Rainer Feistel, 18 Apr 2018:

Reply to the short comments of Hannes Schmidt, 04 Apr 2018

Comment on Page 6 Line 11: The ITS-90 is an empirical temperature scale as described. The thermodynamic temperature T therefore differs from the ITS-90 temperature T_{90}. Based on a request from the Consultive Committee for Thermometry (BIPM-CCT), Fischer et al. (2011)[1] gave updated data (and accuracies) of $\Delta T = T - T_{90}$. For 20 °C (and 30 °C), $\Delta T \approx 2\ \mathrm{mK}$ (and $\Delta T \approx 4\ \mathrm{mK}$) with an accuracy of 0.8 mK.
In addition to the triple point of water, where no difference is expected in the new temperature scale, it may be interesting to know the expected ΔT for other temperatures, say 30 °C, as the 4 mK given by Fischer et al. are usually not considered in calculations.

Reply: Please find more details on the new thermodynamic temperature scale at

- Gavioso RM et al. 2016, Progress towards the determination of thermodynamic temperature with ultra-low uncertainty. Phil. Trans. R. Soc. A 374: 20150046. http://dx.doi.org/10.1098/rsta.2015.0046
- Underwood R, de Podesta M, Sutton G, Stanger L, Rusby R, Harris P, Morantz P, Machin G. 2016 Estimates of the difference between thermodynamic temperature and the International Temperature Scale of 1990 in the range 118 K to 303 K. Phil. Trans. R. Soc. A 374: 20150048. http://dx.doi.org/10.1098/rsta.2015.0048

For higher temperatures, see also the CCT reports of

- Fellmuth et al., *Mise en Pratique* of the definition of the kelvin (MeP-K), https://www.bipm.org/cc/CCT/Allowed/28/CCT_28_MeP-K_cg-2017-32.pdf

and

- Fischer et al., WORKING GROUP FOR CONTACT THERMOMETRY REPORT TO CCT June 2017 https://www.bipm.org/cc/CCT/Allowed/28/WG_CTh_report_2017-57.pdf

Comment on Page 7 Line 26–30: Since the sound speed measurements of Del Grosso & Mader (1972) and Chen & Millero (1977) there has been a discussion, because the datasets have been inconsistent. Any correction or discussion on the measurements of Chen & Millero led to a correction towards the sound speeds of Del Grosso & Mader, especially the correction suggested by Millero & Li (1994). In developing TEOS-10, the sound speeds of Del Grosso & Mader (1972), i.e. those calculated by the equation of Del Grosso (1974), were used instead of those of Chen & Millero (1977) or Millero & Li (1994) (Feistel, 2003, 2008). Since Chen & Millero (1977) measured the sound speed in seawater relatively to those in water, there was the approach to replace the water sound speeds used by Chen & Millero by IAPWS-95 sound speeds. The result of this approach was summarized as (Feistel, 2003, p. 61): "The new IAPWS95 sound speed formula suggested the hope that these problems with Chen-Millero sound speeds may now be eventually resolved in a natural way, but unfortunately this could not be achieved by a simple replacement of the pure water parts [..]." However, in the article under discussion (p. see above): "In TEOS-10, the IAPWS-95 equation replaced the earlier equations of state of liquid water [..]. This change of the pure-water equation made it possible to resolve systematic problems previously encountered with the sound speed of seawater at high pressures (Dushaw et al., 1993; Millero and Li, 1994; Feistel, 2003)."

What is meant by this second statement, as it somehow seems to contradict that first statement?

Reply: In contrast to, say, heat capacity or specific volume, the sound speed expressed in terms of the Gibbs function is a complex nonlinear expression. So is not possible to simply "subtract" an obsolete "pure-water part" from seawater sound speed data and replace it by some improved values, like this was done with the Gibbs function when IAPWS-95 was specified as its pure-water part. As Millero and Li (1994) report, the problems encountered with Chen & Millero (1977) sound speeds resulted from the pure-water reference that Chen and Millero used during their measurements. It turned out that a provisional *a-posteriori* correction of that pure-water part by Millero and Li (1994) was not fully satisfactory because the required raw data are no longer available. Therefore, TEOS-10 has completely refrained from using Chen & Millero (1977) sound speed data and combined for the 2003 and 2008 Gibbs functions the Del Grosso (1974) sound speed with IAPWS-95 density for pure water and with seawater density and thermal expansion data as described in Feistel (2003). In the multi-property fit of the Gibbs function, this combination of data turned out to be mutually consistent and resolved the previous deviations found by Dushaw et al. (1993). So, while it appeared to be impossible to satisfactorily correct Chen & Millero (1976) data by IAPWS-95 (first statement), replacing those data by Del Grosso (1974) in the fit of the Gibbs function resolved the systematic problems encountered previously with the sound speed of seawater at high pressures (second statement).

Comment on Page 10 Line 27: Figure 3 is introduced exemplifying the use of the salinity anomaly dSA. Figure 3 suggests a negative mean salinity anomaly of about -0.008g/kg for Atlantic surface water although TEOS-10 suggests a value of about 0.000g/kg for the region of interest (http://www.teos-10.org/pubs/gsw/pdf/SAAR.pdf, Figure 2).

What are the reasons for the significant negative anomaly shown in Figure 3?

Reply: Actually, answering this question belongs to current research tasks of JCS. Negative density anomalies of similar magnitude as those displayed have meanwhile been found in various regions of the world ocean, and even in some (but not all) certified SSW samples (see e.g. Fig. 6 in www.ocean-sci.net/6/3/2010/). So far, the reasons are elusive; working hypotheses may include unknown chemical (possibly organic?) composition anomalies, isotopic composition anomalies of water, previously unnoticed systematic deviations in the background data of TEOS-10, sample pollution such as by micro-plastic, or measurement errors of other unknown origin. Only after collection and analysis of more data and discovering responsible causes it can be discussed whether the gsw_SAAR library function may need to be updated regionally in the future.

Comment on Page 12 Line 27: "[..] SA is as accurate as SP [..]"

TEOS-10 uses the absolute salinity SA as input variable for calculations. However, SA cannot be measured directly in the ocean. Instead, the practical salinity SP is measured and converted to SA using the factor f=1.004715g/kg. For standard seawater it is assumed that SA matches the reference salinity SR. However, SR is based on measurements of standard seawater with an estimated accuracy of 0.014g/kg (Millero et al., 2008, p. 60)8. By contrast, practical salinity of standard seawater can be measured with an accuracy of 0.002 (=0.002g/kg) or reproduced even more accurately.

How can SR or SA be as accurate as SP?

Reply: While it is correct that SR is an estimate for the mass of dissolved sea salt in SSW with an estimated uncertainty of 7 mg/kg (Millero et al., 2008, p. 60, 70), the questioned sentence, however, begins with the clause "If defined by a fixed conversion factor for a reference composition, S_A is as accurate as S_P". In fact, SR is related to SP by a fixed numerical factor, and this conversion between different salinity units of the input variable of the Gibbs function has no effect on the uncertainty of any derived results.

***Comment on Page 19 Line 19–31*:** Measurements of standard seawater density in addition to salinity „[..] could grant the requisite long-term stability of the SSW standard [..]"

SSW is essential in practical salinity measurement, as it cannot pe prepared artificially with the required accuracy nor stored without changes in its composition in the long term. Density measurement can detect changes in the standard seawater composition or preparation. It is possible to substitute the KCl solution in the preparation process to normalize standard seawater to S=35 with a significant loss in accuracy (0.0004 vs 0.003 in practical salinity).

How can density measurement grant long-term stability of standard seawater?

Reply: This question is discussed in Metrologia 53 (2016) R12–R25, doi: 10.1088/0026-1394/53/1/R12: "A suggested new concept that takes advantage of currently available density measurement technology and at the same time leaves established oceanographic practice largely unaffected is a combination of conductance ratio and density measurement (Seitz et al 2011) [www.ocean-sci.net/7/45/2011/]. In this concept, the salinity of SSW samples can be additionally certified (or at least checked) by density measurements in combination with the TEOS-10 equation of state. At a given reference temperature and pressure, the density of an SSW sample corresponding to a specified salinity is measured by the sample's producer and its Practical Salinity value is calculated via the equation of state and the Reference Salinity, equation (5). This value can be compared directly with the value achieved according to the PSS-78 procedures, which will reveal possible longer-term changes in SSW properties. Recent investigations supported the validity of this procedure (EMRP 2010). However, many practical aspects must still be investigated before it would be feasible to transition to obtaining salinity from density instead of from conductance ratio."

So, the basic idea is to calibrate a CTD conductivity sensor with respect to the certified density of seawater reference samples. The sample density can be verified experimentally at any time against SI standards, independent of any prepared and possibly aging or varying artefacts. The calibration density is a measure of a 'density salinity' intended to be defined in the future (www.ocean-sci.net/7/1/2011/). While this concept does not grant IAPSO standard seawater to become "more stable" than currently, it offers a so-far unavailable option of measuring (and correcting for) suspected long-term (century scale) changes of the reference material against an ultimately stable metrological reference.