The Thermodynamic Properties of Platinum on ITS-90

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Platinum exists in a face-centred cubic structure with a lattice parameter at 20°C of 0.39235 nm and a density of 21.45 g/cm^3 (1, 2). The freezing point is a proposed secondary fixed point on the International Temperature Scale ITS-90 at 1768.1°C (3). Wherever possible values have been corrected to the currently accepted atomic weight of 195.08 (4) and to the ITS-90 temperature scale (5–9), including the further correction to this scale between 630.615 and 1064.18°C (10–12). Previous assessments for platinum were performed by Hultgren and co-workers (13) and by Furukawa, Reilly and Gallagher (14).

Solid

Selected specific heat measurements below 30 K lead to the following values of the electronic specific heat coefficient (γ) and the Debye temperature (θ_D), as shown in Table I.

On average the measurements of Berg, and Boerstoel, Zwart and Hansen agree with the selected curve to 0.6 per cent while earlier measurements of Clusius, Losa and Franzosini (20) 11–274 K are from 7 per cent high to 3 per cent low in this region. Other measurements were rejected in the previous assessments.

Between 30 and 300 K selected values are based on the specific heat measurements of Clusius, Losa and Franzosini (20) 11–274 K and Yokokawa and Takahashi (21) 81–983 K with preference being given to the latter above 80 K and which on average agree with the selected curve to 0.3 per cent, while the former measurements are up to 1.6 per cent too high at the highest temperatures measured. The derived value of the enthalpy $H^\circ_{298.15} - H^\circ_0$ is in exact agreement with that selected by Yokokawa and Takahashi, but the entropy $S^\circ_{298.15}$ is slightly higher due mainly to the adoption of a different value of entropy at 80 K, see Table II and Figure 1.

In the high temperature region values are based on the enthalpy measurements of Kendall, Orr and Hultgren (22) taken between 339 and 1436 K and Macleod (23) 401–1633 K, and the specific heat measurements of Yokokawa and Takahashi (21) 81–983 K, and Righini and Rosso (24) 1000–2000 K. These two different measuring techniques were reconciled by first separately fitting the enthalpy data to the Maier-Kelley equation (25) and then differentiating at sufficient intervals in order to give approximately equal weight to the four sets of data. However derived values of Kendall, Orr and Hultgren above 1200 K were not used since

Table I
Electronic Specific Heat Coefficients and Debye Temperatures

		γ, mJ/mol K^2	θ_D, K
Dixon et al (15)	1.2–4.2 K	6.507 ± 0.006	234.9 ± 0.4
Dixon, Hoare and Holden (16)	1.2–4.2 K	6.517 ± 0.012	235.5 ± 1.6
Shoemake and Rayne (17)	1.2–100 K	6.56 ± 0.03	234.4 ± 2.5
Berg (18)	2.6–20.3 K	6.59 ± 0.03	240.1 ± 2.3
Boerstoel, Zwart and Hansen (19)	1.2–30 K	6.54 ± 0.02	237.0 ± 0.5
Recommended		6.54 ± 0.03	236 ± 2

Table II

Low Temperature Specific Heat Data

T, K	C^o_p, J/mol K	T, K	C^o_p, J/mol K	T, K	C^o_p, J/mol K
1	0.00669	16	0.828	90	18.425
2	0.0143	18	1.155	100	19.559
3	0.0237	20	1.550	120	21.245
4	0.0359	25	2.793	140	22.376
5	0.0518	30	4.323	160	23.185
6	0.0727	35	5.994	180	23.803
7	0.100	40	7.632	200	24.278
8	0.134	45	9.210	220	24.623
9	0.177	50	10.699	240	24.920
10	0.230	60	13.326	260	25.210
12	0.371	70	15.437	280	25.469
14	0.568	80	17.078	298.15	25.648

Overall accuracy above 30 K is ± 0.06 J/mol K

	Solid	Gas
$H^o_{298.15}-H^o_0$ J/mol	5694	6576.6
$S^o_{298.15}$ J/mol K	41.53	192.409

Corrected to one bar standard state pressure

they deviate by up to 1.4 per cent low above this temperature, while similar values for Macleod above 1400 K were not used since they deviate by up to 1.6 per cent low. The selected values were fitted to the following recommended equation, which has an overall accuracy of 0.3 per cent (± 0.09 J/mol K):

$$C^o_p = 23.8992 + 7.89939 \times 10^{-3}T - 3.77463 \times 10^{-6}T^2 + 1.53451 \times 10^{-9}T^3 - 27697.5/T^2 \text{ J/mol K}$$

Specific heat measurements of Yeh and Brooks (26) taken between 350 and 1200 K are on average 2 per cent higher than the selected curve, while those of Wheeler (27) 938–1368 K are 4 per cent higher and those of Vollmer and Kohlhaas (28) 298–1900 K are 2 per cent lower. Specific heat measurements using the modulation technique tend to give values rising sharply above 1600 K, with those of Kraftmakher and Lanina (29, 30), taken between 1000 and 2000 K, being up to 12 per cent high, those of Seville (31) 1280–1860 K (read from graph) up to 6 per cent high and those of Zinov'ev, Korshunov and Gel'd (32) 1100–1900 K (read from graph) up to 14 per cent high. Smoothed true specific heat values, calculated from older mean specific heat measurements, agree closely with the recommended values up to 1300 K, but above this temperature the values of White (33) 373–1573 K are up to 1 per cent low and the values of Jaeger and Rosenbohm (34) 484–1877 K and Jaeger, Rosenbohm and Bottema (35) 681–1664 K are up to 3 per cent low, see Table III and also Figure 2.

Liquid

The liquid enthalpy measurements of Chaudhuri and co-workers (36) 2204–2649 K were fitted to the following equation which is relative to the solid at 298.15 K and which has an overall accuracy of 1.2 per cent (± 1180 J/mol):

$$H^o_T - H^o_{298.15} = 36.432\,T + 637.8 \text{ J/mol}$$

This leads to a constant specific heat value of 36.4 ± 2.2 J/mol K, a value for the heat of

Table III

High Temperature Data

T, K	Condensed Phases Pt(s, l)				Gas Phase Pt (g, bar)			
	C^o_p J/mol K	$H^o_T - H^o_{298.15}$ J/mol	S^o J/mol K	$-\frac{(G^o_T - H^o_{298.15})}{T}$ J/mol K	C^o_p J/mol K	$H^o_T - H^o_{298.15}$ J/mol	S^o J/mol K	$-\frac{(G^o_T - H^o_{298.15})}{T}$ J/mol K
298.15	25.648	0	41.533	41.533	25.531	0	192.409	192.409
300	25.663	47	41.692	41.533	25.577	47	192.567	192.410
320	25.820	562	43.353	41.596	26.031	563	194.233	192.472
340	25.969	1080	44.923	41.746	26.399	1088	195.823	192.623
360	26.112	1601	46.411	41.964	26.684	1619	197.340	192.843
380	26.248	2125	47.827	42.236	26.889	2155	198.789	193.118
400	26.380	2651	49.176	42.549	27.023	2694	200.172	193.437
420	26.508	3180	50.467	42.896	27.095	3235	201.492	193.789
440	26.632	3711	51.703	43.268	27.112	3777	202.753	194.168
460	26.753	4245	52.889	43.661	27.084	4319	203.958	194.568
480	26.870	4781	54.030	44.069	27.108	4860	205.109	194.983
500	26.986	5320	55.130	44.490	26.923	5400	206.210	195.410
600	27.534	8046	60.099	46.688	26.191	8058	211.059	197.628
700	28.049	10826	64.382	48.917	25.349	10635	215.032	199.840
800	28.545	13655	68.160	51.091	24.591	13131	218.366	201.953
900	29.036	16535	71.551	53.179	23.965	15557	221.225	203.939
1000	29.531	19463	74.635	55.173	23.468	17928	223.723	205.795
1100	30.040	22441	77.474	57.073	23.083	20255	225.941	207.528
1200	30.575	25472	80.110	58.884	22.791	22548	227.937	209.147
1300	31.144	28557	82.580	60.613	22.574	24815	229.752	210.663
1400	31.757	31702	84.910	62.266	22.418	27065	231.419	212.087
1500	32.422	34911	87.123	63.850	22.313	29301	232.962	213.428
1600	33.150	38189	89.239	65.371	22.249	31529	234.399	214.694
1700	33.949	41543	91.272	66.835	22.220	33752	235.747	215.893
1000	34.829	44981	93.237	68.248	22.219	35973	237.017	217.032
1900	35.799	48512	95.146	69.613	22.241	38196	238.219	218.116
2000	36.869	52144	97.009	70.937	22.283	40422	239.361	219.150
2041.3(s)	37.314	53677	97.767	71.472	22.305	41343	239.816	219.563
2041.3(l)	36.432	75006	108.216	71.472				
2200	36.432	80788	110.944	74.222	22.412	44891	241.490	221.085
2400	36.432	88075	114.114	77.416	22.584	49390	243.447	222.868
2600	36.432	95361	117.030	80.353	22.784	53926	245.263	224.522
2800	36.432	102647	119.730	83.070	23.001	58505	246.959	226.065
3000	36.432	109934	122.243	85.599	23.226	63127	248.554	227.511
3200	36.432	117220	124.595	87.963	23.453	67795	250.060	228.874
3400	36.432	124507	126.803	90.184	23.678	72508	251.489	230.162
3600	36.432	131793	128.886	92.277	23.898	77266	252.848	231.385
3800	36.432	139079	130.856	94.256	24.111	82067	254.146	232.549
4000	36.432	146366	132.724	96.133	24.318	86910	255.388	233.660
4200	36.432	153652	134.502	97.918	24.517	91794	256.579	234.724

Table IV

Third Law Heats of Sublimation

		$\Delta H^{o}_{298.15}$, kJ/mol
Jones, Langmuir and Mackay (44)	1697–2034 K	564.8 ± 1.7
[a]Dreger and Margrave (45)	1573–1785 K	566.5 ± 1.4
[b]Hampson and Walker (46)	918–2049 K	565.7 ± 0.5
[c]Koch and co-workers (47)	2032–2445 K	559.5 ± 1.1
[d]Plante, Sessoms and Fitch (48)	1675–1977 K	564.4 ± 0.2
Recommended		565 ± 2

[a] Two data points rejected by the authors
[b] Eight data points rejected by the authors
[c] Weighted average of two data sets
[d] Weighted average of eight data sets

Table V

Vapour Pressure Data Pt(s, l) = Pt (g, bar)

T, K	P, bar	ΔG^{o}, J/mol	ΔH^{o}, J/mol	P, bar	T, K
298.15	7.89×10^{-92}	520016	565000	10^{-12}	1489
400	1.26×10^{-66}	504645	565043	10^{-11}	1569
500	7.23×10^{-52}	489540	565080	10^{-10}	1659
600	4.98×10^{-42}	474436	565012	10^{-9}	2759
700	5.29×10^{35}	459354	564809	10^{-8}	1872
800	9.77×10^{-30}	444310	564776	10^{-7}	2002
900	1.21×10^{-25}	429316	564022	10^{-6}	2156
1000	2.27×10^{-22}	414378	563465	10^{-5}	2339
1100	1.07×10^{-19}	399500	562814	10^{-4}	2556
1200	1.80×10^{-17}	384684	562076	10^{-3}	2821
1300	1.37×10^{-15}	369935	561258	10^{-2}	3149
1400	5.57×10^{-14}	355251	560363	10^{-1}	3567
1500	1.38×10^{-12}	340633	559390	1	4122
1600	2.26×10^{-11}	326083	558340	NBP	4125
1700	2.67×10^{-10}	311601	557209		
1800	2.38×10^{-9}	297189	555992		
1900	1.68×10^{-8}	282844	554684		
2000	9.68×10^{-8}	268574	553278		
2041.3(s)	1.90×10^{-7}	262702	552666		
2041.3(l)	1.90×10^{-7}	262702	531337		
2200	1.81×10^{-6}	241901	529103		
2400	2.00×10^{-5}	215915	526315		
2600	1.51×10^{-4}	190161	523565		
2800	8.49×10^{-4}	164614	520858		
3000	3.76×10^{-3}	139264	518193		
3200	1.37×10^{-2}	114085	515575		
3400	4.28×10^{-2}	89075	513001		
3600	0.117	64211	510473		
3800	0.287	39489	507988		
4000	0.639	14892	505544		
4200	1.316	–9585	503142		

NBP: normal boiling point at one atmosphere (1.01325 bar)

ΔH^{o}_{0} = 564.117 ± 2. 000 kJ/mol

$\Delta vapS^{o}_{4122}$ = 122.29 ± 0.29 J/mol K

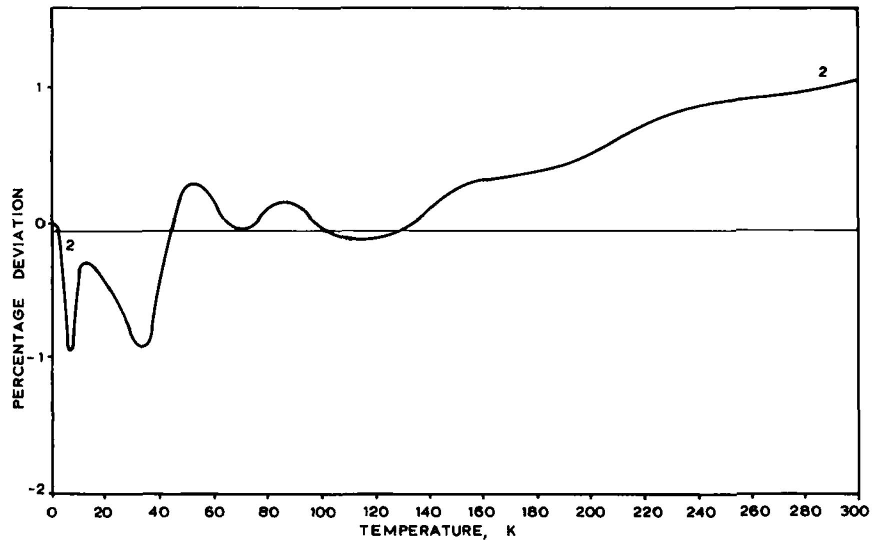

Fig. 1 Low temperature specific heats of platinum from 0 to 300 K
(1) Present selected values
(2)Furukawa, Reilly and Gallagher (14)
Percentage deviation = 100 × (C°_p selected – C°_p calculated)/C°_p calculated

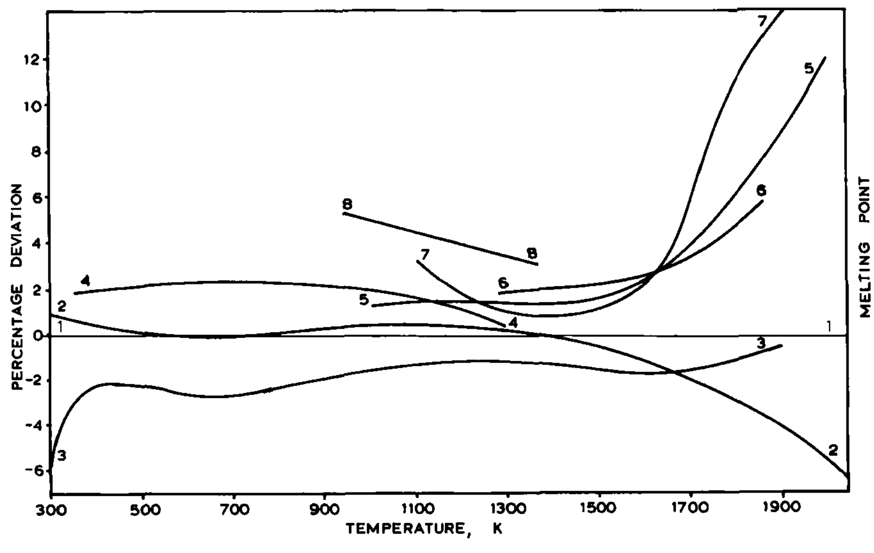

Fig. 2 High temperature specific heats of platinum from 300 K to the melting point
(1) Present selected values
(2) Hultgren and others (13) and references therein
(3) Vollmer and Kohlhaas (28)
(4) Yeh and Brooks (26)
(5) Kraftmakher and Lanina (29, 30)
(6) Seville (31)
(7) Zinov'ev, Kurshunov and Gel'd (32)
(8) Wheeler (27)
Percentage deviation = 100 × (C°_p measured – C°_p calculated)/C°_p calculated

fusion of 21.33 ± 1.19 kJ/mol and an entropy of fusion of 10.45 ± 0.58 J/mol K, see Table III. Rapid pulse heating measurements by Gathers, Shaner and Hodgson (37) 2041–8000 K lead to a higher specific heat of 49 J/mol K and an approximate heat of fusion of 27 ± 6 kJ/mol; while using a similar technique Lebedev, Savvatimskii and Smirnov (38) obtained a heat of fusion of 25 kJ/mol. Improvements in the rapid pulse heating method are eliminating the discrepancies obtained between this technique and drop calorimetry.

Gas

Thermodynamic properties of the monatomic gas were calculated from the 201 energy levels listed by Blaise and colleagues (39) using the method outlined by Kolsky, Gilmer and Gilles (40) together with the 1986 fundamental constants (41) except for the Gas Constant and the Boltzmann Constant which are from the later measurements of Moldover and coworkers (42). Values were corrected to the recommended standard state pressure of one bar (43).

Vapour Pressure

Third Law heats of sublimation were calculated from the following Langmuir determinations, see Tables IV and V.

The recommended value gives most weight to the measurements of Hampson and Walker and Plante, Sessoms and Fitch. Torsion measurements of Peleg and Alcock (49) 1800–2300 K were unfortunately shown only in the form of a graph but lead to a heat of sublimation about 5 kJ/mol higher than the recommended value. However Plante, Sessoms and Fitch have criticised the temperature measuring technique used in these experiments. Mass spectrometric measurements of Norman, Staley and Bell (50) 1752–2045 K lead to a second law heat of sublimation of 538 ± 17 kJ/mol.

Fundamental Constants	
Avogadro's number = 6.0221367 (36) × 10^{23}/mol (41)	Velocity of light = 299,792,458 m/s (41)
Planck's constant = 6.66260755 (40) × 10^{-34} Js (41)	Gas constant = 8.314471 (14) J/mol K (42)
Boltzmann constant = 1.3806513 (25) × 10^{-23} J/K (42)	

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Platinum 1994

Monday, 16th May 1994 saw the launch of "Platinum 1994", the latest in the series of prestigious reviews of the platinum market published annually by Johnson Matthey, which aims to complement the information presented in *Platinum Metals Review*.

"Platinum 1994" is based upon information gleaned from the platinum industry worldwide and provides details of commercial and investment aspects of the platinum group metals. It is beautifully illustrated and well supported by statistical data, summarising events that affected the supply, demand and usage of these metals in 1993. The outlook for 1994 and beyond is discussed.

Once again demands made mainly by the automobile and jewellery industries caused platinum sales to escalate to 4.04 million ounces during 1993. This is a 6 per cent increase over 1992 figures, at an average London fixing price of $374.06 per ounce. Supplies of platinum worldwide rose to 4.38 million ounces resulting in a surplus of 340,000 ounces, mainly due to increased production as additional South African mining capacity came on stream.

Dealing similarly with palladium and rhodium, and the other platinum group metals, "Platinum 1994" also includes surveys on mining and exploration, principally in South Africa, biomedical applications, a comprehensive analysis of the world platinum markets and predictions of increased demand for platinum in 1994.

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