IAPWS Thermophysical Properties of Water and Steam WG
Banff, Canada, 30 September to 3 October 2019

NOTE: These Minutes include many items that were held jointly with the IRS Working Group and/or the Subcommittee on Seawater (SCSW). Items are listed according to their order on the TPWS agenda, which is Attachment A. **Bold print** denotes significant actions.

1-2. The meeting was opened on Monday, September 30, 2019 by the TPWS Chair, Allan Harvey. An additional item 14.2 Discussion of expiring ICRN 28 - Thermophysical Properties of Metastable Steam and Homogeneous Nucleation was added to the agenda (Attachment A). The Chair noted that the 2018 Minutes had been circulated and approved by email shortly after the 2018 meeting. K. Meier was appointed Clerk of Minutes for TPWS.

3. Potential International Collaborative Projects

No new Collaborative Project was suggested at TPWS.

NOTE: Item 4 is reported on in the IRS minutes.

4. Industrial Requirements and Solutions for Steam Property Calculations (joint with WG IRS)

4.1 Report of the Task Group "Categories of industrial requirements"

4.2 Report of the Task Group "Wet steam properties calculation"

4.3 Report of the Task Group "Wet Steam Data from Operating Turbines"

4.4 Requirements for CFD calculations.

5. Heavy Water Properties (joint with WG IRS)

5.1 Density of heavy water at low temperatures - validation of IAPWS standard against Prague experimental data (A. Blahut, J. Hykl, P. Peukert, V. Vinš, J. Hrubý)

A. Blahut reported on density measurements of super-cooled heavy water in the temperature range between 254 K and 298 K up to 100 MPa. The measurements were carried out with a two-capillary instrument developed by J. Hrubý's group in Prague. With the instrument, the density relative to the density on a reference isotherm is measured. The density on the reference isotherm was determined by the method of thermodynamic integration by using very accurate speed-of-sound data measured by Fehres and Rudtsch at PTB in Berlin and data of Wilson at pressures above 60 MPa from the literature as well as thermal expansion and second order thermal expansion coefficients derived from the experimental relative density data. The uncertainty in absolute density is 110 ppm.

Based on the new density measurements and data for density and other properties from the literature, an equation of state (EOS) formulated in Gibbs energy was developed for liquid heavy water that covers the temperature and pressure ranges of the measurements. The new EOS was compared with literature data for various thermodynamic properties and the current and previous IAPWS formulations for heavy water. The new EOS describes the density, isothermal compressibility at high pressure, and maximum of density in the studied region somewhat better than the current IAPWS formulation.

5.2 Report of TG for Heavy Water Transport Properties (J. Sengers, M. Assael, M. Huber, R. Perkins)

J. Sengers reported on the status of the work on the new formulations of the viscosity and thermal conductivity of heavy water. The development of both formulations was mainly carried out after the Release for new formulation for the thermodynamic properties of heavy water was approved in 2018. Available data in the literature for both transport coefficients have been collected, were critically evaluated, and separated in primary and secondary data. The experimental data for the viscosity cover the temperature range between 242 K and 778 K with pressures up to 964 MPa. The viscosity is formulated as a product of three contributions: the viscosity in the limit of zero density, the residual viscosity, and the critical enhancement, which resembles the theoretically well-founded multiplicative critical enhancement. The correlation for the viscosity in the limit of zero density is based on the theoretically calculated values of Hellmann and Bich. It covers the whole temperature range of the calculations between 250 K to 2500 K. The residual viscosity and critical enhancement contributions have the same functional form as for ordinary water. The exponents and correlation length of the critical enhancement are the same as for ordinary water. In the term for the crossover critical behavior, the wavenumber q_c is the same as for ordinary water, but q_d is different as obtained from the fit to the experimental data in the critical region. Only four data points close to the critical point are not represented within the uncertainty of 2%. J. Sengers remarked that the current IAPWS formulation for heavy water does not describe the physical behavior of the correlation length in critical region correctly. An auxiliary equation for the viscosity of heavy water as a function of temperature at ambient pressure was also developed. The uncertainty of the formulation is between 1% and 5% depending on the state point.

K. Meier recommended that more detailed figures with comparisons of the new formulation with experimental data are provided in the publication which e.g. show the representation of data in deviation plots along isotherms as is usually done when assessing the quality of an equation of state. J. Hrubý remarked that his group developed an equation of state for cold and supercooled liquid water which is somewhat more accurate in this region than the current IAPWS formulation for the thermodynamic properties of heavy water.

Subsequently, J. Sengers reported on the progress in the development of the formulation for the thermal conductivity. The primary and secondary data for the thermal conductivity of heavy water cover the temperature range between 270 K to 870 K up to 250 MPa. There are no data for the thermal conductivity of supercooled heavy water. The structure of the formulation is the same as for ordinary water. It is composed of the product of the thermal conductivity in the limit of zero density and the residual thermal conductivity, while the critical enhancement is added. As for the viscosity, the thermal conductivity in the limit of zero density is based on the theoretical values of Hellmann and Bich. The residual thermal conductivity and critical enhancement contributions have the same structure as for ordinary water. The parameters of the critical enhancement are the same as for ordinary water. The available experimental data in the critical region are described well. Next steps are the development of an auxiliary equation for the thermal conductivity at 0.1 MPa, the final assessment of the range of validity and uncertainty of the formulation, and to draft a Release and a manuscript for journal publication.

An evaluation Task Group for the evaluation of the Release for the new viscosity formulation was appointed, consisting of K. Meier (chair), A. Blahut, and H.-J. Kretzschmar. The evaluation of the Release for the viscosity formulation should be finished by the end of December 2019.

The evaluation of the Release for the thermal conductivity will be performed by the same Task Group. The time schedule for the evaluation of the Release for the thermal conductivity will be fixed after the evaluation of the viscosity Release has been completed.

A. Harvey mentioned that there was interest in the static dielectric constant of heavy water; he will look into the issue further before the 2020 meeting.

6. Possible Replacement of IAPWS-95

6.1 Report of Task Group (A. Harvey, D. Friend, J. Hrubý, N. Okita, K. Orlov, R. Span)

A. Harvey reported on behalf of the Task Group examining possible improvement of the IAPWS-95 formulation. His report was structured in three topics: deficiencies in performance of the IAPWS-95 formulation, new data that are not included in the IAPWS-95 formulation, and regions where additional data are needed.

R. Feistel commented that the sea water standard TEOS-10 is based on IAPWS-95 and there is no need to replace TEOS-10 because the changes in the new formulation will be outside of region of interest in oceanography. Moreover, the difference between confidence and prediction intervals should be considered in uncertainty analysis.

6.2 (Item not presented)

6.3 Discussion of proposed ICRN

A. Harvey presented the draft ICRN developed by the task group. It contains the points described in 6.1. J. Sengers suggested not to mention a time when IAPWS-95 is to be replaced. R. Feistel suggested to include investigations on the influence of isotopic composition on the properties of water. The general opinion was that this topic should be considered separately. A. Harvey will prepare this topic for the next meeting. **The WG voted to approve the ICRN with minor editorial changes and recommend that the EC then send it for Postal Ballot.**

7. Report of Task Group on Surface Tension of Ordinary Water (joint with WG IRS and SC SW) (J. Kalová, V. Vinš, A. Harvey, O. Hellmuth, V. Holten, J. Hrubý, R. Mareš, J. Pátek, F. Caupin)

A. Harvey on behalf of J. Kalová reported on the surface tension of ordinary water. The current IAPWS formulation was approved in 1975. Several new data sets were published since then. The selection and analysis of data sets for a new formulation was discussed. A new equation for the surface tension of ordinary water based on Wegner's expansion was developed. The critical exponent was fixed to the theoretical value 1.26. A manuscript for a journal publication will be prepared before the 2020 meeting in Turin. J. Sengers commented that the Wegner expansion refers to the critical region only. It was decided that the Task Group should continue. A sentence will be added to the ICRN for the data needs for the new formulation of the thermodynamic properties of ordinary water stating the need for high-temperature surface tension data.

8. Metastable Water (joint with SC SW)

8.1 Report on the vapor pressure of supercooled water (V. Holten, A. Harvey)

A. Harvey reported that there had been limited progress, but that he hoped he and V. Holten could have a Guideline prepared for next year's meeting in Turin.

NOTE: Items 9, 10, and 11 are reported on in the SC SW minutes.

9. Report of Task Group on Extension of Range of Formulation for Thermodynamic Properties of Sea Water (joint with WG IRS and SC SW) (R. Feistel)

10. Cooperation with other international bodies (joint with SC SW)

10.1 IAPWS/IAPSO/SCOR Joint Committee on Seawater, including updates to TEOS-10

11. Reports on seawater-related topics (joint with SC SW)

11.1 Proposed Guideline on Surface Tension of seawater (K. Nayar, A. Harvey)

11.2 Evaluation Report on proposed Guideline (R. Feistel, M. Duska)

11.3 Formal Working Group consideration of the Guideline

11.4 Density measurements of IAPSO standard seawater by single sinker hydrostatic weighing at atmospheric pressure (A. Giuliano Albo, S. Lago, Y. Kayukawa)

11.5 Density of seawater at low temperatures (including supercooled seawater) and high pressures (A. Blahut, J. Hykl, P. Peukert, V. Vinš, J. Hrubý)

11.6 Seawater Density Anomalies in the Eastern Central Atlantic (S. Weinreben, R. Feistel)

11.7 Report on pH (S. Seitz)

11.8 Progress towards pH Traceability (F. Camoes)

11.9 Liquid Junction Potentials and pH (R. Pawlowicz)

11.10 SI-Traceable Measurement of Relative Fugacity (R. Feistel, J. Lovell-Smith)

12. Reports on miscellaneous TPWS scientific topics (joint with WG IRS and SC SW)

12.1 Anomaly in virial expansion of IAPWS-95 at low temperatures (A. Harvey)

A. Harvey presented an investigation on the behavior of virial coefficients calculated with IAPWS-95. He showed that the calculated virial expansion does not show the correct physical behavior at low temperatures. This effect results from one term in IAPWS-95 with a temperature exponent of 50 causing the fourth virial coefficient to become very large in magnitude at low temperatures. The effect is small, but must be considered when IAPWS-95 is used to derive a virial expansion, which is e.g. done in humidity metrology. A manuscript that describes this investigation has been submitted to the International Journal of Thermophysics.

12.2 (item not presented)

13. Joint session with WG PCAS

13.1 Report and official WG consideration of minor revision of Release on the Ionization Constant of H_2O (A. Harvey)

A. Harvey reported on a minor revision of the Release of the ionization constant of water. An error in the text of the definition of the ionization constant was corrected, the cover page was adopted to the current IAPWS standard, and the definition of activity was added to the nomenclature. The formulation has not changed. The revised document was circulated in both WGs a few months before the meeting, and was also circulated to the EC. **The WGs voted to approve the Revised Release and recommend that the EC give it final approval.**

13.2 Report on progress toward IAPWS Guideline on diffusivity of ordinary water (K. Yoshida, F. Caupin, A. Harvey, R. Hellmann, M. Huber)

K. Yoshida reported on behalf of the Task Group on the progress toward a formulation for the self-diffusion coefficient of ordinary water. Data were collected from the literature and separated into primary and secondary data sets. In summary, 951 data are available, 190 of which were discarded and 487 selected as primary data for preliminary fitting. The product of self-diffusion coefficient and density is formulated as a sum of the zero-density contribution and the residual contribution. Since the self-diffusion coefficient exhibits no anomaly at the critical point, there is no critical enhancement contribution. The functional form of the zero-density contribution is a product of the square root of temperature and a rational function in temperature with 7 adjustable parameters. It is fitted to R. Hellmann's theoretical zero-density values and represents them within 0.1%. The residual contribution is formulated as a product of the square root of temperature and a sum of 17 double polynomials in reduced density and temperature, which are formed with the critical temperature and density. The zero-density contribution does not represent all values derived from experimental data within their uncertainty. In order to assess this discrepancy, experimental viscosity data and theoretically calculated values for the viscosity of Hellmann and Vogel were converted to self-diffusion data by scaling them with the ratio of the cross sections of self-diffusion and viscosity and compared with the self-diffusion data. Based on this comparison, the zero-density contribution was shifted by +0.5%. The preliminary formulation represents the best literature data at high densities within -5% to +10%. Next steps are to improve the data selection and weighing, complete the literature survey, improve the fitting functions, and consider the use of $H_2{}^{18}O$ tracer diffusion data. Moreover, in the supercooled region densities according to the IAPWS Guideline for Supercooled Water will be considered.

In the discussion, K. Meier noted that the two experimental data sets for the product $D{\cdot}\rho$ in the limit of zero density show different dependences on temperature and that the scaling of viscosity to self-diffusion data is only a rough approximation.

13.3 Cross second virial coefficients for industrially and scientifically important mixtures of water vapor and simple gases from *ab initio* intermolecular potentials (R. Hellmann, K. Meier)

K. Meier on behalf of R. Hellmann presented ab initio calculations on the second cross virial coefficients of the mixtures water-nitrogen and water-carbon dioxide. Intermolecular potential functions were developed on the basis of state-of-the-art quantum chemical calculations of the interaction energies of the molecules. Using the intermolecular potentials, cross second virial coefficients were computed semiclassically with the Mayer-sampling Monte-Carlo method in a wide temperature range up to 2000 K. The calculated virial coefficients were represented by simple analytic functions. Comparisons with experimental data for thermal virial coefficients and Joule-Thomson virial coefficients as well as theoretical calculations of other authors show that the calculated cross virial coefficients agree well with the best experimental data and are probably more accurate than previously calculated values. The work on water-carbon dioxide was published in Fluid Phase Equilibria and a manuscript on water-nitrogen has been submitted to the Journal of Chemical and Engineering Data. The project continues with calculations of second cross virial coefficients for further binary mixtures containing water. It was noted in discussion that the water-oxygen binary would be of particular interest to IAPWS for moist air calculations.

13.4 Nucleation in water vapor: Classical nucleation theory and molecular simulation (T. Němec) [joint with IRS]

T. Němec presented an investigation of homogeneous nucleation in steam by molecular dynamics simulations with the SPC/E and TIP4P/2005 models for water. An assessment of experimental and simulation data from the literature shows that there are often large discrepancies between these data and classical nucleation theory. In order to examine these differences, molecular dynamics simulations were performed to detect a single nucleation event. During the simulation the development of the largest cluster is monitored to determine the nucleation rate. Good agreement of the simulation results for the nucleation rate with classical nucleation theory was found. It was concluded that simulations should not be carried out in the *NVT* ensemble. Moreover, experiments must be carried out carefully so that the experimental conditions conform with the assumptions of classical nucleation theory.

14. IAPWS Certified Research Needs (ICRNs)

14.1 Discussion of possible ICRN for acid gas dew points (N. Okita)

N. Okita presented the progress of a survey of models for the prediction of acid dew points in combustion gases. Available data from the literature were collected and compared with prediction methods implemented in the process simulation software ASPEN Plus. It was concluded that the presently available methods are not satisfactory. J. Hrubý noted that a better definition of the requirements for the applications is necessary. A Task Group for the development of an ICRN may be appointed in the 2020 meeting in Turin.

14.2 Discussion of expiring ICRN 28 - Thermophysical Properties of Metastable Steam and Homogeneous Nucleation

It is noted that the part of the ICRN about metastable properties is also contained in the new ICRN on the data needs for the thermodynamic properties of ordinary water. Therefore, it was decided to let the ICRN expire and set up a new ICRN about homogenous nucleation. A Task Group consisting of J. Hrubý and S. Senoo was formed to write the new ICRN before the 2020 meeting. Hrubý will write the closing statement for ICRN 28.

15. Reports on other TPWS activities

15.1 Guideline on Fundamental Constants (A. Harvey)

With the adoption of the new SI system in May 2019 and the 2018 CODATA adjustment, the values of some fundamental constants changed. Consequently, the Guideline must be updated. A. Harvey will prepare an update for the 2020 meeting.

15.2 Advisory Note 2 (J. Cooper, A. Harvey)

No update is needed for this document at this time.

16. Other Business

16.1 Report on International Collaborative Projects

M. Duška worked with Prof. Anisimov on properties of supercooled water. The project was funded as an IAPWS Young Scientist Project. A written report describing the work was recently prepared. It can be accessed via the link: https://arxiv.org/abs/1909.13468 [Duška, M., Water above spinodal, arXiv:1909.13468 [physics.chem-ph] (2019)]

17. Membership

Dr. Patek (Czech Republic) and Dr. J. M. H. Levelt Sengers (U.S.A.) should be removed from the TPWS membership. A. Giuliano Albo (Italy) was unanamously elected as a new TPWS member.

18. Election of Chair and Vice-Chair

K. Meier was elected as Chair, A. Harvey was elected as Vice-Chair, beginning 1 January 2020. H.-J. Kretzschmar on behalf of the WG thanked A. Harvey for serving as Chair of the WG during the last eight years.

19. Contribution to Press Release

The Chair was assigned to prepare the contribution to the Press Release.

20. Preparation of the Formal Motion to the EC

The chair and the clerk of minutes were assigned to prepare the Formal Motion to the EC.

21. Adjournment

The meeting was adjourned at 14:00 on Thursday, October 3.

Agenda for the IAPWS Working Group
Thermophysical Properties of Water and Steam (TPWS)
Banff, Canada, Sept. 30 – Oct. 3, 2019

1. Opening Remarks; Adoption of Agenda
2. Appointment of Clerk of Minutes
3. Potential International Collaborative Projects [Monday]
4. Industrial Requirements and Solutions for Property Calculations, joint with WG IRS
   - 4.1 Report of the Task Group "Categories of industrial requirements" (N. Okita, A. Nový, I. Weber, R. Span, A. Anderko, M. Rziha)
   - 4.2 Report of the Task Group "Wet steam properties calculation" (A. Nový, J. Hrubý, K. Orlov, R. Span, K. Meier)
   - 4.3 Report of the Task Group "Wet Steam Data from Operating Turbines" (N. Okita, A. Nový, I. Weber, S. Senoo)
   - 4.4 Requirements for CFD calculations
5. Heavy Water Properties (joint with WG IRS)
   - 5.1 Density of heavy water at low temperatures - validation of IAPWS standard against Prague experimental data (A. Blahut, J. Hykl, P. Peukert, V. Vinš, J. Hrubý)
   - 5.2 Report of TG for Heavy Water Transport Properties (J. Sengers, M. Assael, M. Huber, R. Perkins)
6. Possible Replacement of IAPWS-95
   - 6.1 Report of Task Group (A. Harvey, D. Friend, J. Hurbý, N. Okita, K. Orlov, R. Span)
   - 6.2 A brief review of density and speed of sound data at high temperatures and pressures (J. Hrubý)
   - 6.3 Discussion of proposed ICRN
7. Report of Task Group on Surface Tension of Ordinary Water (joint with WG IRS and SC SW) (J. Kalová, V. Vinš, A. Harvey, O. Hellmuth, V. Holten, J. Hrubý, R. Mareš, F. Caupin) [presented by A. Harvey]
8. Metastable Water (joint with SC SW)
   - 8.1 Report on the vapor pressure of supercooled water (V. Holten, A. Harvey)
9. Report of Task Group on Extension of Range of Formulation for Thermodynamic Properties of Sea Water (joint with WG IRS and SC SW) (R. Feistel)
10. Cooperation with other international bodies (joint with SC SW)
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12. Reports on miscellaneous TPWS scientific topics (joint with WG IRS and SC SW)

12.1 Anomaly in virial expansion of IAPWS-95 at low temperatures (A. Harvey)

12.2 Cloud service for IAPWS formulations (K. Orlov, V. Ochkov)

13. Joint session with WG PCAS [Thursday morning]

13.1 Report and official WG consideration of minor revision of Release on the Ionization Constant of H_2O (A. Harvey)

13.2 Report on progress toward IAPWS Guideline on diffusivity of ordinary water (K. Yoshida, F. Caupin, A. Harvey, R. Hellmann, M. Huber)

13.3 Cross second virial coefficients for industrially and scientifically important mixtures of water vapor and simple gases from *ab initio* intermolecular potentials (R. Hellmann, K. Meier)

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15.2 Advisory Note 2 (J. Cooper, A. Harvey)

16. Other Business

16.1 Report on International Collaborative Projects

17. Membership

18. Election of Chair and Vice-Chair

19. Contribution to Press Release

20. Preparation of the Formal Motion to the EC

21. Adjournment