

PHYSICAL AND BIOPHYSICAL CHEMISTRY DIVISION REPORT
FIRST YEAR OF THE BIENNIUM 2004-2005

JUNE 2005

REPORT TO THE IUPAC BUREAU: MEETINGS IN BEIJING, P.R.CHINA,
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I. Executive Summary and Highlights

Initiatives to promote projects from those working in the **Biosciences subject area** continued to be made during the biennium following the change in name of Division I in autumn 2000 to Physical and Biophysical Chemistry Division (PBPCD). A major international workshop on the Physical Chemistry of Bio-interfaces was held near Adelaide, South Australia 23–26 May 04 in series with the Seventh World Biomaterials Congress in Sydney, Australia 17-21 May 04. IUPAC was well represented with the Past President of Division I being one of the organisers of the workshop attended by the current President of the Division. Time was allocated for these two individuals to address the attendees about the IUPAC system that provides funding support for projects and to encourage their submission. The workshop was aimed at providing fundamental insights into topics such as interfacial forces and properties involved in protein/surface interactions and the molecular kinetics of drug delivery. It is clear that there is a need for standardisation of terminology and agreement on calibration protocols, both areas where IUPAC can play an important role as the catalyst. The workshop itself was very successful and we wait to see its success in encouraging IUPAC participation. One immediate result is the emergence of a TM nominee representing the field of biophysical chemistry.

The Division continues with its important work of **establishing databases in specific subject areas**. A significant advance has been achieved with one of our several projects on databases, namely that of the evaluated kinetic data for atmospheric chemistry by setting up a website at the University of North Carolina, USA, to mirror the parent site in Cambridge, UK. The site continues to attract some *4000* accesses per week and for the eleven of the publications that have resulted from this database to date, there have been 2599 citations in RED. A substantial number of downloads continues in areas of heterogeneous reactions, thermodynamic data and in guides to the data sheets. The positive spin off is being realised from the decisions taken at the Bureau meetings in Paris to locate all the databases at the University of North Carolina with service support from the IUPAC secretariat and maintenance from the Division. It is at the stage of submission of a project proposal that these matters are to be defined clearly.

The Division remains active with its **chemical thermodynamics** component. You will recall that as a result of the IUPAC restructuring beginning in 2002, the International Association of Chemical Thermodynamics [IACT] was set up. The IUPAC Council at its meeting in Ottawa in August 2003 granted the IACT Associated Organisation status within IUPAC. The IACT has held its biennial meeting, the 18th IUPAC International Conference on Chemical Thermodynamics, in Beijing, P.R. China, during August 2004 with an especially large attendance by scientists from within Asia, many not reachable when the ICCT Conference is held in Europe or the Americas. Topic areas included electrolytes and non-electrolytes, new materials, supercritical fluids, biological applications, medical applications, interfaces, molecular simulation, energetics, industrial thermodynamics and databases, and frontiers in thermodynamics.

The Division is contributing to the final stages of **the revision of the Third Edition of the Green Book [Quantities, Units and Symbols in Physical Chemistry]**, through its membership in the ICTNS. The third edition is to be placed in whole or in part on the Web as well as to be translated into several languages. It is unfortunate that its publication has been delayed. For the biennium 2004-05, the Division has 28 projects underway, which include five nearing completion and seven interdivisional. This total of 28 compares with 35 for the 2003-04 biennium as the Division attempts to focus its efforts on fewer projects but with more financial support for each.

The initiative by the Division to establish **the Advisory Subcommittee of 61 international distinguished scientists and engineers**, some of whom are drawn from industry, is bearing fruit. The members of the subcommittee are listed on the IUPAC website and in the IUPAC Handbook (p29) and all are IUPAC Fellows. The role of the subcommittee is to serve as a sounding board for the Division Committee, suggesting areas that may be dealt with by the Division, drawing attention to the need for experimental protocols in specific subject areas, taking part in IUPAC conferences, and acting as one source of expert referees for IUPAC proposals. The immediate benefit realised from the subcommittee is the reduction of the period needed for the assessment of project proposals to a period of weeks rather than months. It is important to realise that the responsibility for leading and guiding the Division to include encouraging and supporting all its growing activities lies on the shoulders of a relatively few individuals,

who also have heavy responsibilities in their work place and who undertake IUPAC work for public service and service to their profession. The network created by the establishment of our Advisory Subcommittee has been helpful in this regard as well as by the IUPAC Secretariat. The membership of the subcommittee is to be reviewed biennially.

II. Activities of Division I within the IUPAC Framework and its Goals

In their totality, the projects of Division I embody all of the five long-range goals of IUPAC. Some projects support certain goals more strongly than other projects depending on the nature of the project. In terms of **leadership**, the Division continues to exert a strong role through the Interdivisional Committee on Terminology, Nomenclature and Symbols. Its current major project is the production of the new edition of the Green Book, whose influence is very significant in education, research, industry, and publishing through the world. The Division's work with the Chemical Education Committee serves both goals of **leadership** and **chemical education**. Its projects through the International Association of Chemical Thermodynamics promotes connections to **chemistry-related industry** via workshops, **communications** among individuals and the addressing needs of chemistry and applied chemistry in **developing countries** via the rotation of conferences to include these countries with special financial incentives to assist attendance. Several of the Division's current projects are devoted to **advancing research in the chemical sciences** via international **standardisation**, while simultaneously promoting **scientific discussion**.

Scientific **leadership** is further realised by the Division's IUPAC-sponsored projects. One excellent example is the introduction of thermodynamic networks that is changing the way evaluated data will be obtained in the future where experimental redundancies exist. In those cases, a thermodynamic parameter such as the standard heat of formation of an intermediate of transient molecular species may be deduced using different experimental data from various experimental methods. Consistent thermodynamic networks will minimise the individual errors and optimise the fit to all existing data at the same time. The formalism is in the process of being worked out and applied in the near future. Specific examples are the free radical projects 2001-015-1-100 (Standard potentials of radicals) (see Sections III A 3 and IV A 3) and 2003-024-1-100 (Selected free radicals and critical intermediates: thermodynamic properties from theory and experiment) (see Sections III A 12 and IV A 12). It is clear that this procedure applies to "mature" fields where there is large bank of existing data.

The creation of the 61-person Advisory Subcommittee has **broadened the membership base** of the Division significantly with a geographic balance and with an attempt to address the gender and age imbalance.

III. Project List with Updated Progress Reports

This section contains the list of all projects underway together with their current brief progress reports. These include the 16 Current Projects, the five projects nearing completion, the seven other interdivisional projects and the single project in review at the time of preparing this report. The funds awarded for support to the 17 current projects amount to \$205.7k, which compares with the Divisional budget of about \$55k. The large difference has originated from the IUPAC Projects Committee.

PROJECT LIST WITH UPDATED PROGRESS REPORT

A. CURRENT PROJECTS

1. 1999-016-3-100 - [Recommendation for the use of AFM in the direct measurements of colloidal forces](#)

This project for the use of the Atomic Force Microscope (AFM) is nearing completion. The manuscript was submitted July 2004 to the IUPAC ICTNS, is accepted for publication and is in the final stage for printing. The abstract of the paper follows by J. Ralston, I. Larson, M.W. Rutland, A.A. Feiler, and M. Kleijn.

The atomic force microscope (AFM) is designed to provide high-resolution (in the ideal case atomic) topographical analysis, applicable to both conducting and non-conducting surfaces. The basic imaging principle is very simple: a sample attached to a piezoelectric positioner is fastened beneath a sharp tip attached to a sensitive cantilever spring. Undulations in the surface lead to deflection of the spring, which is monitored optically. Usually a feedback loop is employed which holds the spring deflection constant and the corresponding movement of the piezoelectric positioner thus generates the image. From this it can be seen that the scanning AFM has all the attributes necessary for the determination of surface and adhesion forces; a sensitive spring to determine the force, a piezo electric crystal to alter the separation of the tip and surface, which if sufficiently well-calibrated also allows the relative separation of the tip and surface to be calculated. One can routinely quantify both the net surface force (and its separation dependence) as the probe approaches the sample, and any adhesion (pull-off) force on retraction. Interactions in relevant or practical systems may be studied and, in such cases, a distinct advantage of the AFM technique is that a particle of interest can be attached to the end of the cantilever and the interaction with a sample of choice can be studied, a method often referred to as colloid probe microscopy. The atomic force microscope, or, more correctly the scanning probe microscope, can thus be used to measure surface and frictional forces, the two foci of this article. There have been a wealth of force and friction measurements performed between an AFM tip and a surface, and many of the calibration and analysis issues are identical to those necessary for colloid probe work. We emphasise that this article confines itself primarily to elements of colloid probe measurement using the AFM.

2. 1999-037-2-100 - [Evaluation of kinetic data for atmospheric chemistry](#)

The objectives of this project are to enhance the accessibility and availability of the evaluated kinetic database, to develop and implement a way to update material on the website to include various linkages and the creation of a mirror website at IUPAC in North Carolina. All the data sheets for reactions of Ox, HOx, NOx, SOx, organic reactions, the inorganic halogen reactions, and most of the inorganic halogen reactions have now been added. Additional supplementary material has also been posted on the site. The remaining work includes data sheets for the halogen species, heterogeneous reactions and any updates created since June 2005. The current number of accesses is about 4000 per week with 370 subscribers to the mailing list for announcements, which represent an increase of 10% since 2003-04. The mirror site at UNC continues to be operational and is automatically updated when changes are made to the Master site in Cambridge, UK. For 11 of the publications that have flowed so far from this project, there have been 2599 citations in RED.

3. 2001-015-1-100 - [Standard potentials of radicals*](#)

The aim of this project is to evaluate critically the standard potentials of inorganic and organic radicals in the literature, to recommend values, and to identify reduction potentials for further experimentation.

Currently, one set of evaluations and seven summary tables have been prepared, including: Inorganic Standard Potentials, Gibbs Energies of Formation for Radicals, Inorganic Radical pK_a s, Hemicolligation Equilibrium Constants, Organic Standard Potentials, Radical Henry's Law Constants, and Inorganic Radical Equilibrium Constants. Linked to these tables are the 140 individual evaluation sheets. The Technical Report was accepted for publication in February 2005.

One particularly challenging task is to obtain a least-squares optimisation for a thermo-chemical network that links the properties of about 50 radicals, primarily inorganic. Evaluations are complete for about half of these radicals and a robust method has been developed for performing the least-squares optimisation.

4. 2001-028-1-100 - [Electrochemical impedance spectroscopy - terminology, nomenclature and data exchange formats](#)

The aim is to summarize, standardize and disseminate the nomenclature of fast developing new fields of application of electrochemical impedance spectroscopy. It seeks to standardize conventions of formats for experimental data exchange and analysis.

The work is complete and the paper written for two of the three items, namely the aspects of nomenclature and data exchange formats. The first

draft of the paper for terminology or definitions aspect resulted in 70 pages, which is currently being reduced to about 20 pages.

5. 2001-030-1-100 - [Recommendations on the measurement and analysis of results obtained on biological substances with isothermal titration calorimetry](#)

The aim is to prepare recommendations for measurement procedures for isothermal titration calorimetry applied to biological substances, the calibration procedures. The recommendations will include analysis and reporting of the results in order to facilitate universal comparability of ITC data from different laboratories.

Measurements are complete for a working standard NAD/NADH binding to a protein, lactate-dehydrogenase for checking the performance of isothermal titration calorimeters. The first draft of the report is will be complete by December 2005. The 'round-robin' ITC results from 12 laboratories on the binding of 4-carboxybenzene sulfonamide to carbonic anhydrase are complete and they are being evaluated for inclusion in the IUPAC Recommendations.

6. 2001-035-1-100 - [Measurement and interpretation of electrokinetic phenomena](#)

The aim is to prepare recommendations to standardize definitions of the different electrokinetic phenomena, names for the physical quantities, the use of the different experimental methods phenomena and the applicability of the various experimental techniques.

The Technical Report was accepted by the ICTNS on February 2005 for publication in PAC.

7. 2002-005-1-100 - [Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems](#)

The aims of this project are to initiate systematic studies of thermodynamic and thermo-physical properties of Ionic Liquids (IL) based on the needs of industrial chemical processes, to establish a reference system of IL's and (IL + liquid mixtures) with reliable stability and purity and well defined thermodynamic properties, and to define guidelines regarding where research activities and future cooperation should be directed.

At ten different laboratories around the world for the standard reference materials, extensive measurements have been completed for the viscosity, density, thermal conductivity, heat capacity, electrical conductivity,

enthalpy of dilution, gas solubility at high pressure, and speed of sound over the temperature range from 238 K to 378 K. The target date for completion of all experiments is July 2005 and final report is anticipated July 2006.

8. 2002-063-1-100 - [Chemical thermodynamics in industry](#)

The book was published in September 2004 by the Royal Society of Chemistry, Cambridge. It contains 23 chapters that cover 276 pages.

9. 2003-005-1-100 - [Recommended values of the viscosity of molten iron and aluminium](#)

The aims of this project are to reach agreement about the equations used to determine the viscosity by the oscillating cup method, to review critically the widely different data that exist in the literature, and to recommend standard values to be used by the international community.

The round-robin experiments have been completed and the goals of the work are realised. The final manuscript for this Technical Report and IUPAC Recommendation has been approved by ICTNS for publication in PAC and for submission to J Physical Chemical Reference Data.

10. 2003-006-1-100 - [NMR chemical shifts: updated conventions*](#)

The objectives are to update IUPAC Recommendations 2001: NMR Nomenclature, Nuclear Spin Properties and Conventions for Chemical Shifts [[PAC 73, 1795 \(2001\)](#)] by addressing several issues in setting standards for chemical shifts, including temperature variation of the NMR signals of reference compounds, the use of magic-angle spinning for both solutions and solids, solvent effects, and magnetic susceptibility corrections.

Fundamental measurements of the temperature variation of proton chemical shifts versus the signal for He-3 gas are complete and the manuscript is in draft form. The draft paper has also been prepared on shape factors for use with magnetic susceptibility corrections and on high-precision chemical shift measurements. These articles will form the backbone of the final IUPAC Report.

11. 2003-020-2-100 - [Ionic liquids database](#)

The aim is to create an open-access, free, on-line, comprehensive database for storage and retrieval of metadata and numerical data for ionic liquids, including their syntheses, structure, properties, and uses.

The collection of data has been assigned among the seven participating laboratories along with the assignment of the development of the WEB outlet for the system and the storage and retrieval system. The database, storage and retrieval systems have been developed at the Thermodynamics Research Centre at NIST. These systems have been successfully deployed and are undergoing testing. The external launch is planned for December 2005 at which time the collection of data will be interfaced. A meeting of the Task Group is planned for Beijing, P.R. China in August 2005.

12. 2003-024-1-100 - [Selected free radicals and critical intermediates: thermodynamic properties from theory and experiment](#)

The objective of this project activity is the compilation and critical evaluation of published thermodynamic properties, including the computation of accurate thermo-chemical data for selected free radicals that are of importance in atmospheric and combustion chemistry.

A substantial part of the work has been completed and 12 papers have appeared or are in press during 2004-05. See Section IV below. Additional papers are being written as the work progresses. While the scope of this project was originally targeted to perform a systematic critical evaluation of the thermochemistry of important radicals, the scientific problems that are being encountered and formulated as the evaluation effort progresses, have become a unique *spiritus movens*, motivating ground-breaking research and development of new general methods. This is especially the case in the areas of electronic structure calculations (W3 and HEAT), and of dealing efficiently with complex interrelationships inherently present in thermochemistry (ATcT).

Given the fact that the funds originally allocated for this project are being utilized more slowly than planned, and that the scope of the project has expanded beyond the initial intent (both by expanding the target list of radicals and by developing new generalized approaches related to the needs of the project), the project requests a no-cost extension.

13. 2003-036-2-100 - [Thermodynamics and non-equilibrium criteria for development and application of supplemented phase diagrams](#)

The aim of the project is to establish rational links between thermodynamic aspects of phase diagrams supplemented by the non equilibrium curve of the glass transition temperature for mixtures of water with vitrifying agents used in the cryo- and dehydro- preservation of natural (foods, seeds, etc.) and synthetic products (pharmaceuticals).

The update and literature classification on supplemental phase diagrams for relevant aqueous systems for food and pharmaceuticals has been completed. The initial critical evaluation of this database to include the

shortcomings of current practice is to be finished by July 2005. The Technical Report is expected during December 2005.

14. 2004-010-3-100 - [Heat capacity of liquids: critical review and recommended values for liquids with data published between 2000 and 2004](#)

The aims are to update and to extend two publications that contained recommended data on liquid heat capacities for almost 2000 mainly organic compounds, "Heat Capacity of Liquids: Critical Review and Recommended Values", and its "Supplement I" by M. Zábranský, V. Ruzicka, V. Majer (1st work only), and E.S. Domalski published in *Journal of Physical and Chemical Reference Data* in 1996 and 2001. The publications were the product of IUPAC Projects 121/11/87 and [2000-031-1-100](#).

The new literature search has located about 150 papers that report results for calorimetric measurements of liquid heat capacities of about 300 compounds having their melting temperature below 573 K. The existing database for experimental results is being expanded to include these new results and will be complete during November 2005. Their critical assessment and correlation is expected to be complete by April 2006 and manuscript destined for *J Physical Chemical Reference Data* to be ready for ICTNS by September 2006.

15. 2004-026-2-100 - [Categorizing hydrogen bonding and other intermolecular interactions](#)

The aims are to provide a modern definition of the hydrogen bond by examining comprehensively the various intermolecular interactions in the light of all current experimental and theoretical information. Hydrogen bonded systems both in gaseous and condensed phases in chemical and biological systems will be examined.

The first meeting of the Task Group is scheduled for a workshop in September 2005, where all members will present a summary of their recent work.

16. 2004-036-1-100 - [Establishing recommended data on thermodynamic properties of hydration for selected organic solutes](#)

The objectives are to establish a database of thermodynamic properties of hydration for approximately 200 selected organic solutes at reference conditions of $T = 298.15$ K and 0.1 MPa and as a function of temperature and pressure up to the near critical region of water, to calculate from the reliable experimental data the values of hydration properties for solutes

covering different molecular structures, to use the established database as a standard for testing and deriving new physico-chemical models and methods of molecular simulation to include the development of semi-theoretical prediction schemes for chemical engineering, environmental chemistry and geochemistry.

The work has just begun.

* Interdivisional project

B. PROJECTS NEAR COMPLETION OR IN PRESS

1. 110/2/81 - [Revision of "Quantities, Units and Symbols in Physical Chemistry" and the Appendices \(3rd edition\)](#)

The objective is to revise the 2nd edition of "Quantities, Units and Symbols in Physical Chemistry" and the Appendices.

Progress: Its sole project the *Revision of the Green Book: Quantities, Units and Symbols in Physical Chemistry* consists of preparation of the third edition planned. The draft version was circulated at the GA held in Brisbane in 2001. No progress has been reported since that date.

2. 120/15/95 - [Thermochemistry of chemical reactions: nomenclature, symbols and experimental methods for bond energies](#)

The Technical Report describing this project has been submitted, reviewed and accepted by the ICTNS with recommended change in the organisation of the report to reflect both Recommendations and content of a Technical Report. The approved revised title is 'Thermochemistry of Chemical Reactions: I. Terminology and Symbols IUPAC Recommendation 2003, II. Experimental Methods for the Determination of Bond Energies IUPAC Technical Report'. The revisions are being incorporated and the project should be complete by the close of this biennium.

3. 120/16/97 - [New Edition of Experimental Thermodynamics Vol II](#)

The aim of this project is to prepare an updated version of Experimental Thermodynamics. The enormity of the task led to dividing it into two separate volumes. Volume VI appeared in 2003 and Volume VII is due out from the printer in late 2005 or early 2006.

Volume VI. Measurement of the Thermodynamic Properties of Single Phases

Editors: A.R.H. Goodwin, K.N. Marsh and W.A. Wakeham
published - Elsevier, 2003 [ISBN 0-444-50931-3]

Volume VII. Measurement of the Thermodynamic Properties of Multiple Phases

Editors: Th. de Loos and R.D. Weir

The 16 chapters that make up the edition are in the hands of the production department of Elsevier Publishers. Some 24 authors from nine different countries contributed material. This book contains descriptions of recent developments in the techniques for measurement of thermodynamic quantities for multiple phases of pure fluids as well as mixtures over a wide range of conditions. The precision and accuracy of results obtained from each method was regarded as an essential element in each description. Throughout the text, the quantities, units and symbols are those defined by IUPAC for use in the international community.

Anticipated publication date: late 2005 or early 2006.

4. 150/24/95 - [Spectroscopy under extreme conditions of temperature and pressure](#)

The objectives are to obtain international agreement on methods and standards and to prepare documents to guide workers in the field of spectroscopy under extreme conditions. Initially vibrational and electronic spectroscopy will be considered, but the project may be extended to NMR, Mossbauer, and other spectroscopies if the early work reveals interest in these areas. The main issues to be pursued come under the three general headings Instrumentation, Pressure Calibration, and Temperature Calibration. Instrumentation includes the consideration of cell design, the use of membranes with diamond anvil cells, the properties of optical windows under extreme conditions, the design of spectrometers and microscopes, the use of optical fibres for safe access to difficult experimental situations, and the simultaneous generation of high pressure and low temperature in an optical cell. The calibration issues include methods and standards for the calibration of hydrostatic and very non-hydrostatic pressures. Emphasis will be on calibration through the spectroscopic properties, with the intention to make recommendations in the final report of standard substances, inorganic, organic and biological, whose spectroscopic properties can be used for calibration and for establishing the performance of apparatus.

Progress:

A progress report has not been received and the status of this project is unknown.

5. 2000-026-1-100 - [Critical compilation of vapour liquid critical properties](#)

The objective is to review all measurements of vapour-liquid critical properties for pure organic compounds containing **nitrogen**, **halogen(s)**, and **sulphur** and **silicon** and to recommend values for critical temperature, critical pressure and critical densities, with uncertainties.

To date, the project has resulted in eight review papers (Parts 1 to 8) published in the *Journal of Chemical and Engineering Data*. See Section IV below.

Part 9 (nitrogen compounds) has completed the IUPAC review process and will be submitted for publication in June 2005. Part 10 (halogen compounds) will be sent to IUPAC review in June 2005. Part 11 (miscellaneous compounds) is 95% written.

6. 140/6/93 - [Evaluated Chemical Kinetics Data for Combustion Chemistry](#)

This project ended formally several years and was coordinated by Don Baulch and Michael Pilling. It is appropriate at this point of this divisional Report to note that following a fairly long delay, the extensive article regarding the database for chemical reactions is about to be published by Journal of the Physical and chemical Reference Data.

C. OTHER INTERDIVISIONAL PROJECTS

1. 2000-012-1-300 - [Single molecule spectroscopy](#) (Division III)

2. 2001-036-1-300 - [Glossary of terms in photocatalysis and radiation catalysis](#) (Division III)

3. 2002-024-1-300 - [Glossary of terms used in photochemistry](#) (3rd version) (Division III)

4. 2003-056-2-500 - [Standard definitions of terms relating to mass spectrometry](#) (Division V)

5. 2004-005-2-500 - [Comparable pH measurements by metrological traceability](#) (Division V)

6. 2004-035-1-100 - [A database of water transitions from experiment and theory](#) (Division V)

7. 2004-021-1-300 - [Reference methods, standards and applications of photoluminescence](#) (Divisions III and V)

D. PROJECTS IN REVIEW

1. 2005-016-1- [Solubility for Industry](#)

* Interdivisional project

IV. PROJECT DESCRIPTIONS

This section contains a detailed summary of all projects currently underway.

A. CURRENT PROJECTS

1. **Number:** 1999-016-3-100

Title: Recommendation for the use of AFM in the direct measurements of colloidal forces

Task Group Chairman: [John Ralston](#)

Members: [A.A. Feiler](#), [R. Horn](#), [I. Larson](#), [M. Rutland](#), and [J.M. Kleijn](#)

Objectives: To recommend:

- Procedures for the measurement of the inter-particle distance dependence of colloidal force data using the atomic force microscope colloid probe technique
- Methods by which the force-distance data can be compared with existing models of inter-particle forces.

Description:

The colloid probe AFM technique is a promising new method to determine the interactions between colloidal bodies. The technique is based on the general AFM and this equipment is, in principle, available for many research groups (not excessively expensive). In order to avoid confusion in the literature about the use of the AFM equipment for colloid stability measurements (and consequently about the interpretation of

results) recommendations for the use of this equipment for this type of measurement are needed.

Project Contents:

- Principles of atomic force microscopy
- Attachment of colloidal probe to cantilever
- Force measurement Attachment of colloidal probe to cantilever
- Distance separation
- Determination of spring constant
- Determination of colloid probe radius
- Interaction geometry
- Inter-particle forces
- Non-deformable and deformable surfaces
- Symmetric and asymmetric interactions

Progress: Review/update published in [Chem. Int. Nov 2003](#)

In July 2004, a technical report was submitted for publication in *Pure and Applied Chemistry*

Last Update: 12 July 2004

2. Number: 1999-037-2-100

Title: Evaluated kinetic data for atmospheric chemistry

Task Group Chairman: [R.A. Cox](#)

Members: [R. Atkinson](#), [J.N. Crowley](#), [R.F. Hampson](#), R.G. Hynes, M.E. Jenkin, [M. J. Rossi](#), and [J. Troe](#)

Remarks: Continuation and expansion of [141/3/89](#)

Objective

The primary objective of this project is to enhance the accessibility and availability of the evaluated kinetic database, which has been assembled by the IUPAC Subcommittee for Gas Kinetic Data evaluation for Atmospheric Chemistry, by placing the material on an interactive site on the www. A second objective is to develop and implement a scheme for updating the material on the website.

Background

The IUPAC Subcommittee (formally the CODATA Task Group on Chemical Kinetics) was originally tasked to produce an evaluation of the existing chemical kinetics data in 1977, in response to the need to provide an internationally judged data set for modelling the depletion of

atmospheric ozone due to man made pollutants. Since that time the Subcommittee has continued to expand and update the evaluations to aid modelling of a wide range of issues involving Atmospheric Chemistry. The evaluations have been published in a series of nine peer-reviewed articles in *J. Phys. Chem. Ref. Data*. These articles contain two elements: Firstly a summary table which contains a list of recommended rate parameters giving the best available values for rate coefficients for use in models representing atmospheric chemistry explicitly as a system of elementary chemical reactions: Secondly each reaction is discussed in a separate data sheet, in which the key experimental data are summarised and the basis of the recommendation together with its uncertainty is given. These data sheets provide details that are of interest to atmospheric modellers and experimental scientists conducting investigations of kinetics and mechanisms of atmospheric reactions, and chemical kinetics generally. In order to further publicize the accessibility of this web-based material to the scientific community, the evaluation is also being published as a series of journal articles in *Atmospheric Chemistry and Physics*.

Description

In 1998 the IUPAC Subcommittee created a website at the Centre for Atmospheric Science in the Department of Chemistry, University of Cambridge, UK, (<http://www.iupac-kinetic.ch.cam.ac.uk>). This site has attracted very significant interest since its creation, and has now been expanded, and a mirror site has been created at the IUPAC HQ website in N. Carolina, US. Currently there are approximately 4000 connections to the website per week and over 370 subscriptions to the web mailing list for announcements.

The main purpose of the ongoing IUPAC project is to extend the content of the website to include the remaining datasheets for the 850 gas phase reactions, the photochemical reactions (absorption cross sections, quantum yields), and heterogeneous reactions (kinetic uptake coefficients for atmospheric gases on a range of surfaces), for which the data have been evaluated since the first publication by the Group in 1980. In addition to expansion, the website is continually being modified to give improved access, including a simple search facility and implemented hyperlinks between the summary table and the data sheets.

Progress: The database covers over 600 reactions relevant to the chemistry of the stratosphere and the troposphere. The data sheets are grouped in a series of categories that include:

1. Gas phase and photolysis reactions of Ox, HOx, NOx and SOx species.

2. Gas-Phase and photolysis reactions of organic species (including reactions with HOx, NO₃ and halogen radicals).
3. Reactions of organic peroxy radicals, organic alkoxy radicals and other organic radicals with oxygen.
4. Gas Phase and photolysis reactions of inorganic FOx, ClOx, BrOx and IOx species.
5. Gas Phase and photolysis reactions of organic halogen species.
6. Uptake coefficients for non-reactive and reactive heterogeneous processes.

In the future the efforts of laboratory kineticists will continue to provide new data in response to new scientific and societal issues in the field of Atmospheric Chemistry. The IUPAC Group is seeking a more effective way of updating and extending the portfolio of recommended rate coefficients, which will be necessary to maintain an effective and ongoing communication between laboratory scientists and atmospheric modellers. The establishment of web-based material allows for the first time the opportunity of near continuous update of the evaluation. The development and implementation of protocols for the updating of the evaluation, both web-based and archived hard copy will also be carried out.

➤ [Publications listing](#) (including latest supplements)

The number of citations are shown at the end of each entry and are in the sequence of the time history as follows: 3 Mar 2000/3 Nov 2000/16 Apr 2001/20 Nov 2001/19 Apr 2002/11 Jun 2003/16 Jun 2004/9 Jun 2005.

R. Atkinson, D.L. Baulch, R.A. Cox, J.N. Crowley, R.F. Hampson, Jr., R.G. Hynes, M.E. Jenkin, M.J. Rossi, and J. Troe, Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II - reactions of organic species, *Atmos. Chem. Phys. Discuss.*, in open review (2005).

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Last Update: 11 November 2004

3. **Number:** 2001-015-1-100

Title: Standard potentials of radicals

Task Group Chairmen: [David M. Stanbury](#)

Members: [D. Armstrong](#), [J. Butler](#), [R. E. Huie](#), [W.H. Koppenol](#), [Sergei V. Lymar](#), [G. Merényi](#), [Pedi Neta](#), [S. Steenken](#), and [P. Wardman](#)

Objective:

To evaluate critically the standard potentials of inorganic and organic

radicals in the literature, to recommend values, and to identify reduction potentials for further experimentation.

Description:

Radicals play an important role in many chemical transformations. There are presently two fields where more detailed knowledge of the thermodynamic properties of radicals would be extremely useful. The first is biomedicine. The discovery of superoxide dismutase and nitrogen monoxide as a messenger has led to an explosive growth in articles in which one-electron oxidations and reductions are explored. Organic radicals play an important role in the treatment of cancers. The other is atmospheric chemistry where modelling of reactions requires accurate reduction potentials. There are presently two compilations^(1,2) which are now both more than ten years old and in need of updating. We plan to compile new data that has been published since 1989, set up a thermodynamic network and develop in this fashion values for standard potentials that are internally consistent. Per radical we will prepare a data sheet as found in the JANAF tables. The relation of a particular radical to neighbouring (+/- one electron) stable compounds will be shown in oxidation state diagrams. We will start with radicals for which accurate data are known in water and then extend our studies to radicals that have been studied in organic solvents, or for which only estimated data are available.

References

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Progress:

Feb 2005 - So far, a set of evaluations and seven summary tables have been prepared, including: Inorganic Standard Potentials, Gibbs Energies of Formation for Radicals, Inorganic Radical pK_as, Hemicolligation Equilibrium Constants, Organic Standard Potentials, Radical Henry's Law Constants, and Inorganic Radical Equilibrium Constants. Linked to these tables are the individual evaluation sheets. At present we have prepared about 140 evaluation sheets.

One particularly challenging task is to obtain a least-squares optimization for a thermo-chemical network that links the properties of about 50 radicals (primarily inorganic). We have completed evaluations for about half of these radicals and found that we have a robust method for performing the least-squares optimization.

Last update: 24 February 2005

4. **Number:** 2001-028-1-100

Title: Electrochemical impedance spectroscopy – terminology, nomenclature and data exchange formats

Task Group Chairman: [Z. Stoynov](#)

Members: [C. Brett](#), [M. Orazem](#), and [J. Vogelsang](#)

Objective:

The aim of this project is to summarize, standardize and disseminate the nomenclature of fast developing new fields of application of electrochemical impedance spectroscopy. It is also targeted to standardizing conventions of formats for experimental data exchange and analysis.

Description:

The IUPAC recommendations "Impedances of electrochemical systems: terminology, nomenclature and representation. Part I. Cells with metal electrodes and liquid solutions" M. Sluyters-Rehbach (*Pure Appl. Chem.*, **66** (1994) 1831-1891) covered the basic knowledge of the field. Since that time electrochemical impedance (often now known as Electrochemical Impedance Spectroscopy (EIS)) has been developed very actively and now a large variety of systems are investigated by this method. In addition, new types of impedance analysis are being developed - multiple transfer function analysis, local impedance measurements, differential impedance analysis etc.

Many scientists from many different fields - chemistry, physics, biology, materials science, corrosion - are now using EIS as a research tool owing to the ready availability of instrumentation. This is made clear through the success of the triennial series of symposia on Electrochemical Impedance Spectroscopy (the 5th held 17-22 June 2001 in Italy with 200 participants). It is important that conventions and a common data format are implemented in order to facilitate application and understanding of electrochemical impedance data by scientists with different backgrounds and training, including for dissemination through Internet and Virtual Laboratories. These conventions should include: programming of the experiments and obtained data, recommended algorithms for data pre-processing and analysis, and representation of final numerical and graphical results. Such guidelines are important for the chemistry community as a whole.

It is expected to incorporate these recommendations in future ISO standards. A working group has already been formed for this purpose regarding the application of impedance to measurement of the effectiveness of organic coatings (ISO DC35 SC9 WG29, chairman J. Vogelsang).

Progress:

Last update: 11 September 2001

5. **Number:** 2001-030-1-100

Title: Recommendations on the measurement and analysis of results obtained on biological substances with isothermal titration calorimetry

Task Group Chairmen: [Frederick P. Schwarz](#) and [Hans-Jurgen Hinz](#)

Objective: Recommendations for isothermal titration calorimetry measurement procedures on biological substances, calibration procedures, and procedures for testing the performance of isothermal titration calorimeters (ITCs) with a biological test solution are described. Recommendations for the analysis and reporting of the results will be presented to facilitate universal comparability of ITC data from different laboratories.

Description:

Isothermal titration calorimeters (ITCs) have been widely used in the biotechnological and pharmaceutical industry and in academia to determine the thermodynamics of binding reactions of biological substances, including DNA-DNA, DNA-RNA, protein-protein, protein-ligand, and DNA-intercalating drug interactions. ITCs monitor the power exchanged between a reference vessel and a solution vessel as aliquots of a titrant solution are injected into the solution vessel, isothermally. The change in enthalpy, binding affinity, and the stoichiometry for the binding reaction are obtained from an analysis of the power exchanged per each injection and the total concentrations of the reactants in the solution vessel. In addition, the temperature dependence of these quantities can be determined in terms of a heat capacity change for the binding reaction. Thus, the thermodynamics of the binding reaction can be completely characterized over a wide temperature range.

Published results sometimes lack a systematic reporting and analysis of the data and often employ a variety of notation inconsistent with IUPAC recommendations. An important aspect of this project is the fabrication of

a test solution for determination of ITC binding data. ITC test solutions will be distributed to members of the working party to run in their ITCs so that a consensus set of binding data can be developed on a particular system under a specified set of operating conditions. This consensus data can then be used to determine if a particular ITC is being operated properly. This is particularly important for new and in-experienced researchers employing ITC for the first time. The results will also be shared with the MIRG committee of the Association of Biomolecular Research Facilities (ABRF). MIRG is involved in evaluating how well binding affinities determined by ITC, Biacore SPR, and Ultra-analytical centrifugation are in agreement.

Progress:

Last update: 20 November 2002

6. Number: 2001-035-1-100 (previous 160/5/98)

Title: Measurement and interpretation of electro-kinetic phenomena

Task Group Chairmen: [F. Gonzalez-Caballero](#) and [Á. Delgado Mora](#)

Members: A.S. Dukhin, S.S. Dukhin, K. Furusawa, C. Grosse, R.J. Hunter, R. Jack, M. Kaszuba, L.K. Koopal, M. Kosmulski, J. Lyklema, R. Noremberg, V. Ribitsch, V.N. Shilov, F. Simon, C. Werner, A. Zhukov, and R. Zimmerman

Objective:

- Discuss the various electro-kinetic phenomena and give recommendations on the use of the different techniques.
- Discuss briefly the theories of electro-kinetic phenomena.

Description:

Collect and spread the available and updated scientific information about the main electrokinetic phenomena. This includes:

- fundamental background and clarification of notions used in electro-kinetics
- discussion of theoretical models, with emphasis on the validity and usefulness of the various models
- critical evaluation of experimental methods with their ranges of applicability and limitations (electrophoresis, streaming potential/current, electro-osmosis, dielectric dispersion, electro-acoustics)

- description of model systems that can be used as standards for each technique
- elucidation of the physicochemical information that can be obtained from the use of a given method and the corresponding theoretical models

Progress:

The project was first discussed in the Electro-kinetic Phenomena Conference held in Salzburg (1998). A significant number of specialists in the field agreed to contribute and sent their chapters to the coordinator during 1999-2000.

A meeting of the Task Group took place during the Electro-kinetic Phenomena Conference in Dresden, October 2000. The discussion made clear that the project is ambitious with many difficulties that have to be settled. After the workshop, written comments were sent to the coordinator by several members of the task group and a preliminary list of recommended symbols was produced. Restructuring of the draft has been demanding and the second draft was completed just before the GA in Brisbane (July 2001).

A final period is required to produce a document that gives balanced guidelines for the use of electro-kinetic methods and the correct interpretation of the results. There is a

This project was presented at a [poster session](#) at the IUPAC Congress/GA July 2001
>[view pdf - 95KB](#)<

large number of electro-kinetic techniques that all need attention including their theoretical background (which is complicated even for ordinary surfaces).

The 3rd draft will be prepared before July 2002. The working party will meet at the EKP Conference, August 2002, in Cracow (Poland) to discuss the progress and advise on open questions. A final draft is planned for end 2002, resulting in a technical report to be submitted to *PAC*.

Last update: 29 August 2001

7. **Number:** 2002-005-1-100

Title: Thermodynamics of ionic liquids, ionic liquid mixtures, and the development of standardized systems

Task Group Chairman: [Kenneth N. Marsh](#)

Members: [Joan F. Brennecke](#), [Michael L. Frenkel](#), [Andreas Heintz](#), [Joe W. Magee](#), [Cor J. Peters](#), [Luis P.N. Rebelo](#), and [Kenneth R. Seddon](#)

Objective:

1. To initiate systematic studies of thermodynamic and thermo-physical properties of Ionic Liquids (IL) based on the needs of industrial chemical processes.
2. To establish a reference system of IL's and (IL + liquid mixtures) with reliable stability and purity and well defined thermodynamic properties.
3. To define guidelines which research activities and future cooperation should be directed to.

Description:

Ionic liquids (IL's) represent a new class of liquid solvents having the character of molten salts. Recently synthesised compounds are moisture, air and temperature stable. Their melting points are distinctly below room temperature. Most of these IL's consists of cations such as different Alkyl-Imidazolium or Alkyl-Pyridinium ions and anions such as BF_4^- , PF_6^- , $\text{N}(\text{CF}_3\text{SO}_2)_2^-$, CF_3SO_3^- . Chloroaluminate anions are also important provided moisture can be excluded. A large number of ionic combinations is possible for designing special properties.

IL's have gained large interest during the last years. They have no detectable vapour pressure and therefore exhibit an ideal system of solvents for new homogeneous catalytic reactions and other chemical production processes with respect to a "green chemistry". An increasing number of successful applications are described in the literature. The utilization of IL's in industrial chemistry requires a systematic study of their thermodynamic and thermo-physical properties that are of considerable interest for chemical process design. The most important properties are:

- a) solubilities of gases in IL's
- b) miscibility gaps of organic liquids and water with IL's
- c) densities, activity coefficients and excess properties of IL + organic substances (or water) mixtures
- d) viscosities, diffusion coefficients, and electric conductivities of IL + organic substance (or water) mixtures
- e) There is also a strong interest in IL's from the side of theoreticians dealing with statistical mechanical theories and/or computer simulation methods of concentrated electrolyte solutions.

There have been a number of workshops and special sessions at conferences on ionic liquids but they have been specifically directed towards their use as solvent systems for chemical reactions with emphasis on kinetics and homogeneous organometallic catalysis. There has been minimal emphasis on thermo-physical property information.

Three workshops are planned to be held within a period of 3-4 years. Each workshop (2 days) should include at least 4 invited lectures, short oral and poster contributions, and a panel discussion. The aim of the workshop series is to stimulate the discussion and cooperation concerning items a) to e) between chemical engineers, thermodynamicists, organic chemists active in the research field of IL's and those who are dealing with IL's in technical and industrial applications. Standardized IL's and IL + liquid mixture should be developed which can be used as reference systems.

Progress:

Last update: 15 November 2004

8. **Number:** 2002-063-1-100

Title: Chemical thermodynamics in industry

Task Group Chairman: [T.M. Letcher](#)

Members: [Theo de Loos](#), [John Dymond](#), and [Ron Weir](#)

Objective:

To bring to the attention of a wide audience, the pivotal role that Chemical Thermodynamics plays in the Chemical Industry of the 21st century.

Description:

The book is to be written for chemical engineers and industrial chemists, agencies and groups that fund chemical research, and research students and general chemists.

Draft outline

1. Multi-phase thermodynamics of pulp suspensions - scale-up and reactor design with thermochemical models (combining reaction rates with Gibbs energy models)
2. Use of multi-phase thermodynamics in slag metallurgy and steelmaking
3. Metastable coating structures in PVD-coatings

4. Properties of nano-size particles by using multi- phase thermodynamics
5. Distillation (more in particular reactive distillation) (Arlt, Germany)
6. Thermo properties from *ab initio* quantum chemistry (Sandler, USA)
7. Molecular modelling (Cummings, USA)
8. Bioseparations/downstream processing (Van der Wielen, Holland)
9. Fine particle production (Reverchon, France)
10. Polymer synthesis in ScFI's (Beckman, USA)
11. Sustainability (De Swaan Arons, Holland)
12. Ionic liquids (Heintz, Germany)
13. Reactions in ScFI's (Eckert, USA/Poliakoff, UK)
14. Polymer recycling (Kleintjens, Holland)
15. Non-equilibrium thermo (Ratkje, Norway)
16. Process simulation
17. Non-classical critical phenomena (Sengers/ Anisimov, USA)
18. Self-ordering systems
19. CO₂ sequestration
20. Clathrates (Dendy Sloan)
21. Reactive Distillation
22. Molecular Thermodynamics (Prausnitz)
23. Thermodynamic Properties of new materials (Manfred Martin, Aachen)
24. Thermodynamic Properties of Polymers for Industry (Ralf Dohrn, Bayer, Germany)
25. Thermodynamic Properties of Mixing for Industry (Chris Wormold, Bristol)
26. Calorimetric Measurements for Industry (Jean-Pierre Grolier, U of Blaise Pascale)
27. Flow Microcalorimetry measurements and Industry (Tony Beezer, U of Greenwich)
28. Transport Properties and Industry (Bill Wakeham or Hartmut Brueschke, Germany)
29. Viscosity of Refrigerants in Industry (Bill Wakeham)

Progress:

Last update: 29 January 2003

9. **Number:** 2003-005-1-100

Title: Recommended values of the viscosity of molten iron and aluminium

Task Group Chairman: [W.A. Wakeham](#)

Members: [Marc Assael](#), [Michael Banish](#), [Ivan Egry](#), [Ken Mills](#), [Akira Nagashima](#), [Tony Overfelt](#), [Peter Quested](#), [John Redgrove](#), and [Yuzuro Sato](#)

Objective:

The widely different data obtained for the viscosity of molten iron and aluminium will be critically reviewed via an inter-laboratory comparison and recommended values will be proposed.

Description:

Wide ranges of values of viscosity of both molten iron and aluminium are reported in the literature. The most widely used method is some form of oscillating vessel. For the oscillating cup a number of analytical techniques have been used to convert the measurements (logarithmic decrement and time period) to viscosity.

The Roscoe equation (1958) was recommended as providing the most accurate data for molten metals. Ferriss *et al* (2002) have pointed out there is a missing numerator in one of the expansions and a number of workers and standard texts have quoted " $1/2$ " but expansion shows it to be " $3/2$ ".

In a parallel development chemical engineers have adopted a set of equations for oscillating cup viscometers by Kestin and Newell, which have been rarely used for molten metals.

There are two challenges:

1. Agreement about the equations used to determine the viscosity by the oscillating cup method. At present the modified Roscoe equation by Ferriss and the Kestin and Newell appear to give similar results with one laboratory's data.
2. The widely different data obtained for the viscosity of aluminium and iron need to be critically reviewed and recommended values suggested. This may result in the need for an inter-laboratory comparison.

The project should lead to a consistent, internationally approved set of values for the viscosity of these two metals, as an exemplar for the field.

- Roscoe, R (1958), *Proc. Phys. Soc.* **72**, 576

- Ferriss, D H; Quested, P N; Chapman, L A; and Day, A P (2002) "The Choice of Equations for the Measurement of Viscosity by the Oscillating Cylinder Method". Presented at ECTP, London.

Kestin, J and Newell, GF (1957) ZAMP VIII, 433

Progress:

The available experimental data for the density and viscosity of liquid aluminium and iron have been critically examined with the intention of establishing a density and a viscosity standard. All experimental data have been categorized into primary and secondary data according to the quality of measurement specified by a series of criteria. The proposed standard reference correlations for the density of the aluminium and iron are characterized by standard deviations of 0.65 and 0.77% at the 95% confidence level respectively.

A full report is being prepared and will be submitted for publication in *JPCRef Data*.

Last update: 19 April 2005

10. **Number:** 2003-006-1-100

Title: NMR chemical shifts: updated conventions

Task Group Chairman: [Robin K. Harris](#)

Members: [Edwin D. Becker](#), [Sonia M. Cabral de Menezes](#), [Pierre Granger](#), [Roy E. Hoffman](#), and [Kurt Zilm](#)

Objective:

To update IUPAC Recommendations 2001: NMR Nomenclature, Nuclear Spin Properties and Conventions for Chemical Shifts [[PAC 73, 1795 \(2001\)](#)] by addressing several issues still to be resolved in setting standards for chemical shifts, including temperature variation of the NMR signals of reference compounds, the use of magic-angle spinning for both solutions and solids, solvent effects, and magnetic susceptibility corrections.

Description:

Nuclear magnetic resonance [NMR] has long been an invaluable technique for determining molecular structure and for investigating a wide variety of chemical phenomena. The cornerstone of such applications is the *chemical shift* - a quantity that must be measured relative to an agreed reference. For many years, common practice [endorsed by IUPAC in the 1970s] was to use a separate reference for each nuclide. However, as a result of the above-cited publication, IUPAC is now on record as recommending that chemical shifts for all nuclides be expressed on a unified scale relative to the proton [^1H] resonance of tetramethylsilane [TMS] in a 1 per cent solution in CDCl_3 . Since its publication only a year ago, this recommendation has been well received by the international NMR community; has been widely disseminated by republication in NMR

journals and presentations at NMR conferences, as detailed below; and has been publicized by one of the three major NMR equipment manufacturers.

The IUPAC publication in 2001 included extensive tables of data on NMR properties, chemical shift values of secondary references for each nuclide, and detailed explanations of factors affecting measurements of chemical shifts. However, in the interest of bringing that work to closure and publishing the Recommendations, the task group was forced to defer detailed consideration of several important matters:

- The temperature dependence of the primary standard, TMS in CDCl_3 , should be established on the basis of data in the literature and possible new measurements.
- Changes of solvent or concentration are known to have major effects on chemical shifts. These effects should be evaluated for selected systems by use of an external reference, physically separated from the sample being studied.
- An external reference, in turn, requires correction for effects of the magnetic susceptibility of the sample. Methods for measuring magnetic susceptibility and applying the correction in a reliable manner must be analyzed.
- The use of magic-angle spinning [MAS] can, in principle, eliminate the need for magnetic susceptibility corrections, but this method must be evaluated more carefully.
- MAS is widely used for the study of solids. IUPAC has thus far made no recommendations for referencing in solids, a matter that should be rectified.
- Various conventions have been suggested in the literature for shielding and/or chemical shift tensor parameters, and a preferred nomenclature needs to be decided on and recommended.

This project is designed (1) to solicit the views of a broad segment of the relevant NMR community on these and possibly other important matters to be addressed, and (2) to bring together a task group of experienced NMR spectroscopists to analyze the theory and literature data, make experimental measurements where feasible, and prepare a Recommendation that will extend and broaden IUPAC's previous statements.

Progress:

(1 May 2005)

Following a Discussion Forum held during the International Meeting on NMR organised by the Royal Society of Chemistry in Cambridge (England) in the summer of 2003, each of the six task group members was assigned one of the relevant topics and was asked to prepare a briefing paper on it. Progress has been made with all of these, with comments

sought from all members of the task group and from some other experts in the field. The task group concluded that for several areas - temperature variation of chemical shifts, shape factor for magnetic susceptibility correction, and solvent effects - new data or calculations would be needed.

In the case of temperature variations of chemical shifts, it was decided to undertake some new measurements with respect to the He-3 nuclide, and one of the task group members (Dr. Roy Hoffman) has been doing this. The funds supplied by IUPAC for the project sufficed to obtain the necessary helium-3 gas. Fundamental measurements of the temperature variation of proton chemical shifts (vs. the signal for He-3 gas) are now complete, and he has submitted a paper (with Dr. Ted Becker) on this topic for publication in an NMR journal (with acknowledgment of the IUPAC project). Draft papers have also been written on shape factors for use with magnetic susceptibility corrections (Dr. Hoffman) and on high-precision chemical shift measurements (Prof. Pierre Granger). It is intended to use these articles as reference material for the eventual IUPAC report on the project. The briefing paper on shielding tensors has been sent to several experts for comment before recommendations are drawn up and some responses have been received.

At the 46th Experimental NMR Conference, held in Providence (Rhode Island) 10-15 April 2005, four members of the Working Party held a discussion on the progress and future direction of the project. A synopsis for the final report has been agreed, but several matters need to be concluded before a full draft can be produced. It was agreed to add a short section on the vexed question of referencing for nitrogen chemical shifts (to be addressed by Dr. Sonia Cabral de Menezes). The need for new data and calculations has delayed completion of the overall project beyond the initial target date, but the quality of the resultant IUPAC document will be markedly improved by inclusion of these results.

Last update: 4 May 2005

11. **Number:** 2003-020-2-100

Title: Ionic liquids database

Task Group Chairman: [K.R. Seddon](#)

Members: [Andrew Burgess](#), [Michael Frenkel](#), [Marcelle Gaune-Escard](#), [Andreas Heintz](#), [Joseph Magee](#), [Kenneth Marsh](#), and [Roger Sheldon](#)

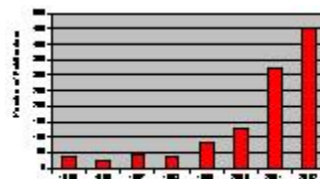
Objective:

Create an open-access, free, on-line, comprehensive database for storage and retrieval of metadata and numerical data for ionic liquids, including

their syntheses, structure, properties, and uses; lack of this information is impeding progress in a burgeoning field of significant current interest.

Description:

Ionic liquids are expanding dramatically in popularity (see inset figure), and the first industrial application (the BASF BASIL process) was announced at the end of March 2003. Crucial to their implementation on a wider scale (and these are green solvents) is



universal access to their physical properties. As there are potentially over one million simple ionic liquids (although fewer than one thousand have yet been reported), the need for a living database, with continuous updating is paramount. This project brings together some of the world leaders in ionic liquid technology with leading thermodynamicists and database technologists.

A task group, that wishes to work under the auspices of IUPAC, has been formed to address the need for international scientific cooperation to implement the design and development of a web-based free-access database for ionic liquids. Taken as a whole, the task group has acquired a critical mass to make the goal of this project a reality. The task group members represent broad interests by organisational type (academic, governmental, and industrial) and geographical location, as well as a wide range of expertise (measurement science, synthesis, enzyme catalysis, data management, structure, and industrial application). To the extent possible, sharing of data and exchange of proposed ideas among group members will be carried out electronically. A total of two in-person meetings of this group will be arranged, preferably around international conferences or at venues provided gratis by a host member's organization, such that expenditures will be held to an absolute minimum. Personal meetings will be used to iron out detailed issues that are crucial to the design of the database, and to divide the larger tasks into those that are more manageable.

The task group is expected to decide on the format of the new database, including its root language, its structure, and the means by which various information types will be stored and retrieved. Seven types of information will be compiled, namely: synthesis; structure; thermodynamic, thermochemical and transport properties; solvent properties and reactions; catalytic properties; and, reviews and bibliography. To ensure that a uniform assessment of each type of information is made, the task group chair will assign primary responsibility for each information type to subgroups. The task group chair will expect each subgroup to take responsibility to assess the available data for its quality and reliability, compile this data, and make regular reports to the full task group. Frequent

interchanges of information among subgroups will prevent repetition of work. Task group members will be expected to provide their own organisation's existing data holdings for the benefit of the project, according to their specialised knowledge and assets. To ensure compatibility of the information coming from various data sources, the output and input formats for each record will be agreed upon in advance. For example, NIST-Thermodynamics Research Centre will extract ionic liquid data for more than 120 properties from its SOURCE data archival system that currently contains over 1.3 million data points on over 17,000 substances and 12,000 mixtures. It is searchable by several means, including CAS registry numbers, chemical name or chemical formulae. In addition to property values in SI units, it stores estimated uncertainties for practically all the stored numerical data, citations of original documents, as well as detailed information about the samples such as their source, method of purification and final reported purity. This information derived from the original sources will contribute to the assessment of overall uncertainties of the data, and will facilitate reports of recommended values. Software has been prepared that will automatically extract ionic liquids data from the SOURCE system. Making this unique tool for automatic data evaluation available to this project will streamline the assessment and compilation of thermodynamic, thermo-chemical and transport properties of ionic liquids.

When each subgroup's data has been compiled into agreed-upon formats, the parts will be combined into a beta version of the entire database. It then will be tested by a wide range of users, whose comments will be solicited to improve the product. When the improvements have been implemented and tested, IUPAC Ionic Liquids Database version 1.0 will be released to the public. NIST will provide web space with a single-entry point for all users of this database, and provide the tools to measure usage and compile a monthly statistical report for the website. As part of an ongoing commitment, NIST will maintain this database on a NIST server and update its holdings on a regular basis. Our long-range operating plan, built upon continuous exchange and cooperation with both data generators and users, will streamline the process of adding new results and making further improvements better to serve the needs of the international chemistry community.

Progress:

Last update: 25 July 2003

12. Number: 2003-024-1-100

Title: Selected free radicals and critical intermediates: thermodynamic properties from theory and experiment

Task Group Chairman: [Branko Ruscic](#)

Members: [Tibor Bérces](#), [J. E. Boggs](#), [A. Burcat](#), [A. Császár](#), [J. Demaison](#), [R. Janoschek](#), [J.M.L. Martin](#), [M. J. Rossi](#), [J. Stanton](#), [P. Szalay](#), [P.R. Westmoreland](#), and [F. Zabel](#)

Objective:

The main objective of this project activity is the continued compilation and critical evaluation of published thermodynamic properties, including the computation of accurate thermo-chemical data for selected free radicals that are of importance in atmospheric and combustion chemistry. A distinguishing feature of the critical data evaluation is the systematic utilization of all available kinetic, spectroscopic and ion thermo-chemical results as well as high-level computations.

Description:

Knowledge of accurate thermo-chemical properties of free radicals is of great importance in many branches of chemistry, in particular atmospheric and combustion modelling. Thermo-chemical kinetic estimations provide sometimes the only possibility for obtaining rate coefficients and branching ratios for reactions of short-lived intermediates such as free radicals. Thermodynamic quantities for stable molecules are relatively well established. These are typically obtained from calorimetric determinations, while heat capacities and entropies are derived from the results of spectroscopic measurements. For free radicals and other short-lived intermediates, direct calorimetric measurements are (in most cases) not possible, while spectroscopic investigations require more skill and sophisticated instrumentation. Consequently, thermo-chemical data for a number of free radicals have a higher uncertainty than the corresponding values of closed shell species. However, computational chemistry has made great progress in reliability and accuracy. A solid basis of thermo-chemistry now comprises the optimized combination of experimental and computational results.

Such type of work has been initiated in our [IUPAC project 2000-013-1-100](#) which comes to a preliminary conclusion at the end of the year 2003. Within this project the critical evaluation of thermodynamic properties of 36 free radicals has been carried out.

The success of this work so far suggests an extension of data evaluation beyond the initial goal to cover an increased number of key radicals that play important part in atmospheric chemistry and combustion. This requires the development of datasheets for about 25 further radicals.

Progress: extension of [project #2000-013-1-100](#)

Last update: 21 October 2003

The following publications have appeared from this project.

W. M. F. Fabian and R. Janoschek

Thermochemical Properties of the Hydroxy-formyl Radical HO-CO, and the Formyloxy Radical, HC(O)O, and their Role in the Reaction $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$: Computational G3MP2B3 and CCSD(T)-CBS Studies. *J. Mol. Struct. TheoChem* **713**, 227 (2005)

P. G. Szalay, A. Tajti, and J. F. Stanton

Ab Initio Determination of the Heat of Formation of Ketenyl (HCCO) and Ethynyl (CCH) Radicals. *Mol. Phys.* **103**, xxx (2005) *in press*

B. Ruscic, J. E. Boggs, A. Burcat, A. G. Császár, J. Demaison, R. Janoschek, J. M. L. Martin, M. L. Morton, M. J. Rossi, J. F. Stanton, P. G. Szalay, P. R. Westmoreland, F. Zabel, and T. Bérces. IUPAC Critical Evaluation of Thermochemical Properties of Selected Radicals: Part I. *J. Phys. Chem. Ref. Data* **34**, xxx (2005) *in press*

X. Tang, Y. Hou, C. Y. Ng, and B. Ruscic

Pulsed Field Ionization Photoelectron-photoion Coincidence Study of the Process $\text{N}_2 + h\nu \rightarrow \text{N}^+ + \text{N} + e^-$: Bond Dissociation Energies of N_2 and N_2^+ *J. Chem. Phys.* **123**, xxx (2005) *in press*

R. Janoschek and M. J. Rossi

Thermochemical Properties of Free Radicals from G3MP2B3 Calculations, Set-2: Free Radicals with Special Consideration of $\text{CH}_2=\text{CH}-\text{C}=\text{CH}_2$, *cyclo-C}_5\text{H}_5*, CH_2OOH , HO-CO, and HC(O)O. *Int. J. Chem. Kinet.* **36**, 661 (2004)

A. D. Boese, M. Oren, O. Atasoylu, and J. M. L. Martin

W3 Theory: Robust Computational Thermochemistry in the kJ/mol Accuracy Range. *J. Chem. Phys.* **120**, 4129 (2004)

B. A. Flowers, P. G. Szalay, J. F. Stanton, M. Kállay, J. Gauss, and A. G. Császár. Benchmark Thermochemistry of the Hydroperoxy Radical. *J. Phys. Chem. A* **108**, 3195 (2004)

A. V. Marenich and J. E. Boggs

Vibrational Spectrum and Thermochemistry of the Formyl (HCO) Radical: A Variational Study by the Coupled Cluster CCSD(T) Method with Complete Basis Set Extrapolation. *J. Phys. Chem. A* **108**, 5431 (2004)

M. Oren, M. A. Iron, A. Burcat, and J. M. L. Martin

Thermodynamic Properties of C_1 and C_2 Bromo Compounds and Radicals: A Relativistic ab Initio Study. *J. Phys. Chem. A* **108**, 7752 (2004)

B. Ruscic, R. E. Pinzon, M. L. Morton, G. Von Laszewski, S. J. Bittner, S. G. Nijssure, K. A. Amin, M. Minkoff, and A. F. Wagner. Introduction to Active Thermochemical Tables: Several “Key” Enthalpies of Formation Revisited *J. Phys. Chem. A* **108**, 9979 (2004)

- B. Ruscic
Active Thermochemical Tables in: 2005 Yearbook of Science and Technology, McGraw-Hill, New York, 2004, pp. 3-7
- P. G. Szalay, L. S. Thøgersen, J. Olsen, M. Kállay, and J. Gauss
Equilibrium Geometry of the Ethynyl (CCH) Radical.
J. Phys. Chem. A **108**, 3030 (2004)
- A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton
HEAT: High Accuracy Extrapolated Ab Initio Thermochemistry. *J. Chem. Phys.* **121**, 11599 (2004)
- A. G. Császár, M. L. Leininger, and A. Burcat
Enthalpy of Formation of ${}^2\Pi_{3/2}$ SH. *J. Phys. Chem. A* **107**, 2061 (2003)
- J. Demaison, L. Margulès, and J. E. Boggs
Equilibrium Structure and Force Field of NH₂. *Phys. Chem. Chem. Phys.* **5**, 3359 (2003)
- A. V. Marenich and J. E. Boggs
Structural and Thermochemical Properties of the Hydroxymethyl (CH₂OH) Radical: A High Precision Ab Initio Study. *J. Chem. Phys.* **119**, 10105 (2003)
- A. V. Marenich and J. E. Boggs
Coupled Cluster CCSD(T) Calculations of Equilibrium Geometries, Anharmonic Force Fields, and Thermodynamic Properties of the Formyl (HCO) and Isoformyl (COH) Radical Species. *J. Phys. Chem. A* **107**, 2343 (2003)
- A. V. Marenich and J. E. Boggs
A Variational Study of Nuclear Dynamics and Structural Flexibility of the CH₂OH Radical. *J. Chem. Phys.* **119**, 3098 (2003)
- R. Janoschek and M. J. Rossi
Thermochemical Properties of Free Radicals from G3MP2B3 Calculations. *Int. J. Chem. Kinet.* **34**, 550 (2002)
- A. G. Császár, P. G. Szalay, and M. L. Leininger
The Enthalpy of Formation of ${}^2\Pi$ CH. *Mol. Phys.* **100**, 3879 (2002)
- J. Demaison, L. Margulès, J. M. L. Martin, and J. E. Boggs
Anharmonic Force Field, Structure, and Thermochemistry of CF₂ and CCl₂.
Phys. Chem. Chem. Phys. **4**, 3282 (2002)

13. **Number:** 2003-036-2-100

Title: Thermodynamics and non-equilibrium criteria for development and application of supplemented phase diagrams

Task Group Chairman: [Horacio R. Corti](#)

Members: [C. Austen Angell](#), [Tony Auffret](#), [Harry Levine](#), [María del Pilar Buera](#), [David S. Reid](#), [Yrjo Roos](#), and [Louise Slade](#)

Objective:

The aim of the project is to establish rational links between thermodynamic aspects of phase diagrams supplemented by the non equilibrium curve of the glass transition temperature for mixtures of water with vitrifying agents used in the cryo and dehydropreservation of natural (foods, seeds, etc.) and synthetic products (pharmaceuticals). It will contribute to improve processing and conservation practices of these important materials. It intends not just to compile information that already exists, but to consider all the sort of basic and applied problems that one should consider when managing these phase/state diagrams.

Description:

The present proposal is prepared as to have a very broad and interdisciplinary scope for impacting on many fields related to chemistry and biophysical chemistry. It would permit promoting IUPAC activities and competence to a wider non-chemistry scientific community. It is largely inspired in early activities of the International Symposia on the Properties of Water (ISOPOW). The applicability of state diagrams is recognized in food chemistry and related areas. However, many basic questions are still open and more precise definitions are needed for a correct interpretation of the involved phenomena. The practical aim of the project is to give solid basis to develop supplemented state diagrams of aqueous glassy formers, such as saccharides, polyols, etc., in order to describe the influence of water content, nature of the vitrifying agent and temperature on the physico-chemical stability of natural and synthetic products.

To fulfil this goal this study proposes to analyze:

1. The areas of food and pharmaceutical processing in which theoretical basis are needed for a better definition of the involved phenomena.
2. The practical/theoretical applicability of equations extensively employed to predict transition temperatures.
3. Which is the best standard procedure to determine the glass transition curve over the water content scale.
4. Differences between methods based on thermodynamics and kinetics to determine the phase/state transitions, and how could they be standardized.
5. What is the effect of water content on the kinetics of phase/state transitions (glass temperature, crystallization temperature) in biomaterials.
6. How can be state diagrams applied to analyze the stability of biomolecules under extreme conditions (i.e. frozen systems, high or low pressures).

7. How can multi-dimensional (ternary systems, pressure coordinate) diagrams be managed. The project will aim to give scientific-based definitions in the detected critical areas.

Progress:

Last update: 5 August 2004

14. **Number:** 2004-010-3-100

Title: Heat capacity of liquids: critical review and recommended values for liquids with data published between 2000 and 2004

Task Group Chairman: [Vlastimil Růžička](#)

Members: [Eugene Domalski](#), [Zdenka Kolská](#), [Milan Zábranský](#)

Objective:

To update and extend two publications that contained recommended data on liquid heat capacities for almost 2000 mostly organic compounds, "Heat Capacity of Liquids: Critical Review and Recommended Values", and its "Supplement I" by M. Zábranský, V. Ruzicka, V. Majer (1st work only), and E.S. Domalski published in *Journal of Physical and Chemical Reference Data* in 1996 and 2001. The publications were the product of IUPAC Projects 121/11/87 and [2000-031-1-100](#).

Description:

Experimental data on heat capacities of pure liquid organic and some inorganic compounds published in the primary literature between 2000 and 2004 will be compiled, critically evaluated and recommended values provided. Recommended data supplemented with an assessment of their uncertainty and presented in terms of parameters of correlating equations for temperature dependence of heat capacities will be developed by critical assessment of literature calorimetrically determined heat capacities. The work will be an update of a two-volume monograph that was published in 1996 as a Monograph No.6 of the *Journal of Physical and Chemical Reference Data*, and of its Supplement I, published in *J. Phys. Chem. Ref. Data* 30, 1199-1689 (2001). The updated and extended database will contain data for about 250 compounds taken from more than 120 literature references. The whole work consisting of the monograph and of its two supplements will also provide an exhaustive survey of the literature for all isobaric and saturation heat capacities for pure organic and inorganic compounds in the liquid state having a melting point below $T = 573$ K. The literature survey includes references to the original paper and to the description of the experimental equipment used for heat capacity data determination and serves as a valuable source of references. The overall

number of compounds in the whole database of recommended data will exceed 2000.

Progress:

Last Update: 2 September 2004

15. Number: 2004-026-2-100

Title: Categorizing hydrogen bonding and other intermolecular interactions

Task Group

Chairmen: [Elangannan Arunan](#) and [Steve Scheiner](#)

Members: [Ibon Alkorta](#), [David C. Clary](#), [Robert H. Crabtree](#), [Joseph J. Dannenberg](#), [Gautam R. Desiraju](#), [Henrik G. Kjaergaard](#), [Roger A. Klein](#), [Karl Kleinermanns](#), [Anthony C. Legon](#), [Benedetta Mennucci](#), [David J. Nesbitt](#), and [Joanna Sadlej](#)

Objective:

To take a comprehensive look at intermolecular interactions and classify them and to give a modern definition of the hydrogen bond, taking in to account all current experimental and theoretical information, and including hydrogen bonded systems both in gaseous and condensed phases as well as in chemical and biological systems.

Description:

Hydrogen bonding has fascinated chemists and biologists for several decades now and it is central to chemistry and biology. The original definition of hydrogen bonding invoked two electronegative atoms (X and Y) interacting through a hydrogen atom as in X-H --- Y. Initially X and Y were found to be mostly N, O and F which led to the mentioning of these atoms as part of the definition of hydrogen bonds in various sources (including the Gold book of IUPAC). Hydrogen bonding was inferred by the difference in physical properties between otherwise chemically similar systems such as found between H₂O and H₂S. However, now it is well known that both H₂O and H₂S form a hydrogen bonded (H₂X)₂ dimer in the gas phase. Spectroscopic red shift in XH stretching frequency was among the first experimental evidence used for inferring hydrogen bonds. Now there are several hydrogen bonded systems that appear to show blue shift in XH stretching frequency. More interestingly, these systems have CH as the hydrogen bond donors, which was against conventional wisdom. The CH --- O interactions have been well established now in organic and biological systems by crystal structure analysis and NMR methods. Traditionally, hydrogen bond acceptors interact through a lone

pair or bonded pair electrons. However, optically active hydrogen bonded complexes involving radicals have been found in the atmosphere. Matrix experiments and theoretical studies have shown that CH₃ radical could form a complex with H₂O, which could be represented as C --- HO? Are these one-electron hydrogen bonds with C as the acceptor? There have been reports on X-H --- interactions where electrons act as hydrogen bond acceptors. Dihydrogen bonds have been observed in which H in XH (X=electronegative) interacts with another hydrogen in MH (typically a metal hydride) with partial negative charge. Moreover, there have been numerous reports on H₂ molecular complexes in the literature - should these be regarded as containing hydrogen bonds?

Electrostatic interaction was identified as the dominant factor for hydrogen bonds. Recent NMR and Compton scattering experiments have given evidence for partial covalency in hydrogen bonds. Dispersion forces have been shown to dominate hydrogen-bonded complexes of second row hydrides (HCl and H₂S). Chlorine monofluoride (ClF) has been shown to form weakly bound complexes with bases very much like HF and these have been identified as chlorine bonded complexes. Such chlorine bonding interactions have been observed in crystal structures as well. Hydrogen bonding, electrostatic interactions and van der Waals interactions are all loosely and interchangeably used in the field. Often van der Waals forces are equated to dispersion forces, though the origin of van der Waals forces (from the equation named after him) should include all intermolecular forces. Should rare gas complexes such as Ar-Ne be called London molecules instead of van der Waals molecules, as only London dispersion forces contribute to stabilization of Ar-Ne? Should Ar-HF be called hydrogen bonded or van der Waals complex? This project will attempt to give a modern definition of a hydrogen bond that is as inclusive as possible. Also, intermolecular interactions will be categorized logically considering the physical forces involved.

Progress:

The Task Group will be having a meeting in Pisa during the week of 5th to 9th September 2005 in the form of a workshop. All the participating members of the Task Group will be presenting a summary of their recent work in the area of hydrogen bonding and molecular interactions and will also give their views about the classification of inter- and intra-molecular interactions. The Task Group will have several rounds of discussion during the Workshop and it is intended that a provisional position paper will be produced at its conclusion. There will also be sufficient place for an additional 25-30 non-task group participants to take part in the Workshop (anyone interested in participating should contact either Elangannan Arunan <arunan@ipc.iisc.ernet.in> or Roger Klein <klein@institut.physiochem.uni-bonn.de>).

The Workshop details are available at the URL address:
http://institut.physiochem.uni-bonn.de/IUPAC_Pisa2005/Workshop.html

Last update: 7 April 2005

16. **Number:** 2004-036-1-100

Title: Establishing recommended data on thermodynamic properties of hydration for selected organic solutes

Task Group Chairman: [Vladimir Majer](#)

Members: [V. Dohnal](#), [R. Fernandez-Prini](#), [M. Frenkel](#), [A.H. Harvey](#), [J. Sedlbauer](#), and [E.L. Shock](#)

Remark: This project is co-funded by the **International Association for Properties of Water and Steam** (IAPWS) <www.iapws.org>

Objective:

The objective of the project is to establish a database of thermodynamic properties of hydration for approximately 200 selected organic solutes at reference condition of $T = 298.15$ K and 0.1 MPa and as a function of temperature and pressure up to the near critical region of water. The values of hydration properties for solutes covering different molecular structures will be calculated from the reliable experimental data for aqueous and pure solutes. The established database will be used as a standard for testing and establishment of new physico-chemical models and methods of molecular simulation as well as for developing semi-theoretical prediction schemes of interest for chemical engineering, environmental chemistry and geochemistry.

Description:

Thermodynamic properties of hydration (TPH) covered in the project are: the Gibbs energy of hydration and its temperature and pressure derivatives (the enthalpy of hydration, the heat capacity of hydration and the partial molar volume at infinite dilution), other TPH result from their combinations; for exact definitions and inter-relationship see Appendix 1 ([pdf](#)).

TPH express the difference between the property of a solute in the standard state of infinite dilution at a given temperature and pressure and that of an ideal gas at the same temperature and reference pressure of 0.1 MPa. Thus they characterise the transfer of a solute from a state where molecules are not interacting to the state where the solute molecules

interact solely with the water solvent. Due to this definition they can be used conveniently in testing and conception of theoretical models and simulation approaches for dilute aqueous solutions developed by physical chemists. At the same time, TPH allow an easy calculation of partition coefficients (such as the Henry's law constant, air-water partition coefficient, relative volatility, etc.) and of the thermodynamic reaction constants for aqueous systems. Therefore they also have a practical value of interest for chemical engineers and environmental chemists. In addition, the high temperature / high pressure TPH are required to characterize phase and chemical equilibria in hydrothermal systems and to guide the development of geochemical prediction schemes for aqueous fluids.

TPH cannot be directly measured but are calculated from the experimental data characterising aqueous and pure solutes, which result from phase equilibrium, calorimetric and volumetric measurements. Appendix 1 ([pdf](#)) summarises equations used to calculate TPH and lists types of experimental data that can be exploited.

The task group will select from the primary literature the best available experimental results for establishing a database of reliable values of TPH for 100 - 200 organic solutes and several common gases. In selecting the solutes, three main criteria will be observed:

- i) coverage of the widest range of molecular structures, indispensable for the development of theoretical models and group contribution prediction schemes,
- ii) availability of reliable experimental data, particularly with regard to the HT/HP region,
- iii) technological and environmental importance of individual solutes.

The database will comprise values at the reference condition for about 200 solutes and at elevated temperatures ($T < 673$ K) and pressures ($p < 40$ MPa) for about 100 solutes. For several solutes the recommended TPH will be given up to the critical region of water where they undergo remarkable changes. A tentative list of the classes of solutes covered and their respective numbers are given in Appendix 2 ([pdf](#)). Every effort will be made to supply a database that will not be biased by use of any particular correlation model for interpolating or extrapolating the data. This project requires collaboration of researchers having complementary knowledge in data evaluation and in different experimental techniques used for obtaining data for aqueous and pure solutes.

Progress:

Last update: 8 February 2005

B. Projects Nearing Completion or in Press

1. **Number:** 110/2/81

Title: Revision of "Quantities, Units and Symbols in Physical Chemistry" and the Appendices (3rd edition)

Coordinator(s): [I.M. Mills](#), [H.L. Strauss](#), [M. Quack](#), and [T. Cvitas](#)

Remarks: Commissions within Division I, ISO/TC12, SUNAMOCO, CIPM

Progress: 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.

Last update: 6 June 2000

2. **Number:** 120/15/95

Title: Thermochemistry of chemical reactions: nomenclature, symbols and experimental methods for bond energies

Coordinator(s): [M. Ribeiro da Silva](#)

Objective:

Nomenclature and symbolism for bond energies are, at the moment, somewhat confusing although these quantities are widely used to estimate the thermo-chemistry of species for which the enthalpies of formation are unknown. The proliferation of designations and symbols for quantities variously known as bond strengths, bond enthalpies, bond energies, bond dissociation enthalpies, bond enthalpy terms, stepwise bond dissociation energies, intrinsic bond energies, BDE, D etc clearly requires some standardisation. Several experimental techniques are available to

determine the parameters named above but can only be used to study the thermo-chemistry of long-lived molecules. However, modern techniques have made possible the study of these species. The correct relationship between the quantities measured with some of these new techniques and thermodynamic functions are often not straightforward and deserve a careful analysis. It is therefore proposed that this project considers in the first stage a comprehensive list of methods that have been used to derive energetic data. A second stage will involve a description of each method with an analysis of its basic assumptions and how thermodynamic data can be derived. In addition recommendations of standard nomenclature and symbols for bond energetics would be prepared.

Progress:

Progress in the first two years has been very good. A draft of the basic information to be included in the report has already been circulated for approval. In the next period comments will be incorporated and the descriptive material added.

A draft of the paper has been now prepared and is awaiting final comments before being submitted for publication.

A manuscript is being prepared for publication in *Pure Appl. Chem.* A final document is submitted to public review comments until 30 September 2002.

> see [provisional recommendations](#)

Last Update: 17 April 2002

3. **Number:** 120/16/97

Title: New Edition of Experimental Thermodynamics Vol II

> [View Series Titles](#)

Coordinator(s): [W.A. Wakeham](#), [R.D. Weir](#), [T.W. deLoos](#) and [A. Goodwin](#)

Remarks: Industrial contact to provide rationale for the task and as authors

Objective:

Experimental Thermodynamics prepared by the Commission in 1970 has been an archival book for nearly 30 years on Thermodynamic Measurement Techniques. It is now out of date; many new techniques have been developed. At the same time many industrial organisations have reduced their expertise in the field. Industrialists and Academic Research

Workers have argued that the volume needs to be updated to provide a reference for the world expertise before it is lost and has to be reinvented. It is proposed to update the volume by including only what is new and relevant. It will comprise two volumes on single and multiple phase separately.

Progress:

- Volume VI. [Measurement of the Thermodynamic Properties of Single Phases](#)

Editors: A.R.H. Goodwin, K.N. Marsh and W.A. Wakeham
published - Elsevier, 2003 [ISBN 0-444-50931-3]

- Volume VII. Measurement of the Thermodynamic Properties of Multiple Phases

Editors: Th. de Loos and R.D. Weir

The 16 chapters that make up the edition are in the hands of the production department of Elsevier Publishers. Some 24 authors from nine different countries contributed material. This book contains descriptions of recent developments in the techniques for measurement of thermodynamic quantities for multiple phases of pure fluids as well mixtures over a wide range of conditions. The precision and accuracy of results obtained from each method was regarded as an essential element in each description. Throughout the text, the quantities, units and symbols are those defined by IUPAC for use in the international community.
Anticipated publication date: late 2005 or early 2006.

Last Update: 19 April 2005

4. **Number:** 150/24/95

Title: Spectroscopy under extreme conditions of temperature and pressure

Coordinator(s): [A..M. Heyns](#)

Remarks: Collaboration with Commission V.4, Max Planck Institute (Stuttgart) and AIRAPTS organisers of Conference series on High Pressure Science

Objective:

To obtain international agreement on methods and standards and to prepare documents to guide workers in the field of spectroscopy under extreme conditions. Initially vibrational and electronic spectroscopy will be considered, but the project may be extended to NMR, Mossbauer, and

This project was presented at a [poster session](#) at the IUPAC Congress/GA July 2001
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other spectroscopies if the early work reveals interest in these areas. The main issues to be pursued come under the three general headings Instrumentation, Pressure Calibration, and Temperature Calibration. Instrumentation includes the consideration of cell design, the use of membranes with diamond anvil cells, the properties of optical windows under extreme conditions, the design of spectrometers and microscopes, the use of optical fibres for safe access to difficult experimental situations, and the simultaneous generation of high pressure and low temperature in an optical cell. The calibration issues include methods and standards for the calibration of hydrostatic and very non-hydrostatic pressures. Emphasis will be on calibration through the spectroscopic properties, with the intention to make recommendations in the final report of standard substances, inorganic, organic and biological, whose spectroscopic properties can be used for calibration and for establishing the performance of apparatus.

Progress:

Much progress has been made on this project. A 6-page summary was presented to the Commission in Berlin, accompanied by a detailed report on the scope of the project.

The final report is submitted for publication in *PAC*.

Last update: 25 January 2002

5. **Number:** 2000-026-1-100 (continuation of [121/10/87](#))

Title: Critical compilation of vapour liquid critical properties

Task Group Chairman: [Kenneth N. Marsh](#)

Members: [C.L. Young](#), [C. Tsonopoulos](#), [J.H. Dymond](#), and [D. Ambrose](#)

Objectives:

Values of vapour-liquid critical properties are essential in corresponding-states treatments of equilibrium thermodynamic and transport property data. The objective is to review all such measurements for pure organic compounds containing **nitrogen**, **halogen(s)**, and **sulphur** and **silicon** and to recommend values for critical temperature, critical pressure and critical densities, with uncertainties.

Progress:

The current project is the continuation of [project 121/10/87](#) which has to date, resulted in 7 review papers published in the *Journal of Chemical and Engineering Data*. These include an introductory survey (which covers experimental methods and effects of impurities and decomposition on the

results; Normal alkanes; Aromatic hydrocarbons: Aliphatic alkanols;
Branched alkanes and cyclo-alkanes; Unsaturated aliphatic hydrocarbons
and Oxygen compounds other than alkanols and cycloalkanols.

Eight papers in the series "Vapour-Liquid Critical Properties of Elements and Compounds" were published in the *Journal of Chemical & Engineering Data*:

- Part 1. An introductory survey, Vol. **40**, 345-350 (1995)
- Part 2. Normal alkanes, Vol. **40**, 531-546 (1995)
- Part 3. Aromatic Hydrocarbons, Vol. **40**, 547-558 (1995)
- Part 4. Aliphatic Alkanols, Vol. **40**, 1025-1036 (1995)
- Part 5. Branched Alkanes and Cycloalkanes, Vol. **41**, 365-372 (1996)
- Part 6. Unsaturated Aliphatic Hydrocarbons, Vol. **41**, 645-656 (1996)
- Part 7. Oxygen Compounds other than Alkanols and Cycloalkanols, Vol. **46**, 457-479 (2001).
- Part 8. Organic Sulfur, Silicon and Tin Compounds, Vol **46** (3), 480-485 (2001).

> [View earlier references in this series](#)

Papers in preparation:

Part 9 - nitrogen compounds

Part 10 - halogen compounds

Part 11 - miscellaneous

Last Update: 14 May 2001

This project was presented
at a [poster session](#) at the
IUPAC Congress/GA July
2001
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