

Revised Crystallographic Properties of Osmium

Assessment of properties from 293.15 K to 3400 K

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PEER REVIEWED

Received 11th July 2022; Revised 3rd August 2022;
Accepted 22nd August 2022; Online 29th March 2023

New dilatometric measurements allow the evaluated thermal expansion of osmium to be increased from the previous limit of 1300 K to the melting point at 3400 K. The new data is reported in the form of Equations and Tables. The revision confirms that osmium is the densest solid at all temperatures above room temperature. A new equation is given for the density of liquid osmium.

Crystallographic Properties

Previous reviews by the present author on the crystallographic properties of ruthenium (1), rhodium (2), palladium (3), iridium (4) and platinum (5, 6) in each case gave values from absolute zero up to their melting points. The exception was osmium (7) where the limited experimental lattice parameter measurements

of Owen and Roberts (8, 9) (323 K to 873 K) and Schröder *et al.* (10) (289 K to 1287 K) only allowed the values to be given up to a rounded temperature of 1300 K. Based on the previous review equations for length values from 293.15 K to 1300 K are given in **Table I** and actual property values covering the range 293.15 K to 1300 K are given in **Tables II** and **III**. Estimated crystallographic properties below 293.15 K were given in the original paper (7). Fixed values at 293.15 K are:

Lattice parameter $a = 0.27342 \pm 0.00002$ nm;
lattice parameter $c = 0.43199 \pm 0.00002$ nm;
molar volume $(8.4214 \pm 0.0013) \times 10^{-6}$ m³ mol⁻¹
and density $22,589 \pm 5$ kg m⁻³

Bulk Properties

Onufriev (11) determined the mean thermal expansion over the range 1631 K to 2572 K. Multiplying these values by $(T - 293)$ K leads to length change values which can be represented analytically by **Table IV**, Equation (vi). At 1600 K this leads to a length change value of 7.12×10^{-3} whilst extrapolation of the average crystallographic equation to this temperature leads to a value of 7.88×10^{-3} , or a difference of 7.6×10^{-4} . Since crystallographic measurements give separate

Table I Thermal Expansion Equations for Osmium 293.15 K to 3400 K

293.15 K to 1300 K

$$\text{Equation (i): } \delta a/a_{293.15 \text{ K}} = -1.32379 \times 10^{-3} + 4.46595 \times 10^{-6} T + 1.69909 \times 10^{-10} T^2$$

$$\text{Equation (ii): } \delta c/c_{293.15 \text{ K}} = -1.53749 \times 10^{-3} + 4.64427 \times 10^{-6} T + 2.04826 \times 10^{-9} T^2$$

$$\text{Equation (iii): } \delta l_{avr}/l_{avr \ 293.15 \text{ K}} = -1.39503 \times 10^{-3} + 4.52539 \times 10^{-6} T + 7.96026 \times 10^{-10} T^2$$

1300 K to 2000 K

$$\text{Equation (iv): } \delta l/l_{293.15 \text{ K}} = -1.21964 \times 10^{-3} + 3.95259 \times 10^{-6} T + 1.49515 \times 10^{-9} T^2 - 3.78070 \times 10^{-13} T^3 + 7.64610 \times 10^{-17} T^4$$

2000 K to 3400 K

$$\text{Equation (v): } \delta l/l_{293.15 \text{ K}} = -3.52394 \times 10^{-4} + 3.41761 \times 10^{-6} T + 1.07522 \times 10^{-9} T^2 + 1.01895 \times 10^{-14} T^3$$

Table II Crystallographic Properties of Osmium 293.15 K to 1300 K

Temperature, K	Thermal expansion coefficient, α_{av} , $10^{-6} K^{-1}$	Thermal expansion coefficient, α_{cr} , $10^{-6} K^{-1}$	Thermal expansion coefficient ^a , α_{avr} , $10^{-6} K^{-1}$	Length change, $\delta a/a_{293.15 K} \times 100$, %	Length change, $\delta c/c_{293.15 K} \times 100$, %	Length change, $\delta a_{vr}/a_{vr_{293.15 K}} \times 100$, %
293.15	4.57	5.85	4.99	0	0	0
300	4.57	5.87	5.00	0.003	0.004	0.003
400	4.60	6.28	5.16	0.049	0.065	0.054
500	4.63	6.68	5.32	0.095	0.130	0.107
600	4.66	7.09	5.47	0.142	0.199	0.161
700	4.69	7.49	5.63	0.189	0.272	0.216
800	4.73	7.89	5.78	0.236	0.349	0.273
900	4.76	8.30	5.94	0.283	0.430	0.332
1000	4.79	8.70	6.09	0.331	0.516	0.393
1100	4.82	9.10	6.25	0.379	0.605	0.455
1200	4.85	9.49	6.40	0.428	0.699	0.518
1300	4.88	9.89	6.56	0.477	0.796	0.583

^aavr = average

Table III Further Crystallographic Properties of Osmium 293.15 K to 1300 K^a

Temperature, K	Lattice parameter, a , nm	Lattice parameter, c , nm	c/a ratio	Interatomic distance, d_1 , nm	Atomic volume, $10^{-3} nm^3$	Molar volume, $10^{-6} m^3 mol^{-1}$	Density, $kg m^{-3}$
293.15	0.27342	0.43199	1.5800	0.26753	13.984	8.421	22,589
300	0.27343	0.43201	1.5800	0.26753	13.986	8.422	22,586
400	0.27355	0.43227	1.5802	0.26754	14.007	8.435	22,552
500	0.27368	0.43255	1.5805	0.26769	14.029	8.448	22,517
600	0.27381	0.43285	1.5808	0.26785	14.052	8.462	22,480
700	0.27394	0.43316	1.5813	0.26818	14.075	8.476	22,443
800	0.27406	0.43350	1.5817	0.26836	14.099	8.491	22,404
900	0.27419	0.43385	1.5823	0.26855	14.124	8.506	22,365
1000	0.27433	0.43422	1.5829	0.26874	14.149	8.521	22,325
1100	0.27466	0.43460	1.5835	0.26894	14.176	8.537	22,284
1200	0.27459	0.43501	1.5842	0.26915	14.203	8.553	22,241
1300	0.27472	0.43543	1.5850	0.26936	14.230	8.570	22,198

^aInteratomic distance $d_2 = a$

values for the a and c thermal expansion then they can be considered to be anisotropically correct. However for dilatometric measurements samples may show preferential orientation leading to values which are not representative of the true average values. It is proposed that the samples used to measure the thermal expansion of osmium may be so affected and in order to overcome this problem it was assumed that in the high temperature region the derived thermal expansion coefficients are independent of the orientation. Therefore crystallographic thermal expansion coefficients at 1300 K and below were combined with dilatometric

thermal expansion coefficients at 2000 K and above and fitted to a perfect equation (four coefficients and four thermal expansion values). This equation was then integrated in order to obtain length change values over the range 1300 K to 2000 K as **Table IV** Equation (vii). Above 2000 K and up to 2600 K initially thermal expansion values are related back to the original equation of Onufriev but corrected for the revised length change values as **Table IV** Equation (viii). However this equation cannot be satisfactorily extrapolated above 2600 K since it leads to a thermal expansion coefficient which varies only linearly with temperature and

Table IV Secondary Equations for Osmium

1631 K to 2572 K

Equation (vi): $\delta/l_{293.15\text{ K}} = -1.06200 \times 10^{-3} + 3.29113 \times 10^{-6} T + 1.13800 \times 10^{-9} T^2$

1300 K to 2000 K

Equation (vii): $\delta/l_{293.15\text{ K}} = -1.21964 \times 10^{-3} + 3.95259 \times 10^{-6} T + 1.49515 \times 10^{-9} T^2 - 3.78070 \times 10^{-13} T^3 + 7.64610 \times 10^{-17} T^4$

2000 K to 2600 K

Equation (viii): $\delta/l_{293.15\text{ K}} = -2.69310 \times 10^{-4} + 3.29113 \times 10^{-6} T + 1.13800 \times 10^{-9} T^2$

298.15 K to 3400 K

Equation (ix): $H^\circ_T - H^\circ_0 (\text{J mol}^{-1}) = -3344.36 + 26.1938 T + 1.32318 \times 10^{-4} T^2 + 3.85960 \times 10^{-7} T^3 + 3.99978 \times 10^{-11} T^4 + 150,378/T$

2000 K to 3400 K

Equation (x): $\ln(L_T) = (H^\circ_T - H^\circ_0) (1.34167 \times 10^{-7} + 4.64912 \times 10^{-11} T - 6.17263 \times 10^{-15} T^2)$

Equation (xi): $\delta/l_{293.15\text{ K}} = -3.52394 \times 10^{-4} + 3.41761 \times 10^{-6} T + 1.07522 \times 10^{-9} T^2 + 1.01895 \times 10^{-14} T^3$

does not take in to account an increase above the linear relationship caused, for example, by the onset of thermal vacancy effects. In order to try and obtain realistic thermal expansion coefficients it was assumed that length change values from 2000 K to 2600 K behaved in a similar manner to thermodynamic properties, specifically absolute enthalpy values, $H^\circ_T - H^\circ_0$, through the relationship, Equation (xii):

$$\ln(L_T) = (H^\circ_T - H^\circ_0) (a + b T + c T^2) \tag{xii}$$

where the length change values are given by Equation (xiii):

$$L_T = 1 + (l_T - l_{293.15\text{ K}})/l_{293.15\text{ K}} \tag{xiii}$$

Values of absolute enthalpy selected by the present author (12) are given in **Table IV**, Equation (ix) and coefficients corresponding to the correlation between length change values and absolute enthalpy are given as **Table IV**, Equation (x). This equation was extrapolated to the melting point at 3400 K. However this equation is clearly cumbersome and it was found that from 2000 K to 3400 K the values could also be represented with a high degree of correlation by use of the cubic equation given as **Table IV**, Equation (xi). Therefore in order to represent the length properties from 1300 K to 3400 K Equations (vii) and (xi) were transferred to **Table I**. Bulk properties based on these equations are given in **Table V**. Above 2000 K the measurements of Onufriev (11) have an average uncertainty of 0.23%. If this value is applied to the melting point values then the density is $21,031 \pm 49 \text{ kg m}^{-3}$ and the molar volume $(9.045 \pm 0.021) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.

Kulyamina *et al.* (13) used an independent approach in which the volumetric thermal expansion value (β) was calculated from Equation (xiv):

$$\beta = C^\circ_p/Q_0 [1 - 2 (H^\circ_T - H^\circ_0)/\Delta H^\circ_{\text{sub}}] \tag{xiv}$$

where values of the specific heat (C°_p) and absolute enthalpy ($H^\circ_T - H^\circ_0$) were given by Cherkhovskoi and Ramanauskas (14) and the value of the enthalpy of sublimation ($\Delta H^\circ_{\text{sub}}$) was from a previous review on osmium by the present author (15). The value of the enthalpy constant Q_0 was determined as 1606 kJ mol^{-1} based on values of β corresponding to the crystallographic values from 800 K to 1300 K. The equation was extrapolated to the selected melting point of 3320 K where the derived molar volume of $9.022 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ is in exact agreement with the value derived in the present review giving some confidence as to the use of both methods.

Properties in the Melting Point Region

Ishikawa *et al.* (16) measured the density of liquid osmium mainly in the undercooled region 2800 K to 3450 K and the results can be expressed as Equation (xv):

$$\rho (\text{kg m}^{-3}) = 22,423 - 0.92 T \text{ K} \tag{xv}$$

leading to a density of $19,295 \pm 162 \text{ kg m}^{-3}$ and a molar volume of $(9.859 \pm 0.083) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ at the selected melting point of 3400 K which compares to the molar volume of the solid as $(9.045 \pm 0.021) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. The increase in molar volume on melting is therefore $\Delta V = (8.14 \pm 0.86) \times 10^{-7} \text{ m}^3 \text{ mol}^{-1}$ and this value can be used in the Clausius-Clapeyron equation to determine the initial slope of the melting curve of osmium as Equation (xvi):

$$dT/dP = T_M \Delta V/\Delta H_M \tag{xvi}$$

where the melting point (T_M) at $3400 \pm 50 \text{ K}$

Table V Bulk Properties of Osmium 1300 K to 3400 K

Temperature, K	Thermal expansion coefficient, α , 10^{-6} K^{-1}	Length change, $\delta l/l_{293.15 \text{ K}} \times 100$, %	Molar volume, $10^{-6} \text{ m}^3 \text{ mol}^{-1}$	Density, kg m^{-3}
1300	6.56	0.583	8.570	22,198
1400	6.71	0.650	8.587	22,154
1500	6.87	0.718	8.604	22,109
1600	7.03	0.788	8.622	22,063
1700	7.20	0.860	8.641	22,016
1800	7.38	0.934	8.660	21,968
1900	7.56	1.009	8.679	21,919
2000	7.76	1.087	8.699	21,868
2100	7.98	1.166	8.719	21,817
2200	8.19	1.248	8.741	21,764
2300	8.41	1.332	8.762	21,710
2400	8.63	1.418	8.785	21,654
2500	8.85	1.507	8.808	21,598
2600	9.07	1.598	8.832	21,540
2700	9.29	1.691	8.856	21,480
2800	9.51	1.787	8.881	21,420
2900	9.73	1.885	8.907	21,358
3000	9.95	1.985	8.933	21,295
3100	10.17	2.088	8.960	21,231
3200	10.38	2.193	8.988	21,166
3300	10.60	2.300	9.016	21,099
3400	10.82	2.410	9.045	21,031

and the enthalpy of fusion (ΔH_M) at $68,005 \pm 1653 \text{ J mol}^{-1}$ were selected by the present author (12). The derived value of $dT/dP = 40.7 \pm 4.5 \text{ K GPa}^{-1}$ is in agreement with the value of 40.4 K GPa^{-1} given by Kulyamina *et al.* (13) but is notably lower than the estimate of 49.5 K GPa^{-1} by Burakovsky *et al.* (17) and the experimental value determined as 58 K GPa^{-1} by Patel and Sunder (18). The discrepancy from the experimental value is almost certainly due to the difficulty in carrying out measurements in the region of the melting point of osmium, for example, the large extrapolation of the thermal expansion values for the solid, the estimates of the melting point and enthalpy of fusion and possible systematic errors in the measurement of the density of the liquid and the initial slope of the melting curve. Clearly far more measurements are required in order to account for the difference.

Is Osmium Always the Densest Metal?

The present author (19) compared the effect of temperature on the densities of osmium

and iridium to evaluate which was the densest metal. Above room temperature the density difference in favour of osmium increased from 27 kg m^{-3} at room temperature to 147 kg m^{-3} at 1300 K, the then limit for osmium, and it was speculated that this difference would continue in to the high temperature region. With the values published in **Table V** the speculation is resolved and the difference increases to 575 kg m^{-3} at the melting point of iridium (2719 K) and thus proving that solid osmium is the densest metal at all temperatures. A comparison of the effect of temperatures on the densities is given in **Figure 1** and on their difference in **Figure 2** where the density values for iridium are those selected by the present author (4) with bulk values above 2000 K to be comparable with the bulk values for osmium.

New Equation for the Density of Liquid Osmium

In the review of the densities of the liquid platinum group metals (20) the values for osmium were based on the measurements of Paradis *et al.* (21). These

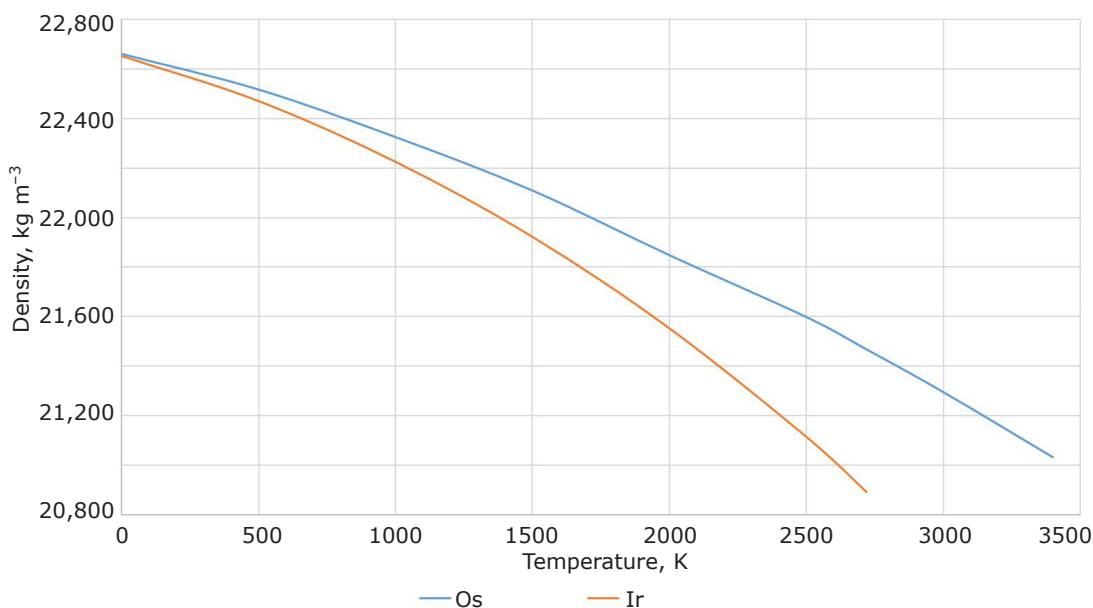


Fig. 1. Variation of density with temperature

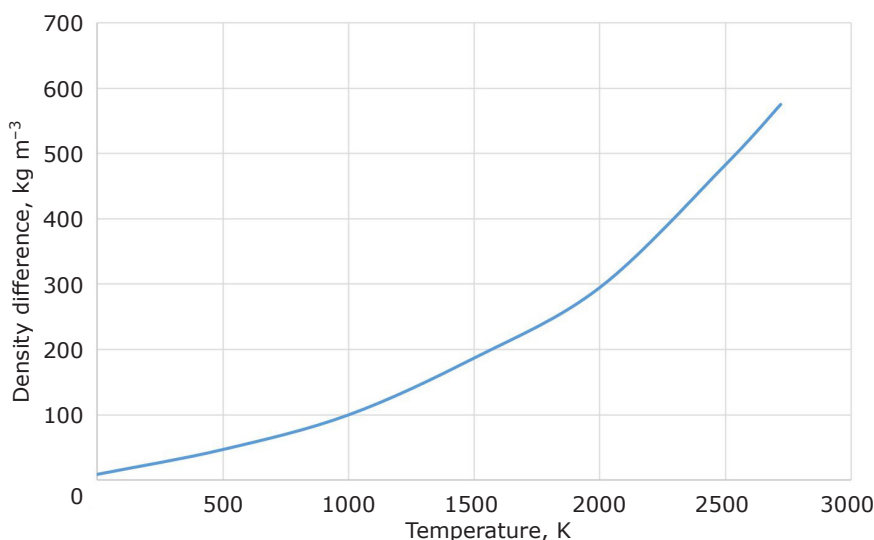


Fig. 2. Variation of density difference with temperature

have now been superseded by the measurements of Ishikawa *et al.* (16) over the range 2800 K to 3450 K which are given by Equation (xvii):

$$\rho \text{ (kg m}^{-3}\text{)} = 19,381 - 0.92 (T - 3306 \text{ K}) \text{ (xvii)}$$

At the selected melting point of 3400 K the calculated density is $19,295 \pm 162 \text{ kg m}^{-3}$ and the derived molar volume is $(9.859 \pm 0.083) \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ leading to the density equation corresponding to the selected melting as Equation (xviii):

$$\rho \text{ (kg m}^{-3}\text{)} = 19,295 - 0.92 (T - 3400 \text{ K}) \text{ (xviii)}$$

applicable over the temperature range 2800 K to 3400 K. Corrected values of density and molar volume are given in **Table VI**.

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Table VI Revised Values of the Densities and Molar Volumes of Liquid Osmium

Temperature, K	Density ^a , ρ , kg m ⁻³	Molar volume, V_m , 10 ⁶ m ³ mol ⁻¹
2800	19,847	9.585
2900	19,755	9.630
3000	19,663	9.675
3100	19,571	9.720
3200	19,479	9.766
3300	19,387	9.812
3400	19,295	9.859

^aEquation (xviii)

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<https://doi.org/10.1595/205651323X16679241042461>

Atomic Weights of the Platinum Group of Elements 2021

NON-PEER REVIEWED FEATURE

Received 20th October 2022; Online 29th March 2023

The publication of the 2021 atomic weights (1) leads to the following updated values for the atomic weights of the platinum group of elements: ruthenium 101.07 ± 0.02 ; rhodium 102.90549 ± 0.00002 ; palladium 106.42 ± 0.01 ; osmium 190.23 ± 0.03 ; iridium 192.217 ± 0.002 ; platinum 195.084 ± 0.009 .

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