Welcome to the Newsletter of Real-K!

Welcome to the third Newsletter of Real-K. The research in Real-K has been progressing apace in the last number of months and there are significant highlights to report. I highlight a few which give just an indication of what has been achieved.

Of particular note are:

a) All required high temperature fixed points (HTFPs), WC-C, Ru-C, Pd-C and Fe-C have been constructed. These have been compared and ranked according to criteria such as melting range, repeatability, plateau shape and value of the inflection point. Preparation is now underway for thermodynamic temperature assignment to the HTFP cells.

b) The primary Magnetic Field Fluctuation Thermometer (pMFFT) has demonstrated smooth overlap between ITS-90 and PLTS-2000 in the range 0.6 K and above 1 K. Germanium based Coulomb Blockade Thermometers (CBTs) have been constructed with 100 nm Al junctions for operation between 1 and 25 K. Comparisons have been performed at PTB between pMFFT and CBT and good agreement found between 2.5 K and 25 K.

c) Great progress has been made on quantifying Type 1 non-uniqueness uncertainties resulting in a recent paper Peruzzi et al (2021) Metrologia 58 035009. Good progress has been made on construction and characterisation of possible alternative fixed points to Hg, namely fixed points based on SF6 or CO2.

d) Great progress has been made in ab initio calculations of thermophysical quantities of gases and facilitating practical gas thermometry in the medium term. One particular highlight is a six-fold improvement in the accuracy of the second virial coefficient B(T) and second acoustic virial coefficient $\beta_a(T)$ for helium-3 and helium-4 between 1 K and 400 K. An open access paper describing these results (P. Czachorowski et al Physical Review A) has been published.

As reported in the last newsletter all our project meetings have moved on-line and are now held over Microsoft teams. Although not a perfect substitute for face-to-face gatherings the meetings have allowed regular reporting of project progress, discussion of technical issues and planning of the next periods research activities. The last on-line meeting was in April 2022 but we hope that the next, and closing meeting, of the project will be held in-person.

The project had its mid-term 18-month review, and I am pleased to report that the expert reviewers endorsed the globally dominant position of the consortium with regards primary thermometry and in realising the redefined kelvin and they agreed that the work we are undertaking is of substantial impact.

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The on-going conflict in the Ukraine has brought some disruption to the project's research and impact activities. The consortium had to take the decision, in line with recommendations from the EURAMET Board of Directors, to suspend project participation of our Russian colleagues from VNIIOFI. In addition, a joint workshop between EURAMET and COOMET, examining the progress in realising the redefined kelvin, was organised and to have been held in Bratislava in April 2022. However, this has had to be postponed and will now be held in April 2023 at the next EURAMET TC-T but without COOMET participation.

As we emerge from the COVID-19 pandemic there will be two very good opportunities in the next year to present, in person, all the good results from the Real-K project. The first is at the 21st International Congress of Metrology to be held in Lyon on 7-10 March 2023, https://www.cim2023.com/en/. The second is at the International Temperature Symposium held at Anaheim California 3-7 April 2023, https://its10.msc-conf.com/. The latter is widely regarded as the premier conference for all things related to temperature measurement and is an event not to be missed. I am looking forward to taking part and seeing many of you there!

Professor Graham Machin FREng

Real-K Project Coordinator

Research highlights

New thermodynamic temperature references based on high-temperature fixed point (HTFP) cells

Thermal effects on high-temperature fixed points

One of the objectives of the work package one is to determine the uncertainty components associated with the thermal conditions of the implementation of the cells. Indeed, it has been proven in former projects that the temperature gradient along the cell, the furnace offsets used for the initiation of the melt and possibly even the inertia of the furnace can have a non-negligible effect on the melting temperature and the repeatability of the phase transition.

To complete the characterisations performed during the first part of the project, further investigations were performed on Fe-C and Pd-C cells in finely-tuneable three-zone furnaces. The idea is to derive the effect of controlled temperature gradient around the cells on the melting temperatures and the plateau shapes.

Figure 1 shows an example of the measurements performed at INRIM showing the effect of the temperature gradient (0 °C being a uniform temperature along the cell, the ideal condition).

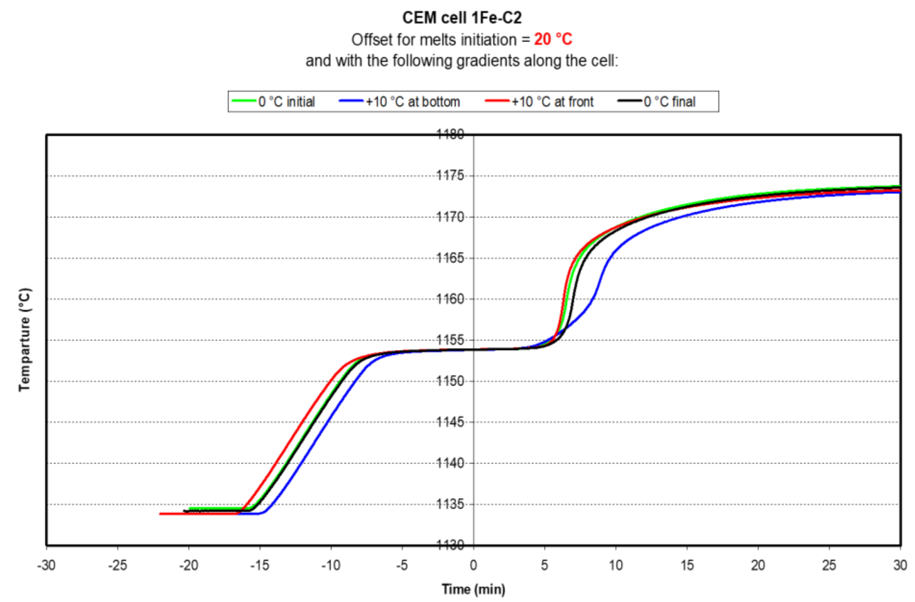

Figure 1- Study of the effect of the temperature gradient on the plateau shapes and the melting temperatures of an Fe-C cell

Selection of cells for thermodynamic temperature assignment

The cells produced and characterised during the first part of the project were gathered in 4 different laboratories, one for each high-temperature fixed point type, to identify the two best performing cells for each point to be used during the collective thermodynamic temperature assignment activity.

The main selection criteria were:

- the melting temperatures: it is commonly agreed that high melting temperatures are a good guarantee of the quality of the cell, especially in terms of purity of the metals. So, the cells with the highest melting temperatures were ranked first.
- the quality of the melting plateaux: the melting range, the shape of the plateau and the repeatability of the melting temperatures are indicators of the quality of the cell, but they can also be affected by the thermal environment.

Each of the testing laboratories (namely INRIM for Fe-C, CEM for Pd-C, NPL for Ru-C and LNE-Cnam for the WC-C) ranked the cells according to these criteria and a set of 8 cells were identified as the best candidates for the thermodynamic temperature assignment.

Thermodynamic temperature assignment

The circulation of the cells was organised in two loops in parallel:

- Loop A: PTB, CEM, LNE-CNAM, NPL
- Loop B: VNIIOFI, TUBITAK-UME, NIM, INRIM

Each laboratory is asked to perform a thermodynamic temperature measurement at the melting point (inflection point) of the 4 circulating cells at the points of Fe-C, Pd-C, Ru-C and WC-C. Figure 2 shows the experimental set-up of CEM devoted to this activity.

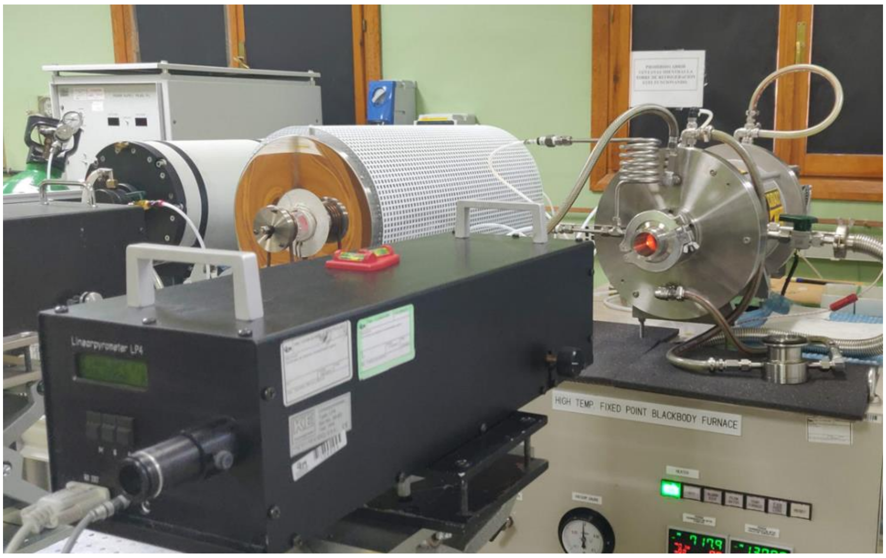

Figure 2- Facilities at CEM devoted to the study of high temperature fixed point cells

Ten months before the end of the project, the cells are still circulating among the participants and the first results are expected in the next weeks. The cells will be gathered in the testing laboratories at the end of the circulation to be compared and to detect any drift to be accounted for during the final assessment of the thermodynamic temperature of the phase transitions.

"Fast" acoustic gas thermometer

WP2 aims at supporting the realisation and dissemination of the kelvin by different kinds of practical primary thermometry in the temperature range from 1 K to 25 K. One of the classical primary thermometers in that temperature range is the acoustic gas thermometer (AGT). Now, LNE-Cnam has developed the fast acoustic gas thermometer ("fast-AGT") for the range from 4 K to 25 K making feasible the application of AGT in practical primary thermometry. Fast-AGT differs from conventional AGT because measurements are performed at one single gas pressure, instead of a set of several pressures. This enables substantially "faster" measurements with respect to conventional AGT and simplifies calibration processes and practical dissemination of thermodynamic temperature. However, a reference thermodynamic temperature is always necessary, and this has to be measured by conventional AGT. LNE-Cnam has first developed the fast measurement technique at microwave frequencies, on a single-pressure refractive index gas thermometer, in cooperation with TIPC of the Chinese Academy of Science [1]. Then, this fast-AGT technique has been transferred to a special pulse-tube cooled cryostat (see figure) at LNE-CNAM, where classical and fast-acoustic measurements have been carried out in parallel. The results have demonstrated good agreement between both methods. In addition, extensive measurements have been carried out at the triple point of neon [2].

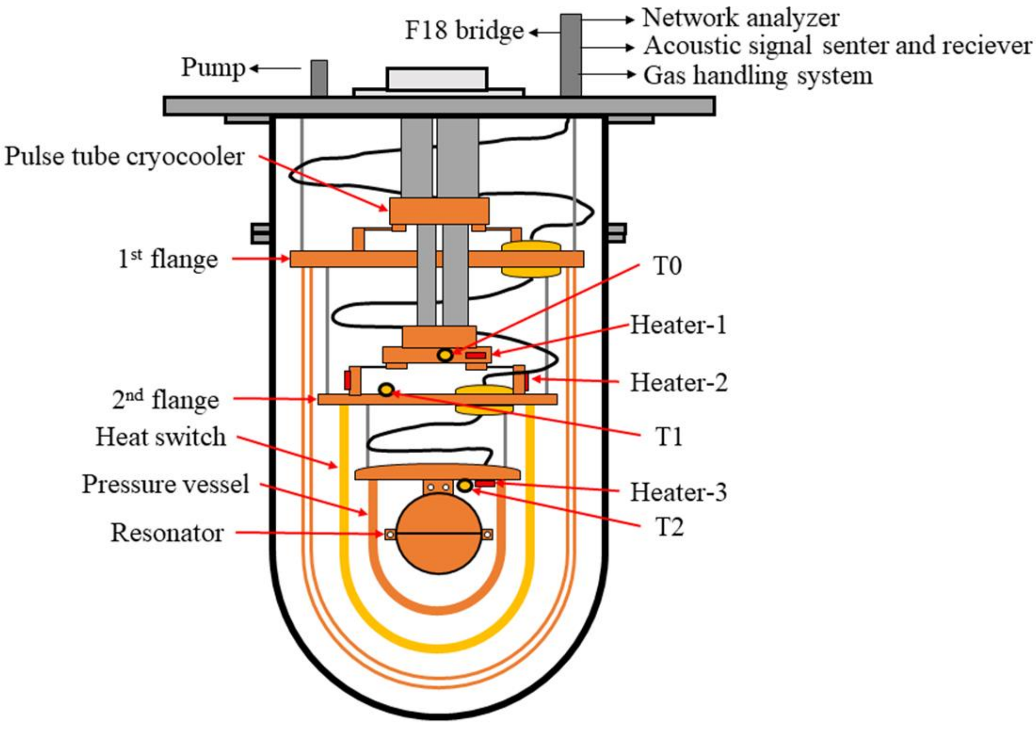

Figure 3: Schematic diagram of the cryogen-free cryostat used for acoustic gas thermometry from [2].

References:

1. Bo Gao et al., Metrologia **57**, 065006 (2020), https://doi.org/10.1088/1681-7575/ab84ca
2. Changzhao Pan et al., Metrologia **58**, 045006 (2021), https://doi.org/10.1088/1681-7575/ac0711

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Extending the life of the International Temperature Scale of 1990

Mercury is a defining fixed-point of the ITS-90 but it is highly toxic and increasingly subject to restrictions on its use. To prepare for the eventuality of such restrictions, two threads are being pursued in Real-K WP3: the development of alternative fixed points, and alternative interpolation schemes to those provided by the ITS-90.

New CO2 fixed-point cell developed

A new CO_2 fixed-point cell has been developed by TUBITAK which has shown a reproducibility of 0.1 mK. The emphasis of this design is on usability for practitioners by being immersed in a stirred liquid bath, which is present in a large number of calibration laboratories, and so does not require specialist equipment. A dedicated thermal enclosure provides temperature homogeneity of a few mK along the sample height. Importantly, the cell can be used to calibrate long-stem SPRTs, which is the calibration service that most end-users need.

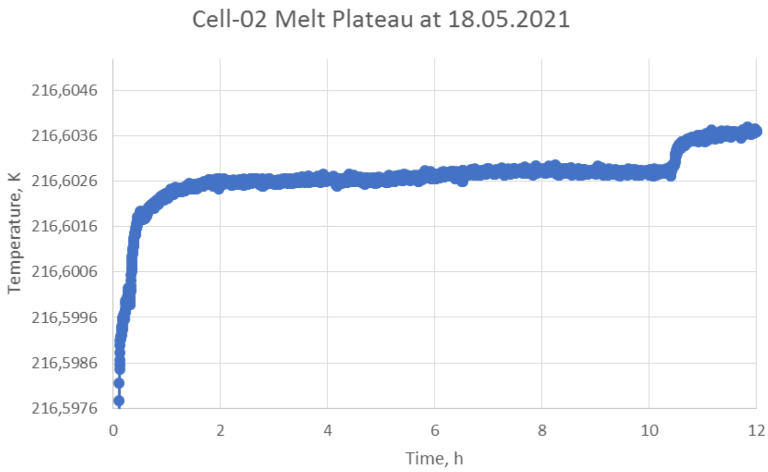

Figure 4: Melt Plateau of CO2 fixed-point cell-02

Alternative ITS-90 interpolation schemes investigated

The effect of eliminating mercury from the ITS-90 interpolation schemes has been investigated using real SPRT calibration data. The difference between interpolations over the ranges Ar-TPW-Ga and Ar-Hg-TPW (TPW is the triple point of water) using the ITS-90 equations 13 and 14 (top figure) were compared with the same difference in interpolations using a quadratic equation (bottom figure). The quadratic interpolation is clearly superior and yields non-uniqueness which is lower by about 20%. The bias away from absolute zero temperature for the ITS-90 equations is due to the well-known inconsistency of the mercury triple point and the gallium melting point. The dispersion values for the SPRTs is partly due to the differences in their characteristics (Type 3 non-uniqueness) but much, or possibly most, is due to the propagated errors or uncertainties in the realisations of the Hg and Ga points. The discontinuity at the TPW is clearly visible; this can be rectified by removing the Hg point from the ITS-90.

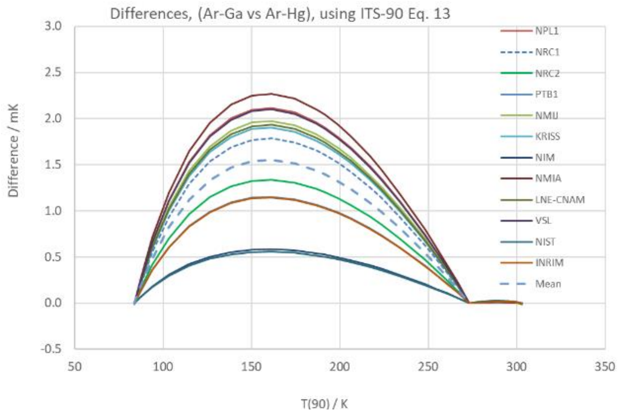

Figure 5: Alternative ITS-90 interpolation schemes, using ITS-90 Eq.13

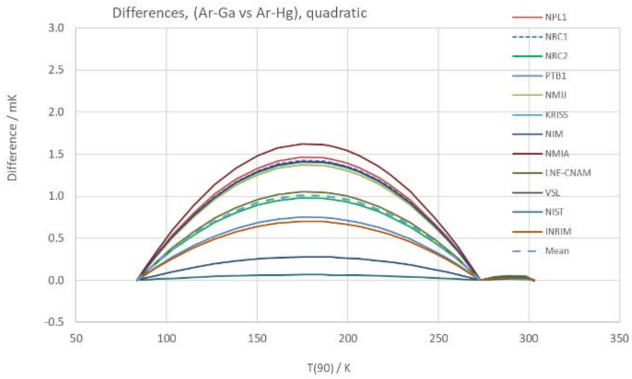

Figure 6: Alternative ITS-90 interpolation schemes: quadratic

Facilitating full range primary thermometry

The aim of this objective is to reduce the uncertainty of several primary thermometry methods, which are included in the Mise en Pratique for the definition of the kelvin, namely acoustic (AGT), dielectric constant (DCGT) and refractive index (RIGT) gas thermometry, and to extend the application range of these methods. These achievements will promote the development of simplified procedures for the direct dissemination of the thermodynamic temperature.

Theoretical ab initio calculation of thermometric gas properties

The improvement and simplification of primary thermometry methods requires the accurate knowledge of several thermophysical properties which enter in the corrections applied to account for the non-ideality of thermometric monatomic gases. For the sake of accurate acoustic thermometry (AGT) these properties include density- and acoustic virial coefficients as well as thermal conductivity. For thermometers based on the experimental determination of electromagnetic properties of gases, like dielectric constant (DCGT) and refractive index gas thermometry (RIGT), accurate estimates of properties like electrical polarizability, magnetic susceptibility and dielectric virials are also needed. The substantial theoretical and computational effort implied by these requirements is being shared among the Real-K and the QuantumPascal EMPIR projects, with a focus of Real-K on the improved determination of thermodynamic and transport properties of He, Ne and Ar.

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Over the last two years, remarkably accurate calculations of the second virial coefficient $B(T)$ and the second acoustic virial coefficient $\beta_a(T)$ of He have been reported by the Quantum Chemistry Laboratory of the University of Warsaw (UW). More recently, the same group has achieved an improved calculation of the three-body potential of He whose publication is expected within 2022. Remarkable progress has also been recently achieved and published by the European Centre for Theoretical Studies in Nuclear Physics (ECT*) of the Bruno Kessler Foundation (FBK) in cooperation with the National Institute of Standards and Technology (NIST), reporting the improved calculation of the 4th density virial coefficient $D(T)$ of helium isotopes (^{4}He and ^{3}He), by path-integral Monte Carlo (PIMC) method and state-of-the-art two-body and three-body potentials between 2.6 K and 2000 K. In 2020, the same collaboration had published corrections to their previous estimates of the 3rd density virial coefficient $C(T)$ of helium. All the progress so far achieved reinforces the choice of He as the reference substance for most accurate thermometric work.

Ongoing work within the Real-K project is focused on the improved calculation of the properties of heavier atomic gas, like Ne and Ar, which are less sensitive to contamination issues and may significantly increase the practical, reliable application of the same primary thermometry methods. New interatomic potential energy and interaction-induced polarizability curves for two ground-state Ne atoms were developed and published in 2021 by the Helmut Schmidt Universität (HSU) and used to predict the second density, acoustic, and dielectric virial coefficients and the dilute gas shear viscosity and thermal conductivity of Ne. In addition to these first-principles calculations, highly accurate dielectric-constant gas thermometry (DCGT) datasets measured at the Physikalisch-Technische Bundesanstalt (PTB) at temperatures from 24.5 K to 200 K were analyzed to obtain the difference between the second density and dielectric virial coefficients with previously unattained accuracy. The agreement of the DCGT values with the calculations from theory resulted to be very satisfactory. Finally, an improved three-body potential for Ar is at an advanced stage of development by UW, expected to be completed within 2022.

Measurement of thermodynamic properties of selected atomic systems

Among thermodynamic properties, speed of sound and density have a special importance, as they allow to determine directly the temperature-dependent deviations from ideality and can be determined experimentally with low uncertainties. These experiments can validate the theoretical results, where they currently suffer larger uncertainties, and drive the selection of appropriate alternative computational tools.

Speed-of-sound measurements in Ne between 200 K and 420 K at pressures up to 100 MPa, previously reported by the Helmut Schmidt Universität (HSU), are expected to be published within 2022. Recently, HSU has completed an apparatus suitable for speed of sound measurements at high pressure and cryogenic temperatures, down to 90 K. Together with the results of speed of sound measurements in argon in the range 120 K to 330 K previously obtained by NPL, the analysis of these sets of data will provide estimates of the acoustic virial coefficients of Ne and Ar which might support the accuracy of improved ab initio calculations of the same properties.

Coupled dielectric constant gas thermometry (DCGT) and Burnett expansion experiments with He and Ar have progressed at the Physikalisch-Technische Bundesanstalt (PTB). For He, measurements at 273.16 K and 296 K were completed allowing to determine the 2nd and 3rd density virial coefficients $B(T)$ and $C(T)$. The relative standard uncertainty of the 2nd virial $u_r(B)$ is lower than 1% and the results found consistent with the most recent theoretical estimates. For Ar, previous measurements in the temperature range between 253 K and 303 K with relative standard uncertainties $u_r(B)$ = 0.5 % and $u_r(C)$ between 1.5 % and 3 % were obtained. In 2021 and 2022 measurements for Ne were also completed using the same apparatus. Publication of all these results is expected in 2022.

An acoustic gas thermometer for use in the cryogenic range down to 10 K has been completed at the Istituto Nazionale di Ricerca Metrologica (INRiM). Measurements of speed of sound in He and Ne have started in April 2021 and will continue throughout

2022 with the aim of providing accurate estimates of the second acoustic virial coefficient $\beta_a(T)$ of these gases before the end of the project. Preliminary results obtained with He at 13.8 K were analyzed and compared to the best theoretical estimates of the second and third acoustic virials. The results of this comparison are illustrated in Figure 7 below.

A RIGT version of the same cryogenic apparatus had been previously used at INRiM to determine the 2nd density virial of Ne in the temperature range between 54 K and 161 K. These determinations, published in 2021, compare favourably with the most accurate theoretical estimates published by HSU and additional measurements of the same property by PTB.

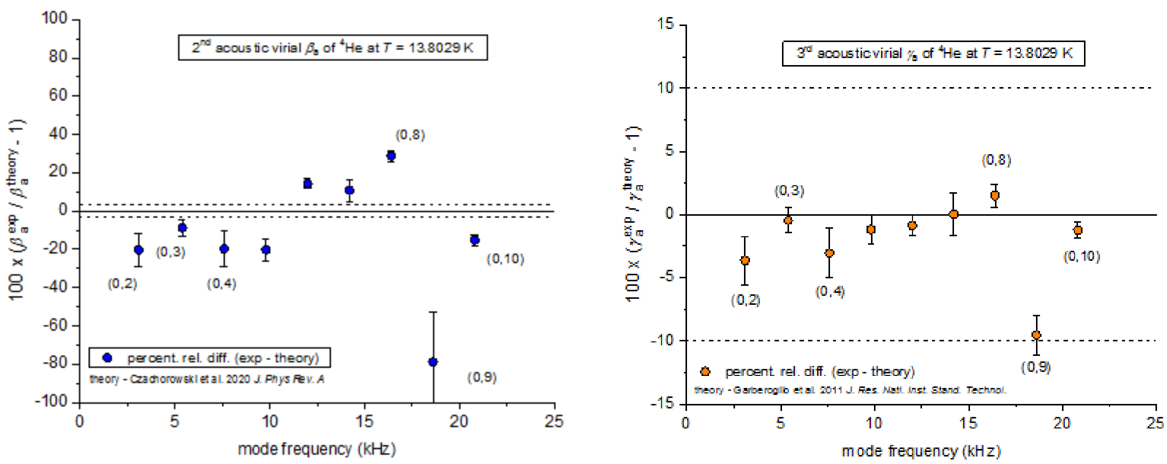

Figure 7: Comparison between experimental determinations of the 2nd and 3rd acoustic virial coefficients of He at 13.8 K and the best theoretical predictions of the same properties. The uncertainty bars and the dashed lines represent the uncertainty of experiment and theory respectively.

Implementing improved primary thermometry

A major objective of the Real-K project regards the simplification of two primary thermometry methods, namely DCGT and RIGT. It has been reported by PTB that a commercial version of DCGT, i.e. an apparatus based on commercially available instrumentation, has performed with absolute uncertainties of a few mK when operated with Ar at temperatures up to 303 K. Further development of the apparatus will continue in 2022.

At INRiM, a RIGT primary thermometer was operated between 13.5 K and 161 K with an absolute uncertainty of 1.8 mK at 161 K. From these measurements, accurate estimates of the differences (T−T90) using He and Ne have been published in 2021. A second RIGT apparatus was used in 2021 to determine the refractive index of He and Ar at 273.16 K, in the pressure range between 200 kPa and 1 MPa. Though the main objective of these measurements is to test the performance of a primary microwave pressure standard, the same data can be analyzed for thermometry when a calibrated pressure balance is used as a reference. This type of analysis, which is currently being completed, provided differences from a calibrated thermometer within ± 3 mK. RIGT measurements over a wider pressure range up to 7 MPa will continue in 2022.

Dissemination of project results

Scientific articles

1. C Gaiser, B Fellmuth Primary thermometry at 4 K, 14 K, and 25 K applying dielectric-constant gas thermometry *Metrologia* https://doi.org/10.1088/1681-7575/ac0d4a

2. Bo Gao, *et al* Measurement of thermodynamic temperature between 5 K and 24.5 K with single-pressure refractive-index gas thermometry *Metrologia* https://doi.org/10.1088/1681-7575/ab84ca

3. O.M. Hahtela *et al* Coulomb Blockade Thermometry on a Wide Temperature Range *CPEM 2020 Proceedings* https://doi.org/10.1109/CPEM49742.2020.9191726 published

4. C. Pan *et al*, Direct comparison of ITS-90 and PLTS-2000 from 0.65 K to 1 K at LNE-CNAM, *Metrologia*, **58** (2021), 025005, https://doi.org/10.1088/1681-7575/abd845

5. A Peruzzi *et al* Survey of subrange inconsistency of long-stem standard platinum resistance thermometers
6. (2021) *Metrologia* **58** 035009 https://doi.org/10.1088/1681-7575/abe8c1

7. D. Madonna Ripa *et al* Refractive index gas thermometry between 13.8 K and 161.4 K *Metrologia* https://doi.org/10.1088/1681-7575/abe249

8. Giovanni Garberoglio *et al* Path-integral calculation of the fourth virial coefficient of helium isotopes *The Journal of Chemical Physics* https://doi.org/10.1063/5.0043446

9. D. Imbraguglio *et al* Comparison of ITS-90 realizations from 13 K to 273 K between LNE-CNAM and INRIM *Measurement* https://doi.org/10.1016/j.measurement.2020.108225

10. M. J. Martín *et al* Construction, Characterization and Measurement of Fe–C and Pd–C HTFPs at CEM *International Journal of Thermophysics* https://doi.org/10.1007/s10765-022-02978-2

11. D. Madonna Ripa *et al* Corrigendum: Refractive index gas thermometry between 13.8 K and 161.4 K *Metrologia* https://doi.org/10.1088/1681-7575/ac2d9e

12. P. Czachorowski *et al* Second virial coefficients for 4He and 3He from an accurate relativistic interaction potential *Physical Review A* https://doi.org/10.1103/PhysRevA.102.042810

13. Changzhao Pan *et al* Acoustic measurement of the triple point of neon T_{Ne} and thermodynamic calibration of a transfer standard for accurate cryogenic thermometry *Metrologia* https://doi.org/10.1088/1681-7575/ac0711

Presentations and other disseminations

1. Poster of Real-K project
2. Coulomb Blockade Thermometry on a Wide Temperature Range, Aug 2020, IEEE Precision Electromagnetic Measurements (CPEM 2020), United States.
3. Current thermometry research directions, invited seminar, January 2020, Aberdeen University, United Kingdom.
4. The kelvin redefinition and its implications, invited keynote, February 2020, European Society of Precision Engineering (EUSPEN), Germany.
5. Redefinition of the SI, November 2020, invited seminar, Glasgow Caledonian, United Kingdom.

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6. Participation of VNIIOFI in EURAMET projects including the Real-K, September 2020, COOMET webinar, Russian Federation.

7. COOMET Tasks in the Light of the redefinition of the International System of Units (SI), October 2019, COOMET Seminar, Russian Federation.

8. Construction of high temperature fixed points of Fe-C and Pd-C at CEM, poster presentation at CIM 2021, September 2021

Forthcoming events

- International Congress of Metrology to be held in Lyon on 7-10 March 2023
- International Temperature Symposium to be held at Anaheim California 3-7 April 2023

Consortium and contact information

The consortium consisting of national metrology, research institutes and universities brings together a critical mass of recognised world leaders in the field.

Project coordinator: Graham Machin (**graham.machin@npl.co.uk**).

Project website: **https://real-k.aalto.fi.**

Newsletter: Every nine months an e-Newsletter will be available via the project website.

Inquiries and more info, Contact Shahin Tabandeh (**shahin.tabandeh@vtt.fi**).

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