

LESZEK LIPIŃSKI, ANNA SZMYRKA-GRZEBYK

Institute of Low Temperature and Structure Research
Polish Academy of Sciences, Wrocław
e-mail: A. Szmyrka@int.pan.wroc.pl

PROPOSALS FOR THE NEW DEFINITION OF THE KELVIN

1. INTRODUCTION

The International Committee for Weights and Measures (CIPM) has had a long-term aim of defining all of the base units in the terms of fundamental physical constants to eliminate any artifact on material dependencies. In 2005, in Recommendation 1, the CIPM approved preparative steps towards new definitions of the kilogram, the ampere, the Kelvin and the mole in terms of fundamental constants [1, 2].

The unit of temperature, the Kelvin, can be defined in terms of the SI unit of energy, the joule, by fixing the value of the Boltzmann constant k which is simply the proportionality constant between temperature T and thermal energy kT [3]. The new definition would be in line with modern science where nature is characterized by statistical thermodynamics, which implies the equivalence of energy and temperature as expressed by the Maxwell-Boltzmann equation. The Boltzmann constant k is not connected with the other fundamental constants, there are no alternatives to the linking of the Kelvin aside from the exact value of the constant k .

In practice, no universal instrument for measuring energy exists while energy appears in different forms, e.g. temperature. Currently, several experiments are underway to determine k using primary thermometers of different types [3, 4].

From the point of view of practical thermometry it is necessary to determine what uncertainty in the measured value of k is needed to apply it as the temperature unit. It would be of the order in the present realization of the triple point of water: $= 1.8 \times 10^{-7}$. At present its uncertainty is about one order of magnitude higher.

2. CURRENT DEFINITION OF THE TEMPERATURE UNIT

The current definition of the unit of the fundamental physical value - thermodynamic temperature - was adopted by the 10th General Conference on Weights and Measures (CGPM) in 1954, based on the proposal of Lord Kelvin from 1854. The

proposal was that the unit of thermodynamic temperature should be defined in terms of the interval between the absolute zero and one fixed point. The single point chosen was the triple point of water which was assigned the temperature of exactly 273.16 K.

For temperatures other than the triple point of water, direct measurements of thermodynamic temperature require a primary thermometry based on a well-understood physical system in which temperature may be derived from measurements of other quantities. In practice, the primary thermometry systems determining thermodynamic temperature directly are few in number and they are difficult in use, time consuming, expensive and much less reproducible than many practical thermometers. As an alternative, the practical temperature scales provide an internationally accepted recipe for realizing temperature in a practical way. The first international temperature scale was adopted in 1927 (ITS-27). The present scale – the International Temperature Scale of 1990 (ITS-90) [5] defined the practical temperature from 0.65 K up to thousands K.

Three main principles characterizing all the international practical scales are:

- thermodynamic temperature is the fundamental temperature to which all temperature measurements should be related
- because of difficulties in precise thermodynamic temperature measurements it is necessary to have for international use a practical scale that agrees with the thermodynamic temperature as closely as present knowledge permits
- the practical scale should be well-defined and easy to realize to allow for world wide uniformity of temperature measurements [6].

The scales have based on sets of fixed points, the defined temperatures of equilibrium states of certain specified substances and methods for interpolating between these points. The majority of present-day temperature measurements is not thermodynamic temperature but T_{90} , as defined by the ITS-90.

The units of practical and thermodynamic temperatures defined by the ITS-90 are identical and equal to $1/273,16$ of the thermodynamic temperature of the triple point of water. Thus, the Kelvin is linked to a material property – water. In practice, as the EUROMET comparisons have shown [7], the water triple point temperatures realized in different water reference cells differ within $50 \mu\text{K}$, what corresponds to an uncertainty $\pm 1.8 \times 10^{-7}$. The value could be even smaller ($\pm 1 \times 10^{-7}$) if a correction for isotopic effects was introduced. Looking for a new way of defining the temperature unit it is necessary to take into account what uncertainty could be achieved.

3. THE VALUE OF THE BOLTZMANN CONSTANT K

The Boltzmann constant k , which is the conversion factor between the thermal and mechanical energies of practice described by the Maxwell-Boltzmann equation :

$$E = k \times T, \quad (1)$$

is for the Kelvin the corresponding fundamental constant. To use the constant k for the redefinition of the temperature unit, k must be known with similar uncertainty as the triple point of water. At present its uncertainty is still about one order of magnitude higher. In 2002 CODATA recommended the value of $k = 1.3806505 \times 10^{-23} \text{ J K}^{-1}$ with the uncertainty 1.8×10^{-6} .

On January 21, 2005, a workshop on new methods for determining the Boltzmann constant k was held at Physikalisch-Technische Bundesanstalt (PTB) in Berlin [8]. The methods for determining k were based on primary thermometry and the thermal equation of state for an ideal gas. Three modern kinds of gas thermometry, constant volume gas thermometry CVGT, acoustic gas thermometry AGT and dielectric-constant gas thermometry DCGT are used for determining k . They are based on different simple relations between the properties of an ideal gas and the thermodynamic temperature T .

CVGT is based on the following equation of state:

$$pV_m = N_A k T, \quad (2)$$

where p is pressure, V_m – the molar volume of gas, N_A – Avogadro constant.

The principle describing acoustic gas thermometry is the relation:

$$c = (\gamma_0 R T / M)^{1/2}, \quad (3)$$

where c is the speed of sound, $\gamma_0 = c_p / c_v$ is the ratio of specific heat capacities at constant pressure and constant volume, $R = k N_A$ – the molar gas constant, M – the molar mass.

The basic idea of DCGT is to replace the density in the state equation of gas by the dielectric constant ε . For an ideal gas, this yields the simple relation between the pressure p and ε :

$$p = k T (\varepsilon - \varepsilon_0) / \alpha_0, \quad (4)$$

ε_0 is the dielectric constant and α_0 is the static electric dipole polarization of the atom.

Other ways of determining k include radiation thermometry TRT based on the Stefan-Boltzmann law and measuring the total radiation without spectral selection using a cryogenic radiometer. It is also possible to use refractive index gas thermometry RIGT, thermometry using quasi-spherical cavity resonators QSCR or Doppler-broadening thermometry DBT.

Uncertainty in determining the Boltzmann constant k by applying different methods of primary thermometry is given in Table 1. The table gives a summary overview of the currently-available primary thermometry and recent information on new developments [4, 8].

Data presented in the table show that within a few years there exists the possibility of achieving a reliable uncertainty of the value of k of the order of one part in 10^{-6} . The two methods of primary thermometry promising the most significant reduction

Table 1. Uncertainty in determining the Boltzmann constant k by applying different methods of primary thermometry.

Method	Present state, ppm	2010 possibility, ppm
AGT	2	1
DCGT	15	2
TRT	32	5
QSCR	40	10
RIGT	300	30
DBT	200	10

of the uncertainty of k are DCGT and AGT. If the experiments to measure R or k currently underway will achieve consistent results it could be expected that the Boltzmann constant k could be used for the redefinition of the Kelvin.

4. PROPOSALS FOR THE NEW DEFINITION OF THE KELVIN

One of the first proposals of the new definition of the Kelvin was given in [3]: *The Kelvin is the change of thermodynamic temperature that results in a change of thermal energy kT by $1.38065XX \times 10^{-23}$ joule.*

The XX will be replaced with the appropriate digits of the Boltzmann constant when the new definition is established. The intention of the redefinition is to move away from any material substance. The definition is to be realized by different types of primary thermometers. However, the symbols k and T are undefined in that definition.

Other proposals for the new definition of the Kelvin which are taken into account are [4]:

The Kelvin is the change of thermodynamic temperature T that results in a change of thermal energy kT by exactly $1,38065XX \times 10^{-23}$ joule, where k is the Boltzmann constant

and the following definition which relates a definition of the Kelvin to a gas:

The Kelvin is the thermodynamic temperature at which the mean translational kinetic energy of atoms in an ideal gas at equilibrium is exactly $(3/2) \times 1,38065XX \times 10^{-23}$ joule.

This definition, by replacing “thermal energy ” with “mean translational kinetic energy” leads to the need of explanation of many details and, therefore, becomes more complicated than it could be expected.

Next definition:

The Kelvin is the thermodynamic temperature at which particles have an average energy of exactly $(1/2) \times 1.38065XX \times 10^{-23}$ joule per accessible degree of freedom

needs to define “particle” further – it cannot apply to all particles, e.g. photons.

These definitions show that it is difficult to produce a satisfactory explicit-unit definition. It seems that the most universal definition for the Kelvin, which is sufficiently

wide to accommodate future developments and does not favor any special primary thermometer for realizing the Kelvin, is that given by Mills et al. [9] and recommended by the task group TG-SI of CCT:

- ***The Kelvin, unit of thermodynamic temperature, is such that the Boltzmann constant is exactly $1,380\ 65XX \times 10^{-23}$ joule per Kelvin.***

5. STATUS OF ITS-90 IN FUTURE

If one of the definitions is adopted and the Boltzmann constant k value is taken to be exact and used to define the Kelvin, there will be a number of consequences for temperature measurements. Presently, the water triple point temperature used for the temperature definition equals 273.16 K **exactly**, but instead of the exact value a standard uncertainty of the water triple point temperature will be given. The smallest uncertainty in k , obtained so far in experiments at the NIST with acoustic thermometry is 1.7×10^{-6} which is equivalent to an uncertainty of temperature measurement of 0.46 mK at the triple point of water. The uncertainty will propagate to thermodynamic temperature measurements because they are defined as ratios with respect to the triple point of water. In practice, the definition will only affect measurements made close to 273 K because the uncertainties of the thermodynamic temperatures well away from this value are much larger than 0.46 mK. Table 2 presents chosen defining fixed points of the ITS-90 with different type of uncertainties.

Table 2. Defining fixed points of the ITS-90 with uncertainty $u(T_{90})$ of the best practical realization in terms of ITS-90, uncertainty $u(T)$ of the thermodynamic temperature and uncertainty $u(T_{k\text{fixed}})$ in the thermodynamic temperature of the phase transitions assuming a new definition for the Kelvin with a fixed value for the Boltzmann constant k .

Fixed point	T_{90} , K	$u(T_{90})$, mK	$u(T)$, mK	$u(T_{k\text{fixed}})$, mK
Cu	1357.77	15	60	60.1
Al	933.473	0.3	25	25.1
Zn	692.677	0.1	13	13.1
Sn	505.078	0.1	5	5.10
In	429.7485	0.1	3	3.11
Ga	302.9146	0.05	1	1.15
H ₂ O	273.16	0.02	0	0.46
Hg	234.3156	0.05	1.5	1.55
Ar	83.8058	0.1	1.5	1.50
O ₂	54.3584	0.1	1	1.00
Ne	24.5561	0.2	0.5	0.50
H ₂	13.8033	0.1	0.5	0.50

All values in the table are quoted as standard uncertainty. The values $u(T_{90})$ and $u(T)$ are taken from the *Supplementary Information for the ITS-90* [10].

The CIPM proposal is to make the international scale as “*mise en pratique*” of the Kelvin [11]. In the aim investigations on improvement of the ITS-90 realization and more accurate determination of fixed points temperature value have been carried out in the word intensely. In a frame of the FW 5 European Project – No G6RD-CT-1999-00114 *Improvement of European traceability in temperature measurements below 0°C using permanently-sealed transportable multicell standards – MULTICELLS* [12, 13] isotopic and other influences on the realization of the triple point of hydrogen were determined [14] and a proposal of amendment of the ITS-90 definition concerning the point temperature was sent to the CCT [15]. An isotopic composition influence on the temperature of the water triple point [16] and cryogenics fixed points [17, 18] is determined at the present. As well the temperature value of other fixed points of the ITS – primary and secondary – are verificated to improve an accuracy of their realization [19, 20].

In the activities of national metrological institutes (NMI’s) the Institute of Low Temperature and Structure Research of the Polish Academy of Sciences in Wroclaw, where the Polish national temperature standard for the temperature range between 13.8033 K and 273.16 K [21] was established on the force of the President of the Central Office of Measures¹ decision in 2001, participates too.

6. CONCLUSIONS

Today, the Kelvin is defined in terms of temperature of the triple point of water and the Boltzmann constant k is a measured quantity. The CIPM proposal is to define a numerical value for k , from which it follows that all temperatures must be measured. If in 2010 the required experimental data are available and the uncertainty of k determination is sufficiently small, the new definition of the Kelvin could be adopted in 2011. The ITS-90 will be the *mise en pratique* of the definition of the Kelvin.

The CIPM publishes guidelines for temperature measurement to help users make accurate and reliable temperature measurements. It comprises recognized approximations to the thermodynamic temperature currently including ITS-90. In future, the *mise en pratique* will be expanded to describe recognized primary thermometers or realizing the scale together with there uncertainties.

REFERENCES

1. *Recommendation 1 (CI-2005): Preparative Steps Towards New Definitions of the Kilogram, the Ampere, the Kelvin and the Mole in Terms of Fundamental Constants* – CIPM, Sevres, 2005.

¹ Główny Urząd Miar.

2. Becker P., De Bievre P., Fujii K., Glaeser M., Inglis B., Luebbig H., Mana G.: "Considerations on future redefinitions of the kilogram, the mole and the other units", *Metrologia*, vol. 44, 2007, pp. 1–14.
3. Fischer J., Fellmuth B., Seidel J., Buck W.: "Towards a new definition of the Kelvin: Way to go", *Proc. of TEMPMEKO 2004, 9th International Symposium on Temperature and Thermal Measurements in Industry and Science*, vol. 2, Zagreb-Croatia, 2005, pp. 13–19.
4. Fischer J., Gerasimow S., Hill K.D., Machin G., Moldover M.R., Pitre L., Steur P., Stock M., Tamura O., Ugur H., White D.R., Yang L., Zhang J.: "Preparative Steps Towards the New Definition of the Kelvin in Terms of the Boltzmann Constant", *Int. J. Thermophys.*, vol.28, 2007, pp. 1753–1765.
5. Preston – Thomas H.: "The International Temperature Scale of 1990 (ITS – 90)", *Metrologia*, vol. 27, 1990, pp. 3–10.
6. Quinn T.: "Temperature scales and units and implications for practical thermometry of a possible redefinition of the Kelvin in terms of the Boltzmann constant",
 1. BIPM, Document CCT/05–26.
 7. Renaot E., et all.: "Comparison of realizations of the triple-point of water; EUROMET project No. 549", *Proc. of TEMPMEKO 2004, 9th International Symposium on Temperature and Thermal Measurements in Industry and Science*, vol. 2, Zagreb-Croatia, 2005, pp. 1009–1016.
 8. Fellmuth B., Fischer J., Gaiser C., Buck W.: "Workshop of Methods for New Determinations of the Boltzmann Constant", *Working Document CCT/05–02 on the 23rd Meeting of the CCT, BIPM*, Sevres 2005.
 9. Mills I. M., Mohr P. J., Quinn T. J., Taylor B. N., Williams E. R.: "Redefinition of the kilogram, ampere, Kelvin and mole: a proposed approach to implementing CIPM recommendation 1 (CI–2005)", *Metrologia*, vol. 43, 2006, pp. 227–246. [10.] Preston – Thomas H., Blombergen P., Quinn T. J.: "Supplementary Information for the ITS-90", *BIPM*, Sevres 1990.
 11. CCT, Document "Mise en pratique for definition of the Kelvin", *BIPM*, 2006, available at www.bipm.org.
 12. Pavese F., Fellmuth B., Head D., Hermier Y., Peruzzi A., Szmyrka-Grzebyk A., Zanin L.: "MULTI-CELLS" the European Project on Cryogenic Temperature Fixed Points in Sealed Cells, *Temperature, Its Measurement and Control in Science and Industry*, vol. 7, American Institute of Physics, Melville, 2003, pp. 161–167.
 13. Fellmuth B., Hermier Y., Pavese F., Szmyrka-Grzebyk A., Tew W.: "Special Problems when Realising the Triple Point of Hydrogen as a Defining Fixed Point of the ITS-90", *Proc. of 8th International Symposium on Temperature and Thermal Measurements in Industry and Science*, TEMPMEKO'2001, pp. 403–410.
 14. Fellmuth B., Wolber L., Hermier Y., Pavese F., Steur P. P. M., Peroni I., Szmyrka-Grzebyk A., Lipinski L., Tew W. L., Nakano T., Sakurai H., Tamura O., Head D., Hill K. D., Steele A. G.: "Isotopic and other influences on the realisation of the triple point of hydrogen", *Metrologia*, vol. 42, 2005, pp. 171–193.
 15. Pavese F., Fellmuth B., Head D., Hermier Y., Sakurai H., Steele A. G., Szmyrka-Grzebyk A., Tew W. L.: "Proposal of amendment of the ITS-90 definition concerning the triple point of equilibrium hydrogen", *Document BIPM – CCT/01-07, 21 Meeting of the CCT, BIPM*, Paris 2001.
 16. Peruzzi A., Kerhof O., de Groot M.: "Isotope and Impurity Content in Water Triple-Point Cells Manufactured at Nmi VSL", *Intern. Journ. of Thermophysics*, 2007, vol. 28, pp. 1931–40.
 17. Tew W. L.: "Estimating the Triple-Point Isotope Effect and the Corresponding Uncertainties for Cryogenic Fixed Point", *Intern. Journ. of Thermophysics*, 2008, vol. 29, pp. 67–81.
 18. Pavese F., Fellmuth B., Hill K. D., Head D., Hermier Y., Lipinski L., Nakano T., Peruzzi A., Sakurai H., Smyrka-Grzebyk A., Steele A. G., Steur P. P. M., Tamura O., Tew W. L., Valkiers S., Wolber L.: "Progress Towards the Determination of the Relationship of the Triple-Point Temperature versus Isotopic Composition of Neon", *Intern. Journ. of Thermophysics*, 2008, vol. 29, pp.57–66.

19. Lipinski L., Kowal A., Szmyrka-Grzebyk A., Manuskiewicz H., Steur P. P. M., Pavese F.: "The triple point of nitrogen", *Metrologia*, vol. 43, 2006, pp. 435–440.
20. Lipiński L., Kowal A., Szmyrka-Grzebyk A., Manuskiewicz H., Steur P. P. M., Pavese F.: "The Transition of Nitrogen", *Intern. Journ. of Thermophysics*, vol. 28, 2007, pp.1904–1912.
21. Szmyrka-Grzebyk A., Lipinski L., Manuskiewicz, Kowal A.: "A National Temperature Standard between 13,8033 K and 273,16 K", *Proc. of the 2nd International Seminar and Workshop on Low Temperature Thermometry*, Wroclaw 2003, pp.79–84. 22. Szmyrka-Grzebyk A., Lipinski L., Manuskiewicz H., Kowal A.: "Cryogenic temperature standards in Poland", *Pribory*, 2007, vol. 85 (7), pp. 16-19. (in Russian).