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Selected Values for the Densities and Molar Volumes of the Liquid Platinum Group Metals and of the Initial Melting Curves of Iridium, Rhodium and Ruthenium

Assessing different determinations of the density of the liquid platinum group metals

John W. Arblaster

Droitwich, Worcestershire, UK

Email: jwarblaster@yahoo.co.uk

Definitive equations are suggested to represent the variation with temperature of the densities and molar volumes of the liquid platinum group metals whilst the previously unknown initial slopes of the melting curves for iridium, rhodium and ruthenium are estimated.

1. Introduction

Paradis *et al.* (1) summarised determinations of the densities of the liquid platinum group metals but a number of important determinations were not included. These are given in **Table I** in which values are presented as $a - b\,(T - T_m)$ where a is the liquid density at the melting point T_m and b represents the density thermal expansion. Unfortunately, in the case of the measurements of Pottlacher (2) volume ratios were considered to vary linearly with temperature so that derived density values could only be fitted to quadratic equations (Equations (i)–(iv)), whereas a very large number of determinations of the densities of medium

and high melting point metals and alloys clearly indicate that liquid density values vary linearly with temperature and this would therefore limit the usefulness of the values of Pottlacher (2). Paradis *et al.* (1) did not suggest definitive values for the densities of the metals but would undoubtedly have given preference to their own electrostatic levitation determinations which are considered to be accurate to about 2%. The problem with the selection was that the differences between various determinations were significant to a certain extent making an objective evaluation difficult. One alternative approach is to indirectly obtain the liquid density at the melting point from the value for the solid density by use of the Clausius-Clapeyron equation (Equation (v)):

$$\Delta V\,(\text{cm}^3\,\text{mol}^{-1}) = \Delta H/(T_m\,\mathrm{d}P/\mathrm{d}T) \qquad (v)$$

where ΔV is the difference between the molar volumes of the solid and the liquid, ΔH is the enthalpy of fusion in J mol^{-1} at melting point T_m, K, and $\mathrm{d}P/\mathrm{d}T$ is the initial slope of the melting curve in MPa K^{-1}. In the case of iridium, rhodium and ruthenium $\mathrm{d}P/\mathrm{d}T$ is unknown so that Equation (v) can be reversed to estimate these values. In applying Equation (v) the densities of the solids at the melting point were all assumed to have an

Table I Additional Determinations of the Densities of Liquid Platinum Group Metals				
Authors	**Ref.**	T_m, K	*a*	*b*
Iridium				
Pottlacher	2	2719	19,722	2.049*
Palladium				
Pottlacher	2	1828	10,690	0.733*
Stankus and Tyagel'skii	3	1827	10,631	0.734
Popel *et al.*	4	1828	10,605	1.056
Platinum				
Pottlacher	2	2042	18,968	1.170*
Stankus and Khairulin	5	2042	18,932	1.168
Rhodium				
Pottlacher	2	2236	11,004	1.022*

*Initial slope $\mathrm{d}D/\mathrm{d}T$ at the melting point from the quadratic fits to the density values (Equations (i) to (iv)):

Ir: D (kg m^{-3}) = 26,665 – 3.058 T + 1.856 × 10^{-4} T^2 (i)

Pd: D (kg m^{-3}) = 12,181 – 0.898 T + 4.504 × 10^{-5} T^2 (ii)

Pt: D (kg m^{-3}) = 21,627 – 1.435 T + 6.490 × 10^{-5} T^2 (iii)

Rh: D (kg m^{-3}) = 13,695 – 1.385 T + 8.124 × 10^{-5} T^2 (iv)

accuracy of ±20 kg m^{-3} which is roughly twice the room temperature uncertainty and therefore equivalent to a 95% confidence level.

2. Platinum

Selected values for the fit to Equation (v) are melting point 2041.3 ± 0.4 K (6), enthalpy of fusion 22,113 ± 940 J mol^{-1} (7) and slope of the melting curve $\mathrm{d}P/\mathrm{d}T$ 22.5 ± 1.3 MPa K^{-1} taken from an average of the $\mathrm{d}T/\mathrm{d}P$ values of 42 K GPa^{-1} as determined by Mitra *et al.* (8) and 47 K GPa^{-1} as determined by Errandonea (9). The resultant value is ΔV = 0.482 ± 0.034 cm^3 mol^{-1} which when combined with the bulk density of the solid as 20,173 ± 20 kg m^{-3} (10, 11) leads to a density of the liquid at the melting point of 19,215 ± 67 kg m^{-3}. This is in extraordinary agreement with the value of 19,200 ± 380 kg m^{-3} determined by Ishikawa *et al.* (12). Other density determinations such as that of Stankus and Khairulin (5) at 18,932 ± 90 kg m^{-3} and that of Pottlacher (2) at 18,968 kg m^{-3} are notably lower but agree with other determinations summarised by Paradis *et al.* (1) suggesting that a possible value for the density could be 18.9 ± 0.1 kg m^{-3} and that the determination of Ishikawa *et al.* (12) would then be an outlying value. However, the indirect density value obtained from the Clausius-Clapeyron equation (Equation (v)) clearly confirms the determination of Ishikawa *et al.* (12) as being the most likely value. The significant difference resulting in the lower density values can be traced to much larger values determined for ΔV at 0.582 cm^3 mol^{-1} by Stankus and Khairulin (5) and 0.696 cm^3 mol^{-1} by Pottlacher (2). The density thermal expansion at b = –0.96 cm^3 mol^{-1} K^{-1} as determined by Ishikawa *et al.* (12) is much lower than previous values but is in reasonable agreement with the value of –1.168 ± 0.062 cm^3 mol^{-1} K^{-1} as determined by Stankus and Khairulin (5). Therefore, a suggested equation (Equation (vi)) to represent the density of liquid platinum over the range from 1700 K to 2200 K with an accuracy of about 0.5% would be:

$$D \,(\text{kg m}^{-3}) = 19{,}215 - 0.96\,(T - 2041.3) \qquad \text{(vi)}$$

3. Palladium

Selected values for the fit to Equation (v) are melting point 1828.0 ± 0.1 K (6), enthalpy of fusion 16,080 ± 740 J mol^{-1} (13) and slope of the melting curve $\mathrm{d}P/\mathrm{d}T$ 21.7 ± 2.2 MPa K^{-1}, equivalent to the $\mathrm{d}T/\mathrm{d}P$ value of 46 K GPa^{-1} as determined by Errandonea (9) and assuming an accuracy of 10%. The resultant value is ΔV = 0.405 ± 0.045 cm^3 mol^{-1} and when combined with the density of the solid of 11,179 ± 20 kg m^{-3} (14) leads to a density of the liquid of 10,723 ± 50 kg m^{-3} which is higher than any of the

experimental values but is encompassed within the accuracy of the determination of Paradis *et al.* (15) at 10,660 ± 210 kg m^{-3} and the value of Pottlacher (2) at 10,690 kg m^{-3}. Two further recent determinations are notably lower with Popel *et al.* (4) obtaining the value 10,605 kg m^{-3} and Stankus and Tyagel'skii (3) obtaining 10,631 ± 45 kg m^{-3}, although in the case of the latter the value of ΔV at 0.506 cm^3 mol^{-1} is again much larger than the value obtained using Equation (v). It is known that the values of the enthalpy of fusion and the density of the solid at the melting point are tentative so that the value obtained from Equation (v) may not be fully representative. It is also noted that the average of the four sets of measurements considered above is very close to the value of Paradis *et al.* (15) and therefore this value is selected since it does include the Equation (v) value in its uncertainty. The density thermal expansion coefficient of $b = -0.77$ cm^3 mol^{-1} K^{-1} as determined by Paradis *et al.* (15) is confirmed by the value of -0.734 cm^3 mol^{-1} K^{-1} obtained by Stankus and Tyagel'skii (3) and by the value -0.733 cm^3 mol^{-1} K^{-1} at the melting point calculated from the quadratic fit to the measurements of Pottlacher (2). Therefore, the equation (Equation (vii)) given by Paradis *et al.* (15) is considered as being representative for palladium over the temperature range 1600 to 1900 K when consideration is given to its 2% accuracy:

$$D \text{ (kg m}^{-3}) = 10,660 - 0.77 \, (T - 1828.0) \qquad \text{(vii)}$$

4. Rhodium

Strong and Bundy (16) determined an initial slope of the melting curve of 62 K GPa^{-1} but the value determined for platinum at the same time, 72 K GPa^{-1}, far exceeds the more recent determinations given above. Therefore, it is assumed that the slope dP/dT is poorly known and can be calculated by reversing Equation (v) with a melting point of 2236 ± 3 K (6), an enthalpy of fusion of 27,295 ± 850 J mol^{-1} (17) and a value of $\Delta V = 0.555 \pm 0.191$ cm^3 mol^{-1} based on the density of the solid at the melting point at 11,491 ± 20 kg m^{-3} (18) and for the liquid at 10,820 ± 220 kg m^{-3} (19). The derived melting curve pressure is 22.0 ± 7.6 MPa K^{-1} or the equivalent dT/dP value of 45 ± 16 K GPa^{-1} which agrees closely with the values obtained for both platinum and palladium. The relatively poor accuracy assigned to dT/dP is due almost entirely to the 2% accuracy assigned to the liquid density value and its effect on ΔV. The density equation given by Paradis *et al.* (19) over the range 1820 to 2250 K has been repeated

as Equation (viii) to remove the ambiguity created by Paradis *et al.* (1) who included two different melting point values. The quadratic fit to the density values of Pottlacher (2) (2236 to 3500 K) leads to a value of 11,004 kg m^{-3} at the melting point which is encompassed within the accuracy assigned to the measurements of Paradis *et al.* (19). Perhaps coincidentally the volume ratios of Pottlacher (2) also lead to $\Delta V = 0.555$ cm^3 mol^{-1} at the melting point although the value obtained of $b = -1.022$ kg m^{-3} K^{-1} is notably higher than the value given by Paradis *et al.* (19) in Equation (viii) below:

$$D \text{ (kg m}^{-3}) = 10,820 - 0.76 \, (T - 2236) \qquad \text{(viii)}$$

5. Iridium

The melting point slope is unknown and was also derived by reversing Equation (v). Initially Ishikawa *et al.* (20) reported that their group (21) obtained a liquid density value of 19,870 kg m^{-3} at the melting point although the actual published value had been reduced to 19,500 kg m^{-3}. For the reverse of Equation (v) input values are melting point 2719 ± 4 K (6), enthalpy of fusion 41,335 ± 1128 J mol^{-1} (22) and $\Delta V = 0.666 \pm 0.197$ cm^3 mol^{-1} based on the density of the solid at the melting point at 20,913 ± 20 kg m^{-3} (23) and for the liquid at the melting point 19,500 ± 390 kg m^{-3} (21). The derived melting curve pressure is 22.8 ± 6.8 MPa K^{-1} or the equivalent dT/dP value of 44 ± 13 K GPa^{-1} which again agrees closely with the values obtained for both platinum and palladium. The relatively poor accuracy assigned to dT/dP is due almost entirely to the 2% accuracy assigned to the liquid density value and its effect on ΔV. The density equation of Ishikawa *et al.* (21) which covers the range 2300 to 3000 K is reproduced as Equation (ix):

$$D \text{ (kg m}^{-3}) = 19,500 - 0.85 \, (T - 2719) \qquad \text{(ix)}$$

Measurements given by Pottlacher (2) were ambiguous since the baseline solid density was given as a value for commercial purity iridium at 22,420 kg m^{-3} rather than the X-ray value of 22,560 kg m^{-3} (23). Using the assigned commercial value, the liquid density value derived from the quadratic fit at 19,722 kg m^{-3} is encompassed by the accuracy assigned to the measurement of Ishikawa *et al.* (20). However, the derived value at the initial slope of the melting curve derived from the quadratic fit at $b = -2.049$ kg m^{-3} K^{-1} differs considerably from the value given in Equation (ix).

6. Ruthenium

The only precision liquid density measurements are those of Paradis *et al.* (24) over the range 2225 to 2775 K. Again the slope of the melting curve was unknown and was derived by reversing Equation (v) using values of melting point 2606 ± 10 K (6), enthalpy of fusion 39,038 ± 1400 J mol^{-1} (25) and ΔV = 0.532 ± 0.189 cm^3 mol^{-1} based on the density of the solid at the melting point 11,396 ± 20 kg m^{-3} (26) and for the liquid 10,751 ± 210 kg m^{-3} (24). The derived melting curve pressure dP/dT is 28.2 ± 10.1 MPa K^{-1} or the equivalent dT/dP value of 36 ± 13 K GPa^{-1} which is lower, but still within the accuracy limits, measured or derived for the face-centred cubic platinum group metals. For comparison theoretical dT/dP values for osmium vary between 40.4 K GPa^{-1} (27) and 49.5 K GPa^{-1} (28) in agreement with the face-centred cubic values. Paradis *et al.* (24) assumed a melting point of 2607 K for ruthenium rather than the International Temperature Scale (ITS-90) value of 2606 K. The published density equation has therefore been adjusted to correspond to the corrected melting point (Equation (x)):

$$D \, (\text{kg m}^{-3}) = 10{,}751 - 0.85 \, (T - 2606) \qquad \text{(x)}$$

7. Osmium

Actual density measurements of solid osmium extend only to 1300 K (29) and therefore estimating possible values above this temperature is speculative. Paradis and Ishikawa (30) measured the liquid density over the range 2670 to 3380 K and assumed that measurements were both undercooled and in equilibrium by taking the melting point to be 3306 K. However, this literature value was obtained on osmium metal of only commercial purity and is considered to be far too low. Arblaster (31) suggested that the true melting point of pure osmium was likely to be in the order of 3400 ± 50 K and the published equation was revised to correspond to this estimated melting point. However, this correction is only formal so that all melting points conform to selected values and the actual derived density values correspond to the experimentally determined values (Equation (xi)):

$$D \, (\text{kg m}^{-3}) = 19{,}047 - 1.16 \, (T - 3400) \qquad \text{(xi)}$$

8. Conclusions

An evaluation of different determinations of the density of the liquid platinum group metals concludes that the determinations using the electrostatic levitation method are possibly the most reliable and derived equations from this method are given in **Table II**, with slight modifications for the density of liquid platinum and the melting points of ruthenium and osmium. Derived molar volume equations are given in **Table III** whilst **Table IV** gives the values of density and molar volume at the melting points. Derived densities and molar volumes at other temperatures are given in **Table V**.

The initial slopes of the melting curves for ruthenium, rhodium and iridium were at first considered to be unknown and were derived using the Clausius-Clapeyron equation (Equation (v)). This showed that the initial slopes derived for rhodium and iridium were very close to the actual experimental values of palladium and platinum suggesting a common value for dT/dP of about 45 K GPa^{-1} for the face-centred cubic platinum group metals. The value of 36 K GPa^{-1} obtained for ruthenium and estimates of 40 to 50 K GPa^{-1} for osmium suggest that a possible common value for the hexagonal close-packed platinum group metals is less certain.

Table II Density Equations for the Liquid Platinum Group Metals[a]				
Element	T_m, K	a	b	Temperature range, K
Ruthenium	2606	10,751	0.85	2200–2800
Rhodium	2236	10,820	0.76	1800–2300
Palladium	1828.0	10,660	0.77	1600–1900
Osmium	3400	19,047	1.16	2600–3400
Iridium	2719	19,500	0.85	2300–3000
Platinum	2041.3	19,215	0.96	1700–2200

[a]Liquid density values are fitted to the equation: $D \, (\text{kg m}^{-3}) = a - b \, (T - T_m)$ where a is the density at the melting point T_m, K, and b is the density thermal expansion. The temperature range approximates to the actual experimental range and therefore the density values mainly correspond to the undercooled region

Table III Molar Volume Equations for the Liquid Platinum Group Metals[a]

Element	Atomic weight	c	d	e
Ruthenium	101.07	7.8532	4.445×10^{-4}	5.734×10^{-8}
Rhodium	102.90550	8.2430	4.660×10^{-4}	5.734×10^{-8}
Palladium	106.42	8.8362	5.338×10^{-4}	5.122×10^{-8}
Osmium	190.23	8.3206	3.730×10^{-4}	3.448×10^{-8}
Iridium	192.217	8.8261	3.288×10^{-4}	1.856×10^{-8}
Platinum	195.084	9.2214	4.052×10^{-4}	2.500×10^{-8}

[a]Because liquid density values vary linearly with temperature then the reciprocal, molar volumes, can only be accurately represented by fitting to quadratic equations. The molar volume is given by V_m (cm^3 mol^{-1}) = $A_r / D = c + d\,T + e\,T^2$ where A_r is the atomic weight and these equations are considered to be valid over the same temperature ranges as adopted for the liquid metals. The 2015 atomic weights were adopted (32)

Table IV Densities and Molar Volumes of the Liquid Platinum Group Metals at their Melting Points[a]

Element	T_m, K	Liquid density, kg m^{-3}	Molar volume, cm^3 mol^{-1}
Ruthenium	2606	10,751 ± 210	9.401 ± 0.19
Rhodium	2236	10,820 ± 220	9.511 ± 0.19
Palladium	1828.0	10,660 ± 210	9.983 ± 0.20
Osmium	3400	19,047 ± 380	9.987 ± 0.20
Iridium	2719	19,500 ± 390	9.857 ± 0.20
Platinum	2041.3	19,215 ± 100	10.153 ± 0.05

[a]Values are based on the equations given in **Tables III** and **IV**. A conservative value for the accuracy of the density of platinum is assumed to be ±100 kg m^{-3} whilst all other density values are assumed to be accurate to 2%. Molar volumes are extended to three decimal places for interpolation purposes

Table V The Variation with Temperature of the Densities and Molar Volumes of the Liquid Platinum Group Metals[a]

Ruthenium

T, K	2200	2300	2400	2500	2600	2700	2800
D	11,100	11,010	10,930	10,840	10,760	10,670	10,590
V_m	9.109	9.179	9.250	9.323	9.397	9.471	9.547

Rhodium

T, K	1800	1900	2000	2100	2200	2300
D	11,520	11,360	11,200	11,040	10,880	10,720
V_m	9.228	9.291	9.356	9.421	9.487	9.554

Palladium

T, K	1600	1650	1700	1750	1800	1850	1900
D	10,840	10,800	10,760	10,720	10,680	10,640	10,600
V_m	9.821	9.856	9.892	9.927	9.963	9.999	10.035

(continued)

Table V Continued

Osmium

T, K	2600	2700	2800	2900	3000	3100	3200	3300	3400
D	19,980	19,860	19,740	19,630	19,510	19,400	19,280	19,160	19,050
V_m	9.523	9.579	9.635	9.692	9.750	9.808	9.867	9.927	9.987

Iridium

T, K	2300	2400	2500	2600	2700	2800	2900	3000
D	19,860	19,770	19,690	19,600	19,520	19,430	19,350	19,260
V_m	9.681	9.722	9.764	9.806	9.849	9.892	9.936	9.980

Platinum

T, K	1700	1800	1900	2000	2100	2200
D	19,540	19,450	19,350	19,250	19,160	19,060
V_m	9.982	10.032	10.082	10.132	10.183	10.234

[a]Liquid density (*D*) is in units of kg m^{-3} and molar volume (*V*$_m$) in units of cm^3 mol^{-1}. The accuracy of these values can be considered to be the same as those determined at the melting point. Molar volumes are extended to three decimal places for interpolation purposes

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The Author

John W. Arblaster is interested in the history of science and the evaluation of the thermodynamic and crystallographic properties of the elements. Now retired, he previously worked as a metallurgical chemist in a number of commercial laboratories and was involved in the analysis of a wide range of ferrous and non-ferrous alloys.