Thermotransport of Solutes in Liquid Silver*

B. N. Bhat and R. A. Swalin
Department of Chemical Engineering and Materials Science
University of Minnesota, Minneapolis, Minnesota 55455

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY J H Kahn lamh
DATE 2/22/71

Abstract

A thermotransport study of liquid silver which contained trace amounts of gold, antimony and sulfur has been made. An alloy sample, encapsulated in narrow quartz capillary, was held in a temperature gradient till the stationary state was attained. The sample was analysed for the solute concentration (C_2) along its length. Gold was observed to migrate to the cold end while antimony and sulfur migrated to the hot end. The net heat of transport, Q^* , was calculated from the expression

$$d \ln C_2 = \frac{Q^*}{R} d \left(\frac{1}{T} \right)$$

The results so obtained are

$$Q_{Au}^* = + 1,690 \pm 225 \text{ cal/gm-atom}$$

$$Q_{Sb}^* = - 6,770 \pm 1,240 \text{ "}$$

$$Q_S^* = - 29,000 \pm 7,000 \text{ "}$$

MASTER

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

The results are discussed by considering Q^* to consist of two parts, 1) extrinsic part, Q_e^* , which arises from the interaction of electrons with solute ion, and 2) intrinsic part, Q_i^* , arising from the interaction of diffusing ion with its neighboring ions. If Q_e^* is calculated by use of Gerl's method which calculates the energy transfer from electron to solute and Q_i^* is calculated by use of Chapman's expression, good agreement is obtained between the experimental and calculated values of heats of transport.

* This research was sponsored by the U. S. Atomic Energy Commission.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Thermotransport of Solutes in Liquid Silver

B. N. Bhat and R. A. Swalin

I. Introduction

If a homogeneous single phase alloy is held in a temperature gradient, matter fluxes are usually generated and a concentration gradient will be created by the temperature gradient. This phenomenon is called thermotransport. de Groot⁽¹⁾ investigated this phenomenon on the basis of the theory of thermodynamics of irreversible processes. This theory characterises thermotransport by a quantity called the heat of transport (Q^*) which, for component i , is defined as

$$Q_i^* = \left(\frac{J_h'}{J_i} \right) \quad J_j = 0, \nabla T = 0 \quad (1)$$

i.e., Q_i^* is the flux of heat J_h' transported per unit flux J_i of species i . J_h' is the excess heat relative to the average partial molar enthalpy of species i which is carried in the absence of a temperature gradient. The value of the heat of transport is influenced by the details of the dynamics of the diffusion process. Some of these details are not evident in ordinary isothermal diffusion experiments. As a consequence, the results of thermotransport experiments have potential theoretical interest.

The study of thermotransport in liquid metals is in its infancy. There is a great need for a better understanding of diffusion process in liquid metals where as yet a generally accepted mechanism of diffusion does not exist. (2, 3) Thermotransport studies in liquid alloy systems may help to provide better understanding of the diffusion

process. In this respect, dilute binary alloys offer distinct advantages over concentrated alloy systems which are the only ones which have been studied so far. Hence it seemed appropriate to investigate thermotransport in a dilute binary alloy system. In view of the paucity of data, this investigation was intended to be exploratory in nature. Silver base alloy system was chosen because a thermotransport study of this system has not been made so far and diffusion coefficients of several solutes in liquid silver have been determined in our laboratory. The solutes chosen were gold, antimony and sulfur. The diffusion coefficients of these solutes in liquid silver have been determined. (4 - 6)

Radioisotopes of these elements are available and hence their concentrations can be determined accurately by radiotracer techniques, even when present in concentrations of a few parts per million. Gold diffuses in silver almost as fast as silver itself. Being noble metals, they both have little chemical affinity. Thus gold would be expected to behave similar to silver in experiments. Antimony is in the same row as silver in the periodic table, but its diffusion coefficient in silver is 40% larger than the self diffusion coefficient of silver. Antimony has a relative valence of +4 in silver, while gold is homovalent in silver. Sulfur was chosen as an extreme case since it is non-metallic and diffuses rapidly in silver.

For a dilute binary system subjected to a temperature gradient, the heat of transport is related to the concentration gradient at the stationary state. (7)

$$d \ln C_2 = \frac{Q^*}{R} d \left(\frac{1}{T} \right) \quad (2)$$

where

C_2 = concentration of solute

$$Q^* = Q_2^* - Q_1^* \frac{\bar{V}_2}{\bar{V}_1}$$

$\bar{V}_1, \bar{V}_2$ = partial molar volumes of solvent and solute respectively

Q_1^*, Q_2^* = heats of transport of solvent and solute respectively

Thus from experimental data one obtains only the difference in the heats of transport of solute and solvent.

II. Experimental

In the technique employed here, a thermotransport experiment consisted essentially in holding a column of liquid alloy of silver and solute in a known temperature gradient for a sufficiently long time for the stationary state to be attained. A brief description of the experimental part is given here.

A. Thermotransport Apparatus

The apparatus designed for the thermotransport experiments is shown in Fig. 1. It consists of two furnaces placed one above the other and controlled separately. The controller employs platinum-1% rhodium and platinum-13% rhodium thermocouples. These thermocouples are housed in protecting alumina tubes which are closed on one end and placed next to the inside wall of the alumina core on which the heating element is wound. The end temperatures of the sample are measured by use of two Pt-1%Rh and Pt-13%Rh thermocouples, placed adjacent to the sample at the hot end and the cold end respectively.

B. Experimental Procedure

1. Preparation of sample

The thermotransport experiments were conducted with silver which contained trace amounts of solute. Silver was obtained from Johnson and Mathey Chemicals Ltd. and was 99.999% pure. The solute elements were radioactive gold-195, antimony-125 (both gamma emitters) and sulfur-35 (a beta emitter). The alloys were prepared by melting together the solute and requisite amounts of silver. The sample consisted of this alloy encapsulated in a narrow, precision bore, quartz capillary with 0.75 mm i.d.

Prior to being filled, the capillary was closed on one end and had a long cup attached to the other end. The inside of the capillary was cleaned with several rinses of acetone and methyl alcohol by means of a needle and a syringe and was then dried in an oven. A clean, weighed piece of alloy was placed in the cup. The amount of alloy was chosen so as to fill the capillary to the desired length which was normally between 2-1/4 and 2-3/4 inches. The sample was placed in the filling apparatus which was evacuated and lowered into a tubular furnace. After the alloy was molten in the cup, argon gas was admitted to the system, thus forcing the metal into the capillary. The alloy was allowed to solidify directionally from the bottom upwards. This was accomplished by simply lowering the filled capillary to the cooler parts of the tubular furnace. This procedure prevented any break in the column of the alloy. After solidification, the cup-end of the capillary was attached to a vacuum system. The capillary was sealed under a vacuum of approximately 10^{-4} Torr. Enough room was left in the sealed capillary to accommodate the expansion during melting.

2. Diffusion Annealing

The sealed sample was lowered into the central hole of the dual furnace assembly, until it rested at the bottom. The hole was then closed with a lava plug. A stainless steel cylinder was fitted to the brass vacuum fitting and the furnace chamber was evacuated and power to the furnaces was turned on. The furnaces were controlled in such a way that the metal in the capillary started to melt at the top first and the liquid front moved downwards to the bottom end. Most of the experiments were conducted with 100°C difference between hot and cold ends and some experiments were conducted with differences of 50°C, 75° and 150°C between hot and cold ends. The cold end was normally at 975°C. The temperature difference between hot and cold ends was maintained within $\pm 2^\circ\text{C}$.

The vacuum in the brass chamber was approximately 25 microns of mercury during the anneal. The approximate time required for achievement of the stationary state (t) is given by⁽⁸⁾

$$t = \frac{\ell^2}{2D} \quad (3)$$

where ℓ = length of the sample

D = diffusion coefficient of solute in silver

A time equal to twice this amount was normally employed in order to ensure that the stationary state was reached. At the end of this period, the sample was allowed to solidify directionally upwards starting from the 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 was maintained at all times while freezing. The freezing process took 3-4 minutes.

C. Radiotracer Analysis

The metal was separated from the quartz capsule and was thoroughly cleaned with a jet of acetone and methyl alcohol and cut into several sections of approximately equal length. Each section was analyzed for the solute concentration by use of a suitable radiotracer analysis technique. Au-195 and Sb-125 were analysed by use of a scintillation counter which used a 2" geometry sodium iodide crystal. The beta activity of S-35 was counted in a liquid scintillation counter.

D. Some Special Considerations

A few experiments were performed to ensure that any segregation obtained in thermotransport experiments was indeed due to temperature gradient and not due to other factors such as convection, solidification and sedimentation. These special experiments are described below.

The effect of convection is to mix the components and to decrease the amount of segregation. This effect is a strong function of the diameter of the capillary. Thermotransport experiments were conducted with 0.75 mm and 1.00 mm diameter capillaries. These experiments yielded essentially the same results. This suggested that the observed segregation was not affected by convection and is in accordance with calculations of Verhoeven. (9)

The process of solidification can in principle influence the segregation process. In order to see if this was important, experiments were run for very short annealing time. This was done by introducing the sample into the thermotransport apparatus which was already at the operating temperature. Sufficient time was allowed for the temperature to reach the desired temperature. The sample was then removed from the apparatus, sectioned and analyzed. The concentration profile so obtained was very similar to that obtained for the sample that had just been filled. This was true of all the solutes which were studied. In the case of antimony and sulfur, the solute concentration decreased slightly along the length of the capillary as one proceeded from the bottom to the top. However, this effect was opposite in sign to the segregation which occurred during a thermotransport experiment. These experiments showed that segregation due to solidification was not significant in the present experiments, in accordance with the calculations of Wagner. (10)

Another factor that can influence segregation is sedimentation. A solute dissolved in a heavier solvent experiences a buoyancy force which tends to concentrate the solute at the top of a vertical capillary. Thus some segregation can occur in an initially homogeneous liquid alloy placed in a gravitational field. In order to see if sedimentation was important in the present investigation, experiments were performed with a negative temperature gradient such that the hot end was at the bottom and the cold end was at the top.

The behavior of the solutes was basically the same as in the positive temperature gradient. Hence it was concluded that sedimentation did not materially affect the experimental results.

III. Results

The concentration of solute in each section is proportional to its specific activity. However, it is not the actual concentration of solute, but the relative concentration that is of interest. The relative concentration (c/c_o) of solute in each section was obtained by dividing its specific activity (c) by the lowest specific activity (c_o) in the sample.

Since the cross-section of the sample was uniform, the length of each section was proportional to its weight. Since the total length as well as the total weight of the sample was known, the length of each section could be accurately determined. The position of each section was then obtained by simply adding the length of the sections, starting from the bottom most section. The length of the sample was corrected for the expansion of metal which occurred on melting.

Since the temperature along the length of the sample was known, the logarithm of relative concentration of each sample can be plotted as a function of the reciprocal temperature. Fig. 2 is a typical plot for gold. Figs. 3 and 4 are similar plots for antimony and sulfur respectively. It is observed that gold segregates to the colder regions while antimony and sulfur segregate to the hotter regions. The magnitude of segregation is rather small for gold but large for antimony and much larger for sulfur. The heat of transport can be obtained from the equation

$$\frac{Q^*}{R} d\left(\frac{1}{T}\right) = d \ln c_2 = d \ln c/c_o \quad (4)$$

$$\text{or} \quad Q^* = R \frac{d \ln (c/c_o)}{d \left(\frac{1}{T} \right)} \quad (5)$$

Since no deviation from linearity can be delineated the plots of $\log (c/c_o)$ vs $\frac{1}{T}$ are fitted with straight lines by use of least mean square method. (11) The slope of the straight line so obtained yields the value of the heat of transport, Q^* .

In Table I are listed the values of Q^* for gold, antimony and sulfur, along with the temperature difference ΔT employed between the hot and cold ends. The values of the heats of transport obtained with different ΔT are the same, within the limits of experimental error. Hence it appears that the heats of transport of the solutes are not strongly dependent on temperature at least in the temperature range employed in the present experiments.

The error in the value of Q^* can be obtained by use of the method of least mean squares (11). The standard error so obtained is listed in the Table I for each sample. The arithmetic mean and the standard deviation of the results as a whole are computed for the solutes. The values are

$$\begin{aligned} \text{for gold, } Q^* &= + 1,690 \pm 225 \text{ cal/gm-atom} \\ \text{for antimony, } Q^* &= - 6,770 \pm 1,240 \text{ cal/gm-atom} \\ \text{for sulfur, } Q^* &= - 29,000 \pm 7,000 \text{ cal/gm-atom.} \end{aligned}$$

IV Discussion

It was pointed out earlier that thermotransport experiments, can, in principle, yield information about the dynamics of the diffusion process. An application of the formalism of irreversible thermodynamics showed the relation between the experimentally observed thermal migration and the heat of transport. The heat of transport, however,

is a kinetic quantity and will depend on the precise nature of the mass transport process which is not made evident by the thermodynamic-phenomenological theory. Hence a kinetic theory of mass transport in liquid metals should be able to explain the heat of transport from an atomistic point of view. Several theoretical models of diffusion have been developed primarily to explain the results of isothermal diffusion experiments and have had varying degree of success. (2, 3) There are other theoretical models developed to describe the force acting on the diffusing species in a temperature gradient. (12) These models are presented and discussed in light of the results obtained in the present investigation. A different theoretical approach to thermo-transport in liquid metals is suggested.

Actually the heat of transport may be considered to consist of two different contributions,

$$Q^* = Q_e^* + Q_i^* \quad (9)$$

where Q_e^* is the extrinsic contribution to the heat of transport. This contribution can arise from a) electrostatic fields created in the metal due to the presence of temperature gradient and b) interaction of diffusing ion with the charge carriers which are electrons and/or holes. Q_i^* represents the intrinsic heat of transport which arises from the asymmetry in the spatial distribution of energy of diffusion. This can also be termed the "ionic contribution" since it is the ions which interact and thus lead to diffusive motion. Sometimes this contribution is also called the "phonon contribution" when the diffusive process is considered to occur through interaction of phonons.

Table I

Solute Element	Temperature Difference (ΔT) $^{\circ}\text{C}$	Heat of Transport Q^* , cal/gm-atom	Standard Error (cal/gm-atom)
Gold	150	1,696	$\pm$ 245
	150	1,931	315
	100	1,791	527
	100	1,254	597
	100	1,766	409
Antimony	100	-7,452	$\pm$ 531
	100	-8,885	1,080
	100	-5,835	589
	100	-5,579	497
	150	-6,091	694
Sulfur	100	-22,410	$\pm$ 6,977
	50	-36,042	4,744

A. Extrinsic heat of transport

The contribution to Q_e^* due to electrostatic fields appears to be small for metals in general⁽¹²⁾ and is neglected here. The contribution of electrons to the heat of transport in metals can be calculated by use of a method described by Gerl.^(13,14) His procedure is used in this paper, but with a slight modification. Gerl assumes a vacancy mechanism for diffusion which probably is not applicable to liquids. It turns out, however, that the presence of a vacancy has little effect on the force acting on the solute atom subjected to a temperature gradient. Hence, the extrinsic contribution to the heat of transport can be written as

$$Q_e^* = \frac{K_e T}{2} \left(\frac{m^*}{m} \right)^{\frac{1}{2}} (E_F)^{-\frac{1}{2}} A_z(E_F) \left[1 + 2 \frac{dA/A}{dE/E} \right]_{E_F} E_F \quad (10)$$

where K_e = electronic contribution to thermal conductivity

m, m^* = rest mass and effective mass of electron

z = effective charge on the diffusing ion

A_z = resistivity scattering cross-section of solute atom for electrons

E = energy of electrons

E_F = Fermi level

The sign of Q_e^* is determined by the term in brackets in expression (10). If this term is positive, that means that the effective scattering cross section of hot carriers is more than that of cold carriers in which case the solute tends to segregate to the colder regions. If the effective scattering cross section of hot carriers is sufficiently

smaller than that of cold carriers, Q_e^* is negative and the solute tends to migrate to the hotter regions.

The method of calculating Q_e^* is described in the appendix. It is calculated that, for gold in silver,

$$(Q_e^*)_{Au} = -480 \text{ cal/gm-atom} \quad (11)$$

Such a calculation requires information about the resistivity and thermoelectric power of silver as a function of solute concentration. This information is available for liquid Ag-Au system⁽¹⁵⁾ but not for liquid Ag-Sb and Ag-S systems. However, in the case of Ag-Sb system, data are available for solid alloys. Assuming that the variation of resistivity and thermoelectric power of liquid silver with the concentration of antimony is the same as in solid, one obtains (see appendix),

$$(Q_e^*)_{Sb} = -6,280 \text{ cal/gm-atom} \quad (12)$$

No such calculation could be made for Ag-S system for want of required information. However, if sulfur has a large resistivity scattering cross section in liquid silver and a sufficiently negative coefficient of thermoelectric power it would result in a large, negative contribution to Q_e^* .

The fact that Q_e^* is negative for the solutes indicates that the effective scattering cross section for resistivity of hot carriers is less than that of cold carriers.

A comparison of the experimental heat of transport (Q^*) with calculated values

of the extrinsic heat of transport (Q_e^*) for solutes shows that the extrinsic contribution accounts for most of the observed Q^* in the case of antimony, but not so in the case of gold. This may be accounted for by the difference in the valence of these two solutes. Antimony has a relative valence of +4 in silver and hence may be expected to have a large scattering cross section for electrons. Gold, on the other hand is homovalent in silver and thus contributes little extrinsically to the heat of transport. Moreover, this contribution is of opposite sign to the observed value. It appears, therefore, that the difference for gold should be accounted for by the intrinsic heat of transport.

B. Intrinsic Heat of Transport

The values for the intrinsic heat of transport (Q_i^*) can be obtained from the models of diffusion. If, for example, diffusion occurs by a jump mechanism, the Wirtz-Brinkman model⁽¹⁶⁻¹⁷⁾ predicts

$$Q_i^* = Q_o - Q_f \quad (13)$$

where Q_o is that part of activation energy for diffusion (Q) received in the original position, Q_f is that part of Q received in the final position of the diffusing atom. However, in liquids, one observes only the difference in the heats of transport of solute and solvent, i. e.

$$Q_i^* = Q_{2i}^* - Q_{1i}^* \frac{\bar{V}_2}{\bar{V}_1} \quad (14)$$

$$= (Q_{2o} - Q_{2f}) - (Q_{1o} - Q_{1f}) \frac{\bar{V}_2}{\bar{V}_1} \quad (15)$$

If the hole theory is applicable to diffusion in liquid metals, $Q_o \approx 0$, $Q_f \approx Q$, the activation energy. This is so because according to the hole theory the energy of hole formation accounts for most of the activation energy in liquids. Further assuming that $\bar{V}_2 \approx \bar{V}_1$, one obtains

$$Q_i^* = - Q_2 + Q_1 \quad (16)$$

Substitution of experimental activation energies into equation 16 yield values of the wrong sign.

The Cohen - Turnbull model⁽¹⁸⁾ assumes that diffusion would occur by redistribution of free volume which is already present in the liquid. If a critical fluctuation occurs, an atom moves with the gas velocity (proportional to $T^{1/2}$) into the void. This assumption would yield values for $Q_2^* = Q_1^* = 0$ and thus is not consistent with observations for gold. Calculations employing the fluctuation model⁽¹⁹⁾ or cluster model⁽²⁰⁾⁽²¹⁾ are not straightforward and will be the subject of further work. In many respects the above models are more solid-like than gas-like in character. It is interesting therefore to examine predictions of Q^* that result from treating liquid metals as a dense gas.

A considerable amount of theoretical and experimental work has been done in the area of thermotransport in dilute gas mixtures (Chapman and Cowling⁽²²⁾, Hirschfelder, Curtiss and Bird⁽²³⁾). The ions in a liquid metal may be considered to form a dense gas. Theoretical study of thermotransport in dense gas mixtures has been rather limited and no experimental data seem to exist. Of the various methods used to treat dense fluids, Enskog's method employs the gas-like formalism and has been used to describe thermotransport in dense binary gas mixtures.⁽²²⁾

In the kinetic theory of dilute gases it is assumed that there are only two body collisions and that the molecular diameter is small compared with the average distance between the molecules. Both these assumptions are valid in dilute gases but in dense gases, however, these assumptions must be reconsidered. Enskog was the first to make an advance in this direction by developing a kinetic theory of dense gases made up of rigid spherical molecules. For this special model there are essentially no three body or higher order collisions. By considering only two body collisions and by taking into account the finite size of the molecules, he was able to graft a theory of dense gases onto the dilute gas theory developed earlier. He showed that the frequency of collisions in a gas made up of rigid spheres differs by a factor χ from that in a gas made up of point particles. This factor χ is intimately related to the equation of state. (23)

The coefficient of self-diffusion in a dense gas is given by (22)

$$D_{(\text{dense gas})} = \frac{D_{(\text{dilute gas})}}{\chi} \quad (17)$$

Such an approach has been used by Ascarelli and Paskin⁽²⁴⁾ to calculate the self-diffusion coefficient of mercury, indium and tin. Their theory employs van der Waals concept of a dense fluid in which the attractive potential energy is thought of as a uniform negative potential. This is justified for liquid metals on the basis of pseudopotential theory according to which the attractive part of the interaction energy between electronically screened ions is comparable to that found in rare-gas liquids. (25)

Enskog's method yields rather complicated expressions for thermotransport in dilute and dense gas binary mixtures. However, simpler expressions have been derived by Clark Jones for dilute isotopic mixtures⁽²⁶⁾ and by Chapman⁽²²⁾ for dilute binary mixtures. For isotopic mixtures. Clark Jones obtains,

$$\frac{Q_i^*}{RT} = \frac{15(C-1)(1+A)}{A(11-4B+8A)} \left(\frac{m_2 - m_1}{m_2 + m_1} \right) = K \left(\frac{m_2 - m_1}{m_2 + m_1} \right) \quad (18)$$

where m_1 , m_2 = mass of components 1 and 2 respectively.

A, B, C = integrals evaluated from the law of force between the atoms.

This expression is correct to the first power of $\left(\frac{m_2 - m_1}{m_2 + m_1} \right)$ which is assumed to be small. The variation in Q^* is indicative of the nature of the attractive potential between the atoms; a weak attractive field increases Q^* while a strong attractive field produces a decrease in Q^* . Chapman⁽²²⁾ extended this to the case of binary mixtures by taking the size effect into account. He obtains the following expression,

$$\frac{Q_i^*}{RT} = \frac{5(C-1)}{11-4B+8A} \left[\frac{3(1+A)}{A} \cdot \frac{m_2 - m_1}{m_2 + m_1} + 2 \left(\frac{s_2^2}{s_{21}^2} - 1 \right) x_2 - 2 \left(\frac{s_1^2}{s_{12}^2} - 1 \right) x_1 \right] \quad (19)$$

where s_1, s_2 , are equivalent molecular diameters (equal to molecular diameters for a rigid sphere model) and x_1 and x_2 are the mole fractions of the components 1 and 2 respectively. The term s_{12} is equal to $(s_1 + s_2)/2$. For a very dilute mixture ($x_2 \ll x_1 \approx 1$), the expression assumes the form

$$\frac{Q_i^*}{RT} = \frac{5(C-1)}{11-4B+8A} \left[\frac{3(1+A)}{A} \left(\frac{m_2 - m_1}{m_2 + m_1} \right) - 2 \left(\frac{s_1^2}{s_{12}^2} - 1 \right) \right] \quad (20)$$

The expression is applicable when $\frac{m_1}{m_2}$, $\frac{s_1}{s_{12}}$ and $\frac{s_2}{s_{12}}$ differ only slightly from unity. When the differences in molecular masses and diameters are large, the expression will give only an approximate estimate of the heat of transport. The first term in equation (20) will underestimate the contribution to Q^* when m_1 and m_2 differ considerably. An average value of the factor $\frac{3(1+A)}{A}$ is estimated to be 10. (22) Hence it is normally the first term involving the mass difference that determines the sign of Q_i^* .

The magnitude of Q_i^* will also depend on the value of the factor K which in turn depends on the value of the integrals A , B and C . These integrals can be evaluated if the interionic potential is known. However, the factor K can also be evaluated from the results of isotope thermotransport experiments. In fact, the latter method will be more accurate than evaluation of K from an arbitrary potential function.

Isotope thermotransport experiments in liquid lithium, potassium, rubidium, gallium and indium have been performed. (27-30) The value of the constant K for these metals are calculated using the expression (18) and tabulated in Table II. The values of K for different metals lie in a rather narrow range. As a first approximation we will consider K to be independent of the atomic mass and the valence. Hence, this value of K is used in the equation (20) and Q_i^* is calculated for different solutes in liquid silver.

In Table III are listed the values of Q_i^* so calculated for gold, antimony and sulfur in silver. Gold is assumed to be monovalent in silver and antimony pentavalent, and the corresponding ionic diameters are used for obtaining s_{12} in equation (20). Sulfur is assumed to accept two electrons (its hexavalent state is unstable under the experimental conditions).

In view of the several approximations made here, the calculated values of the heats of transport of gold and antimony in liquid silver are seen to be in very good agreement with the experimental values. In the case of sulfur, the calculated values of Q_i^* is negative, which is in general accordance with the experiments.

Table II

Reference	Metal	Atomic Weight	$K = \frac{15(C-1)(1+A)}{A(11-4B+8A)}$
(27)	Lithium (6-7)	7	2.03
(28)	Potassium (39-41)	39	1.92
(28)	Rubidium (85-87)	85.5	2.54
(28)	Gallium (69-71)	69.7	2.38
(30)	Indium (113-115)	114.8	2.11

$K(\text{Average}) = 2.2$

Table III

Solute Element	Intrinsic Heat of Transport Q_i^* (cal/gm-atom)	Extrinsic Heat of Transport Q_e^* (cal/gm-atom)	$Q^* = Q_i^* + Q_e^*$ Calculated (cal/gm-atom)	Q^* Experimental (cal/gm-atom)
Gold	+1770	- 480	+1290	+1690
Antimony	-1230	-6280	-7510	-6770
Sulfur	-2160	-----	-----	-29,000

References

1. S. R. de Groot, "L'effet Soret," Northland, Amsterdam (1945), "Thermodynamics of Irreversible Processes," Interscience (1952).
2. N. H. Nachtrieb, "The Properties of Liquid Metals," Taylor and Francis Ltd., London, p. 309 (1967).
3. Y. P. Gupta, Ibid, p. 333.
4. Y. P. Gupta, Acta Met. 14, 297 (1966).
5. R. A. Swalin and V. G. Leak, Acta Met. 13, 471 (1965).
6. T. Ejima, N. Ingaki and M. Kameda, Trans JIM 19, 172 (1968)
7. B. N. Bhat, Ph.D. Thesis, University of Minnesota, Minneapolis, Minnesota (1971).
8. R. E. Jesse, J. Crystal Growth 5, 132 (1969).
9. J. D. Verhoeven, Trans. AIME 242, 1937 (1968).
10. C. Wagner, Trans. AIME 200, 154 (1954).
11. P. G. Guest, "Numerical Methods of Curve Fitting," Cambridge (1961).
12. H. B. Huntington, J. Phys. Chem. Solids 22, 1641 (1968).
13. M. Gerl, ibid 28, 725 (1967).
14. M. Gerl, AEC Report-R 3096, Center of Nuclear Studies, Saclay, France (1966).
15. R. A. Howe and J. E. Enderby, Phil. Mag. 16, 467 (1967).
16. K. Wirtz, Z. Phys. 46, 221 (1943).
17. J. A. Brinkman, Phys. Rev. 93, 343 (1954).
18. M. Cohen and D. Turnbull, J. Chem. Phys. 31, 1164 (1959).
19. R. A. Swalin, Z. Naturf. 23a, 805 (1968).
20. A. Lodding, ibid, 21a, 1348 (1966).

21. A. Lodding, Advan. Chem. Ser., No. 89, 264 (1969).
22. S. Chapman and T. G. Cowling, "The Mathematical Theory of Nonuniform Gases," Cambridge (1952).
23. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley (1964).
24. P. Ascarelli and A. Paskin, Phys. Rev. 165, 222 (1968).
25. W. A. Harrison, "Pseudopotentials in the Theory of Metals," Benjamin (1966).
26. R. Clark Jones, Phys. Rev. 58, 111 (1940).
27. A. Ott and A. Lundeen, Z. Naturf. 19a (1964).
28. A. Lodding and A. Ott, *ibid*, 21a, 1344 (1966).
29. L. Lowenberg, A. Norden-Ott and A. Lodding, *ibid*, 23a, 1771 (1968).
30. A. Ott, L. Lowenberg and A. Lodding, *ibid*, 22a, 2112 (1967).
31. N. F. Mott and H. Jones, "The Theory of the Properties of Metals and Alloys", Dover (1958).
32. R. A. Howe and J. E. Enderby, Phil. Mag. 16, 467 (1967).

List of Figures

- Fig. 1 Thermotransport apparatus. Numbers on Figure refer to specific parts⁽⁷⁾. Sample is No. 23.
- Fig. 2 $\text{Log } c/c_0$ vs the reciprocal of absolute temperature for gold.
- Fig. 3 $\text{Log } c/c_0$ vs the reciprocal of absolute temperature for antimony.
- Fig. 4 $\text{Log } c/c_0$ vs the reciprocal of absolute temperature for sulfur

APPENDIX

A. Calculation of Q_e^* for Gold in Liquid Silver (14)

Gerl derived the following expression for the electronic force acting on a solute ion in solvent matrix,

$$F_z = -M A_z (E_F) (1 + 2E_F \propto) \quad (1)$$

The various quantities on the right hand side of equation (1) are calculated as follows,

$$(a) \quad M = \left(\frac{m^*}{2mE_F} \right)^{\frac{1}{2}} K_e \quad (2)$$

where m^* = effective mass of an electron

E_F = Fermi level

K_e = electronic part of thermal conductivity

Assuming $m^* = m_e$,

$$\begin{aligned} K_e &= 1/2 (K_e)_{\text{solid}} \text{ (from Mott and Jones (31))} \\ &= 1.8 \times 10^7 \text{ erg/cm/deg C} \end{aligned}$$

one obtains, $M = 0.13 \text{ erg/cm}^2$

(b) A_z , the scattering cross section for electrons is obtained from the relation,

$$A_z = \frac{\zeta_i}{0.211 E_F^{1/2}} A^2$$

where $\zeta_i = \frac{\partial \rho}{100 \partial c_i}$, resistivity-concentration coefficient. From the work of Howe and Enderby (32) one obtains

$$\zeta_i = 0.5 \mu\text{V/atom } \%$$

$$E_F = 5.5 \text{ ev for silver}$$

$$\text{Hence } A_z = 1.01 \text{ \AA}^2$$

(c) α_1 is obtained from the expression

$$\frac{dS}{100dc_i} = (\alpha_1 - \alpha_c) \frac{0.0243 \zeta_i}{\rho T} \quad (3)$$

where S = thermoelectric power of liquid silver-gold alloy

ρ = resistivity of silver

$$\alpha_c = \frac{S_T}{0.0243 T} - \frac{1}{2E_F}$$

where S_T = thermoelectric power of pure liquid silver.

For silver-gold system,

$$\frac{dS}{100dc_i} = -0.5 \frac{\mu\text{V}}{^\circ\text{C}} \quad (\text{Howe and Enderby }^{(32)})$$

$$\rho T = 12 \times 10^{-3} T \mu\Omega\text{-cm}$$

and α_1 is then found to be

$$\alpha_1 = -0.27 (\text{ev})^{-1}$$

Hence, the force F_z is calculated to be

$$\frac{F_z}{\nabla T} = +0.162 \times 10^{-4} \text{ ev/deg C} \quad (4)$$

Hence, the extrinsic contribution to the heat of transport is

$$\begin{aligned} (Q_e^*)_{\text{Au}} &= -F_z T \\ &= -0.021 \text{ ev at } 1027^\circ\text{C} \\ &= -480 \text{ cal/gm-atom} \end{aligned} \quad (5)$$