the recesses shown in the Fig. 2 separate thermocouples housed near the capillary for measuring the temperature of the hot and cold ends of the capillary.

These unusual thermocouples were chosen because of their stability in vacuum.

Thermocouples as well as the heater wires enter the chamber through glass-metal seals in the brass vacuum fitting.

B. X-ray Measurements of the RDF of Sodium.

Measurements of the radial distribution function (RDF) of liquid sodium have been carried out as a function of pressure and temperature from atmospheric pressure up to 20,000 psi, and from the melting point up to about 195°C. It was observed that

- 1) The effect of temperature on the X-ray interference function, $I(K)$, and the RDF is much more significant than that of pressure over the ranges of temperature and pressure investigated.
- 2) $I(K)$ is practically insensitive to pressure from atmospheric up to 20,000 psi.
- 3) The height of the first maximum in $I(K)$ decreases linearly with a temperature increase and the low angle scattering appears to increase linearly with temperature.

- 4) At constant volume the position of the first maximum in $I(K)$ remains constant with changes in temperature. The RDF is almost independent of the low angle scattering, with the scattering above $2\theta = 15^\circ$ essentially determining the form of the RDF. Oscillations in the RDF show decreasing amplitude with increasing temperature, which implies a slight randomization of the liquid structure with increasing temperature. The peak position of the first maximum in $I(K)$ remains fixed if the volume is constant. The number of nearest neighbors was found to be about 9.2 atoms in the first shell.
- 5) The most important correction was found to be an absorption - eccentricity correction which was so large that at low angles ($2\theta < 15^\circ$) the measured $I(K)$ data were unreliable.

A full theoretical analysis of the data to determine the RDF and the coordination number is capable of giving only an average distribution of atoms about a central one. No information can be obtained regarding a detailed spatial configuration since the atoms are continually shifting about. That is, diffraction measurements on liquids provide much less information than for solids.

In principle, it is possible to calculate $z(r)$, the RDF, directly from knowledge of the strength and nature of the interatomic interactions (or vice versa). Thus, from $z(r)$ the physical and thermodynamic properties of the liquid may be computed. Actually, various results, including ours, verify that the form of the RDF is independent of the detailed shape of the interaction potential, $\phi(r)$. $z(r)$ depends essentially on the depth and position of the potential well minimum.

The interatomic potential is most sensitive to the values

$$\frac{1}{I(K)} = \frac{\varphi(K)}{kT} + 1$$

where $\varphi(K)$ is the Fourier transform of the interaction potential. Because of this, very precise measurements of the low angle scattering intensity are necessary to accurately determine $\varphi(r)$. However, because of the large effect due to the absorption eccentricity correction our low angle results are not too reliable. At the same time it must be pointed out that though we may not accurately determine $\varphi(r)$ because of this, it does not significantly affect the accuracy of our RDF results. Nevertheless a reasonably accurate determination of the detailed form of $\varphi(r)$ is desirable since in principle it characterizes the nature of the system (whether it's metallic, or an insulator, etc.)

The major distinction between the forms of $\varphi(r)$ for metallic and non-metallic liquids is that the pair potential for metals exhibits long-range oscillations while something like a Lennard-Jones potential appears for non-metals. The long-range nature of the oscillations in metals is related to the fact that the Fermi surface in liquid metals is probably quite sharp contrary to what is usually assumed. A detailed description of the atomic and electronic properties of the system should reflect these distinctions. For example, the processes involved with atom transport (diffusion) should be so affected.

In Figs. 3 - 6 are shown some pertinent information for sodium as obtained from the X-ray diffraction experiments. This work has formed the basis of a completed Ph.D. thesis by M. Daeg and is in the process of being prepared in

Fig. 3 Intensity (cps) as Function of Pressure at $T = 188^\circ\text{C}$, $2\theta = 28.9^\circ$

Fig. 4 $I_{e.u.} \left[s^* = \frac{\sin \theta}{\lambda} \right]$ at Constant Volume for $T = 101.5^\circ, 104^\circ$ and 154° C, Curves are Normalized

Fig. 6 RDF $g(r)$ for Three Different Temperatures at Constant Volume Condition, $c = 0.25$, $s_m = 6$

manuscript form for publication. This work will be submitted later as a Technical Information Document. We had hoped to obtain some experimental information for potassium during the past year but most of the time was expended on computer work in connection with the experimental data for sodium.

C. Resistivity Measurements for Liquid Metals

Measurements have been completed of the electrical resistivity of sodium, potassium and rubidium, as a function of temperature at constant volume over the following temperature ranges:

- a) sodium from 97.5°C to 350°C
- b) potassium from 63.7°C to 250°C
- c) rubidium from 39.0°C to 197°C

Preliminary data were obtained for lithium but difficulty was experienced with reactivity between the lithium and sample holder. All measurements were carried out by the van der Pauw method using a high precision D.C. potentiometer. In general, the constant volume data could be represented by the following linear resistivity - temperature relation.

$$\rho = \rho_0 + \left(\frac{\partial \rho}{\partial T} \right)_v (T - T_0)$$

where ρ_0 = the resistivity at the melting point, and

T_0 = the melting temperature in ° K.

Table I

	ρ_0 (μ ohm-cm)	$\left(\frac{\partial \rho}{\partial T} \right)_v$ (μ ohm-cm/ $^{\circ}$ C)
Na	9.60	0.021
K	13.1	0.030
Rb	22.0	0.046

Our results were obtained over much larger temperature ranges than Endo's results and yet are in good agreement with his earlier results (within 3%) obtained by an A. C. technique. Furthermore, the temperature dependences obtained agree with those predicted for classical correlated density fluctuations in conjunction with the Born Approximation to within 5 to 10%.

The experimental results obtained by M. Budke-Daeg of our group show that to a very good approximation the X-ray interference function $I(K, T)$ may be expressed by

$$I(K, T) = I_0(K) + \left(\frac{\partial I}{\partial T} \right)_v (T - T_0)$$

where K = the scattering vector, T = the absolute temperature, and T_0 = the melting point. This implies that the RDF, $z(r)$, may be written as

$$z(r) = a(r) + b(r) (T - T_0)$$

where $a(r)$ = the Fourier transform of $[I_0(K) - 1]$, I_0 being the interference function at the melting point. $b(r)$ = the Fourier transform of $(\partial I / \partial T)_v$. Now according to the Born Approximation, the scattering responsible for the resistivity depends importantly on $I(K)$, which implies that the small angle scattering part of

I (K) primarily determines the electrical resistivity.

Neutron scattering data and specific heat capacities indicate that high energy vibrational modes exist in liquid metals as well as in solids. Furthermore, it appears that the frequency distribution of the modes in the two states is similar. The liquid has a "smeared-out" Debye spectrum which becomes less distinct as the liquid is heated.

Following Born and Brody, one may define a space-correlation tensor in terms of atomic vibrational displacements. Glauber has applied this approach to a simple Debye model having a single θ_D (characteristic temperature). In this case, the system is isotropic and the correlation tensor is a scalar, $n_{12}(r)$, as is to be expected for liquids. A sum over states becomes an integral over the Debye sphere of radius $q_{\max} = k \theta_D / \hbar C_s$, where C_s = sound velocity, and $q_{\max}$ is the cut-off wave vector. One should then obtain

$$z(r) = n_{12}(r) - \bar{n} = \frac{3\hbar^2}{2mkT} A\left(\frac{\theta_D}{T}, R\right) - \bar{n}$$

$$\text{where } A\left(\frac{\theta_D}{T}, R\right) = \int_0^1 k^2 \coth\left(\frac{1}{2} k \theta_D / T\right) \frac{\sin kR}{kR} dk$$

$$R = q_{\max} r, \text{ and } \bar{n} = \text{mean atom density.}$$

At low temperatures ($T \ll \theta_D$)

$$A\left(\frac{\theta_D}{T}, R\right) = \frac{T}{2\theta_D} \frac{(1 - \cos R)}{R^2}$$

At high temperatures ($T > \theta_D$)

$$A\left(\frac{\theta_D}{T}, R\right) = 2\left(\frac{T}{\theta_D}\right)^2 \frac{1}{R} \int_0^R \frac{\sin x}{x} dx$$

Thus at low temperatures we expect $z(r)$ to be independent of temperature, and at high temperatures $z(r)$ is proportional to T . There can be some criticism of this approach as to its validity in the maximum Debye cut-off region. However, it should result in a small overestimation of the magnitude of the correlation terms. This will be discussed in a forthcoming report.

Now the resistivity calculated by the Born Approximation is given as

$$\rho = C \int_0^{2k_F} |F(K)|^2 I(K, T) K^3 dK$$

Taking $\rho(T) - \rho_0$ gives (for $T > \theta_D$)

$$\rho(T) - \rho_0 = C \int_0^{2k_F} |F(K)|^2 \left(\frac{\partial I}{\partial T} \right)_V K^3 dK$$

Assuming a simple Debye model liquid, and since $T_0 > \theta_D$, we can write

$$\begin{aligned} z_0(r) &= a(r) - \bar{n} \\ &= b(r) T_0 - \bar{n} \end{aligned}$$

at the melting point of the liquid. By substitution we can then obtain the following result

$$\frac{\rho(T) - \rho_0}{\rho_0} = \frac{T - T_0}{T_0}$$

or, equivalently $\frac{\rho(T)}{\rho_0} = \frac{T}{T_0}$. Table II below shows a comparison of

experiment with this result for T = maximum temperature of measurement.

Table II

	<u>Na</u>	<u>K</u>	<u>Rb</u>
$\frac{\rho(T)}{\rho_0}$	1.625	1.42	1.34
$\frac{T}{T_0}$	1.65	1.55	1.48
error	3.85%	8.4%	9.5%

Thus the predictions of the Born Approximation agree with experiment to within 10%.

Some of the experimental data are shown in Figs. 7 - 9.

FIG. 7 RESISTIVITY OF PURE LIQ. Na AT
CONSTANT PRESSURE AND CONSTANT
VOLUME

FIG. 8 RESISTIVITY OF PURE LIQUID K AT
CONSTANT VOLUME

FIG. 9 RESISTIVITY OF PURE LIQUID Rb AT
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