

Academy of Sciences of the Czech Republic

**Institute of Chemical Process  
Fundamentals**

**Prague**

ANNUAL REPORT 1995

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# INSTITUTE OF CHEMICAL PROCESS FUNDAMENTALS

The Institute of Chemical Process Fundamentals (ICPF) is one of the six institutes constituting the Section of Chemical Sciences of the Academy of Sciences of the Czech Republic. The Institute functions as a center for fundamental research in chemical, biochemical, catalytic and environmental engineering. Besides these activities, the Institute acts as a graduate school for Ph.D. studies in the field of chemical engineering, physical chemistry, industrial chemistry, and biotechnology.

## DEPARTMENTS

Department of Diffusion and Separation Processes (page 5)

E. Hála Laboratory of Thermodynamics (page 10)

Department of Catalysis and Reaction Engineering (page 16)

Department of Multiphase Reactors (page 22)

Department of Biotechnology and Environmental Processes (page 29)

Department of Reaction Engineering in Gas Phase (page 35)

Department of Analytical Chemistry (page 43)

## STAFF

(31 December 1995)

Category	Number of Employees
Research	108
Technical	19
Administrative	20
Services	19

**BUDGET 1995**

(in thousands of Kč; 27 Kč = 1 US\$, approx.)

Institutional support from the National Budget	32 343
Research funds from Grant Agencies	11 049
Contracts with industry	1 416
Total	44 808

## Abbreviations used throughout the Report

ASCR	Academy of Sciences of the Czech Republic
GA ASCR	Grant Agency of the Academy of Sciences of the Czech Republic
GA CR	Grant Agency of the Czech Republic
ICPF	Institute of Chemical Process Fundamentals ASCR, Prague
ICTP	Institute of Chemical Technology, Prague
CTU	Czech Technical University, Prague
CU	Charles University, Prague
TU	Technical University

## Department of Diffusion and Separation Processes

Head: H. Sovová  
Deputy: V. Jiříčný  
Research staff: Z. Brož, M. Chačaturjan, L. Hanková, A. Heyberger, K. Jeřábek, J. Procházka,  
Z. Prokop, J. Roček, J. Šťastová, P. Uchýtil, E. Volaufová  
Part time: V. Staněk, H. Vychodilová  
Technical staff: J. Jež, D. Karfík, M. Šoltysová, D. Vlček  
PhD student: J. Vachtová

### Fields of research

- Transport properties of polymer and ceramic membranes, preparation of ceramic membranes
- Relation between the morphology and applicability of polymeric adsorbents and catalyst carriers
- Dynamic behaviour of two-phase gas-liquid flow in packed columns and reactors
- Amine extraction of hydroxycarboxylic acids; extraction and refining of phenols from coal tars
- Supercritical fluid extraction; solubilities of solids and liquids in dense CO<sub>2</sub> with entrainer

### Applied research

- Extractor design for refining cast elastomer reaction mixture
- Preparation of corundum support for ceramic membranes
- Rotating disc stripper design for removal of volatile substances from water

### Research projects

#### **Ceramic membranes - their characteristics and use for waste water purification**

(Z. Brož, joint project with the University of Pardubice; supported by GA CR)

The part of the project solved at ICPF is the critical review of the literature related to the physico-chemical principles of the transport of gases, vapours and liquids in inorganic membranes and methods of membrane modification and characterization.

#### **Investigation of membrane preparation and characterization and study of factors influencing membrane performance in practical applications**

(J. Roček, supported by Elektroporcelán, Louny)

The project solved the problem of preparation and characterization of ceramic membranes made of corundum and  $\gamma$ -alumina. Support, microfiltration and ultrafiltration layers were prepared. Layer structure properties of the samples of supported membranes modified by hardened

resin were tested using mercury porosimetry. Permeation method for the characterization of supports and the first supported layer was developed [Refs. 6, 16]. Permeation models were applied also to polymer membranes [Refs. 3, 9].

### **Polymer-supported ligands for ecological problems**

(K. Jeřábek, joint project with The Weizmann Institute of Science, Rehovot, Israel; supported by the Agency for International Development, Washington, USA)

Solvent impregnated resins prepared by supporting dialkyl dithiophosphoric acid (DADTPA) on porous polymer carriers were investigated [Ref. 8]. Analysis of relations between adsorption of DADTPA from alcoholic solutions and morphology of the polymer supports revealed very unusual mechanism when, instead of a surface adsorption, DADTPA fills the pores gradually from the smallest ones up to those of diameter approx. 10 nm [Ref. 7]. The research was recently expanded to the investigation of supporting of DADTPA on functionalized carriers [Ref. 14].

### **Ion exchanger catalysts with increased lipophilicity**

(K. Jeřábek, joint project with ICTP; supported by GA CR)

Specific properties of functional polymers prepared by copolymerization of p-styrenesulphonyl chloride (SSC) with divinylbenzene (DVB) and styrene were analysed. Copolymerization of SSC with styrene and DVB provides copolymers consisting of functionalized and unfunctionalized domains. These domains result from the possible phase separation of SSC-rich domains due to the strong mutual interaction of the functional monomer molecules or polymer segments [Ref. 4].

### **Molecular accessibility of microporous matrixes**

(K. Jeřábek, joint project with the University of Padua, Italy; Cooperation project CNR/ASCR)

Macromolecular structure and chemical accessibility of swollen polyacrylamide resins were examined with electron spin resonance and inverse steric exclusion chromatography (ISEC). The results in water were interpreted on the basis of a physico-mathematical model [Refs. 1, 17]. ISEC-derived description of the working-state morphology of polymer catalysts was confronted with catalytic experiments [Ref. 2]. Currently available methods for description of the internal morphology of synthetic resins were critically reviewed [Ref. 10].

### **Quasi-stationary regime in packed column close to the flooding point**

(V. Staněk, supported by GA CR)

Transient behaviour of liquid hold up and pressure drop in gas-liquid counter-current packed column was experimentally studied as a response to periodic step changes in gas or liquid flow [Ref. 25]. Experimental data were fitted to mathematical models [Refs. 21, 28] employed in the control theory. The research has also been aimed at constructing physical models of complex multiphase systems [Refs. 12, 13, 20, 26, 27].

### **Effects of solvent composition in reactive liquid extraction**

(A. Heyberger, supported by GA CR)

A model describing the effect of diluents and their binary mixtures on equilibria in systems aqueous solution of citric acid - solution of trioctylamine in the mixture of inert diluent and polar modifier was formulated and experimentally verified [Ref. 30]. Conditions of the third phase formation in these systems were investigated, and a correlation for equilibrium systems (1,1)-acid-amine salt - modifier - inert diluent were developed [Ref. 18].

### **Development of method and equipment for the determination of persistent organic pollutants in food production chains**

(A. Heyberger, joint project with the Institute of Landscape Ecology ASCR; supported by the Ministry of Environment)

A method for quantitative determination of very low concentrations of persistent pollutants (e.g. pesticides and their transformation products) in surface waters was developed. The work included development of an efficient extractor for recovering the pollutants from aqueous samples to suitable organic solvents [Ref. 29].

### **Mass transfer during supercritical fluid extraction of natural products from solids**

(H. Sovová, supported by GA CR)

The effect of operating conditions on the rate of extraction from black pepper, sea buckthorn [Refs. 11, 15] and fennel with dense carbon dioxide was investigated. Mass transfer model including the efficiency of grinding and solvent flow inhomogeneity was used to describe the rate of extraction and the changes of extract composition.

Participation in project "Supercritical fluid extraction - experiment and modelling" (see E. Hála Laboratory of Thermodynamics).

## **International cooperations**

University of Padua, Padua, Italy: Molecular accessibility of microporous matrixes

Laboratoire de Chimie-Physique Macromoléculaire, ENSIC-CNRS, Nancy, France: Membrane separation

Laboratoire des Matériaux Organiques CNRS, Lyon-Solaize, France: Polymer catalysts

Weizmann Institute of Science, Rehovot, Israel: Polymer supported ligands

University of California, Irvine, USA: Morphology of polymer and hybrid materials

MIT, Boston, USA: Modelling of cupola furnace

University of Skopje, Macedonia: Extraction of hydroxycarboxylic acids, supercritical fluid extraction of natural products

## **Visits abroad**

K. Jeřábek: The Weizmann Institute of Science, Rehovot, Israel; University of California, Irvine, USA; University of Padua, Padua, Italy

H. Sovová: Macedonian Academy of Sciences and Arts; University of Skopje, Macedonia

P. Uchytíl: Indian Institute of Chemical Technology, Hyderabad; Bhabha Atomic Research Centre, Bombay, India

## **Visitors**

M. Boaro: University of Padua, Italy (6 months)

V. Raț: Institute of Chemical and Technological Sciences, Timișoara, Romania (3 months)

## **Teaching**

K. Jeřábek: ICTP, postgraduate course "Fundamentals of preparation of heterogeneous catalysts"  
V. Jiříčný: ICTP, laboratory training on "Process control" [Ref. 24]

## Publications

### Papers

1. Biffis A., Corain B., Zecca M., Corvaja C., Jeřábek K.: On the macromolecular structure and molecular accessibility of swollen microporous resins: A combined ESR-ISEC approach. *J. Amer. Chem. Soc.* 117(5), 1603-1606 (1995).
2. Biffis A., Corain B., Cvengrošová Z., Hronec M., Jeřábek K., Králik M.: Relationships between physico-chemical properties and catalytic activity of polymer-supported palladium catalysts. Part I. Experimental investigations. *Appl. Catal. A* 124(2), 355-365 (1995).
3. Clement R., Nguyen Q. T., Grosse J. M., Uchytíl P.: Simulation and modeling of transient permeation of organic solvents through polymer films in the case of a concentration dependent diffusion coefficient. *Macromol. Theory Simul.* 4, 921-933 (1995).
4. Jeřábek K., Hanková L., Revillon A.: Functional polymers prepared from p-styrenesulfonyl chloride as the functional monomer. *Ind. Eng. Chem. Res.* 34 (8), 2598-2604 (1995).
5. Jiříčný V., Staněk V.: Preparation of D-arabinose in a laboratory fluidized bed electrode cell. *Collect. Czech. Chem. Commun.* 60(5), 863-874 (1995).
6. Uchytíl P., Wagner Z., Roček J., Brož Z.: Possibility of pore size determination in separation layer of ceramic membrane using permeation method. *J. Membr. Sci.* 103, 151-157 (1995).
7. Jeřábek K., Hanková L., Strikovský A. G., Warshawsky A.: Solvent impregnated resins: Relation between impregnation process and polymer support morphology: I. Di-(2-ethylhexyl)dithiophosphoric acid. *React. Polym.* 28(2), 201 (1996).
8. Strikovský A. G., Jeřábek K., Cortina J. L., Sastre A. M., Warshawsky A.: Solvent impregnated resins (SIR) containing dithiophosphoric acid on Amberlite XAD-2: Extraction of copper and comparison to the liquid-liquid extraction. *React. Polym.* 28(2), 149 (1996).
9. Uchytíl P., Nguyen Q. T., Clement R., Grosse J. M., Essamri A.: Diffusion of acetic acid and water through poly(vinylalcohol) membranes. Coupling effects. *Polymer* 37(1), 93-100 (1996).
10. Corain B., Jeřábek K.: Macro- and microporous synthetic organic supports in industrial catalysis: Microscopic and nanoscopic morphology and molecular accessibility. *La Chimica e l'Industria* (in press).
11. Sovová H., Jež J., Bártlová M., Šťastová J.: Supercritical carbon dioxide extraction of black pepper. *J. Supercrit. Fluids* 8(4), 295-301 (1995).
12. Staněk V., Katz S., Landefeld C.: Mathematical model of cupola furnace. Part IX: Role of carbon pickup under tuyeres. *AFS Transactions* (in press).
13. Staněk V., Katz S., Landefeld C.: Mathematical model of cupola furnace. Part X: Role of carbon monoxide evolving in the well. *AFS Transactions* (in press).
14. Strikovský A. G., Jeřábek K., Cortina J. L., Warshawsky A.: Solvent impregnated resins via acid-base interaction of poly(4-vinylpyridine) resin and di(2-ethylhexyl) dithiophosphoric acid. *J. Phys. Chem.* (in press).
15. Šťastová J., Jež J., Bártlová M., Sovová H.: Rate of vegetable oil extraction with supercritical CO<sub>2</sub>. III. Extraction from sea buckthorn. *Chem. Eng. Sci.* (in press).



16. Uchytíl P.: Pore size determination in separation layer of ceramic membrane using permeation method. *J. Mater. Sci.* (in press).
17. Zecca M., Biffis A., Palma G., Corvaja C., Lora S., Jeřábek K., Corain B.: Interpenetrating organometallic polymer networks based on poly-dimethylacrylamide-Co-methylene-bisacrylamide: Synthesis and ISEC-ESR Characterization. *Macromolecules* (in press).
18. Procházka J., Heyberger A.: Correlation of ternary liquid-liquid equilibria in systems isobutyl acetate - acetic acid - water. *Chem. Eng. Sci.* (in press).

#### Monographs

19. Jeřábek K.: Inverse steric exclusion chromatography as a tool for morphology characterization. In: *Cross-Evaluation of Strategies in Size-Exclusion Chromatography*, ACS Symposium Series (in press).

#### Conferences

20. Clark D., Moore K., Staněk V., Katz S.: Neural network applications for cupola melting control. 124th TMS Annual Meeting 7 Exhibition, Las Vegas, USA, February 12-16 (1995).
21. Jakeš B., Jiříčný V., Strnad R.: Identification of the dynamic model of packed bed column hydrodynamics. Proc. 10th Conference Process Control '95, Tatranské Matliare, Slovakia, June 4-7 (1995).
22. Jeřábek K.: Inverse steric exclusion chromatography as a tool for morphology characterization. 209th American Chemical Society National Meeting, Anaheim, California, April 2-6 (1995).
23. Jeřábek K.: Sulfonic acid resin catalysts. Invited lecture 35th Moretonhampstead Conference "Reactive polymers and oligomers", Moretonhampstead, UK, April 25-27 (1995).
24. Jiříčný V., Jakeš B., Burianec Z., Strnad R.: Cooperation of the ICPF AS CR with the PICT in the education process. Proc. 10th Conference Process Control'95, Tatranské Matliare, Slovakia, June 4-7 (1995).
25. Staněk V., Jiříčný V.: An experimental study of the response of the counter-current gas-liquid flow to a step change in the gas or liquid velocity. 7th International Summer School of Chemical Engineering, Varna, Bulgaria, September 19-21 (1995).
26. Staněk V., Katz S., Landefeld C.: AFS cupola model: Recent Progress. 99th Casting Congress, Kansas City, Missouri, USA, April 23-26 (1995).
27. Staněk V.: Cupola-state of the art. Scandinavian Conf. on Glass Melting Technology, Vaxjo, Sweden, November (1995).
28. Strnad R., Jakeš B., Jiříčný V.: The methods for development of continuous mathematical models of gas-liquid packed bed column from experimental data sets. Proc. 10th Conference Process Control '95, Tatranské Matliare, Slovakia, June 4-7 (1995).
29. Tříška J., Heyberger A.: Solid-phase extraction and/or continuous liquid-liquid extraction for the isolation of semivolatile pesticides from waters. 8th International Symposium BIOINDICATORS, Č. Budějovice, Czech Rep., May 22-28 (1995).
30. Procházka J., Heyberger A.: Correlating equilibria in ternary liquid-liquid systems. Invited lecture 14th Conference of Chemists and Technologists, Skopje, Macedonia, October 26-28 (1995).

## E. Hála Laboratory of Thermodynamics

Head: I. Wichterle  
Deputy: K. Aim  
Research staff: O. Drábek, J. Fárková, J. Kolafa, J. Linek, M. Lísal, I. Nezbeda, J. Pavlíček,  
M. Strnad, Z. Wagner  
Part time: T. Boublík  
Technical staff: S. Bernatová, Š. Psutka, J. Wolfová  
PhD students: P. Kadlec, M. Předota

### Fields of research

- Development of experimental techniques for the determination of fluid phase equilibria
- Determination of fluid phase equilibrium data at normal and high pressures
- Measurement of data for supercritical fluid extraction
- Thermodynamic modelling and processing of thermodynamic data
- Molecular simulations on model fluids and fluid mixtures
- Formulation of molecular theories of fluids and derivation of bulk thermodynamic models based on the theory
- Application of statistical-mechanical models to real fluids
- Compilation of bibliographic information on vapour-liquid equilibrium data
- Compilation of critically evaluated and correlated data on saturated vapour pressures of pure substances

### Applied research

- Determination of vapour-liquid equilibria in systems containing N-alkylacetamides
- Computerized bibliography of vapour-liquid equilibrium data

### Research projects

#### Molecular theory-based equations of state for real fluids

(K. Aim, supported by GA ASCR)

An algorithm for the direct evaluation of vapour-liquid equilibria of model fluids by the molecular dynamics simulation method based on the Gibbs-Duhem integration has been implemented and applied to the coexistence region of the two-center Lennard-Jones fluid. A semiempirical method improving pure-compound phase equilibrium calculations from pressure-explicit equations of state has been elaborated. Parameters of the Kihara intermolecular potential have been calculated from the full second-order perturbation theory for the homologous series of

real n-alkanes, based on critically evaluated properties of the series of compounds along their vapour-liquid coexistence loci. [Refs. 10, 25, 27, 34, 43]

### **Behaviour of fluids of nonspherical liquid molecules**

(K. Aim, joint project with CU; supported by GA CR)

Thermodynamic excess functions of selected binary mixtures (namely, the n-hexane series) of real n-alkanes differing in chain-length have been successfully calculated from the full second-order perturbation theory of the anisotropic molecule fluids. The theory was applied also to a more general form of the anisotropic intermolecular potential involving the dipole moment term. Promising predictions of thermodynamic properties have thereby been obtained for several real binary systems made up of small molecules of the type 1-chloroalkane + n-alkane. [Refs.: 18, 36, 37, 42]

### **Experimental study of ecologically relevant physico-chemical properties of industrially important compounds**

(K. Aim, joint project with ICTP; supported by GA CR)

Accurate experimental data on vapour pressures of isomeric chlorotoluenes have been determined. Vapour pressure data of ethers have been summarized and processed in a systematic way and the compilation of critically evaluated vapour pressures for selected classes of compounds, important from the environmental viewpoint, has been supplemented with data by mid-1995. [Refs. 16, 17, 35]

### **Molecular theory of phase behaviour of aqueous solutions and its application**

(I. Nezbeda, supported by GA ASCR)

An extended primitive model of associating fluids (primitive model with a mean field term) in the mixture with the van der Waals fluid has been used to determine the global phase diagram of mixtures with one associating component. The model has been shown to give, without any adjustable parameter, the correct (in some cases even semiquantitative) prediction of the phase behaviour of real mixtures of water, ammonia, and methanol with inert gases and n-alkanes, including the presence/absence of azeotropy and of pressure or temperature extreme on critical lines. The primitive model of water has also been used to derive a theoretically based equation of state of real water. [Refs. 4, 8, 28, 29]

### **Molecular theories of homogeneous and inhomogeneous liquid mixtures and their applications**

(I. Nezbeda, joint project with ICTP; supported by GA CR)

The project consists of several subtopics with the following main results: (1) A new integral equation theory of fluids has been developed; (2) A modified insertion particle method has been applied to obtain the chemical potential of the Lennard-Jones fluid and of the ternary mixture of hard nonspherical bodies; (3) Using the insertion particle method, the Gibbs ensemble methodology has been generalized in order to make the simulation of phase equilibria of any system possible; (4) A general methodology of computer simulations has been developed. [Refs. 7, 9, 11, 21, 30, 31]

### **Supercritical fluid extraction - experiment and modelling**

(I. Wichterle, supported by GA ASCR)

Gas-liquid equilibrium data for the CO<sub>2</sub> + ethyl propionate and (methyl and ethyl) methanoate systems were measured at pressures up to 10 MPa and along 3 isotherms in near critical region of CO<sub>2</sub>. Solubility of glycerine and anethole in supercritical CO<sub>2</sub> was determined; then, the influence of entrainers (ethanol, heptane, toluene) on the solubility of glycerine, dinonyl

phthalate, and squalane was investigated. The correlation procedure for fluid phase equilibrium data was generalized for arbitrary analytical equation of state and mixing rules. [Refs. 13, 14, 32; see also Department of Diffusion and Separation Processes, Refs. 11, 15]

### **Phase equilibria and state behaviour of fluid systems**

(I. Wichterle, joint project with ICTP; supported by GA CR)

Experiments: Systematic measurements of vapour-liquid equilibria and excess molar volumes in series of binary, ternary and quaternary systems (methanol + aliphatic ethers, C<sub>4</sub> butylchlorides + C<sub>7</sub> hydrocarbons, systems with N-methylacetamide) have been carried out. Data processing: New disperse and quasichemical contributions were evaluated for the DISQUAC prediction method. Data base: Vapour-liquid equilibrium data bibliography was supplemented by the end of 1994 and published as a book with diskette. [Refs. 1-3, 5, 14, 19, 20, 22, 33, 38]

### **International cooperations**

DICAMP, University of Trieste, Trieste, Italy: Phase equilibria for supercritical fluid technology

University of Guelph, Guelph, Canada: Statistical mechanics of fluids

University of Leipzig, Leipzig, FRG: Simulation of phase and reaction equilibria in homogeneous fluids

University of Odense, Odense, Denmark: PROSIS - Protein simulation software

University of Oldenburg, Oldenburg, FRG: PSRK - Predictive Soave-Redlich-Kwong equation of state

ITODYS, University of Paris, Paris, France: Vapour-liquid equilibrium bibliographic database; Phase equilibria in selected systems

Northwestern University, Evanston, Illinois, USA: Molecular dynamics studies of polymer electrolytes

DSM Research, Geleen, The Netherlands: Vapour-liquid equilibria in N-alkylacetamide systems

### **Visits abroad**

O. Drábek: McGill University, Montreal, Canada (9 months)

J. Kolafa: University of Odense, Odense, Denmark (8 months), Northwestern University, Evanston, Illinois (2 months)

M. Strnad: University of Nancy, Nancy, France (6 months)

### **Visitors**

A. Dahmani: Université de Science et Technologie, Alger, Algeria (7 months)

H. Vörtler: University of Leipzig, Leipzig, FRG (2 weeks)

M. Kettler: University of Leipzig, Leipzig, FRG (3 weeks)

## Teaching

- K. Aim: ICTP, postgraduate courses "Applied statistical analysis and data processing" and "Applied statistical thermodynamics of fluid systems"
- T. Boublík: CU, courses "Basic physical chemistry", "Advanced chemical thermodynamics", and "Statistical thermodynamics"
- I. Nezbeda: CU, courses "Selected topics in theoretical physics", "Computer simulation - principles and applications", and "Applied statistical thermodynamics of fluid systems"

## Publications

### Papers

1. Fárková J., Wichterle I.: Vapor-liquid equilibria of 1, 1, 2, 2-tetrachloroethane + some n-alkyl n-alkanoates (C3-C7). *ELDATA: Int. Electron. J. Phys.-Chem. Data* 1, 13-22 (1995).
2. Fárková J., Wichterle I.: Isothermal vapor-liquid equilibria in five methanol + aliphatic ether systems at temperatures from 310. 15 to 333. 15 K. *ELDATA: Int. Electron. J. Phys.-Chem. Data* 1, 121-130 (1995).
3. Fárková J., Linek J., Wichterle I.: Isothermal vapour-liquid equilibria and excess volumes in the methanol-aliphatic ether systems. *Fluid Phase Equilib.* 109, 53-65 (1995).
4. Kolafa J., Nezbeda I.: The hard tetrahedron fluid: a model for the structure of water? *Molec. Phys.* 84, 421-434 (1995).
5. Linek J.: Excess volume of 1, 1, 2, 2-tetrachloroethane + some n-alkyl n-alkanoates (C3-C7). *ELDATA: Int. Electron. J. Phys.-Chem. Data* 1, 23-28 (1995).
6. Lísal M., Vacek V.: Thermodynamic properties of liquid carbon dioxide modeled by '2-Lennard-Jones centres' pair potentials with quadrupole moment. *Acta Polytech.* 35(5), 23-36 (1995).
7. Nezbeda I., Kolafa J.: The use of control quantities in computer simulation experiments: Application to the exp-6 potential fluid. *Mol. Simul.* 14, 153-163 (1995).
8. Nezbeda I., Kolafa J., Pavlíček J., Smith W. R.: Molecular theory of phase equilibria in model and real associated mixtures. II. Binary aqueous mixtures of inert gases and n-alkanes. *J. Chem. Phys.* 102, 9638-(1995).
9. Nezbeda I., Strnad M.: Monte Carlo simulations in the vicinity of the critical point: vapor-liquid coexistence curve. *Czech. J. Phys.* 45, 793-798 (1995).
10. Pavlíček J., Aim K., Boublík T.: Fluids of the Kihara molecules. 1. Pair potential parameters of n-alkanes from the vapor-liquid coexistence data. *J. Phys. Chem.* 99(42), 15662-15668 (1995).
11. Strnad M., Nezbeda I.: Equation of state and chemical potential of ternary mixtures of hard spheres and heteronuclear diatomics. *Mol. Phys.* 85, 91-101 (1995).
12. Uchytíl P., Wagner Z., Roček J., Brož Z.: Possibility of pore size determination in separation layer of ceramic membrane using permeation method. *J. Membr. Sci.* 103, 151-157 (1995).
13. Wagner Z.: Vapour-liquid equilibrium at high pressure in the system containing carbon dioxide and propyl acetate. *Fluid Phase Equilib.* 110, 175-182 (1995).
14. Wagner Z.: Vapour-liquid equilibrium in the carbon dioxide-ethyl propanoate system at pressures from 2 to 9 MPa and temperatures from 303 to 323 K. *Fluid Phase Equilib.* 112, 125-129 (1995).

15. Lísal M., Vacek V.: Molecular dynamics simulations of fluorinated ethanes. *Mol. Phys.* 87, 167-187 (1996).
16. Aim K.: Vapor pressures of 2-chlorotoluene and 4-chlorotoluene and relative volatility in their binary system. *Thermochim. Acta* (in press).
17. Aim K.: Vapour pressures of some linear and branched dialkyl ethers. *Fluid Phase Equilib.* (in press).
18. Aim K., Pavlíček J., Boublík T.: Applicability of the second-order perturbation theory of anisotropic molecule fluid to real systems of constituents differing in molecular size and/or polarity. *Fluid Phase Equilib.* (in press).
19. Dahmani O., Wichterle I., Ait-Kaci A.: Isothermal vapour-liquid equilibria for binary systems of C4 alkyl chlorides with n-heptane, toluene and methylcyclohexane at 323. 15 and 333. 15 K. *Fluid Phase Equilib.* (in press).
20. Fárková J., Wichterle I., Kehiaian H. V.: Evaluation of the carboxylate/chloric interaction parameters using the DISQUAC group contribution model. *Fluid Phase Equilib.* (in press).
21. Kolafa J.: Numerical integration of equations of motion with a self-consistent field. *Mol. Sim.* (in press).
22. Linek J., Wichterle I.: Isobaric vapour-liquid equilibria in binary systems containing six C4 aliphatic alcohols + n-hexane. *ELDATA: Int. Electron. J. Phys.-Chem. Data* (in press).
23. Linek J., Wichterle I., Marsh K. N.: Vapor-liquid equilibria in systems containing N-methyl-2-pyrrolidone. *J. Chem. Eng. Data* (in press).
24. Linek J., Wichterle I., Marsh K. N.: Vapor-liquid equilibria in the water-diacetone alcohol, ethyl methanoate-water, and ethyl methanoate-phenol systems. *J. Chem. Eng. Data* (in press).
25. Lísal M., Vacek V.: Direct evaluation of vapour-liquid equilibria by molecular dynamics using the Gibbs-Duhem integration. *Mol. Sim.* (in press).
26. Lísal M., Vacek V.: Effective potentials for liquid simulation of the alternative refrigerants HFC-32: CH<sub>2</sub>F<sub>2</sub> and HFC-23: CHF<sub>3</sub>. *Fluid Phase Equilib.* (in press).
27. Nezbeda I., Aim K.: A general method improving phase equilibrium calculations from pressure-explicit equations of state. *Fluid Phase Equilib.* (in press).
28. Nezbeda I., Kolafa J., Smith W. R.: Molecular theory of phase equilibria in model and real associated mixtures. III. Binary solutions of inert gases and n-alkanes in ammonia and methanol. *Fluid Phase Equilib.* (in press).
29. Pavlíček J., Nezbeda I.: Application of primitive models of association: a simple theoretical equation of state of water. *Fluid Phase Equilib.* (in press).
30. Smith W. R., Nezbeda I., Strnad M., Tríska B.: The reaction ensemble method for the computer simulation of chemical and phase equilibria. II. Diatomic formation reactions and chemical potentials of ternary fused-hard-sphere systems. *J. Chem. Phys.* (in press).
31. Strnad M., Nezbeda I.: Extended Gibbs ensemble: a set of Gibbs ensembles with a fluctuating particle. *Mol. Sim.* (in press).
32. Wagner Z.: Vapour-liquid equilibria in CO<sub>2</sub> + (methyl, ethyl) methanoate system. *Fluid Phase Equilib.* (in press).

### Monographs

33. Wichterle I., Linek J., Wagner Z., Kehiaian H. V.: Vapor-Liquid Equilibrium in Mixtures and Solutions. *Bibliographic Database. Integrated Electronic Chemical Databases-Vol. III*, 179 pp., ELDATA SARL, Paris (1995).
34. Aim K., Cortesi A., Fermeglia M.: Solids and liquids in supercritical fluids. In: *The Experimental Determination of Solubilities* (J.-J. Counioux, G. T. Hefter and C. L. Young, Eds.), Butterworth (in press).

35. Boublík T., Aim K.: *The Vapour Pressures of Pure Substances*. Elsevier, Amsterdam (in press).

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36. Aim K., Boublík T.: Vapour pressures of pure substances; systematic treatment of an extensive data compilation. 14th Experimental Thermodynamics Conference, Reading, UK, April 5-7 (1995).
37. Aim K., Pavlíček J., Boublík T.: Applicability of the second-order perturbation theory of anisotropic molecule fluid to real systems of constituents differing in molecular size and/or polarity. 7th Int. Conf. Fluid Properties & Phase Equilibria for Chemical Process Design, Snowmass/Aspen, Colorado, USA, June 18-23 (1995).
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39. Kolafa J.: Realistic force fields for complex molecules. Case study: Poly(ethylene oxide). Internat. Workshop Mol. Phys. Liq.: State-of-the Art, Abertamy, Czech Rep., September, 8-10 (1995).
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42. Pavlíček J., Aim K., Boublík T.: Excess thermodynamic functions from second order perturbation theory of anisotropic molecules. 14th Experimental Thermodynamics Conference, Reading, UK, April 5-7 (1995).
43. Pavlíček J., Aim K.: Equilibrium properties of real fluids by using a simple molecular model. Internat. Workshop Mol. Phys. Liq.: State-of-the Art, Abertamy, Czech Rep., September 8-10 (1995).
44. Slovák J., Nezbeda I.: Modeling of water: A family of primitive models. Internat. Workshop Mol. Phys. Liq.: State-of-the Art, Abertamy, Czech Rep., September, 8-10 (1995).
45. Smith W. R., Kao R., Voertler H., Nezbeda I.: The effects of geometry on chemical and phase equilibria. AIChE Annual Meeting, Miami, USA, November (1995).

## Department of Catalysis and Reaction Engineering

Head: M. Zdražil  
Deputy: P. Schneider  
Research staff: P. Čapek, J. Frimmel, A. Galík, A. Galíková, D. Gulková, V. Hejtmánek, .  
E. Hillerová, K. Jirátová, G. Južakov, K. Klusáček, L. Morávková, R. Ponec,  
H. Šnajdaufová, O. Šolcová, Z. Vít  
Part time: D. Arnošt, L. Beránek, M. Kraus  
PhD students: J. Cinibulk, R. Saidur, F. Uhlík

### Fields of research

- Catalytic combustion of volatile organic compounds in waste gases
- Dynamics of catalytic systems
- Transport processes in porous solids
- Hydrodechlorination over sulphides
- Unconventional sulphide catalysts
- Catalytic combustion of methane
- Laser induced oxidative coupling of methane
- Similarity approach to structure reactivity relationships
- Theoretical analysis of bonding changes and electron correlation in chemical reaction

### Research projects

#### **Dynamics of multicomponent gas transport in porous solids**

(P. Schneider, supported by GA ASCR)

Dynamic transport of ternary mixtures in the dynamic version of the Wicke-Kallenbach diffusion cell was studied. It has appeared that the pulse response due to the step change in gas composition could be safely predicted by the mean transport pore model (MTPM) with parameters determined from measurements with binary gases [Ref. 1].

#### **Extra-column effects in the chromatographic technique**

(P. Schneider, supported by GA CR)

To determine reliable effective diffusion coefficients of gases in porous solids (catalysts, adsorbents, etc.) from the spreading of the tracer response peaks, it is imperative to take into account the tracer spreading in the spaces outside the chromatographic column (connecting elements, detector, etc.). The importance of these extra-column effects (ECE) was experimentally demonstrated. A method, based on convolution of the ECE peaks with column response peaks, was developed which permits accurate determination of rate parameters by the chromatographic technique [Ref. 21].



**Modified BET adsorption isotherm**

(P. Schneider)

By including the micropore volume into the BET adsorption isotherm, it is possible to determine (by a three-parameter non-linear fitting of the experimental physical adsorption data) the BET C-parameter, the specific surface of mesopores and the micropore volume [Ref. 22].

**Nonstationary catalytic and separation processes**

(K. Klusáček, supported by GA CR)

Dynamic models of complex catalytic and separation processes were derived and numerical methods for solution of coupled transport-reaction(-adsorption) systems were developed. Numerical methods were successfully tested for prediction of unsteady behaviour of water-gas-shift reaction. Theory of dynamic behaviour of catalytic systems was extended to reaction systems with periodically controlled feed composition. [Refs. 9, 19, 30]

**Sulphide catalysts for hydrodenitrogenation and hydrodesulphurization**

(M. Zdražil, supported by GA ASCR)

The Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/C sulphide catalysts were prepared by a new clean and simple method of slurry impregnation with molybdic acid. High loading corresponding to monolayer was achieved (18 and 31% MoO<sub>3</sub>, respectively) and the activity of catalysts was the same as that of catalysts prepared by more complicated conventional impregnation with ammonium heptamolybdate [Ref. 16].

**Multiphase catalytic processes for environmental protection**

(M. Zdražil, joint project with ICTP; supported by GA CR)

Parallel hydrodechlorination of dichlorobenzene and hydrodesulphurization of methylthiophene over Ni/C, Mo/C and Ni-Mo/C catalysts were studied as model reactions of hydrogenolysis of organochlorinated pollutants in organic wastes contaminated with sulphur. The synergistic effect in activity between Ni and Mo in the Ni-Mo catalyst was higher in hydrodesulphurization than in hydrodechlorination [Ref. 4].

**Silica-ceria as support for the preparation of NiMo(P) hydrodesulphurization and hydrodenitrogenation catalysts**

(Z. Vít)

Effect of preparation conditions on the properties of NiMo(P) sulphide catalysts based on the new macroporous SiO<sub>2</sub>-CeO<sub>2</sub> support was studied. The catalysts have higher activities and the better C-N bond hydrogenolytic efficiency than alumina-based catalysts [Ref. 5].

**Catalytic combustion of methane**

(K. Jiráťová, joint project with ICTP; supported by GA CR)

In the combustion of methane, the concentrations of NO<sub>x</sub> and CO in the flue gases of a burner have been studied as a function of air excess for various combinations of catalytic components (Pt, Pd, La) [Refs. 7, 18, 34, 35] and perovskites [Ref. 18] supported on ceramic foams.

**Laser induced oxidative coupling of methane**

(K. Jiráťová, supported by GA CR)

Effect of reaction conditions, active components (perchlorates) and supports on catalyst activity and selectivity was studied [Refs. 17, 36]. Low reaction temperature of 120°C was sufficient to obtain 80% conversion of methane. The best selectivity to C<sub>2</sub><sup>+</sup> hydrocarbons was observed at the conversion of methane of 15%.

### **Chemical applications and theoretical interpretation of pair density matrices**

(R. Ponec)

A new original formalism of pair population analysis was proposed and applied to the interpretation and visualization of chemical bonding in molecules with complex bonding patterns [Refs. 10, 11, 14, 20].

### **Chemical application of similarity indices**

(R. Ponec, supported by GA CR)

The project deals with the methodological development of quantitative similarity measures and their application for the rationalization of structure-(re)activity relationships [Refs. 23-25].

### **International cooperations**

Theory of chemical reactivity: University of Liverpool, Liverpool, UK, Universität Hannover, Hannover, FRG, University of Buenos Aires, Buenos Aires, Argentina

Participation in EC project Non-Nuclear Energy JOULE-II: New refining scheme and catalysis for the production of environment-friendly diesel fuels

### **Visits abroad**

P. Čapek: Institut für Angewandte Chemie, Berlin, FRG (3 months)

P. Schneider: Institut für Energieverfahrenstechnik, Jülich, FRG

K. Jiráťová: Indian Institute of Technology, Madras, Indian Institute of Chemical Technology, Hyderabad, National Chemical Laboratory, Puna, India (1 month)

R. Ponec: Central Institute for Chemistry, Budapest, Hungary

R. Ponec: University of Girona, Girona, Spain

### **Visitors**

H. Morishige, Idemitsu Kosan Co., Japan

### **Teaching**

K. Jiráťová: ICTP, postgraduate course "Preparation of heterogeneous catalysts"

M. Kraus: ICTP, postgraduate course "Applied catalysis"

R. Ponec: CU, course "Reaction mechanisms in organic chemistry"

P. Schneider: ICTP, postgraduate courses "Texture of porous solids" and "Applied catalysis"

M. Zdražil: ICTP, postgraduate course "Preparation of heterogeneous catalysts"

## Publications

### Papers

1. Arnošt D., Schneider P.: Dynamic transport of multicomponent mixtures of gases in porous solids. *Chem. Eng. J.* 57(2), 91-99 (1995).
2. Čapka M., Czakoová M., Hillerová E., Petzold E., Oehme G.: [2-(3-trimethoxysilylthio)ethyl]diphenylphosphine - a new agent for transition metal immobilization. *J. Mol. Catal. A* 104, L123-L125 (1995).
3. Damyanova S., Spojakina A., Jiráťová K.: Effect of mixed titania-alumina supports on the phase composition of NiMo/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts. *Appl. Catal. A* 125(2), 257-269 (1995).
4. Frimmel J., Zdražil M.: Hydrogenolysis of organochlorinated pollutants: Parallel hydrodesulfurization of methylthiophene and hydrodechlorination of dichlorobenzene over carbon-supported Ni, Mo, and Ni-Mo sulfide catalysts. *J. Chem. Tech. Biotechnol.* 63, 17-24 (1995).
5. Gulková D., Vít Z.: Silica-ceria as support for the preparation of NiMo(P) hydrodesulfurization and hydrodenitrogenation catalysts. *Appl. Catal. A* 125 (1), 61-70 (1995).
6. Jiráťová K., Paukshtis E. A.: Surface acidity of the La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> system. *React. Kinet. Catal. Lett.* 54(2), 277-280 (1995).
7. Jiráťová K., Morávková L., Malecha J., Koutský B.: Ceramic foam in the catalytic combustion of methane. *Collect. Czech. Chem. Commun.* 60(2), 473-481 (1995).
8. Jiráťová K., Morávková L., Čírová A., Říčanek M.: Katalytické spalování těkavých organických látek. Catalytic combustion of VOC. *Chem. Prum.* 45/70(5), 136-141 (1995).
9. Klusáček K., Stuchlý V.: Increasing of carbon monoxide methanation rate by forced feed composition cycling. *Catal. Today* 25(2), 169-174 (1995).
10. Ponec R., Uhlík F., Cooper D. L.: Population analysis of pair densities. A study of basic set dependence. *Croat. Chim.* 68(1), 149-155 (1995).
11. Ponec R., Bochicchio R.: Nonlinear population analysis from geminal expansion of pair densities. *Int. J. Quant. Chem.* 54, 99-105 (1995).
12. Vít Z., Portefaix J. L., Zdražil M., Breyse M.: Ketones formation during ethylene hydroformylation over sulfided Rh, Ir and NiMo carbon supported catalysts. *Catal. Lett.* 32(1), 55-59 (1995).
13. Vít Z., Gulková D., Novák M.: Preparation of alumina supported Mo catalysts from Mo blue precursor. *React. Kinet. Catal. Lett.* 55(1), 221-226 (1995).
14. Cooper D. L., Ponec R., Thorsteinsson T., Raos G.: Pair populations and effective valencies from ab-initio SCF and spin-coupled wavefunctions. *Int. J. Quant. Chem.* (in press).
15. Frimmel J., Zdražil M.: Comparative study of the activity and selectivity of transition metal sulfides in parallel hydrodechlorination of dichlorobenzene and hydrodesulfurization of methylthiophene. *J. Catal.* (in press).
16. Hillerová E., Zdražil M.: Effect of loading on hydrodesulfurization activity of Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/C sulfide catalysts prepared by slurry impregnation with molybdic acid. *Appl. Catal. A* (in press).
17. Jiráťová K., Morávková L., Urbanová M., Víték J., Pola J.: Laser induced oxidative coupling of methane. *Catal. Lett.* (in press).
18. Jiráťová K., Morávková L., Malecha J., Koutský B.: Perovskites on ceramic foams as catalysts for combustion of methane. *Collect. Czech. Chem. Commun.* (in press).

19. Klusáček K., Hudgins R. R., Silveston P. L.: Forced feed composition cycling of the catalytic reaction with the steady-state multiplicities. *AIChE J.* (in press).
20. Ponec R., Jug K.: Pair population analysis. A new way of visualization of molecular structure. *Int. J. Quant. Chem.* (in press).
21. Šolcová O., Schneider P.: Extra-column effects in determination of rate parameters by the chromatographic technique. *Collect. Czech. Chem. Commun.* (in press).

#### Review papers

22. Schneider P.: Adsorption isotherms of microporous-mesoporous solids revisited. *Appl. Catal. A* 129(2), 157-165 (1995).

#### Monographs

23. Ponec R.: Molecular similarity and LFER. Molecular similarity and reactivity from quantum chemical to phenomenological approaches (Ed. R. Carbo), Kluwer, p. 303-309 (1995).
24. Ponec R.: Similarity models in the theory of pericyclic reactivity. *Topics in Curr. Chem.* 174, 1-26, Springer Verlag, Heidelberg (1995).
25. Ponec R.: Overlap determinant method in the theory of pericyclic reactions. *Lecture Notes in Chemistry Vol. 65*, Springer Verlag, Berlin Heidelberg, 130 p. (1995).
26. Kraus M.: Substituent effects. *Handbook of Heterogeneous Catalysis*, Chapter 5.3.1, Verlag Chemie, Weinheim (in press).
27. Kraus M.: Dehydrogenation of Alcohols. *Handbook of Heterogeneous Catalysis*, Chapter 4.3.3, Verlag Chemie, Weinheim (in press).
28. Kraus M.: Elimination and addition reactions. *Handbook of Heterogeneous Catalysis*, Chapter 4.8, Verlag Chemie, Weinheim (in press).

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29. Czakoová M., Čapka M., Hillerová E., Anderson C.: Catalytic activity of rhodium complexes immobilized to phosphinated poly(trimethylolpropane trimethacrylate). XIth FEICHEM Conference on Organometallic Chemistry, Poster p. 125, Parma, Italy, September 10-15 (1995).
30. Čapek P.: Dynamika vícesložkové difuze a reakce v porézní tabletě katalyzátoru. Dynamics of multicomponent diffusion and reaction in porous catalyst pellet. 22. konference Slovenskej spoločnosti chemického inžinierstva, Vyhne, Slovensko, May 30-June 1 (1995).
31. Frimmel J.: Parallel hydrodechlorination and hydrodesulfurization over carbon supported metal sulfides. 3rd Pannonian Internat. Symposium on Catalysis, P 10, Velem, Hungary, July 6-9 (1995).
32. Hillerová E., Zdražil M.: Preparation of molybdenum catalysts by new slurry impregnation method: Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/C sulfide hydrotreating catalysts. Proc. EUROPACAT-II, 2nd European Congress on Catalysis, P. 57, Maastricht, The Netherlands, September 3-8 (1995).
33. Hillerová E., Zdražil M.: Preparation of molybdena catalysts by new slurry impregnation method: Mo/Al<sub>2</sub>O<sub>3</sub> and Mo/C sulfide hydrotreating catalysts. Proc. of 3rd Pannonian Internat. Symposium on Catalysis, P15, Velem, Hungary, July 6-9 (1995).
34. Jirátová K., Morávková L.: Catalytic combustion of methane. 1st World Conference on Environmental Catalysis, P. 523, Pisa, Italy, May 1-5 (1995).

35. Jiráťová K., Morávková L.: Katalytické spalování methanu. Catalytic combustion of methane. 22. konfer. Slovenskej spoločnosti chemického inžinierstva, Zborník s. 118, Vyhne, Slovakia, May 30-June 1 (1995).
36. Jiráťová K., Morávková L., Urbanová M., Vítek J., Pola J.: Laser induced oxidative coupling of methane. 3rd Pannonian International Symposium on Catalysis, P 08, Velem, Hungary, July 6-8 (1995).
37. Jiráťová K., Morávková L.: Catalytic combustion of VOC in the presence of heterogeneous catalysts. 2nd European Congress on Catalysis Europacat-II, Book of Abstracts P. 286, Maastricht, The Netherlands, September 3-8 (1995).
38. Klusáček K., Čapek P.: Regeneration of hydrodesulphurization catalyst using continuous belt regenerator. 1st World Conf. Environmental Catalysis, P. 471, Pisa, Italy, May 1-5 (1995).
39. Ponec R.: Similarity ideas in the theory of pericyclic reactions I and II. Girona Summer School on Molecular Similarity, Girona, Spain, July 17-19 (1995).
40. Ponec R.: Electron correlation in allowed and forbidden pericyclic reaction of pair densities a similarity approach. 2nd Girona Seminar on Molecular Similarity, Girona, Spain, July 20-22 (1995).
41. Vít Z., Gulková D.: Alumina supported Mo sulfide catalysts from molybdenum blue precursor. Proc. Europacat-II, 2nd European Congress on Catalysis, P. 54, Maastricht, The Netherlands, September 3-8 (1995).

## Department of Multiphase Reactors

Head: J. Drahoš  
Deputy: J. Zahradník  
Research staff: M. Fialová, V. Pěnkavová, M. Punčochář, J. Slezák, M. Růžička, V. Sobolík,  
J. Tihon, O. Wein, J. Wichterlová, K. Wichterle  
Part time: P. Mitschka, J. Vrba  
Technical staff: S. Nováková, A. Zemek (part time)

### Fields of research

- Hydrodynamics and transport phenomena in different types of gas-liquid, liquid-solid or gas-liquid-solid reactors
- Flow of microdispersions and liquids with complex rheological behaviour
- Electrodiffusion diagnostics of flow
- Relation of fractal objects and fuzzy sets

### Applied research

- Removal of heavy metals from waste waters

### Research projects

#### Spatiotemporal dynamics of two-phase chemical reactors

(J. Drahoš, joint project with ICTP; supported by GA CR)

Methods of deterministic chaos were used to analyse the dynamics of wavy film flow and horizontal gas-liquid flow. In the former case, the stability of periodic two-dimensional waves was studied on the liquid film flowing along an oscillating vertical and inclined wall. Depending on the frequency of oscillations, quasiperiodic and chaotic modes were obtained confirming thus a subharmonic instability of the periodic waves. In the latter case, the deterministic chaos was diagnosed within the transitions plug-slug and slug-annular flow [Refs. 2, 13, 14, 15, 21, 29].

#### Chaotic hydrodynamics of bubble columns

(J. Drahoš, supported by GA CR)

Dynamics of bubble formation at a single orifice above a gas chamber was studied by using pressure fluctuations in the chamber. Analysis of the recorded time series showed complicated modes of bubbling ranging from periodic over intermittent to chaotic and random structures [Refs. 17, 34].

**Utilization of coal based materials for removal of heavy metals from waste solutions**  
(J. Drahoš, supported by the Ministry of Environment)

Combustion of metal-loaded low rank brown coal was studied in the classical and recirculating fluidized bed. Attention was paid to the distribution of heavy metals to the slug, ash, and flying ash.

**Application of fuzzy sets for identification of fractal structures**  
(M. Punčochář)

The methodology of fuzzy analysis was applied to the case of self-similar geometrical objects. It was shown that there exists a wide class of fuzzy subsets which can be represented by Cantor sets. A method for decomposition of aggregated fuzzy subsets formed by a superposition (generally non-linear) of two fuzzy quantities was proposed. [Refs. 18, 23, 24]

**Experimental and theoretical study of nonstationary flows through selected singularities**

(V. Sobolík, joint project with CTU, Faculty of Mechanical Engineering; supported by GA CR)

Pulsating flow in a sudden enlargement represents a paradigm of many important situations, e.g. flow in blood vessels. The wall shear stress vector was measured by using a three-segment electrodiffusion probe. Preliminary experiments have shown the existence of stagnation points and recirculation regions. The dependence of the shear stresses on the frequency and amplitude of the flow rate fluctuations has been studied.

**Study of Taylor-Couette instability using three-segment electrodiffusion probe**  
(V. Sobolík, supported by GA CR)

Both azimuthal and axial components of the shear rate were measured by means of a recently developed three-segment electrodiffusion probe, flush-mounted in the wall of the outer steady cylinder. The axial dependence of these components was scanned by sweeping the vortices along the probe by superposed slow axial flow. [Refs. 1, 7, 28]

**Electrochemical sensors for flow measurements**

(V. Sobolík, COST project supported by the Ministry of Education)

Electrodiffusion technique (three-segment probes, software and hardware) has been developed and applied in different flow situations (sudden expansion and contraction, Taylor-Couette flow, impinging jet).

**Transport phenomena in impinging jet**

(V. Sobolík, joint project with CTU, Faculty of Mechanical Engineering; supported by GA CR)

Mass transfer and shear rate in the vicinity of the stagnation point in an impinging jet have been studied using the electrodiffusion diagnostics. Comparison has been made with numerical solutions and experimental results obtained by naphthalene method.

**Apparent wall slip in microdisperse liquids**

(O. Wein, joint project with ICTP and the Institute for Hydrodynamics of ASCR; supported by GA CR)

The apparent slip effect has been studied by using the commercial rotational rheometer RheoStress RS100. The device was recalibrated by using an original computer-aided approach (so-called local filtering), and the necessary software was debugged and tested. The system with coaxial disks is proven to be capable of measuring the strong apparent wall slip effect.

**Dynamics of concentration boundary layer under fluctuating flow**

(O. Wein, supported by GA ASCR)

A new local-similarity theory of the dynamics of the concentration boundary layer successfully predicts the response of electrodiffusion probes in fluctuating flows. The suggested indirect calibration procedure (response to the potential step) was successfully applied for testing the propellers in high-speed centrifugal pumps [Ref. 25].

**New polymers; determination of oxygen permeability**

(K. Wichterle, joint project with ICTP and Inst. Macromol. Chem. ASCR; supported by GA CR)

Transient and steady state mass transfer in the material was examined using the cathodic reduction of oxygen on naked golden electrodes. The method was applied for the evaluation of oxygen permeability in new biocompatible materials.

**Rotational flows of gas - liquid systems**

(K. Wichterle, supported by GA CR)

Circulation of bubbles in impeller induced flow and periodic formation of gas cavities at the impeller blades has been studied. New criteria were suggested for modelling the processes in aerated agitated vessels. [Refs. 9, 10, 26]

**Electrodiffusion diagnostics of high shear rate flows**

(K. Wichterle, supported by GA ASCR)

Extremely high shear rates in liquids have been realized on high speed rotating bodies. Electrodiffusion measurement has confirmed the validity of the laminar boundary layer theory in the corresponding range of variables and can also be used for investigating the effect of turbulence. The method has been applied in the research of shear rates in centrifugal pumps.

**Determination of mass transfer capacity of gas-liquid reactors with ejector gas distributors**

(J. Zahradník, joint project with ICTP; supported by the GA CR)

The effect of ejector configuration on the gas suction rate and on the values of gas holdup in an ejector loop reactor was examined. Experimental evidence demonstrated an essential effect of swirl installation on the mechanism of gas-liquid dispersion formation in the ejector and accordingly on the ejector performance. Correlation of gas holdup data proved adequacy of the slip velocity concept for the description of gas-liquid flow in ejector loop reactors.

**Effect of physical properties of the liquid phase on mass transfer capacity of aerated reactors**

(J. Zahradník, joint project with ICTP; supported by the GA CR).

Experimental evidence proved that the extent of bubble coalescence in aqueous solutions of electrolytes and alcohols can be directly linked with the character of bubble beds containing such solutions and with the values of bubble bed voidage. For all electrolytes studied, the maximum bubble bed voidage was observed at concentrations close to the transition coalescence concentrations of respective electrolytes. The absolute increase of bubble bed voidage was found to be independent of the type of electrolyte and varied only with the mode of gas dispersion. The research project also includes the development and testing of optical light-transmission probes for local measurements in gas-liquid dispersions. [Refs. 4, 11, 31, 32, 35, 36]

**Gas-liquid reactor design and selection for complex rheology fluids in the fine chemicals, bioprocessing and pharmaceutical industries**

(J. Zahradník, COPERNICUS project with UMIST Manchester, UK and the Institute. of



Chemical Engineering, Bulgarian Academy of Sciences Sofia, Bulgaria; supported by the Commission of the European Communities).

Experimental study proved significant effect of bubbling regime variations (homogeneous, transition, and heterogeneous) on the extent of axial mixing in gas and liquid phases in bubble column reactors. Mixing data obtained for both phases in the heterogeneous bubbling regime were adequately described by the model of consecutive circulation cells with backflow between adjacent cells, viewed as a realistic simplified representation of macro-scale flow structures in heterogeneous bubble beds [Ref. 30].

## International cooperations

University of Basilicata, Potenza, Italy: Analysis of chaotic time series

University of Birmingham, Birmingham, UK: Multiphase chemical reactors and bioreactors

Delft University of Technology, Delft, The Netherlands: Chaotic hydrodynamics of bubble columns

University of Hannover, Hannover, FRG: Hydrodynamics of two-phase reactors

University of Tokyo, Tokyo, Japan: Processing of coal sorbents containing heavy metals

Technical University of Munich, Munich, FRG: Shear stresses on rotating bodies

UMIST, Manchester, UK: Gas-liquid reactors for complex rheology fluids

CNRS UPR 15, Paris, France: Electrodiffusion diagnostics of flow

LEGI / IMG, Grenoble, France: Taylor-Couette instabilities

Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, Bulgaria: Gas-liquid reactors for complex rheology fluids

## Visits abroad

J. Drahoš: University of Hannover, Hannover, FRG; Delft University of Technology, Delft, The Netherlands

M. Růžička: University of Birmingham, Birmingham, UK (8 months)

J. Zahradník: University of Birmingham, Birmingham, UK

V. Sobolík: UPR 15, CNRS Paris; LEGI / IMG Grenoble, France; University of Munich, Munich, FRG

K. Wichterle: CNRS, Paris, France; University of Munich, Munich FRG

J. Tihon: IUT, Saint-Nazaire, France (3 months)

## Visitors

S. Ben-Zvi Yona: Ben-Gurion University, Beer Sheva, Israel

J. Chaouki: Ecole Polytechnique, Montreal, Canada

J. Groen: Delft University of Technology, Delft, The Netherlands

M. Letzel: Delft University of Technology, Delft, The Netherlands

C.A.O. Nascimento: University of Sao Paulo, Sao Paulo, Brazil

V. Tovchigrechko: ITMO Minsk, Byelorussia (12 months)

P. Doering (student), TFH Berlin, Berlin, FRG (4 months)  
H. Kuribara (student, IAESTE), Japan (1 month)  
A. Ait Ader, University Tizi Ouzou, Algeria  
A. Alemany, LEGI / IMG Grenoble, France

## Teaching

J. Drahoš: ICTP, postgraduate courses "Applied statistical analysis and data processing" and "Multiphase reactors"  
K. Wichterle: CTU, course "Chemistry"  
K. Wichterle: TU Ostrava, courses "Chemistry" and "Transport Phenomena"  
V. Sobolík: CTU, courses "Fluid mechanics" and "Heat and Mass transfer"  
J. Zahradník: ICTP, postgraduate course "Multiphase reactors"  
O. Wein: TU Brno, postgraduate course "Principles of Rheology"

## Publications

### Papers

1. Cognet G., Martemyanov S., Pascal G., Sobolík V.: Etude d'une interface liquid-liquid par la méthode diffusionnelle. Study of liquid-liquid interface using an electrodiffusional method. C. R. Acad. Sci. Paris 320, Ser. IIB, 505-508 (1995).
2. Drahoš J., Punčochář M., Serio C., Tramutoli V.: Evidence of weak chaos within plug-slug transition in horizontal two-phase flow. Europhys. Letters 30(2), 75-80 (1995).
3. Kuncová G., Zahradník J.: Gas holdup and bubble frequency in a bubble column reactor containing viscous saccharose solutions. Chem. Eng. Process. 34(1), 25-34 (1995).
4. Kuncová G., Fialová M.: Optical oxygen sensor based on metallo-organic compound immobilized by sol-gel technique. Biotechnol. Techniques 9(3), 175-178 (1995).
5. Růžička M., Fridrich M., Burkhard M.: Bacterial colony is not self-similar. Physica A 216, 382-385 (1995).
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## Department of Biotechnology and Environmental Processes

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### Fields of research

- Aerobic bioreactor with immobilized cells - design and scale-up
- Bioremediation of organic pollutants in waste waters
- Detoxification of noxious halogen-containing substances by chemical and biochemical dehalogenation
- Optical fibre sensors for chemical reactors, monitoring of water and soil pollution
- Microwave-induced chemical reactions
- Catalysts for hydrogenation of lipids in cell membranes
- Immobilization of biocatalysts, development of new agents for their chemical bonding to inorganic supports
- Chiral LC phases - their synthesis and performance

### Applied research

- Pilot-scale sorption and biodegradation of PCBs from ground water, performed on an equipment with capacity of 10 m<sup>3</sup> per day [Ref. 4].

### Research projects

#### Materials for chromatographic separation of enantiomers

(M. Čapka, supported by GA CR)

[2-(3-Trimethoxysilylthio)ethyl]diphenylphosphine, a novel silylated phosphine, has been prepared and used for transition metal immobilization to inorganic supports [Ref. 1]. A series of efficient chiral phases has been prepared for enantiomer separation [Ref. 2].

#### Microwave activation of chemical reactions

(M. Hájek, supported by GA CR)

Examination of microwave heating in catalytic reactions proved that heterogeneous reactions were affected by microwaves more than homogeneous ones. It was found that heterogeneous catalysts were activated by microwaves more efficiently than by classical methods. Reactions such as alkylation of sterically hindered amines were therefore activated by microwaves more efficiently than by classical heating. [Refs. 33, 34]

### **Chemical degradation of persistent organic pollutants by catalytic dehalogenation on surfaces of inorganic sorbents**

(V. Pekárek, supported by GA ASCR)

Dehalogenation experiments have been centered on the substances of the type PCB, PCDD, PCDFs by using sheet-like structure of inorganic sorbents within the temperature range of 100-350 °C in a closed system. We have dealt here with the opposite process to the novo-synthetic reactions which take place during incineration [ Refs. 10-12 ].

### **Study of effect of polychlorinated biphenyls on selected technologically important fungi**

(F. Kaštánek, joint project with ICTP; supported by the Ministry of Education)

Accumulation of PCBs on selected types of food fungi of the strain *Penicillium* has been studied. Significant adhesion was found for all the sorts of food fungi, which is important with regard to the participation of these pollutants in food chains. Although efficient for PCBs sorption from solutions, fungi do not biodegrade these pollutants (in contrast to, e.g., white rot fungi). Several other techniques of PCBs disposal, including study of bioreactors and biocatalyst immobilization have been reported [ Refs. 6, 8, 13, 17, 23].

### **Model of movement of solid particles under the condition of creeping flow of liquid in a pipeline network: simulation of the model of flow of blood particles in tissues**

(F. Kaštánek, supported by GA CR)

A novel method for the simulation of the drift and rotation of particles in a viscous liquid near the walls has been developed using Hele-Shaw probe with slanted walls [Refs. 15, 22].

### **Bioreactor technique of production of diagnostic monoclonal antibodies**

(F. Kaštánek, joint project with the Institute of Molecular Genetics ASCR; supported by GA CR)

A new type of bioreactor packed with a layer of the support of hybridomal cells and medium circulation was studied, using hybridom PVA 187 and glass rings SIRAN as models. The reactor suppresses negative effects of shear stresses on cells growth and quality of antibodies production.

### **Biotransformations of xenobiotics by plant tissue-cultures**

(F. Kaštánek, joint project with the Institute of Organic Chemistry ASCR and with the Institute of Experimental Botany ASCR; supported by GA CR)

A new type of submersion bioreactor with circulating medium, utilizing the sorption ability of root cultures, was found to give, under sterile conditions, a favourable biomass breeding and showed long-time performance and high efficiency in ground water decontamination.

### **Complex method of biodegradation of polychlorinated hydrocarbons (PCBs) in soils and ground water**

(G. Kuncová, joint project with ICTP, supported by GA CR)

A novel method for bioremediation of soils and ground water contaminated with PCBs and oil pollutants was developed and applied with success in field experiments [Ref. 4].

### **Ecology 2 - monitoring and optical fibre sensors**

(G. Kuncová, supported by the Ministry of Defence)

In developing optical fibre sensors of organophosphates with evalescent field detection, suitable enzymes were immobilized by sol-gel technique. Lipases and cholinesterases were immobilized both in bulk and as thin layers of organo-inorganic matrices. The activity of the enzymes was preserved in all steps of the sol-gel process. The process was modified for the on-line coating of optical fibres [Ref. 7].

### **International cooperations**

Lajos Kossuth University, Debrecen, Hungary: Ligands for biocompatible hydrogenation catalysts

University of Rostock and Max Planck Gessellschaft Arbeitsgruppe Asymmetrische Katalyse, Rostock, FRG: Synthesis of new chiral phases

University of Lund, Lund, Sweden: Synthesis of heterogenized catalysts bonded to poly-(methacrylates)

E.N.C.S. de Montpellier, Montpellier, France: Synthesis of new biologically active substances, telomerization

University of Padova, Padova, Italy: Immobilization of enzymes by a sol-gel process

### **Visits abroad**

M. Čapka: University of Rostock and MPG Arbeitsgruppe Asymmetrische Katalyse, Rostock, FRG (1.5 months)

M. Čapka: University of Lund, Lund, Sweden (2 months)

J. Čermák: Institute of Chemistry, Academia Sinica, Beijing, China

### **Visitors**

J. Chaouli: BIOPRO, Engineering Reasearch Centre, Montreal, Canada

J.A.C. Teixeira: University of Minho, Minho, Portugal

### **Teaching**

J. Hetflejš: ICTP, postgraduate course "Organometallic Catalysis"

F. Kaštánek: University of Pardubice, Pardubice and ICTP, courses "Bioengineering"

## Publications

### Papers

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14. Šabata S., Včelák J., Hetflejš J.: Biphasic reduction of heptanal and cyclohexanone by sodium formate catalyzed by ether-phosphine ruthenium(II) complexes. *Collect. Czech. Chem. Commun.* 60(1), 127-136 (1995).
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### Fields of research

- Gas-solid reactions
- Gas-solid reactors and operations
- Gas fluidized beds
- Environmental protection
- Laser induced chemistry
- Laser induced chemical vapour deposition (CVD) of novel materials
- Atmospheric chemistry: reactions of ozone with olefinic pollutants
- Experimental study of thermodiffusiophoresis in multicomponent mixtures
- Synthesis of nanoparticles via aerosol process
- Particulate emissions from combustion processes
- Transfer processes in dispersed systems

### Applied research

- Know-how for the combustion of waste organic materials in fluidized bed [Refs. 12, 13]

### Research projects

#### **Interrelationships among the main pollutants in the fluidized bed combustion** (M. Hartman, supported by GA CR)

The axial temperature and concentration profiles of methane, oxygen, carbon dioxide and carbon monoxide in an afterburner chamber equipped with a natural gas burner were measured as functions of the throughput and excess air ratio. A simplified model of the unit was developed which includes the two-step combustion kinetics of methane. Aside from carbon monoxide, formaldehyde and acrolein are among the products formed at low temperature and low stoichiometric air ratio [Ref. 13].

**Thermal decomposition of dolomitic hydrated limes**

(M. Hartman, supported by GA CR)

The measured data were examined empirically by fitting to the  $n$ -th order rate equation of the Arrhenius type, and the kinetic parameters were estimated. A kinetic model has been proposed to correlate the experimental data with the specific surface area of solids. Comparison of the results indicates that particles of magnesium oxide exhibit a surface area which is half an order of magnitude greater than that of calcium oxide sintered under the same conditions [Ref. 26].

**Detection and predicting of different states of fluidization**

(V. Veselý, supported by GA ASCR)

The project is an experimental as well as theoretical effort to explore the intricate hydrodynamic behaviour of larger beds of solid particles fluidized with a gas. Pressure fluctuations have been measured at different positions in a bed by means of sensitive pressure probes. The resultant time series have been analyzed off-line by evaluating their auto-correlations, power spectral density functions and probability density.

**Fuel reactivity and release of pollutants**

(K. Svoboda, supported by the EC in the program PECO: JOU II-CT 92-0037)

A unique experimental facility with a pressurized fluidized bed has been constructed [Refs. 40-43]. The dependence of the  $\text{NO}_x$  and  $\text{N}_2\text{O}$  emissions released by combustion in the pressurized fluidized bed have been explored on such factors as operating conditions (temperature, excess air, pressure) and types of functional bonds of nitrogen in the liquid or solid fuel.

**Emissions of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  in combustion of selected liquid organic compounds, fuels and wastes in pressurized fluidized bed**

(K. Svoboda, supported by the Ministry of Environment)

The experimental apparatus with a pressurized fluidized bed (PFB) has been used for study of relations among experimental conditions of PFB combustion, types of functional nitrogen bonds and nitrogen oxides emissions. Possibilities of co-combustion of coal with nitrogen and/or chlorine containing waste materials have been investigated as well as the effects of nitrogen and chlorine content, catalytic effects of fluidized bed particles and addition of limestone on  $\text{CO}$ , chlorine and nitrogen oxide emissions [Refs. 40-43].

**Studies of atmospheric chemistry and air pollution**

(J. Pola, joint project with the Hebrew University of Jerusalem; supported by the Agency for International Development, Washington, USA)

Initial studies on reaction of ozone with 1-hexene at ppm level in nitrogen atmosphere and air have been carried out in the absence and presence of laser radiation in order to identify products at ambient and increased temperature. The studies are to be extended to 2,3-dimethylbutene.

**SiC chemical vapour deposition via IR laser induced decomposition of silacyclobutane and 1,3-disilacyclobutane**

(J. Pola, joint project with Bergische Universität, Wuppertal; supported by Volkswagen Stiftung FRG)

IR laser induced decomposition of the title compounds was studied at various parameters of laser radiation and found to yield polycarbosilane or  $\alpha$ -SiC:H films. The technique is promising for low temperature chemical vapour deposition of SiC-based materials [Refs. 8, 14, 15].

**Laser chemistry of sila- and disilacyclobutanes for CVD of novel materials**

(J. Pola, supported by GA CR)

IR laser induced decomposition of a series of silacyclobutanes with various substituents at silicon, as well as that of 1,3-disilacyclobutane was revealed to be a very efficient way for chemical vapour deposition of novel organosilicon polymers. The same applies to photolytic decomposition of the silacycles induced by ArF laser [Refs. 22, 23].

**Laser thermolysis of pyridine for CVD of polypyridine films**

(J. Pola, supported by GA CR)

CW CO<sub>2</sub> laser photosensitized decomposition of pyridine in the gas phase was observed to be dominated by dehydrogenative coupling of the heterocyclic rings, and to represent a convenient process for chemical vapour deposition of polypyridine films [Ref. 11].

**Reactive organogermanium films by laser induced decomposition of methyl-(methoxy)germanes in the gas phase**

(J. Pola, supported by GA ASCR)

Organooxogermanium coatings were chemical vapour deposited via IR laser induced decomposition of methyl(methoxy)germanes. The process represents the first successful approach to preparation of polyorganooxo-materials. [Refs. 2, 3]

**Laser chemistry of organosilicon compounds for preparation of novel materials**

(J. Pola, supported by GA ASCR)

Laser induced decomposition of various organosilicon compounds in the gas phase has been carried out to generate, for the first time, very unsaturated organosilicon transients (bis-(ethynyl)silene, ethenylsilene, methyl(hydroxy)silylene, chlorosilyne, etc.) which undergo very efficient polymerization. The technique is a unique approach for CVD of novel organosilicon materials with potential application in microelectronics and catalysis. [Refs. 1, 6, 17, 28]

**Gas phase synthesis of ultrafine particles**

(J. Smolík, supported by GA ASCR)

Synthesis of nanoparticles via aerosol process has been investigated with tetraethylorthosilicate (TEOS) as a precursor. The investigations included oxidation of TEOS vapour in a tube reactor, excimer laser (ArF) photolysis of TEOS vapour and CO<sub>2</sub> laser pyrolysis. The oxidation produced spherical nanoparticles of silica [Refs. 10, 20]. In the photolysis spherical particles of new phase Si/C/O were obtained [Refs. 19, 34].

**Emission fluxes of heavy metals in the fluidized bed combustion of fossil fuels**

(J. Smolík, supported by GA CR)

The project represents both experimental and theoretical effort aimed at solving important relationships in the complex processes of combustion, formation and behaviour of metal pollutants within a fluidized bed and in flue gas cleaning units. Special attention has been devoted to the mechanism of formation of ultrafine particles enriched by toxic elements and organic pollutants. Main part of the measuring device was acquired and the experimental apparatus has been built up [Ref. 38].

**Mass transfer from evaporating droplet**

(J. Schwarz, supported by GA ASCR)

A new mass transfer correlation based on a new definition of the Sherwood number has been proposed including mass transfer due to non-isothermal diffusion, radial efflux of vapour, and

thermal diffusion [Ref. 5]. The effect of individual contributions to the mass transfer was investigated during the evaporation of water and methanol droplets [Ref. 35].

### **Homogeneous nucleation in gaseous phase**

(V. Ždímal, J. Smolík)

The project dealt with the experimental study of homogeneous nucleation in supersaturated vapours of organic substances using a static thermal diffusion chamber. The steps involved were: a) testing of the newly developed method of measurement [Refs. 36, 39, 44, 45], b) comparison with other experimental techniques, and c) testing of the existing nucleation theories.

### **Thermodiffusiophoresis of aerosol particles**

(J. Smolík, V. Ždímal)

A unique technique has been developed that allows to study simultaneous phoresis and droplet growth for arbitrary Knudsen number. The technique has been used for experimental verification of various theories of thermodiffusiophoresis [Refs. 9, 25, 37].

## **International cooperations**

University College London, London, UK: Settling of nonspherical particles

University of Connecticut, Storrs, USA: Reactivity of solids

Delft University of Technology, Delft, The Netherlands: Circulating fluidized beds

Technical University Cottbus, Germany: Pressurized Fluidized Bed Combustion

Institute of Physical Chemistry, Warsaw, Poland: Special regimes of fluidization

The Hebrew University of Jerusalem, Israel: Studies of atmospheric chemistry and air pollution

Bergische Universität, Wuppertal, FRG: IR laser chemical vapour deposition of SiC

Sussex University, Brighton, UK: Siladerivatization of fullerenes

The Glasgow University, Glasgow, UK: IR laser degradation of fluoropolymers

Instituto de Estructura de la Materia, CSIC Madrid, Spain: IR laser deposition of SiC

City University of New York, New York, USA: Laser-produced catalytically active films

Bhabha Atomic Research Centre, Bombay, India: Laser-induced chemistry

Institute of Petrochemical Synthesis, Moscow, Russia: Laser decomposition of silacycles

Centre of Molecular and Macromolecular Studies, Lodz, Poland: Laser generation of silicon containing transients

Fraunhofer Institute for Toxicology, Hannover, FRG: Homogeneous nucleation at higher nucleation rates

Philipps-University Marburg, Marburg, FRG: Experimental study of homogeneous nucleation in supersaturated vapours

University of Helsinki, Helsinki, Finland: Condensation processes as a part of gas-to-particle conversion

## **Visits abroad**

J. Pola: Institute of Materials and Chemical Research, Tsukuba, Japan (1 month)

J. Pola: Bhabha Atomic Research Centre, Bombay, India

V. Ždímal: University of Helsinki, Helsinki, Finland (1 month)

K. Svoboda: Technical University of Tampere, Tampere, Finland

## Visitors

C. Crowley: Sussex University, Brighton, UK (3 weeks)  
A. Laloeuf (IAESTE): University of Maine, France (1.5 months)  
S.F. Ragona (IAESTE): Queens University, Kingstown, Canada (1.5 months)  
H. Rütter (IAESTE): Universidade de Sao Paulo, Sao Paulo, Brazil (3 months)  
T.A.J. Borgström (IAESTE): Royal Institute of Technology, Stockholm, Sweden (1.5 months)  
F.M.C. Villaginez (IAESTE): University of Bergen, Bergen, Norway, (1.5 months)  
E.A. Volnina: Institute of Petrochemical Synthesis, Moscow, Russia (2 months)  
L.E. Guselnikov: Institute of Petrochemical Synthesis, Moscow, Russia (2 months)

## Publications

### Papers

1. Dřínek V., Bastl Z., Šubrt J., Taylor R., Pola J.: IR laser induced decomposition of tetravinylsilane for chemical vapour deposition of Si/C/H materials. *J. Anal. Appl. Pyrol.* 35, 199-206 (1995).
2. Fajgar R., Bastl Z., Tláškal J., Pola J.: Chemical vapour deposition of germanium-containing films by IR laser-induced decomposition of ethoxy(trimethyl)germane. *Appl. Organometal. Chem.* 9, 667-673 (1995).
3. Fajgar R., Jakoubková M., Bastl Z., Pola J.: Germanium-containing coatings by IR laser-induced decomposition of ethoxy(trimethyl)germane and tetramethylgermane. *Appl. Surf. Sci.* 86, 530-532 (1995).
4. Fajgar R., Vitek J., Pola J., Bastl Z., Tláškal J., Gregora I., McGhee L., Stevenson P. R., Winfield J. M.: IR laser degradation of some fluoro-polymers. *J. Fluor. Chem.* 72(1), 111-116 (1995).
5. Kulmala M., Vesala T., Schwarz J., Smolík J.: Mass transfer from a drop-II. Theoretical analysis of temperature dependent mass flux correlation. *Int. J. Heat Mass Transfer* 38(9), 1705-1708 (1995).
6. Pola J., Parsons J. P., Taylor R.: ArF laser photolysis of tetraethyl- and tetravinylsilane. *J. Organometal. Chem.* 489, C9-C11 (1995).
7. Pola J., Darwish A. D., Meidine M. F., Jackson R. A., Kroto H. W., Abdulsada A. K., Taylor R., Walton D. R. M.: Reaction of [60]fullerene with triethylamine. *Fullerene Sci. Technol.* 3, 299-303 (1995).
8. Pola J., Bastl Z., Šubrt J., Taylor R.: Chemical vapour deposition of polycarbosilanes via ArF laser induced photolysis of sila-, 1-methyl-1-sila-, and 1, 3-disilacyclobutane. *J. Mater. Chem.* 5(9), 1345-1349 (1995).
9. Smolík J., Tříška B., Ždímal V. : Thermodiffusiophoresis and droplet growth in ternary gaseous mixtures. *J. Aerosol Sci.* 26(7), 1055-1061 (1995).
10. Smolík J., Moravec P.: Gas phase synthesis of fine silica particles by oxidation of TEOS vapor. *J. Mater. Sci., Lett.* 14, 387-389 (1995).
11. Urbanová M., Vitek J., Pola J.: Laser powered homogeneous decomposition of pyridine for CVD of polypyridine thin films. *J. Mater. Chem.* 5, 849-851 (1995).

12. Veselý V., Hartman M., Kocurek J.: Tlaková ztráta cyklonu pro separaci tuhých částic ze spalných plynů. Pressure drop of a cyclone used for separating solid particles from combustion gases. *Chem. Prum.* 45/70(2), 58-63 (1995).
13. Veselý V., Hartman M., Trnka O., Fetsch D.: Měření účinnosti spalovací komory při spalování methanu. Measurement of combustion chamber performance in methane combustion. *Chem. Listy* 89(7), 448-460 (1995).
14. Bastl Z., Bürger H., Fajgar R., Pokorná D., Senzlober M., Šubrt J., Urbanová M., Pola J.: IR laser induced decomposition of silacyclobutane and 1,3-disilacyclobutane. *Appl. Organometal. Chem.* (in press).
15. Dhanya S., Kumar A., Vatsa R. K., Saini R. D., Mittal J. P., Pola J.: Time resolved study of the transients produced in the CO<sub>2</sub> and ArF laser flash photolysis of silacyclobutane and 1,3-disilacyclobutane. *J. Chem. Soc., Faraday Trans. I* (in press).
16. Jirátovej K., Morávková L., Urbanová M., Vitek J., Pola J.: Laser induced oxidative coupling of methane. *Catal. Lett.* (in press).
17. Pola J., Bastl Z., Šubrt J., Taylor R.: Laser induced chemical vapour deposition of Si/C/H materials from monoorganosilanes. *J. Mater. Chem.* (in press).
18. Samuni U., Haas Y., Fajgar R., Pola J.: Environmental effects in the formation of the primary and secondary ozonides of ethylene at cryogenic temperatures. *Chem. Phys. Lett.* (in press).
19. Smolík J., Moravec P., Kubát P.: Fine particles synthesis in excimer laser assisted decomposition of tetraethylorthosilicate vapour. *J. Mater. Sci., Lett.* (in press).
20. Smolík J., Moravec P.: Aerosolové procesy pro přípravu práškových materiálů. *Aerosol processes for powder synthesis. Silika* (in press).
21. Trnka O., Hartman M.: Solving unsteady-state models for the rapid gas sorption with nonlinear kinetics. *Comput. Chem. Eng.* (in press).
22. Urbanová M., Volnina E. A., Guselnikov L. E., Bastl Z., Pola J.: Laser powered homogeneous pyrolysis of 4-silaspiro(3,3)heptane. A source of 2-silaallene and its polymer. *J. Organometal. Chem.* (in press).
23. Vatsa R. K., Kumar A., Naik P. D., Upadhyay H. P., Pavanaja U. B., Saini R. D., Mittal J. P., Pola J.: UV spectrum and decay kinetics of transient methylsilene produced in the 193 nm photolysis of gaseous methylsilacyclobutane. *Chem. Phys. Lett.* (in press).
24. Veselý V., Hartman M., Trnka O., Fetsch D.: Performance of the afterburner with a natural gas burner. *Fuel* (in press).
25. Ždímal V., Tříška B., Smolík J.: Experiments on thermodiffusiophoresis of droplets in gaseous mixtures. *Colloids Surf.* (in press).
26. Hartman M., Trnka O., Veselý V., Svoboda K.: Predicting the rate of thermal decomposition of dolomite. *Chem. Eng. Sci.* (in press)

#### Review papers

27. Hartman M., Beran Z., Svoboda K., Veselý V.: Operation regimes of fluidized beds. *Collect. Czech. Chem. Commun.* 60(1), 1-33 (1995).

#### Thesis

28. Dřínek V.: Laserová depozice Si/C/H a Si/O materiálů. Kandidátská disertační práce, AV ČR, Praha. Laser deposition of Si/C/H and Si/O materials. Thesis, ASCR, Prague. 80 pp. (1995).



29. Schwarz J.: Vypařování kapky do vícesložkové plynné směsi. Kandidátská disertační práce, AV ČR, Praha. Evaporation of drop in multicomponent gaseous mixture. PhD Thesis, ASCR, Prague. 116 pp. (1995).
30. Svoboda K.: Vlastnosti a využití vysokoteplotní fluidní vrstvy v metalurgii, při spalování a ochraně ovzduší. Habilitační práce, VŠCHT Praha. Properties and application of high temperature fluidized bed processes in metalurgy, coal combustion and air pollution control. Thesis, ICTP, Prague (1996).

#### Conferences

31. Dříněk V., Bastl Z., Šubrt J., Pola J.: Laser induced CVD of silicon dioxide from triethoxysilane and tetraethoxysilane. 2nd International Conference on Materials Chemistry, Canterbury, UK (1995).
32. Jakoubková M., Bastl Z., Fajgar R., Pola J.: Laser induced chemical vapour deposition of polymeric films from thiophene. 2nd International Conference on Photo-Excited Processes and Applications, Proc. p. 56, Jerusalem, Israel, September 17-21 (1995).
33. Jiráťová K., Morávková L., Urbanová M., Vítek J., Pola J.: Laser induced oxidative coupling of methane. 3rd Pannonian International Symposium on Catalysis, P 08, Velem, Hungary, July 6-8 (1995).
34. Moravec P., Smolík J., Kubát P.: Ultrafine particles synthesis by ArF laser photolysis of TEOS vapor. J. Aerosol Sci. 26, Suppl. 1, S821-S822. Poster. European Aerosol Conference, Helsinki, Finland, September 18-22 (1995).
35. Schwarz J., Smolík J., Kugler J., Egami J.: Evaporation of methanol droplet at high ambient temperatures. J. Aerosol Sci. 26, Suppl. 1, S271-S272. Poster. European Aerosol Conference, Helsinki, Finland, September 18-22 (1995).
36. Smolík J.: Study of condensation processes using static diffusion chamber. Staub und Aerosolkolloquium, Vienna, Austria (1995).
37. Smolík J., Ždímal V., Tříška B.: Thermodiffusiophoresis of DOP droplets in ternary gaseous mixtures DOP vapour-He-H<sub>2</sub>. J. Aerosol Sci. 26, Suppl. 1, S249-S250. Poster. European Aerosol Conference, Helsinki, Finland, September 18-22 (1995).
38. Smolík J., Hartman M., Sýkorová I., Kučera J.: Emission fluxes of heavy metals from the fluidized bed combustion of fossil fuels. J. Aerosol Sci. 26, Suppl. 1, S655-S656. Poster. European Aerosol Conference, Helsinki, Finland, September 18-22 (1995).
39. Smolík J., Ždímal V.: Homogeneous nucleation rate measurements by use of a thermal diffusion cloud chamber. Lecture. Workshop "Nucleation Experiments, State of the Art and Future Development", Prague, June 12-15 (1995).
40. Svoboda K., Hartman M., Kocurek J.: Emissions of nitrogen oxides in atmospheric and pressured fluidized bed combustion: Effect of nitrogen functionality, pressure and temperature on NO<sub>x</sub> and N<sub>2</sub>O emissions. Joule II Technical Meeting-Working Party "Pressurized Powder Coal Combustion", Budapest, Hungary, January 23-24 (1995).
41. Svoboda K., Hartman M.: An apparatus for combustion of liquid and solid fuels in a pressurized fluidized bed. The 22nd Conference of SSCHI, Vyhne, Slovakia, May 30-June 1 (1995).
42. Svoboda K., Hartman M., Kocurek J.: Pressurized fluidized bed combustion of model organic liquid mixtures containing pyridine, pyrrole and aniline as sources of organic nitrogen. Effect of total pressure, catalytic properties of quartz sand, lime/limestone and ceramsite, partial pressure of oxygen and carbon dioxide on conversion of organic nitrogen to NO<sub>x</sub> and N<sub>2</sub>O. The Joule II Meeting, Heidelberg, FRG, May 15-16 (1995).
43. Svoboda K., Hartman M., Čermák Ji., Kocurek J., Veselý V., Trnka O.: Formation and destruction of NO and N<sub>2</sub>O in pressurized fluidized bed combustion of model liquid

- organic mixtures containing nitrogen: Effect of nitrogen functionality, pressure, temperature, CO<sub>2</sub> and oxygen on emissions of NO and N<sub>2</sub>O. Internat. Conf. on Minimum Emissions Power Production from Fossil Fuels, Firenze, Italy, November 27-28 (1995).
44. Ždímal V., Smolík J., Uchtmann H.: Critical supersaturations of n-propanol vapor in helium. Effect of the total pressure. *J. Aerosol Sci.* 26, Suppl. 1, S625-S626. Lecture. European Aerosol Conference, Helsinki, Finland, September 18-22 (1995).
45. Ždímal V., Smolík J.: Homogeneous nucleation rates of n-propanol. Effect of the total pressure. Lecture. Short Course III: "Metastable Behaviour of Fluids and Critical Phenomena", Prague, October 30-31 (1995).

#### Research reports

46. Aho M., Hartinger K. T., Hernberg R., Richard J. R., Svoboda K., Varhegyi G.: Fuel reactivity and release of pollutants and alkali vapours in pressurized combustion for combined cycle power generation. Final report covering the period January 1, 1993 - December 31, 1995 Contract No. JOU2-CT92-0037. (1995).

## Department of Analytical Chemistry

Head: J. Schraml  
Deputy: J. Horáček  
Research staff: M. Bártlová, V. Blechta, R. Řeřicha, L. Soukupová  
Part time: L. Fiala, R. Komers  
Technical staff: J. Lněničková, V. Zimová

### Fields of research

- NMR spectroscopy
- Chromatographic separation of enantiomers

### Applied research

- Analytical services to research departments of ICPF

### Research projects

#### Multi-Site Excitation in NMR Spectroscopy

(V. Blechta, supported by GA CR)

An analytical description of the time evolution was derived for a two-spin system under selective, on-resonance irradiation of the two spins by amplitude modulated pulses. This particular case represents the most frequent and the most fundamental one occurring in practice. Additionally, the J-doubling method for the estimation of spin-spin coupling constants was improved [Ref. 1].

#### NMR Spectroscopy of Sterically Demanding Silyl Groups

(J. Schraml, supported by GA CR)

A new mechanism of steric effect in  $^{29}\text{Si}$  NMR spectroscopy was discovered and quantified. The new effect is due to solvent association which in turn is controlled by solvent accessible surface of the solute. The new mechanism allows interpretation of the many until now unrelated observations which are of considerable significance in analytical applications [Ref. 9].

#### Materials for Chromatographic Separations of Enantiomers

(M. Bártlová, supported by GA CR)

By the reaction of 3-(isocyanatopropyl)triethoxysilane with chiral aminocompounds, the stationary phases have been prepared and then covalently bonded to silica gel. We have concluded that the dependence of capacity factors on volume fraction of the more polar

component of mobile phase has been related to the normal phase HPLC system dependence [Refs. 2, 7].

### **Photoelectrically Active Polymers : Synthesis, Structure, Stability Passive and Active Physical Properties**

(J. Schraml, joint project with CU; supported by GA CR)

We have participated in NMR structural analysis of prepared polymers, being a part of an extensive research project aimed at studying the photo-conducting polymers. The project includes the preparation and complex characterization of materials studied by various physical and physico-chemical methods.

### **International cooperations**

University of Ghent, Ghent, Belgium: Study of Neurotoxins as Food Contaminants

University of Rostock, Rostock, FRG: Materials for chromatographic separation of enantiomers

### **Visits abroad**

J. Schraml: Visiting professor at the University of Ghent, Ghent, Belgium (3 months)

### **Teaching**

J. Schraml: CU, course "NMR Spectroscopy"

R. Řeřicha: ICTP, postgraduate course "Chemical Spectroscopy"

### **Publications**

#### Papers

1. Blechta V., Schraml J.: Selective On-Resonance double-pulses applied on IS spin system. *J. Magn. Reson. A* 112, 30 (1995).
2. Čapka M., Bártlová M., Krause H. W., Schmidt U., Fischer C., Oehme G.: Efficient preparation of supports for enantioselective separation. *Amer. Biotech. Laboratory* (April), 13-14 (1995).
3. Kubec R., Velíšek J., Kvíčalová M., Čermák Jan, Schraml J.: <sup>29</sup>Si and <sup>13</sup>C NMR spectra of t-butyltrimethylsilyl derivatives of amino acids. *Magn. Reson. Chem.* 33, 458-460 (1995).
4. Čermák Jan, Kvíčalová M., Blechta V., Čapka M., Bastl Z.: Hydrogenation catalytic activity of substituted cyclopentadienyl titanium complexes anchored on polysiloxanes prepared by a sol-gel procedure. *J. Organomet. Chem.* (in press).
5. Sovová H., Jež J., Bártlová M., Šťastová J.: Supercritical carbon dioxide extraction of black pepper. *J. Supercrit. Fluids* 8(4), 295-301 (1995).

6. Šťastová J., Jež J., Bártlová M., Sovová H.: Rate of vegetable oil extraction with supercritical CO<sub>2</sub>. III. Extraction from sea buckthorn. Chem. Eng. Sci. (in press).

#### Conferences

7. Bártlová M., Čapka M., Fischer C., Oehme G., Popl M.: Úloha selektoru stacionární fáze při enantioselektivní HPLC. 49. Zjazd chemických spoločností, Zborník príspevkov, s. 122-123 (Poster A-P013), Bratislava, Slovakia, September 4-7 (1995).
8. Čermák Jan, Kvíčalová M., Blechta V., Čapka M.: Synthesis and catalytic properties of polysiloxane-supported pentamethylcyclopentadienyl titanium, rhodium, and iron complexes. 6th IUPAC International Symposium on Macromolecule-Metal Complexes, Poster p. 139, Guangzhou, China, November 2-5 (1995).
9. Kvíčalová M., Blechta V., Čermák Jan, Kobyleczyk K., Piekos R., Schraml J.: <sup>29</sup>Si NMR chemical shifts in trimethylsilyl and tert-butyldimethylsilyl derivatives. XIth FECHEM Conference on Organometallic Chemistry, Poster p. 203, Parma, Italy, September 10-15 (1995).

## Miscellaneous

### Organization of International Conferences and Scientific Meetings

International Workshop “Molecular Physics of Liquids - State-of-the-Art”, Abertamy, Czech Rep., September 8-10, 1995

International Workshop “Nucleation Experiments - State of the Art and Future Development”, Prague, June 12-15, 1995

### Memberships in Editorial Boards

K. Jeřábek: “Reactive and Functional Polymers”

T. Boublík: “Molecular Physics”

I. Wichterle: “ELDATA: International Electronic Journal of Physico-Chemical Data”

I. Wichterle: “Fluid Phase Equilibria”

M. Kraus: “Reaction Kinetics & Catalysis Letters”

M. Zdražil: “Applied Catalysis”

K. Klusáček: “Inovační podnikání a transfer technologií” P. Mitschka: “Collection of Czechoslovak Chemical Communications”

J. Hetflejš: “Collection of Czechoslovak Chemical Communications”

J. Hetflejš: “Chemické listy”

Notes: