

# What the Thermophysical Property Community Should Know about Temperature Scales

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**Abstract** Temperature scales have evolved through many decades in order to more accurately represent the thermodynamic temperature. This creates challenges for those who study thermophysical properties, because the temperatures given for literature data may not correspond to the latest international scale. The resulting differences are small, but not necessarily negligible, especially for reference-quality work. Here, we describe the temperature scales that might be encountered in the literature and give guidance for converting them to the International Temperature Scale of 1990 (ITS-90). We pay special attention to the liquid-helium scales used for cryogenic work, where a potentially confusing number of different scales has been used. Advice is given for avoiding common mistakes in dealing with temperature scales in the context of thermophysical property data, including the responsibility of experimentalists to fully document their reported temperatures and the responsibility of modelers to document their handling of any temperature-scale issues.

**Keywords** ITS-90 · temperature scales · thermodynamics · thermophysical properties

## 1 Introduction

We all have a rough idea of what temperature is. For most aspects of life, that is good enough. Even for those of us who do thermophysical property work, it is often adequate to ignore questions about whether a temperature is the thermodynamic

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temperature (which we will denote by  $T$ ) or on a temperature scale such as the International Temperature Scale of 1990 (ITS-90; we will denote such temperatures as  $T_{90}$ ), the International Practical Temperature Scale of 1968 (IPTS-68, denoted by  $T_{68}$ ), etc.

However, for reference-quality work, it is essential to understand temperature scales, at least well enough to decide whether it is necessary to account for their (usually) small differences. Issues of temperature scales should be considered when developing thermophysical property correlations;<sup>1</sup> they are especially relevant to handling older input data. As we will see in Section 4, there are special challenges associated with data at cryogenic temperatures.

The purpose of this paper is to provide readers with a sufficient understanding of temperature scales to use reported temperatures properly in the analysis and correlation of thermophysical property data. Special attention is given to cryogenic temperatures, where there are some additional complications, and some common mistakes are discussed in Section 5. Note that the physical measurement of temperature is outside the scope of this review; a thorough discussion of temperature measurement and the realization of temperature scales is given by Quinn [1] and up-to-date guidance on thermometry is given by the Consultative Committee for Thermometry (CCT). [2]

## 2 The Thermodynamic Temperature

### 2.1 The concept of temperature

We will not attempt to formally define the thermodynamic quantity “temperature.” It arises naturally from the second law of thermodynamics; textbooks on physics or physical chemistry can be consulted for derivations. For our purposes, it is more convenient to think of the (absolute) thermodynamic temperature  $T$  as the quantity in the ideal-gas law:

$$p = \rho RT = \rho N_A k T, \quad (1)$$

where  $p$  is the pressure,  $\rho$  is the molar density,  $R = N_A k$  is the molar gas constant,  $N_A$  is the Avogadro constant, and  $k$  is the Boltzmann constant.

Procedures for measuring the thermodynamic temperature typically involve extrapolating measurements to the ideal-gas limit and/or representing dilute-gas properties by a virial expansion around the low-density limit. Of course the ideal gas is a fictional construct, so care must go into these procedures for real gases.

### 2.2 The absolute temperature and the definition of the kelvin

The thermodynamic temperature appears linearly in the ideal-gas law when it is written in the form of Eq. (1), as a product with the Boltzmann constant. In principle, the value of this constant is arbitrary; we could set  $k$  at half the value and double the

<sup>1</sup> We use the word “correlation” not in the statistical sense, but in the sense of an equation, usually fitted to data, describing a thermophysical property as a function of one or more independent variables.

numerical values of  $T$ . We can unambiguously determine the *ratio* of two temperatures, but extra assumptions must be made to provide actual values.

Since Eq. (1) is linear in  $T$ , it can be defined by two points. It is convenient but not essential to choose one point as absolute zero. Early temperature scales instead fixed two points at finite absolute temperature – the unit for these scales was the centigrade (later renamed Celsius) degree, where  $0\text{ }^{\circ}\text{C}$  was fixed at the ice point of water and  $100\text{ }^{\circ}\text{C}$  at its normal boiling point. That left open the question of the location of absolute zero (or the conversion between K and  $^{\circ}\text{C}$ ).

It is more natural to express the thermodynamic temperature in absolute terms, where absolute zero is defined as 0 K. That leaves only one more point needed to completely define the thermodynamic temperature scale. In 1954, that point was defined by fixing the triple point of pure water (where solid, liquid, and vapor exist in thermodynamic equilibrium) as exactly 273.16 K; that choice was designed to closely match the existing scale based on degrees Celsius. Since it had been previously established that the triple-point temperature of water was very close to  $0.01\text{ }^{\circ}\text{C}$ , the Celsius temperature  $t$  was redefined as exactly 273.15 degrees shifted from the absolute temperature ( $t/^{\circ}\text{C} = T/\text{K} - 273.15$ ). The unit kelvin (symbol K) was defined as  $1/273.16$  the absolute temperature of the triple point of pure water. This definition remained in place for decades.

The redefinition of SI units in 2019 was based on the idea that units should be based on fundamental physics, rather than depending on physical artifacts (such as a piece of metal defining the kilogram) or properties of specific substances (such as a temperature unit based on properties of water). In Eq. (1), the old definition of temperature made the Boltzmann constant an unknown quantity that could, for example, be measured by performing experiments at 273.16 K. In the new SI, the Boltzmann constant is an exactly defined quantity ( $1.380649 \times 10^{-23}\text{ J K}^{-1}$ ); this was the best estimate of  $k$  under the old definition. Now, rather than uncertainty in the Boltzmann constant, there is an equivalent amount of uncertainty (relative standard uncertainty of  $3.7 \times 10^{-7}$ , or approximately 0.1 mK) in the temperature of the triple point of water. [3]

### 2.3 Measuring absolute temperature

Equation (1) immediately suggests a way to make absolute temperature measurements. Careful measurements of the pressure and density of a gas, extrapolated to the low-density (ideal-gas) limit, can determine the absolute temperature. This basic approach, known as *gas thermometry*, was the leading technique for determining thermodynamic temperature for many years; the most commonly used such method is constant-volume gas thermometry (CVGT). [1] More recently, most thermodynamic temperature measurement has used methods that rely on the modern ability to make electrical measurements and frequency measurements very accurately. These include acoustic gas thermometry, [4] dielectric-constant gas thermometry, [5] and refractive-index gas thermometry. [6] In the past, these methods involved extrapolation to the ideal-gas limit by performing experiments at decreasing densities. Recent, state-of-the-art work derives the temperature from measurements at a few densities, or even a

single density, with parameters in the working equation corresponding to low-density gas properties that can be calculated accurately based on fundamental quantum mechanics and statistical physics. An advantage of many of these methods is that the gas density can be determined *in situ* during the experiment.

There are also methods of determining thermodynamic temperature that are not based on gas properties. Johnson noise thermometry [7] measures the electronic noise due to thermal motion of electrons in conductors; its uncertainties are currently not competitive with gas-based thermometry in the temperature regions where they overlap. Radiometric thermometry, which takes advantage of the temperature-dependent emission of radiation by matter (Planck's law), is the primary method of temperature measurement above roughly 1000 °C, and is recommended for realizing the kelvin in the SI at high temperatures. [8]

### 3 Temperature Scales

#### 3.1 Why we need temperature scales

Since we can measure the thermodynamic temperature as mentioned in Sec. 2.3, why do we need temperature scales like ITS-90 at all? First, accurate thermodynamic temperature measurement is difficult. Only a few metrology laboratories have the ability to perform these measurements, at significant time and expense. Second, while thermodynamic measurements are improving, at most temperatures their uncertainty is still significantly larger than the reproducibility of instruments such as the standard platinum resistance thermometer (SPRT). Therefore, comparisons of measurements at different times and places are more accurate if they are based on these instruments rather than on measurements of thermodynamic temperature.

Practical measurement therefore uses *temperature scales*, which are highly reproducible and are designed to match the thermodynamic temperature as well as possible at the time of adoption of the scale. Many laboratories are able to realize the scale (at least the temperature range relevant to their interests), allowing them to calibrate SPRTs against the well-defined scale. This enables consistent measurements around the world, but it should be remembered that these measurements are on a particular scale and are not identical to the thermodynamic temperature.

#### 3.2 History of temperature scales

A review of standardized temperature scales from the late 1800s through the development of ITS-90 is given in the paper of Mangum *et al.* [9] It should be consulted for details and references beyond what we will summarize here.

The earliest standardized scales were reported in degrees centigrade (renamed degrees Celsius in 1948), where the ice point of water (where liquid and ice coexist with atmospheric air at a standard atmospheric pressure of 101.325 kPa) was defined as 0 °C and water's normal boiling point (vapor-liquid equilibrium at 101.325 kPa) was defined as 100 °C. The first widely disseminated international scale was known

as the Normal Hydrogen Scale (NHS) or échelle normale (EN), based on mercury-in-glass thermometers calibrated against a constant-volume gas thermometer that used hydrogen gas.

The invention of a practical platinum resistance thermometer (PRT) by Callendar in the late 1800s enabled more precise and reproducible temperature measurement. This led to the International Temperature Scale of 1927 (ITS-27), [10] which defined temperatures at and above the normal boiling point of oxygen (approximately  $-183\text{ }^{\circ}\text{C}$ ), using PRTs calibrated at specified points up to  $660\text{ }^{\circ}\text{C}$  and applying other methods at higher temperatures. The International Temperature Scale of 1948 (ITS-48) [11, 12] was very similar to ITS-27. ITS-48 for the first time used the triple point of water as a reference point, defining the temperature there as exactly  $0.01\text{ }^{\circ}\text{C}$ .

The International Practical Temperature Scale of 1968 (IPTS-68) [13] was for the first time defined in terms of absolute temperature. ITS-27 and ITS-48 had fixed the temperature of two points in degrees Celsius, leaving unspecified the location of absolute zero. In the interim, the absolute thermodynamic temperature had been defined by fixing the triple point of water at exactly  $273.16\text{ K}$ . This single point and absolute zero provided the two points necessary to define the thermodynamic temperature scale, so the normal boiling point of water was no longer a defined temperature (although IPTS-68 continued to use as a fixed calibration point water's normal boiling point at  $T_{68} = 373.15\text{ K}$ ). IPTS-68 also extended the low-temperature range to the triple point of equilibrium hydrogen at  $13.81\text{ K}$ .

Meanwhile, the lack of a standardized scale for low temperatures, particularly below the  $13.81\text{ K}$  boundary of IPTS-68, was increasingly recognized as a problem. This resulted in the 1976 Provisional  $0.5\text{ K}$  to  $30\text{ K}$  Temperature Scale, known as EPT-76. [14, 15] EPT-76 overlapped in range with IPTS-68 between  $13.81\text{ K}$  and  $30\text{ K}$ , but differed from IPTS-68 below  $27.1\text{ K}$  in order to achieve smooth behavior throughout its temperature range. It also overlapped with, and differed from, the cryogenic helium scales that will be discussed in Sec. 4.

The most recent comprehensive scale is the International Temperature Scale of 1990, known as ITS-90. [16] The thermodynamic calculations and measurements on which ITS-90 is based are described by Rusby *et al.* [17] The temperature range begins at  $0.65\text{ K}$  and is limited at the high end only by the ability to measure temperature according to the Planck radiation law. Below  $5\text{ K}$ , ITS-90 is effectively identical to EPT-76; at higher temperatures the differences reach  $4\text{ mK}$ . Differences from IPTS-68 remain below  $0.1\text{ K}$  up to about  $800\text{ K}$ , exceeding  $1\text{ K}$  above about  $2700\text{ K}$ . Converting measurements made on earlier scales to ITS-90 will be discussed in Sec. 3.5.

Because of the need in some applications to measure temperatures below the  $0.65\text{ K}$  lower limit of ITS-90, a provisional scale for low temperatures was adopted in 2000. [18] The Provisional Low Temperature Scale, PLTS-2000, is defined by the melting pressure of  $^3\text{He}$  and covers the range from  $0.9\text{ mK}$  to  $1\text{ K}$ .

### 3.3 How does a temperature scale work?

A temperature scale can be considered to have two components. The first is a set of *fixed points*, where specific, reproducible conditions are assigned numerical values.

Generally, these values are the best estimates of the thermodynamic temperatures of the fixed points at the time the scale is adopted. The second is specified *interpolation procedures*, where an instrument (such as an SPRT) and interpolation procedure is specified for temperatures between the fixed points.

### 3.3.1 Fixed points

As discussed above, the first fixed points in widespread use were the ice point and normal boiling point of water. Modern temperature scales primarily use triple points (the state point where solid, liquid, and vapor coexist at thermodynamic equilibrium for a pure substance) and, at higher temperatures, melting or freezing points of metals at atmospheric pressure. A table in the paper of Mangum *et al.* [9] summarizes the fixed points used in scales from the NHS through ITS-90.

### 3.3.2 Interpolation

Interpolation between fixed points is specified by describing an instrument to be used and a procedure for constructing an interpolating function. For much of the range of modern temperature scales, the interpolating instrument is an SPRT meeting certain specifications, with constants for the interpolation equation determined by calibration at multiple fixed points. However, other instruments, such as a gas thermometer, may be specified in certain ranges. At the highest temperatures, an extrapolation procedure may be specified for temperatures above the highest fixed point.

### 3.3.3 Nonuniqueness

In some temperature scales, including ITS-90, more than one acceptable interpolation method is specified for certain temperature ranges. For example, there is a low-temperature range where ITS-90 allows either an SPRT or a gas thermometer. This introduces the possibility of *nonuniqueness*, where different interpolation methods may yield different temperatures. A different type of nonuniqueness results when different sets of fixed points may be used to calibrate an interpolating instrument such as an SPRT. Nonuniqueness in ITS-90 is small enough that it is mostly of concern to temperature metrologists; for example Meyer and Reilly [19] found that it was less than 0.3 mK between 1.25 K and 3.2 K where either the vapor pressure of  $^3\text{He}$  or that of  $^4\text{He}$  may be used, and Meyer and Tew [20] found nonuniqueness of up to 1 mK in SPRTs calibrated in different subranges between 24.56 K and 273.16 K. Recent studies have found more significant differences between PLTS-2000 and ITS-90 in their region of overlap between 0.65 K and 1 K; [21,22] PLTS-2000 is believed to be closer to the thermodynamic temperature.

## 3.4 ITS-90

As mentioned previously, the current scale is the International Temperature Scale of 1990, known as ITS-90. [16]

**Table 1** Fixed points for the International Temperature Scale of 1990 (ITS-90)

$T_{90}$ / K	Substance	State
13.8033	e-H <sub>2</sub>	triple point
24.5561	Ne	triple point
54.3584	O <sub>2</sub>	triple point
83.8058	Ar	triple point
234.3156	Hg	triple point
273.16	H <sub>2</sub> O	triple point
302.9146	Ga	melting point
429.7485	In	freezing point
505.078	Sn	freezing point
692.677	Zn	freezing point
933.473	Al	freezing point
1234.93	Ag	freezing point
1337.33	Au	freezing point
1357.77	Cu	freezing point

### 3.4.1 Fixed points and interpolation

Table 1 shows the fixed temperature points on ITS-90. In Table 1, e-H<sub>2</sub> refers to equilibrium hydrogen, where the *ortho* and *para* nuclear spin states are in thermodynamic equilibrium. The melting and freezing points are those at a standard atmospheric pressure of 101.325 kPa. While not exactly fixed points, there are defined temperatures at 5 K and below based on the vapor pressures of <sup>3</sup>He and <sup>4</sup>He, as discussed in Sec. 4. Two places on the vapor-pressure curve of e-H<sub>2</sub>, near 17.0 K and 20.3 K, provide additional low-temperature calibration points.

The use of the triple point of mercury is becoming problematic, due to the desire to eliminate mercury from laboratories for the sake of safety. There are efforts to develop a new fixed point in this region with a non-toxic substance available in high purity; it would also be desirable if the temperature were somewhat lower than the triple point of mercury to reduce the large interpolation range between this point and the triple point of argon (currently almost a factor of 3 in absolute temperature). Candidates being studied include xenon (triple point near 161.4 K), [23–25] carbon dioxide (~216.6 K), [26] and sulfur hexafluoride (~223.6 K). [27–30]

Through most of this range, the specified interpolating instrument is an SPRT. The SPRT may be applied for all temperatures from the triple point of e-H<sub>2</sub> to the freezing point of silver, but in practice a thermometer is calibrated at a subset of points depending on the temperature range of interest. Some small nonuniqueness results because calibrations using different subsets of fixed points do not yield identical results. At temperatures below the triple point of neon and down to 3 K, a gas thermometer (with <sup>3</sup>He or <sup>4</sup>He as the gas) may be used as an interpolating instrument. This produces a region of nonuniqueness between 13.8033 K and 24.5561 K where ITS-90 may also be realized by an SPRT, and nonuniqueness between 3 K and 5 K where there is overlap with temperatures defined by helium vapor pressures. Above

the freezing point of silver, ITS-90 is defined by the Planck radiation law, where the instrument may be calibrated at any of the last three points in Table 1.

### 3.4.2 Differences from thermodynamic temperature

While ITS-90 represented the best knowledge of thermodynamic temperature at the time it was developed, there have since been significant advances in temperature metrology. It has become clear that ITS-90 temperatures differ from the thermodynamic temperature; the differences are on the order of a few mK for temperatures up to 500 K. A recommended function for the difference was given by Fisher *et al.* [31] in 2011, but since that work several studies have further improved the knowledge of  $(T - T_{90})$  (see for example a summary of the data from 30 K to 200 K by Gaiser *et al.* [32]) and a new recommendation is being developed by the CCT.

While some might be tempted to use values of  $(T - T_{90})$  to try to “correct” correlations developed on ITS-90, in general this is a bad idea and attempts to do so are more likely to lead to inconsistencies than to any better modeling of physical reality. If a correlation has been developed on a particular temperature scale, it should be viewed as accurate on that scale; in the rare cases where one is specifically interested in the thermodynamic temperature the conversion between  $T$  and  $T_{90}$  should be done either prior to input or following output.

It might also be tempting to tabulate or report data with the thermodynamic temperature, rather than a scale temperature like  $T_{90}$ , as an independent variable. This is also unwise if the original measurements are made on a temperature scale, because it causes a loss of precision. Over most of the range relevant to thermophysical properties, the uncertainty in the best measurements of thermodynamic temperature (and therefore in  $T - T_{90}$ ) is at least an order of magnitude larger than the uncertainty with which temperatures can be measured on ITS-90. A temperature reported on ITS-90 is unambiguous, and if a future temperature scale is adopted it can be converted to the new scale just as we now convert  $T_{68}$  to  $T_{90}$ . Those specifically interested in the thermodynamic temperature can apply estimates of  $(T - T_{90})$  if desired. Of course in the rare cases where temperature measurement in an experiment corresponds to the thermodynamic temperature, then it is appropriate to report  $T$  rather than converting it to  $T_{90}$ .

## 3.5 Converting from older scales

When analyzing older data, either for comparison to a calculation or for use as input to a correlation, the temperature may be reported on a scale other than ITS-90. If the desired accuracy is such that small changes in temperature are significant, it is necessary to convert the reported temperatures to ITS-90. Even when data are not precise enough for these changes to be significant (for example, if the temperature was only reported to the nearest 0.2 K), it may be wise to convert the temperatures for all input data for the sake of consistency.

The first step is to identify, if possible, the temperature scale corresponding to the data. It is common to assign the scale based on the year of publication of the paper,

but this can produce errors. It takes time for researchers to become aware of a new temperature scale and to begin using instruments calibrated on that scale; it also takes time for reports of experimental work to be written and published. A paper published in 1970 may report experiments performed in 1968 with temperature measurements on ITS-48. If at all possible, information on the temperature scale should be obtained from the original paper; this may involve consulting cited references or an underlying thesis to learn more about the experimental procedure. In many cases, especially for work done in a more engineering-oriented context or for conference publications, this detail is simply not reported. In those cases, it may be necessary to guess the scale based on the year; it is a better guess to use the date of submission (rather than publication) and perhaps the date of the conference for conference papers. Such guesses are speculative, however, and temperatures based on them should be considered to have correspondingly larger uncertainty. It can also be noted that IPTS-68 was only adopted in October 1968, [13] so 1968 publications almost certainly were on ITS-48. ITS-90 was actually adopted in late 1989, [16] so it could have already been used for work in 1990.

### 3.5.1 Converting from IPTS-68 to ITS-90

Most conversions of earlier data involve the difference between ITS-90 and IPTS-68, either as the only conversion needed or as the last step in a chain of conversions for data on earlier scales. When ITS-90 was adopted, detailed comparisons were made, using precise thermometers calibrated on both scales, to estimate the differences between the two scales. Tables for the difference  $T_{90} - T_{68}$  were given in the paper defining ITS-90. [16] Shortly thereafter, it was recognized that these estimates were inaccurate in a range of high temperatures (above roughly 630 °C) where IPTS-68 had been defined by a particular type of thermocouple (Type S). A replacement table was published in 1994 for  $T_{90} - T_{68}$  in that region. [33]

It is more convenient to have an equation that can be programmed for  $T_{90} - T_{68}$  rather than to interpolate from a table. Equations were fitted to the tabulated values by Rusby and published in 1991, [34] and a new equation for the range from 630 °C to 1064 °C was given by Rusby *et al.* in 1994 [33] for the revised differences mentioned in the previous paragraph.

For the range of  $T_{68}$  from 13.81 K to 83.8 K, the difference is represented by

$$(T_{90} - T_{68})/\text{K} = \sum_{i=0}^{12} a_i \left[ \frac{(T_{68}/\text{K}) - 40}{40} \right]^i, \quad (2)$$

where the coefficients  $a_i$  are given in Table 2. For  $T_{68}$  from 73.15 K to 903.89 K, the difference is

$$(T_{90} - T_{68})/\text{K} = \sum_{i=1}^8 b_i \left[ \frac{(T_{68}/\text{K}) - 273.15}{630} \right]^i, \quad (3)$$

where the coefficients  $b_i$  are given in Table 2. Equations (2) and (3) overlap in range and give slightly different results in the range of overlap, but the differences are smaller than the uncertainty in measurements on IPTS-68. Rusby recommended switching between the two formulas at a temperature of 77 K. [34]

**Table 2** Coefficients for Eqs. (2), (3), and (4)

$i$	$a_i$	$b_i$	$c_i$
0	-0.005903		$7.8687209 \times 10^1$
1	0.008174	-0.148759	$-4.7135991 \times 10^{-1}$
2	-0.061924	-0.267408	$1.0954715 \times 10^{-3}$
3	-0.193388	1.08076	$-1.2357884 \times 10^{-6}$
4	1.490793	1.269056	$6.7736583 \times 10^{-10}$
5	1.252347	-4.089591	$-1.4458081 \times 10^{-13}$
6	-9.835868	-1.871251	
7	1.411912	7.438081	
8	25.277595	-3.536296	
9	-19.183815		
10	-18.437089		
11	27.000895		
12	-8.716324		

For temperatures  $T_{68}$  between 903.89 K and 1337.58 K, the revised equation from Rusby *et al.* [33] is

$$(T_{90} - T_{68})/\text{K} = \sum_{i=0}^5 c_i [(T_{90}/\text{K}) - 273.15]^i, \quad (4)$$

where the  $c_i$  are given in Table 2. Note that the temperature on the right side of Eq. (4) is  $T_{90}$ , whereas the previous two equations use  $T_{68}$ . There is additional inherent uncertainty in the conversion represented by Eq. (4), because this temperature range in IPTS-68 (and earlier scales) was only reproducible to about 0.2 K due to limitations of the thermocouples used to define this part of the scale. [1]

At temperatures above  $T_{68} = 1337.58$  K, the freezing temperature of gold, the temperatures on both scales are given by the Planck radiation law. Their difference is simply a function of the offset of the two scales at that freezing point, which is  $(T_{90} - T_{68}) = -0.25$  K. The full relationship is given by [34]

$$(T_{90} - T_{68})/\text{K} = -0.25 \left( \frac{T_{68}}{1337.58 \text{ K}} \right)^2 \frac{1 - \exp\left(\frac{-c_2}{\lambda T_{68}}\right)}{1 - \exp\left(\frac{-c_2}{\lambda \cdot 1337.58 \text{ K}}\right)}, \quad (5)$$

where  $\lambda$  is the wavelength of the radiation and  $c_2$  is the second radiation constant, here taken as  $0.014388 \text{ m} \cdot \text{K}$ . For almost all purposes, the term with the exponentials can be taken to be unity, leaving a simple quadratic function.

To allow readers to test their programming, we supply computational test points; the number of digits given far exceeds the uncertainty with which these differences are known. For  $T_{68} = 70$  K, Eq. (2) yields  $T_{90} - T_{68} = 0.006819$  K. For  $T_{68} = 140$  K, Eq. (3) yields  $T_{90} - T_{68} = 0.013228$  K. For  $T_{68} = 510$  K, Eq. (3) yields  $T_{90} - T_{68} = -0.040455$  K. For  $T_{90} = 1090$  K, Eq. (4) yields  $T_{90} - T_{68} = 0.044543$  K. For  $T_{68} = 1460$  K, Eq. (5) (with the wavelength-dependent term taken as unity) yields  $T_{90} - T_{68} = -0.297856$  K.

It should be recognized that these conversion equations (and others discussed below) have some uncertainty; their accuracy is limited among other things by the reproducibility of the old scale.

### 3.5.2 Converting from EPT-76 to ITS-90

At temperatures below 5 K, ITS-90 was designed to be indistinguishable from the EPT-76 scale, so EPT-76 temperatures may be used directly on ITS-90. A constraint in the development of EPT-76 was that it join continuously with IPTS-68 at the normal boiling point of neon ( $T_{68} = 27.102$  K), [15] so between that point and the upper limit of EPT-76 (30 K)  $T_{76} = T_{68}$ . At other temperatures, a table of  $T_{90} - T_{76}$  was given in the ITS-90 paper, [16] and Rusby [34] gives an equation to approximate the difference, which becomes as large as 4.1 mK at 27 K,

$$(T_{90} - T_{76})/\text{K} = -5.6 \times 10^{-6}(T_{76}/\text{K})^2. \quad (6)$$

### 3.5.3 Converting from older scales

Tables for the difference between IPTS-68 and ITS-48 were given in the paper documenting IPTS-68. [13] Equations approximating these differences were given by Douglas. [35] These formulas for  $T_{68} - T_{48}$  only apply to temperatures above the lower temperature limit of ITS-48, which was approximately 90 K.

Differences between ITS-48 and ITS-27 only appear at temperatures above 630 °C. Estimates of these differences were given in both tabular and graphical form by Corruccini. [36]

Conversion from other, unofficial scales that have been used is discussed in Sec. 3.6. Conversion from the special cryogenic temperature scales used in the past is discussed in Sec. 4.

## 3.6 Other, unofficial scales

Because ITS-27 and ITS-48 did not extend below the normal boiling point of oxygen, work at lower temperatures prior to the adoption of IPTS-68 relied on scales maintained in specific laboratories based on PRTs calibrated with gas thermometers. The most widely used such scales were known as NBS-39 (later shifted by 0.01 K to become NBS-55), NPL-61, PRMI-54, and PSU-54. Further information about these scales may be found in the review of Hust. [37] At the time of adoption of IPTS-68, which extended the range of the international scale down to 13.81 K, extensive work was done to characterize the differences between IPTS-68 and these older scales between  $T_{68} = 13.81$  K and the normal boiling point of oxygen at  $T_{68} = 90.188$  K. Tables of these differences are given by Bedford *et al.*; [38] these tables allow conversion of temperatures from these scales to IPTS-68, from which they can be converted to ITS-90.

### 3.7 Hidden effects on measured properties

For some types of data, simply converting the reported temperature from an old scale to ITS-90 is incomplete. If the original measurement involved a temperature *difference*, a change in the temperature scale also affects this difference if the scales do not have the same slope. The two main examples of this phenomenon are measurements of the thermal conductivity and the heat capacity, where the reported thermophysical property is typically obtained by dividing a measured quantity by a temperature difference. In both cases, a small adjustment proportional to the derivative of the difference between temperature scales,  $d(T_{\text{new}} - T_{\text{old}})/dT_{\text{new}}$ , is needed to convert the quantity to the new scale.

For the isobaric heat capacity, ideally researchers would report an enthalpy difference  $\Delta H$  between two temperatures,  $T_1$  and  $T_2$ , in which case one could simply perform the temperature conversion separately on  $T_1$  and  $T_2$ . Often, however, publications contain only the derived value of the heat capacity at a temperature (usually the midpoint of the temperature range of that experiment), and the numerator and denominator in the original  $\Delta H/\Delta T$  measurement are unknown. Similarly, the thermal conductivity is typically reported without stating the temperatures involved in deriving the quantity. In those cases, the procedure is to consider the property to be a derivative ( $dH/dT$  for the isobaric heat capacity) and recognize that the differential  $dT$  will be affected if the difference between the scales is not constant with temperature. For a property  $X$  where a temperature difference implicitly appears in the denominator, the value on the new scale is [35]

$$X_{\text{new}} = X_{\text{old}} \left[ 1 - \frac{d(T_{\text{new}} - T_{\text{old}})}{dT_{\text{new}}} \right]. \quad (7)$$

The derivative  $d(T_{90} - T_{68})/dT_{90}$  can be obtained by differentiation of Eqs. (2)-(5). We note that differentiating Eqs. (2), (3), and (5) actually yields  $d(T_{90} - T_{68})/dT_{68}$ , but the change from  $dT_{90}$  to  $dT_{68}$  is negligible for what is already a very small correction, so it is adequate to consider these differentiations to yield  $d(T_{90} - T_{68})/dT_{90}$ . As a check for programming,  $d(T_{90} - T_{68})/dT_{68}$  is 0.000331 at 70 K [Eq. (2)],  $-0.000187$  at 400 K [Eq. (3)],  $-0.001675$  at 1200 K [Eq. (4)]; this is  $d(T_{90} - T_{68})/dT_{90}$ , and  $-0.000447$  at 1600 K [Eq. (5), ignoring the wavelength-dependent term].

In 1992, Goldberg and Weir [39] published tables for  $d(T_{90} - T_{68})/dT_{90}$  and for  $d(T_{90} - T_{48})/dT_{90}$ , but it should be noted that their information is obsolete for the range between approximately 630 °C and 1064 °C [corresponding to Eq. (4)] where new values of  $T_{90} - T_{68}$  were given in 1994. [33] Also, readers should beware that their tables for  $d(T_{90} - T_{68})/dT_{90}$  are not always accurate to the number of digits printed.

Equation (7) yields the value of  $X$  at the temperature  $T_{\text{new}}$ , which will be numerically different from the temperature  $T_{\text{old}}$  originally reported for the datum. This is distinct from the conversion of tabulated values of properties in such a way that the tabulated temperature numbers are unchanged, for example with the new table containing a value at  $T_{90} = 300$  K when the old table had a point at  $T_{68} = 300$  K. Such a translation of tables from one scale to another produces different formulas; these other formulas should not be used for the conversion of individual input data points.

The effect on tabulated values of heat capacity, enthalpy, and entropy was analyzed by Douglas [35] and by Goldberg and Weir. [39] The procedure in the latter paper has been criticized by Archer, [40] but this controversy does not affect the conversion of individual measured data points.

This temperature-scale effect is generally small, because  $d(T_{\text{new}} - T_{\text{old}})/dT_{\text{new}}$  is small. Goldberg and Weir [39] found that  $d(T_{90} - T_{68})/dT_{90}$  had a magnitude below 0.04 % for a wide range of temperatures between roughly 60 K and 900 K. They found that  $d(T_{90} - T_{48})/dT_{90}$  reached somewhat larger values, but remained below 0.1 % between roughly 90 K and 860 K. These differences are smaller than the uncertainties of most thermal-conductivity and heat-capacity data, so these effects are marginal at best except for the most precise data.

### 3.8 Calculated “data” are at thermodynamic $T$ , not $T_{90}$

Some data may come not from experiment but instead from statistical mechanical calculations. Examples include ideal-gas heat capacities based on molecular data (such as recent calculations of the ideal-gas heat capacity for heavy water [41] and oxygen [42]) and virial coefficients and dilute-gas transport coefficients calculated from intermolecular potentials (such as the high-accuracy calculation of the second virial coefficient of helium isotopes [43] or calculations of the cross second virial coefficient and dilute-gas transport properties for the  $\text{H}_2\text{O}-\text{CO}_2$  mixture [44]). These calculations produce data as a function of the thermodynamic temperature  $T$ . In principle, before using these data in a correlation based on ITS-90, one could convert these data to  $T_{90}$  based on the best current estimates of  $(T - T_{90})$ . In practice, the differences between  $T$  and  $T_{90}$  are negligible compared to the uncertainties in calculating virial coefficients and transport coefficients (with the possible exception of helium where *ab initio* calculations of these quantities have very small uncertainties [43,45]), and are also small compared to the uncertainty with which ideal-gas heat capacities are known. It should therefore be acceptable in most cases to use such calculated data as if they were on ITS-90, but it should be understood that one is making an approximation when doing so.

## 4 Nuances of Low-Temperature Scales

### 4.1 Background and history

As noted above, prior to the adoption of IPTS-68 there was no official International Temperature Scale below approximately 90 K, and prior to ITS-90 the scale did not extend below roughly 13.8 K. Of course, people still performed cryogenic experiments and reported temperatures during this period, using an assortment of scales. Scales used between roughly 10 K and 90 K have already been discussed in Sec. 3.6; here we will focus on lower temperatures, particularly those relevant to liquid helium.

Early cryogenic researchers recognized that the saturated vapor pressure of helium provided a reproducible measurement of the temperature. This required an independent temperature measurement for at least one point on the vapor-pressure curve

(typically with a gas thermometer); often thermodynamic integration was used to extend the curve to lower temperatures. Beginning in the 1920s, several laboratories developed their own slightly different scales, expressed as equations or tables relating the saturation pressure of helium to the temperature. References and descriptions for eight such early scales are given by Brickwedde *et al.* [46] International consensus was reached with the 1958  $\text{He}^4$  Scale of Temperatures, which provided a table relating the vapor pressure of  $^4\text{He}$  to the temperature between 1 K and 5.2 K. [46,47]

At very low temperatures, the vapor pressure of  $^4\text{He}$  becomes too low to be measured accurately; this led to the use of the vapor pressure of the more volatile  $^3\text{He}$  isotope as a thermometric reference. This was expressed with the 1962  $\text{He}^3$  Scale of Temperatures, which extended from 0.2 K to approximately 3.3 K. [48,49]

After the adoption of IPTS-68, it was observed that there seemed to be a mismatch between temperatures extrapolated upward from the helium vapor-pressure scale and those extrapolated downward from the lowest temperatures of IPTS-68. This led to a reexamination of data, [14] and ultimately to the 1976 Provisional 0.5 K to 30 K Temperature Scale (EPT-76), which was constrained to join smoothly with IPTS-68 above the normal boiling point of neon. EPT-76 was defined by a set of fixed points that included low-temperature superconducting transitions, but also by a table of differences from IPTS-68 and from the 1958 and 1962 helium vapor-pressure scales. [15] The low-temperature portion of EPT-76 (below 5 K) was essentially adopted into ITS-90, although in ITS-90 it is expressed as a set of helium vapor-pressure equations.

#### 4.2 ITS-90 at low temperatures

The low-temperature portion of ITS-90 is defined by equations giving  $T_{90}$  as a function of helium vapor pressure. [16] The equation for the vapor pressure of  $^3\text{He}$  may be used from 0.65 K to 3.2 K. The equation for  $^4\text{He}$  may be used from 1.25 K to 5.0 K; separate sets of coefficients are given for the ranges below and above the  $\lambda$ -point temperature of 2.1768 K.

One consequence of this ITS-90 definition is that, if one is developing an equation of state for  $^4\text{He}$  or  $^3\text{He}$ , the vapor-pressure relationship provides a constraint. If we say that the equation of state is on the ITS-90 scale, we already know the vapor pressure; it should be that given by the defining equation of ITS-90. Any helium equation of state purporting to be on ITS-90 that yields different vapor pressures is by definition in error by the amount of the difference.

#### 4.3 Converting old data

The conversion of old data at liquid-helium temperatures to ITS-90 usually requires careful reading of the paper to see how the temperature was measured. Almost always the measurements involved a helium vapor-pressure scale, but there were enough different scales in use that one cannot use a simple strategy based on the year of publication. Fortunately, it seems that most publications reporting low-temperature thermophysical property data for helium reported the temperature scale used.

If the temperature was reported on the 1958  $^4\text{He}$  scale or the 1962  $^3\text{He}$  scale, these temperatures can be converted to the EPT-76 with a table of differences in the paper describing EPT-76. [15] Since ITS-90 is equivalent to EPT-76 below 5 K, this procedure converts the temperatures to ITS-90.

If the temperature was reported on one of the many  $^4\text{He}$  scales employed prior to the 1958 scale, they should first be converted to the 1958 scale using tables of differences published by Brickwedde *et al.* [46] They can then be converted to ITS-90 as above.

In a few cases, these conversions can be bypassed for papers reporting helium thermophysical properties. Since the temperature may be obtained by measuring the helium vapor pressure, some publications reported that pressure. In those cases, the ITS-90 temperature can be obtained directly from the vapor-pressure equation in the definition of ITS-90. If a temperature on the 1958  $^4\text{He}$  scale was reported with enough precision, a corresponding saturation pressure can be read off from tables in Brickwedde *et al.* [46] and used to obtain an ITS-90 temperature. In these cases where the saturation pressure is given or easily obtained, it is preferable to use the saturation pressure (rather than the temperature) in defining the saturated vapor or liquid data points for input to a correlation.

#### 4.4 The NBS acoustic scale

A unique low-temperature scale was developed at the National Bureau of Standards in the 1960s. This was the National Bureau of Standards Provisional Temperature Scale 2–20. [50] This scale was based on acoustic thermometry in helium gas, and covered the range from 2.3 K to 20 K. Conversion of temperatures on this scale to ITS-90 proceeds in two steps. First, the temperature is converted to the EPT-76 using a table of differences published in the defining paper of EPT-76. [15] Then, the temperature can be converted to ITS-90 using a table of differences published in the defining paper of ITS-90. [16]

## 5 Avoiding Mistakes

In this section, we summarize some common mistakes in the use of temperature scales in thermophysical properties work. These can usually be avoided with careful thought.

The first error is performing a temperature conversion based only on the date of publication. This is especially dangerous for cryogenic data, which often used one of the special scales described in Sec. 4. Even at higher temperatures, the considerations of Sec. 3.5 apply and the date of publication may be misleading. For precise work where differences between temperature scales are significant, there is no substitute for studying the publication to find out (if possible) what the reported temperatures correspond to.

The second error is related – using a conversion routine outside its range. People have programmed formulas to convert from IPTS-68 to ITS-90, etc. These are only

valid for the range of temperature in which both scales were valid. If you try to use a conversion algorithm at an invalid condition (say, converting from IPTS-68 to ITS-90 at 10 K where IPTS-68 was not defined), the result will be unpredictable and meaningless.

There are also cases where rigorous conversion is impossible, because no well-defined scale existed at the time and condition reported. This is particularly a problem for temperatures above the upper limit of liquid-helium scales (about 5 K) but below the lower limit of international scales (about 90 K for ITS-48 and 13.8 K for IPTS-68). In some cases, temperatures in this range were reported on one of the unofficial scales discussed in Secs. 3.6 and 4.4, allowing conversion to ITS-90 as discussed in those sections. Other cases have to be dealt with individually. If a scale was used just slightly below its valid range (say, ITS-48 at 87 K), it may be reasonable to apply a conversion based on the valid end of the scale. In other cases, temperature may have been calibrated by a gas thermometer, which in the absence of other information could be assumed to be the thermodynamic temperature. In many cases, it will have to be recognized that the true temperature of the data on ITS-90 (or any other scale) is unknown, and if appropriate an uncertainty due to lack of knowledge of the scale used should be combined with the uncertainty of the temperature measurement itself to yield the overall uncertainty of the temperature for the data points in question. This additional uncertainty in the temperature will add to the uncertainty of a formulation based on fitting those data.

Another category of error arises from attempting to use thermodynamic temperature where a temperature scale is more appropriate, or vice versa. As discussed in more detail in Sec. 3.4.2, the best practice is to develop thermophysical property correlations and tables within the context of the current state-of-the-art temperature scale so as not to lose precision. As long as the uncertainty in thermodynamic temperature measurements is larger than the reproducibility of ITS-90 (which is still the case except at cryogenic temperatures and very high temperatures), unnecessary uncertainty is introduced if one tries to convert correlations and tables to thermodynamic temperature. This also applies to experimental data, which should be reported on the scale used for the measurement. Conversely, thermophysical data from molecular theory that correspond to the thermodynamic temperature (see Sec. 3.8) should be reported as a function of  $T$  rather than losing precision by attempting to convert them to  $T_{90}$ .

Finally, can we classify simply not converting temperatures of old data as a “mistake”? Not always. If one is comparing theory to experiment and obtaining agreement at the level of 5 %, it will not matter whether a point on a comparison plot is drawn at 373.15 K or 373.12 K. However, when modeling depends on the detailed behavior of highly precise data, failing to consider temperature scales can distort the analysis. For example, it was pointed out [51] that some published work employing precise refractive-index data for water taken at the National Bureau of Standards in the 1930s had neglected temperature-scale effects that were as large as the purported features being analyzed.

In addition, if the product of work is a reference-quality thermophysical property formulation, all possible steps should be employed to ensure correctness of data, including proper consideration of temperature scales. This responsibility does not stop with the development of the input data set; publications that report formulations

should clearly state the temperature scale used and any steps taken to convert temperatures of old data. Documenting how input temperatures were handled is especially important if the conversion is not straightforward, such as with the cryogenic scales discussed in Sec. 4.

While this paper is primarily addressed to those who correlate thermophysical properties, experimentalists also have a responsibility. Experimental measurements should be fully documented, which includes information on the temperature scale. Such detail may not be necessary if the temperature measurement is imprecise, or if the uncertainty in the property measurement is far more than the effect of small temperature changes (for example, if a solubility is reported with 10 % relative uncertainty, temperature differences of a few mK are negligible). However, for data of high precision, full documentation of the reported temperature is essential. When experimentalists omit this detail, they undermine the quality of any reference correlations that might make use of their data in the future.

## 6 Hidden Sources of Thermodynamic Data

The historical development of temperature scales is such that fixed points from old scales can provide good sources of data. For example, because the normal boiling point of oxygen was a fixed point on the ITS-27, ITS-48, and IPTS-68 scales, precise measurements were performed of the vapor pressure of oxygen near standard atmospheric pressure. Similar considerations apply for neon, whose normal boiling point was a fixed point in IPTS-68 and EPT-76. Temperature metrologists have curated a number of these as *secondary reference points* that can be useful for calibrations in some circumstances. Bedford *et al.* [52] collected these points (which also include recommended vapor-pressure equations), along with recommended uncertainties and references to the experimental sources. This paper should be consulted when looking for accurate thermodynamic data on simple substances.

## 7 Conclusion

Differences among temperature scales, and between such scales and the thermodynamic temperature, are generally small. These differences may even be neglected for some thermophysical property work. However, the differences are not in general negligible for precise experimental data and for developing reference-quality correlations. Researchers should at least stop and think about temperature scale issues, even if they turn out to be negligible in a particular context, in order to avoid introducing unnecessary error and/or uncertainty.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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