Progress Report

for the period

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DIFFUSION STUDIES IN LIQUID METALS

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I.   RESEARCH PROGRESS DURING THE PAST YEAR

During the past year, rather extensive progress has been made on our thermotransport program and moderate progress has been made on the measurement of self-diffusion coefficients as a function of temperature under constant volume conditions. In the renewal proposal submitted last year two other avenues of work were mentioned where we planned to put some effort, namely, X-ray diffraction at constant volume and electrical resistivity measurements of liquid lithium. A small amount of staff time was devoted to the first of these two items and none to the last item. The distribution of time devoted to each aspect of the program was governed by consideration as to where the most significant contribution could be made. The research progress made during the past year will be discussed briefly below. Detailed reports are presented in the various Technical Documents which have been prepared or are in the process of being prepared.

A.   Thermotransport Program

In this program a liquid metal which contains a trace quantity of radioactive solute is subjected to a temperature gradient. As a result of the presence of the temperature gradient, a gradient in the solute concentration develops and in the stationary state, a plot of the logarithm of solute concentration versus the reciprocal of absolute temperature (where temperature is a function of distance along the sample) yield a line which has a slope equal to $\triangle Q^* = (Q_2^* - Q_1^* \, \overline{V}_2 / \overline{V}_1)$

where Q_2^* and Q_1^* are the heats of transport of solute and solvent respectively and $\overline{V}_2/\overline{V}_1$ is the ratio of partial molal volumes. As a first approximation $\overline{V}_2/\overline{V}_1$ is equal to unity for substitutionally dissolved solute. Present theoretical ideas suggest that the heat of transport term $\triangle Q^*$ is the sum of several contributions.

$\triangle Q_i^*$ = contribution from the difference in energy transported by solute and solvent during the jumping process (related to the activation energy for an activated state process).

$\triangle Q_e^*$ = contribution from the differential scattering by solute and solvent of electrons at the Fermi level

$\triangle Q_T^*$ = contribution from the effect of Thompson field on a solute of different valence from solvent

$\triangle Q_p^*$ = contribution from differential scattering of phonons.

Theoretical calculations by various scientists indicate that $\triangle Q_T^*$ and $\triangle Q_p$ are probably small and, therefore,

$$\triangle Q^* \cong \triangle Q_i^* + \triangle Q_e^*$$

1. Studies of Liquid Silver Containing Trace Solute Concentrations

Preliminary data for the solutes, Au, Sb and S in liquid silver were provided in the last progress report (COO-841-20). Since that time more measurements have been completed and yield values of $\triangle Q^*$ for Au, Sb and S of +1,690, -6770, and -29,000 cal/g-atom respectively. These numbers, particularly the last two, are surprisingly large and indicate a substantial segregation in a temperature gradient.

For Sb, as an example, in a temperature difference of $100^{\circ}K$, the Sb concentration at the hot end is 12% greater than at the cold end whereas for S, the percentage is 210%. As reported in Technical Documents COO-841-19 and COO-841-22 the electronic term is calculated to be[1]

$$\triangle Q_e^* = \frac{K_e T}{2} \left(\frac{m^*}{m} \right)^{1/2} (E_F)^{-1/2} A_Z(E_F) \left[1 + 2 \left(\frac{dA/A}{dE/E} \right) E_F \right]$$

where K_e is the electronic thermal conductivity, m^* the effective mass of electrons , m is the rest mass of electrons, E_F is the Fermi energy and $A_Z(E_F)$ is the solute scattering cross-section for electrons. Calculations indicate that $\triangle Q_e^*$ is the major term in the net heat of transport for Sb but makes a negligible contribution for Au. Information about the various quantities for S is unavailable.

The $\triangle Q_i^*$ term may be calculated for various models of diffusion. Without going into detail, $\triangle Q_i^*$ is calculated to be zero for all solutes according to the Cohen-Turnbull model of diffusion. For the hole theory $\triangle Q_i^*$ is calculated to have the wrong sign and therefore yield incorrect values of $\triangle Q^*$. The fluctuation model devised by the author has not yet been programmed so as to yield predicted values. Equations, however, have been derived (see COO-841-22) for $\triangle Q_i^*$ in terms of a gas-like model of liquids. This general approach to liquid property calculations based on gas-like assumptions as opposed to calculations based on solid-like models seems at present to be capable of yielding fruitful results. In first-approximation calculations in which masses and sizes of solute and solvent are considered, values of $\triangle Q_i^*$ are calculated which appear quite reasonable. For Au, $\triangle Q_i^*$ is calculated

[1] M. Gerl, J. Phys. Chem. Sol. <u>28</u>, 725 (1967).

according to this approach to be 1770 cal/g-atom and $\triangle Q_e^*$ is calculated to be

- 480 cal/g-atom for a calculated net value of $\triangle Q^*$ of + 1290 cal/g-atom compared

to a measured value of +1690 cal/g-atom. The calculated value of $\triangle Q_i^*$ and $\triangle Q_e^*$

for Sb are -1230 and -6280 cal/g-atom respectively for a calculated value of

$\triangle Q^*$ of -7510 cal/g-atom as compared with the measured value of -6770 cal/g-atom.

As a consequence, this general approach seems fruitful and some solutes have

been chosen this past year for study in order to test the model. The predicted value

of $\triangle Q_e^*$ for transition metal solutes is large and consequently studies have been

initiated on Co, Ni and Pd.

Data have been obtained for cobalt in silver. A typical result is shown in Fig. 1.

The value of $\triangle Q^*$ is -9,000 cal/g-atom and indicates as expected that the electronic

term is large for a transition element in silver.

In addition to the above studies, thermotransport of trace amounts of Ag in

Au are being undertaken as a comparison investigation to our work on Au in Ag. As

expected the values of $\triangle Q^*$ are opposite in sign. A typical result for Ag in Au

is shown in Fig. 2 as the value of $\triangle Q^*$ is -1150 cal/g-atom.

Theoretical calculations indicate that for solutes in which the electronic term

is important there is a relation between $\triangle Q^*$ as obtained from thermotransport

measurement and the electrotransport coefficient as obtained from electromigration

experiments.[2] In order to test the predicted relation, an apparatus has been

constructed for the purpose of making some electromigration measurements of

solutes in liquid silver. Measurements are being initiated at this time. In these

experiments, an electrical current is passed through the alloy under isothermal

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[2] M. Gerl, presented at Europhysics Conference on Atomic Transport in Solids and
Liquids, Marstrand, Sweden, 1970.

conditions and a stationary solute gradient is established. The electrotransport

efficiency is calculated from analysis of the concentration of radioactive solute as

a function of distance and knowledge of the electric current density.

2. Studies in Liquid Sodium Alloys

Part of our attention during the past year has been devoted to thermotransport

studies in liquid sodium. This work has been initiated for two reasons. From a

theoretical point of view (rather than experimental) sodium is an ideal system with

which to work. Pseudopotential concepts may be applied with some justification to

sodium base systems and therefore one is able to get a grasp on the electronic states

of impurities in these systems thus facilitating calculations of properties. Secondly,

these systems are of considerable interest to the Atomic Energy Agency and thus

results could have some immediate significance. In order to test the model discussed

earlier in this section, Hg and C were chosen as the first solutes for study. Hg

is much heavier than Na whereas C is much lighter thus the mass effect can in

principle be more clearly separated. Results to date for Hg indicate that the solute

segregates to the cold end and a preliminary value of $\triangle Q^*$ is calculated to be

2,250 cal/mole.

Thermotransport studies of the Na-K binary system have also been initiated

in our laboratory. A considerable number of electromigration studies have been made

in the past in a variety of laboratories and a cross-over point occurs in electromigration

at about 40 at % K at 373°K. For alloys containing less than 40 at % K, K moves to

the anode whereas for more concentrated alloys, K moves to the cathode[3]. This

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[3] See for example - D. L. Olson et al, Scripta Met. 4, 1023.

problem has been examined theoretically by use of the phase shift approach and differential scattering cross-sections for Na and K have been calculated as a function of composition, temperature and pressure.[3] The calculations are in semi-quantitative agreement with experimental results. This system therefore represents a system for which fairly detailed calculations may be made. Consequently, we have initiated thermotransport measurements on the binary system for various concentrations. If electron back scattering is important in thermotransport we would expect a reversal in sign for $\triangle Q^*$ and should be able to make calculations of $\triangle Q_e^*$ as a function of composition. A few samples have been annealed in the thermotransport apparatus and the concentration as a function of distance (temperature) will be determined by use of an atomic absorption spectrometer which is available in the Department of Chemistry.

The experimental data obtained to date are summarized in Table I.

B. Self-Diffusion at Constant Volume

The purpose of this part of the program is to measure the self-diffusion coefficient of some liquid metals as a function of temperature at constant molar volume. In a constant pressure experiment, as the temperature is varied both the free volume available for diffusion and average energy of the atoms increase. Theoretical calculations of diffusion coefficients are generally performed under constant volume conditions thus there is a closer match between experiment and theory if experiments could be performed at constant volume. A study in our laboratory of liquid sodium

Table I.   Relative Experimental Heats of Transport of Solutes

(Trace Concentrations) in Liquid Metals

Solvent	Solute	$\triangle Q^{*}$ (cal/g-atom)
Ag	Au	+ 1690
	Sb	- 6770
	S	- 29,000
	Co	- 9000 (preliminary)
Au	Ag	- 1150 (preliminary)
Na	Hg	2250 (preliminary)

(Technical Document COO-841-14) yielded results which provided a rather severe test of theory and most models predicted a much different temperature dependence than the one observed. In order to further these studies, In and Hg were chosen for study since they are low melting and have convenient isotopes. These materials have rather low compressibilities as compared to sodium and thus the temperature range for study in our system is restricted ($\triangle T = 30^{\circ}K$ for Hg versus $\triangle T = 100^{\circ}K$ range for Na) because of a limit of 100,000 psi in our apparatus. Nonetheless a program was initiated for indium with the necessity that very precise data would have to be obtained in order that the temperature dependence could be determined adequately. We found, however, that the temperature dependence of diffusion under the condition of constant volume was small so that normal scatter in experimental points precluded an accurate determination of the slope.

Attention was then shifted to Rb. Rb has a very high compressibility and consequently the experimental temperature range is wide ($150^{\circ}K$). The first measurements are in the process of being made at present. We are interested in obtaining results for at least one system in order to show whether or not the general trend observed in the Na study is followed by other systems.

C. RDF Measurements

The work dealing with the RDF of liquid sodium vs. temperature at constant volume has been completed and is the subject of Technical Report No. COO-841-24. The work dealing with the RDF of potassium is uncompleted due to the departure of the graduate student responsible for carrying out the experiment. Several attempts have been made to calculate the RDF of sodium using a theoretically derived pair potential, $\varphi(r)$. From these results it is hoped to obtain $g(r)$, $(\partial g/\partial T)_V$, and $(\partial I/\partial T)_V$ for comparison with experiment. We propose to continue this program to ultimately test the pseudo-potential approach for the liquid alkalis.

II. BIBLIOGRAPHY

Since the last progress report the following technical reports have been either newly issued or published in journals. Reprints of published papers are included with this report.

COO-841-19: B. H. Bhat and R. A. Swalin

Thermotransport of Solute Elements in Liquid Silver
Zeitschrift für Naturforschung Vol. 26a, 45 (1971).

COO-841-21: M. Hsieh and R. A. Swalin

Self-Diffusion in Liquid Indium
Zeitschrift für Naturforschung, Vol. 26a, 328 (1971).

COO-841-22: B. H. Bhat and R. A. Swalin

Thermotransport of Au, Sb and S in Liquid Silver

The principal investigator has devoted about 15% of his time to the project during the present contract period. This will increase to 50% during the period June 16 - August   15 and then become 10 % until the end of the present contract period.
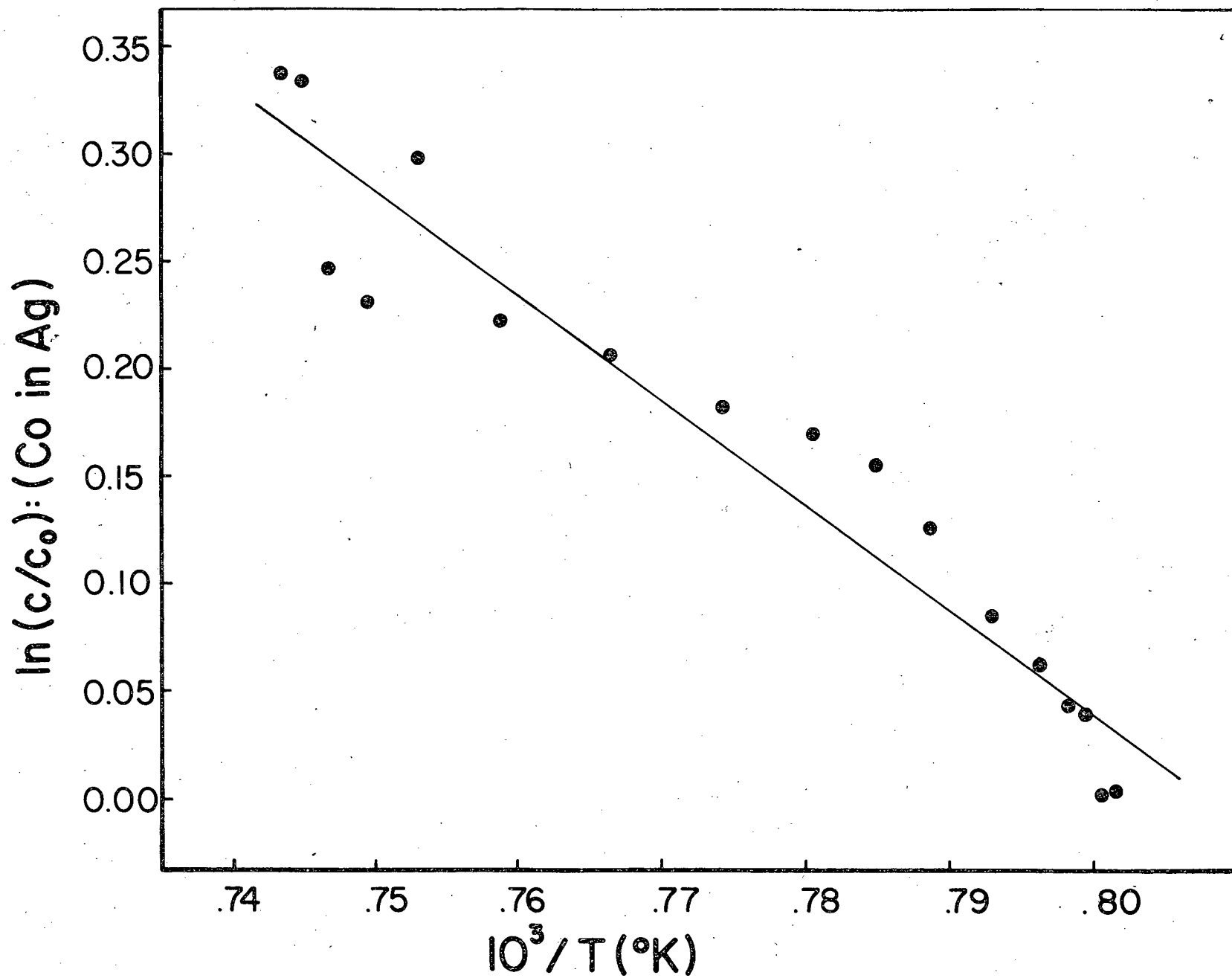
Fig. 1