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Thermotransport of Solutes in Liquid Silver*

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1. Introduction

Investigation of thermotransport or thermal diffusion in liquid metals is in its infancy as compared with such study in solids. In the latter case thermotransport experiments have given information concerning defect mechanisms, energy distribution around an activated configuration and the role of electrons and phonons in diffusion process. The need for such an understanding is even greater in liquids where a generally accepted mechanism of diffusion does not exist. Thermotransport studies yield data which enable us to say more about the mechanism of diffusion than the experiments on isothermal diffusion. Very few attempts have been made to study diffusion in a temperature gradient, especially with metallic systems.

Lodding and Ott⁽¹⁾ have studied the isotope thermotransport in alkali metals. They obtained a rather surprising result that the heat of transport associated with the diffusing species is an order of magnitude larger than the apparent activation energy. However, the observed steady state segregation coefficients were very small because the differences in the diffusivities of the isotopes used in their investigations were small. Hence it was proposed that a system with the diffusivity of solute element considerably different from that of solvent be investigated. Silver base system was chosen because solute elements in silver are known to diffuse as much as 100% faster

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than silver itself. Moreover, conventional radioactive tracer technique can be utilised to measure the concentration and hence a more accurate value of the segregation coefficient can be obtained. Furthermore, considerable work has been done in our laboratory on isothermal diffusion in silver-base systems and it was thought that our past experimental experience could be useful.

The relation between segregation coefficient, temperature gradient and heats of transport of the diffusing species has been derived by Tichacek et al⁽²⁾ using the formalism of irreversible thermodynamics. They obtained the following expression for the steady state condition in a temperature gradient:

$$\left(\frac{Q_1^*}{\bar{V}_1} - \frac{Q_2^*}{\bar{V}_2} \right) \frac{\text{grad } T}{T} = \left[\frac{1}{x_1 \bar{V}_1} + \frac{1}{x_2 \bar{V}_2} \right] x_2 \frac{\partial \mu_2}{\partial x_2} \text{grad } x_2 \quad (1)$$

where $\bar{V}_1, \bar{V}_2$ are the partial molar volumes of components 1 and 2 respectively

x_1, x_2 are mole fractions of component 1 and 2

μ_2 chemical potential of component 1

Q_1^*, Q_2^* molar heat of transport of components 1 and 2 respectively

Here Q_2^* , the heat of transport, is the difference between the total enthalpy transported by one mole of moving molecules of type two in the solution and the average enthalpy of one mole of the type two in the same solution. This Q^* is of special interest because it will depend heavily on the mechanism of atom transport and any theory on diffusion in liquids must explain its magnitude and sign satisfactorily.

Assuming component 2 to be the solute which is present in trace amounts only, we have the situation $x_2 \ll 1$, $x_1 \approx 1$. Also, for a very dilute solution, the solute obeys Henry's law and we can write

$$\mu_2 = (\mu^*)_T, P + RT \ln x_2 \quad (2)$$

$$\left(\frac{\partial \mu_2}{\partial x_2} \right)_{T, P} = \frac{RT}{x_2} \quad (3)$$

equation (1) simplifies to

$$\frac{1}{R} \left(Q_1^* \frac{\bar{V}_2}{\bar{V}_1} - Q_2^* \right) \frac{\text{grad } T}{T^2} = \frac{\text{grad } x_2}{x_2} \quad (4)$$

$$\text{or } \frac{1}{R} \left(Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1} \right) d \left(\frac{1}{T} \right) = d (\ln x_2) = d (\ln C_2) \quad (5)$$

where C_2 is the concentration of solute.

Thus, in a thermotransport experiment, where a column of liquid alloy is held in a known temperature gradient until the steady state is reached, the logarithm of the resulting concentration is related to the reciprocal temperature through the factor $\frac{1}{R} \left(Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1} \right)$ which involves the heats of transport of solute

and solvent. This factor can be assumed to be independent of temperature for short temperature intervals and equation (5) can be integrated to give

$$\ln \frac{x_2^h}{x_2^c} = \frac{K}{R} \left(\frac{1}{T_h} - \frac{1}{T_c} \right) \quad (6)$$

$$\text{where } K = Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1}$$

The symbols h and c stand for hot and cold end respectively.

A plot of $\ln x_2$ vs. $\frac{1}{T}$ will give a straight line with the slope $\frac{K}{R}$.

The solutes gold, antimony and sulfur were investigated. The diffusion coefficients of these elements in liquid silver have been determined^{(3), (4), (5)}. Gold diffuses in silver almost as fast as silver itself. Being noble metals they have very little chemical affinity. Thus gold serves as an index to the experimental conditions prevailing in the set up. Antimony is in the same row as silver but has diffusion coefficient about 40% greater than D_{self} of silver. Sulfur was chosen as an extreme case and it is nonmetallic and is a rapid diffuser in silver.

2. Experimental

The apparatus used for thermotransport studies (shown in Fig. 1) consists essentially of a brass vacuum chamber in which the dual furnace assembly is housed. The upper furnace was wound with platinum and the lower with kanthal. The furnaces were thermally insulated by lava cylinders and plates. Cylinders of graphite form the cores of the furnaces. Controlling and measuring thermocouples were made from Pt-1% Rh and Pt-13% Rh wires, housed in one-end-closed alumina tubes. The furnaces were controlled separately. Electrical connections were taken out of the vacuum chamber through glass-metal seals. A stainless steel cylinder, closed-one-end was fitted to the bottom of the brass chamber through a double O-ring vacuum coupling. The brass chamber was water cooled while in operation. The apparatus was connected to a vacuum system which consists of a mechanical pump and a diffusion pump. A thermocouple gauge is fitted to the vacuum chamber.

Prior to the experimental runs, it was necessary to determine the temperature distribution along the axis of the furnace assembly. This was done by inserting a one-end-closed alumina tube from the top and running it all the way down to the middle of the lower furnace. A thermocouple was introduced in this alumina tube, which now can measure the temperature along the axis as a function of the distance. Actual measurements are made after evacuation of the chamber and allowing the temperatures of the furnaces to reach a steady value. The settings on the controllers were varied to obtain the most desirable temperature profile and the corresponding setting was noted.

The experimental procedure consisted of three steps: 1) sample preparation, 2) diffusion anneal and 3) getting the concentration profile.

Sample preparation. The procedure described here is for antimony -125. Similar procedure was followed for sulfure -35 and gold -195.

Radioactive antimony (Sb) - 125 was obtained in elemental form. Sb-125 is both β and γ active. The γ - activity has a half life of 2.7 years. Two milligrams of this antimony (with approximately one millicurie of radioactivity) was wrapped in a piece of pure silver (99.99% pure) foil and placed in an ultrapure graphite crucible. More silver pieces of 99.999% pure silver were also added to make up the desired percentage of Sb in the alloy. The graphite crucible was placed in a quartz tube closed-one-end. The other end was fitted with a vacuum fitting- which can be connected to a vacuum pump or to a supply of argon dried and then purified by passing through a bed of hot titanium chips.

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The quartz tube containing antimony was evacuated and then filled with argon. This was done several times to drive out all the air in the tube, and finally only pure argon remained in it. It was placed in a vertical tube furnace and slowly heated to 650°C and was held at that temperature for several hours. The temperature was then raised to 1000°C, where antimony formed a homogeneous mixture with silver. The quartz tube was evacuated and the mold made of vycor tubing was lowered into the pool of metal. Argon gas was admitted into the tube, thus forcing the metal into the mold. Power to the furnace was turned off and the metal was allowed to solidify in the mold. Small pieces were cut from this bar. These pieces were the starting material for the experiments.

Sulfur - 35 was diffused into silver at 120°C. The low temperature was used to prevent excessive evaporation of sulfur at high temperature. No such precaution was necessary for gold - 195 which has a very low vapor pressure. Gold-195 was obtained from an aqueous solution of AuCl_2 by slowly heating it to a temperature of 250°C when the chloride decomposes to give metallic gold.

The concentration of gold in the alloy was only about 1 ppm, while sulfur and antimony were present in approximately 10 ppm.

The capillaries used for the experiments were made from precision bore quartz tubing which were 0.75 mm diameter with one end closed. A weighed piece of the alloy was placed in a cup attached to the other end of the capillary. The alloy was melted in vacuum and forced into the capillary by application of argon pressure. The metal was allowed to solidify directionally from the bottom upwards.

The cup-end of the capillary was attached to a vacuum system. The capillary was sealed just below the cup level under a vacuum of approximately 10^{-4} mm of Hg.

Diffusion run. The sealed capillary was attached to a platinum wire and slowly lowered into the center of the dual furnace assembly, until it rested on the bottom end. The open end of the furnace assembly was then fitted with a lava plug. The stainless steel cylinder was fitted to the brass vacuum fitting and the furnace chamber was evacuated. Electrical connections were made and power was turned on. The temperature of the furnaces was controlled in such a way that the metal in the capillary started to melt at the top first and the liquid front moved downwards towards the bottom end. Small adjustment in the settings of the controllers was necessary in order to get the right temperature gradient. The temperatures of both the furnaces were recorded in a temperature recorder during the experiment.

The sample was allowed to remain in the temperature gradient for several days (7 days to 15, depending on the diffusivity of the solute element) until the steady state was reached. The time (t) for steady state is given by⁽⁶⁾

$$t = l^2 / 2D \quad (7)$$

where t = time in seconds

l = length of the liquid column

D = diffusion coefficient of the solute

A time equal twice this amount was employed in order to insure that the steady state had been reached. At the end of this period the sample was allowed

to solidify directionally upwards starting from bottom end. This was accomplished by shutting off the lower furnace first, and then the upper furnace, a few minutes later, so that a positive gradient is maintained at all times while cooling. The sample was removed from the furnace assembly by pulling the attached wire.

Analysis. The concentration profile of the sample was obtained by sectioning the capillary and counting the activity in each section. The solidified capillary of the alloy was freed from the quartz capsules by breaking it and any quartz adhering to the metal was filed off. The capillary was cut into several pieces by use of a shear. Each piece was weighed, put in a glass vial, labelled and put in a photoscintillation counter, for counting the activity. The measured γ activity is converted into specific activity which is proportional to the concentration of antimony in the alloy.

The counting procedure for gold was the same as for antimony except that gold-195 has a different γ spectrum and hence a different setting was needed on the counter. Sulfur-35, on the other hand, has no γ but only β activity. Hence a liquid scintillation counter was used. The procedure adopted was very similar to that used by Jeffay et al⁽⁷⁾. It consisted in (1) dissolving the alloy of silver and sulfur in 1 ml. of modified Pirie's reagent, and evaporating the solution to dryness at 150°C; (2) dissolving the residue in 1 ml. of hot glycerine at 100°C; (3) mixing it with 5 ml. of ethyl alcohol and N-N dimethyl formamide mixture; (4) adding 15 ml. of scintillation solution which is a mixture of PPO and POPOP in toluene; and (5) putting the sample in the liquid scintillation counter which automatically recorded the activity in the sample.

3. Results

The weight of each section of the capillary was converted into length as follows:

$$\text{length} = \frac{\text{wt. of section}}{\text{total wt. of capillary}} \times \text{Total length of capillary}$$

Lengths of sections were added together, starting from bottom, in order to get the distance of each section from bottom end. The relative concentration was obtained for each section by dividing its specific activity by the lowest in the sample. These values are plotted as functions of distance for gold, antimony and sulfur. (figs. 2, 3 and 4).

It is assumed that the temperature profile remains undistorted when the sample is introduced into the furnace assembly. The temperature profile along the length of the capillary is thus known from the plot of temperature vs. distance (fig. 5). Figs. 6, 7 and 8 show plots of $\log C/C_0$ versus $1/T$ for Au, Sb and S. These plots are typical of a number of data obtained in our laboratory. The data are fitted with a straight line by use of least square method. The computer was programmed to give the value of K directly. The values of K thus obtained for each solute element are tabulated in Table I, along with the values of diffusion coefficient in silver (D_{solute}) molar volume of solute in the pure state, "activation energy" for diffusion in silver and the difference in the diffusion coefficients of solute and solvent ($D_{\text{solute}} - D_{\text{Ag}}$).

Table I

Properties	Silver	Gold	Antimony	Sulfur
Diffusion coefficient at 1027°C	3.05×10^{-5}	2.73×10^{-5}	4.54×10^{-5}	7.23×10^{-5}
"Activation energy" cal/mole	7660	8960	5700	11,500
Molar volume, ml	11.66	11.37	19.35	16.7
$(D_{\text{solute}} - D_{\text{Ag}})1027^\circ\text{C}$	-	$- .32 \times 10^{-5}$	1.51×10^{-5}	4.18×10^{-5}
$\left(Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1} \right), \text{calories}$	-	3100 ± 700	-8300 ± 1500	$-76,800 \pm 8400$

In order to determine whether the observed segregation was really due to the presence of the temperature gradient an experiment was conducted for a zero time of anneal. This was done by quickly introducing the sample into the furnace assembly that was already at the working temperature. Sufficient time was given for the temperature to reach equilibrium and the sample was then quickly removed from the furnace, cooled, sectioned and analysed. The resulting activity profile for sulfur is shown in the fig. 9. The concentration falls as one approaches the top. The effect is opposite after diffusion anneal. This kind of profile is probably the result of evaporation during the capillary filling operation. In general, a scatter in the activity of the order of $\pm 5\%$ was observed in the case of antimony and gold; for sulfur, it was higher - of the order of $\pm 15\%$.

It also was desirable to investigate any contribution resulting from buoyancy effects. This contribution would be proportional to the density difference between solute and solvent where the lighter component goes to the top. Sulfur is the extreme case. An experiment with a negative gradient (i.e. hot end at the bottom) was run for sulfur using 50°C difference between hot and cold ends. This kind of set up is generally prone to convection because the density of liquid falls towards the bottom and is basically an unstable system. Verhoeven⁽⁸⁾ has calculated that, under such conditions, convection does not set in until the Rayleigh number reaches a critical value of 68.

This corresponds to a solute gradient of 300 ppm/cm for sulfur. In our case, the total variation of sulfur over 7 cm was less than 300 ppm. Hence it can be reasonably assumed that convection does not affect the results.

Figs. 10, 11 show the concentration profile of such an experiment. The amount of segregation was less than that found for the positive gradients. In fact, the K value is about 1/2 of that obtained for the positive gradient. The trend however is clear - sulfur migrates to the hot end. Similar experiments were performed for gold.

4. Discussion

The results show clearly that the amount of thermotransport of solute in liquid silver varies widely, from almost zero in the case of gold to a large amount in the case of sulfur. Antimony and sulfur segregate to the hot end while gold segregates to the cold end. It is interesting to note that a relation seems to exist between K and $(D_{\text{solute}} - D_{\text{Ag}})$, viz the amount of thermal segregation is more, greater the difference in the solute diffusivity and self diffusivity of silver. This trend is shown in Fig. 12.

One in principle may calculate the heat of transport Q_2^* for various solute elements in silver by use of relation $K = Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1}$. In order to do this one needs information about the partial molar volume ($\bar{V}_2$) of solute in liquid silver and the heat of transport (Q_1^*) of silver. Unfortunately, these data are not available in general.

If, as a first approximation, one assumes that $\bar{V}_1 \approx \bar{V}_2$ for all solute elements, then the following relations are obtained:

$$Q_S^* - Q_{Ag}^* \approx -77,000 \quad \text{cal/mol.}$$

$$Q_{Sb}^* - Q_{Ag}^* \approx -8,300$$

$$Q_{Au}^* - Q_{Ag}^* \approx +3,000$$

There is no straightforward way of calculating Q_{Ag}^* , however.

Winter and Drickamer⁽⁹⁾ have made thermal diffusion measurements on a series of tin-base alloys (50% alloys were used). In all cases except Sn-Hg system solute migrated to the hot end. The amount of segregation varied widely from one system to another.

Lodding and Ott studied isotopic thermotransport in alkali metals. Lodding^{(10), (11)} has attempted to build a theoretical model to interpret these data. In the earlier version of the theory⁽¹⁰⁾ he assumed a cooperative type motion where clusters of atoms make way for a void into which a solute atom can move. The diffusion distance (l) can be much smaller than the distance (φl) between the center of the cluster and the "imperfection", that is responsible for the diffusive jump. In his later paper he devised the following equation for thermotransport at steady state

$$\frac{\partial \ln Q}{\partial T} = \frac{D_2 - D_1}{D_{\text{eff}}} \left[E_D/RT^2 - 2 \frac{\partial \ln f(T)}{\partial T} \right]$$

where $Q = \frac{C_2^h}{C_2^c}$

D_2, D_1 = diffusivity of solute and solvent respectively

D_{eff} = effective diffusivity

D_2 for dilute solution without convection

E_D = apparent activation energy $\frac{\partial \ln D}{\partial (1/RT)}$

$f(T)$ = energy function at the site of diffusing particle

This equation may be written as

$$d \ln C_2 = - \frac{D_2 - D_1}{D_2} \cdot \frac{E^*}{R} \cdot d \left(\frac{1}{T} \right)$$

$$\text{where } E^* = E_D - 2RT^2 \frac{\partial \ln f(T)}{\partial T}$$

E^* is, according to this treatment, the heat of transport associated with the diffusing species 2. Table II gives the values of E^* calculated for Au, Sb and S at 1027°C. The calculation is based on the experimental data presented in the paper.

Table II

Element	$\frac{D_2 - D_1}{D_2}$	$E^* \frac{(D_2 - D_1)}{D_2}$ cal/g-atm)	E^* (cal/g-atm)
Au	- 0.117	+ 3,100	- 27,500
Sb	+ 0.33	- 8,300	- 24,900
S	+ 0.58	- 76,800	- 129,000

The results for E^* are in agreement with Lodding's calculations based on isotopic redistribution in alkali metals. These calculations yielded large negative values for E^* alkali metals. The equation, however, is based on rather specific notions about the nature of the diffusion process and some of the basic assumptions could be questioned.

ADDENDUM

The term $(Q_2^* - Q_1^*) = \Delta Q^*$ may be considered to consist of the following three contributions:

ΔQ_a^* - contribution due to the interaction of the solute ion with the static temperature gradient (this term is related to the anisotropic jump frequency of an atom from "planes" of different temperature.

ΔQ_b^* - contribution from thermoelectric field. This term is very small for a metal.

ΔQ_c^* - contribution from interaction with the heat carriers in the material.

The term ΔQ_a^* may be approximately calculated by employment of a Wirtz type model and for purpose of illustration has been calculated both within the framework of the hole theory and our fluctuation model.

The term ΔQ_c^* has been evaluated by Gerl at Saclay and can be very important for solute ions which have a valence different from the solute. In effect if the scattering cross-section of solute ions is different for cold electrons as compared with hot electrons, net momentum will be exchanged and the solute will be biased toward either the hot or cold end. Gerl has obtained the following expression

$$\Delta Q_c^* = K \left(1 + 2 \frac{dA/A}{dE/E} \right)$$

where K is a constant for a particular solvent metal, A is the scattering cross section and E is electron energy. One would expect that the scattering cross section would decrease as E increases and if $(dA/A) / (dE/E)$ is sufficiently large ΔQ_c^* will be negative in sign and the solute will be driven to the hot end of the capillary. If the term is small ΔQ_c^* will be positive and solute will segregate to the cold end. Estimates of ΔQ_c^* for Au and Sb in Ag are available and results are shown in Table III.

Table III

Solute	ΔQ_a^* (cal/g-atm)		ΔQ_c^* (calc) (cal/mole)	ΔQ^* (calc) (cal/mole)	ΔQ^* (expt) (cal/mole)
	hole theory	fluct. theory			
-			-	-	-
Au	- 1000	- 400	- 200	$\sim$ - 1000	3100
Sb	+ 2000	+ 3000	- 11,000	$\sim$ - 8000	- 8300
S	- 4000	+ 6000	-	-	- 76,340

In Table III, the ΔQ^* (calc) column represents the sum of ΔQ_a^* calculated on the basis of fluctuation theory and ΔQ_c^* . The experimental result for antimony is in agreement with theory and it appears that the principal contribution to ΔQ^* comes from the interaction of the solute with the electronic heat carriers. No estimate of the contribution of ΔQ_c^* to ΔQ^* for sulfur in silver can be made at present. For gold the contribution of ΔQ_c^* is very small and appears to be the wrong sign.

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The point for lithium refers to the isotope redistribution data from reference 1.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12