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Thermophysical Properties of Molybdenum and Rhenium

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Thermophysical properties measurements have been made on the metals molybdenum and rhenium at high temperatures and a pressure of 0.2 GPa. These measured properties include volume, temperature, enthalpy, and electrical resistivity. Values for these quantities are shown for both solid and liquid phases. In addition, sound velocities were measured for liquid molybdenum.

KEY WORDS: density; electrical resistivity; enthalpy; molybdenum; pulse heating technique; rhenium; sound velocity.

1. INTRODUCTION

The measurement of thermophysical properties of metals at high temperatures (>2000 K) is typically done using dynamic techniques because of the difficulties inherent in performing these measurements statically. Such dynamic techniques have been described for several time regimes [1–3].

Properties of metals at high temperatures are useful for many reasons, including applications in which metals are subjected to high-temperature/high-pressure conditions, and for modeling and basic theory. Data on liquid molybdenum and rhenium are sparse, and it appears that further work on these materials is warranted.

We use an isobaric expansion technique (IEX) in which wire-shaped samples are resistively pulse heated in a high-pressure inert gas atmosphere. Experiments are performed in a high-pressure vessel capable of being pressurized up to 1 GPa with helium or argon gas. An inert gas medium is chosen to minimize reaction between the hot liquid metals and the pressure medium. Experiments are performed at high pressure to suppress boiling and allow higher-temperature states to be accessed.

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We report here measurements of sound velocity, enthalpy, density, temperature, and electrical resistivity for solid and liquid molybdenum up to 5243 K and all the above properties except sound velocity for liquid rhenium up to 5725 K.

2. EXPERIMENTAL DETAILS

Samples were taken from 0.75-mm-diameter wire stock, were highly polished, and were approximately 25 mm in length. For molybdenum samples, density was taken as $10.22\,\mathrm{g \cdot cm^{-3}}$, with a purity of 99.97%; for rhenium samples, initial density was $21.04\,\mathrm{g \cdot cm^{-3}}$ and purity was 99.99%.

Our experimental apparatus has been described in detail previously [4]. Briefly, this apparatus consists of a high-pressure vessel, gas-pumping equipment, and a high-energy capacitor bank (50 kJ at 20 kV) to provide heating current. This capacitor bank provides a close approximation to a square current pulse with rise and fall times of $\sim 5\,\mu$s, with adjustable pulse length and amplitude adjustable up to 20 kA. Current through the sample is measured using a high-precision current probe, and voltage along the sample measured using a high-impedance shunt circuit in conjunction with a current transformer. Voltage is measured along a sample length defined by two contacting probes. This length is accurately measured before each experiment. From the currents and voltages, enthalpies are calculated using room temperature and 0.2 GPa as the reference state with ±2% accuracy.

Volumes are measured with a shadowgraph system using an argon-ion laser to backlight the samples. This shadow is imaged onto a slit, which in turn is viewed by an image-converter streaking camera. Volumes are found directly by measuring the resulting streak photograph with ±4% accuracy.

Sound velocities in molybdenum samples were measured (±5%) using a noncontacting method described previously [4]. A ruby laser is focused on one spot on the sample, producing an acoustic disturbance, and a shadowgraph technique is used to detect the arrival on the side opposite the source. From the measured average transit time through the sample and the known sample diameter, the average sound velocity through the sample may be calculated.

Temperatures are measured using an optical pyrometer of our own design. Self-radiation from the sample is collected and imaged onto fast PIN photodetectors. Each photodetector channel has an interference filter to select a specific wavelength band to be observed. Results at several wavelengths are in good internal agreement, so here we report results from the channel with central wavelength maximum at $\lambda = 700$ nm. Both molybdenum and rhenium have melting points that are in our detectable range, and so the thermal arrest point is used as a tie point in our temperature calculations. Temperatures are found from measured intensities by forming ratios of intensity at arbitrary points to the intensity at melt. If $I(\lambda, T)$ is the measured intensity from the pyrometer, and $I(\lambda, T_m)$ is the intensity at melt, then

$$\frac{I(\lambda, T_m)}{I(\lambda, T)} = \frac{\varepsilon(\lambda, T_m)}{\varepsilon(\lambda, T)} \frac{\exp(c/\lambda T_m) - 1}{\exp(c/\lambda T) - 1} \tag{1}$$

In this equation $\varepsilon(\lambda, T)$ is the emissivity, $\varepsilon(\lambda, T_m)$ is the emissivity at melt, and c is the second Planck radiation constant, taken to be 14,388 μm · K. To use Eq. (1) to solve for temperature, T, it is common to take $\varepsilon(\lambda, T_m) = \varepsilon(\lambda, T)$. Recent work by Hansen et al. [5] shows that for molybdenum, this assumption may not cause serious error. Their data on $\varepsilon(\lambda, T)$ for molybdenum over the temperature range 1500–2500 K show a very slowly changing, almost-constant, emissivity at $\lambda = 633$ nm. Similar data for rhenium have not been found.

3. RESULTS ON MOLYBDENUM

Our results for the thermophysical properties of solid and liquid molybdenum are given in Table I.

Table I. Measured Thermophysical Properties of Solid and Liquid Molybdenum

H (MJ · kg^{-1})	T (K)	V/V_0[a]	ρ_{el} ($\mu\Omega \cdot$ m)
0.5	1917	1.035	0.536
0.6	2167	1.041	0.625
0.7	2417	1.048	0.695
0.8	2668	1.052	0.762
0.912 (s)	2896	1.065	0.838
1.290 (l)	2896	1.093	0.988
1.4	3143	1.106	0.999
1.5	3353	1.117	1.012
1.6	3563	1.134	1.026
1.7	3773	1.147	1.050
1.8	3983	1.163	1.062
1.9	4193	1.179	1.075
2.0	4403	1.195	1.094
2.1	4613	1.210	1.111
2.2	4823	1.227	1.130
2.3	5033	1.249	1.170
2.4	5243	—	—

[a] $V_0 = 9.803 \times 10^{-5}$ m^3 · kg^{-1}.

3.1. Temperature

Measured values of enthalpy are shown plotted against temperature in Fig. 1. The best fit for the solid phase is given by

$$H = -2.289 \times 10^{-2} + 1.795 \times 10^{-4}\, T + 4.916 \times 10^{-8}\, T^2 \qquad (2)$$

where H is in $\mathrm{MJ \cdot kg^{-1}}$ and $1917 \leqslant T \leqslant 2896$ K.

The least-squares fit for our data in the liquid phase is

$$H = -9.0244 \times 10^{-2} + 4.748 \times 10^{-4}\, T \qquad (3)$$

for $2896 \leqslant T \leqslant 5243$ K.

Our solid-phase data compare favorably to the values of Betz et al. [6], some of whose data are shown in Fig. 1. In the liquid phase our fit yields a constant value of specific heat at constant pressure of $C_p = 475\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. The review paper by Guillermet [7] lists other measured values of C_p for liquid Mo, and our value compares well with his recommended value of $444.4\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. In addition, Pottlacher et al. [8] have recently performed measurements that yield a value of $560\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$. In Fig. 1 we also show the data of Betz et al. [6], which agree well with our results.

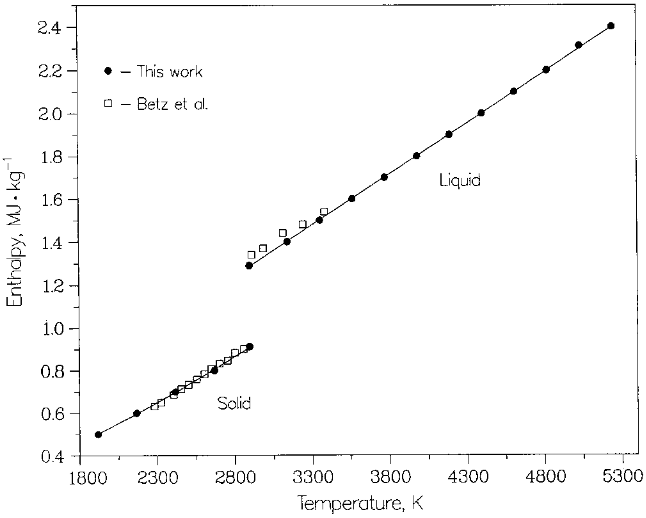

Fig. 1. Enthalpy as a function of temperature for solid and liquid molybdenum.

3.2. Volume

The best fit to our volume data in the solid phase is given by

$$V/V_0 = 1.0304 - 2.2302 \times 10^{-2} H + 6.5076 \times 10^{-2} H^2 \quad (4)$$

for $0.5 \leqslant H \leqslant 0.912$ MJ · kg^{-1}. Our data in the liquid phase is best fit by

$$V/V_0 = 0.9919 + 3.5537 \times 10^{-2} H + 3.2828 \times 10^{-2} H^2 \quad (5)$$

where $1.29 \leqslant H \leqslant 2.3$ MJ · kg^{-1}. This fit is shown in Fig. 2 along with the data of Shaner et al. [9]. Agreement is good, well within error bars.

3.3. Electrical Resistivity

We calculate volume-corrected electrical resistivities from other measured quantities from

$$\rho_e(t) = \frac{V(t)\,A(t)}{I(t)\,l} \quad (6)$$

Here $V(t)$ is our measured voltage along a known length of sample l, $I(t)$ is the measured current through the sample, and $A(t)$ is the time-dependent cross-sectional area of the sample. Results of these calculations for electrical

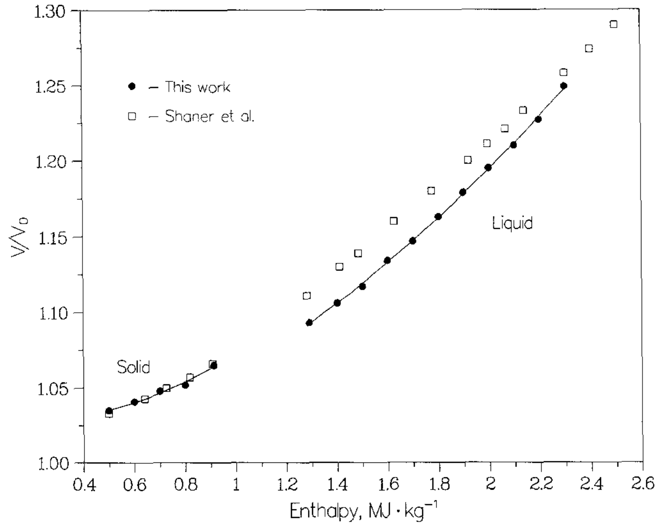

Fig. 2. Volume ratio V/V_0 for solid and liquid molybdenum plotted versus enthalpy, where $V_0 = 9.803 \times 10^{-5}$ m^3 · kg^{-1}.

resistivity are shown plotted in Fig. 3. We show the solid data of Cezairliyan et al. [10] and Shaner et al. [9] and the liquid data of Shaner et al. [9]. We also show the liquid data of Pottlacher et al. [8]. The agreement is reasonably good, except for the highest temperature data of Pottlacher et al. [8]. All results shown in Fig. 3 are volume corrected except that of Cezairliyan [10].

The best fit to our data for ρ_e is

$$\rho_{el} = 3.8101 \times 10^{-2} + 1.1525\,H - 0.3041\,H^2 \tag{7}$$

for $0.5 \leqslant H \leqslant 0.912\ \mathrm{MJ \cdot kg^{-1}}$ in the solid phase with ρ_{el} in $\mu\Omega \cdot \mathrm{m}$. Similarly in the liquid phase we find a best fit of

$$\rho_{el} = 0.9775 - 8.1503 \times 10^{-2}\,H + 7.0599 \times 10^{-2}\,H^2 \tag{8}$$

for $1.29 \leqslant H \leqslant 2.3\ \mathrm{MJ \cdot kg^{-1}}$. The fit in the liquid phase is quadratic, but as seen in Fig. 3, relatively little variation in ρ_{el} is observed.

3.4. Sound Velocity

Sound velocities were measured only for the liquid phase of molybdenum. Our measured values are shown in Fig. 4 plotted versus density. The best fit to these data is

$$C = 0.8537\,\rho - 3.3241 \tag{9}$$

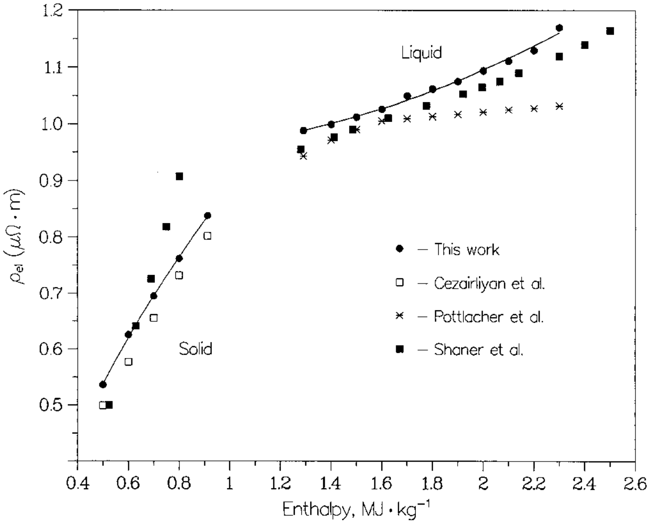

Fig. 3. Electrical resistivities for solid and liquid molybdenum.

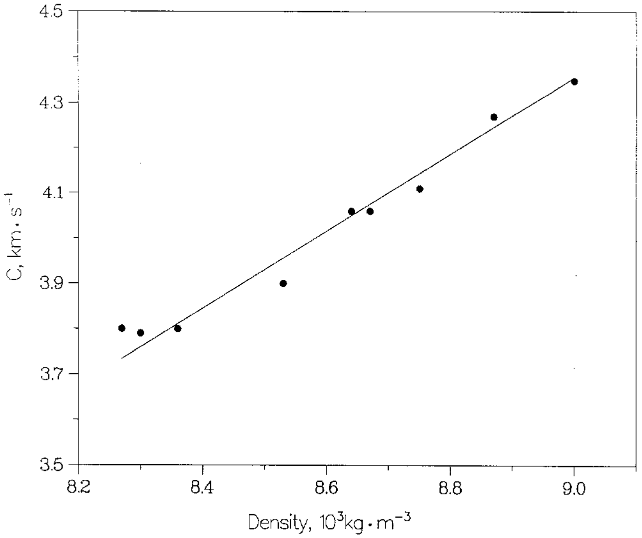

Fig. 4. Measured sound velocities for liquid molybdenum. No literature values were found for comparison.

where ρ is in $g \cdot cm^{-3}$ and C is in $km \cdot s^{-1}$. No literature values for sound velocities in molybdenum at these conditions were found. Estimated uncertainties for sound velocities are $\pm 5\%$.

4. RESULTS ON RHENIUM

Data have been taken on solid and liquid rhenium up to 5725 K using the same techniques applied to molybdenum, but with no sound speeds measured. Our data are compared primarily with the results of Pottlacher et al. [11]. Results are shown in Table II.

4.1. Temperature

We show our measured values of enthalpy plotted versus temperature in Fig. 5 for both the solid and the liquid phases. Shown for comparison is the fit of Pottlacher et al. [11] in the liquid phase. The best fit to our solid data is given by

$$H = -0.1972 + 2.260 \times 10^{-4}\, T \qquad (10)$$

with $2427 \leqslant T \leqslant 3453$ K and H in $MJ \cdot kg^{-1}$. Our liquid data are best fit by

$$H = -0.1253 + 2.670 \times 10^{-4}\, T \qquad (11)$$

Table II. Measured Thermophysical Properties of Solid and Liquid Rhenium

H (MJ·kg^{-1})	T (K)	V/V_0[a]	ρ_{el} ($\mu\Omega\cdot$m)
0.35	2427	1.047	1.289
0.40	2684	1.053	1.337
0.45	2879	1.059	1.386
0.50	3090	1.067	1.396
0.55	3321	1.074	1.431
0.615 (s)	3453	1.081	1.451
0.768 (l)	3453	1.125	1.457
0.80	3535	1.133	1.485
0.85	3699	1.141	1.469
0.90	3840	1.154	1.477
0.95	4042	1.167	1.476
1.00	4216	1.185	1.490
1.05	4386	1.204	1.524
1.10	4605	1.219	1.523
1.15	4800	1.230	1.510
1.20	4977	1.241	1.534
1.25	5180	1.249	1.534
1.30	5350	1.255	1.549
1.35	5569	1.264	1.577
1.40	5725	1.280	1.585

[a] $V_0 = 4.757 \times 10^{-5}$ m^3·kg^{-1}.

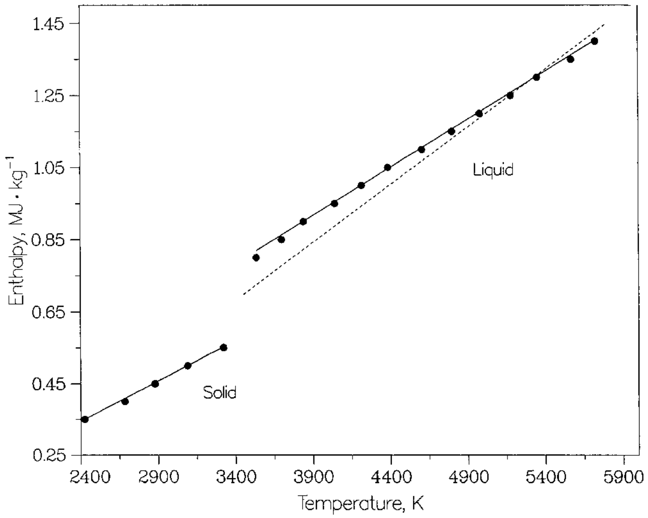

Fig. 5. Enthalpies for solid and liquid rhenium plotted against temperature. The liquid fit of Pottlacher et al. [11] is shown as a dashed line.

for $3453 \leqslant T \leqslant 5725$ K. These fits imply a value of C_p of $226\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ for the solid phase and $267\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$ for the liquid phase. The liquid data of Pottlacher et al. [11] give a value of C_p of $250\ \mathrm{J \cdot kg^{-1} \cdot K^{-1}}$, in close agreement with our result. The recommended value of Hultgren et al. [12] is $225\ \mathrm{J \cdot kg^{-1} \cdot K}$. Our measured enthalpy of fusion is $\Delta H = H_l - H_s = 0.768 - 0.615 = 0.153\ \mathrm{MJ \cdot kg^{-1}}$.

Volumes have been measured for rhenium using our shadowgraph technique. The least-squares fit to our solid data is

$$V/V_0 = 1.0005 + 0.1318\, H \tag{12}$$

for $0.35 \leqslant H \leqslant 0.615\ \mathrm{MJ \cdot kg^{-1}}$. Our liquid results are

$$V/V_0 = 0.9344 + 0.2486\, H \tag{13}$$

for $0.768 \leqslant H \leqslant 1.4\ \mathrm{MJ \cdot kg^{-1}}$. These results are shown in Fig. 6.

4.2. Electrical Resistivity

Our solid-phase results for electrical resistivity (Fig. 7) are best fit by

$$\rho_{el} = 0.7597 + 2.0417\, H - 1.4959\, H^2 \tag{14}$$

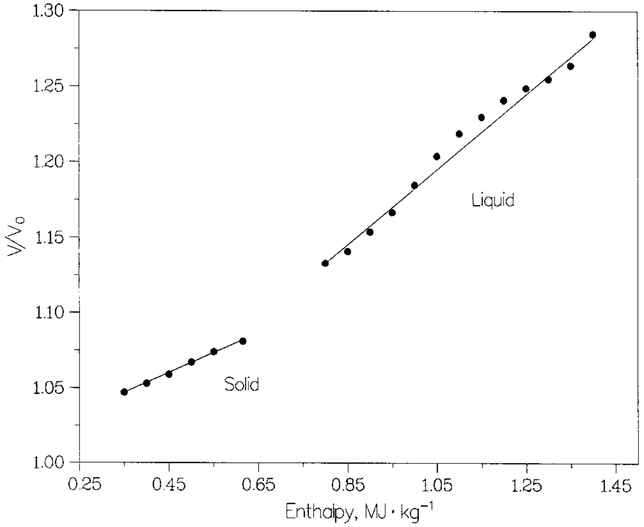

Fig. 6. Volume ratios for solid and liquid rhenium where $V_0 = 4.757 \times 10^{-5}\ \mathrm{m^3 \cdot kg^{-1}}$.

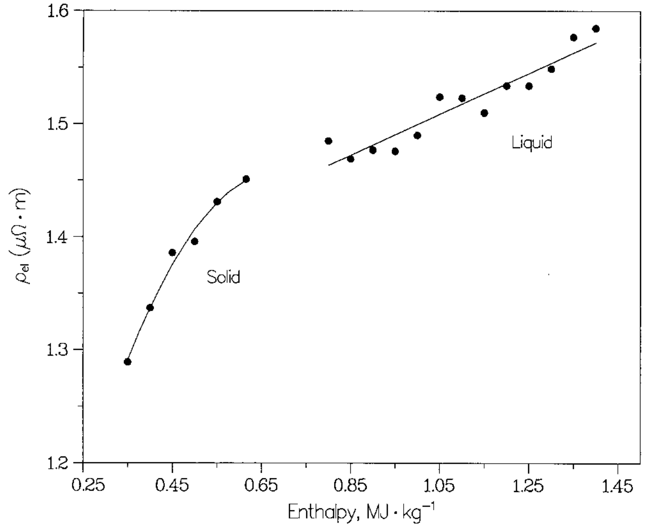

Fig. 7. Electrical resistivities for solid and liquid rhenium.

for $0.35 \leqslant H \leqslant 0.615$ MJ · kg^{-1}, and our liquid results by

$$\rho_{el} = 1.3179 + 0.18162\,H \tag{15}$$

for $0.768 \leqslant H \leqslant 1.4$ MJ · kg · K^{-1}, and with ρ_{el} in $\mu\Omega \cdot$ m. We observe scatter in the liquid resistivities for rhenium, but over a fairly narrow range of values. Additionally, we observe no substantial increase in resistivity upon melting.

5. DISCUSSION

We have measured thermophysical properties of molybdenum and rhenium in the solid and liquid phases with uncertainties quoted in the previous sections. Our measurements are generally in good agreement with values found in the literature. For the solid phase of these two metals, there are many data available for molybdenum, but few for rhenium. In the liquid phase for these metals data are scarce because of their high melting points. Rhenium has a very high melting point, second only to tungsten for metallic elements. We compare reasonably well with other pulse heating results, with the largest differences in the volume measurement. This is to be expected, since these are difficult measurements to make in a fast experiment. Since volumes are used to calculate resistivities, this uncertainty is reflected in the resistivity data as well.

As shown previously by Hixson et al. [13] it is possible to use the measured properties given here to calculate other derivative quantities. These include thermal expansion coefficient, Grüneisen gamma, specific heat at constant volume, and others. We do not show the results of these calculations here.

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