

# Vapor Pressure and Heat of Sublimation of Tungsten<sup>1</sup>

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The vapor pressure of tungsten was measured by the Langmuir method in the temperature range 2574 to 3183 °K using a vacuum microbalance. The least-squares line through the data,  $\log P(\text{atm}) = 7.790 - 44680/T$ , yields a second law  $\Delta H_s^\circ(2850 \text{ °K}) = 204.4 \pm 2.7$  kcal/mol and  $\Delta S_s^\circ(2850 \text{ °K}) = 35.64 \pm 0.97$  cal/mol deg. Our recommended equation for the vapor pressure is  $\log P(\text{atm}) = 7.933 - 45087/T$  based on our experimentally determined mean third law  $\Delta H_s^\circ(298 \text{ °K}) = 203.5$  kcal/mol and tabulated values for the entropies and enthalpies.

## 1. Introduction

This paper is the fourth in a series covering the vapor pressures of refractory metals. Three previous papers [1, 2, 3]<sup>3</sup> gave the vapor pressures and heats of sublimation of Pd, Pt, Ir, Rh, Ru, and Os.

The value of the heat of sublimation of tungsten listed in several reference works [4, 5] is based on the original data of Langmuir [6] which was revised in a later publication by Jones, Langmuir and Mackay [7]. Some reference works [5, 8] have also given weight to the data of Zwikker [9, 10] as reported by Jones, Langmuir, and Mackay [7]. We wish to make it clear here that references [9, 10] contain only smoothed data, and that reference [7] appears to be the only published source of Zwikker's original data.

Although the data from these two studies yield average third law heats of sublimation which are in excellent agreement, little attention has been paid to the ambiguous nature of the temperature scale<sup>4</sup> used by Jones et al. [7], or to the relatively large difference between the second and third law heats of sublimation obtained from the measurements of Zwikker.

The studies of both Langmuir and Zwikker were carried out using the hot wire modification of the Langmuir method. While this method is capable of yielding excellent precision, major disadvantages are encountered in determining temperatures because an emissivity correction must be used and the method of heating can lead to important thermal gradients in the wire.

## 2. Experimental Method

The rate of sublimation of tungsten as a function of temperature was determined using a sample of polycrystalline rod fabricated by arc erosion into a right circular cylinder about 1.5 cm long and 0.25 cm in diameter. A hole 0.1 cm in diameter and 1.0 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 near the other end of the sample.

According to the supplier, the tungsten was 99.9 percent pure. The results of semiquantitative spectrochemical analyses performed at NBS on the material as supplied and on the sample itself after the sublimation experiments were concluded are given in table 1. The results indicate a maximum metallic impurity content of about 0.02 percent before use, and no appreciable purification or contamination due to the vapor pressure measurements. The density determined by weighing a specimen of known volume was  $19.2 \text{ g cm}^{-3}$ , close to the reported x-ray density of  $19.265 \text{ g cm}^{-3}$  at 25 °C [11].

TABLE 1. *Spectrographic analysis of tungsten*

Impurity element	% Before use	% After use
Ag	—	—?
Al	—	—
As	—?	—
B	—	FT
Ba	—	—?
Bi	—	—?
Ca	T	FT
Cu	FT	—?
Fe	T	T
Mg	FT	T
Mo	VW	—
Pb	—	T
Si	VW	VW
Sn	—	—

VW, 0.001—0.01%; T, 0.0001—0.001%; FT, <0.0001%; —, not detected; —?, questionable detection.

Some data were also obtained with an oriented single crystal specimen having an approximately square cross section of about 0.38 cm per edge, a length of 1.9 cm, and blackbody and suspension holes like those in the cylindrical polycrystalline specimen.

It was intended that the faces of this sample be parallel to the (100) crystal planes. Examination of the specimen by an x-ray back reflection technique showed that one of the short and the long sample axes were related to two crystallographic axes by a rotation of approximately 12 deg about the third

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<sup>3</sup> Figures in brackets indicate the literature references at the end of this paper.

<sup>4</sup> All temperatures in this paper are based on the 1948 IPTS unless otherwise noted.

crystallographic axis, while the other short sample axis differed from the third crystallographic axis by a rotation of approximately 4 deg about one of the other crystallographic axes. A noticeable amount of surface roughening took place during the measurements on this sample. The data obtained agreed with that obtained from polycrystalline tungsten but are not reported in detail in this paper because they were considerably less precise than those obtained using the polycrystalline tungsten. We believe that this was due to a temperature gradient of about 30 °K which was measured across the faces of the sample and that the temperature gradient was a result of the sample geometry.

The measurements were made using the vacuum microbalance apparatus previously described [12]. Samples were heated directly by rf induction at 450 kHz. Vacuum in the ultrahigh vacuum range ( $10^{-7}$  to  $10^{-9}$  torr) was maintained by a 90 liter per second ion pump. Weight losses in the microgram range were determined by measuring balance beam displacement with a cathetometer.

The sample was suspended from one arm of an equal-arm quartz beam microbalance at the end of a chain of 0.025 cm diam quartz and sapphire rods by a loop of 0.0075 cm diam tungsten wire which passed through the suspension hole in the sample and over a hook on the lowest rod. The chain of sapphire and quartz rods was connected at each end by V-shaped hooks made by heating and bending the rods.

The arm of the vacuum chamber in which the sample hung was a 16 mm O.D. quartz tube with a graded seal and Pyrex window at the bottom for temperature measurement. The window was protected from vapor deposition during the sublimation experiments by a magnetically operated shutter.

A quartz sleeve of 13 mm O.D. fitted snugly inside the 16 mm O.D. quartz tube of the vacuum system. A thin platinum coating deposited on the inner surface of this sleeve prevented static charge buildup in the vicinity of the sample from interfering with the weighing but did not heat inductively.

An NBS calibrated optical pyrometer with a magnifying objective lens was used to measure temperatures by sighting on the blackbody hole through the calibrated window and mirror. Calibration corrections for the mirror and window were determined in situ, before and after a series of experiments, by sighting the pyrometer on a band lamp located above the vacuum apparatus on a rotatable mount. With the pyrometer and band lamp in one position, readings on the band lamp filament could be made using the same optical path as was used during the vapor pressure measurements except that the source was further away. By rotating the band lamp 90 deg and raising the pyrometer, temperature readings could be made directly on the band lamp filament. The calibration correction was obtained from the difference between reciprocal absolute temperatures with and without the window and mirror in the optical path.

The precision of the temperature measurements, expressed as the standard deviation of the mean temperature of a run, was 8 °K. The uncertainty of the mean temperature 2850 °K is estimated from the precision of the temperature measurements, the uncertainty in window and mirror calibration ( $\pm 6$  °K) and the uncertainty in the pyrometer calibration ( $\pm 7$  °K), to be  $\pm 12$  °K. This estimate does not include the effects of temperature gradients in the sample or the departure of the blackbody hole from blackbody conditions which were not evaluated with sufficient precision to warrant their inclusion.

The overall uncertainty of the mean third law heat of sublimation is estimated to be 0.8 kcal mol<sup>-1</sup> based on the uncertainty of  $\pm 12$  °K in the mean temperature and a value of 70 cal mol<sup>-1</sup> °K<sup>-1</sup> for  $\Delta H_s^0(298)/T$ .

In obtaining each datum point the following sequence of operations was performed: (1) The rest point of the microbalance was determined, (2) the sample was slowly heated to a temperature several hundred degrees below the temperature of the experiment, (3) the sample was rapidly heated to the operating temperature and maintained as near constant as possible, (4) the sample was rapidly cooled to a temperature well below the experimental temperature, the power slowly reduced, and the oscillator then turned off, and (5) the rest point of the balance was redetermined. The slow heating and cooling portions of the cycle were necessary to avoid lateral motion of the specimen caused by the rf field while the rapid heating and cooling portions of the cycle made the measurement of the duration of the experiment more accurate. The mass change of the sample was determined from the displacement of the beam of the microbalance and the previously determined sensitivity of the balance which was about 0.5  $\mu\text{g}/\mu$ .

The change in sensitivity with load was sufficiently small so that the weight change of the sample during a series of experiments had a negligible effect. In general, duplicate rest points agreed to within  $\pm 2$   $\mu$  ( $\pm 1$   $\mu\text{g}$ ) so that the corresponding uncertainty in the weight loss would be approximately  $\pm 1.4$   $\mu\text{g}$ .

### 3. Data and Thermodynamic Treatment

The experimental results obtained using polycrystalline tungsten are summarized in table 2. The vapor pressure was calculated using the equation;<sup>5</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,  $\alpha$  is the projected surface

<sup>5</sup> Values of constants used in the calculations were:  $R=1.98717$  cal mol<sup>-1</sup> deg<sup>-1</sup>, or 8.3143 abs. J deg<sup>-1</sup>mol<sup>-1</sup>; atomic weight of tungsten=183.85; one standard atmosphere=1,013,250 dyn cm<sup>-2</sup>.

area of the sample,  $T$  is the absolute temperature,  $R$  is the gas constant,  $M$  is the atomic weight of tungsten, and  $\alpha$  is the vaporization coefficient, which was assumed equal to unity. The value of the sample area  $a$ , at temperature  $T$  was calculated from the area measured at room temperature  $a_0$  by assuming that the equation  $a = a_0 [1 + 2\beta(T - 300)]$  was valid in the temperature range where vapor pressure measurements were carried out. In this equation,  $\beta$  is the coefficient of linear thermal expansion. Literature values [13] for this coefficient show an appreciable spread for the temperature range of interest here. The value,  $\beta = 6 \times 10^{-6} \text{ }^\circ\text{K}^{-1}$  was used for the present work.

TABLE 2. Vapor pressures and heats of sublimation of tungsten<sup>a</sup> (present study)

Temperature	Duration of run	Weight loss <sup>b</sup>	Vapor pressure	$\Delta H_s^\circ(298)$
$^\circ\text{K}$	min	$\mu\text{g}$	atm $\times 10^9$	kcal mol <sup>-1</sup>
2786	5.0	25.4	5.42	203.7
2773	5.0	24.5	5.21	202.9
2679	20.0	24.1	1.26	203.5
2574	28.0	6.8	0.250	203.7
2925	5.0	141	30.8	203.9
3034	4.9	434	98.3	204.6
2614	45.0	23.2	0.534	203.0
3068	5.0	881	197	202.7
2934	5.0	183	40.0	203.0
3183	4.0	1910	542	204.0

Mean  $\Delta H_s^\circ(298)$  and standard error.....203.5  $\pm$  0.2 kcal mol<sup>-1</sup>  
 Estimated overall uncertainty.....0.8 kcal mol<sup>-1</sup>

<sup>a</sup> Listed in experimental sequence.

<sup>b</sup> Sample surface area at room temperature = 1.332 cm<sup>2</sup>.

In general, the heat of sublimation can be computed from vapor pressure data in two ways. In the second law method, one can make use of the experimental data to evaluate both constants in the equation

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

It should be noted that this equation is only approximate since it ignores the temperature dependence of  $\Delta H^\circ$  and  $\Delta S^\circ$ . Although a more exact second law treatment can be made by inclusion of the temperature dependence of  $\Delta H^\circ$  and  $\Delta S^\circ$ , any error introduced into the second law heat and entropy of sublimation by use of eq (2) in the present case is small in comparison with the error in these quantities resulting from scatter in the vapor pressure data.

In eq (2),  $\Delta H^\circ$  is the heat of sublimation at an average temperature,  $\Delta S^\circ$  is the entropy change at the same temperature and  $R'$  is equal to  $R \ln 10$ . In the third law method, one makes use of absolute entropies, usually obtained from heat content and spectroscopic data, to calculate the entropy change for the assumed sublimation process at each temperature. These values and the experimental pressures can then be substituted in eq (2) to obtain the experimental values of  $\Delta H^\circ$  at the specified temperatures. In practice, use is generally made of free energy functions which allow one to calculate a value for the heat of sublimation at a reference temperature, usually 298.15  $^\circ\text{K}$  (or 0  $^\circ\text{K}$ ) according

to the equation,

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

where  $\left( \frac{G_T^\circ - H_{298}^\circ}{T} \right)$  is the free energy function.

Differences between  $\Delta H_s^\circ(298)$  obtained by the second law and the third law methods can give information concerning the consistency of the vapor pressure data obtained, the free energy function data used, the sublimation reaction assumed or the existence of a vaporization coefficient other than unity. Frequently, a lack of trend in the heat of sublimation calculated as a function of the experimental temperature is taken as an indication that no important systematic errors are present in the data. Actually, this method is quite insensitive to systematic error and it is easier to find a discrepancy by comparing second and third law heats of sublimation or the experimental entropy change with that found from heat content and spectroscopic data.

In the present experiments, a mean third law heat of sublimation at 298  $^\circ\text{K}$  of 203.5  $\pm$  0.2 kcal/mol was obtained<sup>6</sup> using the free energy function data listed in the JANAF Thermochemical Tables [4], while a second law treatment of the data yielded  $\Delta H_s^\circ(2850 \text{ }^\circ\text{K}) = 204.4 \pm 2.7$  kcal/mol. The latter was corrected to 298  $^\circ\text{K}$  using the JANAF enthalpy functions and the value  $\Delta H_s^\circ(298) = 201.6 \pm 2.7$  kcal/mol obtained.

The equation  $\log P(\text{atm}) = 7.790 - 44680/T$  (2574 to 3183  $^\circ\text{K}$ ) is the least-squares line through the data obtained in this study. We believe the vapor pressure of tungsten is best represented by the equation  $\log P(\text{atm}) = 7.933 - 45087/T$  (2574 to 3183  $^\circ\text{K}$ ), obtained using our experimentally determined mean third law heat of sublimation at 298  $^\circ\text{K}$  of 203.5 kcal/mol, a mean temperature of 2850  $^\circ\text{K}$  and the entropy and enthalpy data given by JANAF.

#### 4. Results from Earlier Work

In comparing the values for the heat of sublimation of tungsten listed in several compilations it became apparent that differences in the values were not entirely due to differences in the free energy functions used in these computations. Hence, in view of the date of the original work, it was felt worthwhile to check the conversion of the temperatures reported in the original articles to the 1948 International Practical Temperature Scale. Surprisingly enough, some of the compilations checked had not made any corrections to the temperatures at all.

The corrections to the temperature scale used by Zwicker are easily made. His scale was based on a

<sup>6</sup> Results are given in the form  $a \pm b$  where  $a$  denotes the arithmetic mean or least squares adjusted value and  $b$  is the standard error of  $a$  computed from the scatter of the individual determinations about the mean or fitted line.

gold point of 1063 °C and a second radiation constant value of  $C_2=1.433$  cm deg. It should be noted that this differs slightly from the 1927 ITS in the value of  $C_2$  chosen. The original temperatures reported for Zwikker's data, converted to the 1948 IPTS using the methods outlined by Corruccini [14], are given in table 3.

The method of converting Langmuir's reported temperatures [6, 7] to the 1948 IPTS are not so straightforward. Most of the difficulty stems from the fact that the descriptions of the two scales given by Jones et al. [7, 15], are somewhat sketchy and that the equations given for converting from the original scale to the later scale do not give the results reported. The situation with regard to the original and later scales can be summarized as follows.

The original temperature scale was based on the equation,

$$\log C_w = -\frac{11230}{T} + 7.029 \quad (5)$$

where  $C_w$  is the luminance in candelas per  $\text{cm}^2$  radiated from a tungsten sample. This equation was based on a temperature scale described by Nernst [16]. The revised data published in 1927 [7] were said to be based on the equation

$$\log C_w = -\frac{10957}{T} + 6.797 \quad (6)$$

which was claimed to represent the candlepower-temperature relationship derived from the work of Forsythe and Worthing [17]. However, eq (6) actually represents the candlepower data reported by Zwikker [9, 10] multiplied by 0.917, and leads to temperatures varying nonsystematically from 11 to 28 deg below those reported by Jones et al. [7].

We made a least squares treatment of Forsythe and Worthing's candlepower data to obtain an equation similar to (6). This was used with eq (5) to obtain temperatures which should correspond to those reported by Jones et al. The temperatures obtained in this way differed nonsystematically from zero to 6 deg below those reported. We believe that this indicates that the revised temperatures published by Jones et al. are based on the same temperature scale as was used by Forsythe and Worthing which is the same as the scale used by Zwikker. In view of the relatively small differences between the values reported by Jones et al., and those calculated by us, we have accepted their values and converted these to the 1948 IPTS using the method described by Corruccini [14].

Tables 3 and 4 list the vapor pressures of tungsten calculated from the rate of vaporization data obtained by Langmuir and by Zwikker [7], the temperatures as reported in the 1927 work [7], the temperatures based on the 1948 IPTS and third law heats of sublimation obtained using JANAF [4] free energy functions.

TABLE 3. Vapor pressures and heats of sublimation of tungsten (Zwikker)

$T^a$ (Rept.) [7]	$T$ (1948 IPTS)	Rate of sublimation [7]	Vapor pressure	$\Delta H_s^\circ$ (298)
°K	°K	$g \text{ cm}^{-2} \text{ sec}^{-1} \times 10^9$	$\text{atm} \times 10^9$	$\text{kcal mol}^{-1}$
2389	2383	0.000115	0.00934	203.9
2510	2503	.00099	.0824	203.5
2614	2606	.00525	.446	203.3
2637	2628	.00621	.530	204.1
2657	2648	.00969	.829	203.3
2759	2749	.0427	3.72	203.0
2887	2876	.293	26.1	201.4
2889	2878	.275	24.5	201.9
3017	3004	1.28	117	201.5
3108	3094	3.47	321	201.4
3124	3110	3.82	354	201.9
3129	3115	4.69	435	200.9
3132	3118	4.69	436	201.1
3137	3123	4.95	460	201.1

Mean  $\Delta H_s^\circ$  (298) and standard error ..... 202.3  $\pm$  0.3 kcal mol<sup>-1</sup>

<sup>a</sup> These temperatures are based on a scale defined by  $C_2=1.433$  cm deg,  $t_{Au}=1063$  °C and Wien's law.

TABLE 4.—Vapor pressures and heats of sublimation of tungsten (Langmuir)

$T^a$ (Rept.) [7]	$T$ (1948 IPTS)	Rate of sublimation	Vapor pressure	$\Delta H_s^\circ$ (298)
°K	°K	$g \text{ cm}^{-2} \text{ sec}^{-1} \times 10^6$	$\text{atm} \times 10^9$	$\text{kcal mol}^{-1}$
2518	2511	0.0020	0.167	200.6
2610	2602	.0059	.501	202.3
2913	2901	.39	34.9	201.5
3300	3283	30.0	2860	199.6
2852	2841	0.151	13.4	202.6
2950	2938	.52	46.9	202.3
2950	2938	.59	53.2	201.6
3000	2987	1.01	91.8	201.8
3000	2987	1.14	104	201.0
3060	3047	1.73	159	202.6
3060	3047	2.33	214	200.8
3066	3053	1.84	169	202.6
3066	3053	2.45	225	200.9

Mean  $\Delta H_s^\circ$  (298) and standard error ..... 201.6  $\pm$  0.3 kcal mol<sup>-1</sup>

<sup>a</sup> These temperatures are based on a scale defined by  $C_2=1.433$  cm deg,  $t_{Au}=1063$  °C and Wien's law but see discussion of this scale in text.

Table 5 lists the mean third law heats of sublimation at 298 °K, the second law heats of sublimation obtained from least squares treatment of the vapor pressure data and extrapolated to 298 °K using the enthalpy data of JANAF, and the experimental entropy changes at temperature derived from each set of measurements. Least squares analysis of our data yields a standard deviation in the pressure of approximately 10 percent. This is close to the uncertainty in the pressure that would be expected on the basis of the independently estimated precision in temperature measurement. Hence, it appears that imprecision in temperature measurement is the principal source of random error.

## 5. Discussion and Summary

The heat of sublimation of tungsten obtained in this work is in good agreement with values based on data obtained by Langmuir and by Zwikker. Langmuir's second law heat agrees better with our third law heat than his own, and vice versa, because our experimental entropy change is about as much below the accepted third law entropy change as his

TABLE 5. *Heats and entropies of sublimation of tungsten*

Investigator	$\Delta H_s^\circ(298)$ 2d Law	$\Delta H_s^\circ(298)$ 3d Law	$\Delta S_s^\circ$ 2d Law
	<i>kcal mol<sup>-1</sup></i>	<i>kcal mol<sup>-1</sup></i>	<i>cal mol<sup>-1</sup> °K<sup>-1</sup></i>
Zwikker:			
(Low temp. points)-----	208.5 ± 3.3 (872.4 ± 13.8 kJ mol <sup>-1</sup> )	203.5 ± 0.2 (851.4 ± 0.8 kJ mol <sup>-1</sup> )	38.28 ± 1.28 (160.2 ± 5.4 J mol <sup>-1</sup> °K <sup>-1</sup> )
(High temp. points)-----	206.2 ± 3.4 (862.7 ± 14.2 kJ mol <sup>-1</sup> )	201.4 ± 0.1 (842.7 ± 0.4 kJ mol <sup>-1</sup> )	37.83 ± 1.13 (158.3 ± 4.7 J mol <sup>-1</sup> °K <sup>-1</sup> )
(All points)-----	214.1 ± 1.3 (895.8 ± 5.4 kJ mol <sup>-1</sup> )	202.3 ± 0.3 (846.4 ± 1.3 kJ mol <sup>-1</sup> )	40.44 ± 0.47 (169.2 ± 2.0 J mol <sup>-1</sup> °K <sup>-1</sup> )
Langmuir-----	203.9 ± 3.7 (853.1 ± 15.5 kJ mol <sup>-1</sup> )	201.6 ± 0.3 (843.5 ± 1.3 kJ mol <sup>-1</sup> )	37.04 ± 1.28 (155.0 ± 5.4 J mol <sup>-1</sup> °K <sup>-1</sup> )
This work-----	201.6 ± 2.7 (843.5 ± 11.3 kJ mol <sup>-1</sup> )	203.5 ± 0.2 (851.4 ± 0.8 kJ mol <sup>-1</sup> )	35.64 ± 0.97 (149.1 ± 4.1 J mol <sup>-1</sup> °K <sup>-1</sup> )

<sup>a</sup> The value of the entropy of sublimation at 2850 °K based on heat content and spectroscopic data is 36.30 cal mol<sup>-1</sup> °K<sup>-1</sup> according to JANAF [4] and 35.99 cal mol<sup>-1</sup> °K<sup>-1</sup> according to Kirillin et al. [18].

is above it. Recent work [18] on the heat capacity of solid tungsten yields a value for the third law entropy of sublimation in slightly better agreement with that obtained from the present study. However, we prefer to use the JANAF [4] tabulation until the new data have been critically evaluated.

The large difference between the second and third law heats of sublimation obtained from the work of Zwikker is evidence of appreciable systematic error. Considering the way in which his third law heats vary with temperature it appears likely that his vapor pressure data were obtained in two distinct groups and that a systematic difference existed between the groups. Thus, the first six points listed in table 3 form one group which yield third law heats of sublimation larger than the mean value, while the last eight points yield third law heats of sublimation smaller than the mean value. If these groups of points are treated as independent sets, and second law heats of sublimation calculated, the six low temperature points yield a second law heat of sublimation at 298 °K of 208.5 ± 3.3 kcal/mol while the eight high temperature points give 206.2 ± 3.4 kcal/mol. Hence, the discrepancy between the second and third law heats of sublimation could be partially due to this cause. Similarly, the six low temperature points yield a second law entropy of sublimation of 38.28 ± 1.28 cal/mol deg and the eight high temperature points give 37.83 ± 1.13 cal/mol deg, compared to 40.44 ± 0.47 cal/mol deg for all fourteen points and the JANAF tabulated value at 2850 °K of 36.30 cal/mol deg.

In summary, the results obtained in the present study are in good agreement with those previously obtained. The differences in the mean third law heats of sublimation obtained from this work and from the work of Langmuir correspond to differences in vapor pressures at 3000 °K of about 40 percent, or differences in the observed temperature of about 30°, while the agreement with Zwikker's data is even better.

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