

The Thermodynamic Properties of Platinum

REVISED DATA FOR THE LIQUID STATE AND VAPOUR PRESSURE

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The thermodynamic properties of platinum were reviewed here by the author in 1994. However, the use of superior values for the enthalpy of liquid platinum have resulted in a major revision of the thermodynamic values for the liquid phase. One consequence of the revision is that the boiling point at one atmosphere pressure is altered from 4125 K, as calculated in the 1994 paper, to 4149 K. Previously accepted values for solid platinum are not altered, and there are only very minor changes to the gaseous phase values as a result of using a new atomic weight for platinum and the CODATA 2002 recommended values of the fundamental constants.

Platinum has a face centred cubic structure with a lattice parameter at 20°C of 0.39236 nm and a density of $21.45 \times 10^3 \text{ kg m}^{-3}$ (1). In the present paper the variation of the thermodynamic values of the specific heat at constant pressure, enthalpy, entropy and Gibbs free energy with temperature have been revised in the condensed phases and gaseous phase at a 1 bar standard state pressure. The vapour pressure data was calculated from the selected heat of sublimation of 565 kJ mol^{-1} as shown in Table I and from the nett Gibbs free energy between the condensed and gaseous phases. Values for these properties are reassessed in the light of revised data.

Solid Phase

The thermodynamic properties of platinum were reviewed in this Journal in 1994 (2). The current revision leaves all values for the solid phase unaltered, with equations representing the variation with temperature of enthalpy and specific heat at constant pressure given in the box below. These equations have an overall accuracy of 0.3 per cent, equivalent to a standard deviation of $\pm 0.09 \text{ J mol}^{-1} \text{ K}^{-1}$ for the specific heat values. These equations

were used to generate the thermodynamic properties of the solid phase shown in Table IIA.

The values of enthalpy and entropy at 298.15 K are shown below.

Platinum at 298.15 K	Solid	Gas
Enthalpy: $H_{298.15}^{\circ} - H_{0}^{\circ}, \text{ J mol}^{-1}$	5694	6576.6
Entropy: $S_{298.15}^{\circ}, \text{ J mol}^{-1} \text{ K}^{-1}$	41.53	192.409

Recent measurements of the enthalpy of platinum by Wilthan and colleagues (3, 4) using differential scanning calorimetry (at 473–1573 K) lead to values 3.6% higher falling to 1.7% higher than the selected values, while rapid pulse heating measurements by the same authors (at 1700–2040 K) lead to values of 1.1 to 1.4% lower.

Gaseous Phase

For the gaseous phase the introduction of a new atomic weight for platinum of 195.078 (5) and of the CODATA 2002 fundamental constants (6) have caused only two values (the free energy at 2800 K and the entropy at 3400 K) to be altered, but only by one digit in the last decimal place.

Equations for the Enthalpy and Specific Heat at Constant Pressure of Solid Platinum

$$H_{\text{T}} - H_{298.15}^{\circ} = 23.8992 \text{ T} + 3.949695 \times 10^{-3} \text{ T}^2 - 1.25821 \times 10^{-6} \text{ T}^3 + 3.836275 \times 10^{-10} \text{ T}^4 + 27697.5/\text{T} - 7539.23 \text{ J mol}^{-1}$$

$$C_{\text{p}}^{\circ} = 23.8992 + 7.89939 \times 10^{-3} \text{ T} - 3.77463 \times 10^{-6} \text{ T}^2 + 1.53451 \times 10^{-9} \text{ T}^3 - 27697.5/\text{T}^2 \text{ J mol}^{-1} \text{ K}^{-1}$$

Table I Third Law Heats of Sublimation of Platinum			
Reference	Temperature range, K	$\Delta H^\circ_{298.15}$, kJ mol ⁻¹	Notes
Koch, Calvert, Thomas and Beall (13)	2032–2445	559.4 ± 1.1	a
Jones, Langmuir and Mackay (14)	1697–2034	564.8 ± 1.7	b
Dreger and Margrave (15)	1573–1785	566.5 ± 1.4	c
Hampson and Walker (16)	1918–2049	565.7 ± 0.5	d
Plante, Sessoms and Fitch (17)	1675–1977	564.4 ± 0.2	e
Selected value for the heat of sublimation of platinum at 298.15 K:		<u>565 ± 2*</u>	
<p>a Weighted average of two data sets</p> <p>b Temperatures corrected to ITS-90 from a laboratory temperature scale</p> <p>c Two data points rejected by the authors</p> <p>d Eight data points rejected by the authors</p> <p>e Weighted average of eight data sets</p> <p>* Following the practice of the National Institute of Standards and Technology (the former National Bureau of Standards), the accuracy quoted for the individual heats of sublimation are standard errors not standard deviations. Therefore the value quoted for the “accuracy” of the selected value tries to take into account not only the variations in the quoted values but also individual internal variations in the vapour pressure data sets. This practice is commonly used and represents a “real” accuracy rather than a mathematically derived accuracy which would tend to be lower and not realistic</p>			

Thermodynamic properties of the gaseous phase are shown in Table IIB and the values of enthalpy and entropy at 298.15 K are on the previous page.

Liquid Phase

In 1994, when the original paper was published (2), the melting point of platinum, 2041.3 K, was only tentatively assigned to the ITS-90 temperature scale. It was fully accepted later (7).

However, selected values used in that paper, in the liquid region, were based on the enthalpy values of Chaudhuri *et al.* (8) which were supposedly the measurements made by David Bonnell who was working on his Ph.D. thesis at Rice University. Bonnell’s Ph.D. thesis was published two years later (9) and it was assumed that this was because he was completing work on other metals and that, *as is the usual practice*, the values in the earlier paper were definitive. However, private communication with Bonnell has indicated that this was not the case. In fact, the thesis contains the fully corrected values. The values given in the paper published two years earlier were only preliminary and should not have been given the attention they received.

Therefore, in now selecting the values given in Bonnell’s thesis, his temperature values in the range 2205 to 2650 K are accepted for this review;

while his enthalpy values have been adjusted by 195.08/195.09 to ensure that the atomic weight is the same as that used previously for the solid phase (2). These measurements can then be represented by the following equation which has an overall accuracy of 1.2%, equivalent to a standard deviation of ± 1190 J mol⁻¹:

$$H^\circ_T - H^\circ_{298.15} = 38.9928 T - 3805.63 \text{ J mol}^{-1}$$

Thus, derived values are:

- Specific heat (C_p): 39.0 ± 2.2 J mol⁻¹ K⁻¹
- Heat of fusion: 22.11 ± 0.94 kJ mol⁻¹ and
- Entropy of fusion: 10.83 ± 0.46 J mol⁻¹ K⁻¹.

The difference between the above three values and those tabulated for the liquid phase in Table IIA is due to the values in the Table being taken beyond their true accuracy for interpolation purposes.

Other measurements made on platinum in the liquid region used the rapid pulse heating technique, but the different values obtained show marked differences, and currently this method does not appear to be as accurate as the levitation calorimetry method used by Bonnell.

For instance, Gather, Shaner and Hodgson (10) (at 2041–8000 K) obtained a value for the specific heat of 49 J mol⁻¹ K⁻¹ and for the heat of fusion of

Table IIA

High Temperature Data of Platinum in the Condensed Phase (solid, liquid)

T, K	C_p° , J mol ⁻¹ K ⁻¹	$H_T^\circ - H_{298.15}^\circ$, J mol ⁻¹	S_T° , J mol ⁻¹ K ⁻¹	$-(G_T^\circ - H_{298.15}^\circ)/T$, J mol ⁻¹ K ⁻¹
298.15 (solid)	25.648	0	41.533	41.533
300	25.663	47	41.692	41.533
400	26.380	2125	49.176	42.549
500	26.986	5320	55.130	44.490
600	27.534	8046	60.099	46.688
700	28.049	10826	64.382	48.917
800	28.545	13655	68.160	51.091
900	29.036	16535	71.551	53.179
1000	29.531	19463	74.635	55.173
1100	30.040	22441	77.474	57.073
1200	30.575	25472	80.110	58.884
1300	31.144	28557	82.580	60.613
1400	31.757	31702	84.910	62.266
1500	32.422	34911	87.123	63.850
1600	33.150	38189	89.239	65.371
1700	33.949	41543	91.272	66.835
1800	34.829	44981	93.237	68.248
1900	35.799	48512	95.146	69.613
2000	36.869	52144	97.009	70.937
2041.3 (s)	37.314	53677	97.767	71.472
2041.3 (liquid)	38.993	75790	108.600	71.472
2100	38.993	78079	109.706	72.525
2200	38.993	81979	111.520	74.257
2300	38.993	85878	113.253	75.915
2400	38.993	89777	114.912	77.505
2500	38.993	93676	116.504	79.034
2600	38.993	97576	118.034	80.504
2700	38.993	101475	119.505	81.922
2800	38.993	105374	120.923	83.290
2900	38.993	109273	122.292	84.611
3000	38.993	113173	123.613	85.889
3100	38.993	117072	124.892	87.127
3200	38.993	120971	126.130	88.326
3300	38.993	124871	127.330	89.490
3400	38.993	128770	128.494	90.620
3500	38.993	132669	129.624	91.719
3600	38.993	136568	130.723	92.787
3700	38.993	140468	131.791	93.827
3800	38.993	144367	132.831	94.840
3900	38.993	148266	133.844	95.827
4000	38.993	152166	134.831	96.790
4100	38.993	156065	135.794	97.729
4200 (l)	38.993	159964	136.733	98.647

s is solid, l is liquid

Table IIB

High Temperature Data of Platinum in the Gaseous Phase (gas, 1 bar pressure)

T, K	C_p° , J mol ⁻¹ K ⁻¹	$H_T^\circ - H_{298.15}^\circ$, J mol ⁻¹	S_T° , J mol ⁻¹ K ⁻¹	$-(G_T^\circ - H_{298.15}^\circ)/T$, J mol ⁻¹ K ⁻¹
298.15	25.531	0	192.409	192.409
300	25.577	47	192.567	192.410
400	27.023	2694	200.172	193.437
500	26.923	5400	206.210	195.410
600	26.191	8058	211.059	197.628
700	25.349	10635	215.032	199.840
800	24.591	13131	218.366	201.953
900	23.965	15557	221.225	203.939
1000	23.468	17928	223.723	205.795
1100	23.083	20255	225.941	207.528
1200	22.791	22548	227.937	209.147
1300	22.574	24815	229.752	210.663
1400	22.418	27065	231.419	212.087
1500	22.313	29301	232.962	213.428
1600	22.249	31529	234.399	214.694
1700	22.220	33752	235.747	215.893
1800	22.219	35973	237.017	217.032
1900	22.241	38196	238.219	218.116
2000	22.283	40422	239.361	219.150
2041.3	22.305	41343	239.816	219.563
2100	22.341	42653	240.449	220.138
2200	22.412	44891	241.490	221.085
2300	22.494	47136	242.488	221.994
2400	22.584	49390	243.447	222.868
2500	22.682	51653	244.371	223.710
2600	22.784	53926	245.263	224.522
2700	22.891	56210	246.125	225.306
2800	23.001	58505	246.959	226.064
2900	23.113	60810	247.768	226.799
3000	23.226	63127	248.554	227.511
3100	23.340	65456	249.317	228.202
3200	23.453	67795	250.060	228.874
3300	23.566	70146	250.783	229.527
3400	23.678	72508	251.488	230.162
3500	23.789	74882	252.176	230.782
3600	23.898	77266	252.848	231.385
3700	24.005	79661	253.504	231.974
3800	24.111	82067	254.146	232.549
3900	24.215	84483	254.774	233.111
4000	24.318	86910	255.388	233.660
4100	24.418	89347	255.990	234.198
4200	24.517	91794	256.579	234.724

Table III Vapour Pressure Data of Platinum						
T, K	P, bar	ΔG° , J mol ⁻¹	ΔH° , J mol ⁻¹	P, bar	T, K	
Solid phase	298.15 (solid)	7.89×10^{-92}	520016	565000	10^{-12}	1489
	400	1.26×10^{-66}	506645	565043	10^{-11}	1569
	500	7.23×10^{-52}	489540	565080	10^{-10}	1659
	600	4.98×10^{-42}	474436	565012	10^{-9}	1759
	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}	2558
	1200	1.80×10^{-17}	384684	562076	10^{-3}	2824
	1300	1.37×10^{-15}	369935	561258	10^{-2}	3155
	1400	5.57×10^{-14}	355251	560363	10^{-1}	3580
	1500	1.38×10^{-12}	340633	559390	1	4146
	1600	2.26×10^{-11}	326083	558340	NBP	4149
	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		
Liquid phase	2041.3 (liquid)	1.90×10^{-7}	262702	530553	NBP: normal boiling point at a pressure of one atmosphere (1.01325 bar) $\Delta H^\circ_0 = 564.117 \pm 2.000$ kJ mol ⁻¹	
	2100	4.54×10^{-7}	255013	529574		
	2200	1.80×10^{-6}	241978	527912		
	2300	6.29×10^{-6}	229018	526258		
	2400	1.98×10^{-5}	216130	524613		
	2500	5.65×10^{-5}	203310	522977		
	2600	1.49×10^{-4}	190555	521351		
	2700	3.62×10^{-4}	177863	519735		
	2800	8.27×10^{-4}	165230	518131		
	2900	1.78×10^{-3}	152655	516537		
	3000	3.63×10^{-3}	140134	514955		
	3100	7.06×10^{-3}	127666	513384		
	3200	1.31×10^{-2}	115249	511824		
	3300	2.35×10^{-2}	102880	510276		
	3400	4.06×10^{-2}	90557	508739		
	3500	6.79×10^{-2}	78280	507213		
	3600	0.110	66047	505698		
	3700	0.174	53855	504194		
	3800	0.267	41703	502700		
	3900	0.402	29591	501217		
4000	0.591	17517	499745			
4100	0.852	5479	498282			
4200 (l)	1.205	-6522	496830			

s is solid, l is liquid

Vapour Pressure Equations

$$\text{Solid: } 1200\text{--}2041.3 \text{ K: } \ln(P, \text{ bar}) = 28.3308 - 1.29944 \ln(T) - 69207.9/T$$

$$\text{Liquid: } 2041.3\text{--}4200 \text{ K: } \ln(P, \text{ bar}) = 32.1390 - 1.89944 \ln(T) - 67647.6/T$$

$27 \pm 6 \text{ kJ mol}^{-1}$, while Lebedev, Savvatimskii and Smirnov (11) obtained a heat of fusion of 25 kJ mol^{-1} .

The two most recent sets of measurements: by Hixson and Winkler (12) (at 2041–5100 K) lead to a specific heat of $41.35 \text{ J mol}^{-1} \text{ K}^{-1}$ and a heat of fusion of 24.2 kJ mol^{-1} , and the measurements of Wilthan and colleagues (5, 6) (at 2045–2830 K) lead to a specific heat of $36.5 \text{ J mol}^{-1} \text{ K}^{-1}$ and a heat of fusion of 21.8 kJ mol^{-1} . On average these latter two sets of results show satisfactory agreement with values selected here.

Vapour Pressure

Only the measurements of Koch *et al.* (13) on liquid platinum are affected by the revision, and even in this case the derived heat of sublimation is only lowered by 0.1 kJ mol^{-1} , see Table I. However, these measurements of Koch *et al.* are still discrepant when compared to the other four values obtained on solid platinum as shown in Table I and have again been rejected. In selecting the heat of sublimation most weight is given to the measurements of Hampson and Walker (16) and those of Plante, Sessoms and Fitch (17).

Previous accepted values for the vapour pres-

sure of the solid phase and revised values for the liquid phase are given in Table III.

Vapour pressure equations for both the liquid and the gas are given above. For the solid the values are given over a practical range from 1200 K to the melting point of platinum, while although the values for the liquid are given over a much larger temperature range from the melting point to 4200 K the derived normal boiling point is only 0.2 K higher than that obtained from a proper thermodynamic treatment.

Free Energy Equations

The free energy equations, see below, are derived from those given above for the solid and liquid phases. It is a requirement that the two equations given must be equal at the melting point.

Conclusions

The thermodynamic properties of platinum have been revised by introducing superior values for the enthalpy of the liquid. The vapour pressure curve for the liquid is also reassessed as shown in Table III. Sets of revised values for specific heat at constant pressure, enthalpy, entropy, Gibbs' free energy and vapour pressure are presented.

Free Energy Equations

$$\text{Solid: } G^\circ_T - H^\circ_{298.15} = 120.8910 T - 3.949695 \times 10^{-3} T^2 + 6.29105 \times 10^{-7} T^3 - 1.278758 \times 10^{-10} T^4 + 13848.75/T - 23.8992 T \ln(T) - 7539.23 \text{ J mol}^{-1}$$

$$\text{Liquid: } G^\circ_T - H^\circ_{298.15} = 227.5700 T - 38.9928 T \ln(T) - 3805.63 \text{ J mol}^{-1}$$

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Glossary of Thermodynamic Terms

T	Temperature
R	Gas constant
C_p^0	Specific heat at constant pressure
H^0	Enthalpy = $\int C_p^0(T).dT$ between temperatures T_1 and T_2
S^0	Entropy = $\int (C_p^0(T)/T).dT$ between temperatures T_1 and T_2
G^0	Gibbs free energy = $H^0 - TS^0$
$-G^0/T$	Gibbs free energy/temperature = $S^0 - H^0/T$
$\Delta H_{298.15}^0$	Heat of sublimation at 298.15 K
ΔH^0	Enthalpy of sublimation (solid) or evaporation (liquid)
ΔG^0	Free energy of sublimation (solid) or evaporation (liquid)
P	Vapour pressure in pascals (Pa) or the equivalent bars (10^5 Pa). The terms torr (mm of mercury pressure) and atmosphere are now obsolete although the normal boiling point is still quoted at one atmosphere pressure (1.01325 bar)

Analytical Expressions

Solid

$$C_p^0 = a + bT + cT^2 + dT^3 + e/T^2$$

$$H_T^0 - H_{298.15}^0 = aT + (b/2)T^2 + (c/3)T^3 + (d/4)T^4 - e/T + f$$

$$S^0 = a \ln(T) + bT + (c/2)T^2 + (d/3)T^3 - (e/2)/T^2 + g$$

$$-(G_T^0 - H_{298.15}^0)/T = a \ln(T) + g - a + (b/2)T + (c/6)T^2 + (d/12)T^3 + (e/2)/T^2 - f/T$$

$$G_T^0 - H_{298.15}^0 = -aT \ln(T) + T(a-g) - (b/2)T^2 - (c/6)T^3 - (d/12)T^4 - (e/2)/T + f$$

"f" is evaluated at 298.15 K where $H_T^0 - H_{298.15}^0 = 0$; "g" is evaluated at 298.15 K by fixing the value of $S_{298.15}^0$

Liquid

$$C_p^0 = a$$

$$H_T^0 - H_{298.15}^0 = aT + f$$

$$S^0 = a \ln(T) + g$$

$$-(G_T^0 - H_{298.15}^0)/T = a \ln(T) + g - a - f/T$$

$$G_T^0 - H_{298.15}^0 = -a \ln(T) + T(a - g) + f$$

"f" and "g" are evaluated from the values of enthalpy and entropy for the liquid at the melting point

Calculation of the Thermodynamic Properties of an Ideal Monatomic Gas (as given in Table IIB)

The thermodynamic properties of platinum gas given in Table IIB were calculated using the method of Kolsky, Gilmer and Gilles (18) outlined below. All values given correspond to the 2002 CODATA fundamental constants (6) and to a standard state pressure of one bar.

Velocity of light, $c = 299792458 \text{ m s}^{-1}$ exactly

Avogadro constant, $N_A = (6.0221415 \pm 0.0000010) \times 10^{23} \text{ mol}^{-1}$

Planck constant, $h = (6.6260693 \pm 0.0000011) \times 10^{-34} \text{ J s}$

Gas constant, $R = 8.314472 \pm 0.000015 \text{ J mol}^{-1} \text{ K}^{-1}$

Second radiation constant, $c_2 = 0.014387752 \pm 0.000000025 \text{ m K}$ (metre Kelvin)

Atomic weight, A_r

Energy level = $\nu_i \text{ cm}^{-1}$; Quantum number of energy level, J_i

$\alpha = c_2 = 1.4387752 \text{ cm K}$

$K1 = R\alpha = 11.962656 \text{ J cm mol}^{-1}$

$K2 = 2.5R = 20.786180 \text{ J mol}^{-1} \text{ K}^{-1}$

$K3 = R\alpha^2 = 17.211573 \text{ J cm}^2 \text{ K mol}^{-1}$

$K4 = 1.5R = 12.471708 \text{ J mol}^{-1} \text{ K}^{-1}$

$K5 = S_0 = -9.5758165 \text{ J mol}^{-1} \text{ K}^{-1}$

$K6 = K5 - 2.5R = -30.3619965 \text{ J mol}^{-1} \text{ K}^{-1}$

S_0 , the Sackur-Tetrode constant, is derived from: $S_0 = R[2.5 + \ln(4.980463969 \times 10^{-9} R^{5/2}/h^3 N_A^4)]$, where the numerical value in the equation is equal to $(2\pi/1000)^{3/2}/10^5$

Partition Functions

$$Q = \sum(2J_i + 1)e^{-\alpha\nu_i/T} \quad Q1 = \sum(2J_i + 1)\nu_i e^{-\alpha\nu_i/T} \quad Q2 = \sum(2J_i + 1)\nu_i^2 e^{-\alpha\nu_i/T}$$

Thermodynamic Equations

Values are initially referred to 0 K:

$$C_p^0 = (K3/T^2)(Q2/Q1 - (Q1/Q)^2) + K2 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$H_T^0 - H_0^0 = K1(Q1/Q) + K2 T \text{ J mol}^{-1}$$

$$S^0 = (K1/T)(Q1/Q) + R \ln(Q) + K4 \ln(A_r) + K2 \ln(T) + K5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\begin{aligned} - (G_T^0 - H_0^0)/T &= R \ln(Q) + K4 \ln(A_r) + K2 \ln(T) + K6 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= S^0 - (H_T^0 - H_0^0)/T \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$H_T^0 - H_{298.15}^0 = (H_T^0 - H_0^0) - (H_{298.15}^0 - H_0^0) \text{ J mol}^{-1}$$

$$- (G_T^0 - H_{298.15}^0)/T = - (G_T^0 - H_0^0)/T + (H_{298.15}^0 - H_0^0)/T \text{ J mol}^{-1} \text{ K}^{-1}$$

Vapour Pressure

$$\Delta H^0 = \Delta H_{298.15}^0 + \delta(H_T^0 - H_{298.15}^0)$$

$$\Delta G^0 = \Delta H_{298.15}^0 - T\delta - (G_T^0 - H_{298.15}^0)/T$$

$$\ln(P) = -\Delta G^0/RT$$

$$\delta(H_T^0 - H_{298.15}^0) = (H_T^0 - H_{298.15}^0) \text{ (gas)} - (H_T^0 - H_{298.15}^0) \text{ (solid, liquid)}$$

$$\delta - (G_T^0 - H_{298.15}^0)/T = - (G_T^0 - H_{298.15}^0)/T \text{ (gas)} - - (G_T^0 - H_{298.15}^0)/T \text{ (solid, liquid)}$$

Calculation of the Heat of Sublimation from Vapour Pressure Data (as relating to Table I)

Calculated values are the Second Law heat of sublimation, $\Delta H_{298.15}^0(\text{II})$, and the Third Law heat of sublimation, $\Delta H_{298.15}^0(\text{III})$. Significant differences between these two evaluations may indicate that the vapour pressure measurements are erroneous. The selected heat of sublimation is calculated from the Third Law values.

Third Law Heat of Sublimation

Each data point is evaluated separately and the selected value is based on averaging the derived heats of sublimation:

$$\Delta H_{298.15}^0(\text{III}) = T[\delta - (G_T^0 - H_{298.15}^0)/T - R \ln(P, \text{bar})]$$

Revised Second Law Heat of Sublimation

All data points are fitted to the following equation:

$$\delta - (G^{\circ}_T - H^{\circ}_{298.15})/T - R \ln(P, \text{ bar}) = B + A/T$$

$$\text{where } A = \Delta H^{\circ}_{298.15}(\text{II}) \text{ and } B = \text{entropy drift} = \delta S^{\circ}_{298.15}(\text{III}) - \delta S^{\circ}_{298.15}(\text{II})$$

Ideally B should be zero but if it is an unacceptably large number then this may again indicate that the vapour pressure measurements are erroneous.

Traditional Second Law Heat of Sublimation

All data points are fitted to the Clausius-Clapeyron equation:

$$\ln(P, \text{ bar}) = B + A/T$$

$$\Delta H^{\circ}_{298.15}(\text{II}) = -\delta(H^{\circ}_T - H^{\circ}_{298.15}) - RA$$

Temperature is either the average experimental value or the average value obtained from reciprocal temperatures, but there is no formal definition.

“Pseudo” Third Law Heat of Sublimation

For vapour pressure measurements given only in the form of an equation, usually the Clausius-Clapeyron equation, Third Law values are calculated at the extreme ends of the temperature range and averaged. Where possible the assigned accuracy is that given by the authors who generally carried out a proper Third Law evaluation using previously selected thermodynamic values but reported the results only in the form of the above equation.



The Author

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