IAPWS Thermophysical Properties of Water and Steam WG
Kyoto, Japan, 28–31 August 2017

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, August 28, 2017 by the TPWS Chair, Allan Harvey. The agenda (Attachment A) was adopted after some additions. The Chair noted that the 2016 Minutes had been circulated and approved by email shortly after the 2016 meeting. J. Hrubý was appointed Clerk of Minutes for TPWS.

3. No new Collaborative Project was suggested at TPWS.

4. Possible topics for 17th ICPWS in Prague 2018 have been discussed. Suggested were sessions on uncertainties of thermophysical property formulations, thermophysical properties of aqueous systems, molecular modeling, metastable states. (Other may be included at the IPC meeting.). R. Span stressed that ICPWS should have strong focal points in order to remain a significant meeting. The form of publication of presented research has been discussed. D. Friend suggested that International Journal of Thermophysics may be interested in publishing a special issue dedicated to ICPWS. R. Span suggested that extended abstracts could be published in Energy Procedia.

NOTE: Item 5 except for point 5.5 is reported on in the IRS minutes.

5. Industrial Requirements and Solutions for Steam Property Calculations, joint with WG IRS

5.1 Report of the Task Group “Categories of industrial requirements” (N. Okita, A. Nový, I. Weber)

5.2 Report of the Task Group “Industrial Advisory Note” (M. Hiegemann, B. Rukes, A. Singh, A. Harvey)

5.3 Report of the Task Group “Wet steam properties survey” (I. Weber, H. J. Kretzschmar, N. Okita, A. Nový)

5.4 Acid dew point under low sulfur contents (N. Okita)

5.5 As a result of the discussion on the need of a new industrial formulation initiated by J. Bellows) it has been suggested that the process should start with an updated scientific formulation. A task group for reconsideration of the IAPWS scientific formulation has been established (A. Harvey as chair, members N. Okita, D. Friend, R. Span, K. Orlov, J. Hrubý). The mission of the TG is to explore possible deficiencies of the present scientific formulation, consider new requirements such as modeling mixtures and phase interfaces, and stimulate new research when needed.

6. Heavy Water Properties (joint with WG IRS)

6.1 Stefan Herrig (co-authors R. Span, A. Harvey) reported on the results of the Task Group on Heavy Water Thermodynamic Properties. Collaboration between NIST and RUB in the development of a new formulation started in 2013. The new equation has the form of reduced Helmholtz energy as function of dimensionless temperature and density. It has 24 terms, is valid up to 825 K and 1200 MPa. New ideal gas part is based on recent data by Simkó et al. (2017) and it is accurate to within 0.02%. Many pieces of data such as gas density data by Kell, data for liquid at very high pressures are fitted significantly better than with the present IAPWS formulation. New data was used for second virial coefficient (quantum computations down to 200 K), speed of sound (RUB and PTB), supercooled density data (IT Prague). Draft release submitted, publication is being prepared.

6.2 H.-J. Kretzschmar presented the Report of Evaluation Task Group for Heavy Water Formulation (other members M. Duška, V. Holten, T. Beuthe). After a few amendments the formal aspects fulfill all requirements. correctness: derivatives clearly described, speed of sound equations had to be corrected. Supercooled heavy water with experimental data. High level of experimental data. Minor changes needed. Document appears as complete. Three reviewers implemented independently. Test values were corrected. Computing time is similar to the previous equation. The new equation has smaller number of terms but contains fitted exponents. The evaluation task group recommends to accept the Draft as an IAPWS Release. In discussion: K. Orlov said that he implemented the equation and wants it to be very clear that the molecular weight given in the Release should be used to convert to mass-based properties unless there is special knowledge of a different isotopic composition for the specific system.

6.3 Discussion of procedure toward adoption of Release for Heavy Water Thermodynamics. Because the document was circulated only recently, it was decided that people (especially those not in Kyoto) should be given more time to examine it, although the members present felt it was ready for adoption. **The WG voted to approve the draft Release, with the condition that members be given until the end of October to bring up additional issues. The WG Chair and Chair of the Evaluation TG were authorized to resolve any such issues that are raised. The WG requests the EC to authorize a Postal Ballot to be conducted after this additional period has passed and after the Editorial Committee has approved the draft.**

6.4 Report of TG for Heavy Water Transport Properties (J. Sengers, M. Assael, M. Huber, R. Perkins) A. Harvey reported on behalf of the Task Group that it had collected data but otherwise was just beginning its work.

6.5 R. Romeo (co-authors P. A. Giuliano Albo, S. Lago, L. Rosso) informed about preliminary measurements of density of heavy water through an isochoric method up to 170 MPa. The mass was determined gravimetrically. Coefficients of thermal expansion and pressure expansion for the cell have been determined by comparing the measured data with IAPWS-95 formulation. Estimated standard uncertainty in terms of density is 0.02%. In the discussion, some experimental aspects have been opened, such as the fact that the pressure transducer, containing some volume of the sample, was not immersed in the bath.

7. Possible Improvements of IAPWS-95 Release

7.1 A. Harvey (in collaboration with W. Wagner) reported on possible refinement of uncertainty estimates in the IAPWS-95 Release. Uncertainty estimates for thermodynamic properties in the gas phase may be reduced as the ideal gas limit is approached. In particular, heat capacity, speed of sound and density have been considered. It has been proposed that sentences will be added to the captions of the uncertainty diagrams informing that the uncertainties became smaller at low pressure. The proposal (**TG consisting of Harvey and Wagner**) should be circulated in order that it can be adopted at the 2018 meeting. R. Feistel suggested that more quantitative statements should be possible; he and Harvey will investigate the possibilities.

8. J. Kalová and J. Hrubý reported on behalf of the Task Group on Surface Tension of Ordinary Water (joint with WG IRS and SC SW, members V. Vinš, A. Harvey, O. Hellmuth, V. Holten, J. Hrubý, J. Kalová, R. Mareš, J. Pátek, F. Caupin). R. Mareš performed capillary rise measurements in thin capillary (I.D. 0.097 mm) down to -32 °C. V. Vinš and co-authors measured surface tension of supercooled water using the horizontal capillary method. Both measurements support previous conclusion that the surface tension of supercooled water is close to the extrapolated IAPWS standard. Further, J. Kalová presented results of a literature review. F. Caupin in a message required that the equation should have the proper critical exponent (1.260 is the currently adopted value; neither the present IAPWS equation nor new equation by Pátek et al. use this value). In the following discussion it has been mentioned that new surface tension data should be generated in the high-temperature region, where only old Soviet data is available. **J. Kalová was appointed as the new chair of the TG.** The TG will work towards a new IAPWS equation for the surface tension, but no deadlines were set as it is felt that this is not an urgent task.

9. Humid Air Fugacity and Enhancement Factor, joint with SC SW

9.1 A. Harvey reported on his investigation of explicit approximations to the Poynting factor. The enhancement factor is the ratio between the actual partial pressure of (water) vapor in a mixture equilibrium condition to its saturation pressure in the pure state. The Poynting is a part of the enhancement factor which represents the effect of pressure on the fugacity of a pure liquid or solid phase. Approximations for pressure-independent molar volume ("first order") and considering pressure-independent compressibility ("second order") have been considered. Approximations have been compared with the Poynting factor computed directly from IAPWS-95 or the IAPWS ice formulation up to 20 MPa at temperatures 473 K down to 173 K for ice and down to 235 K for supercooled water. For the second-order correction, the difference to the accurate values was below 0.1 ppm for pressures up to 1 MPa.

10. Metastable Water (joint with SC SW)

10.1 J. Hrubý reported about the progress of measurements of the density of supercooled ordinary and heavy water performed by M. Duška and coworkers. Because M. Duška was in the past year at a research stay in the USA (next item), only evaluation of the 2016 data was performed in this period. The reproducibility of the heavy water measurements was within 0.005%, the standard uncertainty of the "relative density" (the ratio of density at given pressure and temperature to the density at the same pressure and reference temperature of 25 °C) is roughly 0.01%. The data were provided to the developers of the developers of the new IAPWS formulation of thermodynamic properties of heavy water.

10.2 J. Hrubý (main author M. Duška, co-author M. Anisimov) presented a preliminary report on modeling thermodynamic properties of supercooled heavy water. This work has been performed in frame of the Young Scientist IAPWS Fellowship Project "Towards an IAPWS Guideline for the Thermodynamic Properties of Supercooled Heavy Water". A new model based on the two-state concept has been developed. The properties of liquid water are expressed in the form of a Gibbs energy of a mixture, including parts for "pure components", representing the various molecular structures, ideal mixing part and an excess part. In contrast to the model by V. Holten and co-authors which used a high-order empirical polynomial for component A (denser structure), the new model uses a simple expansion around spinodal suggested originally by Speedy (outside the two-state concept). The work is ongoing and final results of the project will be presented at 17th ICPWS in 2018.

10.3 V. Fernicola (coauthors (L. Rosso, G. Beltramino, S. Tabandeh, P. A. Giuliano Albo) informed about vapor pressure measurements over subcooled water down to 255 K. Measurements have been performed with a new setup. The sample cell was formed by a fused silica capillary (I.D. 0.500 mm) forming a U-tube. The sample was outgassed repeated freeze quenching, degassing in vacuum, and thawing under low pressure. The cell is connected to a capacitance pressure transducer, which is at higher temperature. Pressure transducer calibrated at the triple point of water using the IAPWS-adopted value. Combined standard uncertainties range from 0.03% at 273 K to 0.08% at 255 K.

10.4 J. Hrubý reported on behalf of a Task Group on Superheated liquid water (second member R. Feistel, joint with WG IRS and SCSW). The results of comparison of IAPWS-95 computations with experimental data in the superheated liquid region have been presented in Dresden. The main result was that IAPWS-95 can be safely extrapolated to the superheated liquid region. Existing old data on the density and speed of sound for superheated water have large uncertainties and their importance is rather qualitative. R. Feistel informed that the study is not anymore needed for the purpose of the definition of relative humidity, for which it had been required.

10.5 Report on Task Group on ICRN for Interfacial Properties of Supercooled Water (O. Hellmuth, J. Hrubý, J. Sengers) The TG was closed because it had no output.

10.6 A. Harvey (co-author V. Holten) reported on the saturation pressure of supercooled water. Various correlations are used for the saturation pressure of supercooled water. Most of them are extrapolations based on data above the triple point. The saturation pressure can be determined using thermodynamics by starting at the triple point and integrating the Clapeyron equation, or, alternatively, by developing a thermodynamic potential and finding the saturation conditions. The second option has been used and the saturation pressure was computed using the equation in the 2015 Guideline for properties of supercooled water for the liquid phase and IAPWS-95 for the gas phase. Differences with respect to the often used correlation by Murphy and Koop is primarily due to different data for the heat capacity of supercooled water used for the computations. **A Task Group (A. Harvey, V. Holten, R. Feistel) was appointed to develop this into a new section to be inserted into the supercooled water Guideline.** The Chair was authorized to appoint an Evaluation Task Group at the appropriate time; J. Lovell-Smith volunteered for that Task Group.

10.7 A. Harvey reported for the Task Group on possible revision of IAPWS formulations for melting curves (other members V. Holten, H.-J. Kretzschmar) The main point was that V. Holten was working on thermodynamic potentials for various ices which might lead to new melting curves, which would also take advantage of better knowledge of the Ih-III-L triple point. However, there was no progress during the year.

NOTE: Items 11-15 are reported in the SCSW Minutes.

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

12. Cooperation with other international bodies (joint with SC SW) (Tuesday)

13. Reports on seawater-related topics (joint with SCSW) (Tuesday)

(see attached agenda for individual titles)

14. Proposed new IAPWS seawater-related documents (joint with SCSW) (Tuesday)

14.1 Report on Guideline for Electrical Conductivity of Seawater (R. Pawlowicz)

14.2 Report of Task Group on Supplementary Release for a simplified density equation for oceanographic use (R. Pawlowicz, T. McDougall, P. Barker)

14.3 Report of Task Group on Advisory Note on IAPWS documents contributing to TEOS-10 (R. Feistel, A. Harvey, R. Pawlowicz)

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

15.1 Report of Task Group on Covariance in IAPWS work (R. Feistel, J. Hruby, S. Seitz, J. Lovell-Smith, D. Friend)

15.2 Unleashing empirical equations with "Nonlinear Fitting" and "GUM Tree Calculator" (J. Lovell-Smith, P. Saunders, R. Feistel)

15.3 GLS Uncertainty Propagation of Systematic Error (R. Feistel, J. Lovell-Smith)

16. Joint session with WG PCAS [Thursday morning]

16.1 S. Senoo reported on a nonequilibrium condensation model and numerical analysis for wet steam turbines (joint topic with IRS, also presented at IAPWS Symposium on Wednesday). The basic physical principles are nucleation and droplet growth. Homogeneous nucleation is considered, although some effect of heterogeneous nucleation is admitted. Classical nucleation theory with a non-isothermal correction by Kantrowitz was used to predict the nucleation rate. In subsequent discussion it has been said that the processes in wet steam flows are of interest to IAPWS and that relevant ICRNs exist (ICRN

22, Steam Chemistry in the Turbine Phase-Transition Zone and ICRN 28, Thermophysical Properties of Metastable Steam).

16.2 J. Hrubý reported on the progress toward improved ideal-gas properties of ordinary and heavy water performed by a group of authors primarily based in spectroscopy led by Prof. A. Csaszar. Final results for $H_2{}^{16}O$ (the main isotopologue in ordinary water) have been published. Further, final results for deuterated isotopologues $D_2{}^{16}O$, $D_2{}^{17}O$, and $D_2{}^{18}O$, and heavy water (their mixture) were published in 2017 (and used in the new IAPWS formulation for heavy water). The ideal gas properties are computed using a partition function based on a large database of experimental and quantum-mechanically computed energy levels. The developers were encouraged to provide data for the remaining water isotopologues so that the ideal-gas heat capacity for ordinary water could eventually be replaced.

16.3 A. Harvey reported on first-principles calculations of second and third virial coefficients for H_2O and D_2O. Experimentally, the second virial coefficient is known from 350 to773 K, little data exist down to 323 K and up to 1173 K. The third virial coefficient is known from 400 to 773 K. The computations consider quantum effects, flexibility of molecules, and isotopic differences (including D_2O). Significant differences of the new computations with respect to the 2004 formulation by Harvey and Lemmon are only at low temperatures. The quantum correction is needed below about 800 K, semiclassical approach is good down to about 400 K. Preliminary results were shown for the third virial coefficient. Third virial coefficient by IAPWS-95 seems to underpredict the experimental data at low temperatures. The computations with rigid molecules seems to confirm the IAPWS-95 curve, but this is not definitive since flexibility may be significant as it is for the second virial.

16.4 K. Yoshida presented a proposal for IAPWS Guideline on self-diffusion coefficient of water (also presented at IAPWS Symposium on Wednesday). The formulation is based on article J. Chem. Eng. Data 55 (2010) 2815-2823. It has been agreed that an IAPWS document on self-diffusion coefficient is needed. **Task group has been established, including K. Yoshida, K. Maier, and A. Harvey.**

17. IAPWS Certified Research Needs (ICRNs)

17.1 ICRN 27: Thermophysical Properties of Humid Gases and CO2-Rich Mixtures: Closing statement will be prepared by R. Span.

17.2 N. Okita discused a possible ICRN for acid gas dew points. In particular, interest is in dew point under low sulfur contents (SO3 below 1 ppm). Problems occur in combustion of NG containing sulfur. Sulfuric acid and nitric acid are formed causing stress corrosion cracking. Existing empirical formulation predicts dew points more than 25 K lower than a theoretical model. Siemens point of view: apply water dew point when the predicted dew point is below the water dew point. R. Span mentioned that reasonably good correlations can be found for SO2 and SO3. A difficulty is providing the distribution between SO2 and SO3 which depends on complex catalytic effects. **A TG has been established including N. Okita (chair), K. Orlov, and R. Span.**

18. Reports on other TPWS activities

18.1 A. Harvey reported that there are no changes needing an update of the Guideline on Fundamental Constants.

18.2 A. Harvey reported that no amendment is needed to Advisory Note 2.

19. Other Business

19.1 Report on International Collaborative Projects. No new International Collaborative Projects have been proposed.

19.2 Further discussion of ICPWS topics. J. Hrubý acknowledged an update of ICPWS topics based on the contributions of IPC members. He asked the IRS members to reconsider the structure of their topics.

19.3 Ideas for promoting IAPWS has been discussed: Inviting top-level people to other international organizations to ICPWS, translations of TGDs into other languages, online communities, encourage people publishing IAPWS work to mention IAPWS in a prominent place, Wikipedia pages, IAPWS-related software can be a point of contact, mentioning IAPWS when organizing related conferences.

20. Membership and Vice-Chair election: **K. Nayor, R. Romeo and V. Fernicola have been unanimously elected as TPWS members. Prof. Karsten Meier has been unanimously elected as a second TPWS vice chair.**

21. Contribution to Press Release

The Chair and the Clerk of Minutes were assigned to prepare the contribution to the Press Release.

22. 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.

23. Adjournment

The meeting was adjourned at 14:15 on Thursday, August 31.

Preliminary Agenda for the IAPWS Working Group

Thermophysical Properties of Water and Steam (TPWS)

Kyoto, Japan, August 28-31, 2017

1. Opening Remarks; Adoption of Agenda
2. Appointment of Clerk of Minutes
3. Potential International Collaborative Projects [Monday]
4. Discussion of topics for 2018 ICPWS in Prague
5. Industrial Requirements and Solutions for Steam Property Calculations, joint with WG IRS
   - 5.1 Report of the Task Group "Categories of industrial requirements" (N. Okita, A. Nový, I. Weber)
   - 5.2 Report of the Task Group "Industrial Advisory Note" (M. Hiegemann, B. Rukes, A. Singh, A. Harvey)
   - 5.3 Report of the Task Group "Wet steam properties survey" (I. Weber, H. J. Kretzschmar, N. Okita, A. Nový)
   - 5.4 Acid dew point under low sulfur contents (N. Okita)
   - 5.5 Is it time for a new industrial formulation? (J. Bellows)
6. Heavy Water Properties (joint with WG IRS)
   - 6.1 Report of Task Group on Heavy Water Thermodynamic Properties (R. Span, A. Harvey, S. Herrig)
   - 6.2 Report of Evaluation Task Group for Heavy Water Formulation (H.-J. Kretzschmar)
   - 6.3 Discussion of procedure toward adoption of Release for Heavy Water Thermodynamics
   - 6.4 Report of TG for Heavy Water Transport Properties (J. Sengers, M. Assael, M. Huber, R. Perkins)
   - 6.5 Heavy water density through an isochoric method: preliminary results (R. Romeo, P. A. Giuliano Albo, S. Lago, L. Rosso)
7. Possible Improvements of IAPWS-95 Release
   - 7.1 Report on Uncertainty Estimates of IAPWS-95 for vapors at low pressures (W. Wagner, A. Harvey)
8. Report of Task Group on Surface Tension of Ordinary Water (joint with WG IRS and SC SW) (V. Vinš, A. Harvey, O. Hellmuth, V. Holten, J. Hrubý, J. Kalová, R. Mareš, J. Pátek, F. Caupin)
9. Humid Air Fugacity and Enhancement Factor, joint with SC SW
   - 9.1 Report on Investigation of explicit approximations to the Poynting factor (A. Harvey)

10. Metastable Water (joint with SC SW)
    - 10.1 Measurements of the density of supercooled ordinary and heavy water (M. Duška, J. Hrubý)
    - 10.2 Report on modeling thermodynamic properties of supercooled heavy water (M. Duška, J. Hrubý)
    - 10.3 Some difficult, but challenging, vapour pressure measurements over subcooled water down to 253 K (L. Rosso, G. Beltramino, S. Tabandeh, V. Fernicola, P. A. Giuliano Albo)
    - 10.4 Report of Task Group on Superheated liquid water, joint with WG IRS and SCSW (J. Hrubý, R. Feistel)
    - 10.5 Report on Task Group on ICRN for Interfacial Properties of Supercooled Water (O. Hellmuth, J. Hrubý, J. Sengers)
    - 10.6 Report on the vapor pressure of supercooled water (V. Holten, A. Harvey)
    - 10.7 Report of Task Group on possible revision of IAPWS formulations for melting curves (V. Holten, A. Harvey, H.-J. Kretzschmar)
11. Report of Task Group on Extension of Range of Formulation for Thermodynamic Properties of Sea Water (joint with WGs IRS and SC SW) (R. Feistel) (Tuesday)
12. Cooperation with other international bodies (joint with SC SW) (Tuesday)
    - 12.1 IAPWS/IAPSO/SCOR Joint Committee on Seawater, including updates to TEOS-10 (R. Pawlowicz)
    - 12.2 BIPM/IAPWS cooperation (R. Feistel)
13. Reports on seawater-related topics (joint with SCSW) (Tuesday)
    - 13.1 Absolute Salinity measurements by a vibrating tube densimeter and a refractive index salinometer (H. Uchida)
    - 13.1a Current situation of the absolute density measurements of seawater (Y. Kayukawa, H. Uchida)
    - 13.2 Surface Tension of seawater (K.G. Nayar)
    - 13.3 Isothermal compressibility of seawater and predicting seawater properties for desalination applications (K.G. Nayar)
    - 13.4 Progress on pH-related topics (S. Seitz)
    - 13.5 Improving the metrological traceability of seawater pH measurements (A. Dickson – presented by R. Pawlowicz)
14. Proposed new IAPWS seawater-related documents (joint with SCSW) (Tuesday)
    - 14.1 Report on Guideline for Electrical Conductivity of Seawater (R. Pawlowicz)
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16.2 Progress toward improved ideal-gas properties of ordinary and heavy water (J. Hrubý)

16.3 First-principles calculation of second and third virial coefficients for H_2O and D_2O (A. Harvey)

16.4 Possible IAPWS Guideline for self-diffusion coefficient of water (K. Yoshida)

17. IAPWS Certified Research Needs (ICRNs)

17.1 ICRN 27: Thermophysical Properties of Humid Gases and CO_2-Rich Mixtures (closing statement needed) (R. Span, A. Harvey)

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

18. Reports on other TPWS activities

18.1 Guideline on Fundamental Constants (A. Harvey)

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

19. Other Business

19.1 Report on International Collaborative Projects

19.2 Further BRIEF discussion of ICPWS topics (J. Hruby)

19.3 Ideas for promoting IAPWS

20. Membership and Vice-Chair election

21. Contribution to Press Release

22. Preparation of the Formal Motion to the EC

23. Adjournment

August 28, 2017

A.H. Harvey (Chair), J. Hrubý (Vice-Chair)