21st CTAS Annual Workshop & Exhibition

May 10 & 11, 2011
University of Guelph
Guelph, Ontario, Canada
Tuesday May 10, 2011

Training Session
New Science Complex, Room 1511

8:00 – 8:30   Registration (Room 1504)

8:30 – 9:15   Plenary Lecture
The Thermodynamic and Thermal Stability of Amino Acids and Nucleic Acid Bases under Hydrothermal Conditions by Solution Calorimetry, Densimetry and UV-Visible Spectroscopy
E. Balodis, V. Mann and Peter Tremaine, Department of Chemistry, University of Guelph, ON

9:15 – 9:30   Open Forum
Moderator: P. Tremaine

9:30 – 10:00  Advanced Techniques in Thermogravimetry
C. A. Potter, TA Instruments

10:00 – 10:30 Exhibition, Posters & Coffee break (Rooms 1504 and 1508)

10:30 – 11:00 Review of Thermal Conductivity Characterization Techniques
A. Harris, C-Therm Technologies Ltd.

11:00 – 11:30 Sample Preparation for Dynamic Mechanical Analysis
A. Hammer, Mettler-Toledo, Inc

11:30 – 12:00 How Well Do You Know Your Thermal Analysis & Calorimetry Facts?
N. Garcia, Setaram Inc

12:00 – 13:15 Lunch (The Atrium)
### Vendor Presentations

**New Science Complex, Room 1511**

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<td>13:15 – 13:30</td>
<td>Setaram Inc.</td>
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<td>13:45 – 14:00</td>
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<td>14:30 – 16:30</td>
<td>Exhibition, Posters &amp; Coffee break (Rooms 1504 and 1508)</td>
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### Social Event:
The Bullring Pub
Mixer / Dinner
18:00 – 21:00
Wednesday May 11, 2011

Technical Session
New Science Complex, Room 1511

08:00 – 08:30  Registration

08:30 – 09:15  Plenary Lecture
Nanotechnology and its Applications from Medicine to Construction
Subhash C. Mojumdar, Department of Chemical Technologies and Environment, Trencin University of A. Dubcek, Púchov (Slovakia)

G. Zimmerman¹, H. Arcis², P. Tremaine²
¹University of Bloomsburg, Pennsylvania (USA), ²University of Guelph, ON.

09:35 – 09:55  Comparison of Decomposition Gases of Two “Green” Explosives by TG-DSC-FTIR-MS
B. Acheson¹, Q. Kwok¹, R. Turcotte¹ P. Brousseau²
¹Canadian Explosives Research Laboratory, Ottawa, ON, ²Defence R&D Canada, Valcartier, QC.

09:55 – 10:25  Exhibition, Posters & Coffee break (Rooms 1504 and 1508)

10:25 – 10:45  Inclusion Compounds of Leucyl-alanine (Leu-Ala) with Dimethylsulfoxide (DMSO), Guaiacol and Pyridine Derivatives
A. Yazdani, V. V. Chirmanov, D. V. Soldatov
Department of Chemistry, University of Guelph, ON
10:45 – 11:05  Enthalpy of Solution of CO\textsubscript{2} in Aqueous Solutions of Ethanolamines at Temperatures of 50 °C and 100 °C and for Pressures from 0.2 to 5 MPa.

H. Arcis\textsuperscript{1}, K. Ballerat-Busserolles\textsuperscript{2}, L. Rodier\textsuperscript{2}, J.Y. Cozam\textsuperscript{2}.
\textsuperscript{1} University of Guelph, ON, \textsuperscript{2} Laboratoire de Thermodynamique et Interactions Moléculaires, Aubière (France).

11:05 – 11:25  Calorimetry and Thermal Analysis of Cement

Nelson Garcia, Andre A. Levchenko
Setaram Inc., Pleasanton, California (USA).

11:25 – 12:00  Annual General Meeting (35 minutes for discussions)

12:00 – 13:00  Lunch (The Atrium)

13:00 – 13:20  The Decomposition of the Ternary Telluride Tl\textsubscript{2}ZrTe\textsubscript{3} Above Room Temperature

C Raj Sankar, M Guch, H Kleinke
Chemistry Department, University of Waterloo, ON.


Allan Nixon\textsuperscript{1}, Matthew Kaye\textsuperscript{2}, Liliana Trevani\textsuperscript{1}
\textsuperscript{1} Faculty of Science, UOIT, Oshawa, \textsuperscript{2} Faculty of Energy Systems and Nuclear Science, UOIT, Oshawa, ON.

13:40 – 14:00  Application of the MMC 274 to the King’s Lynn Accident

P. Vichos, P. Ralbovsky
Netzsch Instruments North America LLC, Chicago, Illinois (USA).

14:00 – 14:30  Exhibition, Posters & Coffee break (Rooms 1504 and 1508)
14:30 – 14:50  Ionization Constants of Acetic Acid in H₂O and D₂O from 100 °C to 275 °C at 20 MPa: Deuterium Isotope Effects under Hydrothermal Conditions
   K. M. Erickson¹, H. Arcis¹, D. Raffa¹, G. H. Zimmerman², P. R. Tremaine¹
   ¹University of Guelph, ON, ²University of Bloomsburg, Pennsylvania (USA).

14:50 – 15:10  Novel Technique for Measuring Thermal Conductivity of Geological Samples Including Logged Core
   R. Bateman¹, A. F. Park², A. Harris³.
   ¹Department of Chemical Engineering, University of New Brunswick, Fredericton, NB, ²Department of Earth Sciences, University of New Brunswick, Fredericton, NB, ³C-Therm Technologies Ltd., Fredericton, NB.

15:10 – 15:30  Thermal Conductivity of Polyurethane Composites with Silver Nano- and Micro-Particles
   M. Iqbal¹, S. H. Eichhorn¹ and A. Harris²
   ¹Department of Chemistry & Biochemistry, University of Windsor, ON, ²C-Therm Technologies Ltd., Fredericton, NB.

15:30 – 15:50  Melting Properties isotactic Polypropylene at High (1,800,000 °C/min) Heating Rates
   A. Hammer, P. LaPointe, J. Schawe
   Mettler-Toledo, Inc, Columbus, OH (USA).

15:50 – 16:10  Exhibition, Posters & Coffee break (Rooms 1504 and 1508)

16:10 – 16:30  Characterization of Water-in-oil Emulsions by Differential Scanning Calorimetry
   J. Kein, Y. Maham
   Department of Chemical and Materials Engineering, University of Alberta, AB.
16:30 – 16:45 Degradation Mechanism and Thermal Stability of Urea Nitrate Below the Melting Point
S. Désilets\textsuperscript{1}, P. Brousseau\textsuperscript{1}, D. Chamberland\textsuperscript{1}, S. Singh\textsuperscript{2}, H. Feng\textsuperscript{2}, R. Turcotte\textsuperscript{2}, J. Anderson\textsuperscript{3} \\
\textsuperscript{1}Defence R&D Canada, Valcartier, QC, \textsuperscript{2}Canadian Explosives Research Laboratory, Ottawa, ON, \textsuperscript{3}Defence R&D Canada, Suffield, AB.

16:45 – 17:00 Thermal Analysis of Inclusion Compounds: Some Tips and Tricks
D.V. Soldatov, A. Yazdani, V.V. Chirmanov \\
Department of Chemistry, University of Guelph, ON.

17:00 – 17:15 Thermal Conductivity of Advanced Textiles
A. Harris \\
C-Therm Technologies Ltd., Fredericton, NB

17:15 Student Awards Announcement
Poster Session

Thermal Analysis of Highly Unstable Inclusion Materials: Clathrates of a Nickel Complex with Aromatic Guests
V. V. Chirmanov, D. V. Soldatov
Department of Chemistry, University of Guelph, ON

Functionalization of Carbon Nanotubes using a Supercritical Fluid Sol-Gel Aided Method.
D. McGillivray, F. Gaspari, L. Trevani
Faculty of Science, University of Ontario Institute of Technology, Oshawa, ON

Thermal Analysis Techniques for Studying Li-ion Cells and Materials of Construction
P. Vichos, Netzsch Instruments Inc.

Synthesis, Characterization, Magnetic and Electrical Properties of Nanocrystalline Mn$_{0.3}$Ni$_{0.3}$Zn$_{0.4}$Fe$_2$O$_4$ Obtained by Novel Fumarato-hydrazinate Precursor Method
U. B. Gawas$^1$, V. M. S. Verenkar$^1$ and S. C. Mojumdar$^{2, 3}$
$^1$Department of Chemistry, Goa University (India) $^2$Department of Chemical Technologies and Environment, Trencin University of A. Dubcek, (Slovakia),
$^3$Department of Chemistry, University of Guelph, ON

Multiple Mode Calorimeter (MMC) Performance Tests for Material Characterization Studies
P. Vichos, Netzsch Instruments Inc.

Comparative Nanocrystallization Kinetic Study in Two FINEMET Alloys
E. M. Loftfabad, A. Kohandehghan, Y. Maham
Department of Chemical and Materials Engineering, University of Alberta, Edmonton, AB

Influence of Transition Metal V(II)-doping on Thermal and Optical Properties of Magnesium Rubidium Sulphate Crystals
S. Parthiban$^1$, H. Anandalakshmi$^1$, S. Senthilkumar$^2$ and S. C. Mojumdar$^{3, 4}$
$^1$Department of Chemistry, Annamalai University (India), $^2$Chemistry Wing, DDE, Annamalai University (India), $^3$Department of Chemical Technologies and Environment, Trencin University of A. Dubcek, Púchov (Slovakia), $^4$Department of Chemistry, University of Guelph, Guelph, ON
Ion Association in Aqueous MgSO₄ and NiSO₄ from 25 to 275 °C at 19 MPa by AC Conductance and Raman spectroscopy
M. Madekufamba, P. Tremaine
University of Guelph, ON

Crystal Growth, Structure and Characterization of o-hydroxybenzoic acid Single Crystals: Solvent Effects
K. Muthu¹, G. Madhurambal², S. P. Meenakshisundaram¹ and S. C. Mojumdar³, 4
¹Department of Chemistry, Annamalai University, Tamilnadu (India), ²Department of Chemistry, ADM College for Women, Nagapattinam (India), ³Department of Chemical Technologies and Environment, Trencin University of A. Dubcek, Púchov (Slovakia), 4Department of Chemistry, University of Guelph, Guelph, ON

Synthesis and Characterization of Ultrafine Spinel Ferrite Obtained by Precursor Combustion Technique
L. R. Gonsalves¹, S. C. Mojumdar², ³ and V. M. S. Verenkar¹
¹Department of Chemistry, Goa University (India), ²Department of Chemical Technologies and Environment, Trencin University of A. Dubcek, Púchov (Slovakia), ³Department of Chemistry, University of Guelph, Guelph, ON.

Stepwise Formation Constants for Aqueous Copper(II) and Copper(I) Chloro-Complexes from 5 to 150 °C.
L. Applegarth¹, C. Pye², L. Trevani³ and P. Tremaine¹
¹Department of Chemistry, University of Guelph, ON, ²Department of Chemistry, St. Marys University, Halifax, NS, ³Faculty of Science, University of Ontario Institute of Technology, Oshawa, ON

Effect of Alkali Metal Doping on the Properties and Crystalline Perfection of Bis(thiourea)zinc(II) Chloride Crystals
K. Muthu¹, G. Bhagavannarayana², S. P. Meenakashisundaram¹ and S. C. Mojumdar³, 4
¹Department of Chemistry, Annamalai University, Tamilnadu (India), ²Materials Characterization Division, National Physical Laboratory, New Delhi, (India), ³Department of Chemical Technologies and Environment, Trencin University of A. Dubcek, Púchov, (Slovakia), 4Department of Chemistry, University of Guelph, Guelph, ON.
HiTemp 2011 is intended to foster discussion and debate regarding the most recent understanding of high temperature materials and the state of the art in their experimental studies, processes, and diagnostics for scientific and technological applications.

Experimental studies of high temperature materials

- 10 keynote lectures
- 28 contributed lectures
- 3 poster sessions
The Thermodynamic and Thermal Stability of Amino Acids and Nucleic Acid Bases under Hydrothermal Conditions by Solution Calorimetry, Densimetry and UV-Visible Spectroscopy

E. Balodis, V. Mann and P. Tremaine
Department of Chemistry, University of Guelph

The thermodynamic properties and thermal stability of amino acids, nucleic acid bases and nucleosides under hydrothermal conditions are of interest in modelling conditions on the early earth that might have led to the origin of life [1,2]. This paper reviews ongoing experimental research to develop models for predicting the stability of simple pre-biotic molecules in water at elevated temperatures and pressures. Standard partial molar volumes $V_E$ and heat capacities $C_p E$ of aqueous amino acids, nucleic acid bases and their corresponding nucleosides have been determined in acidic and neutral solutions at temperatures from 15 to 90 °C using an Anton Parr DMA 5000 densitometer and TA DSC III nanocalorimeter with methods developed by Woolley [3]. Measurements of $V_E$ for neutral uridine, cytidine, and thymidine were made up to 200 °C, and for $C_p E$ and $V_E$ for several amino acids up to 250 °C, using a custom built platinum vibrating tube densitometer and Picker-type calorimeter, some of which have been reported previously [4,5]. Standard partial molar properties of neutral nucleic acid base and nucleoside species become progressively more positive with increasing temperature, while the zwitterionic amino acids, and the chloride salts of nucleic acid bases and nucleosides become increasingly negative. These experimental results are in contrast with models reported by Amand and Helgeson [1] and LaRowe and Helgeson [2], based on low temperature data, which did not show the correct limiting near-critical behaviour.

The first and/or second acid ionization constants of amino acids, uracil, adenine and adenosine have been measured from 25 to 250 °C at ~10 MPa by UV-visible spectroscopy, using a high pressure flow cell with sapphire windows [6]. Thermal decomposition kinetics of uracil, adenine and adenosine in acidic, neutral, and basic buffer solutions have been determined from 150 to 250 °C at 9.5 MPa by operating the UV-visible cell as a stopped flow system. Interestingly, the decomposition kinetics of neutral and protonated adenine and adenosine in formic acid/formate buffers and mono-hydrogen phosphate/di-hydrogen phosphate buffers show marked differences, despite the fact that the equilibrium buffer pH is very similar, suggesting that phosphate buffers interact with adenine at elevated temperatures in a different way than other buffers [7].

Biography  Peter Tremaine, FCIC

Dr. Peter Tremaine is a Professor in the Department of Chemistry at the University of Guelph, and former Dean of the College of Physical and Engineering Science (2001-2006). Before moving to Guelph, he was Head of the Department of Chemistry at Memorial University of Newfoundland (1990-1996), Manager of the AOSTRA In Situ Oils Sands Research Program, at the Alberta Research Council (1986-1990), and a Research Officer at both ARC (1980-1990) and Atomic Energy of Canada Ltd. (1975-1980). Tremaine’s research is centered on the use of small-scale flow techniques for high-precision measurements on the properties of aqueous chemistry at very high temperatures and pressures. His work has had an impact on both underlying science and on applied problems in thermal and nuclear power generation, heavy oil recovery, geochemistry and materials science. His contributions to basic research are recognized by his Fellowship in the Chemical Institute of Canada (FCIC) and the Calorimetry Conference Stig Sunner Award. Tremaine’s contributions to applied research have been recognized by his appointment as Honorary Fellow by the International Association of Water and Steam (IAPWS) and by the International Water Conference Paul Cohen Award. He is a former President of IAPWS, and current Chair of the R & D Advisory Panel of Atomic Energy of Canada Ltd.
Advanced Techniques in Thermogravimetry

C. Potter, TA Instruments

Biography  Charles A. Potter, Ph.D.

Dr. Potter obtained his PhD in analytical chemistry from the University of Connecticut. Since then he has worked in diverse research environments in thermal analysis and hazard analysis. He is currently a senior application scientist at TA Instruments, helping customers with TA problem solving.
Review of Thermal Conductivity Characterization Techniques

Adam Harris, C-Therm Technologies Ltd.

Biography  Adam Harris

Adam has supported clients in the pharmaceutical, petroleum, ceramics, energetics and electronics industries over the past 8 years in evaluating the adoption of thermal instrumentation for product development and process control. Having contributed to a number of papers on application of the thermal effusivity and conductivity technologies in manufacturing and R&D environments, Adam is well respected for his business and technical acumen on the product line originally developed by Mathis Instruments. Adam graduated from the Dalhousie University School of Business Administration with a Bachelor of Commerce and has completed graduate courses at Harvard University (Summer School) and the University of New Brunswick.
Sample Preparation for DMA Analysis

Angela Hammer, Mettler-Toledo AG Analytical

Obtaining accurate modulus results from Dynamic Mechanical Analysis (DMA) requires careful attention to sample preparation. This course will detail many techniques for the proper preparation of DMA samples for bending, compression, tension and shear modes of deformation.

Biography Angela Hammer, Dr. sc. Nat. ETH

Dr. Hammer holds a degree in ‘Studies of Chemistry’ from Technical University of Clausthal-Zellerfeld (Germany) and, in 1999, obtained a PhD in the field of Analytical Chemistry and Polymers, ETH Zurich (Switzerland). She worked as a R&D chemist in the Analytical department of Sika Technology AG (Switzerland) until 2007. Since then, Dr. Hammer has been an Application Specialist for Thermal Analysis in the Materials Characterization department of Mettler-Toldedo AG, Schwerzenbach (Switzerland).
How Well Do You Know Your Thermal Analysis & Calorimetry Facts?

N. Garcia, Setaram Inc

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Technical Session

Abstracts
Nanotechnology and its Applications from Medicine to Construction

S. C. Mojumdar

Department of Chemical Technologies and Environment, Faculty of Industrial Technologies, Trencín University of A. Dubček, Púchov, Slovakia / Department of Chemistry, University of Guelph (scmojumdar@yahoo.com)

The foundations of nanotechnology have emerged over many decades of research in many different fields. In 1959, the great physicist Richard Feynman suggested that it should be possible to build machines small enough to manufacture objects with atomic precision. His talk, "There's Plenty of Room at the Bottom," is widely considered to be the foreshadowing of nanotechnology. Nanotechnology is the design, characterization, production, and application of structures, devices, and systems by controlling shape and size on the nanoscale. Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular, and macromolecular scales, where properties differ significantly from those at a larger scale. Much interest is also focused on quantum dots, which are semiconductor nanoparticles that can be 'tuned' to emit or absorb particular colors of light for use in solar energy or fluorescent biological labels. Applications of nanotechnology are promising in the longer term. These can be expected to enable drug delivery, detect tumor cells, make hip-joint from biocompatible materials, lead to stronger and longer-lasting implants and sensors that can be used to monitor aspects of human health; and improved artificial cochleae and retinas. Nanotechnology is also enabling the development of smaller, cheaper sensors, which will have a wide range of applications from monitoring environmental pollution, the freshness and quality of foods, or the stresses in a building or a vehicle. It can also be used to produced sun creams, computer disk drives to improve storage (2007 Nobel prize in physics), Organic Light Emitting Diodes (OLEDs) for displays, photovoltaic film that converts light into electricity, fabrics coated to resist stains and control temperature, intelligent clothing to measures pulse and respiration, light but very strong bucky-tubeframe, nano-particle paint to prevent corrosion, thermo-chromic glass to regulate light, magnetic layers for compact data memory, carbon nanotube fuel cells to power electronics and vehicles, and developing stronger construction materials. Nanotechnology will lead to tiny robotic submarines navigating our bloodstream is ubiquitous. Nanotechnology can play a significant role to prevent AIDS. The various applications of nanotechnology from medicine to construction as well as the synthesis, structure and thermophysical properties of various nanomaterials with related examples will be presented.
Biography  Dr. Subhash C. Mojumdar

Dr. S. C. Mojumdar obtained his B.Sc., M.Sc. and Ph.D. degree in Chemical, Biochemical and Biomedical Engineering, respectively. Since then he worked in diverse research environments such as antibiotics, antioxidants, glasses, ceramics, cements, environmental sciences, hydrometallurgy, bio-films and many other bio and nanomaterials. He extended his research activities from medicine through construction to nanotechnology using many thermoanalytical techniques such as TG, DTG, DTA, DSC, DMA, TMA, optical transmittance (light beam) thermal analysis, EGA, calorimetry, conduction calorimetry, isothermal pressure transducer analysis, heating microscopy, thermal conductivity etc. He has already published over 300 articles in the field of medicine, chemistry, biochemistry, materials science, nanotechnology, thermal analysis and many other fields. He is a long time referee for numerous journals and also an editorial board member of many journals such as Journal of Thermal Analysis and Calorimetry, American Journal of Analytical Chemistry, Research Journal of Chemistry and Environment, Advances in Bioscience and Biotechnology, Journal of Environmental Protection, Global Journal of Analytical Chemistry. He is the editor of the Chartered Chemist News (Newsletter of the Association of the Chemical Profession of Ontario). He has delivered over 40 invited and plenary lectures and training seminars throughout the globe and has been selected an examiner for many Ph.D. and M. Sc. theses. He is a Member/Executive Committee Member of 15 professional organizations including the Canadian Thermal Analysis Society (CTAS). He has also a great experience in popularizing thermal analysis and convincing students, faculties and scientists to use thermal analysis for their research who has never used thermoanalytical techniques before.
Thermodynamic and Transport Properties of Aqueous Strontium Salts: Chloride, Hydroxide and Acetate By AC Conductance from 25 to 350 °C at 20 MPa.

G. Zimmerman¹, H. Arcis², P. Tremaine²
¹ Bloomsburg University, Pennsylvania (USA), ² University of Guelph, Guelph, Ontario, Canada

Complexation of metal ions with common ligands in high temperature water is of interest to geochemistry, hydrometallurgy, chemical engineering, materials science and the nuclear industry [1]. Because of its favourable solubility, Sr²⁺ is an attractive model system for predicting the thermodynamic properties of divalent transition metals M²⁺ under hydrothermal conditions. This paper reports the first measurements of the molar conductivity, \( \Lambda \), of aqueous SrCl₂ and Sr(OH)₂ for temperature up to 350 °C. Conductivity measurement of aqueous Sr(Ac)₂ were also obtained up to 275 °C. Experiments were conducted at 20 MPa, using a novel high-precision flow-through AC electrical conductance instrument [2,3] at concentrations \( 5 \cdot 10^{-5} \leq c \leq 0.2 \text{ mol·L}^{-1} \). Association constants were then determined from \( \Lambda \) vs \( c \) using the TBBK model [2,3]. The values for Sr(OH)⁺ and Sr(OH)₂⁰ are greater than those for SrCl⁺ and SrCl₂⁰ ion pairs, and both neutral species are significant above \( 10^{-3} \) mol·L⁻¹ at 350 °C. The limiting molar conductivities, \( \Lambda^\circ \), were found to be a simple exponential function of the solvent viscosity, which can be used to estimate ionic mobilities and diffusion in crevices under hydrothermal conditions.

Comparison of Decomposition Gases of Two “Green” Explosives by TG-DSC-FTIR-MS

B. Acheson¹, Q. Kwok¹, R. Turcotte¹, P. Brousseau²
¹Canadian Explosives Research Laboratory, Ottawa, ON, ²Defence R&D Canada, Valcartier, QC

The “greening” of explosives is a growing trend, as governments seek to reduce exposure of personnel to harmful gases, and of environments to the harmful residues of explosives. Explosive compositions are being sought which produce the best profile of insensitivity, environmental friendliness, and performance. Two such “green” explosives are examined here: PBX (an HMX/HTPB/DOA plastic-bonded explosive), and GIM (Greener Insensitive Material, a TNT/HMX/ETPE mix). The ETPE is an energetic thermoplastic elastomer based on Glycidyl azide polymer. PBX and GIM are both HMX-based explosives. HMX has already been shown to be significantly less aquatically toxic and available than traditional RDX-based explosives (1, 2). In this study, simultaneous TG-DSC-FTIR-MS experiments have been performed on these two HMX-based explosives to investigate differences in evolved gases and thermal decomposition behaviour in both air and helium. This ‘hyphenated’ thermal analysis technique has the advantage of being able to examine evolved gases while simultaneously assessing any changes in the decomposition behaviour of the explosives, under identical experimental conditions. In both explosives, evolution of CO₂, H₂O, formaldehyde, nitrous acid, hydrogen cyanide, and an unidentified absorption at around 590 cm⁻¹ were detected by FTIR. Numerous additional mass spectrometry fragments suggest the presence of additional symmetric gases. In air, DSC onset temperatures were within 20 °C for both samples, with the PBX being slightly more thermally stable, with an onset temperature of approximately 220°C. However, the decomposition enthalpy for the GIM sample was nearly triple that of the PBX sample. TG profiles show that decompositions for both samples are nearly complete, with a low of 92% mass loss in helium for PBX to a high of 100% mass loss for GIM in air.

Inclusion Compounds of Leucyl-alanine (Leu-Ala) with Dimethylsufoxide (DMSO), Guaiacol and Pyridine Derivatives

A. Yazdani, V. V. Chirmanov, D. V. Soldatov
Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

Small peptides are readily available molecules that can be used in the design of versatile biocompatible, environmentally friendly materials [1]. In crystals dipeptides frequently form a 2D layered structure fortified by charge-assisted H-bonds [2]. In our research, we introduce dipeptides with bulky side groups to generate interlayer cavity space in the structure and utilize it as a reservoir for guest molecules.

In this work, inclusion compounds with various (guest) species, including DMSO, guaiacol and pyridine derivatives, were isolated and characterized in order to investigate the inclusion ability of the Leu-Ala dipeptide (host). With all the guests, 1:1 (host:guest) inclusion compounds were identified. The compounds and their properties were studied by thermal analysis techniques. Using TGA and DSC, the phase diagrams of the binary systems Leu-Ala – DMSO and Leu-Ala – Guaiacol were determined in order to investigate stability, limits of existence and modes of decomposition for the inclusion compounds. The inclusion compound Leu-Ala*Guaiacol appears on the phase diagram as a thermodynamically stable phase melting incongruently at ~125°C into solid Leu-Ala (guest-free) and a liquor. Isopiestic and TGA experiments show that the inclusion compounds form reversibly by interacting solid Leu-Ala and gaseous volatile guests.

Enthalpy of Solution of CO₂ in Aqueous Solutions of Ethanolamines at temperatures of 50 °C and 100 °C and for pressures from 0.2 to 5 MPa.

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The capture of carbon dioxide from post combustion emissions is one of the challenges for reducing the release of greenhouse gases into the atmosphere. Aqueous amine solutions are well known to be efficient chemical solvents for this purpose. Energetic effects involved in such processes are of interest to industry as the energy cost for CO₂ removal is directly related to the enthalpy of solution of CO₂ into the absorbing fluid. This paper reports measurements of the enthalpy of solution of carbon dioxide into aqueous solutions of ethanolamines ($w_{\text{ethanolamine}} = 0.1500$ and $0.3000$) at temperatures of 50 °C and 100 °C, and for pressures from 0.2 to 5 MPa for different loading charges (mol CO₂ / mol amine). Experiments were conducted at constant temperature and pressure, using a custom-made flow-mixing unit in a SETARAM C-80 calorimeter [1,2]. Three amines were selected: monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) to examine the impact of amine substitution on the enthalpy of solution. The results are discussed in term of the chemical reactions involved in the capture process and interpreted with a thermodynamic model [3], which was derived only from vapour-liquid-equilibrium properties, considering all reactions taking place at equilibrium. The reactions of amine protonation and carbamate formation (when possible) were found to provide the most important energetic contributions to the enthalpy of solution.

Calorimetry and Thermal Analysis of Cement

Nelson Garcia, Andre A. Levchenko
Setaram Inc., Pleasanton, California, U.S.A.

The capabilities of Calvet calorimeters to study in-situ mixing and materials under the temperature/pressure conditions of real-life applications offer many opportunities in basic and applied research of cement samples. The presentation will deal with applications ranging from cement hydration and effects of additives to stability/reaction studies of cement mixtures under extreme/aggressive environments. Thermal analysis complements the calorimetry data and can be used in conjunction with calorimetry or as an independent method. The Calvet calorimetry is especially used to investigate the kinetics of cement, and the examples of such research will be given.
The Decomposition of the Ternary Telluride Tl₂ZrTe₃ Above Room Temperature

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Tl₂ZrTe₃ crystallizes in the cubic space group $P\bar{4}3$ with $a = 19.118(1)$ ($Z = 36$). The structure consists of distorted ZrTe₆ octahedra, which are edge shared and propagate in a three dimensional fashion. One of the Te atoms is only connected to Tl atoms, forming TeTl₆ distorted octahedra. Our differential scanning calorimetry and high-temperature powder X-ray diffraction experiments reveal that the compound decomposes on heating. This decomposition, occurring well below the compound's peritectic melting point, is irreversible in an open system, likely associated with the loss of tellurium vapour. The anomalies observed in physical properties are also attributed to the decomposition of the sample at high temperatures.
Thermochemical Production of Hydrogen by Splitting of Water: Synthesis of Copper Oxychloride and Thermal Decomposition Studies

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Copper oxychloride (Cu₂OCl₂) is an intermediate in the copper-chlorine cycle for production of hydrogen by splitting of water. The cycle is attractive because it involves very abundant compounds, a small number of reactions, and a relatively low maximum temperature making it compatible with a number of different heat sources and potentially lower cost materials. Below are the reactions of the copper-chlorine cycle.

\[
\begin{align*}
2 \text{CuCl (aq)} + 2 \text{HCl (aq)} & \rightarrow \text{H}_2(g) + 2 \text{CuCl}_2(\text{aq}) & \text{Electrolysis at } < 100 \degree \text{C} \\
2 \text{CuCl}_2(s) + \text{H}_2\text{O (g)} & \rightarrow \text{Cu}_2\text{OCl}_2(s) + 2\text{HCl (g)} & 350-400 \degree \text{C} \\
\text{Cu}_2\text{OCl}_2(s) & \rightarrow 2\text{CuCl (l)} + \frac{1}{2}\text{O}_2(g) & 450-550 \degree \text{C}
\end{align*}
\]

In this study, Cu₂OCl₂ was synthesized from CuCl and CuCl₂ in a tubular furnace using dry air as the oxygen source at temperatures between 350 and 400 °C. Solid products were characterized using X-ray diffraction (XRD), SEM, and Raman spectroscopy. Thermogravimetric analysis (TGA) was used to investigate the thermal stability of Cu₂OCl₂ and identify the conditions under which other possibly reactions by-products such as CuO(s) and Cl₂ (g) are formed.
Application of the MMC 274 to the King’s Lynn Accident
P. Vichos, P. Ralbovsky
Netzsch Instruments North America LLC, Chicago, Illinois (USA).

The Multiple Mode Calorimeter (MMC) is an excellent tool to be used in conjunction with the DSC to provide a more comprehensive look at thermal hazards. The MMC uses samples sizes up to about 3 grams so it is possible to do injection and stirring. In the MMC temperature and pressure are recorded as a function of time. Sample energies measurement of both endotherms and exotherms is possible. Heat capacity can be calculated as a function of temperature. This method offers a quick and inexpensive way to perform isothermal tests which can be used to help design larger scale tests done in 2L+ reaction calorimeters or pilot plant operations.

Thermal Hazards Screening is a primary part of any chemical process safety program. The accident that occurred at the Dow plant in King’s Lynn, UK has been studied and written about in some detail. This accident was chosen as a sample case because of the unusual chemistry and we are able to look at this more openly due to the length of time which has passed since the accident.
Ionization Constants of Acetic Acid in H$_2$O and D$_2$O from 100 °C to 275 °C at 20 MPa: Deuterium Isotope Effects under Hydrothermal Conditions

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CANDU (Canadian Deuterium Uranium) reactors use heavy water (D$_2$O) as a heat transfer medium in the primary coolant circuit. Oxide solubility and hydrolysis reactions in D$_2$O from $T = 250$ °C to $T = 320$ °C can accelerate the unwanted transfer of radioactive corrosion products and shorten the lifetime of reactor components if the coolant pH (“pD”) is not carefully regulated. Methods used by the nuclear industry to determine optimum coolant chemistry conditions in D$_2$O are based on measurements in light water (H$_2$O). Experimental studies to determine accurate differences in acid-base ionization constants ($\Delta pK_a = pK_a(D_2O) - pK_a(H_2O)$) between H$_2$O and D$_2$O are limited to temperatures below 80 °C, with the exception of one paper by Mesmer and Herting [1] who measured the ionization constant of D$_2$PO$_4^-$ up to $T = 300$ °C, and recent UV-visible studies from our laboratory [2].

In this paper, we report experimental values of $\Delta pK_a$ for acetic acid (CH$_3$COOH and CH$_3$COOD) in H$_2$O and D$_2$O using AC conductance methods developed at the University of Delaware [3] over the temperature range $T = 100$ °C to $T = 275$ °C at a pressure of $p = 20$ MPa as a first step towards a predictive model for deuterium isotope effects under primary coolant conditions. We also report a model to calculate deuterium isotope effects on the ionization constant of acetic acid from light water data. This is only the second report of accurate experimental values for $\Delta pK_a$ for any acid at temperatures above $T = 100$ °C.

Novel Technique for Measuring Thermal Conductivity of Geological Samples Including Logged Core

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The modified transient plane source (MTPS) method, developed by C-Therm Technologies Ltd., offers a rapid non-destructive means of measuring thermal conductivity of a variety of solid, liquid and powder materials. The one-sided interfacial sensor is capable of making very rapid precise measurements by surface contact with samples in less than one minute, and consecutive measurements can be repeated on the same time scale. This offers geologists several advantages over more traditional methods of obtaining this type of data, which generally require more complex equipment, elaborate preparation of samples and a longer time-frame.

An interesting area of application of the technology is in the characterization of geological samples, where thermal conductivity measurements are of interest in a number of applications: geothermal energy studies and thermal maturation modelling and formation temperature determination in oil and gas exploration and production are the most obvious. This abstract reports on use of the MTPS firstly, to determine thermal conductivity in a variety of typical geological materials and a comparison of the results with conventional methods, and secondly thermal conductivity from core plug and drill core samples from a complete borehole core retrieved from a hydrocarbon play in southern New Brunswick.

Thermal conductivity determined on over a half dozen geological samples including common igneous, metamorphic and sedimentary rocks are presented and compared to published values obtained by more traditional methods. The second aspect of the study demonstrates that reliable thermal conductivity data can be obtained using the MTPS method from materials commonly subjected to routine core analysis for little extra effort. The use of the MTPS sensors alongside conventional core analytic techniques has the potential to become a routine method for obtaining reliable thermal conductivity determinations from rock samples.
Thermal Conductivity of Polyurethane Composites with Silver Nano- and Micro-Particles

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Polyurethanes are one of the most versatile plastics today. Typical applications range from flexible and rigid foams to thermoplastics used in medical devices, footwear, coatings, adhesives, sealants and elastomers. What all these materials have in common is low thermal conductivity. Presented here is the enhanced thermal conductivity of thermoplastic polyurethane composite materials that contain dispersed silver particles of nanometer and micrometer dimensions. Demonstrated is the effect of different particle sizes and anisotropic particle distributions on thermal conductivity in composites of equal silver content. All composite materials are characterized by TEM, SEM, thermal analysis, and optical spectroscopy.
Melting Properties isotactic Polypropylene at High (1,800,000 °C/min)
Heating Rates

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1Mettler-Toledo AG Analytical (Switzerland), 2Mettler-Toledo Inc, Columbus, OH (USA)

The METTLER TOLEDO Flash DSC 1 revolutionizes rapid-scanning DSC. The instrument can analyze reorganization processes that were previously impossible to measure. The Flash DSC 1 is the ideal complement to conventional DSC. Heating rates now cover a range of more than 7 decades.

Amorphous isotactic polypropylene (iPP) is produced by cooling from the melt at 4,000 °C/s. The material obtained was measured at heating rates between 5 °C/s and 30,000 °C/s. The glass transition occurs just below 0 °C followed by an exothermic peak due to cold crystallization. The crystallites melt above 100 °C. At higher heating rates, the cold crystallization peak is shifted to higher temperatures and melting peak to lower temperatures. From 1,000 °C/s onward, the peak areas become significantly smaller until at 30,000 °C/s recrystallization no longer occurs in the sample.

The Flash DSC 1 is also the ideal tool for studying crystallization kinetics. The Flash DSC 1 allows you to prepare samples with defined structures such as occur during rapid cooling in injection molding processes. The application of different cooling rates influences the crystallization behavior and structure of the sample. The use of high heating rates enables materials to be analyzed without interference from cold crystallization, there is no time for such processes to occur.
Characterization of Water-in-oil Emulsions by Differential Scanning Calorimetry

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The formation of water-in-oil (W/O) emulsions can cause major problems for the oil industry during mining, processing and production. Characterization of emulsion systems, droplet sizes and stability with time are needed for design and processing industry. One of the most important physical properties of these emulsions is droplet size. The droplet size and water content of the emulsions are two important factors for emulsion stability. Normally, droplet size measurements are carried out by light scattering, Coulter counter and optical microscopy but crude oil emulsion systems are opaque and the above techniques are not applicable for this case. The calorimetric method of solidification and melting of water droplets in emulsion can be used for this case and is described in this work. This method consists of measuring the freezing/melting temperatures of water droplets which can help us obtain the droplet sizes. The freezing and melting points of the droplets are directly related to the size of the droplets. Smaller the droplet; lower the melting/freezing point. This is a quite simple method which does not need any dilution, which can change emulsion properties. The samples are cooled to -60°C and kept at this temperature for 10 minute to ensure that all the water droplets present in the emulsion are completely frozen. The samples are then heated back to room temperature. This technique can be used for the characterization of fresh emulsions to check their properties after measurement, to examine their stability during measurement, and also their stability as function of time. This technique can used to determine the amount of water present as bulk water or as droplets of water.
Degradation Mechanism and Thermal Stability of Urea Nitrate Below the Melting Point

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Aging and degradation of urea nitrate at 100°C, which is below the melting point, was studied using thermal analysis and spectroscopic methods including IR, Raman, ¹H and ¹³C NMR techniques. It was found that urea nitrate completely degraded after 72 hrs at 100°C into a mixture of solids (69%) and gaseous species (31%) [1, 2]. The residual solid mixture was composed of ammonium nitrate, urea and biuret while unreacted residual nitric and isocyanic acids, as well as traces of ammonia, were released as gaseous species at 100°C [2].

Thermal Analysis of Inclusion Materials:
Some Tips and Tricks

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Inclusion compounds are formed from two weakly bonded components referred to as host and guest. In crystalline inclusion compounds the molecules of guest occupy cavity space in a host crystal lattice. Since in most cases guest is much more volatile than host, Thermogravimetric Analysis is a very useful technique to study the stoichiometry, stability and dissociation pathways of inclusion materials. Since the host-guest interactions are weak, the inclusion compounds decompose reversibly at relatively low temperatures and Differential Scanning Calorimetry is useful in detecting the corresponding phase transitions (e.g. incongruent melting).

On the other hand, the specificity of inclusion materials often requires the development of special approaches in the thermoanalytical studies, from sample preparation and actual experimental procedure to the interpretation of numerical data obtained. One example is the TG analysis of unstable crystals when the sample is half-decomposed by the time a standard TG experiment could be started. Another problem is the registration of phase transitions in DSC when uncontrollable release of a volatile component leads to irreproducible and non-informative results. Approaches to these and other challenging tasks used or developed in our group will be illustrated.
Thermal Conductivity of Advanced Textiles

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C-Therm Technologies Ltd., Fredericton, NB

An objective means of assessing the heat transfer properties of various advanced fabrics and textiles is of increasing importance as researchers develop new materials for more extreme applications. In high-altitude mountaineering climbers are exposed to extremely frigid conditions and the quality of fabrics applied in the construction of their protective clothing can be of life and death consequence. Different fabrics or textiles used in the clothing industry were evaluated non-destructively by the modified transient plane source (MTPS) technique developed by C-Therm Technologies in characterizing the thermal conductivity property of the material. Each sample tested is placed on the sensor and weighted down by a standard 500g brass weight to ensure a good solid contact between the sensor surface and each sample. Four to five readings are obtained for each sample to ensure precision of the measurement within 1%. The stated accuracy for the technique is better than 5%. This work highlights how the MTPS technique is applied within industry in offering a versatile, rapid and non-destructive testing solution in characterizing the thermal conductivity of various advanced fabrics and textiles.
Poster Session
Abstracts
Thermal Analysis of Highly Unstable Inclusion Materials: Clathrates of a Nickel Complex with Aromatic Guests

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Modified metal dibenzoylmethanates (metal DBMs) are host complexes capable of forming inclusion compounds (clathrates) with the molecules of guest [1]. The attractive features of such 'soft' supramolecular materials are their versatility in structure, selectivity and ease of preparation [2]. The potential uses of these materials for separation, temporary storage and controlled release of guest depend on the knowledge on their stability, structure and dissociation mechanisms.

In this work inclusion compounds of the [Ni(DBM)2(3,5-diMePy)2] complex with benzene, fluorobenzene, chlorobenzene, bromobenzene and iodobenzene as guests have been examined using thermoanalytical methods. Preliminary studies suggested the complex readily forms inclusions that vary in structure, guest capacity, and all are highly unstable. TGA methods were used to examine the guest content, ambient or thermal stability and dissociation modes of bulk crystalline samples of the clathrates. A special two-step TGA experimental procedure was designed where the sample in a closed aluminum pan with a hole in the lid was decomposed isothermally followed by a heating step. It was found that with chlorobenzene the complex forms two inclusions with different structure and stoichiometry (H:G ratios 1:1 and 1:3) resulting in a remarkable difference in stability of the inclusions. Some structural features of the 1:1 inclusion are shown in the Figure.

Functionalization of Carbon Nanotubes using a Supercritical Fluid Sol-Gel Aided Method.

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In this study the growth, purification and functionalization of carbon nanotubes (CNTs) with TiO$_2$ was examined in order to enhance their photoelectrical properties. CNTs were synthesized by chemical vapour deposition using camphor and ferrocene as precursors. The experimental parameters that control the CNTs growth, primarily vaporization temperature, gas flow rate, and pyrolysis temperature, were optimized using Raman spectroscopy and thermogravimetric analysis (TGA). Catalytic particles and amorphous carbon were removed using a standard acid treatment, and finally the “as-purified” SW- and MWCNTs were functionalized with TiO$_2$ using a supercritical fluid sol-gel aided method. The overall experimental procedure was optimized using Raman, FTIR and SEM in conjunction with TGA.
Thermal Analysis Techniques for Studying Li-ion Cells and Materials of Construction

P. Vichos, P. Ralbovsky
Netzsch Instruments Inc.

Thermal analysis and calorimetry play an important role in the development and understanding of safer, high performance Li-ion batteries. The growth of Li-ion battery development field has spurred the introduction of new methods, instruments, and software to help battery researchers manage the increasingly more challenging battery applications. These new approaches offer more insight to the development process, increasing understanding and potentially decreasing development time. Some thermal analysis and calorimetric techniques have been well used but we find often times they are misused or underused. This presentation will address some of the strengths and weakness of current and new techniques being developed and how they can be applied into a development program.

Thermal analysis techniques such as DSC, STA and adiabatic calorimetry have been used to study batteries and battery components. Testing individual material properties, the compatibility of materials used in battery cell as well as testing full battery cells has proven invaluable to the industry. There is a practical limit to using these techniques to study larger battery cells that would be use in areas such as electric cars. Other approaches, such as modeling or large scale thermal test platforms help researchers and engineers make good design choices and safer batteries. Thermal measurements outside of calorimetry also aid in the design of these cells in the ability to measure thermal transport properties and heat capacities. A review of all these techniques in battery development will be reviewed.
Synthesis, Characterization, Magnetic and Electrical Properties of Nanocrystalline Mn$_{0.3}$Ni$_{0.3}$Zn$_{0.4}$Fe$_2$O$_4$ Obtained by Novel Fumarato-hydrazinate Precursor Method

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Carboxylato hydrazinate complex involving mixed metals have been synthesised and used as precursor for preparing the nanocrystalline Mn-Ni-Zn ferrite. Chemical composition of complex was fixed from chemical analysis results, infrared studies, thermogravimetric, differential scanning calorimetric measurement and isothermal weight loss studies. Nanocrystalline Mn-Ni-Zn ferrite particles obtained by thermal autocatalytic decomposition were characterized using X-ray diffraction studies, infrared spectral studies and TEM measurement. Two peaks in the region of 340-420cm$^{-1}$ and 550-660cm$^{-1}$ observed in the infra-red spectrum of 'as synthesized' oxide, are characteristics of spinel ferrites. Average particle size of 'as synthesized' Mn-Ni-Zn ferrite was found to be 10nm. ‘As synthesized’ Mn-Ni-Zn ferrite showed Curie point at 313°C. Saturation magnetization 44.7 emu/gm observed for ‘as synthesized’ Mn-Ni-Zn ferrite is lower than bulk material is indication of its nanocrystalline nature. Seebeck coefficient measurement have shown that the material exhibit n-type semiconducting behavior.
Multiple Mode Calorimeter (MMC) Performance Tests for Material Characterization Studies

P. Vichos, P. Ralbovsky
Netzsch Instruments Inc.

The Multiple Mode Calorimeter or MMC is a new bench top calorimeter platform designed to measure the temperature, pressures, and energies related to physical and chemical changes of pure compounds and chemical mixtures quickly and efficiently. The platform consists of an electronic base which has interchangeable calorimeter assemblies providing users with many modes of operation including constant temperature rate scanning (like a DSC), adiabatic testing (like an ARC), constant power input scanning, or isothermal testing. Sample injection and stirring are also possible. The calorimeter modules can be detached from the electronic base for operation in hoods or glove boxes.

This instrument uses a sample size larger than a DSC, about 1-3 grams, to accommodate sample addition and stirring. The larger sample size facilitates the measurement of multi-component and multi-phase sample systems. Temperature and pressure are recorded as a function of time. From the input energy we are able to measure endotherms, exotherms, and heat capacity, as well as temperature and pressure rates for determination of thermodynamic and kinetic parameters.

Three different modules were tested using a variety of sample types in a variety of operational modes to measure the performance and capability of the instrument. Tests were conducted internationally at different lab sites. Repeats were conducted locally and across the testing community to measure and ensure instrument precision. Well known DSC tests materials as well as some materials listed in the draft version of the new ASTM Kinetic test standard were tested and compared well to the accepted literature value.
Comparative Nanocrystallization Kinetic Study in Two FINEMET Alloys

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In this study nanocrystallization kinetics of the amorphous Fe$_{73.5}$Si$_{13.5}$B$_9$Nb$_3$Cu$_1$ (F1) and Fe$_{77}$Si$_{11}$B$_9$Nb$_{2.4}$Cu$_{0.6}$ (F2) alloys were investigated using isoconversional methods under nonisothermal condition. Magnetic properties of the alloys were measured by a vibrating sample magnetometer (VSM). Differential Scanning Calorimetry (DSC) and X-ray Diffractometry (XRD) were used for thermal and phase characterization, respectively. Bulk and surface crystallization of alloys were investigated by Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM), respectively. DSC results suggest that the smaller amount of Cu and Nb shifts the crystallization onset temperature of F2 alloy toward a lower temperature. Thus, the crystalline volume fraction and grain size for both alloys after annealing were higher for F2 than F1 sample. According to isoconversional methods, the activation energy is changing as a function of crystalline volume fraction; however, the mean values of 350 and 290 kJmol$^{-1}$ were obtained for F1 and F2, respectively. Microstructures evaluations confirm that minor changes in chemical composition affect the kinetics and final microstructure of both alloys. VSM Results show that F2 alloy exhibits higher saturation magnetization and coercivity due to the higher Fe content and the larger grain size than F1 alloy.
Influence of Transition Metal V(II)-doping on Thermal and Optical Properties of Magnesium Rubidium Sulphate Crystals

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We have prepared pure and divalent vanadium doped magnesium rubidium sulphate hexahydrate (MRSH) crystals by using slow-evaporation solution growth technique (SEST). It is interesting to observe that V(II) doping influences the physical properties of MRSH. Presence of V(II) ions in the doped specimen is confirmed by energy dispersive spectroscopy (EDS) and electron paramagnetic resonance spectroscopy (EPR). FT-IR studies reveal that the doping of vanadium ion has not altered the basic structure of MRSH. Scanning electron microscope (SEM) studies of pure and doped samples reveal that structure defect centers are formed in MRSH crystals by the dopant. Steady and gradual decomposition patterns were observed in thermogravimetry (TG) and differential thermal analysis (DTA). The grown crystals were also characterized by UV-Vis and powder X-ray diffraction (XRD). The second harmonic generation (SHG) efficiency tested using Kurtz powder technique is not influenced by the added dopant.
Ion Association in Aqueous MgSO₄ and NiSO₄ from 25 to 275 °C at 19 MPa by AC Conductance and Raman spectroscopy

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AC impedance measurements on dilute aqueous solutions of MgSO₄ and NiSO₄ were carried out in a platinum flow cell [1] from 25 to 275 °C at 19 MPa. An equivalent circuit model [2] was used to derive solution resistivities from the complex impedance data. The resulting molar conductivities were modelled with the Fuoss-Hsia-Fernández-Prini (FHFP) model in order to obtain equilibrium constants for the total association reactions to form of all types of ion pairs: double- solvent-separated ion pairs (SSIP), solvent- separated ion pairs (SIP), and contact ion pairs (CIP).

Temperature-dependant polarization measurements yielded isotropic Raman spectra as a function of concentration, from which the formation constants of the contact ion pairs were determined [3]. The results are being combined with apparent molar volume and heat capacity measurements on the identical solutions to determine a complete thermodynamic description of the ion association reactions as a function of temperature at constant pressure, using the HKF model.

Crystal Growth, Structure and Characterization of o-hydroxybenzoic acid
Single Crystals: Solvent Effects

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Single crystals of o-hydroxybenzoic acid have been grown from water-methanol (1:2 v/v) by slow evaporation solution growth technique. It crystallizes in monoclinic system with two molecular units in the cell (centrosymmetric space group $P2_1/c$). The lattice parameters are $a = 4.8967(6)$ Å, $b = 11.2204(14)$ Å, $c = 11.3027(15)$ Å and $\beta = 92.096(12)^\circ$. The modes of vibrations of different functional groups present were identified by FT-IR studies. Differential scanning calorimetry (DSC) study reveals the purity of the sample and no decomposition is observed up to the melting point. The crystals are further characterized by UV-Vis and powder XRD. Effect of solvents on the growth and morphology has been investigated. The crystalline cohesion is achieved by intra and intermolecular hydrogen bonds.
Synthesis and Characterization of Ultrafine Spinel Ferrite Obtained by Precursor Combustion Technique

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Nanoparticles of the spinel ferrite, Co₀.₆Ni₀.₄Fe₂O₄ have been synthesized by the precursor combustion technique. This synthetic route makes use of a novel precursor viz. cobalt nickel fumarato hydrazinate which decomposes autocatalytically to yield nanosized spinel ferrite. The X-ray powder diffraction of the ‘as prepared’ oxide confirms the formation of monophasic nanocrystalline cobalt nickel ferrite. The thermal decomposition of the precursor has been studied by isothermal, thermogravimetric and differential thermal analysis. The precursor has also been characterized by FTIR and chemical analysis and its chemical composition has been fixed as Co₀.₆Ni₀.₄Fe₂(C₄H₂O₄)₃.₆N₂H₄. The Curie temperature of the ‘as prepared’ oxide was determined by a.c susceptibility measurements.
Stepwise Formation Constants for Aqueous Copper(II) and Copper(I)
Chloro-Complexes from 5 to 150 °C.

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Isotropic Raman spectra were measured for aqueous copper (II) and copper (I) chloride solutions over the very wide range of concentrations required for the electrochemical step in the thermochemical production of hydrogen from Generation IV nuclear reactors. Based on ab initio calculations, and their temperature and pressure dependance in H\textsubscript{2}O and D\textsubscript{2}O, vibrational bands were assigned to the copper (II) species Cu\textsuperscript{2+}, CuCl\textsuperscript{+}, CuCl\textsubscript{2} and CuCl\textsubscript{3}. While the spectra for copper (I) species were much less intense, there is evidence for CuCl\textsuperscript{0} and a mixed oxidation state complex, Cu(II)Cu(I)Cl\textsubscript{x}(\textsuperscript{3-x}+). Formation constants and an appropriate activity coefficient model, for use in modelling copper carryover though polymer electrode materials, are being developed from the concentration dependent data.
Effect of Alkali Metal Doping on the Properties and Crystalline Perfection of Bis(thiourea)zinc(II) Chloride Crystals

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The influence of sodium doping on the properties of bis(thiourea)zinc(II) chloride (BTZC) crystals has been described. The reduction in the intensity observed in powder X-ray diffraction of doped specimen and slight shifts in vibrational frequencies confirm the lattice stress as a result of doping. The incorporation of Na(I) into the crystal lattice was confirmed by energy dispersive X-ray spectroscopy (EDS). Surface morphological changes due to doping of the alkali metal are observed by scanning electron microscopy (SEM). The TG–DTA studies reveal the purity of the material and no decomposition is observed up to the melting point. The high resolution X-ray diffraction studies (HRXRD) reveal that the crystalline quality is improved considerably by doping with alkali metal. The full width at half maximum (FWHM) of the diffraction curve is 18 arc sec which is very close to that expected from the wave theory of dynamical X-ray diffraction. This is further confirmed by a small increase observed in lattice parameter values and the volume. High transmittance is observed and cut off λ is ~270 nm.