Thermophysical Properties Converted from Data and Equations Based on Old Temperature Scales

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Thermophysical properties measured before 1990 are based on obsolete temperature scales. In spite of great progress of experimental technique, there are data measured before 1990 that are still considered as very precious. In similar way it is with correlations of old but reliable thermophysical data. The only change of a parameter, as critical temperature, does not guarantee a correct approach to the right conversion. Comparison of values from an equation based on obsolete temperature scale with a new equation calculated for the same numerical values of temperature gives comparison at two different thermal states. There are thermophysical properties the temperature conversion of which depends on derivatives of equation converting an old temperature scale to the new one. Specific heat capacity, coefficient of thermal conductivity etc. could serve as examples of such properties. Complicated situation is with such properties as entropy and properties derived from it. The paper brings discussion of examples of temperature conversion of experimental data and equations as well.

Introduction

Present-day science and technology need accurate data on material properties. Data come from new measurements or from older ones given in literature. In case of temperature dependent data one should be aware of the differences in temperature standards by which the data were determined. Differences between two different temperature scales are generally small. Nevertheless, in some cases e.g. in measurement of high accuracy and in thermodynamics where first and second derivatives with respect to temperature are applied to calculate derived properties a conversion of data should be made on a common temperature scale.

Temperature scales

A survey of used temperature scales is given by Hust [1]. In 1854 Kelvin [2] proposed a thermodynamic temperature scale based on the Carnot cycle. This scale is independent of the properties of the substance used for the measurement. The first internationally acceptable practical temperature standard was adopted in 1927 as the International Temperature Scale of 1927 (ITS-27) [3]. The ITS-27 was defined in order to approximate the thermodynamic scale as close as experimentally possible. The ITS-27 was changed in 1948 [4] to the International Temperature Scale of 1948 (ITS-48). It was amended in 1960 [5]. However, the numerical values of temperature were the same as on the ITS-48. This amended scale was designated the International Practical Temperature Scale (IPTS-48). Very extensive changes led to the International Practical Temperature Scale of 1968 (IPTS-68) [6]. It was amended in 1975, but without influence on temperature values. Additionally to the ITS-68, the 1976 Provisional 0.5 K to 30 K Temperature Scale (EPT-76) was introduced.

The International Temperature Scale of 1990 [7] (ITS-90) is valid now. This scale superseded the International Practical Temperature Scale of 1968 (amended edition of 1975) and the 1976 Provisional 0.5 K to 30 K Temperature Scale. The thermodynamic bases of the ITS-90 are described in [8].

Conversion of temperature scales

Conversion from IPTS-48 to IPTS-68

The differences between the IPTS-68 and the low temperature national scales, NBS-55, NPL-61,

PRIM-54 and PSU-54 are published in [9]. This allows giving a close approximation to the IPTS-68.

Douglas [10] calculated and tabulated values of $\mu = T_{68} - T_{48}$ and $\mathrm{d}(T_{68} - T_{48})/\mathrm{d}T_{68}$ at rounded temperatures T_{68} from 90 to 10000 K.

Conversion from IPTS-68 to ITS-90

Rusby [11] discussed the conversion of thermal reference values to the ITS-90 and provided analytical equations representing the differences between the ITS-90 and IPTS-68.

A survey of used differences between ITS-90 and EPT-76 (provisional 0.5 to 30 K temperature scale 1976), and ITS-90 and IPTS-68 for specified values of T_{90} and t_{90} according to [6] were revised by Rusby [12]. The revision affects only the range 630 ºC to 1064 ºC, where the IPTS-68 specified the use of Pt -Pt+10% Rh thermocouples.

Weir and Goldberg [13] presented tables of differences: $(T_{90} - T_{76})/K$ (differences between ITS-90 an EPT-76) and the derivatives $\mathrm{d}(T_{90} - T_{76})/\mathrm{d}T$ as a function of T_{76} and also tables of differences $(T_{90} - T_{68})/K$, (differences between ITS-90 and IPTS-68) and the corresponding derivatives $\mathrm{d}(T_{90} - T_{68})/\mathrm{d}T$ as a function of T_{68}.

Temperature differences $T_{90}-T_{68}$ and $T_{90}-T_{48}$ are displayed at Figure 1.
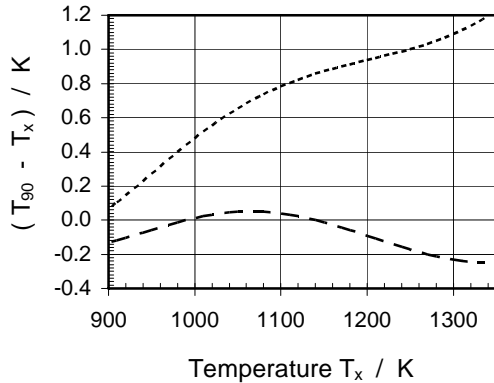
Figure 1: Temperature differences [14], [15]
···· $T_x = T_{48}$, ---- $T_x = T_{68}$

Conversion of experimental thermophysical property values to the ITS-90

This section is limited to a consideration of temperature conversion of experimental values to a fixed-point temperature where the values are different on two different temperature scales.

Simply saying, the conversion we deal with here relates to the same thermodynamic state for both the original and converted value with different values of temperatures in different temperature scales.

With regard to the different temperature dependence of individual thermodynamic properties the experimental data can be divided into three categories.

a) Experimental values with the exception of such values as mentioned in paragraphs b) and c) are dependent on the thermal state only. Thus the conversion involves merely associating them with a different temperature.

   Density can serve as an example. The same relates also to speed of sound, coefficient of viscosity, etc.

Conversion procedures are explained by way of illustrative examples on conversion from IPTS-68 to ITS-90.

   Example 1: Convert an experimental value of density $\rho_{68}(p,T_{68})$ to $\rho_{90}(p,T_{90})$.
Solution: The 'converted' density keeps its experimental value $\rho_{68}(p,T_{68})$, i.e.
$$\rho_{90}(p,T_{90}) = \rho_{68}(p,T_{68}). \qquad (1)$$

Only the associated value of temperature T_{68} indicating the state should be converted to the $T_{90}(T_{68})$.

b) Such thermodynamic properties as enthalpy cannot be assigned absolute values and therefore are usually expressed numerically as the magnitude in excess of the enthalpy at a reference temperature. Thus the correction to be applied to an enthalpy increment involves merely associating it with different boundary temperatures. It should be done in the same way as for properties of category a).

   Example 2: Convert an increment of enthalpy on an isobar measured between temperatures T_{A68} and T_{B68}.
Solution:
$$h_{B90}(T_{B90}) - h_{A90}(T_{A90}) = h_{B68}(T_{B68}) - h_{A68}(T_{A68}).$$

Simply $\Delta h_{90} = \Delta h_{68} \qquad (p=\text{const}) \qquad (2)$

where $T_{B90}(T_{B68})$ and $T_{A90}(T_{A68})$ are converted temperature values.

c) Compound quantities, which involve temperature intervals, such as heat capacity, coefficient of thermal conductivity, coefficient of thermal expansion are affected as values mentioned above, and also by virtue of their correspondence on the derivative $\mathrm{d}\Delta T/\mathrm{d}T$.

   Example 3: Convert an experimental value of the coefficient of thermal conductivity $\lambda_{68}(p,T_{68})$ to $\lambda_{90}(p, T_{90})$.
Solution: Coefficient of thermal conductivity, λ, is defined by the Fourier equation for the heat flux:
$$q = -\lambda \, grad(T) \qquad (3)$$

For one-dimensional heat transfer the equation (3) is expressed with the derivative

$$q = -\lambda \, \frac{dT}{dx} \, . \qquad (4)$$

For the temperature scale ITS-90 the equation (4) becomes

$$q = -\lambda_{90} \, \frac{dT_{90}}{dx} \qquad (5)$$

and for the IPTS-68

$$q = -\lambda_{68} \, \frac{dT_{68}}{dx} \, . \qquad (6)$$

Comparing right sides of equations (5) and (6) we get

$$\lambda_{90} = \lambda_{68} \, \frac{dT_{68}}{dT_{90}} \, . \qquad (7)$$

The derivative of the temperature difference may be expressed as

$$\frac{d(T_{90}\text{-}T_{68})}{dT_{90}} = 1 - \frac{dT_{68}}{dT_{90}} , \qquad (8)$$

and hence

$$\frac{dT_{68}}{dT_{90}} = 1 - \frac{d(T_{90} - T_{68})}{dT_{90}} \, . \qquad (9)$$

This type of data is in the described procedure multiplied by the derivative $\frac{dT_{68}}{dT_{90}}$, here (7).

For conversion from IPTS-48 to ITS-90, the derivative $\frac{dT_{68}}{dT_{90}}$ should be replaced by $\frac{dT_{48}}{dT_{90}}$. It could be obtained by two successive temperature conversions. Each derivative could be calculated either from conversion tables according to equation (9) or derived form a conversion equation. Thus

$$\frac{dT_{48}}{dT_{90}} = \frac{dT_{48}}{dT_{68}} \frac{dT_{68}}{dT_{90}} \, . \qquad (10)$$

The course of the derivatives $\frac{dT_{68}}{dT_{90}}$ and $\frac{dT_{48}}{dT_{90}}$ is displayed in Figure 2 in the temperature interval $903.765 \text{ K} < T_{90} < 1337.33 \text{ K}$.

The maximum absolute values of the derivative, i.e. $\frac{d(T_{90} - T_{68})}{dT_{90}}$, according to the conversion tables [13] do not exceed 0.0017. It means that the percentage deviation of value of any property of category c) converted from IPTS-68 to ITS.90 does not exceed ± 0.2 %. It should be pointed out that it concerns the described conversion procedure when the same thermodynamic state is kept.

Figure 2. also shows that in the temperature interval $903.765 \text{ K} < T_{90} < 1337.33 \text{ K}$ the percentage deviation does not exceed ± 0.43 % when the conversion is performed from the IPTS-48 to the ITS-90.
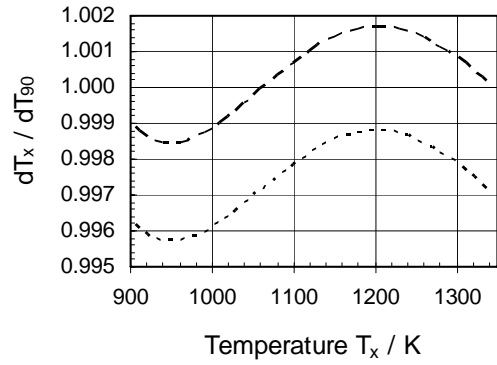
Figure 2: Temperature dierivatives [14],[15]
$\cdots T_x = T_{48}$, $---- T_x = T_{68}$

Conversion of calculated thermophysical property values to the ITS-90

Conversion property data in the same temperature value

Douglas [10] derived formulas for converting the selected thermodynamic properties derived from calorimetric data - enthalpy, heat capacity, entropy and Gibbs free energy - from IPTS-48 to IPTS-68.

Weir and Goldberg [13] revised the Douglas equations [10] and after discarding higher-order terms they obtained simplified equations for conversion of values in IPTS-68 to ITS-90.

In both papers [10] and [13] the conversion procedure to the same temperature values is discussed. For this procedure the Taylor expansion is used.

Conversion of thermophysical property values into the same thermodynamic state

The idea to convert property values to the same thermodynamic state, which was applied to experimental values, will be used also here. Calculated properties could be divided into three categories as well as the experimental properties. Moreover, one extra category was necessary to add for entropy.

Categories of calculated properties:

a) Calculated values like density will be associated with converted temperature value only. It is advisable to use an equation for conversion $T_{68}(T_{90})$ for given value T_{90} and calculate the value of the property with T_{68}.

Example 4: Calculate density $\rho_{90}(p, T_{90})$ from an equation in IPTS-68.

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Solution: Given temperature T_{90} should be converted to $T_{68}(T_{90})$ and density $\rho_{68}(p,T_{68})$ will be calculated from an equation in IPTS-68. According to equation (1) $\rho_{90}(p,T_{90})= \rho_{68}(p,T_{68})$.

b) As for properties like enthalpy, the procedure described above will be used for conversion of both boundary temperatures.

Example 5: Calculate an increment of enthalpy between temperatures T_{A90} and T_{B90}.
Solution: Given temperatures T_{A90} and T_{B90} should be converted to IPTS-68 $T_{A68}(T_{A90})$ and $T_{B68}(T_{B90})$. Enthalpy increment will be calculated from equation in IPTS-68. According to equation (2) $\Delta h_{90} = \Delta h_{68}$.

c) As for properties like coefficient of thermal conductivity, specific heat capacity, thermal expansivity, the procedure described in the paragraph c) can be used.

Example 6: See Example 3.
Solution: For given T_{90} a corresponding temperature in the old temperature scale will be calculated, $T_{68}(T_{90})$, and the property will be calculated with equation in IPTS-68 and multiplied by $\dfrac{\mathrm{d}T_{68}}{\mathrm{d}T_{90}}$ like λ_{68} in (7).

d) A special category should be opened for entropy. It is a property that cannot be measured and is dependent on temperature according the definition equation

$$\mathrm{d}s = \frac{\mathrm{d}q}{T} . \qquad (11)$$

Differential $\mathrm{d}q$ is a small amount of heat introduced reversibly to the system.

It is advisable to calculate the increment of entropy on isobar p_t from triple point temperature T_t to the final temperature T_x and then the increment on the isotherm T_x from pressure p_t to the final value p_x.

According to the international convention the value of entropy of saturated liquid water at the temperature of triple point, i.e. $s_t{'}$ was set equal zero, i.e.

$$s_t{'}=0. \qquad (12)$$

The latent heat of evaporation at the triple point temperature is independent of temperature scale

$$l_{t,\text{evap}90} = l_{t,\text{evap}68}. \qquad (13)$$

Hence

$$T_{t90} (s''-s')_{90} = T_{t68} (s''-s')_{68}. \qquad (14)$$

Because $T_{t90} = T_{t68}$, we get

$$(s''-s')_{90} = (s''-s')_{68}. \qquad (15)$$

With regard to equation (12) we obtain

$$s''_{90} = s''_{68}. \qquad (16)$$

Entropy on the triple point isobar at $T_{x90}>T_t$ in ITS-90 is then

$$s_{90}= s_{68}'' + \int_{Tt}^{Tx90} \frac{c_{p90}}{T}\,\mathrm{d}T \ , \ (p=p_t). \qquad (17)$$

The first law of thermodynamics applied on isobaric process yields

$$\mathrm{d}q = c_{p90}\mathrm{d}T_{90} = c_{p68}\mathrm{d}T_{68} . \qquad (18)$$

Using this expression for substitution in (17) we get in IPTS-68

$$s_{90}= s_{68}'' + \int_{Tt}^{Tx68} \frac{T}{T_{90}}\frac{c_{p68}}{T}\,\mathrm{d}T \ , \ (p=p_t) \qquad (19)$$

with converted upper limit temperature $T_{x68}(T_{x90})$ and $T_{90}(T_{68})$.

Using additivity of integration on intervals, the integration in (19) could be divided in such intervals in which the ratio T_{68}/T_{90} is constant or is possible to consider being constant. It enables to exploit a computer program developed for the old temperature scale (the IPTS-68 serves as an example) for calculations in individual temperature intervals.

$$\int_{Tt}^{Tx68} \frac{T}{T_{90}}\frac{c_{p68}}{T}\,\mathrm{d}T = \left(\frac{T_{68}}{T_{90}}\right)_{tA} \int_{Tt}^{TA68} \frac{c_{p68}}{T}\,\mathrm{d}T +$$

$$+\left(\frac{T_{68}}{T_{90}}\right)_{AB} \int_{TA68}^{TB68} \frac{c_{p68}}{T}\,\mathrm{d}T +...+ \qquad (20)$$

$$+\left(\frac{T_{68}}{T_{90}}\right)_{KX} \int_{TK68}^{Tx68} \frac{c_{p68}}{T}\,\mathrm{d}T .$$

For calculation of entropy increment between the triple point pressure p_t and the final pressure p_x at constant temperature it is possible to exploit an idea that the supplied heat between two states on the same isotherm, here T_{x90} and corresponding converted temperature $T_{x68}(T_{x90})$, is independent of temperature scales. For an arbitrary isotherm T_x holds that

$$q_x = T_{x68}\left(s_{x68} - s_{t68}\right)= T_{x90}\left(s_{x90} - s_{t90}\right). \qquad (21)$$

Hence it follows

$$s_{x90}\left(p_x,T_{x90}\right)-s_{t90}\left(p_t,T_{x90}\right)= \frac{T_{x68}}{T_{x90}}\left(s_{x68} - s_{t68}\right).$$
$$(22)$$

Values $s_{x68} = s_{68}\left(p_x,T_{x68}\right)$ and $s_{t68} = s_{68}\left(p_t,T_{x68}\right)$ could be calculated with converted temperature $T_{x68}(T_{x90})$ using a computer program developed for the old temperature scale (IPTS-68 here).

The converted entropy value is equal to the sum of the right side of equation (19) and equation (22).

Summary and Conclusion

The paper submits methods for temperature conversion of different type of thermophysical property values form an old temperature scale into the new temperature scale ITS-90.

In contrast to published methods based on conversion of the properties when numerical values of the old and the new temperatures are kept equal, authors preferred to convert properties in order to keep both the original and the converted values to the same thermodynamic state.

Submitted methods are based on thermodynamic relations only and tend to reach thermodynamically consistent converted values.

It should be pointed out that the converted properties could be thermodynamically consistent exactly if the dependence between the old temperature scale and the new temperature scale, regarded as the thermodynamic scale, was possible to formulize $T_{68}=k\,T_{90}$, where k is a constant.

Acknowledgements

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