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THE HIGH TEMPERATURE THERMOPHYSICAL PROPERTIES OF RUTHENIUM AND PALLADIUM *

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ABSTRACT

The enthalpy increments of metallic ruthenium have been measured by drop calorimetry between 469 and 879 K. The results can be represented by

$$H^\circ(T) - H^\circ(298.15\ \mathrm{K}) = 21.5070T + 4.28133 \times 10^{-3}T^2 - 6792.9$$

where enthalpy values are in J mol^{-1} and temperatures are in K.

In the same way enthalpy increments of palladium have been measured from 528 to 848 K. These results can be represented by

$$H^\circ(T) - H^\circ(298.15\ \mathrm{K}) = 25.0278T + 2.72019 \times 10^{-3}T^2 + 0.67548 \times 10^5 T^{-1} - 7930.4$$

In both cases the measurements join smoothly to the low temperature heat capacities in the literature and, as a result, smoothed thermodynamic functions from 298.15 to 1000 K are given for both metals.

INTRODUCTION

Professor Westrum has made many important contributions to the understanding of the thermophysical properties of condensed phases. By accurate experimental determinations he was able to resolve the excess heat capacity of transitions and Schottky contributions from the lattice contributions. This, in turn, has led to better understanding of the phonon distribution in the crystalline lattice. Moreover, by quantifying the crystalline vibrational modes the absolute values of the heat capacity and the other thermophysical properties, especially the entropy, can be accounted for. This is particularly important since it enables us to evaluate the thermochemical functions of crystalline materials at temperatures above 298.15 K. To this end the entropy, and also the enthalpy of formation, have to be calculated as functions of temperature using high-temperature heat capacities. In most cases these data were measured in different laboratories and using different

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* Dedicated to Professor Edgar F. Westrum, Jr., on the occasion of his 70th birthday and in honour of his contribution to calorimetry and thermal analysis.

techniques than those used to obtain low temperature capacities. Whereas the latter are determined adiabatically, the former are mostly obtained as enthalpy increments from drop calorimetric measurements.

To judge whether the C_p values from the low temperature adiabatic measurements show continuity with the high temperature measurements, the function

$$H^\circ(T) - H^\circ(298.15\ \mathrm{K})/(T - 298.15\ \mathrm{K})$$

has been proposed [1] which is sensitive enough to show deviations from smooth continuity within the precision attained by the measuring technique. This function, representing the reduced enthalpy increment or mean heat capacity, provides an accurate means of comparing heat capacity data from different sources. At 298.15 K the function has a value which is identical to the true heat capacity, as obtained by adiabatic low temperature heat capacity measurements.

In this paper we present an experimental determination of the high temperature enthalpy increments of the metals ruthenium and palladium. These metals play a role in nuclear technology because they are formed during the fission of uranium. In nuclear fuel Ru and Pd form, together with other transition elements such as Mo, Rh and Tc, a very stable metallic solid solution, the so-called "white inclusions" [2], whereas in fast breeder fuel the formation of the very stable intermetallic compounds URu_3 and UPd_3 has also been observed [3].

The enthalpy increment values obtained here will be compared with data from literature— adiabatic C_p measurements as well as high temperature enthalpy increments—by using the reduced enthalpy function mentioned above. As a result the thermodynamic functions of the light platinum metals Ru and Pd will be given from 298.15 up to 1000 K.

EXPERIMENTAL

Ruthenium used in the present study was purchased as a powder ($<$ 325 mesh) from Highways International; the purity of the material was specified to be 99.9%. Palladium powder (200 mesh; purity 99.95%) was obtained from Drijfhout, Amsterdam. Prior to the measurements, the metal powders were heated at 775 K in an argon atmosphere; X-ray diffraction analysis (Guinier-De Wolff camera, Cu K_α radiation) showed no other phases to be present.

The isothermal diphenyl ether drop calorimeter, in which the enthalpy increments were measured, has been previously described by Cordfunke et al. [4]. Briefly, the sample is enclosed in a spherical vitreous silica ampoule of volume 4.2 cm^3. The ampoule is heated in a furnace whose temperature is measured to within ± 0.1 K with a Pt/(Pt + 10 mass% Rh) thermocouple.

After a reasonable equilibration time, the ampoule is dropped into the calorimeter. The energy of the ampoule plus the sample now melts solid diphenyl ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether is determined by weighing the displaced mercury. The ratio of heat input to mass of mercury making up the volume change is a constant for the apparatus (79.977 ± 0.063) J g^{-1}, and is obtained by calibration with α-SiO_2 and compared with the National Bureau of Standards (NBS) standard reference material (No. 720) synthetic sapphire, Al_2O_3. Our results with sapphire all agree within 0.2% with the data given by NBS. The enthalpy contributions of the vitreous silica were determined separately.

For the present study 9.89008 g of Ru was sealed in the ampoule which had an empty weight of 1.39516 g. A correction was made to the measurements to take account of the difference in enthalpy between the final calorimeter temperature and the standard reference temperature, 298.15 K, using $C_p^\circ(298.15\text{ K}) = 24.06$ J mol^{-1} K^{-1} [5]. A molar mass of 101.07 g was used for ruthenium.

Two different palladium samples were measured. In the first 6.75569 g Pd was sealed in a quartz glass ampoule with an empty weight of 1.47985 g; the other Pd sample was 6.32317 g and was contained in an ampoule of 1.41200 g. The correction for the bath temperature, as mentioned before, was made using $C_p^0(298.15\text{ K}) = 25.89$ J mol^{-1} K^{-1} [5]. A molar mass of 106.4 g was taken for Pd.

All masses were corrected for weighing in argon to values in a vacuum.

RESULTS

Ruthenium

The results of the 15 drop calorimetric measurements are listed in Table 1. The experimental values were fitted by the method of least squares to the polynomial

$$H^\circ(T) - H^\circ(298.15\text{ K}) = 21.5070T + 4.28133 \times 10^{-3}T - 6792.9$$

(enthalpies in J mol^{-1}, temperatures in K) for the interval 469–879 K, applying $C_p^\circ(298.15\text{ K}) = 24.06$ J mol^{-1} K^{-1} [5] and at 298.15 K $H^\circ(T) - H^\circ(298.15\text{ K}) = 0$ as the boundary conditions. The standard deviation is 33 J mol^{-1} or 0.32%.

Palladium

The results of the two sets of enthalpy increment measurements for palladium are listed in Table 2. All experimental values have been fitted to

TABLE 1

Calorimetric enthalpy increment measurements for Ru(s)

T(K)	$H°(T)-H°(298.15\text{ K})$ (J mol^{-1})		δ (%)
	Exp.	Calc.	
469.1	4244	4238	0.14
528.6	5801	5772	0.50
563.5	6696	6686	0.15
601.2	7733	7685	0.62
647.9	8926	8939	−0.15
688.3	10043	10039	0.04
698.1	10299	10308	−0.09
703.7	10409	10462	−0.51
732.4	11209	11255	0.31
768.0	12246	12250	−0.03
784.5	12732	12714	0.14
796.9	13096	13065	0.24
828.5	13969	13964	0.04
847.6	14438	14512	−0.51
879.0	15386	15420	−0.22

TABLE 2

Calorimetric enthalpy increments of Pd(s)

T(K)	$H°(T)-H°(298.15\text{ K})$ (J mol^{-1})		δ (%)
	Exp.	Calc.	
527.6	6128	6159	−0.50
547.4	6701	6708	−0.10
567.2	7264	7260	0.06
587.5	7801	7827	−0.33
606.4	8334	8358	−0.29
627.3	8990	8948	0.47
646.7	9490	9497	−0.07
667.7	10133	10095	0.38
677.3	10349	10369	−0.19
686.8	10639	10640	−0.01
707.2	11243	11225	0.16
726.2	11844	11772	0.61
747.0	12354	12374	−0.16
767.4	12928	12966	−0.29
806.8	14079	14116	−0.26
827.3	14731	14719	0.08
847.7	15329	15320	0.06

the polynomial

$$H^\circ(T) - H^\circ(298.15\ \mathrm{K}) = 25.0278T + 2.72019 \times 10^{-3}T^2 + 0.67548 \times 10^5 T^{-1} - 7930.4$$

for the interval 528 to 848 K, using $C_p^\circ(298.15\ \mathrm{K}) = 25.89\ \mathrm{J\ mol^{-1}\ K^{-1}}$ [5], and $H^\circ(T) - H^\circ(298.15\ \mathrm{K}) = 0$ at 298.15 K as the boundary conditions. The standard deviation is 31 J $\mathrm{mol^{-1}}$ or 0.31%.

DISCUSSION

In a thorough and critical assessment Furukawa et al. [5] reviewed the low temperature heat capacity measurements for ruthenium and palladium in 1974. Since then no new experimental measurements have been published, and we thus take this evaluation as the basis for the high temperature thermochemistry of these metals. Although Furukawa et al. limited their evaluation to the temperature range 0–300 K, they also analysed all known measurements above 300 K as a means of establishing the heat capacity in the region of 300 K, and concluded that more accurate data were needed to resolve values of the heat capacity in that region.

Ruthenium

The only high temperature heat capacity data, available from literature, are from drop calorimetric measurements by Holzmann [6] in 1931 from 573 to 1173 K, and by Jaeger and Rosenbohm [7] in 1932 from 608 to 1811 K. The two sets of measurements not only differ significantly, but are also inconsistent with the assessment of Furakawa et al., which was principally based on the results of Clusius and Piesbergen [8]. Moreover, Jaeger and Rosenbohm reported three structural changes which have not been confirmed with high temperature X-ray diffraction measurements [9].

In Fig. 1 the various data from literature are plotted using the reduced enthalpy function, as mentioned in the introduction, together with our drop calorimetric measurements in the temperature range 525–850 K. It is evident that our measurements disagree seriously with both the measurements of Holzmann and those of Jaeger and Rosenbohm, but join smoothly with the values from the Furukawa assessment. On this basis we have calculated the thermodynamic functions of ruthenium metal up to 1000 K (Table 3).

Palladium

The various measurements for palladium metal are plotted in Fig. 2. The situation differs only slightly from that of ruthenium. The high temperature drop calorimetric measurements by Holzmann [6] as well as the high

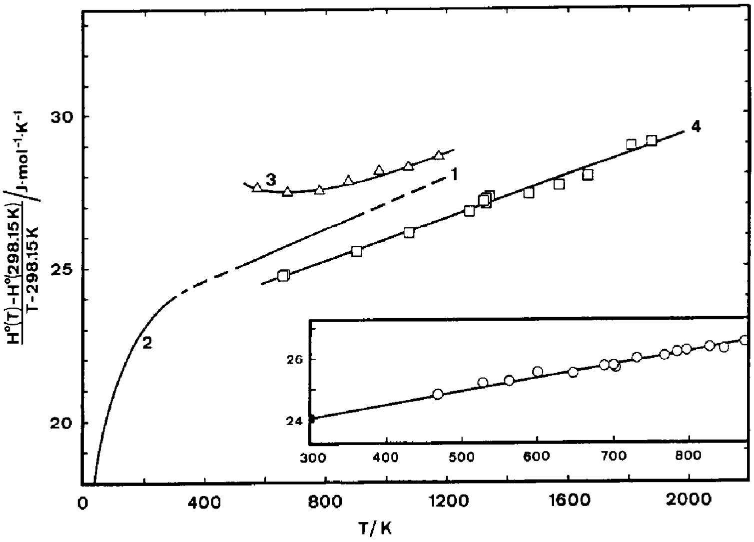

Fig. 1. The reduced enthalpy increments of Ru as a function of the temperature: 1, present results; 2, Furukawa et al. [5]; 3, Holzmann [6]; 4, Jaeger et al. [7]. The insert gives details of the present results.

temperature adiabatic heat capacity measurements by Vollmer and Kohlhaas [10] are in serious disagreement with Furukawa's selection for the low temperature heat capacity of palladium. The agreement of the data of Jaeger and Veenstra [11] with Furukawa's assessment is better but their data are, in turn, in serious disagreement with the present results, which join smoothly with Furukawa's selection. It should be noted that Jaeger and coworkers reported two different sets of data for palladium [11,12], but we consider here only the set for which they performed a stabilization of the sample in vacuum. The purity of their sample is not specified, however. High tempera-

TABLE 3

Thermodynamic functions of Ru(s)

T(K)	C_p° (J mol^{-1} K^{-1})	S° (J mol^{-1} K^{-1})	$-[G^\circ - H^\circ(298)]/T$ (J mol^{-1} K^{-1})	$H^\circ - H^\circ(298)$ (J mol^{-1})
298.15	24.060	28.610	28.610	0
300	24.076	28.759	28.610	45
400	24.932	35.802	29.565	2495
500	25.788	41.458	31.396	5031
600	26.645	46.235	33.481	7653
700	27.501	50.407	35.607	10360
800	28.357	54.135	37.694	13153
900	29.213	57.524	39.712	16031
1000	30.070	60.647	41.651	18995

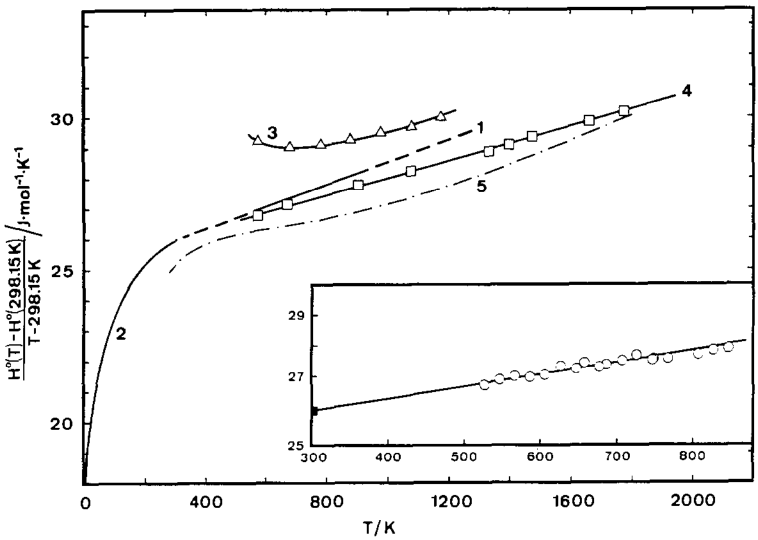

Fig. 2. The reduced enthalpy increments of Pd as a function of the temperature: 1, present results; 2, Furukawa et al. [5]; 3, Holzmann [6]; 4, Jaeger et al. [11]; 5, Vollmer and Kohlhaas [10]. The insert gives details of the present results.

TABLE 4

Thermodynamic functions of Pd(s)

T (K)	C_p° (J mol^{-1} K^{-1})	S° (J mol^{-1} K^{-1})	$-[G^\circ - H^\circ(298)]/T$ (J mol^{-1} K^{-1})	$H^\circ - H^\circ(298)$ (J mol^{-1})
298.15	25.890	37.820	37.820	0
300	25.909	37.980	37.820	48
400	26.782	45.560	38.848	2685
500	27.478	51.613	40.816	5399
600	28.104	56.679	43.049	8178
700	28.698	61.056	45.315	11018
800	29.275	64.926	47.529	13917
900	29.841	68.407	49.659	16873
1000	30.401	71.580	51.695	19885

ture drop calorimetric measurements prior to 1900 by Violle [13] and Pionchon [14] have been excluded from the present discussion.

Using the present results, we have calculated the thermodynamic functions of palladium metal up to 1000 K (Table 4).

CONCLUSIONS

High temperature thermochemical properties of many transition metals are still based on heat-capacity measurements prior to 1950. At that time, Jaeger and coworkers at the University of Groningen, The Netherlands, made a significant contribution in this field. For some metals, for example rhodium, osmium and iridium, their results are still the only ones available at present. By using the function $[H^\circ(T) - H^\circ(298.15\ \mathrm{K})]/(T - 298.15)$, we have shown that their measurements should be used with great caution. Consequently, new experimental determinations of the heat capacity or relative enthalpies would seem desirable in order to establish the thermochemistry of the elements with the precision presently needed for reliable thermochemical calculations.

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