Universität Rostock

Traditio et Innovatio

# Book of Abstracts

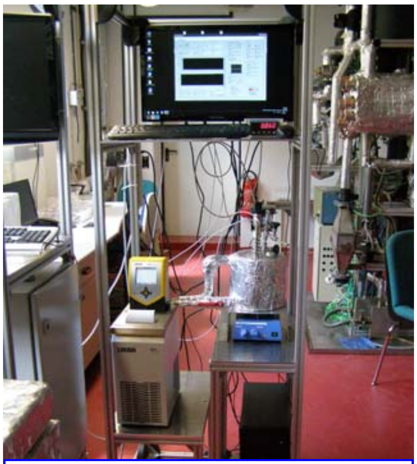
## 2nd Symposium on Thermophysical properties for Technical Thermodynamics

Institute of Technical Thermodynamics
University of Rostock,
Rostock, Germany

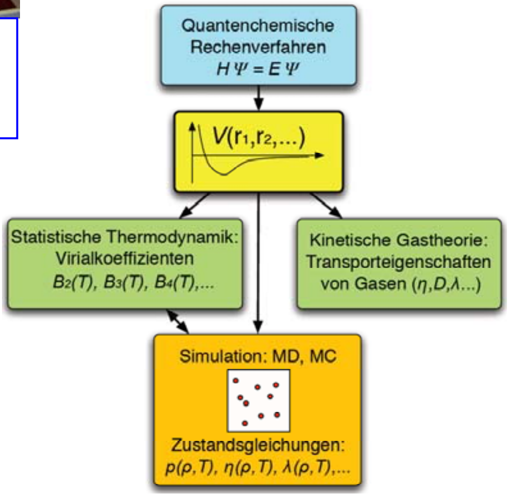
March 27 – 28, 2013

INSTITUTE OF TECHNICAL THERMODYNAMICS

Density measurements at high pressures and temperatures



Vapor pressure measurements at high temperatures



Quantenchemische Rechenverfahren $H\Psi = E\Psi$

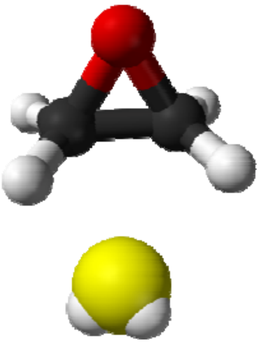
$V(r_1,r_2,\ldots)$

Statistische Thermodynamik: Virialkoeffizienten $B_2(T)$, $B_3(T)$, $B_4(T)$,...

Kinetische Gastheorie: Transporteigenschaften von Gasen ($\eta$,$D$,$\lambda$...)

Simulation: MD, MC

Zustandsgleichungen: $p(\rho,T)$, $\eta(\rho,T)$, $\lambda(\rho,T)$,...



Gas solubility measurements in liquids at high pressures and temperatures

Vapor pressure measurements at small temperatures

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# Book of Abstracts

## 2nd Symposium

## Thermophysical properties for Technical Thermodynamics

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University of Rostock
Institute of Technical Thermodynamics
Albert-Einstein-Str. 2
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# PREFACE

We are here in Technical Thermodynamics in Mechanical Engineering. So we mostly treat subjects like energy technique, internal combustion engines, electrical power plants, refrigeration apparatus, etc.

The basis of all these technical processes are a) the mass-, energy-, momentum-, entropy-, and exergy balances, b) the thermophysical properties of substances and c) the initial and boundary conditions.

The exact knowledge of thermophysical properties of substances plays a crucial role in construction, building, monitoring, running and safety of machines and the underlying processes. Therefore in our institute an important research field is the investigation of thermophysical properties.

Today thermophysical properties are experimentally measured and equations of state are constructed from these results. We also see the first scientific endeavors to calculate thermophysical properties using molecular dynamics theory or molecular modeling, called molecular thermodynamics.

Until now these procedures are mostly limited to simple substances, but with increasing computational power more and more complex questions will be answered.

The Institute of Technical Thermodynamic at the University of Rostock has long time experience with experimental measurement of thermophysical properties, and now molecular thermodynamics has become a new focus area of research.

Examples of our work are the determination of density, vapor pressure, solubility, viscosity and caloric properties for substances like sea water, ionic liquids and fluids for energy processes. Currently we are working on molecular dynamics estimations for pressure, temperature and density for $C_2H_4O$, $H_2S$, $CH_4$ and $N_2O$ etc.

The objective of this symposium is to report on current research development in this active area and serve as a forum for discussions and collaborations between colleagues. The first symposium was held 2012 and we aim to establish a tradition on this field in Rostock.

The team of the Institute of Technical Thermodynamics wish you an interesting and enjoyable meeting during the symposium days in Rostock.

Best regards

E. Hassel

**Prof. Dr.-Ing. Dr. h.c. Egon Hassel**

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# Oral Presentations

# PREDICTIVE THERMODYNAMIC MODELS AND THE DORTMUND DATA BANK – IDEAL TOOLS FOR THE SYNTHESIS AND DESIGN OF CHEMICAL PROCESSES IN PARTICULAR SEPARATION PROCESSES

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Today the synthesis of chemical processes is carried out by solving the resulting balance equations of a mathematical model of the considered unit operation or the whole chemical plant using commercial process simulators.

The quality of the simulation results is mainly influenced by the reliability and correctness of the thermophysical properties used for the pure compounds and their mixtures. For the description of the required phase equilibria, $g^E$-models and equations of state can be applied. These models allow the calculation of the phase equilibrium behavior of multicomponent systems using binary experimental data alone.

Since the number of experimental data for fitting the required binary parameters is limited, both approaches often cannot be applied. Therefore in particular for process development reliable group contribution methods, such as UNIFAC and modified UNIFAC for the estimation of phase equilibria and excess properties were developed. The required group interaction parameters were fitted using the data stored in the worldwide largest factual data bank (Dortmund Data Bank (DDB)).

By combination of cubic equations of state with the group contribution concept, as in PSRK and VTPR the range of applicability was extended to systems with supercritical compounds. At the same time these group contribution equations of state allow the prediction of other important properties (e.g. densities, enthalpies, heat capacities, etc.). With the usage of an adequate electrolyte model (LIQUAC, LIFAC) the group contribution equation of state approach was even extended to systems with strong electrolytes.

The developed predictive thermodynamic tools in combination with factual data banks (e.g. Dortmund Data Bank) are ideal tools for the synthesis of chemical processes.
In the lecture the status of the factual data bank and the different predictive models will be shown. Besides typical results of the predictive thermodynamic models important applications of industrial interest, e.g.:

- examination of model parameters prior to process simulation
- determination of separation problems (azeotropic points)
- construction of residue curves
- selection of suitable solvents for separation processes (azeotropic and extractive distillation, extraction, absorption, ..)
- consideration of the real behavior on the chemical equilibrium conversion
- …….

using the predictive thermodynamic models and/or the Dortmund Data Bank will be presented.

# FROM THE BOCHUM EQUATIONS OF STATE FOR PURE SUBSTANCES UP TO THE COMPLEX MIXTURE EQUATION GERG-2008

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In the period from 1975 to 2006, the Chair of Thermodynamics at the Ruhr-University Bochum was working in the field of the calculation and experimental determination of thermodynamic properties of pure fluid substances and mixtures. Over these 31 years, accurate equations of state had been developed for a number of pure substances. The talk summarizes the ideas and the procedure for the development of these equations of state considered as equations in reference quality for the corresponding pure substances. The experiences and conclusions from these pieces of work were the starting point for the development of an equation of state for multi-component mixtures – the GERG-2004 equation of state for natural gases and other mixtures of an arbitrary combination of the 18 components methane, nitrogen, carbon dioxide, ethane, propane, n-butane, isobutane, npentane, isopentane, n-hexane, n-heptane, n-octane, hydrogen, oxygen, carbon monoxide, water, helium, and argon. Then, this equation was expanded by including the three additional components n-nonane, n-decane, and hydrogen sulfide and was called GERG-2008 [1]. The development of GERG-2008 was our longest and most difficult equation of state project. This equation and its quality are described and a number of insights are given.

## Literature:

1. Kunz, O., Wagner, W. The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004. J. Chem. Eng. Data 57 (2012), 3032-3091 (online publication 31.10.2012).

# THERMOPHYSICAL PROPERTY RESEARCH AT SAOT AND LTT ERLANGEN

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The present work summarizes and reviews the activities performed at the Erlangen Graduate School in Advanced Optical Technologies (SAOT) and the Institute of Engineering Thermodynamics (LTT) of the University of Erlangen-Nuremberg in the field of thermophysical property research. Here, molecular dynamics (MD) simulation and different experimental methods are developed and applied for the characterization of working fluids in chemical and energy engineering. During the past decade, conventional methods of special interest were a guarded parallel-plate instrument for thermal conductivity, the pendant drop technique for surface tension, and a Loschmidt cell combined with holographic interferometry for binary diffusion coefficients in gas mixtures. While conventional methods for the determination of transport properties make use of macroscopic gradients, the application of dynamic light scattering (DLS) gives access to a variety of thermophysical properties in macroscopic thermodynamic equilibrium. Properties accessible by DLS are, e.g., thermal and mutual diffusivity, dynamic and kinematic viscosity, speed of sound, and surface tension.

A compilation of thermophysical property data obtained until now at SAOT and LTT Erlangen by DLS and conventional methods is given. The objects of investigation cover, e.g., industrial standard reference fluids, refrigerants, working fluids for organic Rankine cycles and heat pump systems, ionic liquids as well as systems of pharmaceutical technology and petroleum industry. Besides offering a significant contribution to a reliable database for different working fluids, thermophysical property research could also provide answers to fundamental questions. DLS could contribute to a basic understanding of the behavior of transport properties of fluid mixtures approaching critical points. Furthermore, DLS and conventional techniques could give a close insight into the bulk structure and the fluid structure at the phase boundary of fluid mixtures. The determination of thermophysical properties at SAOT and LTT also allowed contributions to structure property relationships and the development of prediction methods.

# MEASUREMENTS OF THE DENSITY AND VISCOSITY OF ISO-OCTANE AND N-HEPTANE BY A MEMS SENSOR

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Density and viscosity are two important thermophysical properties of fluids. Accurate values of density and viscosity play a key role in the petroleum industry, food productions and pharmaceutical industry. In this work, a fluid density/viscosity sensor has been fabricated with silicon rectangular microcantilever by MEMS (Micro Electro Mechanical System) technology. The density and viscosity of iso-octane and n-heptane have been measured by the MEMS sensor. Measurements were carried out at 5 temperatures in the range from (283.15 to 303.15) K and at one atmospheric pressure. The deviations of the experimental data from the literature values are within 2 % and 10 %, for density and viscosity, respectively. This work has been supported by the National Natural Science Foundation of China (Grant No. 51006083; 50836004) and the Fundamental Research Funds for the Central Universities.

# FAST CALCULATION OF THERMODYNAMIC PROPERTIES OF WATER AND STEAM USING A SPLINE BASED TABLE LOOK-UP METHOD

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For the design and optimization of advanced power cycles and their components extensive process simulations such as Computational Fluid Dynamics (CFD) and the calculation of non-stationary processes are in use. These simulations require very fast and accurate functions for the determination of fluid properties. Furthermore, to meet the demands of numerical solvers, high numerical consistency of forward and backward functions and continuity of these functions and derivatives are required. In order to fulfil these requirements a Spline Based Table Look-up Method (STM) was developed. This paper describes the fundamentals of this method and the generation of a spline based property function for a given range of validity and accuracy.

The generation of a suitable look-up table, the so called grid of nodes, is the crucial step for setting up a spline function. For the desired range of validity and accuracy the amount of data must be minimized whereas the computing speed needs to be maximized. At the same time irregular shaped ranges of validity must be fitted into rectangular grids with equidistant nodes, because this approach simplifies the cell search algorithm in the grid to a straight forward calculation without iterations. The proposed method combines specialized variable transformations and extrapolation techniques to achieve these optimizations. Thereby the shape of the property function is adapted to the shape of the spline-polynomial. Consequently, the number of nodes can be minimized whereas the computational speed is kept as high as possible. The spline based table look-up method also enables the calculation of inverse functions with complete numerical consistency. These inverse functions are the analytic solutions of the spline polynomials solved in terms of one of their independent variables.

In order to demonstrate the applicability of the spline based table look-up method a set of spline functions has been created for superheated steam and wet steam. Accuracies and computing speeds of these functions have been evaluated and compared to IAPWS-IF97. Furthermore, the spline functions have been implemented into TRACE, a CFD software developed at the German Aerospace Agency (DLR). Test calculations show that the proposed approach reduces computing times considerably. Due to the numerical consistency of the spline based property functions the CFD simulations converge with a minimum number of iterations. Consequently, the computing times could be reduced by a factor of ten in comparison with a calculation based on IAPWS-IF97.

For generating spline functions for fluid property calculations, the software FluidSplines has been developed. It makes the spline based table look-up method applicable to all kinds of one- or two-dimensional property functions. Fluid properties can be provided from external databases such as the property libraries of the Zittau/Goerlitz University of Applied Sciences or REFPROP from NIST. The software implements all the features of the spline based table look-up method explained above and assists the user in generating spline functions and inverse spline functions for a given range of validity with the required accuracy.

# MOLECULAR MODELLING AND SIMULATION OF HYDROGEN BONDING FLUIDS

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Hydrogen bonding is a highly complex phenomenon in many respects. Its short-range and ordering effects are responsible for a variety of unusual properties of water. On the other end, H bonds often determine the conformation of macromolecules and influence their function in non-trivial ways. Phenomenological approaches, which disregard statistical mechanics, can therefore at best deliver an accurate *description*, i.e. an empirical correlation, of the thermodynamic properties of H bonding molecules, as far as these are known from experiment.

Molecular modelling and simulation, due to its foundation on a physically sound approach, promises to permit a quantitatively reliable *prediction* of fluid properties, even when experimental data are scarce. Modelling the H bond, however, is particularly challenging due to its hybrid character which combines dispersion and long-range electrostatics with short-range effects from partial covalent bond formation. From previous work [1, 2], it is known that several real H bonding fluids can be adequately modelled by Lennard-Jones interaction sites with additional point charges. For the *beak fluid* model, the present study proves that long-range electrostatics (i.e. the dipole moment) and structural short-range effects (i.e. the dipole elongation) can both significantly influence fluid phase equilibria, cf. Fig. 1, even when they are accounted for by a single modelling approach.

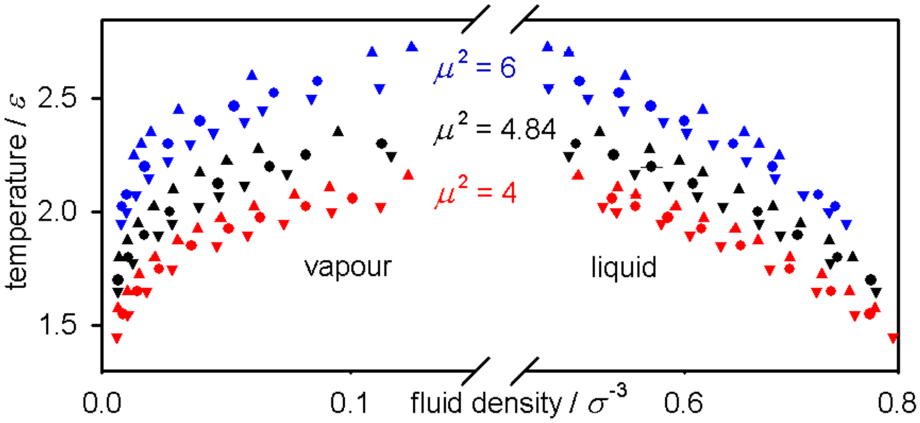

Fig. 1: Vapour-liquid equilibrium of the beak fluid model for various dipole elongations (triangle down: 0.3; bullet: 0.4; triangle up: 0.5) and dipole strengths ($\mu^2$ = 4, 4.84, and 6).

## Literature:

1. T. Schnabel, A. Srivastava, J. Vrabec, H. Hasse (2007), *J. Phys. Chem. B* 111(33): 9871.
2. T. Schnabel, J. Vrabec, H. Hasse (2008), *Fluid Phase Equilib.* 263(2): 144.

# PREPARATION AND THERMAL PROPERTIES OF GRAPHITE REINFORCED POLYMER NANOCOMPOSITES

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In recent years, conducting polymer nanocomposites have attracted considerable attention because of their potential applications in advanced technologies, for example, in light emitting devices, batteries, electromagnetic shielding, anti-static, corrosion resistant coatings, and other functional applications. The introduction of electrically and thermally conductive fillers such as graphite, carbon black, metal and metal oxide powders into the polymeric matrix is a promising approach to fabricate electrically and thermally conductive polymeric materials. The recent advancement of nano-scale compounding technique enables the preparation of highly electrically and thermally conductive polymeric nanocomposites with low loading of conductive fillers. Nanocomposites may offer enhanced physical features such as increased stiffness, strength, barrier properties and heat resistance, without loss of impact strength in a very broad range of common synthetic or natural polymers.

In this study the conductive fillers were untreated natural graphite (UG) and expanded graphite (EG), the base material was ethylene- vinyl acetate copolymer (EVA). Composite samples up to 29.3 % graphite particle volumetric concentrations (50 % mass concentration) were prepared by the melt mixing process in a Brabender Plasticorder PLE 331 internal mixer at 150 ◦C for a total mixing time of 10 min, the mixing chamber capacity being 30 mL. The rotors turned at 35 rpm in a counter-rotating fashion with a speed ratio of 1.1. After 10 min, the mixing chamber of the Brabender apparatus is opened and the resulting mixture is taken out, then after passing through rollers, the mixture is solidified. The resultant mixture in then put in a compression molding die and compressed in a compression molding press at 120 ◦C, under 40 kP pressure for one minute to obtain samples in the form of sheets for electrical-conductivity and thermal-diffusivity measurements. During this mixing process, the EG exfoliates in nanosized graphite layers causing nanocomposites of improved physical properties.

In this study we used two different methods to measure thermal diffusivity: flash method using flash apparatus Netzsch Nanoflash LFA 447/1 and photothermal radiometry (PTR), back detection (in thermal wave transmission across the sample). One may conclude that the diffusivities of EG reinforced composites are higher than the UG ones.

## ACKNOWLEDGEMENT

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# THE THERMODYNAMIC BEHAVIOUR OF SYSTEMS WITH SPECIFIC INTERMOLECULAR INTERACTIONS. THE POTENTIALS OF CENTRAL FORCE, THE DENSITY DEPENDENT POTENTIALS

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Methods of molecular-statistical theory allow us to calculate thermodynamic properties of gases and liquids with the known potentials of the intermolecular interactions. The complexity of the calculations is defined by the complexity of the calculation of these potentials and their dimensions. The most simple case study for the calculation is the system with the spherical form of the molecules. In this case, the intermolecular interaction potential is a function of the distance between the centers of the molecules. Additionally, the methods of the theory of integral equations for the particle distribution functions are useful for the calculation of the thermodynamic properties for the above systems. In contrast to the methods of molecular dynamics and Monte Carlo, the method of partial distribution functions has a much lower computational complexity under the comparable accuracy of the simulation results.

Unfortunately, the thermodynamic behavior of the systems with the spherical-symmetrical intermolecular interactions is quantitatively very different from the thermodynamic behavior of the real substances composed of polyatomic molecules. Here we consider two ways of expanding the capabilities of spherically symmetric potentials of intermolecular interaction to the description of the thermodynamic properties of the real substances.

The first way is based on the model of central forces when the interaction between the molecules is the sum of intermolecular and intramolecular one. This way is similar to the RISM model. The difference consists in the absence of rigid connection between atoms in the molecule which gives the possibility of observing the association and dissociation phenomena. Furthermore, the two-particle correlations in this system are described by theoretically rigorous system of Ornstein-Zernikes' integral equations, when the pressure is defined from the virial equation of state through the two-particle distribution function. The model of central forces has been successfully used for the calculation of the structural and thermodynamic properties of water under the normal conditions. The purpose of this study is to demonstrate the regularities of the behavior for the model of central forces in a wide range of conditions. The possible application of the model for the calculation of the thermodynamic properties of real materials is also shown.

The second way is associated with taking into account the dependence of the intermolecular interaction potential on the density. Various thermodynamic properties including the conditions of the phase transition for a number of pure substances and mixtures are calculated using the method of partial distribution functions. It is shown a satisfactory accuracy for the practical use.

# PHYSICOCHEMICAL PROPERTIES OF GLYME-LITHIUM SALT MIXTURES – EXPERIMENTS AND SIMULATIONS

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Triglyme-lithium salt complexes show low volatility, high thermal stability, high ionic conductivity, and a wide potential window. It has been shown by Yoshida et al. that the mixtures of lithium bis(trifluoromethylsulfonyl)amide [Li][$NTf_2$] and triglyme (G3) behave like conventional room temperature ionic liquids [1,2]. In particular the equimolar triglyme-lithium complexes are presumed to be resistive against oxidation and thus thought to be promising electrolytes for lithium batteries. With a combination of experiments and molecular dynamics simulations we studied the transport properties of G3-lithium salt mixtures. Self-diffusion coefficients, viscosities and ionic conductivities were measured and simulated as a function of salt concentration and temperature. Molecular dynamics simulations provide some insight at molecular level about the change from glyme solutions to quasi-ionic liquids for the binary mixtures. The maximum of the concentration dependent ionic conductivity could be explained by ion pair formation. The results can now be used for tuning better electrolytes for battery systems.

Literature:

1. K. Yoshida, M. Nakamura, Y. Kazue, N. Tachikawa, S. Tsuzuki, S. Seki, K. Dokko, M. Watanabe, *J. Am. Chem. Soc.* 2011, 133, 13121-13129.
2. K. Yoshida, M. Tsuchiya, N. Tachikawa, K. Dokko, M. Watanabe, *J. Phys. Chem. C,* 2011, 115, 18384-18394.

# VIRIAL EQUATION OF STATE FOR METHANE FROM MAYER-SAMPLING MONTE CARLO CALCULATIONS

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Advances in computer technology make it possible to determine the thermophysical properties of simple fluids with high accuracy entirely from theory. For very low and very high temperatures and also for highly corrosive or toxic substances *ab initio* computations represent a reasonable way to obtain accurate values for thermophysical properties.

Virial coefficients of gaseous and supercritical fluids can be calculated up to high order using the Mayer-sampling Monte Carlo method [1]. We will present preliminary results for the virial EOS of methane up to the seventh order based on a two-body potential obtained from quantum-chemical *ab initio* calculations [2] and a semi-empirical nonadditive three-body potential. Quantum effects have been accounted for by using the Feynman-Hibbs effective pair potential [3]. Agreement with the best empirical EOS [4] is very good. Eventually we want to apply an *ab initio* three-body potential instead of a semi-empirical one to further improve the accuracy of the EOS.

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1. J. K. Singh, D. A. Kofke, Phys. Rev. Lett. 92, 220601 (2004)
2. R. Hellmann, E. Bich, E. Vogel, J. Chem. Phys. 128, 214303 (2008)
3. R. P. Feynman, A. R. Hibbs, Quantum Mechanics and Path Integrals (McGraw-Hill, New York, 1965)
4. U. Setzmann, W. Wagner, J. Phys. Chem. Ref. Data 20, 1061 (1991)

# MEASUREMENTS ON N- AND ISOBUTANE USING A VIBRATING-WIRE VISCOMETER AND CORRELATIONS OF THEIR VISCOSITY SURFACES USING A STRUCTURE-OPTIMISATION METHOD

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The exact knowledge of thermophysical properties of fluids with industrial importance is needed for a more accurate basic design of compressors, gas turbines, and gas pipelines. In contrast to the thermodynamic properties, the transport properties of n-butane and isobutane, particularly in the region near to the critical point, are not sufficiently well-known. The current viscosity-surface correlations are characterized by uncertainties of up to 6% in some regions.

New viscosity measurements were performed on n-butane and isobutane using a specially designed vibrating-wire viscometer together with a single-sinker densimeter and with precise measuring devices for temperature and pressure. Isothermal series of measurements were carried out between 298 K and 448 K for n-butane and between 298 K and 498 K for isobutane and at pressures up to 95% of the saturation pressure of the respective isotherm or up to 30 MPa for both fluids. The viscosity measurements are characterized by an uncertainty of (0.25-0.4)% increasing with temperature. The uncertainty of the density determination is estimated to be less than 0.1%, and is increased in the near critical region as well as in the low-density range due to the single-sinker method. The reproducibility of the measurements amounts to 0.05%, for both viscosity and density.

Consequently, the new experimental viscosity data are considered to be primary values. In addition, the density data obtained simultaneously with the viscosity data can be used to refine the current equations of state for n-butane and isobutane [Bücker and Wagner (2006)], which are characterized by uncertainties of 0.5% in pressure in the near critical region due to the experimental data available in the literature when the equations were developed.

The results of our measurements were compared with viscosity values obtained from the surface correlations by Vogel et al. (1999 and 2000) and with density values calculated from the equations of state by Bücker and Wagner (2006) as well as with the best experimental data available in the literature.

New viscosity-surface correlations for n-butane and isobutane were generated using the structure-optimisation method by Setzmann and Wagner (1989). The bank of terms comprises expressions for different regions: the limit of zero density, the moderately dense fluid, the dense liquid phase, and the near critical region. The results are compared to the primary data sets from the literature and from this work which were used in the development of the correlations.

# THERMOPHYSICAL PROPERTIES OF 1-HEXYL-3-METHYLIMIDAZOLIUM BIS(TRIFLLUOROMETHYLSULFONYL)IMIDE AT HIGH TEMPERATURES AND PRESSURES

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An ionic liquid (ILs) is a salt in the liquid state in the room temperature. They are excellent solvents for a broad range of polar organic compounds and they show partial miscibility with aromatic hydrocarbons. As is well known the ILs have been suggested as potentially “green” replacements for conventional organic solvents since they are nonflammable, thermal stable, recyclable and have negligible vapor pressure. ILs are also claimed to be useful as heat transfer fluids in solar heating and absorption refrigerating systems.[1-3] Their applications are successful also in fuel, solar cells, as lubricants and biological reactions media. Beside these, IL’s also apply for the stationary phase for chromatography, as matrices for mass spectrometry, supports for the immobilization of enzymes, in separation technologies, as liquid crystals, templates for the synthesis of mesoporous, nano-materials and ordered films, materials for embalming and tissue preservation.[4]

This work is a continuation of our investigations in the field of $(p,\rho,T)$ properties of ionic liquids. $(p,\rho,T)$ data of ionic liquid 1-hexyl-3-methylimidazolium bis(triflluoromethylsulonyl)imide [HMIM][NTf$_2$] at $T$=(273.15 to 413.15) K and pressures up to $p$=140 MPa are reported with an estimated experimental relative combined standard uncertainty of $\Delta\rho/\rho$= ±(0.01 to 0.08) % in density. The measurements were carried out with a newly constructed Anton-Paar DMA HPM vibration-tube densimeter.

The density measurements at ambient pressure also were carried out using the Anton-Paar DMA 5000 densimeter with an uncertainty of ±0.01 K. The overall uncertainty of the experimental density measurements at ambient pressure was better than $\pm 2\cdot 10^{-2}$ kg·m$^{-3}$

An empiric equation of state for fitting of the $(p,\rho,T)$ data of [HMIM][NTf$_2$] has been developed as a function of pressure and temperature. This equation was used for the calculation of the thermophysical properties of IL, such as isothermal compressibility, isobaric thermal expansibility, differences in isobaric and isochoric heat capacities, thermal pressure coefficient, internal pressure, isobaric and isochoric heat capacities, speed of sound and isentropic expansibility.

# HIGH-PRECISION MEASUREMENTS METHODS. METHODS FOR MEASUREMENT OF PHYSICO-CHEMICAL PARAMETERS OF WATER IN RUSSIA

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Physico-chemical measurements, which under the BIPM's classification fall within the metrology area QM – Amount of Substance (Chemistry), include gas analysis, analysis of components of liquids, including biological fluids, analysis of solids, including metals. Russia has a state verification schedule for instruments measuring components content of solids and liquids, with national primary standards at the top of the traceability chain. In the field of physico-chemical measurement, Russia has 12 national primary standards, and five of them are maintained at VNIIFTRI. As a State Scientific Metrology Centre, VNIIFTRI plays important role in the national system for ensuring the uniformity of measurement. It develops measurement standards and methods of measurement in various areas of metrology. VNIIFTRI carries out measurements of mass concentration of chemical components in liquids using methods of electrochemical analysis; electrical conductivity of aqueous solutions; disperse composition of aerosols, hydrosols and suspensions in natural and technological environments; ionized air parameters. The other primary standards are maintained at other metrology institutes: VNIIM (Saint-Petersburg) has three, including the primary standard for a concentration unit of gas impurities; VNIIOFI (Moscow) has two, including the primary standard for mass (molar) concentration units of components in solid and liquid media; UNIIM (Ekaterinburg) and VNIIR (Kazan) have one each.

Measurements of mass concentration of chemical components in liquids by methods of electrochemical analysis include measuring PH and PX (active concentration of ions of hydrogen, etc) in aqueous media, electrical conductivity, and mass concentration of inorganic components in liquids. Results of these measurements are used in evaluating organic and inorganic materials, foodstuffs, medicines, oil and oil products, in investigating and monitoring the condition of environmental water objects.

To reproduce, maintain and distribute pH and pX values, and reduction-oxidation potentials Eh, VNIIFTRI has created a national primary standard (GET 171-2007), consisting of a measuring device and a set of mono component reference solutions, and has developed a manufacturing technology for buffer solutions that reproduce pH values and serve as Class 1 and 2 working pH standards.

A national primary standard for the units of disperse parameters of aerosols, suspensions and powders (GET 163-2010) ensures the uniformity for measurements of disperse parameters of particles in the size range from 0.03 to 100 µm, and of number concentrations ranging from $10^5$ to $10^{12}$ $m^{-3}$.

A high-precision device for reproducing a concentration unit of oxygen dissolved in water (UVT 108 A 2008) is used as a reference device, having the following metrological characteristics:

- reproduction range: 10-30000 µg/L for oxygen; 10-2000 µg/L for hydrogen;
- mean square deviation (reproduction): 0.5-20 µg/L for oxygen; 1-30 µg/L for hydrogen;
- expanded uncertainty with coverage factor k=2: 1.6-80 µg/L for oxygen; 3.2-120 µg/L for hydrogen.

# SYSTEMATIC DEVELOPMENT OF PREDICTION METHODS

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Experimental data for many substance properties are often not available and measurement is not an option due to costs, time or limited availability of the pure substance. During the development of new processes this lack of information can be closed by predictive models. Furthermore, predictive models for substance properties can be used to identify the best suited substance (or group of substances) for a specific task. A parameter study concerning the influence of different substance properties is an advisable groundwork. Afterwards a huge number of potential substances can be screened for the best suited candidate even if no or only limited experimental data are available.

Quantum chemical methods as well as group contribution methods are the most important options for the estimation of pure substance properties. The huge computing power required for quantum chemical calculations currently limits these methods to small molecules while the description of macromolecules is far from a satisfactory realization. Group contribution methods are not limited to a certain molecule size, but applicability to large molecules has to be demonstrated for each method separately.

The development of new prediction methods necessitates a sufficient number of reliable experimental data points, for parameter fitting as well as for the evaluation of the developed method. The use of separate data for parameter fitting and evaluation is crucial for a reliable conclusion on the prediction quality and the transferability to other substances.

The consideration of other substance properties within the model can have a significant positive effect on the prediction quality compared to a total predictive approach. Correlation coefficients can be a helpful mathematical tool for the identification of associated properties and can indicate interdependencies that do not strike at first glance. Positive as well as strongly negative correlation coefficients can be an indicator for a dependency that can be used to improve predictions.

The screening of huge data sets produced by prediction methods for the best suited substance (or substances class) for a specific task can be enhanced by appropriate mathematic models. Principal component analysis, as an example, allows for a clustering reducing the number of parameters to one or two. Systematic identification of best suited substance classes and even specific substances for e.g. absorption processes is possible based on such technics.

# MOLECULAR SIMULATION STUDIES ON THE THERMOPHYSICAL PROPERTIES OF FLUOROPROPENE REFRIGERANTS AND THEIR MIXTURES

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Hydrofluorolefines such as the tetrafluoropropenes HFO-1234yf and HFO-1234ze(E) are proposed as alternative refrigerants due to their low Global warming potential (GWP). In order to study the performance of these new refrigerants in technical applications, information on various properties such as phase equilibria, transport and caloric properties over a wide range of state points is required.

We have therefore developed a transferable molecular model (force field) for fluoropropenes [1, 2] to enable reliable predictions for the thermophysical properties of this new class of refrigerants by molecular simulation studies to complement experimental data. We will here present simulation results for the phase equilibria and transport properties of different pure fluoropropenes compounds.

However, the use of R-1234yf or R-1234ze(E) as pure component refrigerants cause concern due to their flammability. Furthermore, they usually show smaller volumetric cooling capacities than conventional hydrofluorocarbon (HFC) refrigerants. Thus, blends of HFOs and non-flammable HFC compounds are regarded as suitable choice for refrigerants with GWP and flammability as low as possible and optimal refrigerant capacity. Thus, we will also present molecular simulation studies on refrigerant blends that have recently attracted attention. These are for instance binary mixtures of R-1234ze(E) or R-1234yf with R-32 as refrigerant blends for domestic heat pump or air conditioning systems [3,4], and the ternary mixture AC-6 of $CO_2$, R-134a and R-1234ze(E), which is discussed as mobile air conditioning (MAC) refrigerant blend [5].

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# REALIZATION OF A SUBSTITUTION METHOD TO PERFORM HIGH PRECISION DENSITY MEASUREMENTS OF SEAWATER

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An input quantity for experimental and theoretical determination of thermodynamic properties of seawater is salinity. Due to limitations in experimental equipment and reduction of costs a simplified description of the complex seawater composition is used. Conductivity measurements lead to quantitative values for seawater salinity.

Seitz et al, 2011, showed that the underlying formalism has a risk of inconsistency when measurements are compared over decades. They proposed an empirical relation between conductivity and density measurements.

To overcome the demands for high precision of the density measurements a substitution method introduced by Wolf, 2008, that uses water as a reference fluid and an oscillation-type density meter was realized. Measurements done with seawater resulted in relative measurement uncertainties below 0.002 kg/m$^3$ at atmospheric pressure. A comparison with data calculated with the official standard for thermodynamic properties of seawater, TEOS-10 – Thermodynamic Equation Of Seawater, showed deviations beyond measurement uncertainty that increase with salinity.

Together with conductivity measurements with the same seawater the proposed link between conductivity and density ensures long-term comparability of experimentally gained seawater properties. Also new density information with high precision is provided.

Contemporary work includes high pressure substitution density as wells as conductivity measurements. Measurements that will be carried out on other aqueous substances will ensure broader applicability of the substitution method.

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# REQUIREMENTS FOR THERMOPHYSICAL DATA ON ICES OF ASTROPHYSICAL INTEREST

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Water (-ice) and certain other frozen volatiles (e.g., carbon dioxide, carbon monoxide, methane) play an important role in the solar system. We might find water ice in the regolith of Mercury, the Moon and Mars; there are the polar caps of Mars with water ice and $CO_2$ ice; on the icy moons of the giant planets, we should expect to find ice Ih and at depth, ices II, V, VI, VII and VIII. The Saturnian ring particles are composed of ice Ih, while the Kuiper belt objects (Pluto and beyond) are probably composed of a mixture of ice Ih, amorphous ice, and some ice II under pressure. There maybe also ice XI in the Kuiper belt. Oort cloud objects should be composed of high density amorphous ice ($T$<30 K), while comets, depending on origin and solar heating, will include amorphous ices plus ices Ih and Ic. The properties in particular for high-pressure and amorphous phase as well as for certain clathrates are very poorly known.

Accurate thermophysical properties for wide ranges of temperature and pressure are needed for simulations and in order to describe the formation/thermal evolution of those bodies and the environment for space probes.

What is needed is and physically sound correlation equations for a number of pure and composite substances which are more precise and cover a wider range of temperatures and pressures than the formulations used traditionally in astronomy and planetary research. Requirements for these data are given and explained.

# CALCULATION OF INTERFACIAL PROPERTIES FOR MATERIAL TRANSPORT

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The liquid-liquid extraction is an important method in separation processes. Because of its broad use, even small optimizations can lead to extensive savings in industry. The vital aspects for the simulation and therefore the optimization are the concentrations of the phases in liquid-liquid-equilibria (LLE) and its interfacial properties, especially the interfacial tension and the concentration gradients. The interfacial tension itself is one of the most important quantity needed for the design and optimization of the extraction apparatus. The selective enrichment of one component in the interphase can lead to a large hindrance of the mass transport and requires the input of mechanical energy. Additionally, a large concentration dependence of the interfacial tension can cause undesirable foam formation. Unfortunately, the selective enrichment is not assessable by experimental methods.

Knowing that one key for a successful optimization related to energy consumption is the knowledge of these properties, a prediction of the interfacial properties is highly desirable. The concentrations in the coexisting phase can be computed using a model for the excess Gibbs energy ($G^E$). For this contribution the model of Flory[i] and Huggins[ii] with the extension of Koningsveld-Kleintjens[iii] was chosen to calculate the concentrations in the liquid-liquid equilibrium (LLE). Applying the density gradient theory (DGT)[iv], developed by Cahn and Hilliard[v], to the interface established between two demixed phases of a binary system, permits the calculation of the interfacial properties. Recently[vi], this approach was extended to ternary systems, which are relevant of extraction processes.

In this contribution the developed theoretical approach were applied to two systems, namely water + butan-1-ol + ethanol and water + toluene + acetone. Both ternary systems show one demixing gap; however, the extension of the miscibility gap is quite different.

The used $G^E$-model was able to describe the LLE very close to the experimental data for both systems. The density gradient theory requires a so-called influence parameter. This parameter was fitted to one experimental interfacial tension of the binary system. The theoretical framework allows the prediction of the interfacial tension of the practical relevant ternary system. The predicted interfacial tensions were verified by own experimental data for the system water + butan-1-ol + ethanol and experimental data taken from the literature for the system water + toluene + acetone[vii]. Caused by the different extension of the miscibility gaps of the studied system the selective enrichment of the transfer component differ to a large extend in both systems. The enrichment of ethanol is negligible small; however, the enrichment of acetone is quite large and depends on temperature and feed concentration. With this information it is possible to effectively simulate separation processes, which is the basis for any optimization.

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# AN APPROXIMATE THEORY OF THE TERMAL EQUATION OF STATE

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We proposed an equation of state with pressure expressed as a difference between the current and ideal entropy. The equation has been tested and a satisfactory agreement with experiment. However, application of the equation for pressure is impossible, because there are two unknown functions of pressure and entropy. The advantage of the equation is that the term associated with $\Delta S$ determines the virial part called virial of intermolecular forces, and this part is usually defined as the difference between two large numbers: functionals of repulsion and attraction of functionals. This definition makes a big mistake, so the absence of such differences can reduce it. The second point is that we can use the second principle of thermodynamics analysis. Reciprocity principle in the form of the derivative of the entropy due to volume at constant temperature derivative of pressure with respect to temperature at constant volume. Thus, we have two equations with two unknown functions - pressure and entropy, which can be resolved. The form of these equations is reduced to a single equation in partial derivatives of the first order, and the problem of formulating the thermal equation is reduced to the boundary value problem, which requires the appropriate boundary conditions. The boundary conditions used for expression of the equation of state density are calculated from the second virial coefficient on the basis of pair intermolecular interaction potential. The solution was obtained with parameters in the equation, written in the form $\alpha$ = 2.5.

However, the persistence parameter $\alpha$, which is a power in the complex $e^{\Delta S}$, could not be reached on the entire region of the phase diagram. We found that there is similarity constants in the zone observed similarity of states in the phase diagram. The reported value for the constant is a good approximation for the equation of state. Comparison with experimental data on MK and MD is shown to prove the conclusion.

# THERMOPHYSICAL PROPERTIES OF WORKING PAIRS WITH IONIC LIQUIDS FOR ABSORPTION CYCLES

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Absorption cycles offer the possibility to recover waste heat and thus provide a great potential in primary energy savings. They can either transform the waste heat to a higher useable temperature level or generate ambient cooling. The application of new working pairs with ionic liquids (IL) and water opens new perspectives in operational reliability and economic efficiency. Besides full miscibility with the working fluid, low corrosiveness and negligible vapour pressure, ILs need to exhibit good thermal stability in absorption heat transformers and low viscosity in absorption refrigeration cycles.

To evaluate the performance of an absorption cycle the knowledge of vapour-liquid equilibrium (VLE) data and other thermophysical properties is indispensable. The VLE measurements were conducted via Fourier transform infrared (FITR) spectroscopy at ambient pressure and in a temperature range of 293.15 K to 353.15 K. Density, viscosity and specific heat capacity were also measured over the whole concentration range and the same temperature range. Some diffusion coefficients of water dissolved in ILs were determined via pulsed field gradient-nuclear magnetic resonance spectroscopy (PFG-NMR) and will also be presented.

As the investigated ILs possess either a good vapour pressure lowering ability or a low viscosity which are both relevant for the performance of absorption refrigeration cycles, a mixture of two ILs was analysed. The influence on the thermophysical properties in comparison to the pure ILs will be presented.

# DENSITY AND VOLUME PROPERTIES OF (N-METHYL-1,3-PROPANE DIAME + WATER) OVER THE TEMPERATURE RANGE OF (283.15 TO 363.15) K

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Fossil fuel burning has increasing $CO_2$ concentration in atmosphere over the past 200 years. Researchers over the world have been investigating effective methods to manage $CO_2$ emissions. Chemical absorption are known to be the most reliable and economical for $CO_2$ removal. A wide variety of aqueous alkanolamines, such as monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), or methyldiethanolamine (MDEA) have been extensively studied for this purpose.

The diamine 3-methylaminopropylamine (or *N*-methyl-1,3-propane diamine, MAPA) has low $CO_2$ capacity and absorption rates, however, it has high heat of absorption, this would help lower the energy requirement and could offset its disadvantages. Density is one of the most important properties and it is necessary for determination of physical solubility of $CO_2$ in solvent, mass transfer and solvent kinetics. In addition, the derived volumetric properties can be used to extend our understanding of molecular interactions in mixtures.

Experimental density data of the binary mixtures of 3-methylaminopropylamine (MAPA) with water were reported at atmospheric pressure and various temperatures over the entire composition range. The densities were measured using an Anton Paar digital vibrating U-tube densimeter (model DMA 5000 M). Excess molar volumes of the mixtures were calculated using the experimental densities and correlated as a Redlich-Kister equation. Thermal expansion coefficients for the pure components and excess thermal expansion coefficients of the binary mixtures are represented and discussed.

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# THERMOPHYSICAL PROPERTIES OF SYNTHETIC GEOTHERMAL BRINES

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Investigating the thermophysical properties of geothermal fluids is one of the main issues related to the development of geothermal power as an alternative source of energy. In particular, all components of the power plant need to be designed in accordance with the thermophysical properties of the pumped geothermal fluid. Although the main component is water, geothermal fluid properties generally differ significantly from those of pure water due to varying contents of dissolved ionic species. Combined with changes in temperature and pressure, dramatic impacts on the production efficiency of a geothermal power plant may be caused. Systematic investigations of the properties of a geothermal fluid as a function of pressure, temperature, and composition are therefore essential for an understanding of the processes involved and to avoid disruptions in plant operation. The basis for this laboratory study is the geothermal power plant in Groß Schönebeck, Germany operated by the GFZ. In about 4300 m depth at 450 bars, the temperature of the fluid is about 150°C and its TDS is 265 g/L. Elemental analyses showed that the main solutes are sodium chloride and calcium chloride. Consequently, sodium chloride and calcium chloride solutions and mixtures of both serve as a synthetic analog for this geothermal fluid. Due to large data gaps in the literature, the thermophysical parameters have to be determined systematically in the range between 0 $mol \cdot kg^{-1}$ to saturation and with different mixing ratios of the salts. The final objective is to develop general mixing rules for site-dependently predicting the properties of a fluid having a known composition. The newly installed thermophysical fluid laboratory at the GFZ provides measurements of density, viscosity, heat capacity, electrical and thermal conductivity as well as sonic velocity. Some properties, e.g. density, can be investigated at up to 200°C and 700 bars. In a first series, density, viscosity, and electrical conductivity of these brines were investigated. A combination of an oscillating U-tube density meter, a falling ball viscometer, and a 4-point electrical conductivity probe was used. Concentration series of sodium chloride, calcium chloride, and their mixtures up to saturation were measured between room temperature and 80°C. The results of the pure solutions are in excellent agreement with known literature data and confirm the experimental procedures. In our contribution, we will present the measured data as well as evaluated mixing rules for all three parameters.

# EXCESS THERMODYNAMIC FUNCTIONS OF BINARY MIXTURES FOR SECOND GENERATION BIOFUELS CHARACTERISATION

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The use of biofuels is increasing in the EU with the target of decrease the dependency of the petroleum and also to reduce $CO_2$ emissions and to support the agricultural community. A wide variety of biogenic products is added to fuels and the quality of these products becomes more important requiring an accurate knowledge of the thermodynamic properties of the new fuel blends. Between these properties the heats of mixing or the excess enthalpies are needed to calculate the energy balances.

An automated quasi-isothermal flow calorimeter has been developed for the measurement of high accurate excess enthalpies over the range 250-400 K. The technique was checked for different test binary mixtures and the results were compared with the literature values available [1]. The technique allows us to measure excess enthalpies with an estimated total uncertainty better than 1%. Both binary mixtures have been measured at $T$ = (298.15 and 313.15) K. They show an exothermic behaviour which increases with temperature. The experimental results have been correlated with the Redlich–Kister polynomial equation.

An isothermal total pressure cell has been employed for measuring the vapour-liquid equilibrium at 313.15 K [2]. Data reduction by Barker's method provides correlations for $G^E$ using the Margules equation and Wilson, NRTL and UNIQUAC models. They have been applied successfully to both the binary systems.

Total pressure measurements and excess enthalpies are reported for the binary systems (1-pentanol + cyclohexane) and (1-pentanol + toluene) [3].

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# DIFFUSION OF POLYSTERENE PARTICLES UNDER CONFINEMENT OF POROUS GLASS

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Transport processes inside porous structures are of significant importance in nature and industrial applications like sediment transport or filtration.

To achieve a complete understanding of the transport process in porous media diffusion in combination with the matrix-particle interaction has to be investigated.

Angle-dependent dynamic light scattering (DLS) was applied in this work as a non-invasiv optical method to investigate the transport of polystyrene particles in porous media. By using this method it is possible to differentiate between diffusion and other particle transport processes. Therefore, investigations were performed inside a packed bed of controlled pore glass (CPG), and a monolith of CPG, respectively. These CPGs exhibit a bicontinuous randomly distributed microstructure on a micro- or macroporous scale.

A refractive index matching of the glass matrix and the surrounding fluid were realized to minimize the optical contributions of the porous matrix. Due to the local inhomogeneities of the refractive index of the CPGs, the residual scattered light of the packed bed depends on time and position of the scattering volume. In this study the different contributions on the scattering of matrix and particles are analyzed to determine the impact of the optical properties of the packed bed on the DLS results.

Results obtained by DLS from the packed bed of CPGs show two distinct decay times. These modes result from the particle movement in the voids of the CPG packed bed and inside the pore volume, respectively.

# HIGH PRESSURE VISCOSITIES OF BIOFUELS USING A FALLING BODY VISCOMETER

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Our society's dependence on oil is one of the most serious problems nowadays, which will probably get worse in the future. This problem has become noticeable in recent years, not only because the unending demand for energy resources has led to a shortage of these, but also due to the class and political instability which has affected a number of oil-producing countries, thus causing uncertainty about the future of petroleum. In light of this scenario, biofuels become entirely relevant. Governments, together with the European Union, being aware of this state of affairs, have devised several measures, whose aim is to encourage the use of biofuels. It is worth pointing out that biofuels will not only allow us to become less dependent on oil, but will also help to reduce the amount of carbon dioxide emissions.

There is a wide range of biological origin products that can be added to traditional fuels, but the assurance of quality is an essential requirement and implies the selection of reference materials that must be well characterized. Therefore, there is a need for accurate values of thermophysical properties of the new blends of fuels, viscosity being an essential one [1]. Our research group has a long experience in the measurement of thermodynamic properties, and now, for these purpose, it is involved in the setup of an automated falling body viscometer, a new technique which provides viscosities at high pressure [2].

The equipment can operate from 0.1 to 140 MPa pressure range and a temperature range from -40°C to 250°C. Regarding its working principle, viscosity is obtained through the falling time of a body in a vertical tube which contains the liquid for which the viscosity is to be measured. That falling time is determined using the signal detected by the coil detectors arranged along the tube, which have two circuits. The primary circuit is fed with a wave generator and the induced signal of the secondary circuit is detected by an oscilloscope. After that, a fit was made using polynomial functions in order to obtain the falling time accurately. Finally, a model will allow us to get viscosities from those falling times after a calibration.

## Literature:

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# DETERMINATION METHOD OF INTERMOLECULAR INTERACTION POTENTIAL PARAMETERS BY ZENO LINE

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An adequate description of intermolecular interaction is a key issue, in using the methods of molecular statistics to determine thermodynamic properties of substances. At present a great numbers of force fields with different model potential and level of structure details are used. However, a conventional method of determining the parameters of the potential does not exist.

We propose a method for determining the intermolecular interaction potential parameters by Zeno line. The essence of Zeno line is that the temperature-density dependence is nearly linear at a compressibility factor equal to the unit. This feature allows as to use any two points on the line to determine the parameters of Zeno.

The advantage of using Zeno line is that the parameters characterizing the depth of the potential well ($\varepsilon$) and molecular size ($r_m$ or $\sigma$ for the different model potentials) are defined independently of each other which reduces the required computational resources. Parameter $\varepsilon$ is found by the comparison of experimental value of Boyle temperature with the calculated values obtained from the second virial coefficient. Parameter characterizing the size of the molecule is determined by comparing the experimental and calculated Boyle density.

Correlation expressions of the intermolecular interaction parameters and Boyle density, Boyle temperature and critical temperature are obtained for single-site fluids with modified Lennard-Jones potential and potential Karr-Konowalow. These correlations allow us to define the parameters without additional simulation. It was shown that the parameters found in this way are suitable for the practical application with sufficient accuracy in determining the thermodynamic properties of substances. However, the accuracy of the calculation is reduced when the molecule shape is out of sphere.

The above method had been extended to multi-site molecules. We determined the potential parameters of methane, ethane, propane, ethene and propene. Intermolecular interaction of these substances was described in terms of center-center interaction model with Karr-Konowalow potential. The obtained parameters are shown to provide a satisfactory accuracy in determination of thermodynamic properties in a broad range single phase region and on coexisting lin for further practical application with little required experimental PVT data.

# PREDICTIVE METHODS FOR THERMOPHYSICAL PROPERTIES OF SEWAGE WATERS AND SLUDGE

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The reported research results are part of the activities dedicated to the development of the concept of "Positive Energy Yield Waste Water Treatment Plants" or "Energy + WWTP". For increasing the energy yields there are needed detailed and precise information on the processes and the effects of operational variables on the yields and the thermophysical properties of compounds and mixtures under all conditions in which they can be found in the process itself.

For this purpose there are two major sources: data banks and thermodynamic calculation methods to predict thermophysical properties.

The paper presents the approach that has been followed in the development of process modeling in a WWTP including mass balance, energy balance and exergy analysis and the predictive methods that have been used for required thermophysical properties of sewage waters and sludge.

A critical review of the models used in similar works is reported here. The modeling approaches are discussed and suggestions relative to the current best methodologies for the prediction of each property are presented.

Methods and models are presented for predicting thermophysical properties based solely on data for the composition of the sewage waters and sludge in terms of their basic components. These types of models provide genuine predictions of thermophysical properties and very limited property measurements are required.

Simple guidelines for thermophysical property prediction are presented along with worked examples to serve as illustrations.

# Poster Presentations

# DENSITY OF BUTANOL-1 AT THE HIGH STATE PARAMETERS

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During the last years, butanol-1 has been promoted as an alternative transportation fuel and its application is increased dramatically. It can be successful used as a fuel in an internal combustion engine. Butanol has a higher fuel value than ethanol. It can be blended with traditional fuels in higher amounts.

Current fuel injection systems for diesel engines reach pressures approximately 160 MPa for cars. In future this technology are targeting even higher pressures in excess of 200 MPa. Because, the possible number of injections per cycle from five to nine will be increasing. Under these pressures, the thermophysical properties of the fuel can increase up to approximately 10 times atmospheric levels and also make the fuel very viscous. In this case, the thermophysical properties of butanol-1 (the density, viscosity, speed of sound, heat capacity etc.) are necessary to study of such processes.

In this work, we present the density of butanol-1 at high pressures and wide range of temperature, which measured using a new, modernized high pressure – high temperature Anton-Paar DMA HPM vibrating tube densimeter with an experimental uncertainty of $\Delta\rho/\rho = \pm(0.01 \text{ to } 0.03)$ % in density. The temperature interval was between $T$=(263.15 to 468.15) K and pressure up to 140 MPa. The experimental ($p,\rho,T$) results are helpful to extrapolate the temperature up to $T$=253.15 K and pressure up to 200 MPa using the constructed equation of state.

Density and speed of sound at ambient pressure and temperatures $T$=(278.15 to 363.15) K are also measured using Anton-Paar DMA 5000 vibrating tube densimeter and DSA 5000 M density and sound velocity meter.

An equation of state for fitting of the ($p,\rho,T$) data has been developed as a function of pressure and temperature to calculate the various thermophysical properties of butanol-1, such as isothermal compressibility, isobaric thermal expansibility, differences in isobaric and isochoric heat capacities, thermal pressure coefficient, internal pressure, heat capacities, speed of sound.

# PROPERTY LIBRARIES FOR WORKING FLUIDS, FOR CALCULATING HEAT CYCLES, TURBINES, HEAT PUMPS, AND REFRIGERATION PROCESSES

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The program libraries for calculating the thermophysical properties for working fluids are designed for practical use by engineers who calculate heat cycles, steam or gas turbines, boilers, heat pumps, or other thermal or refrigeration processes. They can calculate thermodynamic properties, transport properties, thermodynamic derivatives and inverse functions.

The following property libraries are being presented here: *LibIF97* for water and steam, *LibIF97_META* for metastable steam, *LibICE* for ice including melting and sublimation, *LibSeaWa* for seawater, also at high temperatures and salinities, for desalination and cooling processes, *LibHuGas* for humid combustion-gas mixtures also at high pressures, *LibHuAir* for humid air also at high temperatures and pressures, *LibAmWa* for ammonia/water mixtures in absorption processes and the Kalina process, *LibWaLi* for water/lithium bromide mixtures in absorption processes, *LibIDGAS* for combustion gas mixtures, *LibIdGasMix* for 25 ideal gases and their mixtures, *LibRealAir* for real dry air, *LibCO2* for carbon dioxide including dry ice, *LibNH3* for ammonia, *LibR134a* for the refrigerant R134a, *LibPropane* for propane, *LibButane_Iso* and *LibButane_n* for isobutane and n-butane, *LibD4*, *LibD5*, *LibD6*, *LibMDM*, *LibMD2M*, *LibMD3M*, *LibMD4M*, and *LibMM* for siloxanes used as ORC working fluids, *LibCH3OH* for methanol, *LibC2H5OH* for ethanol, *LibH2* for hydrogen, *LibN2* for nitrogen, and *LibHe* for helium. In addition, property libraries for a number of hydrocarbons are available.

The libraries contain the most recent and accurate algorithms for calculating thermodynamic and transport properties.

These property libraries can be used in user-specific programs written in Fortran, C++, C#, Java, Pascal (Delphi), Phyton, Visual Basic or other programming languages under the operating systems Windows®, Unix®/Linux® or Mac OS®.

Student versions of certain property libraries are available.

# DENSITY AND SOUND VELOCITY MEASUREMENTS OF GEOTHERMAL WATER RESOURCES OF GABALA-GAKH REGIONS OF AZERBAIJAN

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Azerbaijan possesses rich geothermal energy and mineral water resources. Some of these thermal water groups is located in the Gabala (Gamarvand, Yengije) and Gakh (Moksu, Ilisu and Ilisu-Beshbulag) regions of Azerbaijan. Gamarvan villiage og Gabala region is rich in water springs, rivers and waterfalls. The thermal water deposit 600 meters north of the village with 39 °C comes from under the ground. The thermal water resources of Gakh region are springing around the village of Ilisu and 1,400 to 1,600 m above sea level.

To use the geothermal energy resources as an alternative energy source requires the investigation of the thermophysical properties of a wide range of parameters. In many cases, the temperature of the geothermal water remains high, but pressure quickly becomes equal to ambient pressure. If, we will use the geothermal resources for power generation directly at the source, they can be generating the energy.

The density and speed of sound measurements of five various of geothermal resources of Gabala (Gamarvand, Yengije) and Gakh (Moksu, Ilisu and Ilisu-Beshbulag) regions of Azerbaijan geothermal water resources were experimentally investigated at $T$=(278.15 to 343.15) K and at ambient pressure using the DSA 5000M vibrating tube densimeter (Anton-Paar). The DSA 5000M density and sound velocity meter combines the world's most accurate density measurement, highly accurate sound velocity measurement and a state-of-the-art user interface. The DSA 5000M is equipped with a density and a sound velocity cells thus combining the proven Anton Paar oscillating U-tube method with a highly accurate measurement of sound velocity. Both cells are temperature-controlled by a built-in Peltier thermostat. The accuracies of experiments are: ±0.000005 $\text{g/cm}^3$ for density and ±0.1 $\text{m}\cdot\text{s}^{-1}$ for sound velocity measurements.

Before the experiments, the chemical structure (cations and anions) of the samples also were anaylsed using the IRIS Intrepid II Optical Emission Spectrometer and DX120 ion chromatography. These investigations have been examined for the first time.

The obtained values were fitted to the polynomial equations and compared with the values of pure water. These values will use in future during the calculation of thermophysical properties of them using the additionally measured high pressure-high temperature density values.

# A NEW THERMOPHYSICAL FLUID LABORATORY FOR GEOTHERMAL APPLICATIONS

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An integrated development and use of a geothermal site for sustainable energy provision requires the thermophysical and chemical fluid properties to be known in detail. Due to often highly complex fluid compositions, e.g. high salinity and mineralization of the brines, their properties eventually depart significantly from those of pure water and are often unknown. To close this gap a new laboratory is currently being installed at the German Research Centre for Geosciences that enables measurements of the most important thermophysical and physico-chemical fluid properties at physical and chemical conditions relevant for deep geological and particularly geothermal reservoirs as well as the above-ground installations.

The principal parameters addressed are: density, specific heat, speed of sound, viscosity, thermal conductivity, electrical conductivity, pH-value and redox potential. Off-the-shelf solutions are complemented with in-house constructions where the former are not available, particularly for high pressure measurements. Special attention was given to materials selection issues in connection with the high corrosion potential of geothermal brines. We subdivided the experimental p-T space into three fields, (1) ambient pressure and $T < 80°C$, (2) $p < 20$ MPa and $T < 150°C$, (3) $p < 50$ MPa and $T < 200°C$. For geothermal applications this covers all reservoirs to accessible depths of 5 km having a normal geothermal gradient.

For density, speed of sound, viscosity and electrical conductivity solutions are available for all p-T fields mentioned above. For pH-value and redox potential measurements are possible up to p-T field (2). At this stage, for the thermal properties specific heat and thermal conductivity devices are set up to cover field (1). However, a combination of density and speed of sound measurements also yields values for specific heat up to field (3). Ongoing technical improvements therefore are focused on measurements of thermal conductivity of low viscosity fluids at elevated pressures and temperatures. The laboratory is complemented with a FTIR-Spectrometer equipped with a high pressure cell that enables molecular-spectroscopic investigations of geothermal fluids up to p-T field (2).

In our contribution we will present the installations and the thermophysical research that is ongoing in connection with a larger-scale project on geothermal technologies funded by the German Federal Ministry for the Environment, Nature Conservation, and Nuclear Safety (BMU).

# PROPERTY LIBRARIES SOFTWARE FOR EXCEL, MATLAB, MATHCAD, DYMOLA, SIMULATIONX, LABVIEW, ENGINEERING EQUATION SOLVER, SMART PHONES, TABLETS, POCKET CALCULATORS, AND ONLINE USE

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The software developed for calculating the thermodynamic and transport properties for working fluids have been designed for very convenient use by engineers who routinely calculate heat cycles, steam or gas turbines, boilers, heat pumps, or other thermal or refrigeration processes.

The following software solutions will be presented:
Add-In *FluidEXL^Graphics* for Excel®,
Add-On *FluidLAB* for MATLAB®,
Add-On *FluidMAT* for Mathcad®,
Add-On *FluidDYM* for Dymola® (Modelica) and SimulationX®,
Add-On *FluidVIEW* for LabVIEW™, and
Add-On *FluidEES* for the Engineering Equation Solver®.

The program *FluidDIA* was developed for calculating and plotting large-size and camera-ready thermodynamic charts.

Steam tables are available for iPhone, iPad and iPod touch, and for Android smart phones and tablets.

The software for using steam tables and property software on Texas Instruments®, Hewlett Packard®, and Casio® pocket calculators is particularly interesting for students.

The properties of several working fluids can be calculated at our website:
www.thermodynamics-zittau.de.

# INVESTIGATION OF KINETIC PARAMETERS AND MICROSTRUCTURE IN CuAlMnCr SHAPE MEMORY ALLOY

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In this study, kinetic parameters, phase transformation and microstructure of CuAlMnCr shape memory alloy was investigated. CuAlMnCr SMA was produced from high purity elements by arc melting in an argon atmosphere. The obtained samples were cut from the cast ingot. The specimens were solution-treated at 950 °C for 1 h and quenched in iced-brine water. Then the samples were annealed at 150 °C for 4 h. The evolution of the transformation temperatures was studied by differential scanning calorimetry (DSC) with different heating and cooling rates. Austenite and martensite phase start and finish temperatures are determined ($A_s$=50 °C, $A_f$=72 °C, $M_s$=38 °C and $M_f$=15 °C). The thermodynamic parameters such as enthalpy, entropy values and activation energy of the sample were determined by DSC analysis. The TG/DTA measurement was performed from room temperature to 1000 °C at a heating rate of 20 °C/min to observe the phase transitions at higher temperatures. The chemical composition of the alloy was determined by energy dispersive X-ray (EDX). The structural observation of the sample was studied by optical metallographic microscope and X-ray diffraction (XRD) measurements. Phase identification was performed in a Rigaku RadB-DMAX II diffractometer with CuK$_\alpha$ radiation.

Keywords: Shape memory alloy, Martensitic transformation, Austenitic transformation, Kinetic parameters, Microstructure.

## Acknowledgements

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# ACOUSTIC AND THERMODYNAMIC PROPERTIES OF BINARY LIQUID MIXTURE METHANOL+N.HEPTAHE

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This paper deals with experimental results for the speed of speed in liquid binary methanol+n.heptahe mixtures and the calculation of thermodynamic properties at temperatures from 298.15 to 523.15 K and at pressures up to 60 MPa. The speed of sound has been obtained using a method of direct time measurement of an impulse traveling through the investigated medium in the temperature range 298.15-523.15 and pressure 0.1-60 MPa and concentrations 0-100 %. The pressure was measured by dead weight gauge manometers. The temperature was measured by platinum-resistance thermometer. Mixture composition was prepared by a weight method and was kept under control by chromatography analysis before and after measurements. The error of the experimental data does not exceed 0.08 %.

# THERMODYNAMIC PROPERTIES OF DIESEL FUELS

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To reduce $CO_2$-emissions and the dependence on fossil crude oil resources biodiesel is going to play an important role as an renewable energy source in the future. Since the amount of available biodiesel can not replace the entire fossil diesel fuel, it is decided to blend biodiesel with fossil diesel at certain shares. Currently, the biodiesel portion in a typical EN590 diesel fuel is up to 7% in Europe. In the future shares of up to 10%, 20% and 30% are imaginable and expected for different geographical regions in the world. For particular applications, e.g. agricultural machines, prospectively even a 100% biodiesel operation can be of interest.

Current fuel injection systems for compression-ignition (diesel) engines reach pressures approximately 160 and 140 MPa for passenger car and commercial vehicle systems, respectively. Future systems are targeting even higher pressures in excess of 200 MPa while also expanding the possible number of injections per cycle from five to nine. Under these pressures, the thermophysical properties of the fuel can increase up to approximately 10 times atmospheric levels. Upon injection of the fuel in the cylinder, the large depressurization of the fuel results in a significant gradient of the viscous properties of the fluid. The density, visocisty, speed of sound, heat capacity etc. are the main thermophysical properties for the study of such processes [1].

The density of various diesel fuels and bio diesels were experimentally investigated at $T$=(273.15 to 468.15) K and pressures up to 140 MPa. The measurements were carried out with a newly constructed Anton-Paar DMA HPM vibration-tube densimeter. An empiric equation of state for fitting of the $(p,\rho,T)$ data of diesel fuels has been developed as a function of pressure and temperature. This equation was used for the calculation of the thermophysical properties of diesel fuels, such as isothermal compressibility, isobaric thermal expansibility, thermal pressure coefficient, internal pressure, isobaric and isochoric heat capacities, speed of sound and isentropic expansibility.

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# THERMOPHYSICAL PROPERTIES OF 1-ETHYL-3-METHYLIMIDAZOLIUMBIS(TRIFLLUOROMETHYLSULFONYL)IMIDE AND WATER BINARY MIXTURES

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In times of an accelerated economic growth, humanity and especially scientist are dealing with more and more serious environmental and energy issues. An approach to minimize the ecological impact of new technologies is the use of renewable energy resources and the improvement of energy efficiency. Therefore, absorption chillers and absorption heat pumps are two very interesting energy-saving devices, which can be run totally with low-grade thermal energy (such as solar or geothermal energy) or industrial waste heat supplied from energy-intensive industries (which dissipates into the environment in most cases until now). An increased application of these technologies could lead to a significant reduction of environmental pollution and carbon dioxide emissions.

The efficiency of absorption cycles strongly depends on the thermophysical properties of the used working pairs (consisting of a refrigerant and an absorbent). Unfortunately, the commonly-used working pairs for these applications are $NH_3$ + $H_2O$ and $H_2O$ + LiBr. Although they provide a good Coefficient of Performance (COP), they have some inevitable weaknesses, such as corrosion, crystallization and toxicity (to name three). Therefore, the research for new working pairs combining environmental friendliness with other advantageous properties, like no toxicity, no crystallization, good thermal stability, low viscosity etc. has become more and more important in recent years.

Ionic liquids (ILs) are salts that are liquid at low temperature (<100 °C) and are non-flammable, thermally stable and have no detectable vapor pressure. Their physical and chemical properties can be tailored to meet specific applications by varying the length and branching of the alkane chains of the cationic and anionic parts. In addition to these properties, many ionic liquids are completely miscible with organic solvents. Thus, ionic liquids are characterized as promising solvents for clean processes and green chemistry.

An intensive literature investigation has shown, that the binary mixture of [Emim][$BF_4$]+[$H_2O$] is said to be a promising working pair for the application in absorption cycles. Therefore, in this work, the thermophysical properties of this binary mixture are investigated over a wide range of composition. The density and speed of sound measurements were experimentally investigated at $T$ = (278.15 to 343.15) K and at ambient pressure using the DSA 5000M vibrating tube densimeter (Anton-Paar). The DSA 5000M is equipped with a density and a sound velocity cells thus combining the proven Anton Paar oscillating U-tube method with a highly accurate measurement of sound velocity. The accuracies of experiments are: ±0.000005 g/cm3 for density and ±0.1 m·s-1 for sound velocity measurements. Viscosity measurements have been carried out using a Stabinger SVM 3000 Viscosimeter at ambient pressure in a temperature range from $T$ = (278.15 to 343.15) K with a repeatability of ±0.1 %. In addition, the vapor pressure of the binary mixture was measured from $T$ = 277.15 K up to $T$ = 413.15 K using the static method with a repeatability of $\Delta p$ = ±0.05 % for the temperature interval from $T$ = (277.15 to 333.15) K and $\Delta p$ = ±0.5 % for temperatures from $T$ = 333.15 K up to $T$ = 413.15 K. Furthermore, values for the specific heat capacity can be calculated from the obtained speed of sound and density data.

The next step will be the simulation of the thermodynamic performance of an absorption chiller with typical operating parameters using the received thermophysical data.

# Company Presentations

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The company Anton Paar is committed to long-term partnerships with customers and employees as well as responsibility towards society in general. The Austrian-based company has continuously found new ways to merge high-precision engineering with scientific curiosity. Anton Paar develops, produces, distributes and provides support for analytical instruments used in research, development and quality control worldwide.

Since 2003 Anton Paar has been owned by the charitable Santner Foundation. The foundation is exclusively and directly dedicated to charitable and beneficent causes.

**Customers:** Amongst Anton Paar's customers are universities and research institutes worldwide, major soft drink companies as well as breweries, the petroleum industry, food industry, aerospace industry, Formula One racing, the chemical industry and many more.

Anton Paar offers a range of instruments which provide complete conformity and traceability to meet stringent reference standards and national and international regulatory requirements.

**Innovation:** Anton Paar is constantly working on the development of unique products and continues to expand its product portfolio in close cooperation with the scientific community.
More than 20 % of annual turnover is invested in R&D (Research and Development) to always be one step ahead. The instruments are always innovative and reflect Anton Paar's know-how and cooperation with universities and external research institutes.

This makes Anton Paar the world leader in the fields of density and concentration, rheometry as well as $CO_2$ measurement. The measuring instruments from Anton Paar react to the smallest physical changes from which measuring parameters are derived. Physical quantities such as density, temperature, sound velocity and the optical behavior of light or X-rays form the basis for Anton Paar measuring instruments.

Anton Paar's business fields include

- Density and Concentration Measurement Lab
- Density and Concentration Measurement Process

- Rheometry
- Viscometry
- Chemical and Analytical Techniques
- Material Characterization
- Refractometry und Polarimetry
- Petroleum Testing
- Contract Manufacturing (Anton Paar ShapeTec: High-precision single parts / complex assemblies / custom-tailored complete systems)

Anton Paar's product portfolio for thermophysical measurement includes:

- The DSA 5000 M density and sound velocity meter automatically determines the density and sound velocity of samples. This enables users to determine the concentration of three-component samples and to calculate thermodynamical values such as excess molar volumes, thermal expansion coefficient and isentropic compressibility.

- The DMA HP and DMA HPM external measuring cells measure density at high sample pressures and/or high temperatures. DMA HP is the expert solution for highly viscous samples with high melting points like bitumen.

- The MKT 50 **Millikelvin Thermometer** is designed for the most accurate temperature measurements, comparison calibrations and fixed point calibrations. In combination with standard and industrial platinum resistance thermometers, MKT 50 achieves a measuring uncertainty of 10 mK. Combined with high-end SPRT sensors, a system uncertainty as low as 1.4 mK can be reached.

- The MCR 702 **TwinDrive™ rheometer** is a revolution in rheometry, the practice of testing materials' flow and deformation behavior. This is the first instrument ever to cover all possible rheological applications – with an accuracy of 1 nNm and features like the IsoLign Piezo flange, offering measuring gap control down to an unprecedented size of 10 nm. Anton Paar's groundbreaking TwinDrive™ technology combines two powerful synchronous EC motor units in a modular setup: The upper EC motor in the rheometer is permanent; the lower EC motor can be extracted and integrated at will. Due to the EC motor's renowned dynamism and precision, and building on the different ways these units can be employed and combined, users are given limitless testing options and can break entirely new ground in their research.

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TA Instruments reputation for high technology products, quality manufacturing and unbeatable after sales support is why more customers recommend TA products to their colleagues around the world. Headquartered in New Castle, DE, TA Instruments prides ourselves in the technical competence and professionalism that our sales force offers. We are the only thermal analysis, rheology, TPP (Thermo-physical Properties) and microcalorimetry supplier recognized worldwide for our prompt, courteous and knowledgeable service staff, the hallmark of our company. Our technical support group is committed to handling all of your rheology needs, and is available by phone, email and through the internet.

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- Photo DSC

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- Q600 (Simultaneous DSC-TGA)
- HP-TGA (Pressure TGA)

*Sorption Analysis*

- DVS Q5000SA , VTI-SA

*Dynamic Mechanical Analysis*

- DMA RSA-G2, Q800

*Thermomechanical Analysis*

- TMA Q400

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With more than 400 employees, more than EUR 60 million in annual turnover and eight foreign subsidiaries, LAUDA is the global leader in the manufacture of innovative thermostatic equipment and systems for science, application technology and production, as well as for high- quality measuring devices. With almost 60 years of experience and a unique product portfolio ranging from compact laboratory thermostats to industrial circulation chillers to customized heating and cooling system projects with more than 400 kilowatts of cooling power, LAUDA is the only company that can guarantee optimized temperature throughout the entire value-added chain for its 10,000 plus customers worldwide.

Quality products from LAUDA keep temperatures constant to an impressive 5 thousandth °C or make targeted changes in an area spanning -150 to 400 °C. Through active cooling or warming, production processes are accelerated or, indeed, made possible in the first place. In such cases, LAUDA, for example, replaces the uneconomical mains-water cooling with environmentally friendly and cost-efficient devices or, alternatively, uses existing forms of primary energy such as thermal discharge. LAUDA measuring instruments determine the surface tension, tension limit and viscosity of liquids precisely.

As a highly specialized niche provider, LAUDA ranks either first or second in almost all future-oriented sectors. In the semiconductor industry, all the renowned manufacturers and suppliers place their trust in LAUDA thermostats and heating and cooling systems. LAUDA quality products also enable both the research and mass production of vital medicines. In the growing medical technology market, circulation chillers made by LAUDA cool patients and guarantee safe openheart surgery. LAUDA industrial circulation chillers provide reliable and cost effective cooling for printing machines, injection moulding plants and laser processing machines equipment. Further principle applications include material inspection, biotechnology and the cooling of laboratory instruments and machines. LAUDA thermostats are, naturally, also used in the measuring instruments manufac-

tured by us. For example, in order to determine the viscosity of aviation fuel under real conditions at 10,000-meter altitude, the sample is cooled in the laboratory down to -60 °C.

Through numerous innovations and ongoing investment, LAUDA is sustainably improving its excellent market position and is growing both in the main European market as well as overseas.

*LAUDA – The right temperature worldwide*

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