Thermotransport of Solutes in Liquid Silver *, **

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Thermotransport studies have been made for liquid silver which contained trace amounts of gold, antimony and sulfur. Capillaries containing silver and homogeneously distributed solute were subjected to a temperature gradient and solute redistribution at the stationary state was determined by sectioning and radiotracer technique. The net heat of transport was obtained from the slope of a plot of the logarithm of solute concentrations versus reciprocal of absolute temperature. The segregation was rather small for Au but pronounced for Sb and S. Values of Q^* for Au, Sb and S are 1688 cal/mole, −6768 cal/mole and −29,000 cal/mole respectively. The experimental results are discussed in terms of the various factors which contribute to the heat of transport.

1. Introduction

Investigation of thermotransport (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 diffusion 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.

The silver base system was chosen because a thermotransport study of this system has not been made so far and the diffusion coefficients of several solutes in liquid silver have been determined in this laboratory. 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.

The relation between segregation coefficient, temperature gradient and heats of transport of the diffusing species has been derived by Tichacek et al.[1] using the formalism of irreversible thermodynamics. They obtained the following expression for the steady state condition in a temperature gradient:

$$\left(\frac{Q_1^*}{V_1}-\frac{Q_2^*}{V_2}\right)\frac{\operatorname{grad} T}{T}=\left[\frac{1}{x_1 V_1}+\frac{1}{x_2 V_2}\right] x_2 \frac{\partial \mu_2}{\partial x_2} \operatorname{grad} x_2 \tag{1}$$

where

V_1, 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 2,
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_2^* is of special interest because it will depend strongly on the mechanism of atom transport and any theory on diffusion in liquids must explain its magnitude and sign satisfactorily.

In the case of a very dilute binary alloy, Eq. (1) can be simplified,

$$\frac{1}{R}\left(Q_2^* - Q_1^* \frac{\overline{V}_2}{\overline{V}_1}\right) \mathrm{d}\frac{1}{T} = \mathrm{d}(\ln x_2) = \mathrm{d}(\ln C_2) \tag{2}$$

where subscript 2 refers to the solute and 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

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logarithm of the resulting concentration is related to the reciprocal temperature through the factor $1/R\,(Q_2^* - Q_1^* (\overline{V}_2/\overline{V}_1))$ which involves the heats of transport of solute and solvent. This factor can be assumed to be independent of temperature for small temperature intervals and Eq. (2) can be integrated to give

$$\ln \frac{x_2^{\mathrm{h}}}{x_2^{\mathrm{c}}} = \frac{Q^*}{R}\left(\frac{1}{T_{\mathrm{h}}} - \frac{1}{T_{\mathrm{c}}}\right) \tag{3}$$

where

$$Q^* = Q_2^* - Q_1^* (\overline{V}_2/\overline{V}_1) \,.$$

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

A plot of $\ln x_2$ vs. $1/T$ will yield a line with the slope Q^*/R.

Gold, antimony and sulfur were investigated as solutes. The diffusion coefficients of these elements in liquid silver have been determined [2–4]. Gold diffuses in silver almost as fast as silver itself. Being noble metals they have very little chemical affinity. Antimony is in the same row as silver but has a relative valence of four in liquid silver. Sulfur was chosen as an extreme case because it is nonmetallic and is a rapid diffuser in silver.

2. Experimental

The thermotransport apparatus consisted essentially of a dual furnace assembly housed in a vacuum chamber. The upper furnace was normally operated at a higher temperature than the lower furnace. The temperature distribution along the axis of the furnace assembly was known. The sample was a dilute alloy of silver and solute, encapsulated in a quartz capillary. The samples were normally 0.75 mm in diameter and 7 cm long. The alloy was prepared by melting silver with the appropriate radioisotope of the solute. The solutes were Au-195, Sb-125 and S-35.

The sample was placed along the axis of the furnace assembly, brought to the operating temperatures and held there until the stationary state was reached. The time needed for the stationary state to be reached was obtained by [5] the relation $t = l^2/2\,D$ where l was the length of the sample and D was the diffusion coefficient of solute in liquid silver. A time equal to twice this amount was normally employed. The sample was then quenched, sectioned and analysed. The γ-activity of Au-195, Sb-125 was counted by use of a scintillation counter and the β-activity of S-35 was counted by use of a liquid scintillation counter.

3. Results

The logarithm of concentration of solute is plotted versus reciprocal temperature for each solute. Figures 1, 2 and 3 are typical plots for Au, Sb and S respectively. The heat of transport is obtained from the slope of the line. Table 1 lists the values of the heat of transport so obtained.

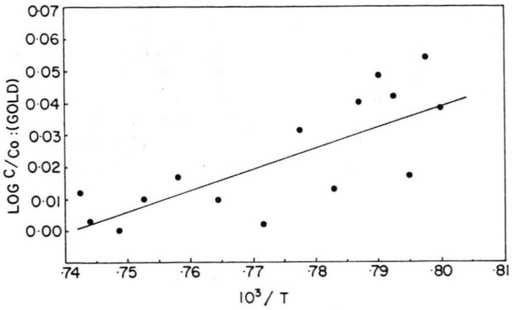

Fig. 1. Logarithm of relative concentration of gold as a function of reciprocal temperature.

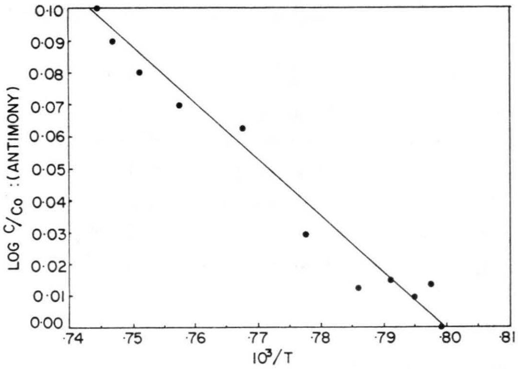

Fig. 2. Logarithm of relative concentration of antimony as a function of reciprocal temperature.

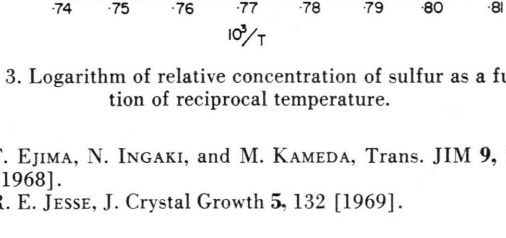

Fig. 3. Logarithm of relative concentration of sulfur as a function of reciprocal temperature.

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Table 1.

Solute	Gold	Antimony	Sulfur
$Q^* = Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1}$ cal/mole	$+1690$ ± 225	-6280 ± 1240	$-29{,}000$ $\pm 7{,}000$

Experiments were performed to ensure that the results were not spurious and due to factors such as gravity or segregation upon freezing.

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 larger amount in the case of sulfur. Antimony and sulfur segregate to the hot end while gold segregates to the cold end.

One in principle may calculate the heat of transport Q_2^* for various solute elements in silver by use of relation $Q^* = Q_2^* - Q_1^* (\bar{V}_2/\bar{V}_1)$. 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:

$$Q_{\mathrm{S}}^* - Q_{\mathrm{Ag}}^* \cong -29{,}000 \text{ cal/mol},$$
$$Q_{\mathrm{Sb}}^* - Q_{\mathrm{Ag}}^* \approx -\ 6{,}768\,,$$
$$Q_{\mathrm{Au}}^* - Q_{\mathrm{Ag}}^* \approx +\ 1{,}688\,.$$

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

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

Q_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).

Q_b^* – contribution from thermoelectric field. This term is very small for a metal.

Q_c^* – contribution from interaction with the heat carriers in the material.

The term Q_a^* may be calculated by employment of either a Wirtz type model or dense gas approximation[6].

The term Q_c^* has been evaluated by Gerl[7] and can be very important for solute ions which have a valence different from the solvent. 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[7]

$$Q_\mathrm{c}^* = K\left(1 + 2\,\frac{\mathrm{d}A/A}{\mathrm{d}E/E}\right)_{E_\mathrm{F}}$$

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 $[(\mathrm{d}A/A)/(\mathrm{d}E/E)]_{E_\mathrm{F}}$ is sufficiently large Q_c^* will be negative in sign and the solute will be driven to the hot end of the capillary. If the term is small Q_c^* will be positive and solute will segregate to the cold end. Estimates of Q_c^* for Au and Sb in Ag are available and results are shown in Table 2.

Table 2.

Solute	Q_a^* (cal/g-atm)		Q_c^* (calc) (cal/mole)	Q^* (calc) (cal/mole)	Q^* (expt) (cal/mole)
	dense gas theory	fluct. theory	—	—	—
Au	$+1770$	-400	-480	1290	1690
Sb	-1230	$+3000$	-6280	-7510	-6770
S	-2160	$+6000$	—	—	$-29{,}000$

In Table 2, the Q^* (calc) column represents the sum of Q_a^* calculated on the basis of dense gas theory and Q_c^*. The experimental results for gold and antimony are in good agreement with the calculation based on the dense gas model and the electronic term. The fluctuation model appears to yield a contribution to Q_a^* which is of the wrong sign and magnitude. Similar incorrect results are calculated from the hole model and free volume theories. These data provide some evidence that it is fruitful to consider liquid metals as dense gases for the sake of calculating atomic transport properties. This was suggested in a different context by Ascarelli and Paskin[8]. No estimate of the contribution of Q_c^* for sulfur in silver can be made at this time.

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