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Thermotransport of Hydrogen and Deuterium in Vanadium, Niobium and Tantalum

Alloys

by

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MASTER

Ph.D. Thesis submitted to Iowa State University

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Thermotransport of hydrogen and deuterium
in vanadium, niobium and tantalum alloys

by

Mark Francis Smith

An Abstract of

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1981

Thermotransport of hydrogen and deuterium
in vanadium, niobium and tantalum alloys¹

Mark Francis Smith

Under the supervision of D. T. Peterson
From the Department of Materials Science and Engineering
Iowa State University

Heats of transport have been determined for thermotransport of hydrogen and deuterium in pure vanadium, niobium and tantalum; in vanadium alloyed with either niobium, titanium or chromium; and in niobium-tantalum alloys. In all cases, thermotransport was toward colder regions and was significantly greater for deuterium than for hydrogen. A mass spectrometric technique was used to simultaneously measure heats of transport for hydrogen and deuterium in a single specimen containing both isotopes. This technique greatly increased the precision with which isotope effects in the heat of transport could be measured. The predominant effect of alloying was to dramatically increase thermotransport; however, thermotransport decreased as niobium was added to tantalum. The heat of transport did not vary linearly with alloy composition, but rather, the changes were always greater at low concentrations of the substitutional element. Close correlations between the heat of transport and the activation energy for diffusion of hydrogen indicate that the temperature dependence of atomic jump frequencies is the predominant factor controlling thermotransport with

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some gradient-related bias in the direction of atomic jumps possibly caused by an electronic mechanism. In tantalum the biasing mechanism could account for up to half of the observed thermotransport; however, in most of the systems studied the biasing is quite small. Heats of transport for hydrogen in pure vanadium, niobium and tantalum are 1.4, 11.9 and 28.5 kJ/mol, respectively, and corresponding values for deuterium are 4.8, 18.0 and 34.8 kJ/mol.

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TABLE OF CONTENTS

	Page
GENERAL INTRODUCTION	1
Explanation of Thesis Format	4
SECTION I. THERMOTRANSPORT OF HYDROGEN AND DEUTERIUM IN VANADIUM, NIOBIUM AND TANTALUM	5
INTRODUCTION	6
EXPERIMENTAL PROCEDURE	9
RESULTS	15
Heats of Transport	15
Isotope Effects	17
Temperature Dependences	19
DISCUSSION	21
SUMMARY	26
REFERENCES	27
SECTION II. THERMOTRANSPORT OF HYDROGEN AND DEUTERIUM IN VANADIUM-NIOBIUM, VANADIUM-TITANIUM AND VANADIUM-CHROMIUM ALLOYS	29
INTRODUCTION	30
EXPERIMENTAL PROCEDURE	32
RESULTS	38
DISCUSSION	44
SUMMARY	49
REFERENCES	50

	Page
SECTION III. THERMOTRANSPORT OF HYDROGEN AND DEUTERIUM IN NIOBIUM-TANTALUM ALLOYS	52
INTRODUCTION	53
EXPERIMENTAL PROCEDURE	55
RESULTS	60
DISCUSSION	63
REFERENCES	66
GENERAL SUMMARY	67
REFERENCES	70
ACKNOWLEDGMENTS	72

GENERAL INTRODUCTION

In 1856, Ludwig (1) made the intriguing discovery that a concentration gradient slowly developed when a temperature gradient was maintained in an aqueous sodium sulfate solution which had initially been homogeneous. Later in the 19th century, similar observations were reported for a number of other electrolyte solutions by Soret (2-4). The establishment of a concentration gradient due to an impressed temperature gradient subsequently came to be called the Soret effect or the Ludwig-Soret effect. Extensive measurements of Soret effects in liquids (5, 6) and in gases (7) have provided information about molecular mechanisms of migration and intermolecular forces. In contrast, significant numbers of Soret effect measurements in crystalline solids have been made only in the last twenty years, and the total number of studies in solids is still relatively small.

The first measurements of Soret effects in solids were reported by Wessels (8) in 1914 and primarily involved noncrystalline materials. However, Wessels did observe a Soret effect in a simple crystalline system consisting of a solid solution of bibenzyl and azobenzene. The first Soret effect in a metallic solid was reported in 1926 by Ballay (9), who had experimented with a lead-thallium alloy. Two years later, Ballay (10) also reported Soret effects in lead-thorium and platinum-rhodium alloys. Although extensive measurements in ionic solids (11-14) were made between 1929 and 1937, only one additional study of Soret effects in metals was published prior to the mid-1950s. In 1953 and 1954, the possibility that Soret effects might prove useful in the investigation of atomistic mechanisms of diffusion was debated in the literature (15-20), and interest

in Soret effects in metals began to increase. In recent years, it has been recognized that the Soret effect, now commonly referred to as thermomigration or thermotransport, may also be of technological importance.

Representative examples of problems which may be related to thermotransport occur in nuclear power reactors and in machine cutting tools. In nuclear reactors, there is evidence that thermotransport may concentrate hydrogen in zirconium cladding alloys and thus, contribute to hydrogen embrittlement (21). Thermotransport of carbon may also be responsible for phase changes in some tool steels and has been implicated as a probable cause of rapid wear of machine cutting tools (22). Due to a need for greater efficiency in modern technology, materials are subjected to progressively higher temperatures and greater temperature gradients for longer periods of time. Thus, the technological importance of thermotransport seems likely to increase in the future.

Despite many years of study, an atomistic explanation for thermotransport in metals has not been established. Proposed atomistic mechanisms for thermotransport may be classified according to whether they are intrinsic to any solid, even if it were a perfect insulator, or whether they are based upon coupling with the heat carriers. The latter may be subdivided according to whether the heat carriers of interest are the phonons or the electrons and holes. Atomistic models for an intrinsic mechanism are the oldest and most highly developed. These models are based solely upon the temperature dependence of the diffusive jump frequency. The frequencies of diffusive jumps should differ among a series of planes normal to a temperature gradient, and a net flux of solute would, therefore, occur until a steady state concentration gradient is established. An

atomistic model for intrinsic thermotransport was first proposed by Wirtz (23) in 1943 and has subsequently been discussed in more than twenty articles. The interested reader is referred to an excellent bibliography of thermotransport literature in a 1967 review article by Allnatt and Chadwick (24). More recent references may be found in review articles by Hehenkamp (25) and Wipf (26). The present consensus seems to be that intrinsic thermotransport probably does occur in metals; however, the relative importance of this mechanism as compared to possible phonon or electron mechanisms has not been established. Indeed, the relative importance of an intrinsic mechanism might vary among different metallic systems.

Phonon mechanisms for thermotransport in metals are based upon scattering interactions between phonons and the transported atoms. A phonon mechanism was first proposed by Fiks (27) in 1961, and major discussions of this mechanism were subsequently presented by Schottky (28) in 1965 and by Sorbello (29) in 1972. Because the details of phonon models are still poorly defined, the importance and even the existence of this mode of thermotransport in metals remains open to question.

Two types of electronic interactions have been suggested as possible mechanisms for thermotransport in metals. First, there may be an electrostatic interaction between an ionic charge associated with a solute atom and a thermoelectric field generated by the Thompson effect. Second, a scattering of electrons and holes with differing thermal kinetic energies at sites of solute atoms might bias the direction of diffusive jumps. These two electronic mechanisms were first proposed by Fiks (30) in 1964. A more detailed treatment for the case of a single conduction band was

presented by Gerl (31) in 1967, and in 1968 Huntington (32) extended Gerl's treatment to a multiple band case. The proposed electronic models are complex and involve several parameters which have never been measured. At present, the existence and importance of electronic thermotransport mechanisms have not been demonstrated.

A major problem in the development of thermotransport theory for solid metals has been a shortage of experimental data. The present investigation of thermotransport of hydrogen and deuterium in vanadium, niobium, and tantalum alloys was done to provide some of the additional data required for the future development and critical evaluation of atomistic thermotransport models. This study provides thermotransport data for several systems that have not been previously investigated. A new high-precision technique has also been used to examine possible isotope effects in thermotransport, and temperature dependence of a characteristic parameter called the heat of transport was studied. Finally, this study is the first systematic investigation of thermotransport in ternary alloy systems.

Explanation of Thesis Format

This thesis has been written in the alternate format as outlined in The Graduate College Thesis Manual. The main body of this thesis consists of three papers which are designated as Sections I, II, and III. These papers are the sole work of Dr. D. T. Peterson and myself and are to be submitted for publication in Metallurgical Transactions.

SECTION I. THERMOTRANSPORT OF HYDROGEN AND DEUTERIUM
IN VANADIUM, NIOBIUM AND TANTALUM

INTRODUCTION

A temperature gradient in an initially homogeneous multicomponent material may cause concentration gradients to develop. Such solute migration induced by a temperature gradient is called thermotransport or thermomigration. Although thermotransport phenomena are poorly understood at present, additional data may provide new insights into the fundamental behavior of solutes in metals. More practically, a redistribution of solute caused by thermotransport may be undesirable in some engineering application of metals. The transport behavior of hydrogen in the Group V B transition metals is of particular interest because hydrogen can severely degrade the mechanical properties of these bcc refractory metals (1, 2).

Existing atomistic models for thermotransport are quite rudimentary and cannot predict even qualitatively the direction or magnitude of thermotransport in any given metal-solute system. Efforts to identify and critically evaluate plausible mechanisms and driving forces for thermotransport have been hindered by a shortage of experimental data. Among the problems which require further investigation are questions concerning isotope effects in thermotransport and concerning temperature dependence of the heat of transport. Apparent isotope effects have been reported (3-5) for thermotransport of hydrogen and deuterium in niobium (columbium), iron, nickel, and zircalloy-2. However, an isotope effect was clearly established only in the case of nickel because in the other metals the observed differences were less than the total uncertainty in the measurements. The heat of transport, Q^* , is a parameter which arises from a phenomenological treatment of thermotransport via irreversible thermodynamics (6-9). The

quantity Q^* has the dimensions of energy, and considerable effort has been expended in attempts to produce an atomistic interpretation of this energy (4, 9-13). Whether or not Q^* has a temperature dependence would seem relevant to such interpretation, and a temperature dependence for Q^* has been reported for hydrogen in iron (4), nickel (4), and β -zirconium (14) as well as for oxygen in tantalum (15). The present study of thermotransport of hydrogen and deuterium in Group V B metals was undertaken to measure Q^* , to look at isotope effects, and to investigate the temperature dependence of Q^* . Determination of the isotopic concentrations and distributions was done by a combination of hot vacuum extraction and mass spectrometric analysis; this approach provides both greater accuracy and better precision than the experimental methods of previous investigations.

If one takes a phenomenological approach, solute migration during thermotransport may be viewed as atomic movement due to applied forces. For a one-dimensional geometry, the force components (11, 12) arise from the logarithmic solute concentration gradient,

$$F_C = - RT (d \ln C/dx), \quad (1)$$

and the logarithmic temperature gradient,

$$F_T = - Q^* (d \ln T/dx), \quad (2)$$

where R is the gas constant and x is a space coordinate. From the form of these two equations, it is evident that Q^* has dimensions of energy; further, the sign and magnitude of Q^* characterize the direction and scale of the thermotransport process. A steady state technique was employed in the present investigation. At steady state, the sum of the two force components, F_C and F_T , is zero so that Eqs. (1) and (2) can be combined and

solved to obtain the following expression for Q^* in terms of measurable changes in solute concentration and temperature,

$$Q^* = R (d \ln C / d(1/T)). \quad (3)$$

This derivation assumes that the mobility of the matrix atoms is negligible and that only the solute atoms move. This constraint was certainly satisfied for the times and temperatures of the present experiments since the pertinent diffusivities for hydrogen and deuterium in Group V B metals are the order of 10^{-8} to $10^{-10} \text{ m}^2/\text{sec}$ (16) while the self-diffusion coefficients for these metals are less than $10^{-39} \text{ m}^2/\text{sec}$ (17). The derivation also assumes the absence of other forces. This second constraint was also satisfied since there were no external electric, magnetic, or other extraneous forces imposed. Finally, the use of concentration rather than activity in Eq. (1) is strictly valid if, and only if, the activity coefficient is constant throughout the concentration range of measurement. For the systems of concern, Sieverts' law is obeyed in the concentration regimes of interest so that this constraint is also satisfied (18).

EXPERIMENTAL PROCEDURE

It is difficult to accurately measure both temperatures and solute concentrations in regions of a test specimen which contain substantial temperature and concentration gradients. This problem is further compounded by the need to correlate the temperature and concentration measurements at various locations in a test specimen in order to determine Q^* . These problems, encountered in previous studies of thermotransport by steady state techniques, have been largely eliminated in the present study through the use of an experimental arrangement shown schematically in Figure 1. The end portions of the test specimens were held at constant temperatures, and the steady state was achieved when concentrations in these isothermal regions were homogeneous and time invariant. With specimens $2.5 \times 1.0 \times 0.08$ cm having a 1.0 cm length clamped in the heat source and a 1.0 cm length clamped in the heat sink, relatively steep temperature and composition gradients could be established across the short (0.5 cm) region between the heat source and heat sink. If these gradients were not too severe, the differentials in the derivative of Eq. (3) could be approximated by finite differences,

$$Q^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln(C_1/C_2) \quad (4)$$

where the subscripts 1 and 2 denote the hot and cold isothermal regions, respectively.

At steady state, Q^* could be evaluated from the readily measurable temperature and composition differences between the segments of a specimen in the heat source and in the heat sink. Temperatures in the heat source

Figure 1. Experimental arrangement (a) with typical sample temperature profile (b) and steady state concentration profile (c)

and heat sink were measured with calibrated chromel-alumel thermocouples. The hydrogen concentrations in the isothermal regions of a specimen were determined by hot vacuum extraction (19). The precision of the determination of hydrogen concentration by the hot vacuum extraction procedure was 2 relative percent. The cutting of a specimen into samples for concentration analysis was completed within two minutes or less after termination of a thermotransport run so that there was no redistribution of solute prior to analysis. For those samples containing only hydrogen or deuterium, the hot vacuum extraction analyses were sufficient, and no mass spectrometric analysis was needed. However, for those samples containing both hydrogen and deuterium, the hot vacuum extraction analyses yielded the combined sum of both hydrogen and deuterium concentrations. For these samples, gas from the hot vacuum extraction was analyzed by mass spectrometry to determine the atom fractions of hydrogen and of deuterium. Atom fractions of hydrogen and of deuterium were determined with an accuracy of better than 2%, and the ratio of these atom fractions had a precision of $\sim 0.5\%$.

Sources for the vanadium, niobium, and tantalum were, respectively, U.S. Bureau of Mines, DuPont Company, and Fansteel, Inc. Specimens were cut and were then given appropriate recrystallization anneals in gettered vacuums at pressures less than or equal to 10^{-4} Pa. Impurity analyses of representative specimens in the annealed condition are shown in Table 1. Carbon concentrations were determined by vacuum fusion analyses. The levels of eighty-two other potential impurities were surveyed with a mass spectrograph, and only tungsten and tantalum appeared in significant amounts.

Table 1. Impurity concentrations in annealed samples

Metal	Carbon (at. %)	Nitrogen (at. %)	Oxygen (at. %)	Tungsten (at. %)	Tantalum (at. %)	Total other (at. %)
Vanadium	0.020	0.010	0.020	0.024	0.010	<0.012
Niobium	0.025	<0.001	0.008	0.013	0.170	<0.046
Tantalum	0.019	0.006	0.040	0.010	---	<0.005

Hydrogen and/or deuterium were introduced into the specimens by electrolytic (cathodic) charging to a level of $0.01 (H+D)/M$, where M represents the matrix metal. In this process, an electropolished specimen formed the cathode, a solution of 10 vol. % $H_2SO_4-H_2O$ or 10 vol. % $D_2SO_4-D_2O$ was the electrolyte, and the anode was platinum. After charging, the specimens were homogenized at room temperature for periods of $\sim 5\tau$ with the relaxation time, τ , evaluated (20) from the relationship

$$\tau = l^2 / \pi^2 D. \quad (5)$$

The specimen length was used for the characteristic distance, l , and values for the diffusivity, D , of hydrogen or deuterium were obtained from the compilation by Völkl and Alefeld (16). After homogenization, segments were cut from the ends of a specimen, and the concentration of hydrogen or deuterium was determined by hot vacuum extraction analysis. The specimens had initially been cut 3.0 cm long with the extra length providing material for analyses of initial hydrogen and deuterium concentrations. For those specimens containing hydrogen-deuterium mixtures, charging was a two-step process with hydrogen being introduced, homogenized, and analyzed to obtain

a level of 0.005 H/M, and an equal amount of deuterium was then introduced and homogenized with final analysis for combined H+D. During the early stages of the investigation, the efficacy of the homogenizing treatments was tested by analyzing some samples along their entire length. It was found that after periods of 5τ , the hydrogen concentrations were homogeneous within the precision of measurement.

Experiments were conducted in two temperature ranges. In one, the heat source was maintained at 60°C and heat sink at 10°C , and in the other, the heat source was maintained at 200°C and the heat sink at 150°C . In all cases, copper blocks served as sources and sinks with elevated temperatures being maintained by resistance furnaces and the 10°C heat sink temperature being maintained by water cooling. A temperature of 10°C was chosen as the lower limit of operation so as to remain well within the solid solubility regimes of the systems under study; at temperatures of 10°C or above, the equilibrium diagrams (21) indicate that the terminal solubilities extend well beyond any concentrations encountered during the present experiments. A temperature of 200°C was chosen as the upper limit of operation so as to avoid any possibility that hydrogen vapor pressures (18) would become sufficiently high to result in hydrogen loss due to outgassing. That no outgassing occurred during thermotransport runs was verified by analyzing several entire specimens after steady state had been reached. The results showed that the total hydrogen content in these samples after thermotransport was the same within experimental error as it was originally.

The effectiveness of the copper blocks in producing an isothermal region at each end of a specimen was tested by measuring the temperature profile along the length of a 0.6 cm thick specimen. This thicker specimen

was used so that a longitudinal hole 0.06 cm in diameter could be drilled into which a thermocouple was inserted to measure the temperature. Temperatures in both the hot and cold ends were uniform within $\pm 0.2^{\circ}\text{C}$ except for a 0.3 cm length where the specimen entered the source or sink. For each isothermal region, the specimen temperature and the temperature of the surrounding source or sink were the same within the 0.2°C resolution of measurement. If the end sections were at uniform temperature in a 0.6 cm thick specimen, temperatures in 0.08 cm thick specimens would certainly be more uniform because there is less heat flow from source to sink with the thinner specimens. Some temperature variation of the heat source or heat sink did occur during the prolonged time span of some thermotransport runs. However, for even the longest experimental run, no source or sink showed a temperature variation exceeding $\pm 1.5^{\circ}\text{C}$.

The degree of approach to steady state may be expressed (22) as

$$\theta = 1 - \exp(-t/\tau) \quad (6)$$

where $\theta=1$ represents the true steady state, t is the time of a run, and τ is the relaxation time (23) of Eq. (5). To evaluate τ , the 2.5 cm sample dimension was used for the characteristic length ℓ , and the value of D at the sink temperature was used. The relaxation times varied from 2.0 hrs for hydrogen in vanadium at 150°C to 11.4 days for deuterium in tantalum at 10°C . No thermotransport run was shorter than 5τ so, according to Eq. (6), no run should have failed to approach within at least 99% of steady state conditions. This prediction was verified by several replicate experiments which ran for times much longer than 5τ with no significant changes in the resulting values of Q^* .

RESULTS

Heats of Transport

In all experiments, hydrogen and deuterium concentrated in the cold end of the specimen. Thus, all heats of transport are positive numbers. Each Q^* value in Table 2 is the mean of a set of results from six or more replicate experiments, and the uncertainty is one standard deviation of the mean. These standard deviations agree closely with uncertainty estimates based upon the previously stated accuracies for temperature measurements, hot vacuum extraction analyses, and mass spectrometer analyses. Values of Q^* for both hydrogen and deuterium increase almost linearly with increasing atomic mass of the host metal. The physical significance of the differing Q^* values becomes apparent if one examines representative concentration ratios between the cold and hot ends of the specimens. Typical ratios of hydrogen concentrations in the 10°C regions, as compared to the 60°C regions in vanadium, niobium, and tantalum specimens, were found to be 1.1, 2.1, and 6.2, respectively, with corresponding values for deuterium of 1.4, 3.2, and 9.2. Thus, concentration differences ranging from 10% to more than 900% resulted from the same 50°C temperature difference in the three Group V B metals.

Two previous studies have examined thermotransport of hydrogen or deuterium in a Group V B metal. In vanadium, Heller and Wipf (24) have reported $Q_H^* = 1.6 \pm 0.3$ kJ/mol. In niobium, Wipf and Alefeld (3) found $Q_H^* = 12 \pm 2$ kJ/mol and $Q_D^* = 13 \pm 4$ kJ/mol. Experiments in these two studies were conducted at temperatures and solute concentrations similar to experimental conditions for the 35°C results in Table 2. Comparison of the earlier Q^*

Table 2. Heats of transport for hydrogen and deuterium in Group V B metals

Metal	Mean specimen temperature (°C)	Q_H^* (kJ/mol)	Q_D^* (kJ/mol)	$Q_D^* - Q_H^*$ by subtraction ^a (kJ/mol)	$Q_D^* - Q_H^*$ via Eq. (9) ^b (kJ/mol)
Vanadium	35	1.4 $\pm$ 0.3	4.8 $\pm$ 0.4	3.4 $\pm$ 0.5	3.8 $\pm$ 0.2
	175	1.8 $\pm$ 0.2	6.1 $\pm$ 0.2	4.3 $\pm$ 0.3	3.9 $\pm$ 0.2
Niobium	35	11.9 $\pm$ 0.3	18.0 $\pm$ 0.2	6.1 $\pm$ 0.4	6.2 $\pm$ 0.2
	175	9.4 $\pm$ 0.4	16.3 $\pm$ 0.2	6.9 $\pm$ 0.4	7.2 $\pm$ 0.3
Tantalum	35	28.5 $\pm$ 0.3	34.8 $\pm$ 0.4	6.2 $\pm$ 0.5	6.3 $\pm$ 0.3
	175	21.5 $\pm$ 0.6	29.5 $\pm$ 0.5	8.0 $\pm$ 0.8	7.3 $\pm$ 0.3

^aCalculated as the arithmetic difference between Q_D^* and Q_H^* results in the preceding two columns.

^bCalculated directly from temperature and isotope ratio data via Eq. (9).

values with respective values in Table 2 shows excellent agreement between hydrogen results and a small, though possibly significant, difference between the previous and present deuterium results. The agreement in the case of hydrogen is particularly noteworthy because the literature Q^* determinations were based upon a resistivity measurement technique which differs greatly from the present experiment method. The difference in the case of deuterium is of the order of the combined uncertainties in the Q_D^* determinations. Also, the experimental technique used by Wipf and Alefeld offers a possible explanation for the lower value of Q_D^* obtained by these investigators. The resistivity technique which they used did not distinguish between hydrogen and deuterium within a single specimen. Since $Q_H^* < Q_D^*$, their technique would yield a low value of Q_D^* if hydrogen were

present in the specimen. Wipf and Alefeld stated that hydrogen may have been present at levels up to 15% of the deuterium content in the specimen used for their Q_D^* determinations; however, the actual isotopic purity of that specimen apparently was not measured.

Isotope Effects

The heat of transport of hydrogen was found to be different from that of deuterium in each of the host metals. It is obvious that this difference can be evaluated by simple subtraction of Q_H^* values from respective Q_D^* values, and such differences are listed in Table 2. However, a second method for evaluating $Q_D^* - Q_H^*$ was found to yield differences with enhanced precision. With the second method, differences between Q_D^* and Q_H^* can be evaluated directly from temperatures and isotope ratios in those samples which contained both hydrogen and deuterium. The enhanced precision of this method results from the cancellation of errors in the hot vacuum extraction analyses and from cancellation of other systematic errors.

The validity of the second method rests upon the fact that the movement of hydrogen was independent of the movement of deuterium in specimens charged with both isotopes. The absence of interactions between solute particles is clearly indicated because Sieverts' law is obeyed within the concentration regimes of interest (18). Also, values for Q_H^* which were determined from specimens charged only with hydrogen agree within experimental uncertainty with values of Q_H^* which were determined from specimens charged with both hydrogen and deuterium. Similar agreement was observed for values of Q_D^* . Since the isotopes move independently, heats of

transport for hydrogen and deuterium may be evaluated from a single specimen as

$$Q_H^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln (C_{H,1}/C_{H,2}) \quad (7)$$

and

$$Q_D^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln (C_{D,1}/C_{D,2}). \quad (8)$$

In these equations, C_H and C_D represent the concentrations of hydrogen and deuterium while the subscripts 1 and 2 refer to the hot and cold regions of the specimen. The concentrations of hydrogen and deuterium may be expressed as $C_H = X_H C_{H+D}$ and $C_D = X_D C_{H+D}$, where X_H and X_D are the atom fractions, respectively, of hydrogen and deuterium in the gas analyzed with the mass spectrometer, and C_{H+D} is the combined concentration of hydrogen plus deuterium as determined by the hot vacuum extraction analyses. If $X_H C_{H+D}$ and $X_D C_{H+D}$ are substituted for C_H and C_D when Eq. (7) is subtracted from Eq. (8), the result is

$$Q_D^* - Q_H^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln (X_{D,1} X_{H,2} / X_{H,1} X_{D,2}) \quad (9)$$

where exact cancellation of C_{H+D} has occurred. Thus, the difference between the heats of transport for the two isotopes can be evaluated solely upon the basis of temperature measurements and mass spectrometric analyses. Values from Eq. (9) are also listed in Table 2, and it may be noted that this method of calculation results in an enhancement of precision by approximately a factor of two.

As noted in the introduction, an isotope effect in thermotransport has been previously established only for the case of hydrogen and deuterium in

nickel (4). While the movement of both hydrogen and deuterium in nickel leads to increased concentrations in hot rather than cold regions, the nickel results are qualitatively similar to the present results in the sense that the magnitude of Q_D^* is greater than the magnitude of Q_H^* . Therefore, in nickel and in the Group V B metals, composition gradients induced by a given temperature difference are greater for deuterium than for hydrogen.

Temperature Dependences

Heats of transport for both hydrogen and deuterium decreased as temperature increased in tantalum and niobium, with the decreases being greater for hydrogen than for deuterium. An inverse situation may exist for vanadium with apparent increases in Q_H^* and Q_D^* as the temperature increased. However, the uncertainties in the Q^* results leave the reality of the positive temperature dependences in vanadium open to question, particularly in the case of hydrogen. Previous studies of thermotransport of hydrogen and deuterium in α -iron and in nickel (4) and of oxygen in tantalum (15) all showed decreases in the magnitudes of the heats of transport with increasing temperature. Only in the case of hydrogen in β -zirconium (14) has there been any other indication of an increase in the magnitude of a heat of transport with increasing temperature, and it should be noted that these zirconium data are for much higher hydrogen concentrations in the range of 30 to 45 at. pct. No other definitive data concerning variations of the heat of transport with temperature have been found, but the possibility of a positive temperature dependence for some systems is

indicated and should be considered in any attempt to develop a model for the understanding of thermotransport phenomena.

DISCUSSION

A general expression which provides insight into the nature of Q^* can be derived from the following atomistic approach. Consider unidirectional heat flow normal to a plane containing solute atoms at a temperature T_1 and another parallel plane containing atoms at a lower temperature T_2 . An equation for the diffusive jump frequency, Γ , may be written for a single atom in each of the two planes (21) as

$$\Gamma_1 = \Gamma_o \exp(-\Delta H_1/RT_1) \quad (10)$$

and

$$\Gamma_2 = \Gamma_o \exp(-\Delta H_2/RT_2) \quad (11)$$

where Γ_o is a temperature independent constant. At steady state, the net flux of atoms between any two parallel planes must be zero, and it may be shown by means of a solute flux balance that

$$\frac{C_1}{C_2} = \frac{\Gamma_2}{\Gamma_1} \quad (12)$$

where C_1 and C_2 are the solute concentrations at planes 1 and 2, respectively. Combination of Eqs. (10), (11), and (12) yields

$$\frac{C_1}{C_2} = \exp\left(\frac{\Delta H_1}{RT_1} - \frac{\Delta H_2}{RT_2}\right). \quad (13)$$

The exponential expression in Eq. (13) may now be substituted for C_1/C_2 in Eq. (4) to obtain

$$Q^* = \left(\frac{\Delta H_1}{T_1} - \frac{\Delta H_2}{T_2} \right) \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1}. \quad (14)$$

Since activation energies for diffusion are essentially constant over extensive temperature ranges (16), it might be expected that $\Delta H_1 = \Delta H_2$. In this case, the temperature terms in Eq. (14) cancel and

$$Q^* = \Delta H. \quad (15)$$

It should be emphasized that this result is based upon a model in which thermotransport arises solely from temperature-related differences in atomic jump frequencies, and the direction of each individual jump is, therefore, totally unbiased with respect to movement up or down the temperature gradient, i.e. a random walk of solute atoms along a temperature gradient. For the more general case where the direction of each jump may not be completely random, Eq. (15) may be rewritten as

$$Q^* = \Delta H + \delta \quad (16)$$

where δ accounts for thermotransport which may arise due to a biasing of the jump direction. Thus, differences between respective values of Q^* and ΔH can be used to evaluate the importance and direction of any biasing of atomic jumps.

The model which was used to derive the ΔH term in Eqs. (15) and (16) is a so-called intrinsic mechanism of thermotransport. For the systems of this study, thermotransport is toward colder regions as predicted by the intrinsic model. A comparison between the Q^* results and diffusion activation energies from a compilation by Völkl and Alefeld (16) provides further evidence that this intrinsic component of Q^* may be of major importance for thermotransport of hydrogen and deuterium in Group V B metals. The

reported activation energies for diffusion of hydrogen in vanadium, niobium, and tantalum are 4.3, 10.2, and 13.5 kJ/mol, respectively, and corresponding values for deuterium are 7.0, 12.3, and 15.4 kJ/mol. Qualitative trends in Q^* and ΔH are the same. Both Q^* and ΔH progressively increase for the sequence vanadium-niobium-tantalum, and both are consistently greater for deuterium than for hydrogen. Quantitative comparisons show that the ΔH term in Eq. (16) accounts for most of Q^* in vanadium and in niobium and for approximately half of Q^* in tantalum. The reported isotope effects in ΔH can account for approximately 70% of the difference between Q_D^* and Q_H^* in vanadium and for roughly 30% of $Q_D^* - Q_H^*$ in niobium and tantalum.

Exact agreement between Q^* and ΔH was not obtained in any of the systems studied. Thus, some biasing of the jump direction is indicated in all cases. In vanadium, Q^* is consistently smaller than ΔH . This would be consistent with a weak bias which favors a jump toward hotter regions and, therefore, reduces the net flux of solute toward the cold end. In tantalum, Q^* is always larger than ΔH by roughly a factor of two. In this case, the bias must favor movement toward colder regions and thus increase the concentration of solute in the cold end. In niobium, three of the four Q^* results are slightly larger than respective values of ΔH and, therefore, weak biasing toward colder regions is indicated. The 175°C result for Q_H^* in niobium is smaller than the respective ΔH but only by 0.8 kJ/mol. Because this difference is so small, it is not clear whether any biasing toward hotter regions actually occurs in this case. In view of the significant temperature dependences of the heats of transport in niobium and tantalum, it seems noteworthy that differences between respective values of

Q^* and ΔH are smaller for the experiments over the higher temperature range. Thus, biasing toward colder regions appears to be smaller at higher temperatures. It is interesting that the larger temperature dependences of Q^* occur in tantalum, which also has the greatest amount of biasing.

At present, an atomistic explanation for the biasing mechanism cannot be established. Because atomic jump frequencies are extremely large, only a small bias in otherwise random jumps is required in order to produce concentration gradients. The biasing mechanism(s) may, therefore, be quite subtle. Proposed atomistic models for electron or phonon mechanisms of thermotransport offer possible explanations for a small bias in the direction of atomic jumps. The electronic mechanisms (10, 25, 26) are based upon electrostatic interactions between an ionic charge associated with a solute atom and the Thompson thermoelectric field or upon scattering of electrons and holes with differing thermal kinetic energies at the sites of solute atoms. The phonon mechanisms (27-29) are similarly based upon scattering interactions between phonons and solute atoms. Estimates for δ based upon electron or phonon mechanisms cannot be calculated because the details of these mechanisms are not well defined, and some of the computational parameters have never been measured.

SUMMARY

Thermotransport of both hydrogen and deuterium is toward the cold end of a temperature gradient in all of the Group V B metals. Heats of transport are greater for deuterium than for hydrogen and progressively increase for the sequence vanadium-niobium-tantalum. A weak temperature dependence of Q^* was observed in tantalum and in niobium. Through an intrinsic mechanism of thermotransport, the activation energy for diffusion seems to be a major component of Q^* . However, there is evidence that some other mechanism, either electronic or phonon, biases the direction of diffusive jumps and thus contributes to thermotransport in the systems of this study.

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SECTION II. THERMOTRANSPORT OF HYDROGEN AND DEUTERIUM IN
VANADIUM-NIOBIUM, VANADIUM-TITANIUM AND
VANADIUM-CHROMIUM ALLOYS

INTRODUCTION

A directed movement of solute atoms caused by temperature gradients in solid metals has been a subject of fundamental and applied research for more than thirty years. At present, an atomistic explanation for such thermotransport phenomena in metals and in other materials has not been established. Previous studies of thermotransport in metals have primarily involved simple binary systems consisting of a dilute concentration of solute in an otherwise pure host metal. Consequently, very little is known about thermotransport in more complex alloys. Since multicomponent alloys are commonly used in engineering applications, thermotransport of solutes in such materials may be of practical interest. In addition, changes in the heat of transport which may result from controlled alloy additions could provide new insight into the fundamental nature of thermotransport. In an earlier investigation, the present authors studied thermotransport of hydrogen and deuterium in pure vanadium and niobium (1). As a logical extension of that research, this study examines thermotransport of hydrogen and deuterium in vanadium-niobium, vanadium-titanium, and vanadium-chromium alloys.

The metal-hydrogen systems of this study are particularly attractive for thermotransport experiments. The vanadium alloys are homogeneous solid solutions in the regimes of interest (2-5) and terminal solubilities for hydrogen in these alloys are quite high (6-10). A concurrent study by Peterson and Herro (11) has shown that diffusivities of hydrogen and deuterium in these alloys are also quite high. Thus, thermotransport experiments based upon steady state techniques can be conducted with single

phase materials at moderate temperatures in reasonable times. The selection of alloy elements from three adjacent columns of the periodic chart also provides a systematic variation in the electron/atom ratio which could prove useful in an evaluation of possible electronic mechanisms (12-14) for thermotransport. In addition, hydrogen and deuterium offer a large ratio of isotopic mass so that isotope effects in thermotransport are more readily observed. Finally, hydrogen can adversely affect the mechanical properties of transition metals. Since vanadium is presently considered to be a possible first wall material for fusion reactors, thermotransport of hydrogen isotopes in vanadium alloys may be of practical concern.

EXPERIMENTAL PROCEDURE

The heat of transport, Q^* , is a phenomenological parameter which is used to describe thermotransport phenomena. The sign and magnitude of Q^* describe the direction and amount of thermotransport in a given system. The heat of transport has dimensions of energy and possible atomistic interpretations of this energy have been reviewed in recent articles by Hehenkamp (15) and Wipf (16). In this study, values of Q^* were determined by means of a steady state technique which has been detailed in an earlier publication (1). Therefore, only a brief description of the experimental method is presented here.

Hydrogen and deuterium were introduced into the alloy specimens by means of electrolytic charging. Each specimen was charged with approximately equal molar amounts of both hydrogen and deuterium to a total concentration of $0.01 (H+D)/M$, where M represents the host metal alloy. A 1.0 cm length at one end of each $2.5 \times 1.0 \times 0.08$ cm specimen was then inserted into a heat source, and an equal length at the opposite end was clamped into a heat sink. The experimental arrangement produced a large 200°C isothermal region at one end of the specimen and a similar 150°C isothermal region at the other end, with a temperature gradient in the portion of the specimen between the heat source and heat sink. Temperatures in the isothermal regions were monitored with calibrated chromel-alumel thermocouples. Hydrogen did not escape from the specimen (1), and after a sufficient time, a steady state was approached wherein the flux of solute due to thermotransport was exactly compensated by an oppositely directed diffusion flux. The steady state concentrations of hydrogen and

deuterium were uniform throughout each isothermal region and were determined by a combination of hot vacuum extraction and mass spectrometric analyses. Heats of transport for hydrogen and deuterium were then computed according to the relations

$$Q_H^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln (C_{H,1}/C_{H,2}) \quad (1)$$

and

$$Q_D^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln (C_{D,1}/C_{D,2}). \quad (2)$$

In these equations, R is the gas constant, T is temperature, C_H and C_D are steady state concentrations of hydrogen and deuterium, and the subscripts 1 and 2, respectively, denote the 200°C and 150°C isothermal regions of a specimen. This experimental method eliminates several problems encountered in other techniques which require measurement and correlation of both temperatures and solute concentrations in regions of a test specimen where there are substantial temperature and concentration gradients. The present method also permits both Q_H^* and Q_D^* to be simultaneously determined with a single specimen so that experimental conditions for the two isotopes are identical.

Vanadium and niobium form a continuous solid solution series (2) and alloys with compositions of 0.10, 0.25, 0.50, 0.75, and 0.90 Nb/(V+Nb) were selected for study. At the temperatures of this investigation, vanadium is bcc and titanium is fcc. Thus, these two metals form homogeneous solid solutions only within limited compositional regimes. Compositions chosen for study were 0.01, 0.05, 0.10, 0.20, and 0.30 Ti/(V+Ti). Within this compositional range, vanadium-titanium alloys are single phase and have bcc

crystal structures (3). Vanadium and chromium do form a continuous solid solution series (4, 5); however, as the chromium content increases, the alloys become very brittle and hydrogen solubility decreases (8, 9). Therefore, only alloys with compositions of 0.10 and 0.20 Cr/(V+Cr) were used.

The vanadium alloys were prepared from pure metals by arc melting on a chilled copper hearth under high-purity argon. The vanadium and niobium in the alloys of this study were taken from the same stock used to prepare specimens for the earlier investigation of hydrogen thermotransport in the pure metals (1). Sources for the vanadium, niobium, titanium, and chromium were, respectively, U.S. Bureau of Mines, DuPont Company, Titanium Metals Corporation, and Chromalloy Corporation. Arc melting of each alloy was done in multiple stages in order to obtain better homogeneity. Several small buttons of an alloy were individually melted and then remelted together to form a single, larger button. Metallographic and X-ray analyses indicated that each alloy was single phase and of uniform composition. The alloy buttons were subsequently rolled to form 0.08 cm thick sheet from which the specimens were cut. The specimens of each alloy were given an appropriate recrystallization anneal at pressures less than 10^{-4} Pa. Carbon, nitrogen, and oxygen concentrations in the specimens were determined after annealing, and representative values are shown in Table 1. Carbon concentrations were determined by combustion analyses. Nitrogen and oxygen were measured by vacuum fusion analyses. The levels of other potential impurities were surveyed with a spark source mass spectrograph. Arc melted samples of the pure metals contained 0.01 to 0.04 at. pct. tungsten, which may have been introduced from the tungsten electrode in the

Table 1. Carbon, nitrogen, and oxygen concentrations in annealed vanadium alloys

Alloy (at. pct.)	Carbon (at. pct.)	Nitrogen (at. pct.)	Oxygen (at. pct.)
0 Nb ^a	0.020	0.010	0.020
25 Nb	0.053	0.013	0.036
50 Nb	0.035	0.021	0.042
75 Nb	0.030	0.038	0.062
100 Nb ^a	0.025	0.001	0.008
5 Ti	0.013	0.001	0.032
10 Ti	0.017	0.002	0.038
20 Ti	0.019	0.004	0.044
30 Ti	0.011	0.007	0.024
10 Cr	0.027	<0.001	0.023
20 Cr	0.013	<0.001	0.016

^aSpecimens used in the earlier pure metal study (1).

arc melting apparatus. The niobium also contained 0.17 at. pct. tantalum. These were the only substitutional impurities found to be present in concentrations greater than 0.01 at. pct.

Evaluations of Q^* via Eqs. (1) and (2) are valid only if certain constraints are satisfied. One constraint is that these equations apply only to single phase materials. The terminal solid solubility of hydrogen in vanadium at 150°C is 0.25 H/M, and the corresponding solubility of deuterium exceeds 1.1 D/M (6). Hydrogen solubilities are even greater in the vanadium-niobium (7) and vanadium-titanium (8, 10) alloys of the present study. Hydrogen solubility in the vanadium-chromium alloys (8, 9) is slightly lower than in pure vanadium. However, the solubility limits in all of the alloys are much greater than any hydrogen or deuterium

concentrations in the experiments of this study. Thus, hydride or deuteride phases should not have been present in the specimens, and none were observed. Another constraint is an assumption required in the derivation (1) of Eqs. (1) and (2) that the mobility of the matrix atoms is negligible and that only the interstitial hydrogen atoms move. This constraint was satisfied for experiments in this study since the interdiffusion coefficients for the metallic alloy components are typically less than $10^{-30} \text{ m}^2/\text{sec}$ (17), whereas the pertinent diffusivities for hydrogen and deuterium in the vanadium alloys are of the order of 10^{-8} to $10^{-10} \text{ m}^2/\text{sec}$ (11). An assumption that the activity coefficients for hydrogen and deuterium are constant throughout the concentration range of measurement is also valid because Sieverts' law is obeyed for hydrogen in the vanadium alloys of this study over the composition and temperature regimes of interest (9, 18). This Sieverts' law behavior also signifies an absence of interactions between the interstitial atoms and, therefore, indicates that hydrogen moves independently of deuterium in a specimen which contains both isotopes. Finally, the use of Eqs. (1) and (2) is valid only if steady state conditions are closely approached. Minimum times necessary to approach within 99% of the steady state were estimated as 5τ with the relaxation time, τ , computed (19) as

$$\tau = \ell^2 / (\pi^2 D). \quad (3)$$

The 2.5 cm specimen length was used for the characteristic distance, ℓ . The diffusivity of deuterium at the 150°C sink temperature was used for D because deuterium diffuses more slowly than hydrogen in the vanadium alloys of this study (11). A close approach to steady state conditions was also

verified by several replicate experiments which ran for times much longer than 5τ with no significant changes in the resulting values of Q^* .

RESULTS

Thermotransport of hydrogen and deuterium in all of the vanadium alloys is much greater than in pure vanadium. Additions of vanadium to niobium also substantially increase thermotransport of hydrogen and deuterium over that observed in pure niobium. Heats of transport in Table 2 and in Figures 1-3 show that changes in Q^* are not linearly related to alloy composition, but rather, the most rapid increases in Q^* occur at low concentrations of the substitutional alloy element. Each heat of transport in Table 2 is the mean of a set of results from three or more replicate experiments, and the uncertainty is one standard deviation of the mean. A representative uncertainty of ± 0.5 kJ/mol shown in Figures 1-3 is also in close agreement with uncertainty estimates based upon the accuracies (1) of the temperature measurements, hot vacuum extraction analyses, and mass spectrometric analyses. As in the earlier experiments with pure vanadium and niobium (1), thermotransport of hydrogen and deuterium is toward the cold end of the specimen in all of the metal alloys of this study. Isotope effects observed for thermotransport in the pure metals also occur in the metal alloys. Isotope effects, expressed as $Q_D^* - Q_H^*$ in Table 2, show that thermotransport of deuterium is significantly greater than thermotransport of hydrogen in all of the alloys. In the vanadium-titanium system, there is a large monotonic decrease in the magnitude of $Q_D^* - Q_H^*$ as the titanium content increases. Similarly, isotope effects in vanadium-niobium specimens which contained substantial amounts of both alloy metals are significantly smaller than isotope effects in pure vanadium or niobium. No significant variations among isotope effects in

Table 2. Heats of transport for hydrogen and deuterium in vanadium alloys with niobium, titanium, and chromium

Alloy (at. pct.)	Q_H^* (kJ/mol)	Q_D^* (kJ/mol)	$Q_D^* - Q_H^*$ (kJ/mol)
0 Nb ^a	1.8 $\pm$ 0.2	6.1 $\pm$ 0.2	4.3 $\pm$ 0.3
10 Nb	8.5 $\pm$ 0.6	12.5 $\pm$ 0.8	4.0 $\pm$ 1.0
25 Nb	13.1 $\pm$ 0.2	16.5 $\pm$ 0.2	3.4 $\pm$ 0.3
50 Nb	15.8 $\pm$ 0.3	18.8 $\pm$ 0.3	3.0 $\pm$ 0.4
75 Nb	16.9 $\pm$ 0.5	20.0 $\pm$ 0.3	3.1 $\pm$ 0.6
90 Nb	15.8 $\pm$ 0.6	20.4 $\pm$ 0.5	4.6 $\pm$ 0.8
100 Nb ^a	9.4 $\pm$ 0.4	16.3 $\pm$ 0.2	6.9 $\pm$ 0.4
1 Ti	3.5 $\pm$ 0.2	7.6 $\pm$ 0.1	4.1 $\pm$ 0.2
5 Ti	7.7 $\pm$ 0.3	10.9 $\pm$ 0.4	3.2 $\pm$ 0.5
10 Ti	10.4 $\pm$ 0.4	13.4 $\pm$ 0.3	3.0 $\pm$ 0.5
20 Ti	12.2 $\pm$ 0.2	14.2 $\pm$ 0.2	2.0 $\pm$ 0.3
30 Ti	12.1 $\pm$ 0.4	13.2 $\pm$ 0.3	1.1 $\pm$ 0.5
10 Cr	4.8 $\pm$ 0.1	9.2 $\pm$ 0.2	4.4 $\pm$ 0.2
20 Cr	5.8 $\pm$ 0.2	10.0 $\pm$ 0.2	4.2 $\pm$ 0.3

^aData from the earlier pure metal study (1).

vanadium-chromium alloys were observed over the limited compositional range of this investigation.

There are few published data which are relevant to the present Q^* results for vanadium alloys. Sawatzky and Duclos (20) have reported $Q_H^* = 2.6$ kJ/mol for 20 to 40 at. pct. hydrogen in β -titanium over the temperature range from 320 to 590°C. This value, shown in Figure 2, is lower than any of the present Q^* results for vanadium-titanium alloys. The heat of transport for hydrogen in chromium apparently has never been measured. Only one previous thermotransport study has been done in alloy systems comparable to those of the present investigation. Mathuni, Kirchheim, and Fromm (21) have studied thermotransport of oxygen in

Figure 1. Heats of transport for thermotransport of hydrogen and deuterium in vanadium-niobium alloys

Figure 2. Heats of transport for thermotransport of hydrogen and deuterium in vanadium-titanium alloys. Literature value for β -titanium is from Sawatzky and Duclos (20)

Figure 3. Heats of transport for thermotransport of hydrogen and deuterium in vanadium-chromium alloys

tantalum separately alloyed with up to 12 at. pct. tungsten, 6 at. pct. rhenium, or 1.2 at. pct. nitrogen. Thermotransport of oxygen in each of the alloys and in pure tantalum is toward the hot end of a temperature gradient, i.e. Q^* values are negative numbers. However, in each case the ternary alloy addition significantly decreased the magnitude of Q^* . Behavior in these systems is qualitatively similar to the present results in the sense that ternary alloy additions in both studies caused heats of transport to become more positive. Physically this means that thermotransport toward hotter regions was reduced or that thermotransport toward colder regions was increased. Indeed, Mathuni et al. state that Q^* for the 1.2 at. pct. nitrogen alloy is very close to zero and may be slightly positive. Thus, the ternary addition of nitrogen may have changed the direction of thermotransport of oxygen in tantalum.

DISCUSSION

For thermotransport along a one-dimensional temperature gradient, an expression for the heat of transport may be written (1) as

$$Q^* = \Delta H + \delta \quad (4)$$

In this equation, ΔH is the activation energy for diffusion of the mobile species, and δ represents a small energy difference which tends to bias the direction of a diffusive jump with respect to movement up or down the temperature gradient. The ΔH term in Eq. (4) may be readily identified as a so-called intrinsic component of Q^* if intrinsic thermotransport is considered to arise solely from temperature related differences in atomic jump frequencies with no bias in the direction of any given jump, i.e a random walk under the influence of a temperature gradient (1, 22). In this case, δ would be zero and Q^* would be identically equal to ΔH . For the case where the heat of transport does not equal the respective activation energy for diffusion, the difference between Q^* and ΔH is a measure of the bias represented by δ .

For the systems of this study, the dominant effect of alloying upon Q^* is a dramatic increase in Q^* with increasing solute concentration. This increase is observed for all three substitutional solutes added to vanadium and for additions of vanadium to niobium. The only atomistic model that makes a definite prediction of the change in Q^* upon alloying is the random walk model for intrinsic thermotransport. This model predicts that Q^* will follow changes in the activation energy for diffusion. Fortunately, Peterson and Herro (11) have made a concurrent investigation of activation energies for diffusion of hydrogen in the same alloys which were used for

the present thermotransport study. Plots of their ΔH values versus alloy composition are qualitatively similar to the respective plots for Q^* shown in Figures 1-3. In each alloy system, both Q^* and ΔH increase most rapidly at low concentrations of the substitutional alloy element, and the maximum values of Q^* and ΔH occur at the same composition. Thus, the simple random walk model correctly predicts the qualitative trends in Q^* for all of the systems studied.

A quantitative comparison shows that respective values of Q^* and ΔH for the two vanadium-chromium alloys agree within the combined uncertainty of the measurements. Thus, thermotransport of hydrogen in both of the vanadium-chromium alloys could be accounted for solely upon the basis of the random walk model for intrinsic thermotransport. In the vanadium-niobium and vanadium-titanium systems, ΔH is larger than Q^* by amounts which increase with solute concentration. The maximum differences between Q^* and ΔH are about 30% of Q^* in 50 and 75 at. pct. niobium alloys and about 50% of Q^* in 20 and 30 at. pct. titanium alloys. In both alloy systems, the magnitude of $Q^* - \Delta H$ in the more dilute alloys is smaller but still meaningful. It must, therefore, be concluded that the biasing factor, δ , is small but nonzero for thermotransport of hydrogen in the vanadium-niobium and vanadium-titanium alloys, and thus the simple random walk model must be modified. Because ΔH is consistently greater than Q^* , δ in Eq. (4) represents a negative contribution to Q^* and indicates that the biasing favors a jump toward the hot end of a temperature gradient thereby reducing the net mass flow toward the cold end. Any meaningful model for δ must allow for this direction of bias.

Several possible explanations for a small bias in the direction of an atomic jump have been advanced. Wirtz (23) and others (24, 25) have proposed intrinsic thermotransport models in which the jump direction as well as the jump frequency is influenced by the temperature gradient. No evaluation of the Wirtz type models can be made from the present experimental results because the details of the jump process for diffusion of hydrogen in bcc transition metals are unknown. However, such models have been criticized for a number of reasons (13, 21, 26), and it appears questionable whether this type of model is totally consistent with basic phenomenological relationships between temperature and concentration (27). Other potential explanations for the directional bias represented by δ are possible interactions between a jumping atom and electrons or phonons. Proposed electronic mechanisms (12-14) are based either upon electrostatic interactions between an ionic charge associated with a solute atom and the Thompson thermoelectric field or upon scattering of electrons and holes with differing thermal kinetic energies at sites of solute atoms. Possible phonon mechanisms (28-30) are similarly based upon scattering interactions between phonons and solute atoms.

At their present state of development, electron and phonon models do not provide a basis for quantitative comparison with the results of this study; however, a few qualitative comparisons have been attempted. At comparable alloy compositions, the electron/atom ratio progressively increases for the alloy sequence vanadium-titanium, vanadium-niobium, and vanadium-chromium. The difference $Q^* - \Delta H$ becomes smaller as the electron/atom ratio increases. This observation, while not conclusive, favors an interpretation of the biasing factor, δ , in terms of an electronic

mechanism. Additional evidence for a meaningful contribution from electronic interactions comes from Mathuni et al. (21) who have noted that nearly linear relationships between Q^* and the thermoelectric power occur in some transition metal alloys. These authors have argued that interaction of electrons and holes with the transported atoms is of major importance in thermotransport. Unfortunately, values of the thermoelectric power for the alloys of the present study have not been determined.

Atomic mass affects vibrational amplitudes and changes in the mass of a solute species could, therefore, influence a phonon dependent mechanism for thermotransport. An attempt to evaluate possible phonon contributions to thermotransport was made by searching for correlations between trends in the Q^* results and the relative atomic masses of niobium, chromium, and titanium. However, differences in the atomic masses of the alloy elements did not correlate with any obvious trend in the heats of transport. A similar attempt to investigate possible strain effects which might result from differences in the atomic diameters of the alloy elements also failed to show any meaningful correlation. Thus, the data generally favor an interpretation of thermotransport arising primarily from the intrinsic temperature dependence of atomic jump frequencies with a small but significant directional biasing via an electronic mechanism.

There is some evidence that isotope effects in the present Q^* results might be related to differences in the activation energies for diffusion of hydrogen and deuterium. In the earlier study (1) of thermotransport of hydrogen and deuterium in pure vanadium and niobium, it was found that differences between Q_H^* and Q_D^* could be largely accounted for by reported (31) isotope effects in ΔH . Although activation energies for diffusion of

deuterium in the alloys of this study are not currently available, it is known that diffusion of deuterium is slower than diffusion of hydrogen in these alloys (11). Thus, diffusion activation energies could be greater for deuterium than for hydrogen and may at least partially account for isotope effects in Q^* via the ΔH term in Eq. (4).

SUMMARY

Thermotransport of hydrogen and deuterium in vanadium alloyed with niobium, titanium, or chromium is much greater than in pure vanadium, and additions of vanadium to niobium similarly increase thermotransport of hydrogen and deuterium over that observed in pure niobium. The most rapid increases in Q^* always occur at low concentrations of the substitutional alloy element. Heats of transport are consistently larger for deuterium than for hydrogen, and thermotransport of both isotopes is always toward the cold end of a temperature gradient.

The observed results are consistent with a model in which the temperature dependence of the atomic jump frequency is the dominant factor controlling thermotransport. Heats of transport in the vanadium-chromium alloys are equal to respective activation energies for diffusion and may be entirely accounted for via a simple random walk model for intrinsic thermotransport. In the vanadium-niobium and vanadium-titanium systems, ΔH is typically larger than Q^* , and the atomistic model must, therefore, be modified to reflect a small bias in the direction of any given atomic jump. For both of these systems, the small directional bias favors a jump toward the hot end of a temperature gradient. Although the present results appear to favor an electronic biasing mechanism, the actual nature of the biasing mechanism cannot be established. As in the previous study (1) of the thermotransport of hydrogen and deuterium in pure vanadium and niobium, differences between Q_H^* and Q_D^* are possibly a reflection of isotope effects in the activation energies for diffusion.

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SECTION III. THERMOTRANSPORT OF HYDROGEN AND DEUTERIUM
IN NIOBIUM-TANTALUM ALLOYS

INTRODUCTION

Thermotransport is a poorly understood phenomenon characterized by mass transport along temperature gradients. Thermotransport in metals is of both fundamental (1-3) and technological (3, 4) interest; however, only a small number of systems have been studied. Additional experimental investigation is needed to provide a basis for the development of atomistic models which correctly predict the direction and extent of thermotransport in a specified system.

Several investigators have studied thermotransport of a dilute solute in a pure host metal, and a few have examined the movement of markers along temperature gradients in pure metals. However, there has been very little investigation of thermotransport in more complex systems. Thermotransport of solutes in multicomponent alloys is of interest because such materials are commonly used in engineering applications and because insight into the fundamental nature of thermotransport might be gained by investigating changes in the direction or extent of thermotransport after controlled alloy additions. In a recent study (5), the present authors found that thermotransport of hydrogen and deuterium in vanadium alloyed with either niobium, titanium, or chromium is much greater than in pure vanadium and that additions of vanadium to niobium similarly increase thermotransport of hydrogen and deuterium over that observed in pure niobium. In these systems, thermotransport always increases most rapidly at low concentrations of the substitutional alloy element, and transport of deuterium is significantly greater than transport of hydrogen in all cases. These interesting results were interpreted according to a model in which the

temperature dependence of the atomic jump frequency is the dominant factor controlling thermotransport with a small, gradient-related bias in the direction of atomic jumps possibly caused by an electronic mechanism.

The present study of thermotransport of hydrogen and deuterium in niobium-tantalum alloys was undertaken in order to further investigate thermotransport in multicomponent systems. Niobium and tantalum are both Group V B transition metals and form a continuous series of solid solutions (6). The atomic density in niobium-tantalum alloys is essentially independent of composition (7, 8), but the differing atomic weights cause the mass density to increase by a factor of two upon going from niobium to tantalum (8). Although these two metals are similar in many respects, it has been shown (9) that thermotransport of hydrogen and deuterium is much greater in pure tantalum than in pure niobium. Therefore, it seems of interest to determine how thermotransport varies with alloy composition in the niobium-tantalum system.

EXPERIMENTAL PROCEDURE

The heat of transport, Q^* , is a phenomenological parameter which is used to describe thermotransport phenomena. The sign and magnitude of Q^* indicate the direction and extent of thermotransport in a given system. The heat of transport has dimensions of energy, and atomistic interpretations of this energy have been reviewed in recent articles by Wipf (2) and Hehenkamp (3). In an earlier study (9), the present authors used a steady state technique to determine heats of transport for thermotransport of hydrogen and deuterium in pure niobium and tantalum. The same measurement technique was used for the present investigation of thermotransport of hydrogen and deuterium in niobium-tantalum alloys. Since the experimental method has already been detailed in the publication describing the results for pure niobium and tantalum, only a brief outline of the procedure is presented here.

Hydrogen and deuterium were introduced into the alloy specimens by means of electrolytic charging. Each specimen was charged with approximately equal molar amounts of both hydrogen and deuterium to a total concentration of $0.01 (H+D)/M$, where M represents the host metal alloy. A 1.0 cm length at one end of each $2.5 \times 1.0 \times 0.08$ cm specimen was then inserted into a heat source, and an equal length at the opposite end was clamped into a heat sink. The experimental arrangement produced a 200°C isothermal region at one end of the specimen and a similar 150°C isothermal region at the other end, with a temperature gradient in the portion of the specimen between the heat source and heat sink. Temperatures in the isothermal regions were monitored with calibrated chromel-alumel thermocouples.

Hydrogen did not escape from the specimen (9), and after a sufficient time, a steady state was approached wherein the flux of solute due to thermotransport was exactly compensated by an oppositely directed diffusion flux. The steady state concentrations of hydrogen and deuterium were uniform throughout each isothermal region and were determined by a combination of hot vacuum extraction and mass spectrometric analyses. Heats of transport for hydrogen and deuterium were then computed according to the relations

$$Q_H^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln (C_{H,1}/C_{H,2}) \quad (1)$$

and

$$Q_D^* = R \left(\frac{1}{T_1} - \frac{1}{T_2} \right)^{-1} \ln (C_{D,1}/C_{D,2}). \quad (2)$$

In these equations, R is the gas constant, T is temperature, C_H and C_D are steady state concentrations of hydrogen and deuterium, and the subscripts 1 and 2, respectively, denote the 200°C and 150°C isothermal regions of a specimen. This experimental method eliminates several problems encountered in other techniques which require measurement and correlation of both temperatures and solute concentrations in regions of a test specimen where there are substantial temperature and concentration gradients. The present method also permits both Q_H^* and Q_D^* to be simultaneously determined with a single specimen so that experimental conditions for the two isotopes are identical.

Niobium-tantalum alloys with compositions of 25, 50, and 75 at. pct. tantalum were prepared from pure metals by arc melting on a chilled copper hearth under high-purity argon. The niobium and tantalum were obtained

from DuPont Company and Fansteel, Inc., respectively, and were the same as used in the earlier study of hydrogen thermotransport in the pure metals (9). Several small buttons of each alloy were individually melted and then remelted together to form a single, larger button. The alloy buttons were subsequently rolled to form 0.08 cm thick sheet from which the specimens were cut. The sheet specimens of each alloy were annealed at 1700°C for 30 minutes at pressures less than 10^{-4} Pa. Representative impurity concentrations in specimens of pure niobium and tantalum which had been arc melted, rolled, and annealed are shown in Table 1. Carbon concentrations were determined by combustion analyses. Nitrogen and oxygen concentrations were measured by vacuum fusion analyses. The levels of eighty-two other impurities were surveyed with a spark source mass spectrograph. Tungsten was present in both the niobium and tantalum in concentrations of approximately 0.01 at. pct. and may have been introduced from the tungsten electrode in the arc melting apparatus. The niobium also contained an initial 0.17 at. pct. tantalum prior to alloying. No other substitutional impurities were found in concentrations greater than 0.01 at. pct.

Evaluations of Q^* via Eqs. (1) and (2) are valid only if certain constraints are satisfied. One constraint is that these equations apply only to single phase materials. Westlake and Miller (10) have determined terminal solubilities for hydrogen and deuterium in niobium-tantalum alloys at 23°C. Their results indicate that terminal solubilities for hydrogen in 25, 50, and 75 at. pct. tantalum alloys are approximately 0.035, 0.095, and 0.120 H/M, respectively, and that solubilities for deuterium are very similar to the values for hydrogen in each of these alloys. Even higher terminal solubilities would be expected for the 150°C to 200°C temperatures

Table 1. Impurity concentrations in annealed specimens of the pure metals

Metal	Carbon (at. pct.)	Nitrogen (at. pct.)	Oxygen (at. pct.)	Tungsten (at. pct.)	Tantalum (at. pct.)	Total other (at. pct.)
Niobium	0.024	<0.001	0.008	0.013	0.170	<0.046
Tantalum	0.019	0.006	0.040	0.010	--	<0.015

of the present study, so that the solubility limits in all of the alloys are much higher than any hydrogen or deuterium concentrations in the thermotransport experiments. Thus, hydride or deuteride phases should not have been present in the specimens and none were observed. Another constraint is an assumption required in the derivation (9) of Eqs. (1) and (2) that the mobility of the matrix atoms is negligible and that only the interstitial hydrogen atoms move. This constraint was satisfied for the experiments of this study because binary interdiffusion coefficients for niobium and tantalum at 200°C should be less than $10^{-45} \text{ m}^2/\text{sec}$ (11), whereas the pertinent diffusivities for hydrogen and deuterium are of the order of 10^{-9} to $10^{-10} \text{ m}^2/\text{sec}$ (12, 13). An assumption that the activity coefficients for hydrogen and deuterium are constant throughout the concentration range of measurement also seems justified because available data indicate that Sieverts' law is obeyed for hydrogen and deuterium in niobium-tantalum alloys over the composition and temperature regimes of interest (10, 14-16). This Sieverts' law behavior also signifies an absence of interactions between interstitial atoms and, therefore, indicates that hydrogen moves independently of deuterium in a specimen which

contains both isotopes. Finally, the use of Eqs. (1) and (2) is valid only if steady state conditions are closely approached. Minimum times necessary to approach within 99% of the steady state were estimated as 5τ with the relaxation time, τ , computed (17) as

$$\tau = l^2/(\pi^2 D). \quad (3)$$

The 2.5 cm specimen length was used for the characteristic distance, l . Diffusivities for deuterium at the 150°C sink temperature were used for D because deuterium diffuses more slowly than hydrogen in Group V B metals. According to the compilation by Völkl and Alefeld (12), the diffusivities of deuterium in both niobium and tantalum at 150°C are 40% lower than respective diffusivities for hydrogen. Diffusivities for deuterium have not been measured in niobium-tantalum alloys, however, Peterson and Jensen (13) have determined diffusivities for hydrogen in the alloys of the present study. Reasonable estimates for the diffusivities for deuterium in these alloys could, therefore, be made upon the basis of the known relationship between diffusion of hydrogen and deuterium in the pure metals and the measured data for hydrogen in the metal alloys. A close approach to steady state conditions was also verified by several replicate experiments which ran for times much longer than 5τ with no significant changes in the resulting values of Q^* .

RESULTS

As in the earlier experiments with pure niobium and tantalum (9), thermotransport of hydrogen and deuterium in the niobium-tantalum alloys of the present study is toward the cold end of a temperature gradient. Heats of transport in the alloys are larger than in pure niobium and are smaller than in pure tantalum; however, Q^* does not vary as a simple linear function of alloy composition. A comparison of results in Table 2 shows that the heats of transport are approximately the same in the 25, 50, and 75 at. pct. tantalum alloys. In Figure 1, these alloy results are compared to dashed lines which represent values of Q_H^* and Q_D^* estimated by linear interpolation of results for the pure metals. The observed values of Q^* are larger than the interpolated values for the niobium-rich specimens and are smaller than the interpolated values for the tantalum-rich specimens. In all cases, heats of transport are significantly greater for deuterium than for hydrogen. However, isotope effects expressed at $Q_D^* - Q_H^*$ in Table 2 are smaller in the metal alloys than in the pure metals.

It should be noted that each heat of transport in Table 2 is the mean of a set of results from at least three replicate experiments, and the stated uncertainty is one standard deviation of the mean. A representative uncertainty of ± 0.5 kJ/mol illustrated in Figure 1 is also in close agreement with uncertainty estimates based upon the accuracies (9) of the temperature measurements, hot vacuum extraction analyses, and mass spectrometer analyses.

Table 2. Heats of transport for hydrogen and deuterium in niobium-tantalum alloys over the 150°C to 200°C temperature range

Alloy (at. pct.)	Q_H^* (kJ/mol)	Q_D^* (kJ/mol)	$Q_D^* - Q_H^*$ (kJ/mol)
0 Ta ^a	9.4 $\pm$ 0.4	16.3 $\pm$ 0.2	6.9 $\pm$ 0.4
25 Ta	16.9 $\pm$ 0.3	21.0 $\pm$ 0.2	4.1 $\pm$ 0.4
50 Ta	17.5 $\pm$ 0.2	21.6 $\pm$ 0.2	4.1 $\pm$ 0.3
75 Ta	17.1 $\pm$ 0.3	21.5 $\pm$ 0.2	4.4 $\pm$ 0.4
100 Ta ^a	21.5 $\pm$ 0.6	29.5 $\pm$ 0.5	8.0 $\pm$ 0.8

^aData from the earlier pure metal study (9).

Figure 1. Heats of transport for thermotransport of hydrogen and deuterium in niobium-tantalum alloys. Dashed lines indicate values predicted by linear interpolation of results for the pure metals (9)

DISCUSSION

There are interesting similarities and differences between the results of the present study and the results of the earlier study (5) of thermotransport of hydrogen and deuterium in vanadium alloyed with either niobium, titanium, or chromium. Thermotransport of hydrogen and deuterium in the alloys of both studies is toward colder regions, and heats of transport are significantly larger for deuterium than for hydrogen in all cases. However, the additions of substitutional elements to vanadium and to niobium always increase Q_H^* and Q_D^* , whereas additions of niobium to tantalum have the opposite effect and substantially decrease Q_H^* and Q_D^* .

The only atomistic model which makes a definite prediction of the change in Q^* upon alloying is the random walk model (5, 9, 19) for so-called intrinsic thermotransport. This model is based upon the temperature dependence of the frequency of diffusive jumps and predicts that Q^* should be equal to ΔH , where ΔH is the activation energy for diffusion of the mobile species. In the vanadium alloy study (5), changes in Q^* upon alloying were found to closely parallel changes in ΔH , although respective values of Q^* and ΔH were equal only in a few cases. These results have been interpreted according to a model in which the temperature dependence of the atomic jump frequency is the dominant factor controlling thermotransport with a small, gradient-related bias in the direction of atomic jumps possibly caused by an electronic mechanism.

Unfortunately, activation energies for diffusion of hydrogen and deuterium in niobium-tantalum alloys have not been determined so that quantitative comparisons between Q^* and ΔH cannot be made for the alloys of

the present study. However, Peterson and Jensen (13) have measured diffusivities of hydrogen in the niobium-tantalum system at 23°C. Their results indicate a monotonic decrease in diffusivity from approximately $7.5 \times 10^{-10} \text{ m}^2/\text{sec}$ in pure niobium down to $1.7 \times 10^{-10} \text{ m}^2/\text{sec}$ in a 75 at. pct. tantalum alloy with little further change in the diffusivity from 75 to 100 at. pct. tantalum. Although no definite statements about ΔH can be made on the basis of diffusivity data at one temperature, the substantial decrease in diffusivity from pure niobium to 75 at. pct. tantalum could be at least partially due to an increase in ΔH . An increase in ΔH as tantalum is added to niobium would help to explain the observation that Q^* values are larger in the niobium-tantalum alloys than in pure niobium. Also, a compilation by Völkl and Alefeld (12) indicates that activation energies for diffusion of hydrogen and deuterium in niobium are 10.2 and 12.3 kJ/mol, respectively, and the corresponding values in tantalum are 13.5 and 15.4 kJ/mol. A comparison between these activation energies and respective heats of transport in Table 2 shows that differences between Q^* and ΔH are small in niobium, and thus the gradient-related bias in the direction of atomic jumps must be small. However, Q^* is larger than ΔH by roughly a factor of two in tantalum. Thus, the random walk model can only account for about half of the thermotransport effect in tantalum, and some other mechanism must significantly bias the direction of atomic jumps toward the cold end. Decreases in Q_H^* and Q_D^* upon going from pure tantalum to 75 at. pct. tantalum could be explained by a rapid decrease in the biasing as niobium is added. The nature of the biasing mechanism cannot be established at present; however, Mathuni et al. (18) have presented evidence that an electronic mechanism is of major importance for thermotransport of oxygen

in pure tantalum and in tantalum alloys containing small amounts of either tungsten, rhenium, or nitrogen.

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GENERAL SUMMARY

Heats of transport have been determined for thermotransport of hydrogen and deuterium in pure vanadium, niobium, and tantalum; in vanadium alloyed with either niobium, titanium, or chromium; and in niobium-tantalum alloys. In all cases, thermotransport was toward colder regions and was significantly greater for deuterium than for hydrogen. Heats of transport in the pure metals increased almost linearly with atomic mass for the sequence vanadium-niobium-tantalum, and differences in solute concentration resulting from a 50°C temperature difference ranged from 10% to more than 900%. Isotope effects, expressed as $Q_D^* - Q_H^*$, were of the order of 3 to 4 kJ/mol in vanadium and were approximately 6 to 8 kJ/mol in both niobium and tantalum. The predominant effect of alloying was to dramatically increase thermotransport; however, thermotransport decreased as niobium was added to tantalum. The heat of transport did not vary linearly with alloy composition, but rather, the changes were always greater at low concentrations of the substitutional element. In most cases, the difference between Q_D^* and Q_H^* decreased upon alloying; however, no change in the isotope effect was observed for additions of 10 or 20 at. pct. chromium to vanadium.

The following expression was developed for the heat of transport and was found to be very useful in the interpretation of Q^* results

$$Q^* = \Delta H + \delta \quad (1)$$

According to a random walk model, the ΔH term in this equation is due to intrinsic thermotransport arising from temperature related differences in atomic jump frequencies. The random walk model correctly predicted qualitative trends in Q^* for all cases where ΔH data were available, and in the

two vanadium-chromium alloys, respective values of Q^* and ΔH were equal. Differences between Q_D^* and Q_H^* could also be partially explained by reported isotope effects (33) in ΔH . For the case where $Q^* \neq \Delta H$, the direction of each atomic jump was not completely random, and thus a biasing mechanism must have influenced the jump process. A bias in the jump direction accounted for up to half of the thermotransport effect in tantalum but was much smaller in most of the other systems. The fundamental nature of the biasing process could not be established, but the evidence seemed to favor an electronic mechanism.

The success of the random walk model in predicting qualitative and, in some cases, quantitative changes in Q^* is perhaps the most significant new information gained from the research described in this thesis. In the past, so-called intrinsic thermotransport has been primarily associated with the more complex and much maligned Wirtz type models (23, 34) which have provided little basis for substantive comparison with experimental results. Based upon the results of the present research, an intrinsic mechanism may be much more important for thermotransport in metallic systems than has been previously thought. Because there has been very little previous investigation of thermotransport in ternary systems, the results of the present alloy studies also represent particularly interesting new information. Finally, the results of these three studies clearly indicate that isotope effects in the heat of transport do occur and must, therefore, be explained in any acceptable atomistic model for thermotransport.

As is often the case in scientific investigation, the present research has suggested other studies which might offer further insight into the

problem of thermotransport in metals. There is need for additional diffusion measurements to provide activation energies for comparison with Q^* results. It may also be useful to investigate the concentration dependence of Q^* in systems where the activation energy for diffusion is known to be concentration dependent. Examples of such systems are diffusion of hydrogen in tantalum (35) and in vanadium-titanium alloys (36). Measurements of the thermoelectric power in niobium-tantalum alloys might help to establish whether the biasing of atomic jumps in tantalum is caused by an electronic mechanism. Some of the proposed electronic mechanisms for thermotransport (31, 32) predict that the heat of transport should be closely related to the thermoelectric power. Also, additional measurements of Q^* are needed since the total number of thermotransport studies in metallic systems is still relatively small. Finally, there is the somewhat more general problem of developing a better understanding of the fundamental behavior of solutes in metals. Even if variations in Q^* can be correlated with variations in ΔH , an atomistic explanation for these variations remains to be determined.

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