

## NEW DEFINITION OF THE KELVIN

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**Abstract:** The current definition of the kelvin refers to a property of a special substance, the triple-point temperature of water. However, the stability of triple point realisations in space and time and the agreement between different cells can not be warranted as shown by experimental indications. Therefore, as a base unit of the SI the kelvin should better be defined by fixing the value of a fundamental constant, a definition already successfully exercised with the metre relying on the speed of light in vacuum. The fundamental constant linked with the kelvin is the Boltzmann constant  $k$ , which relates the temperature  $T$  to the thermal energy  $kT$ . Different methods to determine the Boltzmann constant with sufficient accuracy are reviewed with a view to their present and future limits of uncertainty. Acoustic and dielectric-constant gas thermometry seem to be the most promising candidates, supported by measurements of the total thermal radiation. Finally, a new and universal definition for the kelvin is suggested, including a discussion of its consequences.

**Keywords:** Kelvin, SI units, Boltzmann constant.

### 1. PRESENT SITUATION

Since 1954, when the General Conference on Weights and Measures (CGPM) adopted the proposal made about a century before by William Thomson, the later Lord Kelvin, the kelvin, called degree Kelvin in those days, has been defined by the temperature distance between absolute zero and another fixed point, the triple point of water (TPW), with an assigned temperature value of exactly 273.16 K [1].

The use of the TPW as a fixed point in the definition of the Kelvin links this unit to the property of a special substance and inevitably hands it over to unpredictable changes in space and time. This situation is clearly demonstrated e.g. by three recent comparisons of TPW cells. During a EUROMET comparison [2] only half of the 27 investigated cells agreed with the circulated sample to within  $\pm 50 \mu\text{K}$  ( $\pm 1.8 \cdot 10^{-7}$ ). Two cells even deviated by more than 200  $\mu\text{K}$  and were excluded from further analysis. Another study of also 27 different cells performed by the National Research Council of Canada [3] reports the indication of a long-term drift of 4  $\mu\text{K}$  per year presumably caused by the slowly increasing solution of minerals and silicon from the walls of the borosilicate glass containers. Nine cells had to be ruled out for contamination reasons with excess air or some other strange behaviour. Thus, the drift of the better cells was sufficient to create within ten

years a deviation of the same order of magnitude as that found in the previous comparison. The most recent study, the CIPM Key Comparison of water triple point cells CCT-K7 [4], yielded a standard deviation of the triple-point temperatures of the transfer cells from 20 metrological institutes of 50  $\mu\text{K}$ . In this case it could be shown that the observed differences result essentially from variations in the isotopic composition of the water samples, in agreement with earlier reports of isotope effects of some 10  $\mu\text{K}$  or often much more [5, 6]. In this respect, the situation will soon be improved, since the Consultative Committee for Thermometry (CCT) of the International Committee for Weights and Measures (CIPM) recommended to clarify the definition of the kelvin by explicit, sufficiently accurate specification of the isotopic composition of the water samples to be used in TPW cells [7, 8]. The favoured isotopic composition follows the concentration values of Vienna Standard Mean Ocean Water (V-SMOW). As a consequence, a reduction of the spread of TPW realisations by a factor of about two for this temporally stable uncertainty contribution seems to be possible. The time-dependent effect of impurities, however, has to be treated separately, and the statistical basis for such a treatment is not large at present. Probably, the long-term drift can be reduced by using other materials for the containers. Due to the small size of the effect, corresponding investigations will require several years of observation.

In this situation one should aspire to a new definition of the kelvin not based on an artefact or a special material's property. Following the model of other base units like the second or the metre, where a fixed value is assigned to an atomic transition or a fundamental constant, the kelvin should be related to the thermal energy  $kT$  with the Boltzmann constant  $k$  as a fixed conversion factor. Similar efforts are under way for other units, since the CIPM recommended recently that National Metrology Institutes should pursue their work aimed at providing the best possible values of the fundamental constants needed for redefinitions of the four base units kilogram, ampere, kelvin and mole [9].

There are four guidelines which should be observed in redefining a major part of the base units [10]. First, the structure of the SI should remain unchanged. There is no real need to choose different base units or to increase or reduce their actual number. The important aim is not to disturb the global measurement system. Second, it is not

necessary in principle to reduce the uncertainty with the new definition of a unit, since already the benefit of a definition free of drift forever is a most promising advantage. Third, a new definition of a unit should improve the benefits to both metrology and science, that is everyday commerce and physics in general or quantum physics in particular. Fourth, a new definition of a unit should not cause a discontinuity in the value of the unit in order to have a smooth change for the users and to avoid recalibrations or recalculations. In order not to lose too much accuracy, the uncertainty of the fundamental constant should finally be in the same order of magnitude as that of the current definition.

As shown by the recently published CODATA values for fundamental physical constants [11] the present uncertainty of the Boltzmann constant of 1.8 parts in  $10^6$  (ppm) is based mainly on the results of a single experiment using acoustic gas thermometry to measure the gas constant  $R$  at NIST [12]. This is not considered to be sufficient for the replacement of the present definition of the kelvin related to the TPW. Therefore, further independent measurements, preferably based on different physical laws, are needed to improve the reliability of a fixed value of  $k$ . In order to get an overview of the state of the art of thermodynamic (primary) measurement methods for temperatures near the TPW temperature  $T_{\text{TPW}}$ , a workshop on ‘‘Methods for new determinations of the Boltzmann constant’’ was held at PTB, Germany, on January 21, 2005 [13].

In the following such methods are described in some detail and their future attainable uncertainties are considered.

## 2. METHODS FOR DETERMINATION OF THE BOLTZMANN CONSTANT

Since the microscopic thermal energy  $kT$  cannot be measured directly, macroscopic quantities have to be investigated the temperature dependence of which is explicitly related to this energy [14]. For gases, the microscopic energy is the mean kinetic energy of the atoms or molecules they consist of. In a closed volume this energy determines the gas pressure  $p$ , and at constant pressure the density of the gas is inversely proportional to  $kT$ . Therefore, all kinds of gas thermometers are suited in principle to determine the Boltzmann constant. The kinds expected to achieve the lowest uncertainties for measuring the density are the acoustic gas thermometer (AGT) detecting the speed of sound  $u_0$ , the dielectric constant gas thermometer (DCGT) determining the dielectric constant  $\epsilon$ , and the refractive index gas thermometer (RIGT) and the quasi-spherical cavity resonator (QSCR), both exploiting the refractive index  $n$ .

Quite different methods are Johnson noise thermometry, measuring the thermal movement of carriers in an electrical resistor  $R_{\text{el}}$  (JNT), and radiation thermometry based on the spectral distribution of photons with energy  $h\nu$ . The latter method can be performed as total (TRT) or spectral (SRT) radiation thermometry. Finally, Doppler-broadening thermometry (DBT) evaluates the broadening of an atomic or molecular spectral line by means of laser absorption spectroscopy applied to the measuring gas.

**Table 1:** Overview of the different methods of primary thermometry for the determination of the Boltzmann constant, the fundamental formulas they are based on, and the uncertainty estimates for the present state and the mid-term progress. ( $u_0$  zero-frequency zero-pressure limit of the speed of sound,  $M$  molar mass of the gas,  $R$  molar gas constant,  $T$  temperature,  $\gamma_0 = c_p/c_v$  heat-capacity ratio,  $p$  pressure,  $k$  Boltzmann constant,  $\epsilon$  dielectric constant,  $\epsilon_0$  electric constant,  $\alpha_0$  static electric dipole polarizability,  $L$  total radiance,  $M_{\text{rad}}$  total radiant exitance,  $c_0$  speed of light in vacuum,  $h$  Planck constant,  $L_\nu$  spectral radiance,  $\nu$  frequency,  $\langle U^2 \rangle$  mean square noise voltage,  $R_{\text{el}}$  electrical resistance,  $n$  refractive index,  $\Delta\nu_D$  Doppler width,  $\nu_0$  absorption frequency,  $m$  atomic mass)

Method	Physical law	Relative standard uncertainty	
		Present state	Mid-term estimate
AGT	$u_0 = \sqrt{\frac{\gamma_0 RT}{M}}$	2 ppm	1 ppm
DCGT	$p = kT \frac{(\epsilon - \epsilon_0)}{\alpha_0}$	15 ppm	2 ppm
TRT	$L = \frac{M_{\text{rad}}}{\pi} = \frac{2\pi^4}{15c_0^2 h^3} (kT)^4$	32 ppm	5 ppm
SRT	$L_\nu = \frac{2h}{c_0^2} \nu^3 \left[ \exp\left(\frac{h\nu}{kT}\right) - 1 \right]^{-1}$		50 ppm
JNT	$\langle U^2 \rangle = 4kTR_{\text{el}}\Delta\nu$		10 ppm
QSCR	$p = kT \frac{(n^2 - 1)\epsilon_0}{\alpha_0}$	40 ppm	10 ppm
RIGT	$p = kT \frac{(n^2 - 1)\epsilon_0}{\alpha_0}$	300 ppm	30 ppm
DBT	$\Delta\nu_D = \sqrt{\frac{2kT}{mc_0^2}} \nu_0$	800 ppm	10 ppm

All the methods mentioned are primary methods since they rely on fundamental physical laws (listed in Table 1). All other quantities in these laws beside  $kT$  can be determined independently or are fundamental constants. Table 1 gives also an overview of the uncertainties of the different methods attained today and expected in near future, and permits the selection of the most promising candidates [15]. Considering the mid-term uncertainty estimates, a group of three thermometers is clearly separated from the others: AGT, DCGT and TRT. These are discussed in the following section because they offer the prospect of determining the Boltzmann constant with different methods and a relative uncertainty of the order of 1 ppm required for replacement of the present definition of the kelvin via the TPW within the next years. The other methods should not be neglected, but chosen to deliver supporting results.

### 3. METHODS PROVIDING SUFFICIENT ACCURACY

#### 3.1. Acoustic gas thermometry

Applying AGT at the TPW, the determination of the Boltzmann constant is based on the relation

$$k = \frac{Mu_0^2}{N_A \gamma_0 T_{\text{TPW}}} \quad (1)$$

valid for an ideal gas, where  $u_0$  is the zero-frequency, zero-pressure limit of the speed of sound, and  $\gamma_0$  is the zero-pressure limit of the ratio  $c_p/c_V$  of the specific heat capacities at constant pressure ( $c_p$ ) and constant volume ( $c_V$ ). In principle, Eq. (1) could be written in the form  $k = mu_0^2/(\gamma_0 T_{\text{TPW}})$  with the microscopic mass  $m$  of a gas particle. As given above, Eq. (1) describes the situation better because the amount of substance is defined via the molar mass of  $^{12}\text{C}$ , i.e., a macroscopic quantity. This is the reason why the determination of the Boltzmann constant by means of AGT requires the knowledge of the Avogadro constant  $N_A = R/k$ . The pressure dependence of the speed of sound is of secondary influence, which is one main advantage of the AGT. In a real gas it may be expressed by a virial expansion

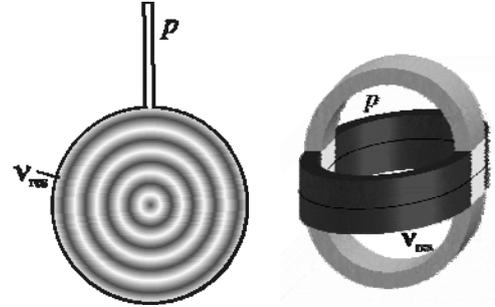
$$u^2 = u_0^2(1 + \alpha p + \beta p^2 + \dots) \quad (2)$$

The acoustic virial coefficients  $\alpha$  and  $\beta$  can be expressed in terms of the temperature-dependent density virial coefficients  $B(T)$  and  $C(T)$ . Applying Eq. (2),  $u_0$  is determined by extrapolation to zero pressure and  $k$  is calculated using equation (1). Another advantage of AGT is the small influence of the deformation of the apparatus under pressure. Compared with the other kinds of gas thermometry, AGT has quite different sources of error [15].

Mainly two methods have been used to measure the speed of sound [1, 16]. Until recently most AGTs used cylindrical interferometers with fixed frequency and variable path. Nowadays, variable-frequency, fixed-path spherical or quasi-spherical resonators are preferred. Their figure of merit is about an order of magnitude higher than that of cylindrical resonators. Furthermore, boundary layer effects and problems due to the excitation of different modes are smaller. The application of AGTs with spherical or quasi-spherical resonators for primary thermometry in the temperature range from 7 K to 505 K is described in [17–25]. The quasi-spherical shape retains the advantages of spherical resonators while simplifying the determination of the resonator's thermal expansion using microwave resonances.

Moldover *et al.* [12] assembled a 3 litre, steel-walled spherical resonator and used it to re-determine the gas constant  $R$  with an estimated relative uncertainty of 1.7 ppm (increased to 1.8 ppm in [26], based on a more detailed consideration of an additional uncertainty component due to the contamination of the measuring gas argon with nitrogen). This was a factor of 5 smaller than the uncertainty of the best previous measurement. The acoustic resonance frequencies of the argon-filled resonator were measured applying electro-acoustic transducers. The main uncertainty

components of this determination of  $R$  arose from the necessary link to the TPW temperature (0.89 ppm), the determination of the resonator volume using high-purity mercury of known density (0.80 ppm), the molar mass of the argon working gas sample (0.81 ppm), and the extrapolation to zero pressure together with the thermal boundary-layer correction and a possible error in the location of the transducers (0.92 ppm).



**Figure 1:** Left-hand: principle of acoustic gas thermometry applying a spherical resonator ( $v_{\text{res}}$  resonance frequency). Right-hand: cut-away schematic of a quasi-spherical cavity resonator with a “race-track” shape used by May *et al.* [27]. The overall shape of the quasi-spherical cavity is a triaxial ellipsoid. It is composed of two quasi-hemispheres of oxygen-free high-conductivity copper bolted together at their “equator”. This design was already used for acoustic gas thermometry by Pitre *et al.* in the range 7 K to 273 K [25].

At the workshop [13] mentioned at the end of section 1, Moldover analysed the state-of-the-art measurement techniques and claimed that they would allow to obtain a relative uncertainty of  $k$  of 1 ppm by repeating the NIST experiments described in [17] and [12]. The main uncertainty components of such a repeated experiment (with the estimated limits of the standard uncertainty in parentheses) would be the traceability to the TPW (0.36 ppm), the determination of the dimensions of the spherical resonator (0.39 ppm), the molecular weight of the measuring gas argon (0.42 ppm), and the zero-pressure limit of and corrections to frequency (0.69 ppm). For the first component it might be a problem that all determinations of the density of mercury used for measuring the resonator volume are many years old and a new determination with the necessary accuracy is currently not possible. The use of helium as an alternative measuring gas was proposed because the number of necessary parameters in the virial expansion is smaller and because the uncertainty of the molecular weight is negligible.

In their talks at the workshop [13], Marcarino and Gavioso described that new AGT measurements of the Boltzmann constant will be performed in a collaboration of Istituto di Metrologia “Gustavo Colonnetti” (IMGC-CNR) and Istituto Elettrotecnico Nazionale Galileo Ferraris (IEN), Italy (recently merged with one another and now forming Istituto Nazionale di Ricerca Metrologica (INRIM)). It is intended to derive the dimensions of the spherical or quasi-spherical resonator from the resonance frequencies of microwave modes in the resonator without referring to the

density of mercury, which would be an essential progress compared with the method used at NIST. Several microwave modes will be used to evaluate the perturbations of the modes by various effects. The achievable uncertainty of the final result is not yet known. In [24], even the mode-dependent deviations of the calculated radius values were of the order of 10 ppm. Recent progress is described in the Proceedings of the CPEM 2006 [28].

### 3.2. Dielectric-constant gas thermometry

The basic idea of DCGT is to replace the density in the equation of state (EOS) of a gas by the dielectric constant  $\varepsilon$ , and to measure this by incorporating a capacitor in the gas bulb. The dielectric constant of an ideal gas is given by  $\varepsilon = \varepsilon_0 + \alpha_0 N/V$ , with  $\varepsilon_0$  the exactly known electric constant,  $\alpha_0$  the static electric dipole polarizability of the gas atoms, and  $N/V$  the number density. The EOS of an ideal gas can thus be written in the form  $p = kT(\varepsilon - \varepsilon_0)/\alpha_0$ . Just as AGT, DCGT avoids the troublesome density determination of conventional gas thermometry, that is complicated by gas contained in dead spaces not at the measuring temperature  $T$  and by gas adsorption in the system. In addition, the pressure sensing tubes can be of any convenient size and the thermometric gas can be moved into or out of the bulb without the need to determine the amount of gas involved. A compensating disadvantage of DCGT is the need to measure a dielectric constant which is very close to unity.

Absolute DCGT requires knowledge of the static electric dipole polarizability  $\alpha_0$  with high accuracy. Today this condition is fulfilled for helium, which has become a model substance for evaluating the accuracy of *ab initio* calculations of thermophysical properties. Recent progress decreased the uncertainty of the *ab initio* value of  $\alpha_0$  to well below 1 ppm [11, 29, 30]. Since the molar polarizability  $A_\varepsilon$  is defined as  $A_\varepsilon = N_A \alpha_0 / (3\varepsilon_0)$ , the Boltzmann constant is related to  $\alpha_0$ ,  $A_\varepsilon$  and the molar gas constant  $R$  by

$$k = \frac{R}{A_\varepsilon} \frac{\alpha_0}{3\varepsilon_0} \quad (3)$$

Measuring the ratio  $A_\varepsilon/R$  of two macroscopic quantities (see below) therefore allows to determine  $k$  without knowledge of the Avogadro constant. Since *ab initio* calculations give the static electric dipole polarizability of the  $1^1S$  ground state of  $^4\text{He}$  in the  $^4\text{He}$  reduced atomic unit of polarizability  $\alpha_0^*(^4\text{He}) = \alpha_0(^4\text{He}) / (4\pi \varepsilon_0 a_0^3 (1 + m_e/m_\alpha)^3)$ , with  $a_0$  the Bohr radius and  $m_e/m_\alpha$  the electron to  $\alpha$ -particle mass ratio, the complete expression for  $k$  becomes

$$k = \frac{4\pi}{3} a_0^3 \left(1 + \frac{m_e}{m_\alpha}\right)^3 \frac{\alpha_0^*(^4\text{He})}{(A_\varepsilon/R)_{^4\text{He}}} \quad (4)$$

In the 2002 set of fundamental constants recommended by CODATA [11], the standard uncertainties of  $a_0$  and  $m_e/m_\alpha$  are only  $3.3 \cdot 10^{-9}$  and  $4.4 \cdot 10^{-10}$ , respectively.

For a real gas, the interaction between the particles has to be considered by combining the virial expansions of the EOS and the Clausius-Mossotti equation. Neglecting higher-

order terms and the very small dielectric virial coefficients, this yields

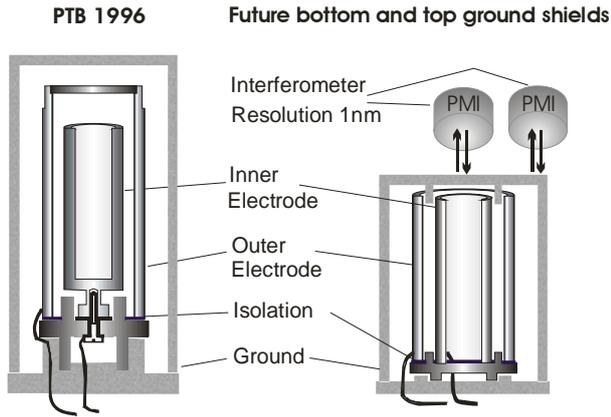
$$p \approx \frac{\chi}{\frac{3A_\varepsilon}{RT} + \kappa_{\text{eff}}} \left[ 1 + \frac{B(T)}{3A_\varepsilon} \chi + \frac{C(T)}{(3A_\varepsilon)^2} \chi^2 + \dots \right], \quad (5)$$

where  $\chi = \varepsilon/\varepsilon_0 - 1$  is the dielectric susceptibility,  $B(T)$  and  $C(T)$  are the second and third density virial coefficients taking into account the pair and triplet interactions, and  $\kappa_{\text{eff}}$  is the effective compressibility of a suitable capacitor used to measure  $\chi$ . For determination of  $3A_\varepsilon/RT$ , isotherms have to be measured, i.e., the relative change in capacitance  $[C(p) - C(0)]/C(0) = \chi + (\varepsilon/\varepsilon_0)\kappa_{\text{eff}}p$  of the gas-filled capacitor has to be determined as a function of the gas pressure  $p$ . This is done by measuring the capacitance  $C(p)$  with the space between the capacitor electrodes filled with the gas at various pressures and evacuated. A polynomial fit to the resulting  $p$  vs.  $(C(p) - C(0))/C(0)$  data points (cf. Eq. (5)), together with the knowledge of the pressure dependence of the dimensions of the capacitor (effective compressibility  $\kappa_{\text{eff}}$ ), yields  $3A_\varepsilon/RT$ . Since the susceptibilities of gases are very small (merely  $7 \cdot 10^{-5}$  at the TPW and a pressure of 0.1 MPa for helium), they cannot be determined by absolute capacitance measurements. Even relative measurements of corresponding capacitance changes with an uncertainty of a few parts in  $10^9$  cause extreme demands on the parameters of the audio-frequency capacitance bridge.

Up to now, two research groups performed primary DCGT using conventional cylindrical capacitors (left hand side of Fig. 2) for the determination of  $\varepsilon$  in the range from about 3 K to 27 K [31–33] with relative uncertainties of the order of 10 ppm. The measurements described in [33] resulted in the value of  $k$  which presently has the smallest uncertainty for a direct determination without knowledge of the Avogadro constant [11]. Applying Eq. (4), the values of  $a_0$  and  $m_e/m_\alpha$  recommended in [11], and a copy of the gas-thermometer scale NPL-75 as thermodynamic reference [34, 35], the measured ratio  $A_\varepsilon/R$  of  $6.22112(19) \cdot 10^{-8}$  K/Pa leads to a value of  $k = 1.38065(4) \cdot 10^{-23}$  J/K. The relative difference of this value of  $k$  from the CODATA-recommended value [11] of  $1.3806505(24) \cdot 10^{-23}$  J/K is no more than 0.4 ppm, far below the uncertainty level of about 30 ppm.

The main deficiency of the conventional cylindrical capacitors used to date is the fact that the whole length of the capacitor electrodes affects the effective compressibility  $\kappa_{\text{eff}}$ . For the system described in [33], for instance, the main uncertainty components result from the measurements of pressure  $p$  (5 ppm), relative capacitance changes  $[C(p) - C(0)]/C(0)$  (3 ppm), temperature (2 ppm), the determination of  $\kappa_{\text{eff}}$  (13 ppm), the possible influence of impurities in the gas (5 ppm), and surface layers on the capacitor plates (0.5 ppm) [33, 36]. An evaluation of the results obtained so far, considering especially the state-of-the-art level of accuracy of the measurements of pressure and capacitance shows that DCGT has the potential for both decreased relative uncertainty and increased application

## DCGT-Capacitors



**Figure 2:** Cross sections of different cylindrical capacitors for DCGT. The conventional design shown on the left has the deficiency that the whole length of the capacitor electrodes influences the estimation of the effective compressibility. On the contrary, the new design shown on the right has a ground shield also at the top that is not connected with the electrodes. This design allows the determination of the change of the most important dimension, the effective capacitor length, under pressure from outside, i.e. the determination of the main part of the effective compressibility *in-situ*. (The effective length is given by the distance between the small bottom and top ground-shield spacers located between the inner and outer cylindrical electrodes.) The plane mirror interferometers (PMIs) yield data on the deformation (movement and bowing) of the top plate of the outer ground shield. Since the bottom plate is rigidly mounted on a block (not shown), in first order, the change of the effective length of the capacitor is derived from the interferometer signals. A remaining uncertainty component results from the correction of the compression of the spacers. But since they are much shorter than the capacitor electrodes, the uncertainty of the compressibility correction is significantly reduced compared to the conventional design.

range at least up to the TPW. In the next few years the uncertainty can be reduced by an order of magnitude or more by the following measures: (i) optimising the capacitor design (using materials such as tungsten carbide, applying new design principles like cross, spherical or toroidal capacitors, etc., if possible with the same pressure in the surroundings as in the measuring capacitor), (ii) improving the parameters of the audio-frequency capacitance bridge, (iii) working with higher pressures up to about 7 MPa, and (iv) measuring  $\kappa_{\text{eff}}$  *in situ* by using, e.g., specially designed cylindrical capacitors and interferometric measurements [13, 36], see right-hand side of figure 2. The interferometric measurements allow to correct for the main part of the change of the effective capacitor dimensions under pressure caused by the movement of the ground shields. The remaining uncertainty results primarily from the pressure dependence of the length of the ground shield spacers.

Furthermore, the uncertainty of the pressure measurement will be decreased by a better calculation of the effective area of piston-cylinder assemblies of pressure balances from dimensional measurements recording also the distortions under pressure. For piston-cylinder assemblies with an effective area of 5 cm<sup>2</sup>, an uncertainty level of 5 ppm has already been achieved [37]. Though international

intercomparisons could not verify this level up to now, it is well supported up to 2 MPa by a comparison with a high-pressure mercury manometer and by intercomparisons with quite different pressure balances. These pressure balances were made by different manufactures, had different designs and widths of the piston-cylinder gap and different sources of the piston-cylinder materials (tungsten carbide), and were operated with gas as well as oil [38]. Further progress is expected by utilising piston-cylinder assemblies with larger effective areas and applying new techniques of length-measurement. These developments will allow the determination of  $k$  with an uncertainty comparable with that obtained with AGT.

### 3.3. Total radiation thermometry

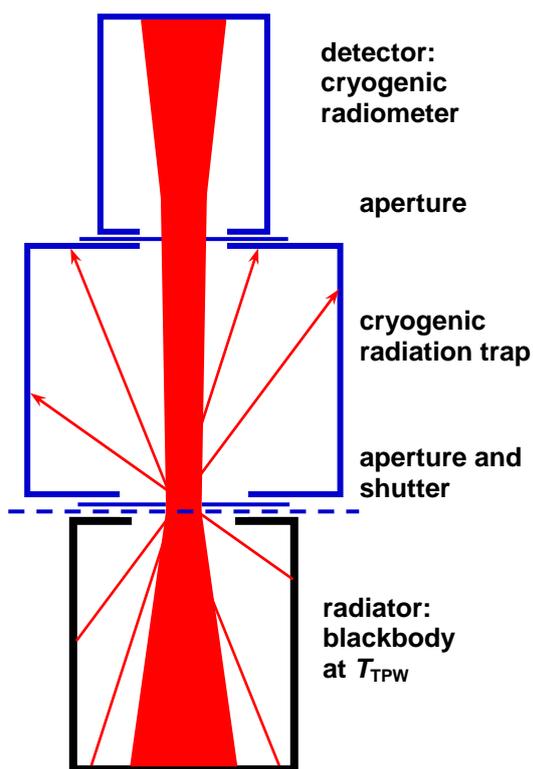
Absolute radiant power measurements of the radiation emitted by a blackbody with known temperature  $T$  (preferably  $T_{\text{TPW}}$ ) also provide another method of primary thermometry and allow to determine  $k$ . The total radiance  $L$  of an ideal blackbody (or the total radiant exitance  $M_{\text{rad}} = \pi L$ ) is given by the Stefan-Boltzmann law obtained by integration over all frequencies of Planck's law [39] for the spectral radiance (versus frequency  $\nu$ )  $L_{\nu} = (2h\nu^3/c_0^2) \{\exp[h\nu/(kT)] - 1\}^{-1}$ :

$$L = \frac{M_{\text{rad}}}{\pi} = \int_0^{\infty} L_{\nu} d\nu = \frac{\sigma}{\pi} T^4. \quad (6)$$

Here,  $\sigma = 2\pi^5 k^4 / (15c_0^2 h^3)$  is the Stefan-Boltzmann constant.

This kind of measurement is done with an "electrical substitution radiometer" (ESR) employing substitution of the radiative heating of the radiation detector by equivalent electrical heating (resulting in the same rise in temperature). After the ESR had been invented – independently, but practically simultaneously – by Kurlbaum and Ångström in 1892/93 [40], it took nearly a century before the UK's National Physical Laboratory (NPL) succeeded in distinctly reducing the measurement uncertainty of the device to well below 0.1% or even below 0.01% by developing and operating an ESR with a cavity detector (an "inverse blackbody" with absorptivity very close to 1) at cryogenic temperature [41]. Quinn and Martin [42, 43] used the very first "cryogenic radiometer" as an "Absolute Radiation Thermometer" (ART) for a determination of the Stefan-Boltzmann constant. A relative standard uncertainty of 130 ppm was stated for the value of  $\sigma$  obtained by combining the results of five series of measurements done with two sets of apertures of different diameters. This corresponds to a relative standard uncertainty of  $k$  of 32 ppm.

Figure 3 schematically shows the measuring set-up. Ideally, the set-up would do without the radiation trap, and radiator and detector would be separated by only a single aperture. However, the trap seems to be imperative in order to thermally separate the "hot" blackbody from the cryogenic cavity detector, and corresponding uncertainties seem to be unavoidable. The main contributions to the uncertainty of  $k$  in the Quinn-Martin measurements made with the larger-diameter aperture set [43, 44] were due to the



**Figure 3:** Schematic illustration of the measuring set-up for the determination of the Stefan-Boltzmann constant by means of total radiation thermometry at the TPW.

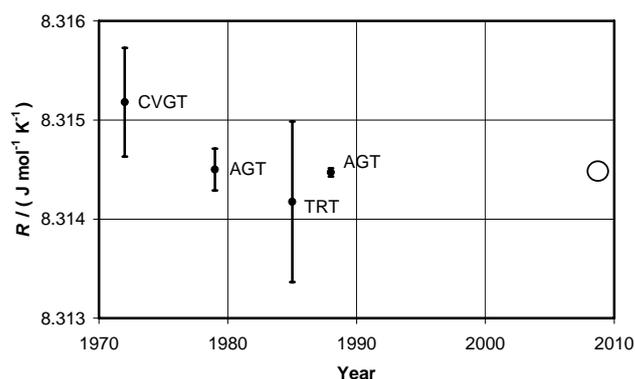
radiation transfer function giving the net emissivity and absorptivity of the combined radiator and detector assembly (35 ppm), the determination of the aperture geometry (22 ppm), diffraction effects (17 ppm), scattering from the side walls of the radiation trap (5 ppm), and absorption by the aperture land (5 ppm). According to today's knowledge, diffraction and scattering may have been even larger than estimated at that time [45].

Based on the experience gained in the earlier work, and in particular on the identification of the major sources of uncertainty, a significant improvement in the measured value of  $\sigma$  (and, thus,  $k$ ) seems to be possible today. Therefore, the NPL has undertaken to design and construct a second generation “Absolute Radiation Detector” (ARD) [46] similar to the Quinn-Martin ART, but incorporating design improvements of the blackbody, the geometrical system, and the cavity detector [44, 46–49]. As reported by Fox at the workshop [13], these improvements, together with a recent modification of the radiation trap, are expected to drastically reduce all of the major uncertainties of the Quinn-Martin measurement listed above, so that the combined uncertainty is expected to become 20 ppm for  $\sigma$  and 5 ppm for  $k$ .

The ARD is presently under evaluation at the NPL, and more results concerning its actual performance should soon become available. If it can in fact be used for a determination of the Boltzmann constant with reliable relative uncertainty of 5 ppm, this would certainly be a major advance of absolute radiation thermometry.

#### 4. THE UNIVERSAL NEW KELVIN

In order to illustrate the progress of measurements the history of determining the gas constant  $R = kN_A$  (where  $N_A$  is the Avogadro constant) is shown in Figure 4 [15]. In 1972 Batuecas [50] reviewed the last determinations based on absolute constant-volume gas thermometry (CVGT). The determination by acoustic gas thermometry (AGT, see Section 3.1) of Colclough *et al.* [51] was performed using a cylindrical interferometer. The determination by total radiation thermometry (TRT) of Quinn and Martin [43] is described in Section 3.3. Moldover *et al.* determined the gas constant by AGT with a spherical resonator in 1988 [12] (see Section 3.1).



**Figure 4:** Determinations of the gas constant  $R = kN_A$  in the past and prospects for the near future. The abbreviations are explained in the text. For clear readability, the error bars here indicate the uncertainties at the confidence level of 99%.

As shown by the recently published CODATA values for fundamental physical constants [11], the 2002 recommended value of the Boltzmann constant  $k$  with  $u_r(k) = 1.8 \cdot 10^{-6}$  is to a very large extent determined by the NIST result [12] and, therefore, is not yet regarded as sufficiently corroborated to replace the present definition of the kelvin. The important point to note here is that the measurement uncertainty of any value of  $k$  would be transferred to the value of  $T_{\text{TPW}}$ , if that  $k$  value were taken to be the exact value of the Boltzmann constant and used to define the kelvin. Hence, if the 2002 CODATA recommended value would be fixed as the exact value of  $k$  tomorrow, the best estimate of  $T_{\text{TPW}}$  would still be 273.16 K. However, this value would no longer be exact (as it is now as a result of the current definition of the kelvin), but would become uncertain by  $u_r(T_{\text{TPW}}) = 1.8 \cdot 10^{-6}$ , which corresponds to 0.49 mK. The issue to be decided by the thermometry community is whether or not this uncertainty is acceptable, and if not, how small an uncertainty is required.

Considering the aforementioned uncertainty estimates, the two most promising methods for reduction of the uncertainty of  $k$  currently are dielectric-constant gas thermometry (DCGT, Section 3.2) and acoustic gas thermometry (AGT, Section 3.1). It seems to be possible that the DCGT method at PTB or the AGT work of different groups will have been advanced so far by the end of 2009, that they can contribute to an improved value of  $k$  or  $R$  with similar relative uncertainty as that obtained by Moldover *et al.* [12] with the AGT in 1988. Thus, an improved value

of the Boltzmann constant proposed for definition of the kelvin would ideally have been determined by at least these two fundamentally different methods and be corroborated by other – preferably optical – measurements with larger uncertainty. We shall assume here that the experiments currently underway to measure  $R$  or  $k$  [15] will achieve a relative standard uncertainty by the end of 2009, which is a factor of about two smaller than the current  $u_r$  of approximately  $2 \cdot 10^{-6}$ , so that  $u_r(T_{\text{TPW}})$  will be reduced to about  $1 \cdot 10^{-6}$ , corresponding to about 0.25 mK, and that this will be small enough for the redefinition of the kelvin to be adopted by the 24<sup>th</sup> General Conference on Weights and Measures (CGPM) in 2011.

In the discussion about the new definition of the kelvin, it should also be recognised that the “practical” International Temperature Scale of 1990, ITS-90, is a defined temperature scale which assigns an exact temperature value  $T_{90}$  to each defining fixed point. Hence, the ITS-90 value of the TPW temperature will remain 273.16 K, that is,  $T_{\text{TPW}-90} = 273.16$  K exactly. The value and uncertainty of  $T_{\text{TPW}}$  would only need to be taken into account if for some critical reason one has to know how well the thermodynamic temperature scale is represented by the ITS-90 at a particular temperature or in a particular temperature range. In fact, although the consistency of  $T_{\text{TPW}}$  as realised by different TPW reference cells can be as low as 50  $\mu$ K (and even less if the isotopic composition of the water used is taken into account), the uncertainties of the thermodynamic temperatures of all other defining fixed points, which are the basis for all practical thermometry, are significantly larger [35]. In contrast to other units, the uncertainty of the realisation of the kelvin varies greatly with temperature: at 1300 K, for instance, the uncertainty is roughly 1000 times greater than at  $T_{\text{TPW}}$ . Hence, the fact that  $T_{\text{TPW}}$  will not be exactly known but have a standard uncertainty of 0.25 mK will have negligible practical consequences.

To support new determinations of the Boltzmann constant, the CCT recommended “that national laboratories initiate and continue experiments to determine values of thermodynamic temperature and the Boltzmann constant” [52], which is also asked for by the recent recommendation of the CIPM concerning preparative steps towards new definitions of the kilogram, the ampere, the kelvin and the mole [9]. As one result of the workshop held at PTB [13] in 2005, an iMERA/EUROMET joint research project [53] is now coordinating the European activities to determine the Boltzmann constant in France (LNE-INM/CNAM, LPL), Italy (INRIM, Universities of Naples and Milan), United Kingdom (NPL) and Germany (PTB). Since several NMIs are undertaking great efforts to determine the Boltzmann constant with high precision, a new and more accurate value based on AGT and DCGT is in fact to be expected about 20 years after the NIST result [12].

To put the new definition of the kelvin into practice a *mise-en-pratique* has already been recommended to the CIPM by the CCT [54]. These practical guidance notes will contain, in due course, “recommendations concerning the direct determination of thermodynamic temperature, the text of the ITS-90, the text of the Provisional Low Temperature

Scale PLTS-2000, a Technical Annex of material deemed essential for the unambiguous realisation of both the ITS-90 and the PLTS-2000, and a section discussing the differences  $T - T_{90}$  and  $T - T_{2000}$  together with their uncertainties.” In addition, the CCT asked for “approval by the CIPM of the text entitled ‘Technical Annex for the *mise-en-pratique* of the definition of the kelvin’, adopted by the CCT at its 23<sup>rd</sup> meeting, as initial entry to the Technical Annex.” This recommendation was approved by the CIPM at its 94<sup>th</sup> meeting in October 2005.

Consequently, the *mise-en-pratique* will allow direct determination of thermodynamic temperatures particularly at temperatures far away from the triple point of water in parallel to the realisation described in the International Temperature Scale. In the high temperature range this will considerably reduce the uncertainty of the realisation of the kelvin for many purposes for which the need to refer back to the TPW is anomalous, such as radiation thermometry.

It should also be recognized that experiments previously be aimed to determine the value of a fundamental constant with reduced uncertainty now become experiments be aimed at the realisation of a unit. For example, molar gas constant or Boltzmann constant experiments will no longer be carried out to determine  $R$  or  $k$  but rather to realise the kelvin. NMIs will undertake new experiments leading to knowledge of thermodynamic temperatures in terms of the new definition of the kelvin with uncertainties such that, on the long term, the International Temperature Scale might be dispensed with.

In Ref. [10], two alternative new definitions are suggested for each of the units kilogram, ampere, kelvin and mole to be chosen by the CGPM in 2011. The first type explicitly defines a unit in terms of a particular quantity of the same kind as the unit and, through a simple relationship implied by the definition itself or one or more basic laws of physics, implicitly fixes the value of a fundamental constant; we call these “explicit-unit definitions.” The second type explicitly fixes the value of a fundamental constant and, through a simple relationship implied by the definition itself or one or more laws of physics, implicitly defines a unit; we call these “explicit-constant definitions.” It should be understood that the alternative definitions for the same unit are in fact equivalent; they are only different ways of stating the same definition, and in no way should the choice of words be regarded as final at this stage.

The “explicit-unit definition” for the kelvin, as proposed for the first time in [14], could be as simple as “The kelvin is the change of thermodynamic temperature that results in a change of the thermal energy  $kT$  by exactly  $1.38065XX \cdot 10^{-23}$  joule.” This definition is comparable with the current definitions of other base units. The “explicit-constant definition” has no evident direct physical meaning and reads “The kelvin, unit of thermodynamic temperature, is such that the Boltzmann constant is exactly  $1.38065XX \cdot 10^{-23}$  joule per kelvin.”

Whichever definition will finally be chosen, we now come into the position that the kelvin and the other physical units considered are no longer related to human reach and

experience or restricted to human artefacts or special material's properties. In future, they will rely on fundamental constants and physical laws valid throughout the universe and should be stable in space and time. That means they are both, universal and sustainable.

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