

# Thermophysical data of liquid vanadium

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Available online 14 December 2006

## Abstract

Although vanadium is commonly used as an additive in the steel production, literature data for thermophysical properties of vanadium around the melting point are sparse and show, where available a variation over a wide range. This manifests especially in the melting temperature (variation of  $\pm 30$  K), heat of fusion, or specific enthalpy.

This recent work presents the results of thermophysical measurements on vanadium including normal spectral emissivity at 684.5 nm. The aim was to obtain another full dataset of properties (enthalpy, heat of fusion, electrical resistivity, thermal conductivity, emissivity) of liquid vanadium to either confirm existing recommendations for certain properties or presenting newer measurements for comparison leading towards such recommendations.

Summarizing, the following results for thermophysical properties at the melting point have been obtained: radiance temperature at melting (650 nm)  $T_{r,m} = 1993$  K, melting temperature  $T_m = 2199$  K, normal spectral emissivity at melting (684.5 nm)  $\varepsilon = 0.353$ . An observed feature of all measured data and results is, that a much better agreement with literature references exists for the liquid phase than in the solid state, thus we have restricted the presentation to liquid vanadium.

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*Keywords:* Heat of fusion; Melting temperature; Normal spectral emissivity; Pulse heating; Thermophysical properties; Vanadium

## 1. Introduction

Pure vanadium is a bright white metal with good corrosion resistance to, i.e., alkalis and salt water and is therefore commonly used as an additive in producing rust resistance in springs, and highspeed tool steels, since it is an important carbide stabilizer in making steels [1]. Despite its widespread use as a steel-additive, only few measurements on thermophysical properties of pure vanadium are reported in literature. A good example for this lack of precise data for vanadium is the melting point, which is only known and reported in a temperature range covering values from 2163 to 2223 K (see Table 1 for more details).

At the subsecond thermophysics laboratory in Graz thermophysical properties determinations are performed for many years and vanadium was one of the pure metals which have been investigated recently. The results of pure vanadium are presented within this paper which – by comparison to literature data – should either help to find some recommendations for thermophysical properties or act as an initial point for more or even more accurate measurements on vanadium.

Within this study, thermophysical properties of vanadium like specific enthalpy, electrical resistivity and isobaric heat capacity have been measured under containerless conditions by using a ohmic pulse-heating apparatus whereas the temperature determination combined with normal spectral emissivity measurements have been performed by pyrometry and the use of an ellipsometric approach with  $\mu$ s-resolution. This paper briefly describes the facilities used, presents all data with estimated uncertainties compared to available literature values, and discusses the results for vanadium in the liquid state.

## 2. Experiment setup and data reduction

### 2.1. Pulse-heating setup

The apparatus itself and the specific details on the data reduction used in these measurements have been extensively described elsewhere [10,11], wherefore a detailed description is omitted in this paper. In principle, a wire sample (typically 0.5 mm diameter and 40 mm in length) is clamped between two sets of brass jaws and resistively heated in an inert-gas-filled discharge chamber while the heating current, the sample

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Table 1  
Values for the melting temperature  $T_m$  of pure vanadium from different sources [2–9]

| Source of melting temperature               | $T_m$ (K)      |
|---|----------------|
| Goodfellow Cambridge Limited (supplier) [2] | 2163           |
| Desai [3]                                   | 2202 (IPTS 68) |
| McClure and Cezairliyan [4]                 | 2201 (ITS 90)  |
| Aesar [5]                                   | 2183           |
| Storms and McNeal [6]                       | 2161           |
| Oriani and Jones                            | 2192           |
| Hultgren et al. [8]                         | 2199           |
| Kocherzhinskii et al. [9]                   | 2223           |

Note: The value given by McClure and Cezairliyan [4] is the value from [3] (2202 K) adapted to the ITS 90.

voltage drop, and the surface radiance are recorded. Since the volume of the inert gas is much larger than the volume of the sample it provides not only an isobaric environment but also helps preventing possible electrical discharges and/or contaminations.

The heating current, provided by a capacitor bank, is chosen to allow heating rates of about  $10^8$  K/s which result in an average experimental duration of about 30–60  $\mu$ s per single measurement.

## 2.2. Temperature determination

Temperature measurements are performed with an optical pyrometer operating at 650 nm (FWHM 37 nm) to record the sample surface temperature as a function of experimental duration. Two possible techniques can be applied to obtain the thermodynamic temperature of the sample from its radiance temperature. Either an assumed melting temperature is assigned to the melting plateau in the radiance temperature records to determine the relative emissivity at this point whose value is

assumed to stay constant throughout the liquid state or emissivity and its behaviour is directly measured (see section  $\mu$ s-DOAP) and temperature is calculated from Planck's radiation law and the actual measured emissivity. In this second case, the pyrometer has to be calibrated, e.g. against a tungsten striplamp (see Section 3.2.2).

Both mentioned methods lead to the same results in temperature, if emissivity is actually constant throughout the liquid phase but can lead to erroneously differing results in temperature for the first method if emissivity changes during the liquid state. As results have shown [12], a constant emissivity at 684.5 nm is the exception as almost all materials investigated so far show either an increase or a decrease in emissivity. To overcome this problem, only the latter method was used for determining the actual sample temperature within this work.

## 2.3. $\mu$ s-Division-of-amplitude-photopolarimeter ( $\mu$ s-DOAP)

Normal spectral emissivity at a wavelength of 684.5 nm is directly measured by using a division-of-amplitude-photopolarimeter. The photopolarimeter uses an ellipsometric measurement approach but without any rotating with regard to the timescale used for pulse-heating devices, based on the Stokes formalism for polarized light.

Basically, a polarized laser beam is focused on the surface of the sample wire and the change in polarization of the reflected beam is analyzed. As a result normal spectral emissivity at the given laser wavelength is obtained as a function of experimental direction which is used (as described in Section 2.2) to obtain the sample temperature. For more details on the  $\mu$ s-DOAP and the data reduction used see [13,14].

For easier understanding, a schematic display of the experimental setup including the DOAP can be seen in Fig. 1.

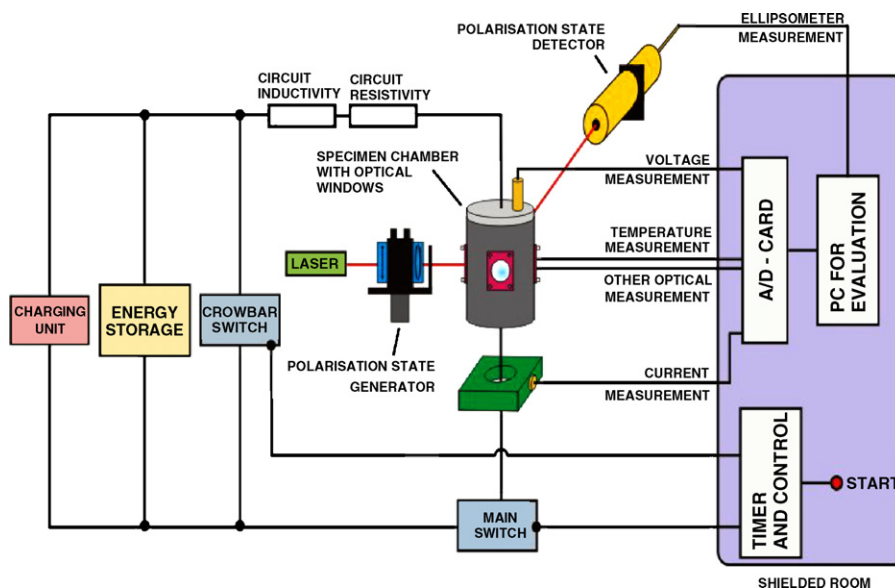


Fig. 1. Schematic overview of the experimental setup in Graz used to obtain thermophysical properties and emissivity of liquid vanadium.

### 3. Experimental data and results

#### 3.1. General information

All measurements reported within this work have been performed on wire shaped vanadium specimens with a diameter  $\varnothing = 0.515$  mm and an average length of about 60 mm total (40 mm active length). The material was purchased by Goodfellow Cambridge Limited with the following specifications – diameter: 0.5 mm, purity: 99.8+%, hardness: as drawn. As can be seen from the numbers above, the actual diameter of the wire differed from the nominal value given by Goodfellow. After surface preparation the diameter was measured again leading to values down to 0.470 mm. According to [15] a density at room temperature of  $6100 \text{ kg m}^{-3}$  has been used for all evaluations.

As mentioned earlier in the introduction section, the melting temperature,  $T_m$ , of vanadium varies strongly throughout the published literature. Wherever it was necessary, we decided to use a value of  $T_m = 2201 \text{ K}$  from [4] which equals the value of [3] ( $2202 \text{ K}$ )<sup>1</sup> but was converted to the ITS-90 by the authors.

All results given within the graphs of the following section represent mean values of different measurements. For thermophysical properties nine independent measurements (with a deviation better than 1% between each of the experiments) have been used to obtain the averaged results. For normal spectral emissivity six independent measurements have been used to obtain the results. Further 17 experiments with varying surface preparation have been performed to enhance the determination of melting-temperature via melting plateaus.

#### 3.2. Experimental data

##### 3.2.1. Normal spectral emissivity (Fig. 2)

The results of the emissivity investigations can be seen in Fig. 2, which shows normal spectral emissivity for vanadium at 684.5 nm at melting and in the liquid state as a function of radiance temperature  $T_r$ . The linear least-squares fit for the liquid phase is

$$\varepsilon(T) = 0.358 - 2.471 \times 10^{-6} T_r, \quad 1997 \text{ K} < T_r < 3300 \text{ K} \quad (1)$$

At the end of melting, this results in an emissivity value of  $\varepsilon(T_m) = 0.353$ .

The plot shows a decrease of emissivity at the melting transition, which is the usual behaviour of metals, related to the smoothening of the surface area due to surface tension (see Section 4). The solid-state value on the other hand does strongly depend on the surface preparation (i.e. grinding) and does in this kind of experimental setup not represent a property of pure vanadium.

##### 3.2.2. Melting temperature

The voltage output at the melting plateau of a pyrometer operating at a centerwavelength of 650 nm has been used in

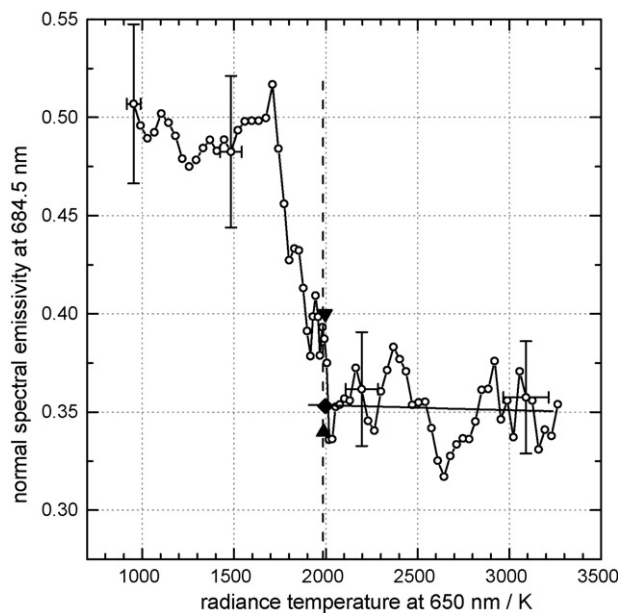


Fig. 2. Normal spectral emissivity at 684.5 nm of vanadium vs. radiance temperature. Open circles: values from this work (mean value of six independent sets of data); solid line: linear least-squares fit for the liquid state; vertical dashed line: radiance temperature at melting (1997 K); up-triangle: literature value from [4] interpolated for 684.5 nm; solid square: reference value at 650 nm taken from [16]; solid down-triangle: value at 650 nm taken from [17].

combination with the normal spectral emissivity value at melting to determine the melting temperature for vanadium. Therefore, the pyrometer was calibrated against a certificated tungsten striplamp (OSRAM WI 17/G) to obtain the so-called *pyrometer-constant* or *calibration-factor*.<sup>2</sup> The radiance temperature of melting at 650 nm was found to be  $T_r = 1993 \text{ K}$ , and as a final result, a melting temperature of  $T_m = 2199 \text{ K}$  was experimentally obtained for vanadium.

##### 3.2.3. Enthalpy and isobaric heat capacity (Fig. 3)

Fig. 3 presents enthalpy at the end of the solid and in the liquid state as a function of temperature obtained with the pulse-heating system. Additionally, enthalpy for solid vanadium in the temperature range from 473.15 to 1573.15 K has also been measured with a DSC (differential scanning calorimeter, Netzsch 404) to show that a combination with a completely different method – related to the timescale (microsecond-resolution pulse heating versus quasistatic DSC measurement) – is possible.

The linear fit for the liquid state is given by

$$H_l(T) = -503.525 + 0.964T, \quad 2199 \text{ K} < T < 2900 \text{ K} \quad (2)$$

where  $H$  is given in  $\text{kJ kg}^{-1}$ .

At melting we observe  $H_s(T_m) = 1210.4 \text{ kJ kg}^{-1}$  and  $H_l(T_m) = 1616.3 \text{ kJ kg}^{-1}$ ; thus a heat of fusion of  $\Delta H = 405.9 \text{ kJ kg}^{-1}$  is obtained.

<sup>1</sup> Desai [3] did also not measure this value for  $T_m = 2202 \text{ K}$  himself, but converted the value recommended in [7] (2199) to the ITPS-68.

<sup>2</sup> The name pyrometer-constant is misleading, as the calibration-factor is not constant but varies with temperature, which is mostly caused by the temperature dependence of the mean effective wavelength of the pyrometer.

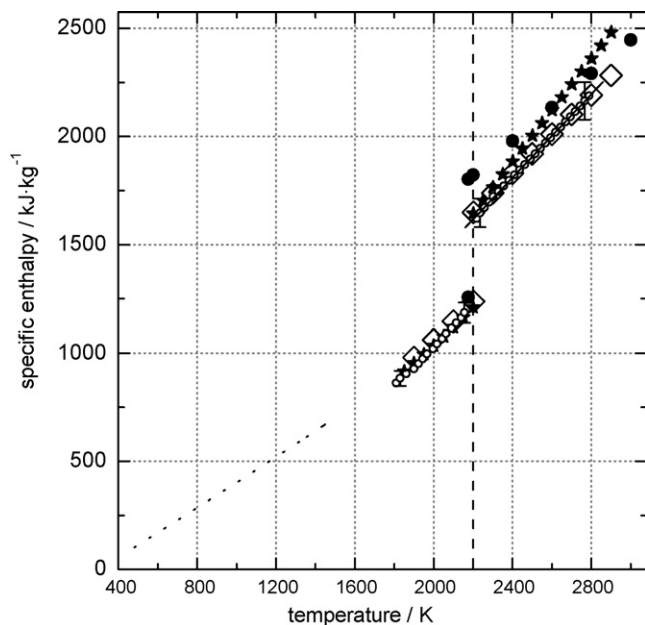


Fig. 3. Specific enthalpy of vanadium as a function of temperature. Open circles: values taken from measurement number 15 (see Fig. 6); solid line: linear least-squares fits to measured values obtained by pulseheating; dotted line: second order polynomial fit to DSC measurements; vertical dashed line: melting temperature (2199 K); full stars: literature values from [18]; open squares: reference values from [3]; solid circles: values from [19].

The values for isobaric heat capacity is obtained from the slope of the linear fit given in Eq. (2). A constant value of  $c_{p,l} = 964 \text{ J kg}^{-1} \text{ K}^{-1}$  can be reported for the liquid phase.

### 3.2.4. Electrical resistivity (Fig. 4)

Fig. 4 shows the results for specific electrical resistivity,  $\rho$ , both with initial room temperature geometry and resistivity including volume expansion in the liquid state. The volume expansion for vanadium in the liquid state used for evaluation has been taken from [20], although [18] gives values for both the solid and the liquid states. The values in the latter publication have been measured under initial pressure of 0.3 GPa and thus, according to the authors, tend to higher values.

The second order polynomial fit for electrical resistivity with initial geometry in the liquid state is ( $\rho_{IG}$  in  $\mu\Omega \text{ m}$ ):

$$\rho_{IG,l}(T) = 1.486 - 2.305 \times 10^{-4} T + 5.188 \times 10^{-8} T^2, \quad 2199 \text{ K} < T < 2900 \text{ K} \quad (3a)$$

The second order fit for electrical resistivity including volume expansion from [20] is given by ( $\rho$  in  $\mu\Omega \text{ m}$ ):

$$\rho_l(T) = 1.417 - 1.781 \times 10^{-4} T + 6.740 \times 10^{-8} T^2, \quad 2199 \text{ K} < T < 2900 \text{ K} \quad (4a)$$

The resistivity at the initial room temperature geometry at the onset of melting is  $\rho_{IG,s}(T_m) = 1.195 \mu\Omega \text{ m}$ , at the end of melting  $\rho_{IG,l}(T_m) = 1.230 \mu\Omega \text{ m}$ , which gives – after including thermal expansion – values of  $\rho_s(T_m) = 1.277 \mu\Omega \text{ m}$  (expansion at melting onset taken from [18]) and  $\rho_l(T_m) = 1.352 \mu\Omega \text{ m}$ , respectively.

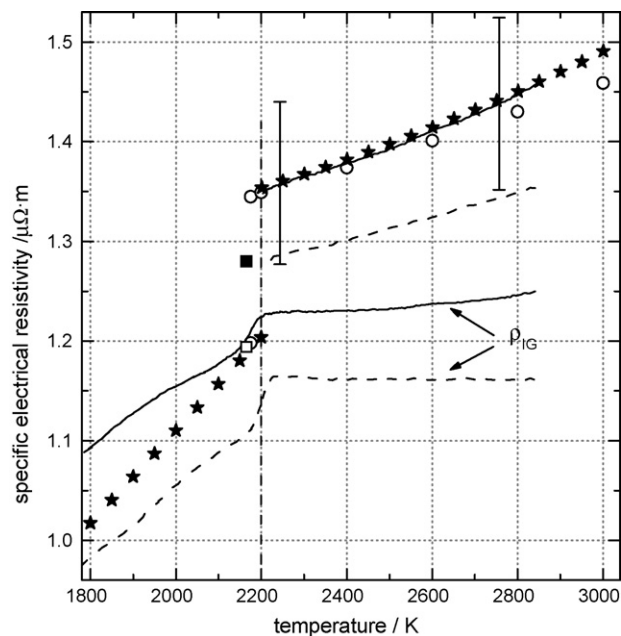


Fig. 4. Specific electrical resistivity with initial room temperature geometry ( $\rho_{IG}$ ) and including thermal expansion as a function of temperature. Solid lines: measured values; dashed lines: values obtained after strong grinding; vertical dashed line: melting temperature (2199 K); full square: resistivity value at the melting onset including expansion; open square: resistivity value at the melting onset including expansion after strong grinding; full stars: literature values from [18]; open circles: reference values taken from [19].

In the measurements, performed to obtain flat plateaus in the pyrometer signals, the vanadium wire was treated with abrasive paper (grain 1200). This changed the surface and it caused a significant drop of electrical resistivity. Hence we provide a second set of values, belonging to strongly ground vanadium wire.

The second order polynomial fit for electrical resistivity with initial geometry in the liquid state is ( $\rho_{IG}$  in  $\mu\Omega \text{ m}$ ):

$$\rho_{IG,l}(T) = 1.244 - 6.020 \times 10^{-5} T + 1.098 \times 10^{-8} T^2, \quad 2199 \text{ K} < T < 2900 \text{ K} \quad (3b)$$

The second order fit for electrical resistivity including volume expansion from [20] is given by ( $\rho$  in  $\mu\Omega \text{ m}$ ):

$$\rho_l(T) = 1.172 + 6.225 \times 10^{-7} T + 2.234 \times 10^{-8} T^2, \quad 2199 \text{ K} < T < 2900 \text{ K} \quad (4b)$$

The resistivity at the initial room temperature geometry at the onset of melting is  $\rho_{IG,s}(T_m) = 1.117 \mu\Omega \text{ m}$ , at the end of melting  $\rho_{IG,l}(T_m) = 1.165 \mu\Omega \text{ m}$ , which gives – after including thermal expansion – values of  $\rho_s(T_m) = 1.194 \mu\Omega \text{ m}$  (expansion at melting onset taken from [18]) and  $\rho_l(T_m) = 1.282 \mu\Omega \text{ m}$ , respectively.

Calculations of thermal conductivity and thermal diffusivity are done with the values described in (3a) and (4a), for which the wire has not been modified.

### 3.2.5. Thermal conductivity and thermal diffusivity

Thermal conductivity ( $\lambda$  in  $\text{W K}^{-1} \text{ m}^{-1}$ ) and thermal diffusivity ( $a$  in  $\times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ ) of vanadium in the liquid state are

Table 2  
Tabular presentation of the thermophysical properties presented within this work in fits at melting and in the liquid state

| Temperature (K) | Thermophysical property    |                              |                         |  |   |
|-----------------|----------------------------|------------------------------|-------------------------|--|---|
|                 | $H$ (kJ kg <sup>-1</sup> ) | $\rho_{IG}$ ( $\mu\Omega$ m) | $\rho$ ( $\mu\Omega$ m) | $\lambda$ (W K <sup>-1</sup> m <sup>-1</sup> ) | $a$ ( $\times 10^{-5}$ m <sup>2</sup> s <sup>-1</sup> ) |
| 2199 (s)        | 1210.4                     | 1.195                        | 1.277                   | 41.35  | 0.752   |
| 2199 (l)        | 1616.3                     | 1.230                        | 1.351                   | 39.08  | 0.819   |
| 2250            | 1665.5                     | 1.230                        | 1.358                   | 39.80  | 0.837   |
| 2300            | 1713.7                     | 1.230                        | 1.364                   | 40.49  | 0.855   |
| 2350            | 1761.9                     | 1.231                        | 1.371                   | 41.17  | 0.873   |
| 2400            | 1810.1                     | 1.231                        | 1.378                   | 41.82  | 0.891   |
| 2450            | 1858.3                     | 1.233                        | 1.386                   | 42.46  | 0.909   |
| 2500            | 1906.5                     | 1.234                        | 1.393                   | 43.08  | 0.927   |
| 2600            | 1954.7                     | 1.235                        | 1.401                   | 44.26  | 0.944   |
| 2650            | 2002.9                     | 1.237                        | 1.410                   | 44.83  | 0.961   |
| 2700            | 2051.1                     | 1.239                        | 1.419                   | 45.37  | 0.978   |
| 2750            | 2099.3                     | 1.242                        | 1.428                   | 45.91  | 0.994   |
| 2800            | 2147.5                     | 1.244                        | 1.437                   | 46.42  | 1.011   |
| 2850            | 2195.7                     | 1.247                        | 1.447                   | 46.91  | 1.027   |
| 2900            | 2243.9                     | 1.250                        | 1.457                   | 47.39  | 1.043   |

$H$ : specific enthalpy;  $\rho_{IG}$ : electrical resistivity with initial geometry;  $\rho$ : electrical resistivity including thermal expansion;  $\lambda$ : thermal conductivity;  $a$ : thermal diffusivity.

not shown in a separate graph as the behaviour is strictly polynomial and shows no important features for both properties. For evaluation of  $\lambda$  via the Wiedemann–Franz–Lorentz relation a value of  $2.45 \times 10^{-8}$  V<sup>2</sup> K<sup>-2</sup> [21] has been used for the Lorentz number  $L$ . Measurements of  $L$  reported in [22] approve, that this theoretical value is applicable to vanadium at high temperatures. The second order fits for the liquid state are represented by

$$\lambda_1(T) = -9.680 + 0.030 T - 3.559 \times 10^{-6} T^2, \\ 2199 \text{ K} < T < 2900 \text{ K} \quad (5)$$

and

$$a_1(T) = -2.190 \times 10^{-6} + 5.686 \times 10^{-9} T - 4.416 \times 10^{-13} T^2, \\ 2199 \text{ K} < T < 2900 \text{ K} \quad (6)$$

Thermal conductivity at the end of melting gives a value of  $\lambda_s(T_m) = 40.0$  W K<sup>-1</sup> m<sup>-1</sup>, and thermal diffusivity a value of  $a_1(T_m) = 0.82 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup>, respectively.

The collected results presented as linear or polynomial fits within this section are explicitly given in steps of 50 K in Table 2.

#### 4. Discussion

The most interesting fact for all measurement results is, that the values in the liquid state are in much better agreement with values presented in various literature references than the solid state values. This is believed to originate from the fact that vanadium starts to oxidize at 660 °C (~933 K) [1] which actually causes some difficulties with accurate voltage measurements as an oxidized surface can lead to changing voltage signals due to different electrical resistance and contact resistivity. Oxidation of the samples was favored by the fact, that only a mixture of nitrogen and air has been used as inert-gas atmosphere, since pure nitrogen caused even more experimental difficulties. This problem could probably be overcome by using argon as inert-gas, which was not available at the time of the experiments but

is expected to work well in combination with vanadium, as can be seen from the DSC measurements.

##### 4.1. Normal spectral emissivity

Most pure metals show a sudden decrease in emissivity at the onset of melting. This drop stops at the end of the melting transition and passes into the liquid phase behaviour of emissivity which could be either increasing, constant, or decreasing [12]. This drop is most likely caused by a smoothening of the surface upon melting which results in a higher reflectance and thus a lower emissivity of the surface (Kirchhoff's law).

Some hundred degrees (~200 K) before the melting onset, normal spectral emissivity at 684.5 nm of vanadium starts to drop (as can nicely be seen from Fig. 2) but shows two intermediate breakpoints before it reaches the actual melting temperature. A similar behaviour was found for zirconium [23] and was interpreted as a mixture of sample impurities and an oxide layer (with a higher melting temperature) floating on the liquid metal obstructing the actual liquid sample surface. For zirconium, it took a couple hundred degrees of overheating until the oxide layer disappeared (due to combustion or diffusion) and the pure metal surface was unveiled. This explanation is likely to hold just as well for vanadium, as vanadium tends to readily oxidize above 660 °C (see remark above). After reaching the liquid state, vanadium shows a very slight decrease in normal spectral emissivity. The liquid state has been approximated by a linear least-squares fit and based on this fit, the value of emissivity at 684.5 nm at the melting temperature  $\varepsilon = 0.353$  is obtained.

Although there is some scattering in the emissivity values at melting and two reference values have been determined at 650 nm, our recently obtained result fits quite good the already established data. Interestingly, the absolute value obtained by [17] at 650 nm coincides exactly with the second breakpoint during the emissivity-drop at melting, as mentioned before. Probably, this value of [17] also originates from an oxide layer

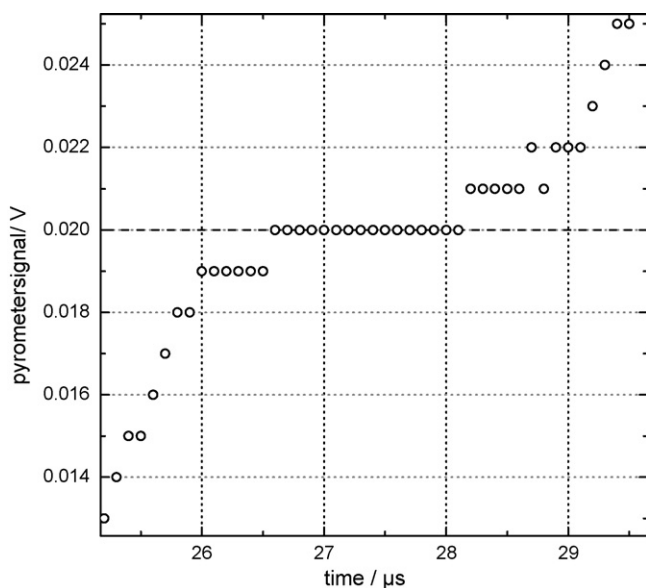


Fig. 5. Pyrometer signal vs. time for a single experiment. Horizontal dashed line: melting plateau in signal delivers 0.020 V. The discrete resolution of the digitized pyrometer signal can already be seen in the trace of the melting signal.

covering the liquid metal. If this applies, it would be much better for further experiments on vanadium to either pre-heat the sample in an inert-gas atmosphere before the experiment or to use the solidification plateau of the cooling curve in an inert-gas to avoid oxide layers and to obtain better emissivity values at melting.

During the last years, it was believed that a connection between emissivity and electrical resistivity with initial geometry similar to the Hagen–Rubens relation ( $\varepsilon \propto f(\rho)$ ) [24] for the mid-IR might exist. Recent results, like vanadium, show that liquid phase behaviour of emissivity cannot be guessed from the resistivity behaviour and a Hagen–Rubens presumption is not applicable for the visible spectra, as, i.e.,  $\varepsilon$  and  $\rho_{IG}$  (see Fig. 4) show opposite trends throughout the liquid state.

#### 4.2. Melting temperature

Values for the melting temperature of vanadium show a broad scattering (see Table 1). Even in the comprehensive list of ITS-90 secondary reference points [25] only radiance temperatures but no direct value for  $T_m$  of vanadium are given. The melting temperature determined within this work was obtained – as described above – from the signal output of a calibrated pyrometer at the melting plateau and the directly measured emissivity. For more accuracy, the signals from all 17 experiments have been independently used to calculate  $T_m$  (see Figs. 5 and 6). With laborious surface preparations it was possible to get flat signal plateaus. As the obtained values did not differ from values obtained with not perfectly flat plateaus all 17 measurements were used to calculate the average. Fig. 6 also depicts a comparison to literature data.

The melting temperature of  $T_m = 2199$  K is found within the uncertainty range, in good agreement with the value recommended by [3] and adopted to ITS-90 by [4]. Nevertheless,

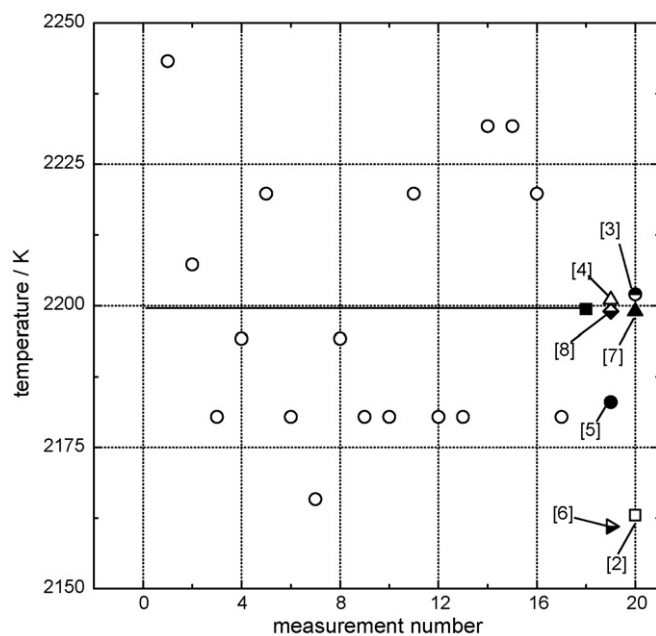


Fig. 6. Evaluated melting-temperatures of single measurements. Solid line and filled square: average of 17 measurements (2199 K); open square: reference value from [2]; half-filled circle: value from [3]; open triangle: [4]; filled circle: [5]; half-filled triangle: [6]; filled triangle: [7]; half-filled diamond: [8].

more accurate measurements should be performed to approve the value of  $T_m$  for vanadium.

To go further into the details, Fig. 5 shows a single experiment. This gives information about the time scale and the digitalization process.

#### 4.3. Specific enthalpy

As already stated in the general remarks at the beginning of this section, thermophysical properties for vanadium measured within this work show a much better agreement in the liquid state than in the solid phase. This is especially true for electrical resistivity in the solid.

The averaging of several results containing slightly differing melting plateaus leads to a not perfect vertical course of enthalpy at  $T_m$ . Therefore a measurement with perfect melting plateau was used to obtain correct values in the region of  $T_m$  (see Fig. 3).

The obtained isobaric heat capacity (in the liquid phase) of  $c_{p,l} = 964$  J kg<sup>-1</sup> K<sup>-1</sup> delivers the highest value, but is in agreement with literature references, 907 J kg<sup>-1</sup> K<sup>-1</sup> [3], 957.5 J kg<sup>-1</sup> K<sup>-1</sup> [17], 780 J kg<sup>-1</sup> K<sup>-1</sup> [19], and 822 J kg<sup>-1</sup> K<sup>-1</sup> [8].

The heat of fusion  $\Delta H = 405.9$  kJ kg<sup>-1</sup> is in good agreement with literature values, such as 412 kJ kg<sup>-1</sup> [3], 430 kJ kg<sup>-1</sup> [18], 340 kJ kg<sup>-1</sup> [17], or 453 kJ kg<sup>-1</sup> [26]. The low value reported in [17] could originate from an oxide layer as discussed in the emissivity section.

Additionally, enthalpy in the solid state has also been obtained by a DSC technique. The most interesting fact is, that these enthalpy values measured in a high-purity argon inert-gas atmosphere show excellent agreement with the solid state enthalpy values of [3,18].

#### 4.4. Electrical resistivity

Both results for electrical resistivity (with initial geometry and including thermal expansion) suffer from the same problem as described for enthalpy in the solid state. Therefore, the results do almost not compare to the reported literature data from [18] or [19]. The liquid phase electrical resistivity has been calculated by including thermal expansion values from [20] and the obtained results are once again in good agreement with the data reported by [18,19]. As discussed with enthalpy, the increase in resistivity at melting is found to be smaller than the values in literature for the same reasons.

Although the reported results are not reliable in the solid state, the results for enthalpy and electrical resistivity show the validity and reliability of the measured data in the liquid phase.

The additional measurements with strongly ground wire show a lower resistivity. As these measurements have no indication of irregularity, we must conclude, that changing the wire means changing its resistivity. This could on the one hand be the positive effect of removed disturbing oxide layers, but on the other hand it is a very individual specimen preparation that is hard to copy.

Finally there is to say, that the specimen specifications (see Section 3.1) are of great interest for the experimenter and are necessary for reproducibility.

#### 4.5. Thermal conductivity and thermal diffusivity

Thermal conductivity has been calculated by using the W–F–L and furthermore thermal diffusivity is based on the conductivity result. Since  $\rho$  is used during the W–F–L calculations, the present results are only restricted to liquid state of vanadium. Within this work a value of  $\lambda_l(T_m) = 39.0 \text{ W K}^{-1} \text{ m}^{-1}$  is found at the end of the liquid phase. This value is about 9% lower than the recommended value from NPL [27] ( $\lambda_l(T_m) = 43.5 \text{ W K}^{-1} \text{ m}^{-1}$ ), but the recommendation itself is based on only one set of data [28], as high temperature thermal conductivity measurements for pure vanadium are extremely sparse.

The result for thermal diffusivity  $a_l(T_m) = 0.82 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$  is not compared to any literature data, as no appropriate references have been found for the liquid state (solid state values can be found in [29]).

### 5. Conclusion

Within this work, a measured value for the melting temperature, normal spectral emissivity at 684.5 nm, and a complete set of thermophysical properties including uncertainties is presented for vanadium.

Unfortunately, thermophysical properties in the solid state do not compare very well to literature data due to some possible problem with oxidation of the vanadium samples. This fact is also assumed to be a source of ambiguity in published data on vanadium in the temperature range before melting. It still has to be checked if this effect can be suppressed under pulse-heating conditions by using a high-purity argon inert-gas atmosphere.

However, the liquid state properties show excellent agreement with previously published data on vanadium, a fact that consolidates the results. It seems that there are enough published data available now to give some ‘recommendations’ for pure vanadium data in the liquid state.

Normal spectral emissivity for liquid vanadium was found to decrease only slightly during the liquid phase. Since this change in emissivity during the liquid phase is small, all measurements from other authors without consideration of the actual behaviour of emissivity are not expected to differ significantly from values including the directly measured emissivity.

### 6. Estimation of uncertainty

According to the guide to the expression of uncertainty in measurement [30] uncertainties reported here are expanded relative uncertainties with a coverage factor of  $k=2$ . From the directly measured quantities, only the temperature,  $T$  with an uncertainty of 4% should be noted within this section. Excluded from this estimation is the uncertainty for the melting temperature, which is  $\pm 20 \text{ K}$  and therefore smaller than the regular temperature uncertainty due to lower individual deviations of the different signals and a more precise calibration of the pyrometer.

For the calculated thermophysical properties the following uncertainties have been obtained and should be applied: enthalpy  $H$ , 4%; enthalpy of melting  $\Delta H$ , 12%; specific heat capacity  $c_p$ , 8%; specific electrical resistivity with initial geometry  $\rho_{IG}$ , 4%; resistivity considering volume expansion  $\rho_{Vol}$ , 6%; thermal conductivity  $\lambda$ , 12%; thermal diffusivity  $a$ , 16%.

An estimation of uncertainty for normal spectral emissivity,  $\epsilon$ , is performed by determining the signal-to-noise ratio of different individual measurements and by analyzing the reproducibility of different measurements. For investigations on liquid vanadium the signal-to-noise of a single experiment does not exceed 8%. By averaging several different measurements to minimize the noise of the emissivity signals and applying a linear least-squares fit to the liquid phase behaviour of normal spectral emissivity, the uncertainty can be reduced up to a factor of 2, thus yielding an uncertainty of  $\pm 4\%$ . By including the coverage factor of  $k=2$  one obtains a realistic uncertainty for normal spectral emissivity for liquid vanadium of  $\pm 8\%$ , respectively.

### Acknowledgement

This work has been supported by the FFG-ASAP Project ‘Electrical Resistivity Measurement of High Temperature Metallic Melts’ and FWF P15055.

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