

# Vapor Pressure and Heat of Sublimation of Platinum

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(May 21, 1970)

The vapor pressure of platinum was measured by the Langmuir method in the temperature range 1700–2000 K using a vacuum microbalance. Eight series of data gave concordant results and an average third-law heat of sublimation of  $564.49 \text{ kJ mol}^{-1}$  with an estimated overall uncertainty of  $2.1 \text{ kJ mol}^{-1}$  ( $134.92 \pm 0.5 \text{ kcal mol}^{-1}$ ). Three out of eight second-law heats agreed with the third-law heats within one standard error but there was a tendency for second-law heats to be low. This was attributed to small systematic errors in the measurements. A vapor-pressure equation representing the data is  $\log P (\text{atm}) = -29020/T + 7.502$ , based on our third-law heat and tabulated entropies evaluated at 1800 K. Our data agree well with several previous Langmuir determinations but significantly decrease the error in the heat previously accepted.

Inability to obtain saturation pressures at lower temperatures, previously reported in the literature, was confirmed. It was shown that microgram quantities of carbon are capable of blocking the sublimation reaction.

Key words: Heat of sublimation; Langmuir vaporization; platinum; rate of vaporization; vapor pressure.

## 1. Introduction

This study was undertaken as part of an NBS contribution to a program involving the measurement of vapor pressures of selected standard materials in various cooperating laboratories. The object of these measurements is to determine reliable standard vapor pressure data and to reveal, if possible, any systematic differences in vapor pressures which might be attributable to different methods of measurement. Data leading to vapor pressures or heats of sublimation of platinum have been reported by a number of investigators [1–10]<sup>1</sup> using several methods of measurement over a wide temperature range. Results from some of these data are listed in table 2 and comments on these studies are reserved for section 4 of this paper.

## 2. Experimental Method

Data were obtained by Langmuir rate of sublimation measurements using a vacuum microbalance. Techniques and procedures were similar to those used previously [11]. Vacuum in the range of  $10^{-7}$  to  $10^{-9}$  torr was maintained and indicated by a commercial sputter-ion pump. Preliminary data were obtained using Standard Reference Material, SRM 680, but this material is not generally available in a convenient form for Langmuir measurements. Later measurements were made on SRM 747 stock which will be certified as a vapor-pressure standard. Samples were machined from the stock materials, both of about five 9's purity,

into right circular cylinders having nominal diameters of 0.25 or 0.20 cm and lengths of 1.9 cm. A hole 0.1 cm in diameter and 1.5 cm long, assumed to represent blackbody conditions, was drilled along the cylinder axis and a suspension hole 0.025 cm in diameter was drilled along a diameter about 0.20 cm from the other end. Machining was accomplished by ordinary machining methods using oil cutting fluid on the 0.25-cm-diam samples except that designated SRM 747–17, which was machined using oil-free tools and trichloroethylene cutting fluid. The blackbody hole of the 0.20-cm sample was machined by arc erosion. Samples machined using oil cutting fluids were rinsed in acetone or ethanol to remove any residual traces of oil. However, this procedure was not effective, as two of the three samples treated in this way gave evidence of contamination as discussed later.

The sample was suspended from one arm of an equal-arm quartz beam microbalance by a chain of 0.025-cm-diam sapphire or quartz rods connected together by V-shaped hooks made by heating and bending the rods. The lower 10 cm of the suspension was 0.0075-cm platinum wire, which passed through the suspension hole in the samples and over the hook on the lowest suspension rod.

The appendage of the vacuum chamber in which the sample hung was a 22-mm o.d. Vycor<sup>2</sup> tube made with a fused silica window at the bottom. The window could be protected during sublimation experiments with a magnetically actuated shutter. The shutter was used to

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>2</sup> Reference to trade names is made only for completeness of description and does not imply in any way the endorsement of the product by the National Bureau of Standards.

protect the window during the first three experiments but was not used during the remaining five. For our experimental arrangement it was found that the increase in the window correction factor was not significantly greater when the shutter was not used than when it was. This is because the shutter must be kept open for a large fraction of the time during short experiments when the rate of sublimation is highest. Data were designated as belonging to a new experimental series when new window and/or mirror correction values were determined, when a different observer made temperature measurements, when the sample was changed, or when a combination of these changes was made.

Prior to experiments, a thin platinum coating which did not heat inductively was deposited on the interior surface of the Vycor tube and a grounding device consisting of a split circular stainless steel ring, about 1 cm wide and having a magnetically actuated wire hinge, was inserted into the Vycor tube so that it made contact with the platinum coating. The Vycor tube was connected to the system by means of a standard taper joint using Apiezon W sealant. A wire connected the grounding device to an electrical ground. With the sample in place, the hinge of the grounding device could be magnetically deflected until it made contact with the wire supporting the sample. This allowed for removal of any static charge generated during the high-temperature heating. Heating was accomplished by induction at 450 kHz. The metal sample served as its own susceptor.

Temperatures were measured with an NBS-calibrated optical pyrometer through a calibrated window and mirror. Calibration corrections for the window and mirror were determined in separate experiments using a band lamp. Corrections were determined in terms of "A" values where  $A = (1/T) - (1/T_w)$ ;  $T$  is the brightness temperature in Kelvins of the source; and  $T_w$  is the brightness temperature of the source with the window or mirror in the optical path. Window corrections were determined before and after each series of measurements and the average value accepted. Mirror corrections were determined less frequently; an average of two independent sets of determinations was used.

In obtaining each datum point the following sequence of operations was followed: (1) the rest point of the balance was determined, (2) the sample was heated to a temperature about 100 K below the lowest temperature where vapor pressure measurements were practicable, (3) the power of the oscillator was adjusted to a predetermined setting and held constant, (4) the power was turned off, (5) the sample and platinum coating on the Vycor sleeve were grounded, and (6) the rest point of the balance was redetermined.

The mass change of the sample was determined from the displacement of the beam of the microbalance and the previously determined sensitivity, which was about  $0.5 \mu\text{g}/\mu\text{m}$ . The change in sensitivity with load is sufficiently small so that the weight change during a series of experiments (about 2 mg) has negligible effect on it. Data during these experiments were obtained with two different but similar balances. One was gold

plated and had been used for previous experiments. The second was unplated and had slightly higher sensitivity. Both balances exhibited excellent zero-point stability in contrast to some previous drift problems [11]. This is attributed to a more nearly constant ambient temperature at our new NBS facility, use of a narrower slot on the kinematic table which supported the gold-plated balance, and the grounding procedure which eliminates static charge on the sample and its surroundings.

Initial time for an experiment was taken when the brightness of the blackbody hole matched the preset brightness of the pyrometer filament set for a temperature 50 K or so below the expected temperature for a particular power setting. Final time was taken as the time the power was turned off. The first temperature measurement was usually obtained within the first minute of the experiment, at which time the sample had attained its ultimate temperature. This method of determining the duration of the experiment represents a slight change from our previous practice and was made because the rate of heating is slower than the rate of cooling. Qualitatively, the time required to heat from the base temperature to the operating temperature is inversely proportional to the temperature difference between them. For low-temperature runs the length of time to go from the base temperature to 50 K below the operating temperature would be about 15 s, while for high-temperature runs about 3 s would be required. We believe that systematic error resulting from this approximation is small.

Some difficulties were encountered in achieving linear  $\log P$  versus  $1/T$  relationships in two of the platinum samples which had been exposed to oil during the machining process. These samples exhibited the same type of behavior as described by Hampson and Walker [4] with platinum and by Carrera et al. with ruthenium [12]; that is, below about 1800 K the apparent vapor pressure deviated negatively from the normal curve. This behavior is apparently due to carbon contamination as a result of pyrolysis of oil residue introduced during machining, since a sample of the same reference material did not exhibit this behavior when machined using trichloroethylene cutting fluid. In addition, after the sample showing abnormal behavior was heated in air it gave normal vapor-pressure measurements. Finally, after the vapor-pressure measurements were completed, the 0.25-cm sample 747-15, which weighed 1.74 g, was heated in contact with graphite powder at 1735 K for half an hour. During this process it gained  $72 \mu\text{g}$ . Microscopic examination of the sample at  $75\times$  showed a uniform darkening of the surface. Attempts at measuring the vapor pressure of this sample showed complete blocking of the vaporization process at temperatures up to 1860 K, while at 1900 K and above, the vaporization rate was normal. Measurements in the transition range were not very satisfactory because the sample temperature tended to increase or decrease at constant power setting. This behavior differs greatly from that of a pure sample, whose temperature would remain constant within a few degrees. These observations would seem to indi-

cate that the carbon contamination stays close to the surface of the sample and that the extent of diffusion into the sample during the measurements is negligible. We can speculate that above the transition temperature the rate of sublimation is normal because the carbon is dissolved by the platinum and the rate of platinum diffusion through the solution is high, while below the transition temperature, the carbon would precipitate, and the rate of platinum diffusion through the carbon would be low.

### 3. Data and Thermodynamic Treatment

Vapor pressures were calculated using the equation<sup>3</sup>

$$P = \frac{m}{\alpha at} \left( \frac{2\pi RT}{M} \right)^{1/2} \quad (1)$$

where  $m$  is the mass of material sublimed,  $t$  is the duration of the experiment,  $a$  is the projected surface area of the sample,  $T$  is the absolute temperature on the 1968 IPTS [13],  $R$  is the gas constant,  $M$  is the atomic weight of the vaporizing species, monatomic platinum, and  $\alpha$  is the vaporization coefficient which we assumed equal to unity. The value of the sample area at temperature,  $A_T$ , was calculated using the equation

$$A_T = A_R [1 + 2\beta(T - 300)]$$

where  $A_R$  is the area calculated from measurements made at room temperature and  $\beta$  is the linear thermal expansion coefficient. For platinum,  $\beta$  was taken to be  $11.3 \times 10^{-6} \text{ K}^{-1}$ . This correction amounts to an increase in the surface area at temperature of 2 to 4 percent.

Sample areas at room temperature for the various samples were 1.60 cm<sup>2</sup>, 1.64 cm<sup>2</sup>, 1.64 cm<sup>2</sup>, and 1.27 cm<sup>2</sup> for the platinum SRM 747 I through IV series, respectively, and 1.64 cm<sup>2</sup> for the platinum SRM 680 data.

A linear equation was fitted to the data by least squares solution of the approximate integrated form of the Clausius-Clapeyron equation

$$\log P(\text{atm}) = -\frac{\Delta H^\circ}{R'T} + \frac{\Delta S^\circ}{R'} \quad (2)$$

where  $\Delta H^\circ$  and  $\Delta S^\circ$  are the heat and entropy changes at an average temperature and  $R'$  is  $R \ln 10$ .

In addition, third-law heats of sublimation were calculated using the equation

$$\Delta H_{298}^\circ = T \left[ \Delta - \left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) - R \ln P(\text{atm}) \right] \quad (3)$$

where  $\Delta - \left( \frac{G_T^\circ - H_{298}^\circ}{T} \right)$  is the difference in free-energy functions of product and reactant. Free-energy function data for platinum were from Hultgren et al. [14]. Finally, accurate second-law heats and entropies were

obtained using a method suggested by Horton [15] which is similar to Cubicciotti's method [16]. This consists of fitting by least squares  $\Delta - \left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) - R \ln P$  versus  $1/T$  and allowing for non-zero intercept. The slope corresponds to an accurately adjusted second-law heat, while the intercept corresponds to  $\Delta S_{298}^\circ$  (3d law)  $- \Delta S_{298}^\circ$  (2d law). To show this, add and subtract each of the quantities  $\Delta(H_T^\circ - H_{298}^\circ)/T$  and  $\Delta(S_T^\circ - S_{298}^\circ)$  from the negative of eq (2). Combining appropriate terms, the result is

$$-R \ln P = \frac{\Delta H_{298}^\circ(2)}{T} + \Delta \left( \frac{H_T^\circ - H_{298}^\circ}{T} \right) - \Delta S_{298}^\circ(2) - \Delta(S_T^\circ - S_{298}^\circ), \quad (4)$$

which is equivalent to Cubicciotti's [16] eq (4) or Horton's [15] eq (22). Here, the (2)'s and (3)'s following heats or entropies are used to designate second-law or third-law values. The quantity  $\Delta(S_T^\circ - S_{298}^\circ) - \Delta(H_T^\circ - H_{298}^\circ)/T$  equals  $\Delta - (G_T^\circ - H_{298}^\circ)/T - \Delta S_{298}^\circ(3)$ . Therefore, collecting temperature-dependent terms, we can write

$$-R \ln P + \Delta - \left( \frac{G_T^\circ - H_{298}^\circ}{T} \right) = \Delta S_{298}^\circ(3) - \Delta S_{298}^\circ(2) + \frac{\Delta H_{298}^\circ(2)}{T}. \quad (5)$$

By subtracting the intercept from  $\Delta - (G_{298}^\circ - H_{298}^\circ)/T = \Delta S_{298}^\circ$  (3d law), we can also obtain  $\Delta S_{298}^\circ$  (2d law). The convenience of this method results from the fact that the  $\Delta - (G_T^\circ - H_{298}^\circ)/T - R' \log P$  terms are used in evaluating the third-law heats so that the data necessary for calculating an accurate second-law heat are already available. This method gives the same results as that described by Cubicciotti [16]. We should note also that the difference between the third-law entropy and the second-law entropy is a constant and is independent of temperature. The second-law entropy can, therefore, be determined at any temperature by subtracting the intercept from  $\Delta S_T^\circ$  (3d law). We have, however, chosen to evaluate the second-law entropy at 298 K for convenience.

### 4. Results

Basic data used in the calculation, the vapor pressures, and individual third-law heats are listed in table 1. Table 2 lists the average second-law heat and entropy change at 298.15 K and their standard errors, the coefficients of eq (2) and their standard errors, the standard deviation in the pressure in log units, and the average third-law heat and its standard error for each series of data. The mean third-law heat, calculated as the average of the means for each run, is 564.49 kJ mol<sup>-1</sup> (134.92 kcal mol<sup>-1</sup>).

The overall uncertainty in this value is estimated to be  $\pm 2100 \text{ J mol}^{-1}$  ( $\pm 0.5 \text{ kcal mol}^{-1}$ ). This is calculated using an uncertainty in the pyrometer calibration

<sup>3</sup> Values of constants used in the equation were:  $R = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$  or  $1.98717 \text{ cal mol}^{-1} \text{ K}^{-1}$ , atomic weight of platinum = 195.09; one standard atmosphere =  $101.325 \text{ Nm}^{-2}$

TABLE 1. *Compilation of platinum data*<sup>a</sup>

VAPOR PRESSURE OF PLATINUM SRM 680 .25 CM. SAMPLE SERIES I						
Temp.	Time	Wgt. loss	Pressure		$\Delta H_{298}^{\circ}$	$\Delta H_{298}^{\circ}$
<i>Kelvins</i>	<i>seconds</i>	<i>micrograms</i>	<i>atmospheres</i>		<i>cal/mol</i>	<i>J/mol</i>
1809	1500	112	2.98	E-9	134796	563987
1781	2100	74.2	1.40	E-9	135416	566580
1866	900	168	7.57	E-9	135521	567018
1735	6600	95	5.64	E-10	135106	565285
1835	1200	133	4.46	E-9	135234	565817
1777	3000	102	1.35	E-9	135245	565865
1852	900	130	5.84	E-9	135475	566826
1821	1200	97.6	3.26	E-9	135352	566312
1704	7200	54.6	2.95	E-10	134922	564515
1675	10800	38.5	1.37	E-10	135210	565718
1909	300	135	1.84	E-8	135221	565767
1902	240	83.8	1.43	E-8	135688	567719
1807	1500	93.6	2.49	E-9	135294	566072
1978	180	210	4.86	E-8	136192	569826
1978	180	284	6.57	E-8	135007	564868
1759	3600	73.7	8.08	E-10	135690	567729
1945	210	190	3.74	E-8	134979	564751
1930	210	148	2.90	E-8	134935	564566
1752	4800	104	8.53	E-10	134970	564714
1802	1800	113	2.50	E-9	134911	564469
1697	9000	68.1	2.94	E-10	134387	562276
1875	600	136	9.21	E-9	135433	566652
1748	4800	81.3	6.66	E-10	135526	567041
1951	210	194	3.82	E-8	135305	566114

  

VAPOR PRESSURE OF PLATINUM SRM 680 .25 CM. SAMPLE SERIES II						
1823	1200	111	3.71	E-9	135030	564964
1949	150	182	5.02	E-8	134111	561119
1755	2400	57.1	9.38	E-10	134866	564281
1879	600	162	1.10	E-8	135054	565067
1700	9000	65.3	2.82	E-10	134762	563846
1790	1800	89.3	1.97	E-9	134875	564315
1838	900	116	5.19	E-9	134898	564411
1727	7200	88.4	4.80	E-10	135046	565033
1908	240	115	1.96	E-8	134912	564474

  

VAPOR PRESSURE OF PLATINUM SRM 680 .25 CM. SAMPLE SERIES III						
1833	1200	139	4.66	E-9	134929	564541
1882	600	163	1.11	E-8	135232	565813
1906	240	105	1.79	E-8	135117	565331
1939	210	169	3.32	E-8	135030	564965
1841	900	128	5.73	E-9	134752	563803
1827	1200	105	3.51	E-9	135523	567027
1692	9000	56.8	2.45	E-10	134610	563207
1781	2100	83.6	1.58	E-9	134988	564789
1732	7200	102	5.55	E-10	134932	564554

  

VAPOR PRESSURE OF PLATINUM SRM 680 .25 CM. SAMPLE SERIES IV						
1933	180	130	2.98	E-8	135036	564989
1833	1200	132	4.42	E-9	135121	565347
1903	300	132	1.80	E-8	134888	564371
1822	2400	246	4.11	E-9	134586	563108
1753	3600	86.5	9.46	E-10	134685	563524
1699	10800	70.5	2.53	E-10	135051	565052
1873	900	256	1.16	E-8	134432	562464
1817	1500	130	3.47	E-9	134834	564143
1797	2400	153	2.54	E-9	134486	562690
1733	7200	108	5.88	E-10	134810	564043

TABLE 1. *Compilation of platinum data*<sup>a</sup>—Continued

## VAPOR PRESSURE OF PLATINUM SRM 747-15 .25 CM. SAMPLE SERIES I

1864	600	114	7.89	E-9	135224	565778
1912	240	114	2.00	E-8	135113	565313
1806	1800	121	2.75	E-9	134864	564272
1698	10800	70.9	2.61	E-10	134867	564284
1750	4800	96.8	8.14	E-10	134981	564760
1932	180	130	3.05	E-8	134878	564329
1837	1200	158	5.43	E-9	134660	563419
1781	2700	116	1.75	E-9	134626	563276
1726	7200	94.4	5.26	E-10	134655	563398
1890	300	107	1.49	E-8	134692	563552

## VAPOR PRESSURE OF PLATINUM SRM 747-17 .25 CM SAMPLE SERIES II

1936	180	164	3.76	E-8	134346	562105
1854	1200	216	7.28	E-9	134807	564031
1823	1800	176	3.92	E-9	134830	564130
1794	2700	150	2.21	E-9	134761	563841
1889	480	174	1.48	E-8	134647	563365
1726	7200	88.5	4.81	E-10	134962	564681
1780	3600	150	1.65	E-9	134760	563836
1748	5400	113	8.23	E-10	134791	563965
1932	180	120	2.75	E-8	135275	565993
1706	10800	89.4	3.22	E-10	134781	563926
1930	180	139	3.18	E-8	134581	563087

## VAPOR PRESSURE OF PLATINUM SRM 747-17 .25 CM. SAMPLE SERIES III

1869	600	143	9.67	E-9	134826	564110
1836	1200	159	5.33	E-9	134656	563400
1731	5400	78.7	5.71	E-10	134757	563824
1924	180	117	2.67	E-8	134839	564168
1781	2700	113	1.66	E-9	134813	564058
1807	1800	123	2.73	E-9	134964	564689
1701	10800	93.4	3.36	E-10	134248	561695
1903	300	139	1.90	E-8	134683	563516
1963	120	156	5.39	E-8	134777	563905
1753	3600	80.7	8.83	E-10	134925	564528

## VAPOR PRESSURE OF PLATINUM SRM 747-15 .20 CM. SAMPLE SERIES IV

1925	240	111	2.46	E-8	135221	565767
1830	1800	150	4.32	E-9	134987	564784
1876	600	115	1.01	E-8	135160	565510
1780	3000	93.6	1.60	E-9	134869	564291
1945	180	119	3.52	E-8	135202	565686
1800	1800	87.8	2.51	E-9	134749	563792
1894	360	104	1.52	E-8	134898	564411
1708	10800	67.1	3.12	E-10	135044	565025
1746	7200	112	7.90	E-10	134781	563924
1858	900	127	7.37	E-9	135048	565039

<sup>a</sup> Data are listed in experimental sequence.

of  $\pm 5$  K, an uncertainty in the window and prism correction of  $\pm 4$  K, and three standard errors in the mean third-law heat. This estimation neglects two possible sources of systematic error about which little is known; namely, deviation of the blackbody hole from blackbody conditions, and temperature inhomogeneity of the sample. Error in the third-law heat resulting from

errors in the free-energy function data is considered negligible.

The average third-law heats for each series of measurements are reasonably consistent within the expected error limits. There is a tendency for second-law heats and entropies to be lower than the respective third-law values, but the significance of this is questionable.

TABLE 2. *Derived quantities for platinum*<sup>a</sup>

Source	Second-Law Values									Third-Law Values	
	$\Delta H_{298}^{\circ}$	<sup>b</sup> S.E.	<sup>c</sup> $\Delta S_{298}^{\circ}$	S.E.	$-\Delta H_{7}^{\circ}/R'$	S.E.	$\Delta S_{7}^{\circ}/R'$	S.E.	<sup>b</sup> S.D. (log <i>P</i> )	$\Delta H_{298}^{\circ}$	S.E.
	<i>kJ mol<sup>-1</sup></i>	<i>kJ mol<sup>-1</sup></i>	<i>J mol<sup>-1</sup>K<sup>-1</sup></i>	<i>J mol<sup>-1</sup>K<sup>-1</sup></i>	<i>K</i>	<i>K</i>				<i>kJ mol<sup>-1</sup></i>	<i>kJ mol<sup>-1</sup></i>
SRM 680 I	555.20	6.16	144.85	3.38	28520	321	7.189	0.176	0.042	565.85	0.31
SRM 680 II	553.82	4.77	144.66	2.63	28457	254	7.184	.140	.018	564.78	.26
SRM 680 III	552.48	5.09	144.07	2.79	28393	264	7.156	.145	.018	564.56	.27
SRM 680 IV	564.76	8.62	151.11	4.76	29034	454	7.524	.250	.031	563.97	.32
SRM 747-15 I	558.56	6.41	147.56	3.53	28710	335	7.338	.185	.025	564.24	.27
SRM 747-17 II	568.25	6.39	153.06	3.50	29208	334	7.621	.183	.027	563.91	.29
SRM 747-17 III	557.23	6.11	147.09	3.35	28629	316	7.307	.174	.025	563.79	.26
SRM 747-15 IV	554.95	4.67	145.30	2.55	28514	247	7.216	.135	.017	564.82	.22
Mean, This Work										564.49	.24
Jones et al. [2]	537.51	26.37	135.99	14.12	27564	1385	6.708	.742	.131	565.13	1.71
D & M [3]	606.45	32.31	173.95	18.81	31285	1683	8.759	.980	.118	566.38	1.36
H & W [4]	539.54	23.40	137.60	11.71	27571	1220	6.742	.611	.051	565.71	0.46
NSB [6]	536.97	17.20	.....	.....	27518	896	.....	.....	.....	.....	.....
P & A [7] (s)	536.29	25.15	133.53	12.69	27411	1311	6.534	.662	.040	570.30	.45
P & A [7] (l)	582.93	14.56	156.14	6.56	28684	760	7.147	.342	.039	570.79	.44
Koch et al., I [9]	617.04	26.95	176.74	11.97	30433	1406	8.208	.624	.094	558.11	1.64
Koch et al., 1A [9]	601.94	23.32	169.01	10.46	29653	1219	7.808	.547	.119	560.87	1.43

<sup>a</sup> All temperatures were converted to the 1968 IPTS.

<sup>b</sup> S.E.=standard error; S.D.=standard deviation.

<sup>c</sup> Based on tabulated data,  $\Delta S_{298}^{\circ} = 150.68 \text{ J mol}^{-1}\text{K}^{-1}$ .

This could be understood in terms of a non-unit evaporation coefficient or error in the free energy function data for *Pt*(s), but it is more likely that small systematic errors in our measurements are responsible. Specifically, the method of establishing the duration of each experiment could lead to larger negative deviations in the observed pressure as the time of an experiment is shortened. However, such systematic error, if it occurred, cannot be seen in the present data, possibly because of insufficient precision.

One set of data, series I on SRM 747, shows a trend in the third-law heats and residuals with order of experiment which could be indicative of a changing "A" value of the window during the series. However, measurements showed a "normal" increase of about 10 percent in the "A" value, which corresponds to a change in temperature of about 1° at 1800 K. To remove the trend in residuals, the "A" value would have had to change systematically by about 70 percent during the experiments. Several other possibilities to account for trend could be put forward but discussion of this point seems futile. The data for this series are normal in that they give heats and entropies in good agreement with the other series but are abnormal because of the trend in third-law heats and residuals.

Below the melting point, the vapor pressure of platinum can be adequately represented by the equation

$$\log P(\text{atm}) = -\frac{29020}{T} + 7.502,$$

which is based on our mean third-law heat and tabulated entropies evaluated at 1800 K. At 1500 K, an accurately calculated vapor pressure will deviate from

the pressure predicted by this equation by only 3 percent. The poorest agreement with this equation occurs in the SRM 680 III data. At 1600 and 2000 K, the approximate temperature extremes for this series, the least squares equation representing the SRM 680 III data gives pressures deviating by +10 percent and -10 percent, respectively. In terms of temperature this corresponds to an error of +5° at 1600 and -5° at 2000 K.

Table 2 also contains some derived quantities obtained from other studies. These data were reevaluated after conversion of temperature scales to the 1968 IPTS. This increased the average third-law heats by approximately 800 J and had negligible effect on second-law heats. Data rejected by the original authors were also rejected in our calculations. Second-law heats based on the data of Dreger and Margrave [3] and Norman, Staley, and Bell [6] differed significantly from those reported. However, it was not clear that their reported second-law heats were evaluated by least squares.

Data obtained by Langmuir sublimation studies include the original work of Langmuir and Mackay [1] corrected by Jones, Langmuir, and Mackay [2]; Dreger and Margrave [3]; and Hampson and Walker [4]. A preliminary analysis of Hampson and Walker's data was also published by Diamond et al. [5]. These three studies give average third-law heats in substantial agreement with our data. Some mass spectrometric Knudsen effusion data were presented by Norman, Staley, and Bell [6], who reported a second-law heat in fair agreement with the Langmuir data. Peleg and Alcock [7] carried out some torsion Langmuir and torsion Knudsen experiments. Their data were

published only in graphical form but evaluation of the graphical data indicates pressures lower by roughly 40 percent at 2000 K than those obtained in the classical Langmuir experiments. This difference was attributed by Peleg and Alcock to errors arising in determining the duration of the experiment in the classical Langmuir experiments. They argue that weight losses occurring during the preheating and cooling cycles, as well as outgassing of the sample during the experiment, lead to high pressures. However, errors of this magnitude resulting from measurement of the duration of the experiment or outgassing are unlikely. A systematic difference in temperature measurement of about 20 K would account for the difference in measured pressures. Errors of this magnitude are frequently encountered and the arrangement used by Peleg and Alcock, which consisted of sighting an optical pyrometer on the surface of a specimen heated by radiation, can lead to significant errors in either direction depending on the geometric relationship of heater to specimen and the emittance of the specimen. Very high temperature measurements in the range 3400 to 3900 K were reported by Falk [8], who used a shock tube technique. These measurements yielded pressures agreeing within a factor of two with extrapolated pressures based on the classical Langmuir experiments. This agreement is excellent considering the length of the extrapolation, the extremely high temperatures, and the complexity of the experimental method. However, these data are subject to greater interpretive error than those of the simpler experiments and no attempt has been made to derive thermodynamic quantities from them. Recent Langmuir measurements carried out on molten platinum by Koch et al. [9] by a novel technique give average third-law heats somewhat below our average third-law heat. However, lack of knowledge of the emittance of molten platinum as a function of temperatures makes their result relatively unreliable. Finally, some rate of vaporization data by Rytvin and Ulybysheva [10] were noted but were too fragmentary to be considered further.

In summary, our data give good agreement with those of three previous Langmuir determinations. The

major contribution of our data is that they significantly decrease the error in the heat previously accepted, primarily because of improved precision. Unanswered questions remain concerning the effect and importance of temperature gradients in our sample, extent of deviation from blackbody conditions in the blackbody sight hole, and whether or not apparent systematic errors are experimental artifacts or are properties of platinum. Questions of this sort can be answered only by systematic studies which yield improved precision.

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