

APPENDIX A:

Background and theory underlying the use of the Gibbs function of seawater

A.1 ITS-90 temperature

In order to understand the limitations of conversion between different temperature scales, it is helpful to review the definitions of temperature and of the international scales on which it is reported.

A.1.1 Definition

When considering temperature, the fundamental physical quantity is thermodynamic temperature, symbol T . The unit for temperature is the kelvin. The name of the unit has a lowercase k. The symbol for the unit is uppercase K. One kelvin is 1/273.16 of the thermodynamic temperature of the triple point of water. (A recent evolution of the definition has been to specify the isotopic composition of the water to be used as that of Vienna Standard Mean Ocean Water, VSMOW.) The Celsius temperature, symbol t , is defined by $t/^{\circ}\text{C} = T/\text{K} - 273.15$, and 1 $^{\circ}\text{C}$ is the same size as 1 K.

A.1.2 ITS-90 temperature scale

The definition of temperature scales is the responsibility of the Consultative Committee for Thermometry (CCT) which reports to the International Committee for Weights and Measures (often referred to as CIPM for its name in the French language). Over the last 40 years, two temperature scales have been used; the International Practical Temperature Scale 1968 (IPTS-68), followed by the International Temperature Scale 1990 (ITS-90). These are defined by Barber (1969) and Preston-Thomas (1990). For information about the International Temperature Scales of 1948 and 1927 the reader is referred to Preston-Thomas (1990).

In the oceanographic range, temperatures are determined using a platinum resistance thermometer. The temperature scales are defined as functions of the ratio W , namely the ratio of the thermometer resistance at the temperature to be measured $R(t)$ to the resistance at a reference temperature R_0 . In IPTS-68, R_0 is $R(0^{\circ}\text{C})$, while in ITS-90 R_0 is $R(0.01^{\circ}\text{C})$. The details of these temperature scales and the differences between the two scales are therefore defined by the functions of W used to calculate T . For ITS-90, and in the range $0^{\circ}\text{C} < t_{90} < 968.71^{\circ}\text{C}$, t_{90} is described by a polynomial with 10 coefficients given by Table 4 of Preston-Thomas (1990).

We note in passing that the conversions from W to T and from T to W are both defined by polynomials and these are not perfect inverses of one another. Preston-Thomas points out that the inverses are equivalent to within 0.13mK. In fact the inverses have a difference of 0.13 mK at 861 $^{\circ}\text{C}$, and a maximum error in the range $0^{\circ}\text{C} < t_{90} < 40^{\circ}\text{C}$ of 0.06 mK at 31 $^{\circ}\text{C}$. That the CCT allowed this discrepancy between the two polynomials immediately provides an indication of the absolute uncertainty in the determination, and indeed in the definition, of temperature.

A second uncertainty in the absolute realization of ITS-90 arises from what is referred to as sub-range inconsistency. The polynomial referred to above describes the behaviour of an 'ideal' thermometer. Any practical thermometer has small deviations from this ideal behaviour. ITS-90 allows the deviations to be determined by measuring the resistance of the thermometer at up to five fixed points: the triple point of water and the freezing points of tin, zinc, aluminium and silver, covering the range $0.01\text{ }^{\circ}\text{C} < t_{90} < 961.78\text{ }^{\circ}\text{C}$. If not all of these points are measured, then it is permissible to estimate the deviation from as many of those points as are measured. The melting point of Gallium ($t_{90} = 29.7646\text{ }^{\circ}\text{C}$) and the triple point of Mercury ($t_{90} = -38.8344\text{ }^{\circ}\text{C}$) may also be used if the thermometer is to operate over a smaller temperature range. Hence the manner in which the thermometer may be used to interpolate between the points is not unique. Rather it depends on which fixed points are measured, and there are several possible outcomes, all equally valid within the definition. Sections 3.3.2 and 3.3.3 of Preston-Thomas (1990) give precise details of the formulation of the deviation function. The difference between the deviation functions derived from different sets of fixed points will depend on the thermometer, so it is not possible to state an upper bound on this non-uniqueness. Common practice in oceanographic standards laboratories is to estimate the deviation function from measurements at the triple point of water and the melting point of Gallium ($t_{90} = 29.7646\text{ }^{\circ}\text{C}$). This allows a linear deviation function to be determined, but no higher order terms.

In summary, there is non-uniqueness in the definition of ITS-90, in addition to any imperfections of measurement by any practical thermometer (Rudtsch and Fischer (2008), Feistel *et al.* (2008a)). It is therefore not possible to seek a unique and perfect conversion between IPTS-68 and ITS-90.

Goldberg and Weir (1992) and Mares and Kalova (2008) have discussed the procedures needed to convert measured thermophysical quantities (such as specific heat) from one temperature definition to another. When mechanical or electrical energy is used in a laboratory to heat a certain sample, this energy can be measured in electrical or mechanical units by appropriate instruments such as an ampere meter, independent of any definition of a temperature scale. It is obvious from the fundamental thermodynamic relation (at constant Absolute Salinity), $du = Td\eta + Pd v$, that the same energy difference $Td\eta$ results in different values for the entropy η , depending on the number read for T from a thermometer calibrated on the 1990 compared with one calibrated on the 1968 scale. A similar dependence is found for numbers derived from entropy, for example, for the heat capacity,

$$c_p = T \eta_T \Big|_{S_A, p}.$$

Douglas (1969) listed a systematic consideration of the quantitative relations between the measured values of various thermal properties and the particular temperature scale used in the laboratory at the time the measurement was conducted. Conversion formulas to ITS-90 of readings on obsolete scales are provided by Goldberg and Weir (1992) and Weir and Goldberg (1996).

Any thermal experimental data that entered the construction of the thermodynamic potentials that form TEOS-10 were carefully converted by these rules, in addition to the conversion between the various older definitions of for example calories and joules. This must be borne in mind when properties computed from TEOS-10 are combined with historical measurements from the literature.

A.1.3 Theoretical conversion between IPTS-68 and ITS-90

Having understood that the conversion between IPTS-68 and ITS-90 is not uniquely defined, we review the sources of uncertainty, or even flexibility, in the conversion between t_{90} and t_{68} .

Consider first why t_{90} and t_{68} temperatures differ:

- 1) The fixed points have new temperature definitions in ITS-90, due to improvements in determining the absolute thermodynamic temperatures of the melting/freezing physical states relative to the triple point of water.
- 2) For some given resistance ratio W the two scales have different algorithms for interpolating between the fixed points.

Now consider why there is non-uniqueness in the conversion:

- 3) In some range of ITS-90, the conversion of W to t_{90} can be undertaken with a choice of coefficients that is made by the user (Preston-Thomas (1990) Sections 3.3.2.1 to 3.3.3), referred to as sub-range inconsistency.
- 4) The impact of the ITS-90 deviation function on the conversion is non-linear. Therefore the size of the coefficients in the deviation function will affect the difference, $t_{90} - t_{68}$. The formal conversion is different for each actual thermometer that has been used to acquire data.

The group responsible for developing ITS-90 was well aware of the non-uniqueness of the conversion. Table 6 of Preston-Thomas (1990) gives differences $(t_{90} - t_{68})$ with a resolution of 1 mK, because

- (a) the true thermodynamic temperature T was known to have uncertainties of order 1 mK or larger in some ranges,
- (b) the sub-range inconsistency of ITS-90 using the same calibration data gave an uncertainty of several tenths of 1 mK.

Therefore to attempt to define a generic conversion of $(t_{90} - t_{68})$ with a resolution of say 0.1 mK would probably be meaningless and possibly misleading as there isn't a unique generic conversion function.

A.1.4 Practical conversion between IPTS-68 and ITS-90

Rusby (1991) published an 8th order polynomial that was a fit to Table 6 of Preston-Thomas (1990). This fit is valid in the range 73.15 K to 903.89 K (-200 °C to 630.74 °C). He reports that the polynomial fits the table to within 1 mK, commensurate with the non-uniqueness of IPTS-68.

Rusby's 8th order polynomial is in effect the 'official recommended' conversion between IPTS-68 and ITS-90. This polynomial has been used to convert historical IPTS-68 data to ITS-90 for the preparation of the new thermodynamic properties of seawater that are the main subject of this manual.

As a convenient conversion valid in a narrower temperature range, Rusby (1991) also proposed

$$(T_{90} - T_{68})/K = -0.00025(T_{68} / K - 273.15) \quad (\text{A.1.1})$$

in the range 260 K to 400 K (-13 °C to 127 °C). Rusby (1991) also explicitly reminds readers (see his page 1158) that compound quantities that involve temperature intervals such as heat capacity and thermal conductivity are affected by their dependence on the derivative $d(T_{90} - T_{68})/dT_{68}$. About the same time that Rusby published his conversion from t_{68} to t_{90} , Saunders (1990) made a recommendation to oceanographers that in the common oceanographic temperature range $-2\text{ °C} < t_{68} < 40\text{ °C}$, conversion could be achieved using

$$(t_{90}/\text{°C}) = (t_{68}/\text{°C})/1.00024. \quad (\text{A.1.2})$$

The difference between Saunders (1990) and Rusby (1991) arises from the best slope being 1.00024 near 0 °C and 1.00026 near 100 °C (recall that t_{68} for the boiling point of water was 100 °C while its t_{90} is 99.974 °C). Thus Rusby (1991) chose 1.00025 over the wider range of 0 °C to 100 °C.

In considering what is a ‘reasonable’ conversion between the two temperature scales, we must recall that the uncertainty in conversion between measured resistance and either temperature scale is of order a few tenths of mK, and the uncertainty in the absolute thermodynamic temperature T is probably at least as large, and may be larger than 1 mK in some parts of the oceanographic range. For all practical purposes data converted using Saunders’ 1.00024 cannot be improved upon; conversions using Rusby’s (1991) 8th order fit are fully consistent with Saunders’ 1.00024 in the oceanographic temperature range within the limitations of the temperature scales.

A.1.5 Recommendation regarding temperature conversion

The ITS-90 scale was introduced to correct differences between true thermodynamic temperature T , and temperatures reported in IPTS-68.

There are remaining imperfections and residuals in $T - T_{90}$ (Rusby, pers. comm.), which may be as high as a couple of mK in the region of interest. This is being investigated by the Consultative Committee for Thermometry (CCT). At a meeting in 2000 (Rusby and White (2003)) the CCT considered introducing a new temperature scale to incorporate the known imperfections, referred to at that time as ITS-XX. Further consideration by CCT WG1 has moved thinking away from the desirability of a new scale. The field of thermometry is undergoing rapid advances at present. Instead of a new temperature scale, the known limitations of the ITS-90 can be addressed in large part through the ITS-90 Technical Annex, and documentation from time to time of any known differences between thermodynamic temperature and ITS-90 (Ripple *et al.* (2008)).

The two main conversions currently in use are Rusby’s 8th order fit valid over a wide range of temperatures, and Saunders’ 1.00024 scaling widely used in the oceanographic community. They are formally indistinguishable because they differ by less than both the uncertainty in thermodynamic temperature, and the uncertainty in the practical application of the IPTS-68 and ITS-90 scales. Nevertheless we note that Rusby (1991) suggests a linear fit with slope 1.00025 in the range -13 °C to 127 °C, and that Saunders’ slope 1.00024 is a better fit in the range -2 °C to 40 °C while Rusby’s 8th order fit is more robust for temperatures outside the oceanographic range. The difference between Saunders (1990) and Rusby (1991) is less than 1 mK everywhere in the range -2 °C to 40 °C and less than 0.03mK in the range -2 °C to 10 °C.

In conclusion, the algorithms for PSS-78 require t_{68} as the temperature argument. In order to use these algorithms with t_{90} data, t_{68} may be calculated using Eqn. (A.1.3) thus

$$(t_{68}/^{\circ}\text{C}) = 1.00024 (t_{90}/^{\circ}\text{C}). \quad (\text{A.1.3})$$