TECHNICAL REPORT

ISO/TR 20461

First edition
2000-11-01

Determination of uncertainty for volume measurements made using the gravimetric method

Détermination de l'incertitude de mesure pour les mesurages volumétriques effectués au moyen de la méthode gravimétrique

Reference number
ISO/TR 20461:2000(E)

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Foreword

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ISO/TR 20461 was prepared by Technical Committee ISO/TC 48, *Laboratory glassware and related apparatus*, Subcommittee SC 1, *Volumetric instruments*.

Determination of uncertainty for volume measurements made using the gravimetric method

1 Scope

This Technical Report gives the detailed evaluation of uncertainty for volume measurements according to the *Guide to the Expression of Uncertainty in Measurement* (GUM) [1]. It uses the gravimetric method specified in ISO 8655-6 [2] as the reference method for calibrating piston-operated volumetric apparatus. It has been arranged in paragraphs to facilitate direct access to different aspects of this kind of evaluation as follows:

— modelling the measurement by describing the physical equations necessary to calculate the volume using the gravimetric method of measurement;

— determination of the standard uncertainty of measurement associated with the volume V_{20} by describing the calculation procedure according to the GUM;

— determination of the sensitivity coefficients with an example of the calculation of all sensitivity coefficients by using complete equations, approximations of equations and by giving numerical values for standard conditions;

— determination of the standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus giving the combination of the standard uncertainty associated with the volume V_{20} measured using the gravimetric measuring system and the experimental standard deviation associated with the volume delivered by the apparatus;

— determination of the standard uncertainties of measurement with a brief insight into the calculation of uncertainties of measuring devices according to GUM;

— determination of the expanded uncertainty of measurement associated with volume V_{20};

— example of the determination of the uncertainty for volume measurements.

2 Modelling the measurement

The equation for the volume V_{20} of the delivered water at 20 °C is given by

$$V_{20} = m \times Z \times Y \tag{1}$$

with

$$m = m_2 - m_1 - m_E \tag{2}$$

where

m is the balance reading of delivered water;

m_1 is the balance reading of the weighing vessel before delivery of the measured volume of water;

m_2 is the balance reading of the weighing vessel after delivery of the measured volume of water;

m_E is the balance reading of the mass loss due to evaporation of liquid during the measurement;

Z is the combined factor for buoyancy correction and conversion from mass to volume;

Y is the thermal expansion correction factor of the delivering device.

Equation (1) combines the measurement results yielded by the balance (m), air and liquid densities yielded by measurements of air and liquid temperatures, air pressure and relative humidity of air in conjunction with tables or equations for the factor (Z), and parameters of the delivering device (Y).

Z is given by

$$Z = \frac{1}{\rho_w} \times \frac{1 - \frac{\rho_a}{\rho_b}}{1 - \frac{\rho_a}{\rho_w}} = \frac{1}{\rho_b} \times \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \tag{3}$$

where

ρ_w is the density of water;

ρ_a is the density of air;

ρ_b is the density of the standard weight used to calibrate the balance [according to OIML (Organisation Internationale de Métrologie Légale), ρ_b = 8 000 kg/m^3 for steel weights].

The density of water ρ_w (in kg/m^3) is given by an equation [3] which is a very useful approximation of the equation of Kell [4],[5] in the temperature range 5 °C to 40 °C. The relative deviation between this equation and the original equation of Kell (given in reference [5] in terms of the ITS-90 temperature scale and valid for temperatures between 0 °C and 150 °C) is less than 10^{-6} in the temperature range 5 °C to 40 °C.

$$\rho_w = \sum_{i=0}^{4} a_i t_w^i \tag{4}$$

where

t_w is the water temperature in degrees Celsius;

with the constants (ITS-90 temperature scale):

a_0 is equal to 999,853 08 kg/m^3;

a_1 is equal to $6{,}326\,93 \times 10^{-2}$ °C^{-1} kg/m^3;

a_2 is equal to $8{,}523\,829 \times 10^{-3}$ °C^{-2} kg/m^3;

a_3 is equal to $6{,}943\,248 \times 10^{-5}$ °C^{-3} kg/m^3;

a_4 is equal to $3{,}821\,216 \times 10^{-7}$ °C^{-4} kg/m^3.

Any additional corrections for the pressure dependence and gas saturation of the water density are negligible as they are very small.

The density of air ρ_a (in kg/m^3) is given by [5]:

$$\rho_a = \frac{k_1 p_a + \varphi \left(k_2 t_a + k_3\right)}{t_a + t_{a0}} \qquad (5)$$

where

t_{a0} is equal to 273,15 °C;

p_a is the pressure, expressed in hectopascals (hPa);

φ is the relative humidity, expressed as a percentage;

t_a is the air temperature, expressed in degrees Celsius;

with the constants (ITS-90 temperature scale):

k_1 is equal to 0,348 44 (kg/m^3) °C/hPa;

k_2 is equal to –0,002 52 kg/m^3;

k_3 is equal to 0,020 582 (kg/m^3) °C.

The correction for the thermal expansion of the delivering device is given by

$$Y = 1 - \alpha_c \left(t_d - t_{d20}\right) \qquad (6)$$

where

α_c is the cubic expansion coefficient in °C^{-1};

t_d is the device temperature in degrees Celsius;

t_{d20} is equal to 20 °C.

The temperatures t_w, t_a, and t_d are assumed to be uncorrelated, as the actual values of t_w and t_d do not only depend on t_a, but also strongly depend on the handling by the user. Considerable effects of evaporation-cooling and hand-warming when using handheld apparatus are to be taken into account. The resulting temperature differences are often larger than the uncertainty in the temperature measurement.

Equations (1) to (6) show that one may write:

$$V_{20} = \frac{m}{\rho_b} \cdot \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \cdot \left[1 - \alpha_c \left(t_d - t_{d20}\right)\right] \qquad (7)$$

This model shows that the measured volume V_{20} is a function of m, t_w, t_a, p_a, φ, α_c, t_d, and some constants.

$$V_{20} = F(x_i) = F(m, t_w, t_a, p_a, \varphi, \alpha_c, t_d; \text{constants}) \qquad (8)$$

3 Standard uncertainty of measurement associated with the volume V_{20}

According to the GUM the standard uncertainty of measurement associated with the value V_{20} may be written as:

$$u^2(V_{20}) = \sum_i c_i^2 \times u^2(x_i) = \sum_i \left(\frac{\partial F}{\partial x_i}\right)^2 \times u^2(x_i) \tag{9}$$

$$u^2(V_{20}) = \left(\frac{\partial F}{\partial m}\right)^2 \times u^2(m) + \left(\frac{\partial F}{\partial t_w}\right)^2 \times u^2(t_w) + \left(\frac{\partial F}{\partial t_a}\right)^2 \times u^2(t_a) + \left(\frac{\partial F}{\partial p_a}\right)^2 \times u^2(p_a) + \ldots \tag{10}$$

where

$u^2(x_i)$ are the standard uncertainties referred to the measurement of each quantity which contributes to the final result (described by the model);

c_i^2 are the sensitivity coefficients giving the weight of each individual standard uncertainty.

The sensitivity coefficients may be determined by calculating the partial derivatives as indicated in equation (9), by numerical calculations, or by experiment.

As the uncertainties of the constants [equation (8)] and the uncertainties of equations (4) and (5) for ρ_w and ρ_a are very small compared to other uncertainties, they may be neglected in the evaluation of uncertainty.

4 Sensitivity coefficients

The evaluation of the uncertainty of measurement does not require such exact values and exact solutions of the mathematical model for the measurement, as the determination of the volume V_{20} itself. Approximations are tolerable, but they have to be used only for this uncertainty evaluation.

In the following the approximations $\rho_w - \rho_a \approx \rho_w$, $\rho_b - \rho_a \approx \rho_b$, $\rho_w \approx 1\,000$ kg/m^3, $1 - \alpha_c(t_d - t_{d20}) \approx 1$, and $\rho_b - \rho_w \approx \rho_b$ are used without special notation. Keep in mind that the first approximations are of the order 10^{-3} or less, whereas the last approximation is of the order 10^{-1}. This last approximation is justified as it is affecting only the air buoyancy correction.

The sensitivity coefficients c_i in equation (9) are calculated as partial derivatives using equations (11) to (29).

The sensitivity coefficient c_w related to the balance reading m is calculated as follows:

$$c_w = \frac{\partial F}{\partial m} = \frac{V_{20}}{m} \tag{11}$$

$$c_w = \frac{\partial F}{\partial m} \approx \rho_w \tag{12}$$

$$c_w = \frac{\partial F}{\partial m} \approx 10^{-3}\ \frac{\text{m}^3}{\text{kg}} = 1\,\frac{\text{nl}}{\mu\text{g}} \tag{13}$$

The sensitivity coefficient c_{α_c} related to the cubic expansion coefficient α_c of the piston-operated volumetric apparatus is calculated as follows:

$$c_{\alpha_c} = \frac{\partial F}{\partial \alpha_c} = -\frac{m}{\rho_b} \times \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \times (t_d - t_{d20}) \tag{14}$$

$$c_{\alpha_c} = \frac{\partial F}{\partial \alpha_c} \approx -\frac{m}{\rho_w} \times (t_d - t_{d20}) \tag{15}$$

$$c_{\alpha_c} = \frac{\partial F}{\partial \alpha_c} \approx -10^{-3} \left(\frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \times (t_d - 20\ °\text{C}) \tag{16}$$

It should be emphasized that α_c is not a well defined value for a compound system.

The sensitivity coefficient c_{t_d} related to the temperature t_d of the piston-operated volumetric apparatus is calculated as follows:

$$c_{t_d} = \frac{\partial F}{\partial t_d} = -\frac{m}{\rho_b} \times \frac{\rho_b - \rho_a}{\rho_w - \rho_a} \times \alpha_c \tag{17}$$

$$c_{t_d} = \frac{\partial F}{\partial t_d} \approx -\frac{m}{\rho_w} \times \alpha_c \tag{18}$$

If $\alpha_c = 10^{-5}\ \text{K}^{-1}$ is used:

$$c_{t_d} = \frac{\partial F}{\partial t_d} \approx 10^{-8} \left(\frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \tag{19}$$

It should be emphasized that the temperature t_d of the piston-operated volumetric apparatus is neither spatially nor temporally constant because of hand-warming at the middle and the top, and evaporation-cooling at the bottom of the apparatus.

The sensitivity coefficient c_{t_w} related to the water temperature t_w is calculated as follows:

$$c_{t_w} = \frac{\partial F}{\partial t_w} = -\frac{m}{\rho_b} \times \frac{1 - \alpha_c (t_d - t_{d20})}{(\rho_w - \rho_a)^2} \times (\rho_b - \rho_a) \times \left(\sum_{i=1}^{4} i a_i t_w^{i-1} \right) \tag{20}$$

$$c_{t_w} = \frac{\partial F}{\partial t_w} \approx -\frac{m}{\rho_w^2} \times \frac{\partial \rho_w}{\partial t_w} = -\frac{m}{\rho_w^2} \times \left(\sum_{i=1}^{4} i a_i t_w^{i-1} \right) \tag{21}$$

It is possible to use the expression $\frac{\partial \rho_w}{\partial t_w} = -2{,}1 \times 10^{-4} \text{K}^{-1} \times \rho_w$ instead of the sum given in equation (21) in the temperature range of 19 °C to 21 °C with sufficient accuracy.

$$c_{t_w} = \frac{\partial F}{\partial t_w} \approx \frac{m}{\rho_w} \times 2{,}1 \times 10^{-4}\ \text{K}^{-1} = 2{,}1 \times 10^{-7} \left(\frac{\text{kg}}{\text{m}^3} \text{K} \right)^{-1} \times m \tag{22}$$

It should be emphasized that t_w may also be affected by evaporation-cooling as by hand-warming.

The sensitivity coefficient c_{p_a} related to the air pressure p_a is calculated as follows:

$$c_{p_a} = \frac{\partial F}{\partial p_a} = \frac{m}{\rho_b} \cdot \left[1 - \alpha_c (t_d - t_{d20}) \right] \times \frac{\rho_b - \rho_w}{(\rho_w - \rho_a)^2} \times \frac{k_1}{t_a + t_{a0}} \tag{23}$$

$$c_{p_\mathrm{a}} = \frac{\partial F}{\partial p_\mathrm{a}} \approx \frac{m}{\rho_\mathrm{w}^2} \cdot \frac{k_1}{t_\mathrm{a} + t_\mathrm{a0}} \tag{24}$$

If t_a = 20 °C is used:

$$c_{p_\mathrm{a}} = \frac{\partial F}{\partial p_\mathrm{a}} \approx 1{,}2 \times 10^{-9} \left(\frac{\mathrm{kg}}{\mathrm{m}^3}\mathrm{K}\right)^{-1} \times m \tag{25}$$

The sensitivity coefficient c_φ related to the relative air humidity φ is calculated as follows:

$$c_\varphi = \frac{\partial F}{\partial \varphi} = \frac{m}{\rho_\mathrm{b}} \times \left[1 - \alpha_\mathrm{c}(t_\mathrm{d} - t_\mathrm{d20})\right] \times \frac{\rho_\mathrm{b} - \rho_\mathrm{w}}{(\rho_\mathrm{w} - \rho_\mathrm{a})^2} \times \frac{k_2 t_\mathrm{a} + k_3}{t_\mathrm{a} + t_\mathrm{a0}} \tag{26}$$

$$c_\varphi = \frac{\partial F}{\partial \varphi} \approx \frac{m}{\rho_\mathrm{w}^2} \times \frac{k_2 t_\mathrm{a} + k_3}{t_\mathrm{a} + t_\mathrm{a0}} \tag{27}$$

If t_a = 20 °C is used:

$$c_\varphi = \frac{\partial F}{\partial \varphi} \approx -1 \times 10^{-10} \left(\frac{\mathrm{kg}}{\mathrm{m}^3}\%\right)^{-1} \times m \tag{28}$$

The sensitivity coefficient c_{t_a} related to the air temperature t_a is calculated as follows:

$$c_{t_\mathrm{a}} = \frac{\partial F}{\partial t_\mathrm{a}} = \frac{m}{\rho_\mathrm{b}} \cdot \left[1 - \alpha_\mathrm{c}(t_\mathrm{d} - t_\mathrm{d20})\right] \times \frac{\rho_\mathrm{b} - \rho_\mathrm{w}}{(\rho_\mathrm{w} - \rho_\mathrm{a})^2} \times \frac{\varphi k_2 t_\mathrm{a0} - k_1 p_\mathrm{a} - \varphi k_3}{(t_\mathrm{a} + t_\mathrm{a0})^2} \tag{29}$$

$$c_{t_\mathrm{a}} = \frac{\partial F}{\partial t_\mathrm{a}} \approx \frac{m}{\rho_\mathrm{w}^2} \times \frac{\varphi(k_2 t_\mathrm{a0} - k_3) - k_1 p_\mathrm{a}}{(t_\mathrm{a} + t_\mathrm{a0})^2} \tag{30}$$

If φ = 50 %, p_a = 1 013 hPa, and t_a = 20 °C are used:

$$c_{t_\mathrm{a}} = \frac{\partial F}{\partial t_\mathrm{a}} \approx -4{,}5 \times 10^{-9} \left(\frac{\mathrm{kg}}{\mathrm{m}^3}\mathrm{K}\right)^{-1} \times m \tag{31}$$

5 Standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus

As mentioned in annex B of ISO 8655-6:—[2] there are two sources of uncertainty. One source is the uncertainty of the measurement of the delivered volume by the gravimetric method, the other is the uncertainty of the delivery process itself. By combining both, the standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus is obtained.

Equations (7) to (31) give the standard uncertainty associated with the volume V_{20} measured with the gravimetric measuring system. To derive the standard uncertainty associated with the volume delivered by a piston-operated volumetric apparatus (pipette, burette, etc.), the square of the experimental standard deviation (square of the random error of measurement, see 8.5 in ISO 8655-6:—[2]) of repeated measurements has to be treated as an additional term in equation (9). The sensitivity coefficient is 1 in this case ($c_{V_{20}} = \frac{\partial V_{20}}{\partial V_{20}}$).

The standard uncertainty associated with the volume V_{20} measured with the gravimetric measuring system should be less than one third of the (expected) standard uncertainty associated with the volume delivered by the piston-operated volumetric apparatus which has to be calibrated. This ensures that the uncertainty obtained in the calibration is due mainly to the uncertainty caused by the piston-operated volumetric apparatus.

6 Standard uncertainties of measurement

It is possible to determine the standard uncertainties of measurement $u(x)$ by making calibrations under repeatability conditions so as to obtain the experimental standard deviation associated with the repeatability (GUM: type A evaluation) or by considering the manufacturer's specifications of the measuring devices (e.g. for resolution, linearity, drift, temperature dependence).

In the second case, the manufacturer's specifications are often given as an interval covering the measurement value. The probability of finding the value within this interval is equal to 1. The distribution of possible values is uniform in this interval. This distribution is called rectangular (constant distribution inside the interval, zero distribution outside the interval). The interval should be used to give the variance in the form (GUM: type B evaluation) of:

$$u^2(x_i) = \frac{\left[\frac{1}{2}(a_{i+} - a_{i-})\right]^2}{3} = \frac{a_i^2}{3} \tag{32}$$

where a_{i-} and a_{i+} give the lower and the upper limits of the interval of the device i.

a_i is half of this interval, typically the interval is denoted as $\pm a_i$ in this case. The standard uncertainty is given as the square root of the variance.

7 Expanded uncertainty of measurement associated with volume V_{20}

The expanded uncertainty of the volume V_{20} is expressed as:

$$U = k \cdot u(V_{20}) \tag{33}$$

where the standard uncertainty is multiplied by the coverage factor k. The value $k = 2$ is recommended for calibrations. In the case of a normal distribution, this means that when measuring the value of V_{20}, it can be found within the interval given by $V_{20} \pm U$ (k = 2) at a level of confidence of approximately 95 %.

The result of the measurement will therefore be given as:

$$V_{20} \pm U \ (k = 2) \tag{34}$$

The coverage factor has to be stated.

8 Example for determining the uncertainty of the measurement

8.1 Measurement conditions

The measurement conditions are as follows:

- tenfold measurement of a nominal 100 µl volume of water, delivered by a piston-operated pipette;
- balance: 200 g balance with a readability of 10 µg;
- mean volume: V_{20} = 100,3 µl;

- random error of measurement (experimental standard deviation): $s(V_i)$ = 0,4 µl;
- experimental standard deviation of the mean: $s(V_{20}) = s(V_i)/\sqrt{n}$ = 0,13 µl;
- systematic error of measurement: $V_{20} - V_s$ = 0,3 µl.

The determination of the uncertainty for these conditions is given in Table 1.

Table 1 — Determination of uncertainty

Parameter		Interval	Distribution	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Uncertainty
		Equation (32)			Equations (11) to (31)	$c_i \times u(x_i)$
Balance	uncertainty	± 100 µg	rectangular	57 µg	1 nl/µg	57 nl
	linearity	± 20 µg	rectangular	11,4 µg	1 nl/µg	11,4 nl
1st value	reproducibility	± 20 µg	rectangular	11,4 µg	1 nl/µg	11,4 nl
2nd value	reproducibility	± 20 µg	rectangular	11,4 µg	1 nl/µg	11,4 nl
1st value	readability	10 µg	rectangular	2,9 µg	1 nl/µg	2,9 nl
2nd value	readability	10 µg	rectangular	2,9 µg	1 nl/µg	2,9 nl
	temperature drift	0,1 µg	rectangular	0,029 µg	1 nl/µg	0,029 nl
	correction for evaporation loss	± 20 µg	rectangular	11,4 µg	1 nl/µg	11,4 nl
Water	temperature	± 0,1 K	rectangular	$5{,}7\times10^{-2}$ K	20 nl/K	1,14 nl
Air	temperature	± 0,1 K	rectangular	$5{,}7\times10^{-2}$ K	0,45 nl/K	$2{,}6\times10^{-2}$ nl
	pressure	± 5 hPa	rectangular	2,9 hPa	0,12 nl/hPa	0,35 nl
	relative humidity	± 10 %	rectangular	5,7 %	0,01 nl/%	$5{,}7\times10^{-2}$ nl
Delivering device	cubic expansion coefficient	$\pm 10^{-5}$ K^{-1}	rectangular	$5{,}7\times10^{-6}$ K^{-1}	-2×10^{5} nl K	1,14 nl
	temperature	± 2 K	rectangular	1,15 K	1 nl/K	1,15 nl
Standard uncertainty associated with the volume V_{20} measured with the gravimetric measuring system						61,6 nl
Experimental standard deviation of the mean of the calibration				$400/\sqrt{10}$ nl	1	126 nl
Standard uncertainty of the calibration (for the mean delivered volume)				$(61{,}6^2 + 126^2)^{1/2}$ nl		141 nl

8.2 Results

8.2.1 Standard uncertainty of the measurement

$u(V_{20})$ = 0,14 µl

8.2.2 Result of measurement

V_{20} = 100,30 µl ± 0,28 µl (k=2)

8.2.3 Standard uncertainty of the calibration for one single delivered volume:

$u(V_{20}) = (61{,}6^2 + 400^2)^{1/2}$ nl = 405 nl ≈ 0,4 µl.

Only a single dispensed volume is considered in this example. Therefore the experimental standard deviation is not divided by $\sqrt{n}$ (see clause 5). This value has to be compared to values in the tables of maximum permissible random errors given in ISO 8655 (parts 2 to 5) [6], [7], [8], [9].

8.2.4 General remarks

It should be kept in mind that some of the numerical values of the sensitivity coefficients are volume dependent. It is not possible to use the values given in the example for other volumes.

The uncertainty contributions of the balance reproducibility and the balance readability are listed twice as there are two readings giving the mass value before and after the delivery procedure.

The readability of the thermometer, the barometer, and the humidity measuring device are much smaller than the given intervals and are thus neglected.

The uncertainty associated with the gravimetric measurement is mainly attributed to the uncertainty associated with the result given by the balance.

The uncertainties attributed to the lack of knowledge of air temperature, pressure and humidity are often so small, that in most cases it is justifiable to work with standard values rather than the measured values.

For the same reason, it is often justifiable to neglect the uncertainty due to the thermal expansion of the piston-operated volumetric apparatus.

It should be kept in mind that, although the thermal expansion coefficient and the temperature of the piston-operated volumetric apparatus have been taken into consideration in this example, other factors have not been taken into consideration (e.g. the effect of an air interface of a piston-operated pipette which is non-saturated with water vapour).

For delivered volumes smaller than 100 µl, it may be important to consider the error resulting from the evaporation of liquid. Nonetheless, the uncertainty due to evaporation has been calculated for this example (100 µl volume measurement), as given in Table 1, and can be considered negligible.

The standard uncertainty associated with the volume V_{20} measured using the gravimetric measuring system is much smaller than the standard uncertainty associated with the calibration. This means the standard uncertainty is primarily attributed to the standard uncertainty of the volume delivered by the delivering device.

8.2.5 Note on the conformity of ISO 8655 with GUM

Random error of measurement is equivalent to the term “experimental standard deviation” used in GUM. There is no direct equivalent to systematic error of measurement in GUM. But a simple way to be in conformity with the GUM is to expand the model (paragraph 2) defining a new quantity $V_d = V_{20} - V_s$, where V_s is the selected volume of the piston-operated volumetric apparatus. In this case the result of the measurement is equivalent to the systematic error of measurement defined in ISO 8655-6. The measurement uncertainty will be unchanged as V_s has a zero uncertainty.

The systematic error of measurement does not influence the measurement uncertainty of the volume V_{20} measured with the gravimetric measuring system. It is the result of a measurement made using the gravimetric measuring system and has to be referred to the piston-operated volumetric apparatus. It is a measure characterizing the volume delivered by the piston-operated volumetric apparatus.

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[8] ISO 8655-4, *Piston-operated volumetric apparatus — Part 4: Dilutors.*

[9] ISO 8655-5, *Piston-operated volumetric apparatus — Part 5: Dispensers*.

1) To be published.

2) This review gives all constants based on the temperature scale ITS-90.

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