FINAL REPORT

DIFFUSION STUDIES IN LIQUID METALS

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Abstract

A summary of the results obtained throughout the duration of the contract is presented in this report along with a list of publications and a list of students who have worked on the project. Twenty papers have been prepared for a variety of technical journals. Seventeen of these have already been published and three are in the process. Nine graduate students have received degrees which were based on research performed in connection with the project. Six of the students have received the Ph. D. degree and three have received the M. S. degree. These students have been employed as research assistants. In addition, several postdoctoral fellows have worked on the program.

The technical work itself may be divided into three broad categories.

- I. Self-diffusion in liquid metals as a function of temperature and pressure
- II. Solute diffusion in liquid metals
- III. Thermotransport studies in liquid alloys

The principal concern of Part I was the use of self-diffusion data obtained over a wide temperature interval under constant volume conditions to test models which were based on a variety of possible mechanisms of diffusion in liquid metals.

Part II involved the systematic diffusion study of a variety of trace concentrations of solutes in liquid silver. Altogether ten solutes were investigated and the results were compared to theoretical predictions and to work on the same systems in the solid state.

Part III involved the study of thermal segregation of solutes in liquid silver and various alkali metals. The experimental effects observed could be very large and a model has been developed to explain the observed effect. Solutes may segregate at either the hot end or the cold end.

FINAL REPORT

AEC Contract AT(11-1)-841

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The research program was initiated in November 1959 and thus has encompassed a period of 13 1/2 years. During this period 17 papers have been published and three more are in process. Thus, a total of 20 papers based on this AEC project will have been published. A list of these publications is appended to this report. Nine graduate students have worked on the program. Six of these have received the Ph. D. degree and three have received the M.S. degree. Some of the students have worked as postdoctoral fellows for a period of time after receipt of their degrees. A list of students is appended to the report. In addition to the students, two postdoctoral fellows have been employed on the project after receiving their degrees from other universities.

By 1959, the year the research program was initiated, self-diffusion studies had been performed for several metallic systems. These studies were all characterized by large diffusion coefficients (of the order of 10^{-5} cm²/sec), low values of the frequency coefficient D_0 (of the order of 10^{-4} cm²/sec) and values of the apparent activation energy of a few thousand kilocalories/mol. Given the success of the vacancy mechanism theory for solid state diffusion, it was perhaps natural for interpreters to attempt to apply the general features to liquid metals. These attempts were based on the hole theory approach in which it was assumed that a large number of holes (analogous to vacancies in solids) existed in liquid metals. The interpretation broke down completely when the hole theory model was employed to explain the low D_0 values for diffusion.

Also by 1959, several solute diffusion studies had been performed in liquid base systems although no systematic approach had been developed.

In November 1959, two papers were published which took a new viewpoint of the liquid diffusion mechanism. One published by M. Cohen and D. Turnbull was based to some extent on the hole theory. They took the viewpoint that the diffusion jump distance is one interatomic spacing but that the holes into which an atom diffused could be variable in size but had to be above some critical dimension. This approach yielded a standard exponential diffusion equation of the form

$$D = D_0 \exp (-Q/RT)$$

The model did explain the experimentally observed small values of D_0 . The other paper published by R. A. Swalin was based on a density fluctuation approach and assumed that jump distance could be variable and that under the correct atomic packing conditions no critical void size was necessary. This led to diffusion equations that did not vary exponentially with temperature but had the form

$$D = KT^2$$

where K is constant for a particular metallic system. All of the diffusion data which had been obtained experimentally had been obtained over a rather narrow range of temperature and, given the normal experimental scatter, either equation could be employed to interpret the results.

Our first approach then was to attempt to extend, in an experimental investigation, the temperature interval of measurement. Results from our experiments were published in Paper No. 1. The data when plotted as $\log D$ versus $1/T$ showed considerable curvature and were compatible with a $D \sim T^2$

relation. After our paper was published, I received several letters from investigators who had detected curvature on $\log D - 1/T$ plots in their data. Some of these investigators subsequently published their work in the literature.

Often a T^2 relation was not obtained by investigators. Sometimes $D \sim T^n$ where n could be one for one system and some other value for a different system. As theoretical models were developed and applied, it became clear that results could be better interpreted theoretically if constant volume data in addition to constant pressure data could be obtained. Under constant volume conditions, the Cohen-Turnbull model predicted that $D \sim T^{1/2}$, and according to the Rice-Nachtrieb model $D \sim T^{3/2}$. Our model employed pair potential considerations between ions. In the version published in 1959, quasi-chemical pair potentials were employed. These attractive potentials were all quite large and negative in sign when compared with kT . There is considerable evidence, however, for materials such as sodium that the effective pair potential is oscillatory in character and has an effective attractive interaction which is of the same magnitude of kT . This problem was examined in Paper No. 10. For materials with large attractive interactive potentials (where the attractive interactive energy $\gg kT$), D was predicted to vary linearly with T at constant volume. On the other hand, for a material like sodium, no simple relationship was directly obtainable. Rather, one had to substitute the actual parameters of the potential into a rather involved mathematical expression.

We decided, therefore, to experimentally investigate self-diffusion as a function of temperature under constant volume conditions. This involved the use of high pressure diffusion apparatus. A base molar volume was established

which was characteristic of some temperature somewhat above the melting point and one atmosphere pressure. At a higher temperature enough pressure was applied to counteract the normal thermal expansion of the liquid metal. Experimental results for liquid sodium were published in Paper No. 11. In this work, neither the $T^{1/2}$ or $T^{3/2}$ dependence was observed to hold. The temperature dependence predicted by our model was quite closely followed although the actual magnitude of D measured was not identical to calculated values.

This work was followed up in Paper No. 20 in which liquid potassium and rubidium were investigated over a wide temperature interval. Precise data under constant volume conditions could not be obtained for these systems but the constant pressure data yielded an excellent proportionality between D and T^2 in accordance with our model. The shape of the $D - T^2$ curve differed significantly however from the calculated values. This is not particularly surprising in view of our general lack of knowledge of pair potential parameters for various materials. Pair potential theory is at best semi-quantitative and the only good calculations appear to have been done for sodium.

Another approach was initiated in about 1964. Detailed calculations had been made by Ziman of the temperature dependence on the electrical resistivity of alkali metals. For sodium it was concluded that local density fluctuations gave rise to electron scattering and accounted for much of the temperature dependence of the electrical resistivity for sodium. The remainder of the scattering is due to changes in the structure factor as a function of temperature. The fluctuations which contribute to electron scattering are presumably the same ones which, according to our model, may facilitate diffusion. It was decided,

therefore, to investigate the electrical resistivity of alkali metals as a function of temperature under constant volume conditions and further to investigate the X-ray radial distribution function of liquid sodium as a function of temperature under constant volume conditions. The electrical resistivity results were presented in Paper No. 13. Precise X-ray scattering data were obtained in a pressure cell under constant volume conditions. These very precise data were presented in Technical Document COO-841-24 but unfortunately we found that a low angle correction term was in error and thus the quantitative deductions are open to question.

II Solute Diffusion

Very little systematic study has been given to the study of solute diffusion in liquid metals. In solid metals, on the other hand, a wide variety of systems had been systematically studied. One of the most successful of these investigations was the study of trace concentrations of various solutes in silver. Lazarus showed that the ratio of the solute diffusion coefficient to the self-diffusion coefficient could be explained in terms of the relative valence of solute and solvent. In these calculations, it is not necessary to know the pair potentials between solvent ions. What is important in the calculations is the change in pair potential between solute and solvent as affected by the valence difference. This perturbation may be estimated by various techniques.

We decided, therefore, to investigate the same systems in the liquid state. It was thought further that the quantitative experimental results could be employed to shed light on the diffusion mechanism. The experimental results

of these studies were presented in a series of papers: Papers No. 2, 3, 4, 8, 9, and 12. A summary of most of the work was presented in Paper No. 7.

Several effects were found, namely:

- (a) The relative behavior of solutes in liquid silver was qualitatively the same as the behavior in solid silver. That is to say, solutes with positive relative valence diffused faster in liquid silver than silver itself.
- (b) As in the case of solid silver-base alloys, the agreement between theory and experiment for electropositive solutes such as Cd, In, Sn, Sb is much better than that for electronegative solutes such as Ru, Fe, Co, Ni.
- (c) The ratio of $D(\text{solute}) : D(\text{self})$ was closer to unity in liquids than it is in solids. For example, a solute such as antimony which has a relative valence of +4 in silver yields a ratio of about 1.5 in liquid silver whereas in solid silver the ratio is about 10. This attenuation in the ratio $D(\text{solute}) : D(\text{self})$ for liquids is to be expected in view of the intrinsically large high magnitude of self-diffusion of liquids.
- (d) The experimental results could not be used definitely to determine the diffusion mechanism in liquids. Calculations, for example, based on our fluctuation model and classical hole theory yielded equally good agreement with the experimental results.

III Thermotransport Studies

From a basic point of view, ordinary studies of diffusion have gone about as far as they can in elucidating the detailed mechanism of diffusion. Further knowledge for the fine structure of the activated state mechanism will probably come as a result of insight obtained from the study of cross-effects. Such phenomena as the isotope effect, electromigration and thermomigration are explainable only in terms of detailed models of the diffusion process. Various groups have been active in isotope work and electrotransport studies but no careful work had been done on thermotransport studies in liquid metals. The phenomenon of thermotransport is the redistribution of solute in an otherwise homogeneous alloy which results from the presence of a temperature gradient. In principle the solute may segregate at the hot end or the cold end of a capillary tube, for example, and until recently the theory of the process was extremely crude. The thermotransport effect is important in systems which operate at elevated temperatures and which contain thermal gradients. Such a system, of course, is a nuclear reactor.

Our first experimental work, published in Paper No. 14, was published in 1971. This was a study of the redistribution of trace amounts of various solutes in liquid silver. When we began the work, since we had little to go on, we were concerned that the thermal segregation might in fact be too small to measure and thus attempted to survey a variety of solutes. Gold, antimony and sulfur were chosen for this study. Since this was the first thermotransport study of dilute liquid metal alloys performed, in view of the closeness of solute diffusion coefficients to self-diffusion coefficients in liquids, we expected the effect of

a temperature gradient on the redistribution to be small in view of the closeness of solute and solvent diffusion coefficients. We were quite surprised to observe that in a temperature difference of 100° K, the sulfur concentration was 15 times greater at the hot end than at the cold end. For antimony, the ratio was 1.2 and gold concentrated at the cold end with a ratio of about 1.05. Since that time thermotransport of silver as a solute in gold has been studied (Paper No. 16) and cobalt in silver has been investigated (Paper No. 17). In addition, a variety of liquid alkali alloy systems have been studied and results are to be published. Recently we have been investigating the magnitude of thermal segregation in the sodium-potassium binary system as a function of alloy composition. The reason for this study is that electromigration has been carefully investigated both experimentally and theoretically for this system. Interestingly, a sign reversal occurs for the migration of the species and thus at one intermediate composition there is zero electrotransport. Interestingly, we find the sign reversal also for thermotransport in this system but the composition at which the thermotransport cross-over occurs is not identical to that for electromigration. Recent theory predicts a relation between electrotransport and thermotransport and we are interested to see whether or not we can rationalize the two sets of experimental results.

In thermotransport studies, the important quantity which is obtained is the heat of transport Q^* . Q^* is obtained from a plot of $\log C$ versus $1/T$ where C is the solute concentration. Theoretical work done in other laboratories indicates that Q^* is composed of two terms Q_e^* and Q_i^* . Q_e^* results from the momentum exchange between electrons and solute ions. The solute has a

scattering cross-section which depends on electron energy. Thus, the high energy electrons which move down the temperature gradient will exchange a smaller fraction of their momentum than will the low energy electrons which are moving up the gradient. This results in a net force which will tend to move the solute to the high temperature end of the sample. The other component of Q^* , Q_1^* , is due to the diffusion process itself and may simplistically be considered to represent the net amount of activation energy (positive or negative) carried by the solute as it moves. We find that a gas-like treatment of the liquid diffusion process gives calculated results for Q_1^* that are in reasonable agreement with experiment. The most important variable in these calculations is the relative mass of solute and solvent. If the mass of solute is greater than that of the solvent, Q_1^* will tend to be positive (solute will move to the cold end) whereas if the mass of the solute is less than that of the solvent Q_1^* will tend to be negative. The sign of Q^* depends then on the sum of Q_e^* which tends to be negative and Q_1^* which may be either positive or negative. Results of our calculations for several systems along with experimental data are presented in Papers No. 14, 16, 17, 18 and 19. The model for Q_1^* which is based on the Chapman equation for dense gases is presented in Paper No. 16. The apparent success of the gas-like approach to thermotransport calculations is consistent with recent use of the gas-like approach for ordinary diffusion calculations. There is considerable evidence now that it is more fruitful to consider liquid metals as analogues of dense gases than as quasi-solids.

List of Publications

1. Self-Diffusion in Liquid Tin, C. H. Ma and R. A. Swalin. J. Chem. Physics 36, 3014 (1962)
2. Diffusion of Silver and Tin in Liquid Silver, V. G. Leak and R. A. Swalin. Trans. AIME 230, 426 (1964)
3. Diffusion of Heterovalent Solutes in Liquid Silver, R. A. Swalin and V. G. Leak. Acta Met. 13, 471 (1965)
4. Diffusion of Gold in Liquid Silver, Y. P. Gupta. Acta Met. 14, 297 (1966)
5. On Solute Diffusion in Liquid Tin, Y. P. Gupta. Acta Met. 14, 1007 (1966)
6. Correlation of Thermodynamic and Atomic Transport Properties, R. A. Swalin, in Thermodynamics, Vol. II, International Atomic Energy Agency (1966)
7. Solute Diffusion in Liquid Metals, Y. P. Gupta. Advances in Physics 16, 333 (1967)
8. Diffusion of Ru, Fe and Co in Liquid Silver, H. S. Wang and Y. P. Gupta. Acta Met. 16, 53 (1968)
9. Diffusion of Nickel in Liquid Silver, Y. P. Gupta and H. S. Wang. Scripta Met. 2, 21 (1968)
10. On the Fluctuation Model of Diffusion in Liquid Metals, R. A. Swalin. Zeitschrift für Naturforschung 23a, 805 (1968)
11. Self-Diffusion in Liquid Sodium at Constant Volume and Constant Pressure, M. W. Ozelton and R. A. Swalin. Philosophical Magazine 18, 441 (1968)
12. Diffusion of Zinc and Germanium in Liquid Silver, Y. P. Gupta and H. S. Wang. Trans. AIME 245, 619 (1969)
13. The Resistivity versus Temperature at Constant Volume of Liquid Na, K and Rb, S. Y. Lien and J. M. Sivertsen. Phil. Mag. 20, 759 (1969)
14. Thermotransport of Solutes in Liquid Silver, B. N. Bhat and R. A. Swalin. Zeit. für Naturf. 26a, 45 (1971)
15. Self-Diffusion in Liquid Indium, M. Hsieh and R. A. Swalin. Zeit. für Naturf. 26a, 328 (1971)

16. Thermotransport of Silver in Liquid Gold, B. N. Bhat and R. A. Swalin.
Acta Met. 20, 1387 (1972)
17. Thermotransport of Cobalt in Liquid Silver, B. N. Bhat and R. A. Swalin.
Scripta Met. 6, 523 (1972)
18. Thermotransport of Be and Hg in Liquid Sodium, B. N. Bhat and
R. A. Swalin. Scripta Met. (in press)
19. Thermotransport Studies in Liquid Alkali Metal Alloys, S. Murarka, T. Kim
and R. A. Swalin (in preparation)
20. Self-Diffusion in Liquid Potassium and Rubidium, M. Hsieh and R. A. Swalin
(in preparation)

List of Student Research Assistants

1. C. H. Ma, Ph.D. -- now with New Mexico College of Science and Technology, Socorro, New Mexico
2. V. G. Leak, M.S. -- now with U. S. Bureau of Mines Research Center, Minneapolis, Minnesota
3. H. S. Wang, M.S. -- previously with Northrop Corporate Research Laboratory; address presently unknown
4. S. Y. Lien, M.S., Ph.D. -- now with Bell Telephone Laboratories, Allentown, Pennsylvania
5. B. N. Bhat, Ph.D. -- now with George C. Marshall Space Flight Center, NASA, Huntsville, Alabama
6. S. Murarka, Ph.D. -- now with Bell Telephone Laboratories, Murray Hill, New Jersey
7. T. Kim, M.S. -- now predoctoral student, University of Minnesota
8. M. Hsieh, Ph.D. -- now postdoctoral fellow, University of Minnesota
9. M. Daeg, Ph.D. -- previously with Northrop Corporate Research Laboratory; now with industrial research laboratory in Germany