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The sublimation temperature of carbon dioxide

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Abstract. The technique of realizing the sublimation temperature of carbon dioxide at standard atmospheric pressure is described and its value on the International Practical Scale of Temperature (I.P.S.T.) is found to be $-78.5103 \pm 0.003^\circ\text{C}$, and on the thermodynamic Celsius scale $-78.475 \pm 0.005^\circ\text{C}$ (194.675°K). It is concluded that it is a suitable fixed point, in addition to the boiling point of oxygen and the triple point of water, for the realization of a practical scale over the temperature range from -182.97°C to 0°C . The vapour-pressure-temperature relation is deduced for a small range of pressures near to one standard atmosphere. Comparisons are made with previous determinations.

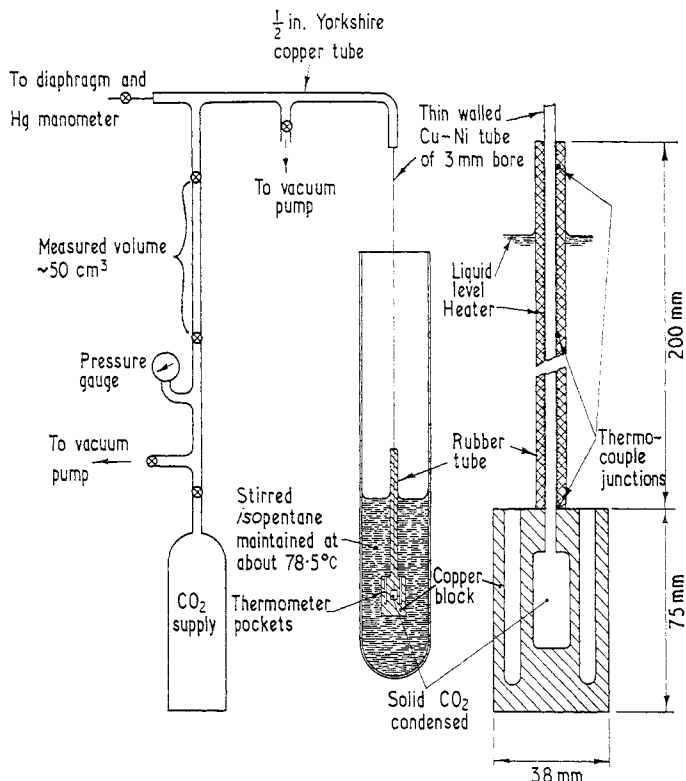
1. Introduction

Recent work (Barber and Horsford 1965) has shown that the Callendar-Van Dusen equation for the relation between the resistance and temperature of platinum over the temperature range from 0°C to -183°C used in the definition of the International Practical Scale of Temperature (I.P.S.T.) leads to interpolated temperatures which differ considerably (by up to 0.04 deg C) from thermodynamic temperatures. It is necessary, therefore, to re-define the I.P.S.T. over this temperature range and the International Committee of Weights and Measures has under consideration the use of a standard reference table of $W(=R_T/R_{273.15})$ against T for interpolation with platinum resistance thermometers instead of the Callendar-Van Dusen equation. Such a table of values would be based on a re-assessment of the properties of present day pure platinum and of the realization of the thermodynamic temperature scale. The calibration of a particular thermometer would be made by calibrating it at a few thermometric fixed points and then taking differences from the reference table. The results of the comparisons made at the National Physical Laboratory of a number of thermometers over this range of temperature shows that two points, the triple point of water (0.01°C) and the boiling point of oxygen (-182.97°C , 90.18°K), and a straight-line difference from a reference table would suffice to give a calibration in which the maximum error would be ± 0.004 deg C, provided that the α coefficient of the thermometer exceeded 3.925×10^{-3} . The inclusion of a third fixed point, ideally at the mid-point of the range, would clearly increase the precision obtainable provided the point could be adequately realized. A very conveniently placed fixed point for this purpose is the sublimation point of carbon dioxide (-78.5°C , 194.65°K); the realization of the CO_2 point and its value on the I.P.S.T. and thermodynamic scales is the subject of this paper.

2. The vapour pressure thermometer

In precision thermometry the boiling points of liquids are often realized by the static method in which a vapour pressure thermometer containing a very pure sample of the liquid is maintained at a constant temperature and the vapour pressure of the liquid is measured. This technique can be applied with the sublimation point of carbon dioxide, though, since we are now dealing with a solid instead of a liquid, care must be exercised to avoid blockage of the pressure transmitting tube. The method of ensuring this is to heat the transmitting tube and measure its temperature as described below.

The design of the vapour pressure thermometer is as shown in the figure. The solid carbon dioxide is condensed into a central cavity in a cylindrical copper block and platinum resistance thermometers of the capsule type are inserted into closely fitting holes in the block adjacent to the cavity. The cavity is connected by a thin-walled copper-nickel



Apparatus for the realization of the sublimation temperature of CO_2 .

tube, 3 mm bore, to a pressure-sensitive diaphragm by means of which the vapour pressure can be balanced against an external pressure which is measured by a mercury manometer. The pressure-transmitting tube has also connections to the supply of carbon dioxide through a measured volume (50 cm^3) and a pressure gauge, and to a vacuum pump. By these arrangements known volumes of gas may be condensed into, or withdrawn from, the cavity.

In order to ensure that the temperature of the copper-nickel tube is always higher than that of the cavity a heater is wound on the tube and insulated with a rubber tube, and thermocouples are placed on the tube to measure its surface temperature. The thermocouple junctions (copper-constantan) were located at the junction of the tube with the copper block and at 10 and 18 cm above the block. The heater (16Ω) was wound over a length of 14 cm, above the block, and the insulating rubber tube was 20 cm long. The copper block was suspended in a stirred *isopentane* bath (Barber and Horsford 1965) to a depth of 12.5 cm above the block; the temperature of the bath could be maintained at a uniform and steady temperature near to the normal sublimation temperature.

3. Experimental procedure

Carbon dioxide, of a special high purity grade, was supplied in a high pressure cylinder by the Distillers Co. Ltd, who stated that the liquid phase in the cylinder had been analysed and residual gases were found to be less than 25 parts per million by volume and water was found to be less than 50 parts per million by weight. The vapour pressure thermometer, diaphragm and manometer were carefully evacuated and then the system was filled with CO_2 directly from the cylinder, to a pressure of one atmosphere. The copper block was cooled to a temperature slightly above the sublimation temperature and the temperature of the connecting tube was adjusted to be higher than that of the copper block, as indicated by the relative readings of a copper-constantan thermocouple attached to the block and the thermocouples on the tube. A measured volume of CO_2 at a known pressure was then admitted to the cavity so that the volume of condensed CO_2 could be computed. The

Table 1, Typical observation of vapour pressure and temperature

Time	Manometer reading (millibar scale)	Manometer temperature, thermocouple readings (μv)	Thermocouple on vapour pressure bulb (μv)	Thermocouples on vapour pressure connecting tube (μv)	Bridge readings of resistance thermometers
04.18	1016.18	2097.7	-2850.9	0 cm: -2847.8	No. 141478 1-6-8-8-9-0 (reversed) 8-0-6
	6.07			10 cm: -2845.8	
	6.02			18 cm: -2698.3	No. 141479 1-6-9-3-9-10-8 (reversed) -8
	1015.91				
	5.92				
04.24	1016.00				1-6-8-8-8-8-2 (reversed) 7-9-2
	1015.97				
	5.97				1-6-8-8-8-8-1 (reversed) 7-8-2
	5.91	2100.4			
corrected for <i>g</i>	1015.995	2099.1		1-6-8-8-8-4-2	1-6-9-3-9-10-4 $t_{\text{int}} = -78.5044^\circ\text{C}$ $t_{\text{int}} = -78.5051^\circ\text{C}$
	-3.097	+0.2			
	-0.203	18.743°C			
	+0.105				
	+0.208				
	1013.008				-78.5048°C int 0.0035
	1013.543 mb				Corrected to 1013.250 mb - 78.5083°C int

F, K, Fortin and Kew corrections for temperature; M, meniscus height correction; I, index correction.

condensed volume of CO_2 was initially 6 mm^3 . The temperature of the cryostat was adjusted so that the vapour pressure was close to one standard atmosphere ($101\,325 \text{ N m}^{-2}$). The temperature of the connecting tube was adjusted so that there was a positive gradient of temperature upwards from the bulb. A series of ten simultaneous readings of the vapour pressure and the resistance of the two platinum thermometers (Nos 141478 and 141479) were made. The details of a typical measurement are set out in table 1.

The measurement is seen to have taken 6 min to complete and during this time the temperature has fallen by 0.003 deg c , as indicated both by the change of resistance of the thermometers and the change in vapour pressure ($0.1 \text{ mb} = 0.0012 \text{ deg c}$). The thermocouple on the outside of the bulb (column 4) was $3.1 \mu\text{v}$ lower than that at the bottom of the pressure connecting tube (0 cm, column 5), showing the latter to be warmer than the bulb by about 0.1 deg c .

The method of testing the purity of the carbon dioxide was to examine the vapour pressure with different volumes of condensate; the volume could be reduced by allowing the gas to expand into the measured volume which was at a pressure of less than one atmosphere. The values recorded in table 2 were obtained in this way, showing the temperature to rise initially at constant pressure with change of volume and then to become constant.

Table 2. Variation of sublimation temperature with volume of condensed CO_2

Date	Time	Sublimation temperature	Volume of solid CO_2
		t_{int} ($^{\circ}\text{C}$)	(mm^3)
5 Jan. 65	03.06	-78.5213	6
	03.30	-78.5209	6
	04.18	-78.5083	5
	04.54	-78.5079	4
6 Jan. 65	11.24	-78.5521	3
	11.44	-78.5231	2.4
	12.05	-78.5110	1.6
	12.25	-78.5101	1.1
	14.15	-78.5108	1.1
	16.12	-78.5116	1.1
	17.33	-78.5119	1.1

This behaviour is consistent with a purification process, probably by the removal of permanent gas. The constancy of the reading with change of volume was taken as an indication that a sufficiently pure condition had been reached.

4. Results

When the carbon dioxide in the vapour pressure thermometer had been purified in the manner described above, a series of pressure-temperature readings were obtained over a small range on each side of standard atmospheric pressure. The values obtained are set out in table 3.

Table 3. Experimental values of vapour pressure and temperature

Vapour pressure (N m^{-2})	Temperature on I.P.S.T. (t_{int}) Mean of platinum thermometers Nos 141478 and 141479
97 647.8	-78.9657
99 453.8	-78.7408
101 351.6	-78.5048
101 270.5	-78.5141
101 355.4	-78.5062
101 373.6	-78.5055
101 359.8	-78.5074
102 336.7	-78.3888
103 338.4	-78.2698
104 279.8	-78.1588

Apart from the normal correction of the pressure readings of the manometer as set out in table 1, a small correction was applied for the difference in height between the reference surface of the mercury manometer and the vapour pressure bulb and also for the increased density of carbon dioxide in the tube above the bulb, where it was cooled by the liquid of the cryostat. The total correction for these differences was 2.7 N m^{-2} , corresponding to about $3 \times 10^{-4} \text{ deg C}$ in the sublimation temperature. By graphical means a curve was fitted to the data in table 3 showing the relation between vapour pressure and temperature, and the value of the sublimation temperature at one standard atmosphere was deduced to be -78.5097°C . Since it is known that different thermometers give slightly different interpretations of the I.P.S.T., an average of a group of thermometers, including the two used in the determination, was taken. These thermometers had been compared in a cryostat of stirred *isopentane* and on the results obtained the following values of the normal sublimation temperature were deduced.

Table 4. Sublimation temperature values given by seven platinum thermometers

Thermometer No.	Sublimation temperature ($^\circ\text{C int}$)
143372A	-78.5115
141474	-78.5121
141478	-78.5092
141479	-78.5102
141480	-78.5117
141483	-78.5093
141485A	-78.5079
mean:	-78.5103

Thermometer No. 141480, among those listed in table 4, had been compared with the helium gas thermometer and its I.P.S.T. value at -78°C was lower than the value on the thermodynamic scale by 0.0364 deg C . Hence the thermodynamic temperature of the normal sublimation point of CO_2 is given by $-78.5117 + 0.0364 = -78.4753^\circ\text{C}$. Applying the limits calculated for the gas thermometry mentioned above and taking into consideration the range of values on the I.P.S.T. with different thermometers, we may state the following values for the CO_2 point:

$$t_{\text{th}} = -78.4753 \pm 0.005^\circ\text{C} (194.675^\circ\text{K})$$

$$t_{\text{int}} = -78.5103 \pm 0.003^\circ\text{C}.$$

The reproducibility of the point as realized in these experiments was $\pm 0.001 \text{ degC}$.

5. Previous results

5.1. I.P.S.T. values

Meyers and Van Dusen (1933) computed a value of -78.515°C for the normal sublimation temperature from vapour-pressure-temperature measurements. From Heuse and Otto (1932) one can deduce a value on the I.P.S.T. of -78.506°C on the mean of two platinum thermometers having α coefficients of 3.915×10^{-3} . Lovejoy (1962), using modern platinum resistance thermometers ($\alpha = 3.926 \times 10^{-3}$), obtained a value of -78.5097°C .

5.2. Thermodynamic scale values

The only determination on the thermodynamic scale previously reported is that of Heuse and Otto (1932) who found a value of -78.471°C , using a helium gas thermometer; they give the corresponding Kelvin temperature as 194.689°K , i.e. they assume $T_0 = 273.16^\circ\text{K}$. The pressure coefficient of the normal helium gas thermometer (i.e. where $p_0 = 1000 \text{ mmHg}$) used in their calculations is given as $\alpha_{\text{nHe}} = 0.0036606$. According to Keesom (1942) the corresponding fundamental pressure coefficient for a perfect gas, when the gas is said to be in the Avagadro state, is $\alpha_{\text{A}} = 0.00366092$ and this is equivalent to

Table 5. Vapour-pressure-temperature relationship of solid CO₂ near one standard atmosphere

P (kN m ⁻²)	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
97						-78.9497	-78.9372	-78.9247	-78.9122	-78.8997
98	-78.8873	-78.8748	-78.8623	-78.8499	-78.8374	8.8250	8.8125	8.8001	8.7876	8.7752
99	8.7628	8.7503	8.7379	8.7255	8.7130	8.7006	8.6881	8.6757	8.6632	8.6508
100	8.6384	8.6260	8.6136	8.6012	8.5888	8.5764	8.5640	8.5517	8.5394	8.5271
101	8.5184	8.5026	8.4905	8.4784	8.4663	8.4542	8.4422	8.4302	8.4182	8.4062
102	8.3942	8.3823	8.3704	8.3585	8.3466	8.3347	8.3228	8.3110	8.2992	8.2874
103	8.2756	8.2638	8.2520	8.2402	8.2284	8.2166	8.2048	8.1930	8.1812	8.1694
104	8.1576									

Temperatures derived from the above table are on the thermodynamic Celsius scale; they may be converted to the International Practical Scale of Temperature by subtracting 0.035 degc.

Table 6. Comparison of table 5 with I.P.S.T. (1948) values

Pressure (kN m ⁻²)	97.5	98.0	99.0	100.0	101.0	102.0	103.0	104.0
(a) I.P.S.T. (1948) (°C)	-78.9669	-78.9048	-78.7816	-78.6596	-78.5390	-78.4196	-78.3013	-78.1845
(b) Table 5-0.035 (°C)	-78.9847	-78.9223	-78.7978	-78.6734	-78.5534	-78.4292	-78.3106	-78.1926
(a)-(b) (degc)	0.0178	0.0175	0.0162	0.0138	0.0144	0.0096	0.0093	0.0081

0.01 degc of the difference (a)-(b) is due to the value of -78.5°C for the normal sublimation temperature in the I.P.S.T. definition, compared with our value of -78.510°C.

$T_0 = 273.155^\circ\text{K}$. On this basis -78.471°C corresponds to 194.684°K and is reduced to 194.680°K for $T_0 = 273.15^\circ\text{K}$, from which we get the thermodynamic Celsius temperature of -78.470°C .

Summarizing, we have the following values:

	I.P.S.T. $t_{\text{int}} (^\circ\text{C})$	Thermodynamic $t_{\text{th}} (^\circ\text{C})$	$t_{\text{th}} - t_{\text{int}}$ (degC)
Heuse and Otto 1932	-78.506	-78.470 (corrected)	0.036
Meyers and Van Dusen 1933	-78.515		
Lovejoy 1962	-78.5097		
Present results	-78.5103	-78.4753	0.0350

6. Vapour-pressure-temperature relation for solid carbon dioxide

From the measurements reported in table 3, the equivalent thermodynamic temperatures were deduced and the values of vapour pressure and temperature in table 5 were computed over a short range of pressures close to one standard atmosphere.

The temperature of equilibrium between solid carbon dioxide and its vapour is quoted as a secondary fixed point of the I.P.S.T. as follows:

$$t_p = -78.5 + 12.12 \left(\frac{P}{P_0} - 1 \right) - 6.4 \left(\frac{P}{P_0} - 1 \right)^2 (^\circ\text{C})$$

where P_0 is one standard atmosphere. On the basis of this formula, and making the necessary correction to table 5 to give I.P.S.T. values, we obtain the comparison shown in table 6.

7. Conclusions

The experiments show that by using a small quantity of carbon dioxide in a vapour pressure thermometer its sublimation temperature may be realized to ± 0.001 degC provided suitable arrangements are made for achieving uniformity of temperature around the thermometer bulb and avoiding cold spots on the pressure-transmitting tube. It is concluded that the value of the sublimation temperature on the I.P.S.T. is $-78.5103 \pm 0.003^\circ\text{C}$; this value agrees with that determined by Lovejoy in 1962 to better than 0.001 degC. The value on the thermodynamic Celsius scale was found to be $-78.475 \pm 0.005^\circ\text{C}$; the only previous determination (Heuse and Otto 1932) was -78.470°C . Thus the CO_2 point to which has been assigned an agreed value, would be suitable for use as a fixed point in the realization of a practical temperature scale.

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