

Physical Chemistry Division (I)

Report of Activities

August 1997 to July 1998

The IUPAC Division I on Physical Chemistry consists of 7 Commissions with a total of $7 \times 6 = 42$ Titular (TM), 46 Associate Members (AM) 44 National Representatives (NR) and 40 additional members within subcommittees. The work is coordinated by the Division Committee consisting of 7 TM and 4 AM. There is an additional Subcommittee on Plasma Chemistry attached directly to the Division Committee with its Chairman as an AM. The seven Commissions cover different fields of Physical Chemistry. This working force is engaged in 51 projects some of which are ongoing while most of them are time-limited between 2 and 12 years.

Commission I.1 on symbols, terminology and units is exceptional in that it deals with Physical Chemistry as a whole and covers the aspects of terminology, symbols and units of physical quantities. Its work strongly depends on the recommendations produced in other Commissions including some from other Divisions of IUPAC (especially II.1, III.2, III.3, and some commissions from Division V). Its sole project the Revision of the Green Book: Quantities, Units and Symbols in Physical Chemistry consists of preparation of the third edition planned for 1999. The typing of the whole text into a standard computer-readable format (Revtex) is taking time. It is being carried out under the supervision of M. Quack and a meeting of I.1 is planned for January 1999 in order to finalize the text and get it to the printers. The main changes with respect to the second edition, except for producing the book on a computer, involve extensions in the field of surface chemistry and the treatment of uncertainties of measurement.

The largest **commission** in the Division (**I.2**) covers the field of thermodynamics. In the period since the General Assembly in Geneva it has produced numerous publications covering different types of work:

Evaluated data compilations

- Electrolyte Solution Data: Book publications in the Dechema Chemistry Data Series

Electrolyte Data Collection Volume XII.

Viscosities of non-aqueous solutions

Part 3. Alcohols published in 1997

Part 3a. Non-alcohols C1-C3 1997

Part 3b. Non-alcohols C4-C8 1997

- Thermodynamic data

- Critical compilation of vapour-liquid critical properties: 6 papers published in the period 1996-98.
- Critical compilation of vapour-liquid critical properties: papers in preparation for 1999.
- Critical compilation of heat capacities of pure liquids: publications completed in 1997.
- Critical compilation of activity coefficients at infinite dilution: publications planned for 1999 and 2000.
- International Thermodynamic Tables of the Fluid State published by Blackwell Science

Volume 14 in the series on benzene will be prepared by 1999.
Volume 15 in the series on carbon dioxide will be prepared by 2000.

- Vapour-Liquid Equilibria and Related Properties in Binary and Ternary Mixtures
Mixtures of Ethers, Alkanes, Alkanols

Workshop 1: July 1996 with 20 papers published Fluid Phase Equilibria in 1997.

Workshop 2: July 1998 with several papers to be published in 1999.

- Transport Properties

- Standards of Viscosity and Thermal Conductivity
Joint meetings with Commission I.2 and ISO re liquid water were held in 1997/98 and final agreement was reached for accepted values. Values for other fluids will be prepared by 2000.
- Correlation of Transport Properties of Fluids
The publication of standard accepted values for propane, toluene and carbon dioxide is planned in 1999 and for water, butane and ethane in 2000.
- The book Theory and Prediction of Transport Properties got published by Cambridge University Press in 1997.

Terminology

- Standardised Phase Diagram Nomenclature: Equilibrium for Vapour-Liquid and Liquid-Liquid

Joint meeting with Commissions I.1 was held in 1997, comments were received from external reviewers and final draft of manuscript will be prepared for submission in *Pure Appl. Chem.* in 1998.

- Standardised nomenclature, symbols and experimental methods for bond energies.

The second draft is being completed during 1998 and the final manuscript is expected to be ready for submission in *Pure Appl. Chem.* in 1999.

Recommendations and guidelines

- Legendre Polynomials in Chemical Thermodynamics

Joint meetings with Commission I.3 were held in 1997 and the final drafts of papers for *J. Chem. Thermodyn.* and *Pure Appl. Chem.* will be prepared during 1998.

- Guidelines for Publication of Equations of State

Publications to standardize the field.

I. Pure Fluids. *Pure Appl Chem.* **69**(6), 1237-1249, 1997

II. Fluid Mixtures. The feasibility study is under way.

Conferences

The Rossini Lecture is delivered at each two year meeting of the International Conference on Chemical Thermodynamics which the I.2 Commission sponsors and organises. In addition, it arranges for the nominations and selection of the Rossini Lecturer. The next lecture will be given at the 16th ICCT meeting in Halifax, Canada in August 2000 and the project is again under way to get the nomination and make the selection.

IUPAC Workshop: Thermodynamic and Thermophysical

Properties of Halocarbons - Properties of the new environmentally safe refrigerants.

The first Workshop will be held in Pisa, Italy in September 1999, and the second is planned in Fontainebleu, France in 2000.

Monographs

Chemistry for the 21st century

A book entitled *Chemical Thermodynamics in the 21st Century* consisting of 27 chapters has been prepared and is with the printers and publication is expected in 1999

A new edition of *Experimental Thermodynamics* Volume II (1965) is being prepared

- Vol 6: Single Phases is edited by Goodwin, Marsh and Wakeham
10 chapters are defined, authors obtained, first draft of ca. 400 pages is due late in 1999.
- Vol 7: Multiple Phases is edited by de Loos and Weir
10 chapters are defined, authors obtained, first draft of ca. 400 pages is due late in 1999.

A new 1000-pages book entitled *Theory of Equations of State for Fluids and Fluid Mixtures*, has been written and all 19 chapters are with the printer (Blackwell Science). Publication is expected in 1999.

Commission I.2 at its meeting in Porto, Portugal (15th ICCT, July '98), agreed to enter a Joint IUPAC/CODATA project on Standardisation of Physico-Chemical Properties: Electronic Data Files with Professor Kehiaian as the CODATA project officer. From Commission I.2, the active participants will be Professor Grolier, Drs Stolen, Deiters and Vogel.

Commission I.3 on Electrochemistry completed two projects:

Spectroelectrochemistry: a survey of in situ spectroscopic techniques with publication due in *Pure Appl. Chem.* **70** (7) (1998) and Nanostructures in electrochemistry: in situ local probe techniques in electrochemistry which resulted in the publication of a book with the same title by Wiley - Verlag Chemie in March 1998.

In Geneva the commission made a critical assessment of the unfinished older projects. Two projects will be continued: Measurements of redox potentials of proteins (F. M. Hawkrige) and Electrocrystallization and electroplating (M Sluyters-Rehbach, A. A. Milchev). Since Bulgaria is not represented in IUPAC any more, Milchev could not contribute as expected. The project will be continued under the new title and W. Plieth will try to prepare a new draft.

Three new projects: Electrochemistry at the interface between two immiscible electrolyte solutions (Z. Samec), Electrochemistry for the environment (Ch. Brett) and State of the art of the waste water treatment for industrial plating facilities (M. De Vogelaere) have been started and first draft manuscripts will be discussed at the off-year meeting in October 1998.

Commission I.4 on Chemical Kinetics has a very active subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. They have an ongoing project and produced two evaluations under IUPAC sponsorship in the reporting period:

R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr (Chairman), M. J. Rossi, J. Troe, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. Supplement V. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, *J. Phys. Chem. Ref. Data* **26** (1997) 509-1011;

{disk version of Summary Table published in *Atmos. Environ.* **30** (1996) 3903}.

R. Atkinson, D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr (Chairman), M. J. Rossi and J. Troe, Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. Supplement VI. IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry, *J. Phys. Chem. Ref. Data* **26** (1997) 1329-1499.

The subcommittee on evaluation of rate constants for atmospheric chemistry met in corpore in October 1997 in Vallon de Villars near Montreux, Switzerland, in order to finalize yet another Evaluation, namely "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. Supplement VII (Organics)" and discuss in detail the draft on Supplement VIII on heterogeneous atmospheric processes. Roger Atkinson indicates that he should be able to get the manuscript of Suppl VII (Organics) sent off to *J. Phys. Chem. Ref. Data* by about the end of June, 1998.

The subcommittee met in June 1998 at the same place in order to finalize the draft on Supplement VIII, heterogeneous chemistry. We expect the manuscript submission towards the end of 1998 with a publication date of early 1999. Part of the delay has to do with the fact that the secretary of R. Atkinson has to retype all data sheets.

The next meeting of the IUPAC subcommittee on Data Evaluation will deal with the planning of additional Evaluation volumes in light of the possibility of putting information on a specially dedicated Website. Early indications are that this is more difficult than expected also in view of considerable quality control and quality assurance problems. It is likely that the format of presenting the evaluations is going to change significantly also in light of changes in involvement of several members of the subcommittee.

Commission I.5 on Molecular Structure and Spectroscopy is working on 11 projects

- Practical Standards for NMR (R. K. Harris)

A report entitled "Recommendations for NMR nomenclature A. Nuclear Spin properties and Conventions for Chemical Shifts", has been reviewed by the Commission. The report contains a table of consistent NMR reference frequencies for all nuclei, and recommended definitions of the local chemical shift scale zero values. After Geneva, it was necessary to reconcile differences with Commission I.7 which arose because biophysical chemists have to use water solvent instead of non-aqueous solvents and, hence, different standards. These differences have been resolved. It was then necessary to obtain additional detail about some of the measurements. Much of this has also been done since Geneva, but additional material from Professor Granger of Strasbourg is still awaited. The document will be finalized when all of the additional material has been received. It is hoped to publish the final report in 1999.

- Guidelines for the Presentation of Instrumental Parameters in Optical and Nuclear Magnetic Resonance Fourier Transform Spectroscopies (J. E. Bertie, R. K. Harris)

The project is completed apart from publication. Originally, there were 2 parts of this project. One concerned optical spectroscopy and one NMR spectroscopy. In Guildford, the NMR part was transferred to project 150/22/95. The final report concerning optical FTS was accepted by the Commission in Geneva subject to minor changes. While these changes were made it became desirable to send the document to concerned scientists for a final review. This has been done and the replies are expected by the end of June. The document will be finished in July and submitted to PAC for publication. It contains no recommendations about nomenclature and symbols, so IDCNS is expected to rule that it does not require the extensive community review. Thus publication is expected in late 1998.

- Nonlinear Spectroscopy for Molecular Structure Determination (S. Tsuchiya)

The project is completed. The final report of this project is the 268-page book entitled Nonlinear Spectroscopy for Molecular Structure Determination edited by R. W. Field, E. Hirota, J. P. Maier and S. Tsuchiya, published by Blackwell Science, January 1998.

- Parameters and Symbols for use in Nuclear Magnetic Resonance (R. K. Harris)

The final report of the same title has been published in PAC 69 (1997) 2489 - 2495.

- Spectroscopic Intensities; Related Quantities, Nomenclature, and Symbols (J. E. Bertie)

An initial draft on which the final report will be based has been circulated among physical and analytical spectroscopists. The report will be modified on the basis of the many resulting discussions. The final report will be submitted to the Commission at the 1999 General Assembly.

- Spectroscopy under Extreme Conditions of Temperature and Pressure (A. M. Heyns)

The project leader has been ill, and has been heavily occupied for the past 9 months organizing the International Conference on Raman Spectroscopy, ICORS, to be held in Cape Town in August 1999. There has, thus been little progress in this time frame. It is understood that the first 2 parts of a 3-part project have been completed. After the ICORS conference, the Commission Chairman will request that the final reports of these two parts be sent to Commission members for review and comment. The project is expected to be completed in 1999.

- Quantities, Terminology and Symbols in Photothermal and Related Spectroscopies (Noboru Hirota, M. Terazima)

Eight of the leading workers in the field have been asked to join the project. To date, two have accepted and other acceptances are anticipated. The original plans for the project have been further developed and drafts for review, discussion and development will be commenced in the summer of 1998.

Members of the Subcommittee on Notations and Conventions for Molecular Spectroscopy have arranged a meeting during the Symposium on Molecular Spectroscopy, Columbus, Ohio, USA in June 1998. Two projects are being worked on:

- Notations and Conventions in Molecular Spectroscopy - Part 4. Vibrational-Rotational Spectroscopy (R S McDowell, J K G Watson)

Excellent progress has been made. Robin McDowell has circulated two drafts for review and discussion, and the second, 36-page, draft will be discussed at the Columbus 1998 meeting of the Sub-committee. The final report is expected at or before the 1999 General Assembly

- Notations and Conventions in Molecular Spectroscopy - Part 5. Electronic-Vibrational-Rotational Spectroscopy (J. K. G. Watson, R S. McDowell)

This project depends heavily on the preceding project. Discussions have been held, and drafts will be started after the Columbus 1998 meeting of the Subcommittee.

The Subcommittee on Theoretical Chemistry held a useful meeting at the Austin Symposium on Molecular Structure, March 2-4, 1998. Work is in progress on two projects:

- Guidelines for the Presentation of Methodological Choices in the Publication of Computational Results (J. E. Boggs)

This project has evolved to include three parts.

Part A is for ab initio electronic structure calculations. The final report has been published in Pure Appl. Chem. 70 (1998) 1015-1018, and is being put onto the IUPAC web page. The reprints will be distributed to journal editors to help them to guide authors and referees on the appropriate presentation.

Part B is for semi-empirical calculations. A draft report was reviewed by the Commission in Geneva and is in the process of revision. Following review by the leading practitioners in the field, its publication is expected in 1999.

Part C is for molecular dynamics, molecular mechanics and empirical force-field calculations. It is being pursued in collaboration with Commission I.7 which initiated a similar project in Geneva. Dr. Terry Stouch leads the I.7 project and has been made a member of the Subcommittee to avoid duplication of effort.

- The Computation of Experimental Structure and Properties of Small Molecules by Ab Initio Calculation (R. Janoschek)

The Commission Chairman has requested that this project be transferred to the Commission from the Subcommittee. A 79-page report was reviewed by the Commission in Geneva. Valuable suggestions were made and have been pursued; among these J. K. G. Watson of the NRC of Canada was consulted about the effect of the breakdown of the Born-Oppenheimer approximation on the comparison of computed and experimental values, and advised that the effect is very small. The final report is in preparation and will be circulated to the community and then to the Commission for approval. Publication is expected in 1999.

The projects/activities of **Commission I.6** can be grouped under the headings: General, Environmental Protection and Advanced Materials.

General

- Pillared clays and pillared layers (R. Schoonheydt)

Project is focused on nomenclature and characterization and is forwarded for final refereeing.

Four more preliminary projects have been accepted by Commission I.6:

- Measurement and Interpretation of Electrokinetic Phenomena (Gonzalez-Caballero; L. K. Koopal)

To initiate this project a special IUPAC workshop has been held as part of the Electrokinetic Phenomena Conference in Salzburg (April 1998). About 25 specialists have attended the workshop from all over the world. At the workshop the various aspects of a possible document have been discussed and a preliminary working party

has been established under the chairmanship of Gonzalez-Caballero from the University of Granada. This group has produced a Feasibility Study Document. This document has been sent out for review by the Division.

- Recommendations for the use of Atomic Force Microscopy in the Direct Measurements of Colloidal Forces (J. Ralston)

The AFM technique offers the possibility to measure surface forces between colloid particles. A Feasibility Study Document focused on the measurement of colloidal interactions using AFM has been prepared by Ralston, Hayes and Rosenholm and it will be sent out for review to the Division.

- Colloidal stability and flow properties of concentrated dispersions (Rosenholm)

This is a new subject; Rosenholm will propose a preliminary working party and the outline of a feasibility study. The proposed project has relevance for ceramics and many other fields where concentrated suspensions are used.

Environmental Protection

- Environmental Protection: Surface, Colloid and Catalytic Aspects (J. Ralston)

This project comprised the involvement in 3 meetings: (1) "Colloids in the Aquatic Environment" (Gregory, London 1992, proceedings: Colloids Surfaces A, 73 (1993); (2) "Soil Pollution" (Iyer, Madras 1994); (3) "Environmental Catalysis" (Misono, Tokyo 1995, proceedings: Catalysis Today, 35, 1-2, (1997). The project is now ended.

- Colloid Chemical and Catalytic Processes for the control and Protection of Environmental Pollution (L. K. Koopal, M. Misono, I. Dékány)

This project has been centered on the IUPAC sponsored International Conference "Interfaces Against Pollution" (Koopal, Wageningen 1997). 130 participants attended the conference. The final task is to publish the proceedings in Colloids and Surfaces A, 1998. About 50 papers are offered for review. The majority of these papers has been accepted and the special issue of Colloids and Surfaces is due before the end of 1998.

Advanced Materials

- Nomenclature of structural and compositional characteristics of ordered microporous materials (K. K. Unger, Liebau, Delmon, R. Schoonheydt)

The title of this project has changed somewhat in the course of the project. The recommendation document regarding this project will be sent out for refereeing to the Division.

Two preliminary projects have been accepted by Commission I.6:

- Nomenclature and Recommendations for the Characterization of Powders for Advanced Materials Manufacture (R. Schoonheydt)

At the international meeting "Powder characterization for advanced materials manufacture" (Delmon, Gijon 1997) a discussion was held regarding an action on this topic, several attendees of the meeting were willing to contribute to the action. A

feasibility study on this activity is under way. Several older initiatives of Commission I.6 are joined in this project.

- Recommendation for the Characterization of Inorganic Membranes

This activity is to be carried out as joint project with Commission IV.3 (Albertsson). A feasibility study will be proposed in the near future.

IUPAC Strategic Initiative in Materials: An important part of the projects of Commission I.6 are connected with the preparation or characterization of new advanced materials. This domain is not exclusively that of our commission and certainly in this field collaboration with other Commissions and Divisions through the Inter Divisional (limited lifetime) working party co-chaired by Professor John Corish (Inorganic Division) and Professor Robert Gilbert (Macromolecular Division) is important. All initiatives regarding new materials have been reported to this working party.

Further collaboration: Other fields of collaboration emerge with the Commissions on Electrochemistry (e.g., electrochemistry at interfaces, nanostructures, poisons for catalysts), Fundamental Environmental Chemistry (see Subcom. E) and Biophysical Chemistry (e.g., microcalorimetric techniques, the role of adsorption at interfaces, terminology of liquid vesicles and membranes).

The relatively new **Commission I.7** on Biophysical Chemistry works on 6 projects.

- Recommendations for the presentation of NMR structures of proteins and nucleic acids (K Wüthrich)

The final document was published in *Pure Appl. Chem* 70 (1998) 117-142. It will also appear shortly in leading structural journals *Biochemistry*, *J. Mol. Biol.* and *J. Biomol. NMR*. This document will be useful and valuable in the standardization of reporting of NMR structures of proteins, nucleic acids and macromolecules in general.

- Recommendations for reporting the results of computations in biophysical chemistry (T. Stouch)

The working party has met twice at conferences and plans to meet again (6 members) with J E Boggs (SC 155) in New Jersey in autumn 1998 in order to produce (i) an educational paper and (ii) a draft of recommendations.

- Terminology in the field of lipid vesicles (liposomes) (H. Hauser)

A 3-day meeting of the six-membered working party was organized in April 1998. General consensus has been achieved among the members on most points and a document containing recommendations on nomenclature and symbols in the field of liposome science is being drafted.

Three more projects are all expected to be finished at the General Assembly in 1999:

- Electrochemical biosensors (D. Thévenot),

- Recommendations for the measurement and for the presentation of results obtained on biological substances with scanning calorimetry (F Schwarz, H-J Hinz) and
- Nomenclature for lipid mesophases (M. Caffrey).

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