British and Irish Association for the Properties of Water and Steam

Report to IAPWS of technical activities– July 2002

Technical Meetings

BIAPWS held a further Power Plant Chemistry Symposium at the University of Birmingham in October 2001.

The following papers were presented:

Discussion on degassed conductivity after cation exchange – Theory and practice,
A.G.L. Zeijseink and H.M. Van Deelen.

A Sensitive, versatile monitor for the measurement of CO_2 in High Purity Water,
K. Tittle.

Steam purity considerations for combined cycle power plants, R Svoboda, H. Sandmann,
S. Romanelli and F. Stoffel.

TOC Practical experience - A collection of case studies, M. Rziha.

Development of chemistry policy for power generation, P.Colman.

Practical experience with high efficiency reverse osmosis (HERO) technology,
J. Brown and S. Radford.

A development arising out of the interest in CO_2 and TOC measurements and their application is a programme of further work by K. Tittle on practicable simple methodologies for making key measurements in plant.

Other activities

BIAPWS Committee meetings continue on a basis of three per annum. Sponsorship and support from the major power generators and power plant manufacturers remains strong. Links with major universities and research establishments remain active.

BIAPWS plans to hold a further symposium early in 2003 with associated workshops to be held before and after the main event.

BIAPWS will launch its web-site to advertise its activities shortly.

BIAPWS will also announce an award for high achievement in undergraduate final year projects of relevance to the issues covered by IAPWS. The first award will be presented at the end of the 2002/3 academic year.

G J Bignold
July 2002

Attachment 15

The Czech National Committee

International Association for the Properties of Water and Steam

REPORT on IAPWS related activities - September 2001 / July 2002

Submitted to the EC Meeting of IAPWS, Buenos Aires - July 2002.

National Committee Contacts:

CZ NC PWS - Institute of Thermomechasnics, Dolejskova 5, 182 00 Prague 8, Czech Republic
Fax: + 420 2 858 4695, E-mails: sifner@it.cas.cz; secr.czncpws@it.cas.cz
Prof. R.Mareš, Fax: + 420 19 7429986, E-mail: maresr@kke.zcu.cz

Following Institutions participated in the research into the thermophysical properties and chemical processes:

Institute of Thermomechanics (IT) AS CR, Department of Thermodynamics, Dolejskova 5, CZ-182 00 Prague 8

Czech Technical University in Prague (CTU), Faculty of Mechanical Engineering, Department of Fluid Mechanics and Power Engineering, Technická 4, CZ-166 07 Prague 6

Technical University Brno (TU), Faculty of Mechanical Engineering, Department of Thermomechanics and Nuclear Energetics, Technická 2, CZ-616 69 Brno

Institute of Chemical Technology Prague (ICT), Power Engineering Department and Department of Physical Chemistry, Technická 5, CZ-166 28 Prague 6

University of West Bohemia (UWB), Faculty of Mechanical Engineering, Department of Theory and Design of Power Plants, Univerzitní 8, CZ-306 14 Plzen

SKODA ENERGO, Turbines, Plzeň, Inc., Tylova 57, CZ-316 00 Plzen

Nuclear Research Institute plc. (NRI), Rez, CZ-250 68 Rez

Technical University of Liberec (TUL), Department of Chemistry, CZ-461 19 Liberec.

Activities were sponsored by the Grant Agency of the Academy of Sciences and Grant Agency of the Czech Republic, SKODA ENERGO-Turbines, Plzen Inc., Ministry of Education, Youth and Physical Training, and Ministry of Industry and Trade.

- Mares (UWB) and Sifner (IT) prepared a short information about temperature conversion and recalculation of the thermal conductivity for discussion in the TG on transport properties Ref.[1].

- The international standards for computation of thermophysical properties of water and steam and the authorized software were presented at the Seminar Power Engineering-2002 organized by University of West Bohemia, Refs.[2,3]
- Prof. Marsik (IT) with co-authors modified the manuscript of the Chapter 7: Binary Homogeneous Nucleation in Selected Aqueous Solutions for the ATLAS, Ref. [4]. The modifications respected recommendations of Dr. Palmer and reviewers.

The particular results of investigations into condensation, evaporation, and cavitation are presented by the same working team in Refs.[5 to 7].

- Dr. Sedlbauer within his Young Scientists IAPWS Fellowship collaborated also with Profs. Majer and Wood on preparing the ATLAS Chapter "Calculation of Standard Thermodynamic Properties of Aqueous Solutes in a Wide Range of Temperatures and Pressures" Ref.[8].
- Research activities at the CTU have continued during the period 9/2001 – 7/2002 in further study of the droplet nucleation process occurring in LP steam turbines.

  The diagnostics of wet steam at the exit of L-0 turbine stage (from the root to the blade tip) consisted in measurement and prediction of droplet size spectra and moisture level, electrostatic charge of the droplet population, and chemical impurities in the steam. The droplet size spectra and moisture level were measured by means of the optical extinction probe, redesign to enable to measure electrostatic charge of the droplet population as well. At the same probe positions the steam was sampled and analyzed providing concentration of chemical impurities. The data obtained in the turbine tests have been used in improving computational model of the droplet nucleation in LP steam turbines.

  The expansion chamber for controlled heterogeneous droplet nucleation of steam was developed. It consists of cylindrical test section equipped with the controlled valves. The onset of the steam droplet nucleation on existing heterogeneous impurities is realized by controlled pressure decrease in the test section in a way preventing the onset of the homogeneous nucleation. As a result, these nuclei increase to the measurable values. The expansion chamber can measure concentration of the steam impurities at the inlet of LP steam turbines and enables to predict and to develop the computational models of the liquid phase formation in LP steam turbines.

  Information on the both items is being prepared for presentation at the 5th European Conference on TURBOMACHINERY, Fluid Dynamics and Thermodynamics, which will be held in March 2003 in Prague.

- Jiricek (ICT) studied the typical behavior of organic compounds in steam/water cycle. Specific behavior, fate, structural factors and limit values in makeup water, condensate and superheated steam samples were summarized. Procedures for sampling and measurement at low concentration were evaluated. Two different power cycles alkalizing chemicals (ammonia and ethanolamine) were compared. Refs.[9,10].
- Ing Kodl, SKODA-Turbines, carried out the TTSE test based on calculation of 10 schemas (15 operations) of conventional power plants and combined cycles with or without regeneration, reheat and external extractions and for various operation parameters. The schemas were chosen to cover usual and special cases and operations. In general, they are the same as used in the previous tests TTSE97/IF97. Compared were the specific heat consumption (shc), its relative values and the computing time ratio. The results were submitted to Ing. I. Weber, who will include them into the Test report on TTSE-95d.
- Dr.Vosta (ICT-IE) with collaborators is concerned with power cycle chemistry, which is divided into water treatment for coal and nuclear power plants, problems of electrochemistry and questions of material and corrosion. Published articles are under Refs. [11 to17].
- Dr.Hnedkovsky (ICT-IPC) with collaborators investigated properties of organic solutes in water. The solute vapor absorption technique was applied at measurement of aqueous solubility of hydrophobic volatile organic compounds. Solution and transfer processes were modelled in non-polar solutes in water and aqueous solutions of protein denaturants. Published articles are under Refs.[18 to 22].
- Stastny (SKODA ENERGO) with co-workers studied effects of deposits on the blades of HP and MP parts of steam turbine by chemical analysis, degradation of steam turbine blade surfaces by deposits of chemicals, and tested numerical models of the water steam flow with condensation in nozzles Refs.[23 to 26].
- Research activities of the NUCLEAR RESEARCH INSTITUTE ŘEŽ plc - Power Cycle Chemistry Working Group (PCC WG) included investigations of corrosion products under conditions of primary cycle of VVER and surface prconditionary and its effects on the radiation situation.

Young Scientists IAPWS Fellowships:

Sedlbauer finished the project *" Correlation and Prediction of Standard Thermodynamic Properties of Aqueous Solutes over a Wide Range of Temperatures and Pressures"* under supervisors Profs. Kadrnozka, Majer and Wood. The project was focused on three areas of interest in the description of standard thermodynamic properties of aqueous solutions at elevated conditions:

- acquisition of experimental data for non-electrolyte organic aqueous solutes,
- testing and comparison of different models for correlation of standard thermodynamic properties and their extrapolation beyond the regions where experimental data were obtained,
- development of software tool for an easy calculation of standard thermodynamic properties in a wide range of conditions.

His Final report for the Young Scientists IAPWS Fellowship is in Appendix 1.
The new publications of the fellowship holder are in Refs.[27 to 31].
The CZ NC PWS reviewed and recommends the Proposal for Young Scientists IAPWS Project for the years 2002-2003 "Thermodynamics of Binary Homogeneous Nucleation in Superheated Steam" (applicant. T. Nemec) to submit to the Evaluation Committee. The project is in Appendix 2.

- **References:**

[1] Mares R., Sifner O.: *Temperature Conversion of the Coefficient of Thermal Conductivity*, Paper for the IAPWS Annual Meeting, Buenos Aires, July 2002

[2] Sifner O., Mares R.: *International Standards for Calculation of the Thermophysical Properties of Water and Steam*, Paper for the Seminar Power Engineering – 2002, Pilsen, June 2002 (in Czech)

[3] Mares R., Sifner O.: *Authorized Software for the Thermodynamic Properties of Water and Steam*, Paper for the Seminar Power Engineering – 2002, Pilsen, June 2002 (in Czech)

[4] Marsik F., Hruby J., Demo P., Kozisek Z., Petr V., Kolovratnik M.: Chapter 7. *Homogeneous Nucleation in Selected Aqueous Solutions* (prepared for ATLAS *The Physical and Chemical Properties of Aqueous Systems at Elevated Temperatures and Pressures: Water, Steam and Hydrothermal Solutions*, Editors: Palmer D.A., Fernandez-Prini R., Tremaine P.)

[5] Sedlar M., Marsik F., Safarik P.: *Numerical Analysis of Cavitated Flows in Mixed-Flow Pump Impellers*, The Third International Conference *HEAT 2002, Transport Phenomena in Multiphase Systems*, Kielce-Baranow, 2002

[6] Delale C.F., Hruby J., Marsik F.: *Homogeneous Bubble Nucleation in Liquids : The Classical Theory Revisited* (in print Journal of Physical Chemistry)

[7] Marsik T., Delale C.F., Sedlar M.: *Condensation and Cavitation in the Water and Water Mixtures*, invited lecture, The Third International Conference *HEAT 2002, Transport Phenomena in Multiphase Systems*, Kielce-Baranow, 2002

[8] Majer V., Sedlbauer J., Wood R.H.: Chapter for ATLAS *Calculation of Standard Thermodynamic Properties of Aqueous Solutes in a Wide Range of Temperatures and Pressures*, (prepared Chapter for *The Physical and Chemical Properties of Aqueous Systems at Elevated Temperatures and Pressure: Water, Steam and Hydrothermal Solutions*, Editors: Palmer D.A., Fernandez-Prini R., Tremaine P.)

[9] Jiricek I., Kalivodova J.: *Principles for Cycle Water Organic Contamination Measurement*, Proceedings of *Maintenance of NP SG VVER*, Organized by Nuclear Power Research Institute at Rez, Velke Losiny, Czech Republic, 2001, pp.98-102

[10] Jiricek I., Macak J., Sajdl P., Machnikova E.: *When Organic Compounds Serve as Contaminants and When as Correction Chemicals*, Proceedings of *Maintenance of NP SG VVER*, organized by Nuclear Power Research Institute at Rez, Znojmo, Czech Republic, 2002, pp. 78-93

[11] Vosta J., Sajdl P., Schneeweis O., Novotny R.: *Hydrogen Embrittlement and Mossbauer Effect*, International Conference on *Hydrogen Effect on Material Behaviour and Corrosion Deformation Interactions*, Jackson, Wyoming USA, 2001

[12] Novotny R., Sajdl P., Vosta J.: *The Initiation and Propagation of Stress Corrosion Cracks in High Temperature and High Pressure Conditions*, International Conference on *Hydrogen Effect on Material Behaviour and Corrosion Deformation Interactions*, Jackson, Wyoming USA, 2001

[13] Vedral J., Vosta J.: *Determination of Iron Oxides by Help of Mossbauer Spectroscopy*, Diploma Thesis, Institute of Chemical Technology, Prague, 2002

[14] Dudr V., Novotny R., Vosta J.: *Study of Generation of Oxide Layers on Fe and its Alloys*, Institute of Chemical Technology, Prague, 2002

[15] Kucera P., Novotny R., Sajdl P.: *Electrochemical Noise During Corrosion Phenomena*, Institute of Chemical Technology, Prague, 2002

[16] Racek J., Sajdl P.: *Stress Corrosion Cracking of Steels Used for Pipelines*, Institute of Chemical Technology, Prague, 2002

[17] Trapl K., Sajdl P.: *Acoustic Emission During Corrosion of Steels*, Institute of Chemical Technology, Prague, 2002

[18] Hnedkovsky L., Cibulka I., Hynek V.: *Partial Molar Volumes of Organic Solutes in Water. VI. O- and p-Chlorophenols at Temperatures = (298 to 573) K and Pressures up to 30 MPa*, Journal of Chemical Thermodynamics, 2001, 33, pp.1049-1057

[19] Bendova M., Rehak K., Matous J., Novak J.P.: *Liquid – Liquid Equilibrium in the Ternary Systems Water + Ethanol + Dialkyl Phthalate (Dimethyl, Diethyl, and Dibuthyl Phthalate) at 298.15 K*, Journal of Chemical Engineering Data, 2001, 46 pp. 1605-1609

[20] Dohanyosova P., Fenclova D., Vrbka P., Dohnal V.: *Measurement of Aqueous Solubility of Hydrophobic Volatile Compounds by Solute Vapor Absorption Technique : Toluene, Ethylbenzene, Propylbenzene, and Butylbenzene at Temperatures from 273 K to 328 K*, Journal of Chemical Engineering Data, 2001, 46, pp. 1533-1539

[21] Dohnal V., Costas M., Carrillo-Nava E., Hovorka S.: *Non-Polar Sloutes in Water and Aqueous Solutions of Protein Denaturants. Modeling of Solution and transfer processes*, Biophysical Chemistry, 2001, 90, pp. 183-202

[22] Carrillo-Nava E., Dohnal V., Costas M.: *Infinite Dilution Activity Coefficients for Toluene in Aqueous Solutions of the Protein Stabilizers Glycerol, Ethylene Glycol, Glucose, Sucroese and Trehalose*, Journal of Chemical Thermodynamics, 2002, 34, pp. 1-14

[23] Stastny M.: *Effect of Cooper Deposition on the Steam Turbine*, Joint Workshop PCC/PCAS on *Copper in Water/Steam Cycle*, IAPWS Annual Meeting in Gaithersburg, USA, 2001

[24] Stastny M.: *Effect of Copper Deposition on the Steam Turbine Efficiency and Capacity*, Power Plant Chemistry, Vol.3, No.11, pp.669-673, Germany, 2001

[25] Stastny M.: *Numerical Modeling of Water Steam Flow with Condensation*, Course on *Modeling and Measurement in Continuum Mechanics*, West Bohemia University, Nectiny, Czech Republic, 2002 (in Czech)

[26] Stastny M., Sejna M.: *Numerical Modeling of the Steam Flow with Condensation in Nozzles*, IAPWS Annual Meeting, Buenos Aires, 2002

[27] Sedlbauer J., Bergin G., Majer V.: *Group Contribution Method for the Henry's Law Constant $K_H(T,p)$ of Aqueous Hydrocarbons*, AIChE Journal, 2002 (submitted)

[28] Majer V., Bergin G., Sedlbauer J.: *Predicting the Henry's Law Constant and Related Partition Coefficients of Aqueous Hydrocarbons: A Software Tool for Calculations in a Wide Range of Temperatures and Pressures*, Fluid Phase Equilib., 2002 (to be submitted)

[29] Sedlbauer J., Bergin G., Majer V.: *Towards a Prediction Scheme for Hydration Propertes of Aqueous Hydrocarbons up to the Critical Region of Water,* Solution Chemistry, Vaals, Netherlands, 2001

[30] Sedlbauer J., Majer V.: *Semi-Theoretical Approaches to Modeling Thermodynamic Properties of Aqueous Solutions in a Wide Range Conditions*, EURESCO Conference on *Molecular Liquids : Water at New Millenium*, Obernai, France, 2001

[31] Sedlbauer J.: *Semi-Empirical Models for Standard State Properties of Aqueous Solutes*, Sixth Liblice Conference on *The Statistical Mechanics of Liquids*, Spindleruv Mlyn, Czech Republic, 2002

Attachment 15
Appendix 1

Correlation and Prediction of Standard Thermodynamic Properties of Aqueous Solutes over a Wide Range of Temperatures and Pressures

final report for the Young Scientists IAPWS Fellowship

prepared by **Josef Sedlbauer**
Department of Chemistry, Technical University, 46119 Liberec, Czech Republic

IAPWS Sponsors:
Jaroslav Kadrnozka
Faculty of Mechanical Engineering, Technical University Brno, 61969 Brno, Czech Republic

Vladimir Majer
Laboratory of Thermodynamics and Chemical Engineering, Blaise Pascal University
63170 Aubiere, France

June 5, 2002

Overview

The project was focused on three areas of interest in the description of standard thermodynamic properties of aqueous solutions at elevated conditions:

- acquisition of experimental data for non-electrolyte organic aqueous solutes,
- testing and comparison of different models for correlation of standard thermodynamic properties and their extrapolation beyond the regions where experimental data were obtained,
- development of software tool for an easy calculation of standard thermodynamic properties in a wide range of conditions.

An integral part of the project was collaboration on preparing the chapter "Calculation of standard thermodynamic properties of aqueous solutes in a wide range of temperatures and pressures" (co-authored by V. Majer, J. Sedlbauer and R.H. Wood) for the "ATLAS" book. Some of the results, databases and recommendations obtained in the course of this Fellowship are included in this chapter.

ACTIVITIES AND RESULTS

Research visits of J. Sedlbauer at the Blaise Pascal University, France:

- June – July 2000 (two months, *costs:* $4000)
- May – June 2001 (six weeks, *costs:* $3000)
- January – February 2002 (one month, *costs:* $2000)
- Total budget: $9000

Papers with acknowledgement of the IAPWS support:

- Sedlbauer J., Majer V.: „Data and models for calculating the standard thermodynamic properties of aqueous nonelectrolyte solutes under hydrothermal conditions“, *Europ. J. Mineral.*, **12**, 1109-1122 (2000). The paper is focused on application of the standard derivative thermodynamic properties of aqueous solutes for predicting standard chemical potential in a wide range of conditions. An overview of recent sources of experimental data is given for non-electrolyte solutes and a set of tests is reported regarding the ability of several thermodynamic models to correlate and predict the standard chemical potential.
- Sedlbauer J., Bergin G., Majer V.: „Group contribution method for the Henry's law constant $K_H(T,p)$ of aqueous hydrocarbons“, *AIChE J.*, submitted (2002). A new group contribution scheme was proposed for calculating the standard thermodynamic properties of aqueous hydrocarbons (aliphatic, cyclic and aromatic). About 2000 data points were retrieved from the literature in the course of this study, most of them refer to vapor-liquid equilibrium of aqueous hydrocarbons.
- Majer, V., G. Bergin and J. Sedlbauer, "Predicting the Henry's law Constant and Related Partition Coefficients of Aqueous Hydrocarbons: A Software Tool for Calculations in a Wide Range of Temperatures and Pressures ", *Fluid Phase Equilib.*, to be submitted (2002). Implementation of the new group contribution method is not quite straightforward. To accommodate its use in applications a freeware program was prepared and is presented in this paper along with some thermodynamic background regarding the Henry's law constant and its different variants.

Conference contributions with acknowledgement of the IAPWS support:

- Sedlbauer J., Majer V.: „Predictions of Henry`s constant for environmental chemicals at elevated temperatures“, *18-th European Seminar on Applied Thermodynamics*, Kutná Hora, Czech Republic, 2000.

- Sedlbauer J., Majer V.: „Correlation and prediction of standard thermodynamic properties of aqueous solutes over a wide range of temperatures and pressures“, *IAPWS Meeting*, Prague, Czech Republic, 2000.
- Sedlbauer J.: „Predictions of thermodynamic properties of aqueous organic solutes at elevated temperatures“, *CZ-PL-D Younger Chemist Meeting*, Regensburg, Germany, 2001.
- Sedlbauer J., Bergin G., Majer V.: “Towards a prediction scheme for hydration properties of aqueous hydrocarbons up to the critical region of water”, *Solution Chemistry*, Vaals, Netherlands, 2001.
- Sedlbauer J., Majer V.: “Semi-theoretical approaches to modeling thermodynamic properties of aqueous solutions in a wide range of conditions”, *Molecular liquids: Water at the new millennium (EURESCO conference)*, Obernai, France, 2001.
- Sedlbauer J.: “Semi-empirical models for standard state properties of aqueous solutes”, *Sixth Liblice conference on the statistical mechanics of liquids*, Spindleruv Mlyn, Czech Republic, 2002.

Other results, conclusions and future prospects:

- Draft of the chapter “Calculation of Standard Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes“ for ATLAS was prepared and will be presented by V. Majer at the IAPWS annual meeting in Buenos Aires or before.
- Collaboration between J.S. and V.M. was supported during this period also by the Czech – French bilateral program “Barrande” (2000 – 2002) and by a project under auspices of American Chemistry Council. New support was obtained from the Grant Agency of Czech Republic (joint project 2002 – 2004) and by French program “GEOMEX” (2003, to be continued).
- In our view all aims of this IAPWS project were addressed by the published or submitted materials and represent a solid basis of continuing collaboration of the partners. This will be focused in the next years mainly on further development of the group contribution scheme for aqueous organic solutes, including other types of compounds – oxygen and nitrogen derivates, organic ions, amino acids and peptides.

Attachment 16

Danish National IAPWS Committee - DIAPWS
c/o IDA, Kalvebod Brygge 31 - 33, 1780 Copenhagen V

18 February 2002

IAPWS report 2001

The research activities in 2000 in Denmark in the field of properties of water and steam were mainly concentrated on continuation of activities started in the previous year. Due to the difficult economic situation new research has not been initiated.

The investigation of solubility of salts in superheated steam was finished in 2002. Earlier reported measurements on sodium sulphate and sodium chloride were complemented with measurements on copper oxide. The work was performed as an international collaboration project with 5 participants. The final report is accessible to the participants only. The publication of the results will be possible after 3 years.

Mathematical modelling of thermodynamic properties of ammonia / water mixtures is in progress at the Technical University of Denmark, Copenhagen. The model takes the chemical interaction between ammonia and water into account, which improves its fit to the experimental data.

Measurements and modelling of density and viscosity of multicomponent aqueous electrolyte solutions is started at the Technical University of Denmark, Copenhagen.

Publications in 2001:

K. Daucik, Accumulation of Ionic Impurities in the Plant Cycle, Power Plant Chemistry, 3(2001), 5, p. 280-282.

Attachment 17

FRENCH National Committee

Report on the IAPWS related scientific activities
Buenos Aires, July 2002

National Committee Contacts:

Dr. Vladimir MAJER, National President, Fax: 33 (0)4 73 40 71 85, vladimir.mayer@univ-bpclermont.fr
Dr. Dominique YOU National Secretary, Fax: 33 (0)1 69 08 15 86, dominique.you@cea.fr

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Laboratoire de Physique Theorique des Liquides, Université Paris VI

Address: 4 place Jussieu, boite courrier 121
75252 Paris cedex 05, France
Contact: Bertrand GUILLOT
Fax: 33 (0)1 44 27 51 00
E-Mail: guillot@lptl.jussieu.fr

OBJECTIVES

(1) Determination of an accurate empirical potential for simulated water.
(2) Comparison between molecular dynamics simulations and various experimental data; thermodynamics, structure, transport properties and dynamics, dielectric constant.
(3) Understanding supercritical water, supercooled and glassy water.

PRINCIPAL RESULTS, CURRENT PROJECTS

- A new water model for computer simulations taking into account the electronic penetration by the use of diffuse charges on O and H atoms.
- Evaluation of liquid -liquid equilibrium in aqueous solutions by the Gibbs ensemble method: investigation of reapparent phases.

RECENT PUBLICATIONS

How to build a better pair potential for water
B.GUILLOT and Y.GUISSANI
J. Chem. Phys, 114, 6720 (2001)

Simulation of the liquid-liquid coexistence curve of tetrahydrofuran+water mixture in the Gibbs ensemble
I. BROVCHENKO and B.GUILLOT
Proceedings of the 14th Symposium on Thermophysical Properties (Boulder,2000),
Fluid Phase Equilibria, 46-48, 1 (2001)
A reappraisal of what we have learnt during three decades of computer simulations on water
B.GUILLOT
J. Mol. Liq., 101,.1 (2002)

Percolation of water in aqueous solution and liquid-liquid immiscibility
A. OLEINIKOVA, I. BROVCHENKO, A. GEIGER and B.GUILLOT
J. Chem. Phys., 117, issue of August 15 (2002)

Laboratoire de Thermodynamique des Solutions et des Polymères, Université Blaise Pascal (Clermont II) / CNRS

Address: avenue des Landais, 63177 Aubière Cedex FRANCE
Fax: +33 (0)4 73 40 71 85
E-Mail: vladimir.majer@univ-bpclermont.fr
Contact: Vladimir MAJER
WEB Page: http://ltsp.univ-bpclermont.fr

OBJECTIVES

(1) Development of instruments and techniques for data acquisition at high temperatures and pressures

(2) Experimental determination of volumetric and calorimetric properties of aqueous solutions over a wide range of temperatures and pressures (*T* between 273 and 723 K, *p* between 1 and 40 MPa), measurement of solubilities up to 200°C

(3) Correlation and prediction of standard state properties of aqueous nonelectrolytes as a function of state parameters up to the critical region of water

(1) Thermodynamics of systems strong electrolyte-acid gas-water

(2)

PRINCIPAL RESULTS, CURRENT PROJECTS

- Treatment of experimental data for heat capacities of aqueous hydroxy and aminoderivatives of benzene and toluene (phenol, cresols, aniline, toluidines, aminophenols, diaminophenols, dihydroxybenzenes) up to 350 °C and 30 MPa.

- Testing of models for correlating and predicting standard thermodynamic properties of aqueous organic nonelectrolytes, development of a group contribution method for predicting hydration properties of hydrocarbons (aq) up to 300°C and 100 Mpa, Henry's law constant for aqueous organics

- Developing methodology for determining solubility of highly hydrophobe nonelectrolytes in water by saturation column technique, new measurements for n-alkanes C12, C14, C16 and C18 up to 200°C were carried out in spring 2001 in collaboration with the Claude Bernard University, Lyon (prof. Jose), new investigation regarding solubility of mono halogenated octanes and selected hydrocarbons (cyclooctane, cyclooctene, 1,2 cis-dimethylcyclohexane, 1,2 trans-dimethylcyclohexane, ethyl cyclohexane) between 0 and 50°C were carried out in the academic year 2001-2002.

- Critical evaluation of thermodynamic data on aqueous polyaromatics and n-alkanes as a function of temperature (solubilities, temperatures and heats of fusion).

- Measurement of volumetric and heat capacity data for triflates of lanthanides(La, Nd, Ga, Yt) started in 2002 for determining the standard thermodynamic properties of noncomplexed lantahanides^{3+} up to 350 °C et 35 MPa

RECENT PUBLICATIONS

A new version of differential flow heat capacity calorimeter; heat capacities of aqueous NaCl from 303 to 623 K. L. HNEDKOVSKY, V. HYNEK, V. MAJER, R.H. WOOD. J. Chem. Thermodyn. 2002, 34, 759-785.

Méthodes à écoulement pour mesures des propriétés calorimétriques et volumetriques HT/HP des systèmes aqueux. V. MAJER, V. HYNEK, J-Y. COXAM, K. BALLERAT-BUSSEROLLES. Technologie des Hautes Pressions, 3ème Forum Collonges-la-Rouge. Eds. J.-P. Petitet, T. de Resseguier. Réseau Hautes Pressions – CNRS 2002, pages 187-197.

Measurement of densities using vibrating bodies. V. MAJER and A. PADUA, in Experimental Thermodynamics Volume VI, Measurement of the thermodynamic properties of single phases, under auspices of IUPAC Editeurs K. Marsh, W.A. Wakeham, A.R.H. Goodwin, Elsevier Amsterdam to be published in 2002 (30 pages).

Group contribution method for the Henry's law constant $K_H(T,p)$ of aqueous hydrocarbons. J. SEDLBAUER, G. BERGIN, V. MAJER. AIChE J. submitted

CEA-DEN/DPC/SCCME

Address: CEA-DEN/DPC/SCCME
Bât 458 - CEA/Saclay
91191 GIF-SUR-YVETTE CEDEX FRANCE
Contact: Dominique YOU
Fax: 33 (0)1 69 08 15 86
E-Mail: dominique.you@cea.fr

OBJECTIVES

- Prediction of the behaviour of corrosion product (spinels solubility measurements) in the PWR primary coolant circuit.
- Understanding the formation of concentrated solutions in local crevices of PWR steam generators.

PRINCIPAL RESULTS, CURRENT PROJECTS

(1) Solubility behaviour of cobalt, zinc and nickel ferrites of different compositions was studied. A thermodynamic model was developped to obtain nickel release during shutdown and the chemical conditions of formation of metallic nickel in the primary circuit. The solubility data were used to obtain the thermodynamic functions. The new data has been extensively used in the PACTOLE code to predict formation, activation, migration and deposition of activated corrosion products.

(2) In local crevices of PWR steam generators, the formation of concentrated solutions is the precursor phenomena to corrosion and degradation of S.G. tubes. The concentration processes, due to the boiling phenomena and to the thermal gradient between the primary and the secondary temperatures, are strongly dependent on the mass transfer processes and also on the chemical equilibrium in the liquid phases and on the equilibrium between the liquid and the vapour phases. A special apparatus has been developed to study the evolution of crevice chemistry and of the chemical equilibrium during concentration processes (EVA device). In order to be able to interpret chemical equilibrium, concentration process is performed in EVA device at constant temperature and constant volume and the mass balance is calculated (isochore and isotherm concentration process).
This investigation is in progress on the concentration processes of sodium, aluminium and silicon with or without boron. The following main results are:
   - EVA facility appears to be a simple and good tool for crevice chemistry investigations (chemical equilibrium and thermodynamic purposes). Good agreement between mass balance calculations and direct chemical analyses on samples has been observed.
   - Simultaneous hideout of boron with aluminium, silicon and sodium leads to the following main observations:
      - boron, aluminium and sodium concentrate in the crevice liquid phase. The good hideout of boron leads to a limitation of the crevice pH, as expected;
      - silicon reacts with nickel of the apparatus to form a solid compound $Ni_3Si_2O_5(OH)_4$. It is needed to verify if the same compound is formed with nickel base alloy (alloy 600, 690 or 800);
      - differences appear between the EVA experimental results and code (MULTEQ®) data, mainly due to the fact that the precipitation of nickel silicon solid phase occurs during EVA tests, while a sodium alumina silicate compound is predicted by the code.

   Evolution of the EVA facility is needed to measure crevice pH and redox potentials, which are considered as the main parameters for IGA/IGSCC.

INSTITUT DES SCIENCES DE LA TERRE D'ORLÉANS (ISTO) / CNRS

Address: 1A rue de la Férollerie, 45071, Orléans cedex 2
Contact: Gleb S. POKROVSKI
Fax: +33 (0)2 38 63 64 88 Phone: +33 (0)2 3825 53 89
E-Mail: gleb@cnrs-orleans.fr

OBJECTIVES

1/ Study of the identity, stoichiometry, and structure of aqueous and gaseous complexes of geochemically relevant metals and metalloids in high-temperature geothermal fluids (to 500°C).
2/ Prediction of the stability, solubility and thermodynamic properties of minerals and aqueous/gaseous species in high-temperature aqueous and mixed (H_2O-CO_2...) fluids; calculations of chemical equilibria between minerals and fluids, study of water-rock interactions.
3/ Development of special chemical reactors and spectroscopic cells (Raman, XAFS) for study of metal speciation and solubility in (super)critical fluids and high-temperature vapours.

PRINCIPAL RESULTS, CURRENT PROJECTS

- Experimental determination (liquid/vapour partition coefficient measurements coupled with XAFS spectroscopy) of the stoichiometry and stability of As gaseous species to 500°C. It was found that $As(OH)_3°$ is the main As-bearing complex in both hydrothermal boiling systems and volcanic gases, responsible for the As fractionation and transport during magmatic-to-hydrothermal fluid evolution and ore deposit formation.

- Experimental determination of arsenopyrite (FeAsS) stability and solubility in aqueous solution at temperatures from 300 to 450°C and pressures from 100 to 1000 bar. Results permitted to generate a consistent set of FeAsS thermodynamic properties, and to apply these data to predict As transport in natural hydrothermal fluids.

- XAFS in situ study of Sb speciation and solubility of Sb2O3 in high-temperature aqueous fluids (in coll. with J.L. Hazemann, Laboratoire de Cristallographie/ESRF, Grenoble).

- Measurements of vapour/liquid partition coefficients for Ag, Cu, Sb, Fe and Zn at 350-450°C and saturation pressure of the system H_2O-NaCl±HCl±H_2S, using recently developed high T-P chemical reactors and XAFS spectroscopic cells.

- Experimental study of gold solubility in the system Au-H_2O-H_2S-NaCl±As(III), and gold incorporation into arsenopyrite at hydrothermal conditions (300-500°C, 500 bar).

- Measurements of partial molal heat capacities and volumes for $As(OH)_3°$(aq) and $AsO(OH)_3°$(aq) up to the critical point of water (in coll. with V. Mayer, Laboratoire de Thermodynamique des Solutions et Polymers, Clermont-Ferrand).

- Development of hydrogen sensors based on Au-Pd membranes for in situ measurements of hydrogen fugacity in high-temperature hydrothermal fluids.

RECENT PUBLICATIONS

Stability and solubility of arsenopyrite, FeAsS, in crustal fluids.
G.S. POKROVSKI, S. KARA, & J. ROUX
Geochimica et Cosmochimica Acta (2002), 66, 2361-2378

Experimental study of arsenic speciation in vapor phase to 500°C: Implications for As transport and fractionation in low-density crustal fluids and volcanic gases.
G.S.POKROVSKI, I.V. ZAKIROV, J. ROUX, D. TESTEMALE, JL. HAZEMANN, A.Y. BYCHKOV., & G.V. GOLIKOVA. Geochim. Cosmochim. Acta (sous presse).

Laboratoire Chimie et Procédés, Ecole Nationale Supérieure de Techniques Avancées (Paris, 15ème)

Address: 32 boulevard Victor
75739 Paris Cedex 15, France
Contact: Walter FÜRST
Fax: 33 (0)1 45 52 83 22
E-Mail: furst@ensta.fr

OBJECTIVES

(1) Development of predictive equations for the calculation of equilibrium properties involving electrolyte solutions
(2) Measurement of speciation in complex electrolytes solutions using Raman or IR spectroscopy.
(3) Determination of mean activity coefficients in mixed solvent electrolyte solutions.
(4) Determination of gas hydrate stability conditions by calorimetry.

PRINCIPAL RESULTS, CURRENT PROJECTS

- Determination of speciation in the water – CO2 – H2S – Amine systems as a function of loading, amine concentration and temperature.
- Determination of a method allowing to predict the temperature effect on excess properties in electrolytes solutions.
- Study of the Gibbs energy of transfer allowing adapting electrolyte models to mixed solvent systems: experimental determination and choice of the best expression.
- Experimental determination of gas hydrate stability conditions in drilling mud.

RECENT PUBLICATIONS

Use of a predictive electrolyte equation of state for the calculation of the gas hydrate formation temperature in the case of systems with methanol and salts Q.V. VU, P. DUCHET SUCHAUX AND W. FÜRST Proceedings of the 9th Conference on Properties and Phase Equilibria for Product and Process Design (Kurashiki,2001) Fluid Phase Equilibria, 194-197, 361 (2002)

Representation of VLE and liquid phase composition with an electrolyte model : application to $H_3PO_4 – H_2O$ and $H_2SO_4 – H_2O$. M. CHERIF, A. MGAIDI., M. N. AMMAR, M. ABDERRABBA AND W. FÜRST Proceedings of the 9th Conference on Properties and Phase Equilibria for Product and Process Design (Kurashiki,2001) Fluid Phase Equilibria, 194-197,285 (2002)

Experimental Determination of the Molecular CO_2 Composition in the Liquid Phase of CO_2 / Alkanolamine / H_2O Systems R. SIDI-BOUMEDINE, E. PROVOST AND W. FÜRST Proceedings of the 3th European Congress of Chemical Engineering (Nüremberg,2001) Chemie-Ingenieur-Technik, 73, 6, 605 (2001)

Extension of the electrolyte EOS of Fürst and Renon to mixed solvent electrolyte systems J. Y. ZUO, D. ZHANG AND W. FÜRST Fluid Phase Equilibria, 175 (1-2), 285 (2000).

Prediction of LLE in Mixed Solvent Electrolyte Systems Using an Electrolyte EOS J. Y. ZUO, D. ZHANG AND W. FÜRST AIChE J.,46, 11, 2318 (2000)

Attachment 17

Modeling of the Equilibrium Properties of the system H_3PO_4-H_2O System: representation of VLE and liquid phase Composition M. CHERIF, A. MGAIDI, M. N. AMMAR, M. ABDERRABBA AND WALTER FÜRST Fluid Phase Equilibria, 175, 1-2, 197 (2000)

Attachment 18

Research Activities on the Thermodynamic Properties of Water Substance in Germany 2001/2002

University of Applied Sciences of Zittau and Görlitz
Prof. Dr.-Ing. habil. H.-J. Kretzschmar

1. Supplementary backward equations $T(p,h)$, $v(p,h)$, and $T(p,s)$, $v(p,s)$ for the critical and supercritical regions of water and steam
   - The backward equations $T(p,h)$, $v(p,h)$, and $T(p,s)$, $v(p,s)$ for the critical and supercritical regions were completed and successfully tested in process modelling. They can be used in combination with the Industrial Formulation IAPWS-IF97.
   - The Draft of "Supplementary Release on Backward Equations for the Functions $T(p,h)$, $v(p,h)$, and $T(p,s)$, $v(p,s)$ for the Critical and Supercritical Regions to the IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam" was formulated and sent to the IAPWS Working Groups "Industrial Requirements and Solutions" and "Thermophysical Properties of Water and Steam"
2. Supplementary backward equations $p(h,s)$ for the critical and supercritical regions of water and steam
   - The division of IAPWS-IF97 region 3 into subregions was investigated.
   - First equations $p(h,s)$ for IAPWS-IF97 region 3 were developed.
3. Supplementary backward equations $v(p,T)$ for the critical and supercritical regions of water and steam
   - The division of IAPWS-IF97 region 3 into subregions was investigated.
4. Supplementary backward equations $p(h,s)$ for water and steam
   - The comprehensive publication:
     Kretzschmar, H.-J., Cooper, J. R., Dittmann, A., Friend, D. G., Gallagher, J., Knobloch, K., Mareš, R., Miyagawa, K., Stöcker, I., Trübenbach, J., Wagner, W., and Willkommen, Th., "Supplementary Backward Equations for Pressure as a Function of Enthalpy and Entropy $p(h,s)$ to the Industrial Formulation IAPWS-IF97 for Water and Steam" for the Journal of Engineering for Gas Turbines and Power was completed.
5. Test of the TTSE method for calculating the thermodynamic properties of water and steam in process modelling
   - The accuracy and numerical consistency of the TTSE functions based on IAPWS-95 was investigated.
   - The computing speed of the TTSE functions was investigated and compared with that of IAPWS-95.
   - The results were described in the Test Report:
     Knobloch, K., Kretzschmar, H.-J., "Test Report of Documentation and Software of TTSE Method applied to IAPWS-95 as an Example" .

6. Preparation of program packages including the Industrial Formulation IAPWS-IF97 for the power industry
   - The property library LibHuAir for humid air calculated as ideal mixture of the real fluids air, steam, and water was prepared. The air is calculated by the NIST standard of Lemmon at al., and water and steam are calculated by IAPWS-IF97.
   - The property library LibHuGas for humid combustion gas mixtures calculated as ideal mixture of real fluids was prepared. The components carbon dioxide, carbon monoxide, sulfur dioxide, nitrogen, oxygen, argon, and neon are calculated by fundamental equations and water and steam are calculated by IAPWS-95.
7. Implementation of the Industrial Formulation IAPWS-IF97 on pocket calculators
   - The program FluidCASIO for the models CFX 9850G and CFX 9850GB Plus of Casio® was prepared.
8. Property libraries for water and steam, combustion Gas mixtures, and humid air for education
   - The Versions for students of the programs

     Add-In FluidEXL for Excel®

     FluidMAT for Mathcad®

     FluidTI for the pocket calculators TI 92 and TI 89

     FluidHP for the pocket calculators HP 48 and HP 49G

     FluidCASIO for the pocket calculator Casio FX 880P

     were revised.

Attachment 19

Current Status of Research Activities in Japan Submitted to the Executive Committee Meeting, IAPWS, Buenos Aires, Argentina, July 2002

by

Japanese National Committee
International Association for the Properties of Water and Steam
c/o The 139th Committee on Steam Properties
Japan Society for the Promotion of Science (JSPS)
6, Ichiban-cho, Chiyoda-ku,
Tokyo 102-8471, Japan

The Japanese National Committee to the IAPWS is playing an active function as the 139th Committee on Steam Properties chaired by Professor Koichi Watanabe, Keio University, at the Japan Society for the Promotion of Science (JSPS), Tokyo.

The following research projects on the thermophysical and physico-chemical properties of water substances including various aqueous systems of technological importance are currently in progress at several universities and institutions in Japan.

At the Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo, Prof. S. IKAWA and coworkers are engaged in spectroscopic measurements of water-hydrocarbon mixtures at high temperatures and pressures. In a recent paper, infrared and near infrared measurements of water-aromatic hydrocarbon mixtures in the temperature range 473 – 648 K and the pressure range 10 – 35 MPa have been reported [*Bull. Chem. Soc. Japan*, **74** (10) (2001), 1775-1788]. By use of these experimental results, π-hydrogen bonding between water and aromatic hydrocarbons at high temperatures and pressures has been discussed on the basis of a charge transfer theory [*J. Chem. Phys*., **117** (3) (2002) in press]. In addition, anomalous volume behavior of water-benzene mixtures has been found in the vicinity of the critical region of the mixtures [*J. Chem. Phys*., **117** (5) (2002) in press]. [contact: Prof. S. Ikawa; E-mail: sikawa@sci.hokudai.ac.jp].

At the Department of Quantum Science and Energy Engineering, Graduate School of Engineering, Tohoku University, Sendai, Prof. S. UCHIDA is promoting a new project on IASCC (Irradiation Assisted Stress Corrosion Cracking) of BWR core internals as a part of studies on life management of aged nuclear power plants. High temperature high pressure water loops with controlling hydrogen peroxide concentrations and lower possible oxygen concentrations are operated to determine the effects of hydrogen peroxide on IASCC. Theoretical approaches to understand crack tip water chemistry under gamma and neutron irradiations are also promoted. The paper (1) was awarded the 2001 Preeminent Monograph Award by Atomic Energy Society of Japan [Latest publication: (1) Y. Wada, et al., *J. Nucl. Sci. Technol*., **37** (2000), 901-912, (2) Y. Wada, et al., *J. Nucl. Sci. Technol*., **38** (2001), 621-632 and (3) T. Satoh, et al., *J. Nucl. Sci. Technol*., **38** (2001), 773-779]. [contact: Prof. S. Uchida; E-mail: shunsuke.uchida@qse.tohoku.ac.jp].

At the Department of Geoscience & Technology, Graduate School of Engineering, Tohoku University, Sendai, Profs. N. YAMASAKI, H. ENOMOTO, K. TOHJI, Assoc. Prof. N. TSUCHIYA, and their group are studying the hydrothermal preparation of advanced materials such as diamond, the stratified material on carbon nano- tube using hydrothermal process, and the water-rock interaction under SCW conditions for geothermal power plant, the liquefaction and gasification of heavy oil, the SCWO of rice husk for production of sodium acetate, the separation and extraction of useful materials from bio-mass using superheated steam, and the formation of organic materials by the hydrothermal reduction of carbon dioxide. [contact: Prof. N. Yamasaki; e-mail: yamasaki@igt.earth.tohoku.ac.jp].

At the Material Properties and Metrological Statistics Division, National Metrology Institute of Japan (NMIJ, formerly NRLM), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, a group of Dr. K. FUJII is working on the density and viscosity standards. An absolute density measurement of silicon crystals with a relative uncertainty of 1×10^{-7} and a determination of the Avogadro constant by the x-ray crystal density (XRCD) method for an atomic mass standard are conducted [K. Fujii, A. Waseda, and M. Tanaka, "Development of a silicon density standard and precision density measurements of solid materials by hydrostatic weighing," *Meas. Sci. Technol*., **12** (2002), 2031-2039]. Using this solid density standard the density of standard liquids are measured by a magnetic suspension density meter. A relative uncertainty of 1×10^{-5} has been achieved in the density measurement of organic liquids that are used as Certified Reference Materials (CRMs) for calibrating vibrating-tube density meters. In his group a new absolute viscosity measurement using the falling ball method is in progress. Nanometer measurements of the falling distance and diameters of small silicon balls are performed for providing reference data of transport properties of liquid water with a relative uncertainty of 0.01 %. Dr. K. FUJII is working as a chairman of the WG-Density, CCM (Consultative Committee for Mass and Related Quantities) to organize the research activities on the density standards at national metrology institutes. A new density-of-water table that has a specified isotopic abundance was proposed by the WG-Density and recently approved by CCM [M. Tanaka, G. Gerard, R. Davis, A. Peuto, and N. Bignel, "Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports", *Metrologia*, **38** (2001), 301-309]. This new table is recommended as a metrological standard for the density of SMOW [contact: Dr. K. Fujii, Group Leader, Density and Viscosity Standards, NMIJ; E-mail: fujii.kenichi@aist.go.jp].

At the Department of Environmental Science & Technology, Faculty of Engineering, Shinshu University, Nagano, Prof. H. TAKAKU works since Feb. 1 of 2000, and previously worked at Central Research Institute of Electric Power Industry (CRIEPI). In the simulated geothermal waters containing the mixed corrosive chemicals of chlorides, sulfides, carbon dioxide and others, he and coworkers are studying the corrosion of the steam turbine materials for geothermal power plants and also the corrosion of the Ti-Ni base shape memory alloys for the geothermal engine actuators. Recently, they start the study on the water management and corrosion monitoring of boiler materials for fossil power plants operated with the oxygenated water treatment, using mainly the electrochemical techniques such as the corrosion potential, polarization behaviors and others [Latest publications: (1) N. Kawai, H. Takaku, et al., *Zairyo-to-Kankyo* (*J. Corrosion Eng. in Japan*), **49** (2000), 612-618, (2) T. Sakuma, H. Takaku, et al., *Transactions of Materials Research*

Society of Japan, **26** (2001), 167-170, (3) L. Niu, H. Takaku, et al., *Materials Transactions*, **43** (2002), 840-845] [contact: Prof. H. Takaku; E-mail: takakuh@gipwc.shinshu-u.ac.jp].

Mr. K. MIYAGAWA is developing Tubular Taylor Series Expansion Method (TTSE) for rapid calculation of thermodynamic properties of water substance and other fluid. In the IAPWS meeting in Gaithersburg in 2001, it was decided that the TTSE method should be evaluated as an IAPWS product entitled "Documentation and Software of TTSE Method applied to IAPWS-95 as an example". Following the decision, he submitted a draft of the IAPWS product to the evaluation task group. The draft and the test report of the task group will be reported and discussed in upcoming IAPWS meeting in Buenos Aires [contact: Mr. K. Miyagawa; E-mail: miyagawa. kiyoshi@nifty.ne.jp].

At the Department of Mechanical Sciences and Engineering, Tokyo Institute of Technology, Tokyo, Assoc. Prof. S. OKAWA, Prof. A. SAITO and their group are studying the effect of oxidation on freezing of supercooled water, and finding that the oxidation of the surface restrain the supercooled water on the surface from freezing [*Int. J. Refrigeration*, **25** (6) (2002) in press]. They are also studying the crystal growth of dendrite ice in water and in solution, and finding the difference in shape depending on the concentration and the degree of supercooling [*Int. J. Refrigeration*, **25** (2) (2002), 218-225], and the effect of bubble nuclei on freezing of supercooled water [*Int. J. Refrigeration*, **25** (2) (2002), 243-249]. [contact: Dr. S. Okawa; E-mail: sokawa@ mech.titech.ac.jp].

At the Department of Surface Science, Central Research Institute of Electric Power Industry (CRIEPI), Komae, Tokyo, Dr. H. HIRANO and his coworkers are studying transformation of coal into smaller molecules in supercritical fluid. The study is in progress, and it has been found that the decomposition of coal in supercritical water (SCW) is more effective in the presence of hydrogen. They are also conducting feasibility study on the separation of metal in supercritical water. It has been found that solubility of metal in SCW strongly depends on the density of water. A study on the corrosion of materials in SCW will be started in near future. [contact: Dr. H. Hirano, Director; E-mail: hirano@criepi.denken.or.jp].

At the Energy & Mechanical Engineering Department, Central Research Institute of Electric Power Industry(CRIEPI), Yokosuka, Mr. E. KODA and Mr. TAKAHASHI are developing a computer software to calculate the heat and mass balance of fossil power generation system. In this research, IF97 was enhanced so as not to indicate an abnormal value also outside the range of approval, and built into the program. [contact: Mr. E. Koda; E-mail: kouda@criepi.denken.or.jp].

At the Center for Mechanical Engineering and Applied Mechanics, Keio University, Yokohama, Prof. M. UEMATSU and his group are constructing two apparatuses for measuring thermophysical properties of aqueous mixtures: apparatus for measuring isobaric heat capacity in a temperature range from 250 K to 500 K at pressures up to 20 MPa, and that for *PVT* properties from room temperature to 800 K up to 200 MPa. The measurements of *PVT* properties for methanol + water mixtures in a temperature range up to 420 K at pressures up to 200 MPa have been completed. The measurements of thermodynamic properties of ammonia + water mixtures will be published in the

Journal of Chemical Thermodynamics. A paper entitled "Equation of state for fluid mixtures based on the principle of corresponding states with two-fluid model. (Application to fluid mixtures of water + ammonia system)" by J. Suzuki and M. Uematsu will be published in *Heat Transfer - Asian Research*. [contact: Prof. M. Uematsu; E-mail: uematsu@mech.keio.ac.jp].

At the Department of System Design Engineering, Prof. A. NAGASHIMA and coworkers are studying measurement of transport properties of liquids including aqueous solutions and correlations of fluids properties of environmental concern. [contact: Prof. A. Nagashima; E-mail: nagasima@sd.keio.ac.jp].

At the Department of Mechanical Engineering, Keio University, Yokohama, Dr. K. YASUOKA and his group are studying the molecular dynamics simulation to clarify the mechanism for the dissociation and formation of methane hydrate. Some of the results were presented at International Conference of Gas Hydrate, Yokohama. [contact: Dr. K. Yasuoka; E-mail: yasuoka@mech.keio.ac.jp].

At the Department of Mechanical Engineering, Kanagawa Institute of Technology, Atsugi, Prof. K. OGUCHI and his group are measuring the *PVTx* properties of ammonia + water mixtures. They have measured 230 data points of *PVTx* properties of aqueous dilute solutions of ammonia along 13 isochores in the range of temperatures from 253 K to 333 K, pressures from 0.46 MPa to 17.0 MPa, densities from 954 kg□m^{-3} to 997 kg□m^{-3}, and compositions from 0.014 mol% to 0.139 mol% of ammonia, focusing their attentions on the maximum density phenomena. [contact: Prof. K. Oguchi; E-mail: oguchi@me.kanagawa-it.ac.jp].

At the Research Center for Computational Science, Okazaki National Research Institutes, Prof. S. OKAZAKI and his group started quantum-classical molecular dynamics calculation for vibrational relaxation of solute in supercritical water. They are interested in understanding relaxation machanism in terms of time-dependent couplings between solute and solvent in supercritical fluids. They also published their calculation of dielectric constant of supercritical water [N. Yoshii et al., *Chem. Phys. Lett*., **345** (2001), 195-200]. [contact: Prof. S. Okazaki; E-mail: okazaki@ims. ac.jp].

At the Department of Applied Chemistry, Ritsumeikan University, Shiga, Prof. S. SAWAMURA is measuring the solubility of cesium chloride and monosodium L-gutamate monohydrate in water at high pressures up to 400 MPa and the visicosity of water and heavy water at low temperature and high pressure region [Y. Suzuki, et al., *High Press. Res*., **21** (2001), 93-104; Matsuo, H. et al., *Fluid Phase Equilibria*, **189** (2001), 1-11; S. Sawamura et al., *J. Phys. Chem*., **B105** (2001), 2429-2436]. At the same department, Prof. Y. TANIGUCHI and Assoc. Prof. M. KATO are measuring the infrared, Raman, and NMR spectra for biological compounds at high pressures [M. Kato, et al., *Biochim. Biophys. Acta*, **1595** (2002), 131-144; 963-967; M. Kato, et al., *Biospectroscopy*, **62** (2001), 29-39]. [contact: Prof. S. Sawamura; E-mail: sawamura@se. ritsumei.ac.jp].

At the Institute for Chemical Research, Kyoto University, Uji, Kyoto, Prof. Masaru NAKAHARA, Dr. Nobuyuki MATUBAYASI, Dr. Chihiro WAKAI, and their coworkers study the structure, dynamics, and reactions in super- and subcritical water by means of multinuclear NMR (nuclear magnetic resonance) spectroscopy, Raman spectroscopy, and computer simulation. Their current

focuses are (1) the structure and dynamics of aqueous electrolyte solutions in the high-temperature regime ["Chloride ion hydration and diffusion in supercritical water using a polarizable water model", M. Kubo, R. M. Levy, P. J. Rossky, N. Matubayasi, and M. Nakahara, *J. Phys. Chem*., **B106** (2002), 3979-3986] and (2) the molecular mechanism of noncatalytic reactions in hydrothermal conditions. It should also be noted that Dr. MATUBAYASI received 2001 IAPWS Helmholtz Award for his "distinguished achievement in fundamental physico-chemical approach to elucidate the static and dynamic structure of supercritical water and related aqueous systems with the aid of NMR spectroscopy and computer simulations". [contact: Prof. M. Nakahara; E-mail: nakahara@scl.kyoto-u.ac.jp].

Department of Molecular Science and Technology, Doshisha University, Kyotanabe, Prof. M. UENO and his group are studying on the electrolyte solutions at high temperature and pressure in collaboration with Prof. M. Nakahara, Kyoto University, Uji. Reliability and limitations of the Hubbard-Onsager (HO) continuum dielectric friction theory are examined for the limiting ionic mobility in sub- and supercritical water [*J. Mol. Liq*., **98-99** (2002), 129-144]. The HO theory explains the general trends of the experimental results along the liquid-vapor coexistence curve, the isochores, and the isotherms. At lower densities and supercritical temperatures, however, the HO theory fails to reproduce the density dependence of the limiting electrolyte conductance. They are also trying to measure the viscosities of water-organic compound mixtures at high pressure. [contact: Prof. M. Ueno; E-mail: mueno@mail.doshisha.ac.jp].

At the Department of Mechanical Engineering Science, Kyushu University, Fukuoka, Prof. T. ITO (retired) and Dr. Y. TAKATA have released the newest 12.1 version of the Computer Program Package for Thermophysical Properties, PROPATH, which includes those of water substances. This software is available free of charge to any non-profit organizations. [contact: Dr. Y. Takata; E-mail: takata@mech.kyushu-u.ac.jp or http://propath.mech.kyushu-u.ac.jp/].

At Mitsubishi Heavy Industries, Ltd., Nagasaki R&D Center, Mr. T. MORIMOTO and his coworkers are studying the oxygenated water treatment for super- and sub-critical thermal power plants and Mr. M. TATEISHI and his coworkers are studying the hydrothermal decomposition of organic compounds such as poly-chlorinated bi-phenyl (PCB) and Dr. J. IZUMI and his coworkers are studying the water treatment for geothermal plants, studying the solubility of hydroxy- and fluoro-apatite in hot water for radioactives storage, and also studying the molecular simulation to assume the solubility of inorganic compounds in hot water [contact: Dr. J. Izumi; E-mail: junizumi@ngsrdc.mhi.co.jp].

Attachment 20

US Activities Report, IAPWS Meeting
Buenos Aires, Argentina
July 22-26, 2002

The Energy Institute's Electrochemical Laboratory
The Pennsylvania State University
Program Coordinator: Professor S.N. Lvov (814-863-8377, lvov@psu.edu)

Research Directions and Key Publications: 2001-2002

- **High Temperature Polymer Electrolyte Fuel Cells**

1. Allcock H.R., Hofmann M.A., Lvov S.N., Zhou X. Y., Chalkova E., and Weston J.A. Phenyl Phosphonic Acid Functionalized Poly[aryloxyphosphazenes] as Proton-Conducting Membranes for Direct Methanol Fuel Cells, *J. Membr. Sci.*, 2001, v. 201, p. 47-54.

2. Fedkin M.V., Zhou X.Y., Hofmann M.A., Chalkova E., Weston J.A., Allcock H.R., Lvov S.N. Evaluation of Methanol Crossover in Proton-Conducting Polyphosphazene Membranes, *Materials Letter*, 2002, v. 52, p.192-196.

3. Chalkova E., Zhou X.Y., Ambler C., Hofmann M.A., Weston J.A., Allcock H.R., Lvov S.N. Sulfonimide Polyphosphazene-Based H_2/O_2 Fuel Cells*, J. Electrochem. Soc.*, 2002 (in press).

4. Hofmann M.A., Ambler C.M., Maher A.E., Chalkova E., Zhou X.Y., Lvov S.N., Allcock H.R. Synthesis of Polyphosphazenes with Sulfonimide Side Groups, *Macromolecules*, 2002 (in press).

5. Zhou X.Y., Hofmann M.A., Weston J.A., Chalkova E., Allcock H.R., Lvov S.N. High Temperature Methanol Crossover in Proton-Conducting Polyphosphazene Membranes, *Proceedings of the 199 ECS Meeting*, 2002 (in press).

- **Electrochemistry of High Temperature Aqueous Systems**

6. Zhou X.Y., Lvov S.N., Wei X.J., Benning G., and Macdonald D.D. Quantitative Evaluation of General Corrosion of Type 304 Stainless Steel in Subcritical and Supercritical Aqueous Solutions via Electrochemical Noise Analysis, *Corrosion Science*, 2001, v. 44/4, pp. 841-860.

7. Zhou X.Y., Lvov S.N., Macdonald D.D., Wei X.J., and Benning L.G., Measuring Corrosion Rate in Subcritical and Supercritical Aqueous Solutions via Electrochemical Noise Analysis", CORROSION 2001, Paper# 368, NACE, Houston, Texas, March, 2001.

8. Zhou X.Y., Ulyanov S.M., Lvov S.N., Advanced Yittria-Stabilized Zirconia pH Sensing Electrode for Chemistry Monitoring in SCWO Environments, CORROSION 2001, Paper #359, NACE, Houston, Texas, March, 2001.

9. Lvov S. N., Ulmer G. C., Zhou X. Y., Barnes H. L., Macdonald D. D., Ulyanov S.M., Benning L. G, Grandstaff D. E., Manna M., and Vicenzi E., Electrochemistry and Structure of Yttria-Stabilized Zirconia Sensors for Hydrothermal pH Measurements, *Chemical Geology*, 2002 (in press).

10. Seneviratne D.S., Papangelakis V.G., Zhou X.Y., Lvov S.N. Potentiometric pH Measurements in Process Sulfate Solutions at 250°C, *Hydrometallurgy*, 2002 (in press).

Department of Earth and Planetary Sciences, Washington University, Campus Box 1169 St. Louis, MO 63130-4899. Phone: (314) 935-7435
e-mail: andreyp@zonvark.wustl.edu
Andrey V Plyasunov

The project on the estimation of the second cross virial coefficients for interactions involving water

There are data in the literature (second cross virial coefficients, B_{12}, and the cross isothermal Joule-Thomson coefficients) for about 29 interactions between water and other compounds (among these are simple fluids, nonpolar and polar compounds, and "hydrogen-bonded" compounds). Practically always the available data can be successfully reproduced by the Tsonopoulos corresponding-states correlation, provided that the mixture-specific parameter, k_{12}, is determined from the data. Therefore, we concentrated our efforts on the search of ways to estimate the k_{12} parameter. The approximate theory of k_{12} is available for the case of interactions between nonpolar molecules, and this theory gives k_{12} as the product of the "Size" and "Energy" term. We found (on an empirical basis) possible to extend this relation to the case of interactions involving water by replacing the "Energy" term with an empirical function proportional to the Gibbs energy of hydration of a compound at 298.15 K, 0.1 MPa. Certainly, the Gibbs energy of hydration at 298.15 K, 0.1 MPa is not a perfect measure of the extent of the attractive forces between water and a solute in the gas phase. However, pragmatically it is probably the best choice from single descriptors. On this basis the B_{12} values are estimated for interactions between water and many volatile inorganic and organic compounds, including many functional groups of organic compounds.

The following manuscripts are prepared:
Plyasunov A.V., Shock E.L. Second cross virial coefficients for interactions involving water. Critical data compilation. Submitted to *Fluid Phase Equil.*

Plyasunov A.V., Shock E.L., Wood R.H. Second cross virial coefficients for interactions involving water. Correlations and group contribution values. Submitted to *Fluid Phase Equil.*

A project on the estimation of vapor-liquid distribution coefficients for neutral solutes in high-temperature water.

The vapor-liquid distribution coefficient of a solute at infinite dilution, K_D^o, can be calculated from the following equation

$$K_H^o = K_D^o \Phi_2^o P_1^o ,$$

provided that Henry's constant, K_H^o, and the fugacity coefficient of a solute at infinite dilution, Φ_2^o, are known. The fugacity coefficient of a solute at infinite dilution in the gaseous phase can be calculated from the virial equation of state truncated at the second virial coefficient (this approximation is expected to be sufficiently accurate up to 550-575 K for the case of solutes in water). Our preliminary runs show that the values of Henry's constants for aqueous solutes can be reliably (errors less than 0.03-0.05 log units) predicted up to 550-575 K provided that the values of the Gibbs energy, enthalpy and heat capacity of hydration are known for a solute under consideration at 298.15 K. Therefore, we may predict reasonably accurate K_D^o values up to at least 550 K. Values of K_D^o at 450-550 K can be used to estimate the Krichevskii parameter by assuming (and we have ample empirical evidences of that) that the asymptotical near-critical relations are valid at these temperatures. Preliminary results are looking good, and we expect to generate reliable values of K_D^o and the Krichevskii parameter for many volatile compounds in water. Unfortunately, the requirement to know the values of the enthalpy and heat capacity of hydration of a solute at 298.15 K strongly limits the number of solutes for which such estimates are possible (some correlations to estimate the enthalpy and heat capacity of hydration of a solute at 298.15 K would be helpful).

This project was just recently started.

National Institute of Standards and Technology, NIST, Boulder CO
Contributors: D. G. Friend, A.H. Harvey, E.W. Lemmon, J.W. Magee, R.D. Mountain, L.A. Watts, I.M. Abdulagatov, M.M. Aliev
Daniel.friend@nist.gov, allan.harvey@nist.gov

In collaboration with theoretical chemists at the University of Nottingham, we have derived intermolecular pair potentials from quantum mechanics for water with helium, neon, and argon, and used them to calculate second cross virial coefficients for the water/gas binaries. The resulting second virial coefficients cover a larger range of temperature and have smaller uncertainties than those obtainable from experiment. We are beginning to work on water's interactions with diatomic gases, which are of more
practical interest for areas such as humidity standards and combustion gases.

A new correlation for the vapor pressure of D2O, consistent with the ITS-90 temperature scale and the IAPWS-adopted critical parameters, has been published in the Journal of Physical and Chemical Reference Data.

In collaboration with researchers in Argentina, high-temperature solubility data have been analyzed for 14 solutes in H2O and 7 solutes in D2O. These data, expressed both in terms of Henry's constant and the vapor-liquid distribution coefficient, have been correlated to expressions that exhibit the theoretically correct high-temperature behavior as the critical temperature of the solvent is approached.

Molecular simulation has been used to estimate the diffusivity of NaCl in steam at turbine conditions. This property is effectively impossible to measure, and our results suggest that simple hard-sphere estimation techniques are substantially in error. In the future, we hope to extend these calculations to NaOH and silica.

Work is continuing on the joint IAPWS and IUPAC efforts to update the formulations for the transport properties of water and steam.

The formulation for the thermodynamic properties of ammonia-water mixtures that was recently adopted as an IAPWS Guideline has been incorporated into Version 7 of the NIST refrigerants database (NIST REFPROP) that will soon be available for distribution.

Selected measurements of VLE and density (from about 308 to 348 K) on the 4-component system of water + acetone + isopropyl alcohol + sodium nitrate have been completed. Papers describing the experimental results and a model to describe the thermodynamic surface of this system and similar mixed solvent electrolyte systems are being prepared.

NIST is assisting in the coordination of a Fluid Properties Simulation Challenge (http://www.cstl.nist.gov/FluidSimulationChallenge/) to help promote developments in the areas of force fields and algorithms for molecular simulation techniques. The specific test problems on the density of water, water + methanol mixtures, and aqueous choline chloride may be of interest to IAPWS participants.

NIST is in the process of helping to organize the 15th Symposium on Thermophysical Properties to be held in Boulder in June of 2003. As in past Symposia, there will be a special focus on Properties of Aqueous Systems.
Please see http://symp15.nist.gov for details.

We are collaborating with the Dagestan Scientific Center of the Russian Academy of Sciences (DSCRAS) in the areas of thermophysical properties measurements and models. Five papers have been published, or are currently in press, a sixth has been submitted,
and a seventh is in internal review concerning our joint studies of aqueous systems. The two most recent papers concern pressure-volume-temperature and isochoric heat capacity behavior of light and heavy water mixtures in the near-critical and supercritical regions. IAPWS awarded financial support for experimental studies of methanol + water mixtures with calorimeters at NIST and at the DSCRAS. Mr. Aliev, a doctoral candidate at the DSCRAS, has completed a six-month visit to NIST during which he carried out heat capacity measurements in the NIST labs.

Attachment 20

A collaboration has been established with the National Defense Academy (NDA) in Japan in the area of calorimetry of fluid mixtures.
After successful validationests with pure light water, graduate students at the NDA carried out measurements of isochoric heat capacity for the methanol + water mixture system. The results were published in the Proceedings of the 22nd Japan Symposium on Thermophysical Properties.

University of Maryland, Institute for Physical Science and Technology and Department of Chemical Engineering, College Park, MD.
M. A. Anisimov, and J. V. Sengers
Collaborators: Kh. S. Abdulkadirova, A. Kostrowicka Wyczalkowska

(1) A.Kostrowicka Wyczalkowska, M.A. Anisimov, and J.V. Sengers, "Impurity effects on the two-phase isochoric heat capacity of fluids near the critical point", J. Chem. Phys. 116, 4202-4211 (2002).

(2) Kh.S. Abdulkadirova, A. Kostrowicka Wyczalkowska, M.A. Anisimov, and J.V. Sengers, "Thermodynamic properties of mixtures of H2O and D2O in the critical Region", J. Chem. Phys. 116, 4597-4610 (2002).

Attachment 21

The Hellenic National Committee
International Association for the Properties of Water and Steam

REPORT on IAPWS related activities

Submitted to the EC Meeting of IAPWS, Buenos Aires - July 2002

National Committee Contact:
Prof. Marc J. Assael, Chemical Engineering Department, Aristotle University
54124 Thessaloniki, Greece
Tel. +30310.996163, Fax. +3031.996190, EMail. assael@auth.gr

The work concentrated in the area of transport properties. More specifically:

As part of a joint project between the International Association for the Properties of Water and Steam and the International Association for Transport Properties (formerly known as Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry Commission I.2 on Thermodynamics), all available and reliable experimental data on the viscosity and thermal conductivity of ordinary water and steam, as well as heavy water, have been collected and converted to the current temperature scale (ITS-90) and a common set of units. The data are grouped according to state into four regions: liquid phase (excluding data at 0.101 325 MPa), steam (vapor) phase, supercritical phase ($T>T_c$ for any pressure), and liquid at ambient pressure (0.101 325 MPa) between the triple point temperature and the normal boiling point temperature. Moreover, in the case of water, for each point with measured temperature and pressure (or at specified saturation conditions) a density has been computed with the current scientific standard thermodynamic formulation (IAPWS95), and each experimental datum has been compared with the viscosity or thermal conductivity calculated from the current standard formulations for these properties.

The water database contains 3993 points for viscosity in the range of temperatures from 254 K to 1316 K with pressures to 346 MPa and 5095 points for thermal conductivity in the range of temperatures from 255 K to 1072 K with pressures to 785 MPa. The heavy water database contains 1244 points for viscosity in the range of temperatures from 277 K to 779 K with pressures to 468 MPa, and 2380 points for thermal conductivity in the range of temperatures from 277 K to 1043 K with pressures to 250 MPa.

Both collections include all data considered for the current IAPWS formulations as well as measurements published since those were completed. The study has identified new data which were not available for the previous reviews of the transport properties of water, has identified regions in which the current standard transport property formulations can now be improved, and is intended to facilitate the development of new, more accurate, international formulations for the viscosity and thermal conductivity of water and steam and heavy water.

Current facets of the research involve further temperature conversions (with Czech collaborators), evaluation of Russian equation (with Czech collaborators), development of formal statistical methods to achieve correlations (at NIST), and theoretical calculation of low-density viscosity (with British collaborators).