

# A Re-assessment of the Thermodynamic Properties of Osmium

## Improved value for the enthalpy of fusion

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The thermodynamic properties were reviewed by the author in 1995. A new assessment of the enthalpy of fusion at  $68.0 \pm 1.7 \text{ kJ mol}^{-1}$  leads to a revision of the thermodynamic properties of the liquid phase and although the enthalpy of sublimation at 298.15 K is retained as  $788 \pm 4 \text{ kJ mol}^{-1}$  the normal boiling point is revised to 5565 K at one atmosphere pressure.

## Introduction

The thermodynamic properties of osmium were reviewed by the author in 1995 (1) with a further review in 2005 (2) to estimate a most likely value for the melting point at  $3400 \pm 50 \text{ K}$  to replace the poor quality experimental values which were being quoted in the literature. More recently Burakovsky *et al.* (3) have estimated a value of  $3370 \pm 75 \text{ K}$  in good agreement with the above selected value. In the 1995 review the enthalpy of fusion was unknown but was estimated from a relationship between the entropy of fusion and the melting point which showed a high

degree of correlation for the platinum group metals (pgms). However the derived entropy of fusion value for osmium was based on values for the other pgms available at that time but since then the values for both palladium and platinum have been revised so that the entropy of fusion value for osmium would also be revised leading to a new estimate of  $68.0 \pm 1.7 \text{ kJ mol}^{-1}$  for the enthalpy of fusion. This would then require the thermodynamic properties of the liquid phase to also be updated. A comment is included on an independent much lower estimate of the enthalpy of fusion. Wherever possible measurements have been corrected to the International Temperature Scale (ITS-90) and to the currently accepted atomic weight of  $190.23 \pm 0.03$  (4).

## Low Temperature Solid Phase

Selected values in the normal and superconducting states are based on the specific heat measurements of Okaz and Keesom (0.18 K to 4.2 K) (5) including a superconducting transition temperature of  $0.638 \pm 0.002 \text{ K}$ , an electronic specific heat coefficient ( $\gamma$ ) of  $2.050 \pm 0.003 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and a limiting Debye temperature ( $\Theta_D$ ) of  $467 \pm 6 \text{ K}$ . Specific heat values up to 5 K in both the normal and superconducting states are given in **Table I**.

**Table I Low Temperature Specific Heat Data Up To 5 K**

Temperature, K	$C^{\circ s^a}$ , $\text{mJ mol}^{-1} \text{ K}^{-1}$	$C^{\circ n^b}$ , $\text{mJ mol}^{-1} \text{ K}^{-1}$	Temperature, K	$C^{\circ p}$ , $\text{mJ mol}^{-1} \text{ K}^{-1}$
<b>0.2</b>	0.093	0.410	<b>1.0</b>	2.07
<b>0.3</b>	0.525	0.616	<b>2.0</b>	4.25
<b>0.4</b>	1.19	0.821	<b>3.0</b>	6.67
<b>0.5</b>	1.94	1.03	<b>4.0</b>	9.43
<b>0.6</b>	2.79	1.23	<b>5.0</b>	12.7
<b>0.638</b>	3.14	1.32	–	–

<sup>a</sup>Superconducting state

<sup>b</sup>Non-superconducting state (in magnetic field)

Above 4 K selected specific heat values are initially based on the measurements by Naumov *et al.* (6 K to 316 K) (6). However above 280 K these measurements show an abrupt increase of  $0.5 \text{ J mol}^{-1} \text{ K}^{-1}$  and a further abrupt increase of  $0.3 \text{ J mol}^{-1} \text{ K}^{-1}$  above 300 K. Naumov *et al.* attempted to accommodate these values but the selected specific heat curve showed an unnatural sharp change in slope above 270 K. Therefore the selected values of Naumov *et al.* above 250 K were rejected and instead specific heat values to 298.15 K were obtained by joining smoothly with the high temperature enthalpy measurements of Ramanauskas *et al.* (7). In the original review of the low temperature data only the specific heat values were given consisting above 50 K of 10 K intervals to 100 K and then 20 K intervals above this temperature as well as the value at 298.15 K. This minimalist approach is now considered to be unsatisfactory and therefore comprehensive low temperature thermodynamic data are now given at 5 K intervals from 5 K to 50 K and at 10 K intervals above this temperature up to 290 K and then the value at 298.15 K as given in **Table II**.

## High Temperature Solid Phase

In the high temperature region, after correction for temperature scale and atomic weight, the enthalpy measurements of Ramanauskas *et al.* (1155 K to 2961 K) (7) were fitted to the following equation with an overall accuracy of  $\pm 200 \text{ J mol}^{-1}$  (0.4%) (Equation (i)):

$$H^0_T - H^0_{298.15 \text{ K}} (\text{J mol}^{-1}) = 26.1938 T + 1.32318 \times 10^{-4} T^2 + 3.85960 \times 10^{-7} T^3 + 3.99978 \times 10^{-11} T^4 + 150378/T - 8336.36 \quad (\text{i})$$

This equation was used to represent selected enthalpy values from 298.15 K to 3400 K. Equivalent specific heat and entropy equations corresponding to the above equation are given in **Table III**, the free energy equations in **Table IV**, transition values associated with the free energy functions in **Table V** and derived thermodynamic values in **Table VI**. The actual equation given by Ramanauskas *et al.* to represent the enthalpy measurements over the experimental temperature range agrees with Equation (i) to within 0.2%.

The only other enthalpy measurements were obtained by Jaeger and Rosenbohm (693 K to 1877 K) (8) and compared to the selected values vary from 1.6% low at 693 K to an estimated 1.2% low at 1600 K to 1.4% low at 1877 K.

## Liquid Phase

Selected values of the enthalpies and entropies of fusion of the Groups 8 to 10 elements with a close-packed structure are given in **Table VII**. Only the enthalpy of fusion of osmium is unknown. References (10–14) represent the latest reviews on the thermodynamic properties of the pgms by the present author. From an evaluation of the entropies of fusion of the elements, Chekhovskoi and Kats (15) proposed that the entropy of fusion ( $\Delta S^0_M$ ) and the melting point ( $T_M$ ) could be related by the equation  $\Delta S^0_M = A T_M + B$ . In the previous review (1) different values were proposed for the entropies of fusion of palladium ( $8.80 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and platinum ( $10.45 \text{ J mol}^{-1} \text{ K}^{-1}$ ) leading to an estimate of the entropy of fusion for osmium of  $20.6 \text{ J mol}^{-1} \text{ K}^{-1}$ . With the revised values it is clear that, although of the right order, the entropy of fusion of nickel is discrepant and has therefore been disregarded. The other six values were fitted to the equation with  $A = 6.6954 \times 10^{-3}$  and  $B = -2.7630$  and a standard deviation of the fit of  $\pm 0.193 \text{ J mol}^{-1} \text{ K}^{-1}$ . However in order that the derived entropy of fusion of osmium has a similar accuracy to those of the input values then the accuracy is expanded to a 95% confidence level leading to an entropy of fusion of  $20.0014 \pm 0.387 \text{ J mol}^{-1} \text{ K}^{-1}$  and based on a melting point  $3400 \pm 50 \text{ K}$  to an enthalpy of fusion of  $68,005 \pm 1653 \text{ J mol}^{-1}$ . Based on neighbouring elements then a liquid specific heat of  $50 \text{ J mol}^{-1} \text{ K}^{-1}$  was proposed in the original paper (1) and therefore the enthalpy of liquid osmium can now be expressed as Equation (ii):

$$H^0_T - H^0_{298.15 \text{ K}} (\text{J mol}^{-1}) = 50.0000 T + 816.2 \quad (\text{ii})$$

Equivalent specific heat and entropy equations corresponding to the above equation are given in **Table III**, the free energy equation in **Table IV** and derived thermodynamic values in **Table VI**. It should now be possible to accurately determine the melting point and enthalpy of fusion of osmium since the metal is available in high purity in a coherent form whilst the enthalpies of fusion of other high melting point elements such as rhenium (3458 K) and tungsten (3687 K) have been successfully determined.

## Gas Phase

Based on a standard state pressure of 1 bar the thermodynamic properties of the monatomic gas were calculated from the 295 energy levels listed by Van Kleef and Klinkenberg (16) and

**Table II Low Temperature Thermodynamic Data Above 5 K**

Temperature, K	$C_p^{\circ a}$ , J mol <sup>-1</sup> K <sup>-1</sup>	$H_T^{\circ} - H_{0K}^{\circ b}$ , J mol <sup>-1</sup>	$S_T^{\circ c}$ , J mol <sup>-1</sup> K <sup>-1</sup>	$-G_T^{\circ} - H_{0K}^{\circ d}$ , J mol <sup>-1</sup>	$-(G_T^{\circ} - H_{0K}^{\circ})/T^d$ , J mol <sup>-1</sup> K <sup>-1</sup>
5	0.0127	0.0286	0.0111	0.0266	0.00532
10	0.0417	0.153	0.0272	0.119	0.0119
15	0.116	0.519	0.0559	0.319	0.0213
20	0.290	1.475	0.110	0.719	0.0360
25	0.636	3.704	0.208	1.490	0.0596
30	1.252	8.302	0.374	2.910	0.0970
35	2.104	16.61	0.628	5.376	0.154
40	3.139	29.65	0.975	9.346	0.234
45	4.322	48.25	1.412	15.27	0.339
50	5.604	73.03	1.933	23.60	0.472
60	8.205	142.2	3.186	48.99	0.817
70	10.563	236.2	4.631	87.96	1.257
80	12.661	352.6	6.182	142.0	1.775
90	14.448	488.4	7.780	211.8	2.353
100	15.939	640.6	9.381	297.6	2.976
110	17.182	806.4	10.961	399.3	3.630
120	18.231	983.6	12.502	516.7	4.305
130	19.132	1170	13.997	649.2	4.994
140	19.912	1366	15.445	796.4	5.689
150	20.577	1568	16.842	957.9	6.386
160	21.085	1777	18.187	1133	7.082
170	21.533	1990	19.479	1322	7.774
180	21.975	2207	20.722	1523	8.459
190	22.377	2429	21.921	1736	9.136
200	22.695	2655	23.078	1961	9.804
210	22.928	2883	24.191	2197	10.463
220	23.178	3113	25.263	2445	11.111
230	23.441	3346	26.928	2702	11.749
240	23.715	3582	27.302	2970	12.377
250	23.929	3820	28.275	3248	12.993
260	24.119	4061	29.217	3536	13.599
270	24.290	4303	30.130	3832	14.195
280	24.444	4546	31.017	4138	14.780
290	24.584	4791	31.877	4453	15.355
298.15	24.688	4992	32.560	4715	15.816

<sup>a</sup> $C_p^{\circ}$  is specific heat<sup>b</sup> $H_T^{\circ} - H_{0K}^{\circ}$  is enthalpy<sup>c</sup> $S_T^{\circ}$  is entropy<sup>d</sup> $-G_T^{\circ} - H_{0K}^{\circ}$  and  $-(G_T^{\circ} - H_{0K}^{\circ})/T$  are free energy functions

Gluck *et al.* (17) using the method outlined by Kolsky *et al.* (18) together with the 2018 Fundamental Constants (19). Derived thermodynamic values are given in **Table VIII**.

## Enthalpy of Sublimation

No temperature scales were given with the measurements of the vapour pressures by Panish

and Reif (20) and Carrera *et al.* (21). Normally the experimental temperature values would therefore be accepted but in the case of such values above 2000 K the difference from the current scale, ITS-90, becomes significant. Since the measurements were carried out in 1962 and 1964 then they would ultimately be associated with the International Practical Temperature Scale (IPTS-1948) and were therefore corrected to the

**Table III Thermodynamic Equations Above 298.15 K****Solid: 298.15 K to 3400 K**

$$C_{p}^{a}, \text{ J mol}^{-1} \text{ K}^{-1} = 26.1938 + 2.64636 \times 10^{-4} T + 1.15788 \times 10^{-6} T^2 + 1.599912 \times 10^{-10} T^3 - 150378/T^2$$

$$H_{T}^{0} - H_{298.15 \text{ K}}^{0b}, \text{ J mol}^{-1} = 26.1938 T + 1.32318 \times 10^{-4} T^2 + 3.85960 \times 10^{-7} T^3 + 3.99978 \times 10^{-11} T^4 + 150378/T - 8336.36$$

$$S_{T}^{c}, \text{ J mol}^{-1} \text{ K}^{-1} = 26.1938 \ln(T) + 2.64636 \times 10^{-4} T + 5.78940 \times 10^{-7} T^2 + 5.33304 \times 10^{-11} T^3 + 75189/T^2 - 117.6597$$

**Liquid: 3400 K to 5600 K**

$$C_{p}^{a}, \text{ J mol}^{-1} \text{ K}^{-1} = 50.0000$$

$$H_{T}^{0} - H_{298.15 \text{ K}}^{0b}, \text{ J mol}^{-1} = 50.0000 T + 816.2$$

$$S_{T}^{c}, \text{ J mol}^{-1} \text{ K}^{-1} = 50.0000 \ln(T) - 281.5442$$

<sup>a</sup> $C_{p}$  is specific heat<sup>b</sup> $H_{T}^{0} - H_{298.15 \text{ K}}^{0}$  is enthalpy<sup>c</sup> $S_{T}^{c}$  is entropy**Table IV Free Energy Equations Above 298.15 K****Solid: 298.15 K to 3400 K**

$$G_{T}^{0} - H_{298.15 \text{ K}}^{0a}, \text{ J mol}^{-1} = 143.8535 T - 1.32318 \times 10^{-4} T^2 - 1.92980 \times 10^{-7} T^3 - 1.33326 \times 10^{-11} T^4 + 75189/T - 26.1938 T \ln(T) - 8336.36$$

**Liquid: 3400 K to 5600 K**

$$G_{T}^{0} - H_{298.15 \text{ K}}^{0a}, \text{ J mol}^{-1} = 331.5442 T - 50.0000 T \ln(T) + 816.2$$

<sup>a</sup> $G_{T}^{0} - H_{298.15 \text{ K}}^{0}$  is the free energy function

ITS-90 scale on this basis. Derived enthalpies of sublimation are given in **Table IX**. The selected enthalpy of sublimation of  $788 \pm 4 \text{ kJ mol}^{-1}$  is basically an unweighted average but slightly biased towards the measurements of Carrera *et al.* (21).

## Vapour Pressure Equations

The vapour pressure equations are given in **Table X**. For the solid the evaluation was for free energy functions for the solid and the gas at 50 K intervals from 1700 K to 3400 K and for the liquid at 50 K intervals from 3400 K to 5600 K and were fitted to Equation (iii):

$$\ln(p, \text{ bar}) = A + B \ln(T) + C/T + D T + E T^2 \quad (\text{iii})$$

A review of the vapour pressure data is given in **Table XI**.

## Discussion of Alternative Estimates of the Enthalpy of Fusion of Osmium

Based on various assumptions Fokin *et al.* (22) proposed that the enthalpy of fusion for osmium was only in the range  $30 \text{ kJ mol}^{-1}$  to  $40 \text{ kJ mol}^{-1}$  or half of the above derived value. One of the main arguments was that by using the Chekhovskoi-Kats equation the entropy of fusion for rhenium was estimated to be  $20.0 \text{ J mol}^{-1} \text{ K}^{-1}$  whereas the actual value is only  $9.85 \text{ J mol}^{-1} \text{ K}^{-1}$  (23) and therefore if the estimate for rhenium was so completely wrong then it would also be possible that the estimate for the neighbouring element osmium at  $19.0 \text{ J mol}^{-1} \text{ K}^{-1}$  could also be wrong. However, Fokin *et al.* completely misunderstood how the estimated values were arrived at. It was initially assumed that Group 7 rhenium would behave like Groups 8 to 10 (the pgms) whereas all that the experimental value proved was that Group 7 elements behaved completely independently of Groups 8 to 10 and therefore showed the same deviations as other transition metal groups. For example, the entropies of fusion of Group 5 elements vanadium, niobium and tantalum at  $10.46 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $11.13 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $10.25 \text{ J mol}^{-1} \text{ K}^{-1}$  (24) showed no trend with temperature whilst the entropies of fusion of the Group 6 elements chromium, molybdenum and tungsten at  $13.89 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $13.53 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $13.66 \text{ J mol}^{-1} \text{ K}^{-1}$  (24) were virtually identical. Therefore it would not be surprising if Group 7 elements would also behave completely independently. In fact for the transition metals only the Groups 8 to 10 elements showed a high degree of correlation with the Chekhovskoi-Kats equation. However in order to prove their point that osmium does behave differently to the other pgms, Fokin *et al.* used the equation:  $\sigma_{\text{M}} = Z \Delta H_{\text{M}} \rho_{\text{SM}} d$  where  $\sigma_{\text{M}}$  is the surface tension at the melting point,  $\Delta H_{\text{M}}$  is the enthalpy of fusion,  $\rho_{\text{SM}}$  is the density of the solid at the melting point and  $d$  is the interatomic distance. This equation was applied to a number of elements but there is virtually no correlation for the values of  $Z$  with values varying between 1.2 to 3.3. For osmium Fokin *et al.* selected an arbitrary rounded value of  $Z = 2$  for osmium and values of surface tension and liquid density determined by Paradis *et al.* (25) to arrive at an enthalpy of fusion of only  $32 \text{ kJ mol}^{-1}$  which is considerably less than the value of  $39.0 \pm 1.4 \text{ kJ mol}^{-1}$  (9) selected for the analogue element ruthenium whereas for the other pgms the enthalpy of fusion is always greater for the heavier analogue. This much lower

**Table V Transition Values Involved with the Free Energy Equations**

Transition	Temperature, K	$\Delta H_M, \text{J mol}^{-1}$	$\Delta S_M, \text{J mol}^{-1} \text{K}^{-1}$
<b>Fusion</b>	3400	68005.00	20.0014

**Table VI High Temperature Thermodynamic Data for the Condensed Phases**

Temperature, K	$C_p^a, \text{J mol}^{-1} \text{K}^{-1}$	$H_T^o - H_{298.15 \text{ K}}^o, \text{J mol}^{-1}$	$S_T^o, \text{J mol}^{-1} \text{K}^{-1}$	$-(G_T^o - H_{298.15 \text{ K}}^o) / T^d, \text{J mol}^{-1} \text{K}^{-1}$
<b>298.15</b>	24.688	0	32.560	32.560
<b>300</b>	24.711	46	32.712	32.560
<b>400</b>	25.555	2564	39.951	33.541
<b>500</b>	26.034	5145	45.709	35.419
<b>600</b>	26.386	7767	50.488	37.543
<b>700</b>	26.694	10,421	54.579	39.692
<b>800</b>	26.994	13,105	58.163	41.781
<b>900</b>	27.301	15,820	61.360	43.782
<b>1000</b>	27.626	18,566	64.253	45.687
<b>1100</b>	27.975	21,346	66.902	47.497
<b>1200</b>	28.351	24,162	69.352	49.217
<b>1300</b>	28.757	27,017	71.637	50.855
<b>1400</b>	29.196	29,914	73.784	52.417
<b>1500</b>	29.669	32,857	75.814	53.909
<b>1600</b>	30.178	35,849	77.745	55.339
<b>1700</b>	30.724	38,894	79.591	56.712
<b>1800</b>	31.308	41,996	81.363	58.033
<b>1900</b>	31.932	45,157	83.073	59.306
<b>2000</b>	32.597	48,383	84.727	60.536
<b>2100</b>	33.303	51,678	86.335	61.726
<b>2200</b>	34.053	55,045	87.902	62.880
<b>2300</b>	34.846	58,490	89.432	64.002
<b>2400</b>	35.684	62,016	90.933	65.093
<b>2500</b>	36.568	65,628	92.407	66.156
<b>2600</b>	37.499	69,331	93.859	67.193
<b>2700</b>	38.478	73,130	95.293	68.208
<b>2800</b>	39.506	77,028	96.710	69.200
<b>2900</b>	40.583	81,032	98.115	70.173
<b>3000</b>	41.712	85,147	99.510	71.128
<b>3100</b>	42.892	89,377	100.897	72.066
<b>3200</b>	44.125	93,727	102.278	72.988
<b>3300</b>	45.412	98,203	103.655	73.897
<b>3400 (solid)</b>	46.751	102,811	105.031	74.792
<b>3400 (liquid)</b>	50.000	170,816	125.032	74.792
<b>3500</b>	50.000	175,816	126.482	76.249
<b>3600</b>	50.000	180,816	127.890	77.664
<b>3700</b>	50.000	185,816	129.260	79.040
<b>3800</b>	50.000	190,816	130.594	80.379
<b>3900</b>	50.000	195,816	131.892	81.683
<b>4000</b>	50.000	200,816	133.158	82.954
<b>4100</b>	50.000	205,816	134.393	84.194
<b>4200</b>	50.000	210,816	135.598	85.403

(Continued)

Table VI Continued

Temperature, K	$C_p^o$ , J mol <sup>-1</sup> K <sup>-1</sup>	$H_T^o - H_{298.15\text{ K}}^o$ , J mol <sup>-1</sup>	$S_T^o$ , J mol <sup>-1</sup> K <sup>-1</sup>	$-(G_T^o - H_{298.15\text{ K}}^o)/T^d$ , J mol <sup>-1</sup> K <sup>-1</sup>
4300	50.000	215,816	136.774	86.585
4400	50.000	220,816	137.924	87.738
4500	50.000	225,816	139.047	88.866
4600	50.000	230,816	140.146	89.969
4700	50.000	235,816	141.222	91.048
4800	50.000	240,816	142.274	92.104
4900	50.000	245,816	143.305	93.139
5000	50.000	250,816	144.306	94.152
5100	50.000	255,816	145.311	95.146
5200	50.000	260,816	146.276	96.120
5300	50.000	265,816	147.229	97.075
5400	50.000	270,816	148.164	98.012
5500	50.000	275,816	149.081	98.933
5600	50.000	280,816	149.982	99.836

<sup>a</sup> $C_p^o$  is specific heat<sup>b</sup> $H_T^o - H_{298.15\text{ K}}^o$  is enthalpy<sup>c</sup> $S_T^o$  is entropy<sup>d</sup> $-(G_T^o - H_{298.15\text{ K}}^o)/T$  is the free energy functions

Table VII Enthalpies and Entropies of Fusion for the Groups 8 to 10 Elements

Element	Melting point, K	Enthalpy of fusion, J mol <sup>-1</sup>	Entropy of fusion, J mol <sup>-1</sup> K <sup>-1</sup>	Reference
Cobalt	1768	16056 ± 369	9.08 ± 0.21	(9)
Nickel	1728	17042 ± 376	9.86 ± 0.22	(9)
Ruthenium	2606	39040 ± 1400	14.98 ± 0.54	(10)
Rhodium	2236	27295 ± 850	12.21 ± 0.38	(11)
Palladium	1828.0	17340 ± 730	9.48 ± 0.40	(12)
Iridium	2719	41335 ± 1128	15.20 ± 0.41	(13)
Platinum	2041.3	22110 ± 940	10.83 ± 0.46	(14)

Table VIII Thermodynamic Properties of the Gaseous Phase

Temperature, K	$C_p^o$ , J mol <sup>-1</sup> K <sup>-1</sup>	$H_T^o - H_{298.15\text{ K}}^o$ , J mol <sup>-1</sup>	$S_T^o$ , J mol <sup>-1</sup> K <sup>-1</sup>	$-(G_T^o - H_{298.15\text{ K}}^o)/T^d$ , J mol <sup>-1</sup> K <sup>-1</sup>
298.15	20.788	0	192.579	192.579
300	20.788	38	192.707	192.579
400	20.810	2118	198.689	193.394
500	20.901	4203	203.341	194.936
600	21.102	6302	207.168	196.665
700	21.432	8428	210.444	198.404
800	21.887	10,592	213.334	200.093
900	22.453	12,809	215.944	201.712
1000	23.104	15,086	218.342	203.256
1100	23.812	27,431	220.577	204.731
1200	24.545	29,849	222.680	206.140
1300	25.278	22,340	224.674	207.489

(Continued)

Table VIII Continued

Temperature, K	$C_p^o$ , $J mol^{-1} K^{-1}$	$H_T^o - H_{298.15 K}^o$ , $J mol^{-1}$	$S_T^o$ , $J mol^{-1} K^{-1}$	$-(G_T^o - H_{298.15 K}^o)/T$ , $J mol^{-1} K^{-1}$
1400	25.988	24,904	226.574	208.785
1500	26.659	27,537	228.390	210.032
1600	27.283	30,234	230.130	211.234
1700	27.854	32,991	231.802	212.395
1800	28.374	35,803	233.409	213.518
1900	28.844	38,665	234.956	214.606
2000	29.269	41,571	236.446	215.661
2100	29.656	44,517	237.884	216.685
2200	30.009	47,501	239.272	217.681
2300	30.337	50,518	240.613	218.649
2400	30.642	53,567	241.911	219.591
2500	30.931	56,646	243.167	220.509
2600	31.207	59,753	244.386	221.404
2700	31.473	62,887	245.569	222.277
2800	31.732	66,047	246.718	223.130
2900	31.986	69,233	247.836	223.962
3000	32.234	72,444	248.925	224.776
3100	32.480	75,680	249.986	225.573
3200	32.722	78,940	251.021	226.352
3300	32.961	82,224	252.031	227.115
3400	33.197	85,532	253.019	227.862
3500	33.430	88,864	253.984	228.595
3600	33.660	92,218	254.929	229.313
3700	33.885	95,596	255.855	230.018
3800	34.107	98,995	256.761	230.710
3900	34.323	102,417	257.650	231.389
4000	34.535	105,860	258.522	232.057
4100	34.742	109,324	259.377	232.713
4200	34.943	112,808	260.217	233.357
4300	35.138	116,312	261.041	233.992
4400	35.327	119,835	261.851	234.616
4500	35.510	123,377	262.647	235.230
4600	35.687	126,937	263.429	235.834
4700	35.858	130,514	264.199	236.430
4800	36.023	134,108	264.956	237.016
4900	36.182	137,719	265.700	237.594
5000	36.325	141,345	266.432	238.164
5100	36.483	144,986	267.153	238.725
5200	36.625	148,641	267.863	239.278
5300	36.762	152,311	268.562	239.824
5400	36.895	155,993	269.251	240.363
5500	37.022	159,689	269.929	240.894
5600	37.145	163,398	270.597	241.419

<sup>a</sup> $C_p$  is specific heat<sup>b</sup> $H_T^o - H_{298.15 K}^o$  is enthalpy<sup>c</sup> $S_T^o$  is entropy<sup>d</sup> $-(G_T^o - H_{298.15 K}^o)/T$  is the free energy functions;  $H_{298.15 K}^o - H_{0 K}^o = 6197.4 J mol^{-1}$

**Table IX Enthalpies of Sublimation at 298.15 K**

Authors	Reference	Method <sup>a</sup>	Temperature range, K <sup>b</sup>	$\Delta H^{\circ}_{298.15\text{ K}}(\text{II})^{\text{c}}$ , kJ mol <sup>-1</sup>	$\Delta H^{\circ}_{298.15\text{ K}}(\text{III})^{\text{c}}$ , kJ mol <sup>-1</sup>
Panish and Reif	(19)	L	2376–2718	807 ± 35	784.3 ± 1.3
Carrera <i>et al.</i>	(20)	L	2159–2595	773 ± 13	790.7 ± 0.7
				Selected	788 ± 4

<sup>a</sup>L: Langmuir free evaporation<sup>b</sup>Temperature ranges corrected to temperature scale ITS-90<sup>c</sup> $\Delta H^{\circ}_{298.15\text{ K}}(\text{II})$  and  $\Delta H^{\circ}_{298.15\text{ K}}(\text{III})$  are the Second Law and Third Law enthalpies of sublimation at 298.15 K**Table X Vapour Pressure Equations<sup>a</sup>**

Phase	Temperature range, K	A	B	C	D	E
Solid	1700–3400	26.82612	-1.17464	-95030.60	$5.68917 \times 10^{-4}$	$-6.25849 \times 10^{-8}$
Liquid	3400–5600	45.02206	-3.41958	-93542.51	$2.64385 \times 10^{-4}$	$-5.78416 \times 10^{-9}$

<sup>a</sup> Equation (iii)**Table XI Vapour Pressure**

Temperature, K	Pressure, bar	$\Delta G^{\circ}_{\text{T}}^{\text{a}}$ , J mol <sup>-1</sup>	$\Delta H^{\circ}_{\text{T}}^{\text{b}}$ , J mol <sup>-1</sup>	Pressure, bar	Temperature, K
298.15	$2.03 \times 10^{-130}$	740,290	788,000	$10^{-15}$	1780
300	$1.44 \times 10^{-129}$	739,994	787,992	$10^{-14}$	1861
400	$2.81 \times 10^{-95}$	724,059	787,554	$10^{-13}$	1950
500	$1.03 \times 10^{-74}$	708,242	787,058	$10^{-12}$	2048
600	$5.14 \times 10^{-61}$	692,527	786,535	$10^{-11}$	2156
700	$3.09 \times 10^{-51}$	676,901	786,007	$10^{-10}$	2277
800	$6.59 \times 10^{-44}$	661,350	785,487	$10^{-9}$	2411
900	$3.28 \times 10^{-38}$	645,863	784,989	$10^{-8}$	2563
1000	$1.18 \times 10^{-33}$	630,430	784,520	$10^{-7}$	2736
1100	$6.23 \times 10^{-30}$	615,043	784,085	$10^{-6}$	2934
1200	$7.88 \times 10^{-27}$	599,693	783,687	$10^{-5}$	3163
1300	$3.31 \times 10^{-24}$	584,375	783,323	$10^{-4}$	3435
1400	$5.86 \times 10^{-22}$	569,084	782,990	$10^{-3}$	3792
1500	$5.19 \times 10^{-20}$	553,816	782,680	$10^{-2}$	4235
1600	$2.62 \times 10^{-18}$	538,568	782,385	$10^{-1}$	4804
1700	$8.32 \times 10^{-17}$	523,338	782,097	1	5559.70
1800	$1.80 \times 10^{-15}$	508,126	781,807	NBP <sup>c</sup>	5564.74
1900	$2.81 \times 10^{-14}$	492,929	781,508	-	-
2000	$3.33 \times 10^{-13}$	477,749	781,188	-	-
2100	$3.12 \times 10^{-12}$	462,586	780,839	-	-
2200	$2.38 \times 10^{-11}$	447,439	780,456	-	-
2300	$1.52 \times 10^{-10}$	432,312	780,028	-	-
2400	$8.32 \times 10^{-10}$	417,204	779,551	-	-
2500	$3.97 \times 10^{-9}$	402,117	779,018	-	-
2600	$1.68 \times 10^{-8}$	387,052	778,422	-	-
2700	$6.36 \times 10^{-8}$	372,012	777,757	-	-
2800	$2.19 \times 10^{-7}$	356,998	777,019	-	-
2900	$6.92 \times 10^{-7}$	342,011	776,201	-	-
3000	$2.02 \times 10^{-6}$	327,054	775,297	-	-
3100	$5.51 \times 10^{-6}$	312,129	774,303	-	-
3200	$1.41 \times 10^{-5}$	297,237	773,213	-	-

(Continued)



Table XI Continued

Temperature, K	Pressure, bar	$\Delta G_T^{\circ a}$ , J mol <sup>-1</sup>	$\Delta H_T^{\circ b}$ , J mol <sup>-1</sup>	Pressure, bar	Temperature, K
3300	$3.39 \times 10^{-5}$	282,381	772,021	-	-
3400 (solid)	$7.75 \times 10^{-5}$	267,563	770,721	-	-
3400 (liquid)	$7.75 \times 10^{-5}$	267,563	702,716	-	-
3500	$1.58 \times 10^{-4}$	254,788	701,048	-	-
3600	$3.08 \times 10^{-4}$	242,061	699,402	-	-
3700	$5.78 \times 10^{-4}$	229,380	697,780	-	-
3800	$1.05 \times 10^{-3}$	216,742	696,179	-	-
3900	$1.84 \times 10^{-3}$	204,146	694,601	-	-
4000	$3.15 \times 10^{-3}$	191,590	693,044	-	-
4100	$5.23 \times 10^{-3}$	179,073	691,508	-	-
4200	$8.48 \times 10^{-3}$	166,593	689,992	-	-
4300	$1.34 \times 10^{-2}$	154,148	688,496	-	-
4400	$2.08 \times 10^{-2}$	141,739	687,019	-	-
4500	$3.15 \times 10^{-2}$	129,363	685,561	-	-
4600	$4.69 \times 10^{-2}$	117,018	684,121	-	-
4700	$6.84 \times 10^{-2}$	104,706	682,698	-	-
4800	$9.87 \times 10^{-2}$	92,422	681,292	-	-
4900	0.140	80,169	679,903	-	-
5000	0.195	67,943	678,529	-	-
5100	0.269	55,745	677,170	-	-
5200	0.365	43,574	675,820	-	-
5300	0.490	31,428	674,495	-	-
5400	0.651	19,307	673,177	-	-
5500	0.854	7,210	671,873	-	-
5559.70	1.000	0	671,100	-	-
5600	1.110	-4,863	670,582	-	-

<sup>a</sup> $\Delta G_T^{\circ}$  is the free energy of formation at 1 bar standard state pressure and temperature T

<sup>b</sup> $\Delta H_T^{\circ}$  is the enthalpy of sublimation at temperature T enthalpy of sublimation at 0 K:  $\Delta H_0^{\circ} = 786.795 \pm 4.000$  kJ mol<sup>-1</sup>

<sup>c</sup>NBP is the normal boiling point at one atmosphere pressure (1.01325 bar)

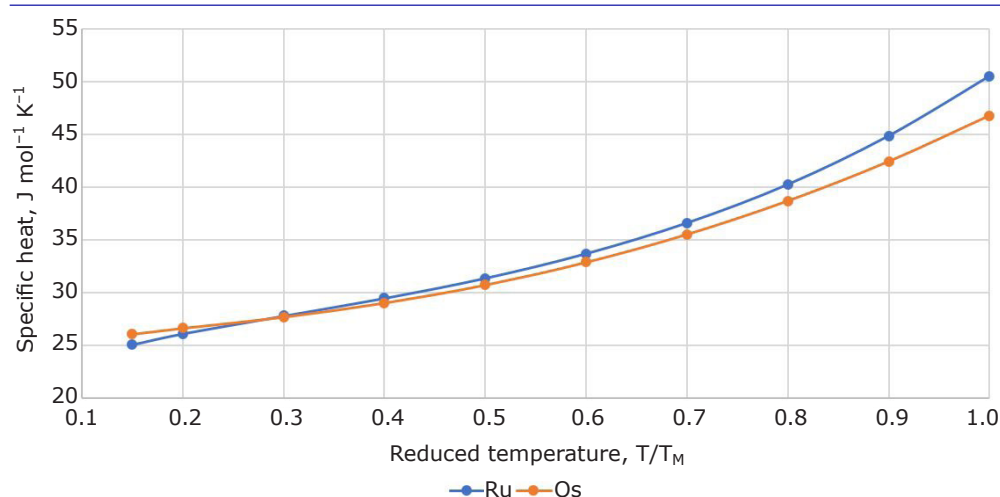


Fig. 1. The specific heat values of ruthenium and osmium at reduced temperature ( $T/T_M$ )

value for the enthalpy of fusion would suggest that the thermal properties of osmium should then be distinct from those of the other pgms but this is not the case. For example, the specific heat values of ruthenium (10) and osmium at reduced temperature

( $T/T_M$ ) as indicated in **Figure 1** are very similar and show virtually the same behaviour suggesting that they are genuine analogues of each other whilst the extrapolated melting point of osmium obtained by applying the same incremental difference as

between iridium and platinum agrees closely with the selected value and again suggesting a common Groups 8 to 10 behaviour.

Further, the chemical properties of ruthenium and osmium are virtually identical forming the same type of compounds with similar properties. These are examples where osmium behaves exactly like the other pgms and on these grounds it is suggested that the very low value for the enthalpy of fusion as suggested by Fokin *et al.* is inconsistent with this behaviour and that osmium would obey the same periodic trend as suggested by the other pgms and that its entropy of fusion can be determined by the Chekhovskoi-Kats equation. This would suggest anomalies in the input values selected by Fokin *et al.*, especially in the selection of  $Z = 2$  for osmium since the value for the analogue ruthenium is only 1.5 whilst the value for the neighbouring element iridium is only 1.2 where the selection of such values would lead to higher enthalpies of fusion for osmium. It is suggested that in view of the lack of any real correlation for  $Z$  that the value for osmium may well be independent and could even be 1.0 leading to an enthalpy of fusion similar to that obtained from the Chekhovskoi-Kats equation. Therefore until the actual enthalpy of fusion of osmium is determined it is assumed that it behaves as a normal Groups 8 to 10 element.

## Conclusions

Estimated entropy and enthalpy values of fusion of osmium have been revised leading to corrections of the thermodynamic properties of the liquid phase and therefore to the vapour pressure curve above the melting point. The revisions are based on the assumption that osmium behaves as a normal Group 8 to 10 element and contradicts recent suggestions that its behaviour could be abnormal.

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