REALIZATION OF THE SUBLIMATION TEMPERATURE POINT OF CARBON DIOXIDE

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Received 14 January 2013; revised 19 April 2013; accepted 20 June 2013

Possibilities for realization of the sublimation temperature point (−78.464 °C) of carbon dioxide at standard atmospheric pressure are investigated. A simple methodology is demonstrated, and experimental results consistent with those obtained by other authors who used much more sophisticated methods are presented.

Key words: sublimation point, triple point, reference point, carbon dioxide, International Temperature Scale ITS-90

PACS: 06.20.fb

1. Introduction

Phase transitions, or phenomena when a substance changes its state from liquid to solid, etc. are very common. They find a range of applications, such as growing crystals from the liquid phase, and many others.

Usually, there exist conditions (temperature and pressure) at which all the three (gaseous, liquid, and solid) phases of a substance can coexist in thermodynamic equilibrium. Such a state is called the triple point of the substance. Triple points of some pure substances have been used as the reference points for realization of both former international temperature scales and the ITS-90 in effect now. In practice, triple points are realized by melting the solid phase or freezing the liquid. E. g. the triple point of water, where the liquid, ice, and gas (vapour) coexist, is at 273.16 K (0.01 °C) and 611.73 Pa. ITS-90 and its reference points are described in [1]. Supplementary information for the ITS-90, including its relation to earlier temperature scales, can be found in [2].

The phase transition when a substance changes its state from the solid to the gaseous one, or vapour, without appearing in the liquid state, is called sublimation. This is a specific case of evaporation. Sublimation takes place at temperatures below the triple point, where the liquid phase cannot exist. For instance, snow and ice gradually disappear by means of sublimation even in winter colds. If a substance below the triple point contains both solid and gaseous states and is in thermodynamic equilibrium, the dependence of gas pressure on temperature \( p(T) \) is a monotonous function. Thus, if \( p(T) \) is known, and the system is in thermodynamic equilibrium, one can unambiguously determine temperature from pressure and \textit{vice versa}. In thermometry, the dependence is usually considered to be \( T(p) \), which implies determining temperature from pressure.

An important substance in this respect is solid carbon dioxide (\( \text{CO}_2 \)), otherwise called dry ice. Due to its large molar heat of sublimation (about 26 kJ/mol), it is widely used for a variety of applications, such as keeping food cold for a long time, etc. A comprehensive overview of properties and applications of various phases of \( \text{CO}_2 \) can be found in [3]. \( \text{CO}_2 \) is relatively inexpensive; its sublimation with conditions close to equilibrium between
the solid and the gaseous phase is a phenomenon easy to realize at pressures close to atmospheric. Therefore, as \( T(p) \) for \( \text{CO}_2 \), in the range has been measured precisely [1, 3], sublimation offers a possibility for realization of reference temperatures in the vicinity of \(-78.5 \, ^\circ\text{C} \) (194.65 K) provided accurate measurements of pressure can be made. The sublimation point of \( \text{CO}_2 \) at the pressure of one atmosphere (101325 Pa) (its temperature determined in [4] and recalculated to ITS-90 in [7] is 194.686 K, or \(-78.464 \, ^\circ\text{C} \)) is included into the description of ITS-90 as a second quality reference point [7]. However, the methods for realizing the sublimation point and measuring \( T(p) \) for \( \text{CO}_2 \) employed in [1, 3] were too complex and required sophisticated equipment, which made them inapplicable to simple metrological applications. On the other hand, reference points in the range of low temperatures are of interest because the international temperature scale ITS-90 used now lacks low-temperature reference points convenient for long-stem thermometry. Namely, there is only one primary reference point between the water triple point (0.01 °C) and the triple point of argon (\(-189.34 \, ^\circ\text{C} \)) – the triple point of mercury (\(-38.83 \, ^\circ\text{C} \)). There are also some secondary reference points of the first and second quality (see Tables 1 and 2 of [3]). However, most of them are not easy to realize, especially if using precision long-stem thermometers. Without a doubt, thermometry would benefit from a simple realization of a reference point in this range.

Our effort aims at elaborating a simple method for realizing stable arbitrary reference temperatures in the vicinity of \(-78.5 \, ^\circ\text{C} \), which could be used for calibration of, e.g. platinum resistance thermometers, as well as comparing between the \( T(p) \) obtained by us and those obtained in the abovementioned work.

Success in simple and reliable realization of the sublimation point of \( \text{CO}_2 \) could finally lead to its wider application to practical metrology and science.

2. Description of the state of substance

The state of substance in various conditions can be determined by a point on its \( p-T \) phase diagram, defining temperature and pressure (the phase diagram for \( \text{CO}_2 \) can be found in p. 63 of [3]). The phase diagram is divided into domains of different phases by the abovementioned \( p(T) \) dependences. Such dependence defines the pressures and temperatures at which the two coexisting phases can coexist at thermodynamic equilibrium and thus is called a coexistence curve. A coexistence curve can be described by the Clausius–Clapeyron relation:

\[
\frac{dp}{dT} = \frac{L}{T \Delta V},
\]

where \( L \) is the molar latent heat of the phase transition, and \( \Delta V \) is the change of the molar volume during the phase transition. The Clausius–Clapeyron relation is derived directly from thermodynamic principles, without additional assumptions [3]. It is valid for any two phases coexisting in equilibrium: solid and liquid, solid and gaseous, or gaseous and liquid.

Let us apply the relation to equilibrium between the solid and the gaseous state. If we assume that the molar volume of the solid is much smaller than that of the gas, i.e. \( \Delta V = V_{\text{gas}} - V_{\text{solid}} \approx V_{\text{gas}} \), and also that the gas obeys the state equation for the ideal gas \( pV_{\text{gas}} = RT \), with \( R \) being the universal gas constant, we get

\[
\frac{dp}{dT} = \frac{Lp}{RT^2}.
\]

In this case, \( L \) is the molar latent heat of the phase transition from the solid state to gaseous, or sublimation. If we assume that it can be considered constant over a finite range of temperatures, we may integrate the equation and rearrange it to obtain expressions relating equilibrium temperature and pressure in their conventional form:

\[
T = \frac{B}{A - \ln \frac{p}{p_0}},
\]

where \( p_0 \) is a normalization constant used for convenience, \( A \) is an integration constant, and \( B = L/R \). The constants \( A \) and \( B \) can be found from experimental data by means of the least squares method. However, Eq. (3) does not fit experimental data over relatively large temperature ranges to the highest precision. This can be explained by the fact that the latent heat of sublimation actually depends on temperature, molar volume is not necessarily infinitesimal compared to that of gas, and, finally, saturated vapour is not a perfectly ideal gas. To obtain a better approximation, we can introduce an additional degree of freedom – constant \( C \) – to obtain
\[ T = \frac{B}{A - \ln \frac{p}{P_0}} - C. \]  

Eq. (4) is called the Antoine equation. When we introduce an additional degree of freedom to our least squares approximation procedure, we allow it to make a shift along the temperature axis to find an interval of the hyperbola with the curvature closer reflecting the character of experimental results. However, the shifted hyperbola needs to be rescaled, which causes constants \( A \) and \( B \) to change. Therefore, the third constant allows better approximation but constant \( B \) in this case does not correspond to the latent heat of sublimation. An alternative way to describe \( T(p) \) is the Zhokhovskii equation \( [5] \), which describes \( T(p) \) along the coexistence curve between two points – initial and final – with \( T \) and \( p \) known. The Zhokhovskii equation does not need the assumption that \( L \) is constant over the range, but it requires to determine some empirical constants. Empirical relations between \( p \) and \( T \) for various coexisting phases of \( \text{CO}_2 \) can be found in \( [10] \), and calculation of vapour pressure and sublimation heat in \( [11] \).

The dependence of sublimation temperature on the pressure of gaseous \( \text{CO}_2 \) at pressures near atmospheric was investigated and described in \( [4] \) in terms of ITS-48. Much later, the sublimation of \( \text{CO}_2 \) was investigated over a large range of temperatures and pressures, and the dependence of the sublimation temperature on pressure was presented in \( [5] \) in terms of ITS-68. The dependence recalculated to ITS-90 was given in Table 4 of \( [7] \) for the secondary reference point of \( \text{CO}_2 \) sublimation:

\[ T_{\text{w}} \text{ / K} = \frac{4120.8642}{16.064649 - \ln \left( \frac{p}{\text{MPa}} \right)} - 29.8365, \]  

where \( p \) is the pressure of gaseous \( \text{CO}_2 \). Eq. (5) is the Antoine equation applied to \( \text{CO}_2 \) in terms of ITS-90. However, although the \( T(p) \) relation is known, at present time the sublimation point of \( \text{CO}_2 \) is not widely used in metrology because a simple realization of the measurement has not yet been proposed.

We have performed a number of investigations of \( \text{CO}_2 \) sublimation, which made possible developing an acceptably simple methodology for realization of the sublimation temperature of \( \text{CO}_2 \) and calibration of long-stem standard platinum resistance thermometers (SPRTs) at arbitrary temperatures in the vicinity of \(-78.5 \text{ °C}\) by means of stabilizing the pressure of \( \text{CO}_2 \) gas close to atmospheric pressure.

3. Experiment

The set-up of the fully assembled measurement system is shown on Fig. 1. Our methodology for realization of the sublimation point of \( \text{CO}_2 \) employs in part the methodology and equipment for realization of the boiling point temperature of nitrogen, which is often used in thermometry for replacing a reference point of ITS-90, the triple point of argon. It is to be noted that the substances known as impurities to liquid \( \text{CO}_2 \) (\( \text{O}_2, \text{~N}_2, \text{~Ar, Ne, CO, Kr} \)) are gaseous under sublimation conditions. Therefore, they are unlikely to appear in the \( \text{CO}_2 \) snow produced by means of solidifying liquid \( \text{CO}_2 \). Moreover, \( \text{CO}_2 \) gas is heavier than all the listed impurity gases (except for krypton), and it forces them, even if present, out. There can be little amounts of dissolved impurities; however, their effect on sublimation temperature has to be investigated. Our results obtained with \( \text{CO}_2 \) of technical purity of 99.97% imply that the effect is insignificant.

First of all, we inject liquid \( \text{CO}_2 \) from a balloon into a sack made of a piece of cloth through a tube ending with a funnel-shaped nozzle. A strongly endothermic Joule–Thomson expansion causes the liquid to freeze to the solid. In this way, some amount (about half a kilogram) of solid-state \( \text{CO}_2 \) (\( \text{CO}_2 \) snow) appears in the sack. We put the snow to an open Dewar vessel, model 7196 (Hart Scientific) wrapped into a layer of thermally isolating material and fixed in a polystyrene box. We press the snow gently to form a homogeneous mass filling the vessel almost to the full. The temperature of the snow deep inside the vessel just after loading is about \(-80 \text{ °C}\). Then, we put on a polystyrene cover having two holes. Through the first hole, we insert a long (just a little shorter than the height of the vessel) metal tube with its bottom end closed, and into this tube we insert a calibrated standard long-stem platinum resistance thermometer, model 5681 (Hart Scientific). The long tube, while being inserted, pierces the snow and makes a well of the tube’s diameter. Through the second hole, we insert a short metal tube of small diameter. After that, we connect the thermometer to a high-precision temperature measurement bridge, model 6010 T (Measurements International), put a flexible rubber hose tightly over
the metal tube, and connect the hose to the divider, with one branch going to a DPI 150 pressure gauge, and the other to the pressure stabilization system (see Fig. 1 for the overall experimental layout (top) and for the pressure stabilization system in detail (bottom)). The pressure stabilization system is just the lower part of a conventional plastic bottle of 5 litres capacity filled with water from a tap roughly to the half, a glass cylinder immersed in the water upside down, and a low capacity diaphragm pump (ASF Thomas). There is also a flexible hose coming from the divider and ending in the upper area of the cylinder and the other hose beginning near the end of the first hose and going to the pump. The pressure gauge is positioned at the level of the sensitive element of the thermometer and is connected to the computer, which saves the readings at the specified time intervals.

With inserting the long tube and the thermometer, the snow surrounding the thermometer’s tube receives some amount of heat, while the tube and the thermometer cool down. Since then, a small amount of heat is coming from the outer part of the thermometer, which has a contact with ambient air. A tiny amount of heat is created by the thermometer’s wire (the current of 1 mA is flowing through the resistance of about 18 Ω).

As the snow in contact with the tube heats to the temperature defined by the Clausius–Clapeyron relation for the pressure of ambient air, the sublimation producing CO₂ gas begins. The snow starts evaporating from a tiny area surrounding the thermometer, and the gas pressure indicated by the DPI 150 and saved by the PC starts increasing, while the water level in the cylinder starts lowering. Finally, we launch a computer program
to control the diaphragm pump and to maintain the pressure at the value desired (the pump can also be controlled manually by reading the changing value on the DPI's screen and switching the pump on/off). After about half an hour, a state of relative thermal stationarity is reached, and thermometer's readings become stable to about 1 mK. This implies that the gas around the thermometer’s pipe has come into equilibrium with the snow at the vapour–snow interface. The temperature indicated by the thermometer corresponds to the value defined by the Clausius–Clapeyron relation for the pressure maintained. The difference between water levels inside and outside the cylinder indicates visibly the difference between the ambient air pressure and the pressure of CO₂ gas in the Dewar vessel.

Another sublimation area appears at the walls of the vessel, where sublimation is driven by a little amount of heat coming through the outer isolation and the walls of the vessel.

We have measured the temperature at some values of pressure and repeated the measurements many times in various conditions: with the vessel freshly loaded as well as when CO₂ snow is at expiry (as the rate of sublimation in our case is low, we manage to keep the snow for several days after loading). Each \((p, T)\) value reported is an average of a set of values saved over a time period of about 15 min.

4. Results and discussion

Table 1 gives the values of \(p\) and \(T\) measured in the immediate vicinity of 101325 Pa as well as the values of \(T\) when \(p\) is recalculated to the pressure of exactly 101325 Pa by using the differential expression \(\Delta T = \frac{\partial T}{\partial p} \Delta p\). The mean value of temperature is 194.684 K, i.e., it is lower by 2 mK than the reference value specified in Table 3 of [7]; however, it coincides with the value obtained using the approximating Eq (5) taken from Table 4 [ibid].

Table 1. The values of \(p\) and \(T\) measured at pressures near 101325 Pa and the values of \(T\) recalculated to the pressure of exactly 101325 Pa.

<table>
<thead>
<tr>
<th>Average pressure (Pa)</th>
<th>Average temperature (K)</th>
<th>Temperature (K) recalculated to the pressure of 101325 Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>101325.86</td>
<td>194.6842</td>
<td>194.6841</td>
</tr>
<tr>
<td>101325.74</td>
<td>194.6841</td>
<td>194.684</td>
</tr>
<tr>
<td>101325.61</td>
<td>194.6841</td>
<td>194.684</td>
</tr>
<tr>
<td>101325.66</td>
<td>194.6841</td>
<td>194.684</td>
</tr>
<tr>
<td>101325.85</td>
<td>194.684</td>
<td>194.6839</td>
</tr>
<tr>
<td>101325.99</td>
<td>194.6844</td>
<td>194.6843</td>
</tr>
<tr>
<td>101325.26</td>
<td>194.6837</td>
<td>194.6837</td>
</tr>
<tr>
<td>101325.24</td>
<td>194.6836</td>
<td>194.6835</td>
</tr>
<tr>
<td>101325.86</td>
<td>194.6844</td>
<td>194.6843</td>
</tr>
<tr>
<td>101325.94</td>
<td>194.6844</td>
<td>194.6843</td>
</tr>
<tr>
<td>101325.88</td>
<td>194.6844</td>
<td>194.6843</td>
</tr>
</tbody>
</table>

Table 1. The values of \(p\) and \(T\) measured at pressures near 101325 Pa and the values of \(T\) recalculated to the pressure of exactly 101325 Pa.

<table>
<thead>
<tr>
<th>Average of recalculated temperature</th>
<th>194.684</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean standard deviation</td>
<td>(2.5 \cdot 10^{-4})</td>
</tr>
</tbody>
</table>

Eq. (5) and the difference between our results and approximation of those presented in [4]. To obtain an ITS-90 approximation of the data of [4] presented in ITS-48, at first we have interpolated the tabular relation between ITS-68 and ITS-48 given in Table 1.4 of [2] in the Celsius scale and added 273.15 to obtain an approximate transition from ITS-48 in Celsius to ITS-68 in Kelvin degrees in the range of interest:

\[
T_{68} / K = t_{68} / ^\circ C - 0.043 - 2.15 \cdot 10^{-5} t_{48} / ^\circ C - 1.5 \cdot 10^{-5} t_{48}^2 / (^\circ C)^2 + 273.15.
\]

Having recalculated the results of [4] to ITS-68, we have recalculated them to ITS-90 using an expression derived from the tabular relation between ITS-90 and ITS-68 given in Table 1.5 of [2]:

\[
T_{90} / K = (T_{68} / K + 0.031) / 1.0001.
\]

The results in [4] comprise a rather small range of temperatures and pressures. They approximate well with the expression

\[
T_{90} / K = \frac{3083.295}{15.83743 - \ln(p/101325 \text{ Pa})},
\]

having only two constants (we use the value of one standard atmosphere as the reference pressure). Our results approximate with
thus yielding the value of the molar heat of sublimation of about 25.9 kJ/mol, which is close to the values given in [3] and many other sources. It is seen that the two differences depicted have a little bit different trends caused by slight differences in the results of [4] and [5].

Consider the main components of uncertainty of the sublimation temperature at the pressure of 101325 Pa, which budget is given in Table 2. Expanded uncertainty in calibration of the DPI pressure gauge has been taken from the recent calibration certificate. Yet, we have to take into account the fact that the DPI placed outside the Dewar vessel at the same level as the thermometer’s wire inside yields the pressure slightly different from its actual value at the place of interest. Namely, the pressure both inside and outside is level dependent. As the temperature outside is different from that inside, the dependences are different. We evaluate the limiting value of the pressure difference as $g \frac{\mu p}{R} \left( \frac{1}{T_{subl}} - \frac{1}{T_{room}} \right) \Delta h$.

Table 2. Uncertainty budget for the realization of the sublimation temperature point of CO$_2$ at the pressure of 101325 Pa.

<table>
<thead>
<tr>
<th>Component of uncertainty</th>
<th>Value at the 95% confidence level</th>
<th>Sensitivity coefficient</th>
<th>Contribution to the uncertainty of the sublimation temperature point (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calibration error of SPRT</td>
<td>1.5 mK</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>Calibration error of the pressure gauge</td>
<td>4 Pa</td>
<td>$\frac{dT}{dp} = 0.12$ mK/Pa</td>
<td>0.5</td>
</tr>
<tr>
<td>Possible difference in pressures inside and outside the cryostat at the same level</td>
<td>$g \frac{\mu p}{R} \left( \frac{1}{T_{subl}} - \frac{1}{T_{room}} \right) \Delta h = 4$</td>
<td>$\frac{dT}{dp} = 0.12$ mK/Pa</td>
<td>0.6</td>
</tr>
<tr>
<td>Other systematic and random effects</td>
<td>2</td>
<td></td>
<td>2.6</td>
</tr>
<tr>
<td>Scattering of the results (reproducibility)</td>
<td>0.5 mK</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Total expanded uncertainty of a single measurement series and the sublimation temperature value given in Table 1: 2.7 mK
where \( g \) is the free falling acceleration (9.8 m/s\(^2\)), \( \mu \) is the molar mass of CO\(_2\), \( \Delta h \) is the distance between the thermometer's wire and the cover of the vessel.

However, there are some other uncertainty components – hard to estimate and having both systematic and random character. Namely, the thermometer serves as a thermal conductor for the heat flow (dependent on the length of the outside part of the thermometer), which implies temperature gradients along its axis. Resistance thermometry itself is not a perfect instrument for a medium with finite thermal conductivity, e. g. gas, because of the tiny heating effect by electric current. Sublimation is not a state of thermal equilibrium – it is a process related to the heat flow across the boundary between the two phases, with \( p \) and \( T \) being close to the equilibrium between them only at the boundary, while the detailed distribution of temperature depends on the sublimation rate. Deeper layers of snow remain colder by roughly 1 K even after a long time. Thus, we have to maintain the sublimation rate not too high and not too low, which is not easy to control. Experience shows that in order to avoid significant deviations, we have to avoid fast decrease of gas pressure. With sublimation going on, the amount of snow slowly goes down, while the gap between the well and the phase boundary increases, which is slightly changing the thermal conditions around the thermometer. As we made our measurements until the snow was several days old, this also contributed to uncertainty. All those components, subject to further investigation, are termed other systematic and random effects in Table 2. We consider the component related to impurities negligible.

All the factors enlisted make up the full expanded uncertainty of sublimation temperature at the atmospheric pressure of about ±2.7 mK.

The evaluation of scattering is of type A (i. e. from measurement statistics), while evaluation of other components is of type B.

The difference between our results and the approximations of the data obtained earlier does not exceed ±2 mK.

The scattering generally does not exceed ±1 mK. A little larger scattering at about 99.6 kPa can be explained by the conditions of operation below atmospheric pressure. Namely, when we operate above the ambient pressure, we do not need our system to be perfectly hermetic. If the cover is not tight enough, we just cannot exceed a certain value of pressure (another limitation for pressure is the fragility of the Dewar vessel). However, when we operate below the ambient pressure, the ambient air and water vapour can get into the system, thus disturbing our operating conditions.

Measures of precaution shall be taken to protect the vessel from too large gas pressures, which could explode it, as well as one’s eyes from any wreckage in the case of an accident.

5. Conclusion

We demonstrate a possibility for a simple realization of the sublimation point of carbon dioxide at pressures near atmospheric, which enables obtaining the values of temperature between 194.4 K and 194.8 K. The value of sublimation temperature at one standard atmosphere (101325 Pa) is found to be 194.684 K, which coincides with the value obtained using the approximating equation (5) taken from Table 4 of [7]. The overall expanded uncertainty of sublimation temperature realized at the pressure of 101325 Pa is about ±2.7 mK, which is consistent with the uncertainties stated in [7]. The differences between the values of temperature obtained by us and those reported in [4, 5] are within the uncertainty.

Although sublimation is slow and some snow in the Dewar vessel survives for several days, the best results are achieved on the first day.

The methodology employed requires the substance of only technical purity and conventional laboratory equipment as well as commercially available devices and materials.

Acknowledgement

We wish to thank the company Lietuvos dujos for cooperation and lending their DPI 150 pressure gauge.

References


**ANGLIES DVIDGEGINIO SUBLIMAVIMOSI TAŠKO TEMPERATŪROS ATKŪRIMAS**

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Santrauka

Tikslų temperatūros verčių atkūrimas žemoje temperatūroje tebėra kebus, kadangi dabar naudojama tarptautinė temperatūros skalė ITS-90 šiame ruože turi nedaug pamatinių taškų. Tarp vandens trigubo taško (0,01 °C) ir argono trigubo taško (–189,34 °C) tėra vienintelis pirminis pamatinis taškas – tai gyvūs vidri trubą ne leiskite bet kokiems įtakos,šių prietaisams keliant įvairių temperatūrų režimą. Tačiau šių pastarųjų įrankių atkurimą per daug stulbinantis įrangos kaip antroji įvairių temperatūrų apskaičiavimą tik pradžiose skaidrumo vertinimas.