Thermophysical properties of rhodium obtained by fast pulse-heating

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Abstract

The so-called *platinum metals* are Ru, Rh, Pd, Os, Ir and Pt. Our workgroup has already published data on Pd, Ir and Pt. The present work will focus on measurements of the thermophysical properties of rhodium, which have been carried out recently. The scarce literature data available emphasize the need for new measurements.

Using a rapid pulse-heating technique, wire-shaped specimens are ohmic-heated by the passage of a large current pulse. This fast heating drives the sample from room temperature up into the liquid phase in typically 50 μs and thus prevents chemical reactions and gravitational distortions. Enthalpy, electrical resistivity and volume expansion can be obtained as a function of temperature. From these results, heat of fusion, heat capacity and change of density can be calculated as a function of temperature. A set of data of the mentioned quantities will be presented and the comparison to literature values will be discussed within this study. Additionally we will contrast the results for rhodium with the respective results for Pd, Ir and Pt.

The conformity of data published decades ago with our new measurements is fairly high. Rhodium does not show unexpected behaviour regarding the comparison to Pd, Ir and Pt.

1. Introduction

The workgroup of Subsecond Thermophysics at TU Graz has a long tradition in performing measurements on metals up to very high temperatures by means of a fast pulse-heating method. Heating rates of typically 10^8 K s^{-1} allow investigations of the liquid phase.

In the course of our collaboration project with the DLR in Cologne, Germany, we have started to recapitulate our measurements and work on those elements which still have not been investigated at our laboratory. One of them is rhodium (Greek, *rhodon*: rose). The colour is associated with many rhodium alloys [1] and its salts give a rosy solution [2]. Wollaston discovered rhodium in the years 1803–1804 in crude platinum ore [3].

The metal is silvery white and at red heat slowly changes in air to the sesquioxide. At higher temperatures it converts back to the element. Rhodium has a higher melting point and lower density than platinum. (T_m: 2236 K [4] density at RT: 12 423 kg m^{-3} [5]). Its major use is as an alloying agent to harden platinum and palladium. Such alloys are used for furnace windings, thermocouple elements, bushings for glass fibre production, electrodes for aircraft spark plugs and laboratory crucibles. It is useful as an electrical contact material as it has a low electrical resistance, a low and stable contact resistance and is highly resistant to corrosion. Plated rhodium, produced by electroplating of evaporation, is exceptionally hard and is used for optical instruments. It has a high reflectance and is hard and durable. Rhodium is also used for jewelry, for decoration and as a catalyst.

2. Experiment and data reduction

The measurements were performed during fast resistive pulse-heating experiments. Herein the electrical energy is stored in a capacitor bank of 500 μF which is then discharged over the sample. Its ohmic resistivity leads to a rapid self-heating. This process is so fast (10^8 K s^{-1}) that the sample maintains its initial position during the transition from room temperature up to the end of the liquid phase where the wire explosion takes place. The experimental duration of such an experiment is typically 50 μs. This has two advantages: on the one hand, the manipulation of the samples can be done without a container—and without any crucible reactions—and, on the

Table 1. Results of the present study given as least squares fits (where applicable) including the temperature range of applicability. (Fits are given in the form $a + bT + cT^2$, where a, b and c are the fitted parameters and T is the temperature.) H: enthalpy, ρ_{IG}: electrical resistivity with initial geometry, ρ: electrical resistivity considering thermal volume expansion, $V(T)\,V_0^{-1}$: volume expansion, λ: thermal conductivity, a: thermal diffusivity. Temperature range for λ and a see section 3.

	Solid state			Liquid state		
	a	b	T range (K)	a	b	T range (K)
H (kJ kg^{-1})	−486.154	0.523	$1950 < T < 2236$	−98.980	0.448	$2236 < T < 3150$
ρ_{IG} ($\mu\Omega$ m)	−0.126	3.085×10^{-4}	$1950 < T < 2236$	0.635	6.975×10^{-5}	$2236 < T < 3150$
ρ ($\mu\Omega$ m)	−0.202	3.617×10^{-4}	$1950 < T < 2236$	0.516	1.680×10^{-4}	$2236 < T < 3150$
$V(T)\,V_0^{-1}$ (1)	0.943	5.994×10^{-5}	$1400 < T < 2236$	0.893	1.055×10^{-4}	$2236 < T < 3500$
	a	b	c	a	b	c
λ (W m^{-1} K^{-1})	157.611	−0.046	7.255×10^{-6}	10.661	0.029	-2.932×10^{-6}
$a \times 10^{-5}$ (m^2 s^{-1})	2.349	-6.157×10^{-4}	1.046×10^{-7}	0.071	6.052×10^{-4}	-3.558×10^{-8}

other hand, chemical reactions like oxidation can be avoided. The surrounding atmosphere in our case was nitrogen with a pressure of 2.3 bar.

Our rhodium samples were purchased from Goodfellow Cambridge Limited. The wire was cut into pieces of about 50 mm length. The diameter was 0.509 mm and the purity 99.9% (lot no. RH005120/9).

In all the measurements *temperature* was determined with pyrometers working at either 1570 nm or 650 nm, selected by interference filters with a bandwidth of 84 nm and 37 nm, respectively. The melting plateau in the temperature records was used to assign the voltage output of the pyrometer to the freezing point of rhodium of 2236 K [4]. Then the temperature was calculated by Planck's radiation law using the assumption of a constant emissivity in the liquid phase. The contribution of a possible change of emissivity throughout the liquid phase is not considered in the uncertainty analysis. This enables the researcher to recalculate temperature and its uncertainty with any supplementary data on emissivity. In our experience the influence thereof on thermophysical data is small [6, 7].

Due to the electronics of the pyrometer used the temperature range is limited from 1000 to 3500 K.

Furthermore *current* was measured with an induction coil and the *voltage drop* along the wire was measured with two molybdenum foil knife-edges directly placed on the wire.

All these quantities were recorded as a function of experimental duration. The simultaneous temperature measurement allows a description of all quantities as a function of temperature, which will be presented subsequently.

During the investigations, two values for a series resistor were used (0.25 and 0.50 Ω), leading to two different heating rates and two different experimental durations (40 and 80 μs).

The two different heating rates have no influence on the *electrical* data obtained (specific enthalpy, specific electrical resistivity and quantities derived from them), but the experimental duration is one of the parameters which has to be optimized in matters of the *optical* measurements.

The *volume expansion* of the wire is measured optically with a CCD camera. Thereby the wire is backlit with a photoflash and a magnified picture is mapped on a multi-channel plate which acts as a fast shutter. This picture is then imaged one by one on the CCD. As the picture rate of this device is limited, a longer experimental duration means
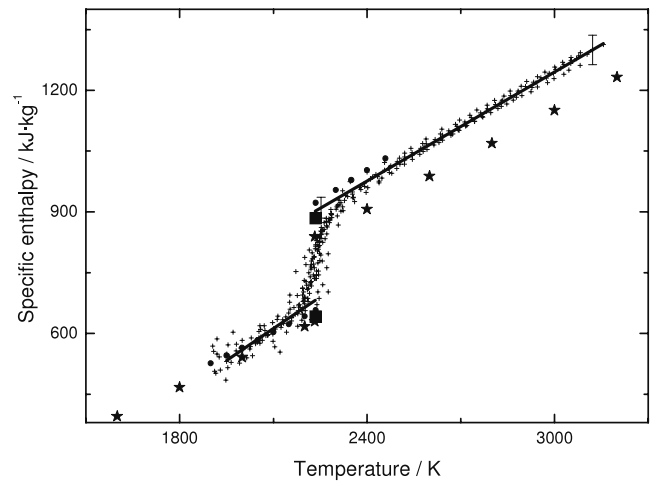

Figure 1. Specific enthalpy of rhodium versus temperature. Crosses: measurement data from the present study, solid lines: linear fits to the data points, filled squares: values of Martynyuk [9], stars: values of Jaeger [10], filled dots: values of Chekhovskoi [11].

more pictures per experiment and consequently an increased accuracy. Therefore two different heating rates have been used.

A detailed description of the apparatus can be found in [8].

3. Results

All the calculations were done with a melting temperature T_m of 2236 K [4] and a density at RT of 12 423 kg m^{-3} [5].

Specific enthalpy, H, given in kJ kg^{-1} is plotted in figure 1 as a function of temperature. It was calculated using the equation

$$H(t) = \frac{1}{m} \int I(t) U(t)\, \mathrm{d}t \tag{1}$$

where m is the mass of the sample, I: current and U: voltage drop. The polynomials for the linear fits are given in table 1. Numerical results are given in table 2. Values at the melting transition: $H_s\,(T_m)$ 683.3 kJ kg^{-1} and $H_l\,(T_m)$ 902.7 kJ kg^{-1}, which deliver a heat of fusion ΔH of 219.4 kJ kg^{-1}.

In figure 1 the enthalpy values at the beginning and at the end of the melting transition measured by Martynyuk are also depicted (ΔH: 242.9 kJ kg^{-1}) [9], as well as literature values

Table 2. Numerical results of the present study. H: enthalpy, ρ_{IG}: electrical resistivity with initial geometry, ρ: electrical resistivity considering thermal volume expansion, $V(T)\,V_0^{-1}$: volume expansion, λ: thermal conductivity, a: thermal diffusivity.

T (K)	H (kJ kg^{-1})	ρ_{IG} ($\mu\Omega$ m)	ρ ($\mu\Omega$ m)	$V(T)V_0^{-1}$ (1)	λ (W m^{-1} K^{-1})	$a \times 10^{-5}$ (m^2 s^{-1})
1950	533.7	0.476	0.503	1.060	95.5	1.55
2000	559.8	0.491	0.521	1.063	94.6	1.54
2050	586.0	0.506	0.539	1.066	93.8	1.53
2100	612.1	0.522	0.558	1.069	93.0	1.51
2150	638.3	0.537	0.576	1.072	92.2	1.51
2200	664.4	0.553	0.594	1.075	91.5	1.50
2236s	683.3	0.564	0.607	1.077	91.0	1.50
2236l	902.7	0.791	0.892	1.129	60.8	1.25
2250	909.0	0.792	0.894	1.130	61.1	1.25
2300	931.4	0.795	0.902	1.136	61.9	1.27
2400	976.2	0.802	0.919	1.146	63.4	1.32
2500	1021.0	0.809	0.936	1.157	64.8	1.36
2600	1065.8	0.816	0.953	1.167	66.2	1.40
2700	1110.6	0.823	0.970	1.178	67.6	1.45
2800	1155.4	0.830	0.986	1.188	68.9	1.49
2900	1200.2	0.837	1.003	1.199	70.1	1.53
3000	1245.0	0.844	1.020	1.210	71.3	1.57
3100	1289.8	0.851	1.037	1.220	72.4	1.61
3150	1312.2	0.855	1.045	1.225	72.9	1.62

of Jaeger [10] and Chekhovskoi [11], which yield a ΔH of 208.9 kJ kg^{-1} and 265.2 kJ kg^{-1}, respectively. Paradis [12] reports a heat of fusion of 223.5 kJ kg^{-1}.

The enthalpy records, as shown in figure 1, show very good agreement in the solid state and at the melting transition. In the liquid phase our values are in between the results of Chekhovskoi [11] and Jaeger [10] (regardless of the fact that Jaeger's values for rhodium are only guiding values in this temperature range). Our heat of fusion outcome matches the result of Paradis best.

This work obtains for *isobaric heat capacity c_p* in the solid state right before melting $c_{p,s}$ 523 J kg^{-1} K^{-1} and in the liquid phase $c_{p,l}$ 448 J kg^{-1} K^{-1} (calculated from the slope of the $H(T)$ curves). Paradis [12] reports 312.9 J kg^{-1} K^{-1} at T_m (liquid phase). The values of Jaeger [10] are 384.0 J kg^{-1} K^{-1} (solid) and 406.7 J kg^{-1} K^{-1} (liquid).

The isobaric heat capacity shows large variations: our value for the solid state is higher than the recommended value of Touloukian [13]. In the liquid state the correlation to Touloukian is better. Values from Paradis [12] for the supercooled liquid are lower.

Figure 2 plots the results for *specific electrical resistivity*, ρ, as a function of temperature. It was calculated using the equation

$$\rho_{IG}(t) = \frac{U(t)\pi r_0^2}{I(t)l} \qquad (2)$$

where r_0 is the sample radius at room temperature and l the length. The average of different measurements was fitted with linear least squares fits. This gives the results for electrical resistivity with initial geometry (index IG). But the volume expansion has to be taken into account to obtain ρ.

According to equation (3), this is achieved via a multiplication of two independent measurements: electrical resistivity (with initial geometry) and thermal expansion (square of the relative change of diameter). As the temperature in this kind of dynamic experiments is a measured
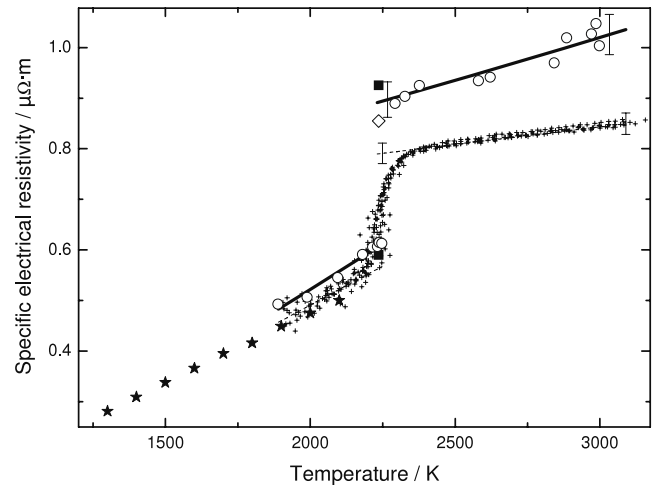

Figure 2. Specific electrical resistivity of rhodium versus temperature. Crosses: measurement data from the present study, dashed lines: linear fits to the specific electrical resistivity with initial geometry (IG), open circles: values including volume expansion, solid lines: linear fits to specific electrical resistivity including volume expansion, filled squares: values of Martynyuk [9], open diamonds: values of Savvatimskii [14], filled stars: values of Filippow [15].

quantity—not an 'applied' one—the experimental points from independent measurements happen to be located at slightly different temperatures. Consequently a multiplication of quantities can only be performed on the basis of fits or interpolations.

To preserve the characteristic distribution of points, which can be used to estimate the quality of the measurement, we combined the fit for electrical resistivity at initial geometry with the data points of thermal expansion. In this way it is also possible to follow the uncertainty contribution of thermal expansion as the basic value for derived quantities. It can be seen in figures 2 and 4 that its influence, though it seems to be
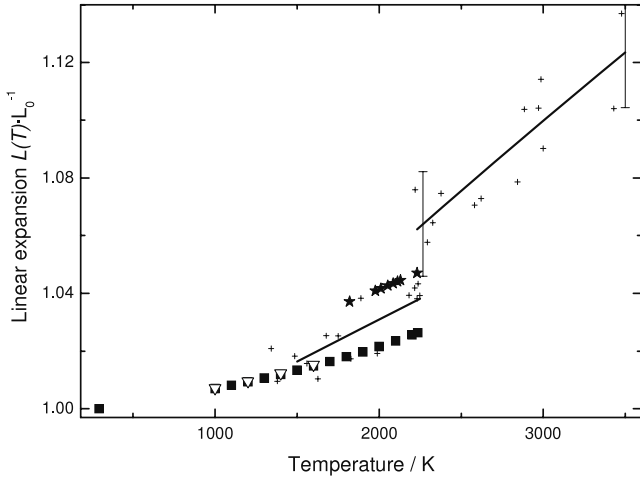
Figure 3. Linear thermal expansion of rhodium versus temperature. Crosses: measurement data from the present study, solid lines: linear fits to the data points, full stars: values of Paradis [12] for supercooled liquid Rh, full squares: values of Arblaster [5], open down triangle: recommended values of Touloukian [13].
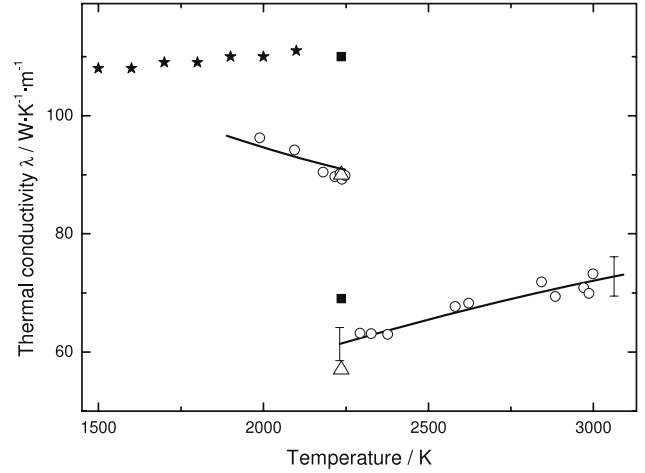

Figure 4. Thermal conductivity of rhodium versus temperature. Open circles: data from the present study, solid lines: fits to the data points, solid squares: value from the NPL report [16], open triangle: values of Vlasov [17], full stars: values of Filippow [15].

a highly scattered measurement with high uncertainty, on the derived quantities is small (GUM vocabulary: its index in the uncertainty budget is small).

The relevant polynomials for ρ are given in table 1. Numerical results are given in table 2. The values at the melting transition are for resistivity with initial geometry: $\rho_{IG,s}$ 0.564 $\mu\Omega$ m and $\rho_{IG,l}$ 0.791 $\mu\Omega$ m and with the volume expansion included: ρ_s 0.607 $\mu\Omega$ m and ρ_l 0.892 $\mu\Omega$ m (an increase of $\Delta\rho_{IG}$ 0.227 $\mu\Omega$ m and $\Delta\rho$ 0.285 $\mu\Omega$ m is observed).

The plot also shows the results of Martynyuk [9] and Savvatimskii [14], who have measured ρ_s: 0.590 $\mu\Omega$ m, ρ_l: 0.925 $\mu\Omega$ m ($\Delta\rho$: 0.335 $\mu\Omega$ m) and ρ_s: 0.610 $\mu\Omega$ m, ρ_l: 0.855 $\mu\Omega$ m ($\Delta\rho$: 0.245 $\mu\Omega$ m), respectively. Filippow [15] did measurements in the solid phase.

The results (see figure 2) do almost coincide when approaching the melting temperature. Our value for ρ_l lies in between the results of Martynyuk [9] and Savvatimskii [14].

To be able to account for the *volume expansion* of the wire it is necessary to know the cross section at a given temperature. This is done via a measurement of the diameter during the heating process as described in section 2. For the comparison to literature values we chose the quantity $L(T)L_0^{-1}$ (length of the sample at temperature T divided by the length at room temperature L_0) and converted each result accordingly (the length in our case is the diameter, shown in figure 3).

Notice that for the calculation of ρ out of ρ_{IG} (see equation (3)) the square of this quantity has to be used. The (squared) data points were fitted linearly, separated into the solid and liquid phase.

These polynomials are given in table 1. Numerical results are given in table 2:

$$\rho(t) = \rho_{IG}(t)\frac{L(t)^2}{L_0^2} \tag{3}$$

where L_0^2 is the diameter at room temperature squared. A conversion from density to $L(T)/L_0$ (which was necessary for the levitation measurements of Paradis [12]) was done using 12 423 kg m^{-3} as the value for density at 293.15 K [5]. Figure 3 compares our measurements to values for the supercooled liquid [12] and to recommended values of Touloukian [13] and values of Arblaster [5] for the solid phase.

In the low temperature regime scattering is high and values of Arblaster [5] and recommended values of Touloukian [13] are lower than the values of the present work. At the onset of melting the situation is the same for the comparison to the measurements of Paradis [12]. The values are still within the error bars: however, he has measured supercooled liquid rhodium.

Thermal conductivity, λ, may be estimated by using the Wiedemann–Franz law:

$$\lambda(T) = \frac{LT}{\rho(T)}. \tag{4}$$

With a Lorentz number $L = 2.45 \times 10^{-8}$ V^2 K^{-2} a value of 91.0 W K^{-1} m^{-1} is obtained at the onset of melting and 60.8 W K^{-1} m^{-1} at the end of melting.

Figure 4 only depicts thermal conductivity, because the behaviour of *thermal diffusivity*, a, is very similar:

$$a(T) = \frac{\lambda(T)}{c_P(T)d(T)} \tag{5}$$

where c_p is the isobaric heat capacity and $d(T)$ the density. The relevant polynomials are given in table 1. Numerical results are given in table 2. At the onset of melting the value for a_s is 1.50×10^{-5} m^2 s^{-1} with a decrease to a_l: 1.25×10^{-5} m^2 s^{-1} at the end of melting. It has to be considered that, due to the fact that we obtain just one constant value for the isobaric heat capacity c_p in the solid phase, the relevance of a is limited to the region near the melting point. The thermal diffusivity of the liquid state does not suffer from this situation.
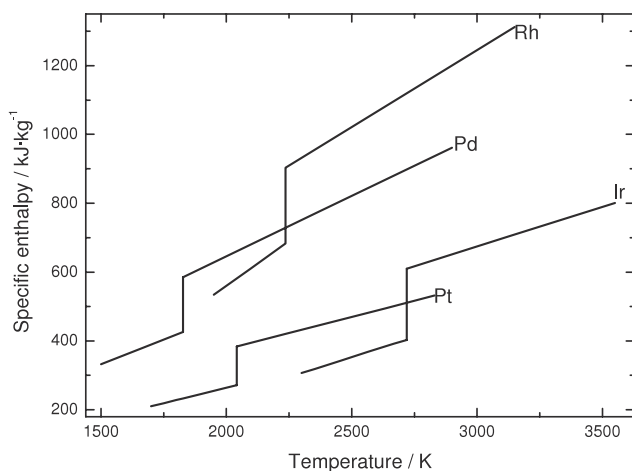
Figure 5. Specific enthalpy of Rh, Pd, Pt and Ir as a function of temperature. Rh: values from the present work. Pd, Pt and Ir: values from [18–20].

Figure 6. Specific electrical resistivity of Rh, Pd, Pt and Ir as a function of temperature. Rh: values from the present work. Pd, Pt and Ir: values from [18–20].

The plot shows the values at melting from the NPL report [16] (λ_s 110 W K^{-1} m^{-1} and λ_l 69 W K^{-1} m^{-1}) and values from Vlasov [17] (λ_s 90 W K^{-1} m^{-1} and λ_l 57 W K^{-1} m^{-1}). Filippow [15] reports values for the solid state. Surprisingly the solid state values of Filippow [15] do precisely aim at NPL's value for λ_s whereas our measurements hit the value of Vlasov. At the beginning of the liquid state our results lie in between the NPL and Vlasov.

4. Discussion

The available data of thermodynamic properties of rhodium, especially in the liquid state, are very scarce. However, the existing data give quite a good match to the values reported in this work (see section 3).

To set rhodium in context with the other platinum metals, we have compared the results to our already published data on Pd, Ir and Pt [18–20].

Figure 5 shows *specific enthalpies* as a function of temperature. The conformity of the results is high. It can be observed (as described for the first time in [21]) that Rh is linked with Pd and Pt with Ir. This can be explained by their position in the periodic table of the elements (fifth period and sixth period elements).

Figure 6 shows *specific electrical resistivities* as a function of temperature. The graph shows that Pd differs from Pt, Rh and Ir, which are very similar regarding their electrical resistivities. The trace for Pd is almost constant throughout the liquid phase, whereas the traces for Pt, Rh and Ir are increasing with similar slopes and the absolute resistivity value of Pd is significantly lower. A possible reason for the diverse behaviour of Pd is the electron configuration: it is the only element (out of Rh, Pd, Ir and Pt) with an empty outermost s orbital (Rh: [Kr]$4d^85s^1$, Pd: [Kr]$4d^{10}5s^0$, Ir: [Xe]$4f^{14}5d^76s^2$, Pt: [Xe]$4f^{14}5d^96s^1$).

In summary, the infrequent appearance of rhodium in the literature is more likely to be a result of its seldom occurrence on Earth than 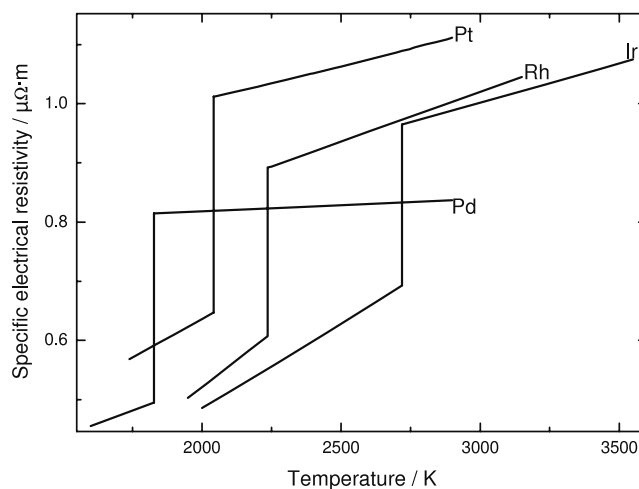of its peculiar thermodynamic properties, because the latter are not peculiar but 'good-natured' for they are very similar to those of the other platinum metals.

5. Uncertainties

In accordance with the guide to the expression of uncertainty in measurement (GUM 1999 [22]), uncertainties reported here are expanded relative uncertainties with a coverage factor of $k = 2$. For the calculated thermophysical properties the following uncertainties have been obtained (liquid phase): enthalpy, H_l: 2.8%, volume expansion, $V(T)V_0^{-1}$: 3%, electrical resistivity with initial geometry, ρ_{IG}: 2.5%, electrical resistivity including volume expansion, ρ: 3.9%, thermal conductivity, λ: 4.6% and thermal diffusivity, a: 8.8%.

6. Conclusion

The present study describes measurements on rhodium. It delivers a complete dataset of thermophysical properties, as literature values for liquid rhodium are sparse.

However, the accordance with these literature values— some published decades ago—is high (see figures 1–4).

In figures 5 and 6 rhodium is set in context with the other platinum metals Pd, Ir and Pt, measured under the same experimental conditions. Again, consistency is high. Rhodium shows no unexpected behaviour.

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