

Academy of Sciences of the Czech Republic

**Institute of Chemical Process
Fundamentals**

Prague

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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. 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 11)
Department of Catalysis and Reaction Engineering (page 17)
Department of Multiphase Reactors (page 24)
Department of Biotechnology and Environmental Processes (page 30)
Department of Reaction Engineering in Gas Phase (page 37)
Department of Analytical Chemistry (page 45)

STAFF

(31 December 1994)

Category	Number of Employees
Research	92
Technical	20
Administrative	18
Services	24

BUDGET 1994

(in thousands of Kč; 26 Kč = 1 US\$, approx.)

Institutional support from the National Budget	30 766
Research funds from Grant Agencies	13 353
Contracts with industry	889
Total	45 008

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
ICTP	Institute of Chemical Technology, Prague
CTU	Czech Technical University, Prague
CU	Charles University, Prague

Department of Diffusion and Separation Processes

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

Fields of research

- Transport properties of gases in polymer membranes in the course of their plasticization and swelling; methods for preparation and characterization 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 phenols from coal tars
- Extraction from ground plant materials with supercritical carbon dioxide; solubilities of solids and liquids in dense carbon dioxide

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.

Effect 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 the 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. 4]. 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.

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 Ministry of Environment CR)

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.

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. 20]. 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 the pores with diameter approx. 10 nm [Ref. 16].

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. The results obtained suggest that copolymerization of SSC with styrene and DVB does not provide polymers composed of randomly alternating monomer units but rather copolymers consisting of functionalized and unfunctionalized domains. These domains result from a possible phase separation of SSC-rich domains due to the strong mutual interaction of the functional monomer molecules or polymer segments [Ref. 15].

Polymer-supported catalysts

(K. Jeřábek, joint project with the University of Padua, Italy; Cooperation project CNR/ASCR 1992-94)

A series of differently crosslinked polyacrylamide resins was examined with two conceptually and experimentally quite independent methods which are able to provide information on the macromolecular structure and chemical accessibility of these materials in the swollen state. Electron spin resonance and inverse steric exclusion chromatography gave quite consistent results in water which were interpreted on the basis of a physico-mathematical model that fits the experimental data nicely [Ref. 14].

Identification of regime of packed gas-liquid flow column

(V. Jiříčný, joint project with ICTP; supported by Ministry of Education CR)

Transient behaviour of hydrodynamics of counter-current packed column (in terms of liquid hold up and pressure drop) was experimentally studied as a response to periodic step changes in gas or liquid flow. Experimental data were fitted to mathematical models [Ref. 35] employed in the control theory. A practical laboratory training of students of the Faculty of Computer and Control Technique on the pilot-plant packed column equipped with sophisticated measuring and computer technique was one of the goals of the project.

Investigation of membrane preparation and characterization and study of factors influencing membrane performance in practical application

(J. Roček; supported by GA CR)

The project solved the problem of preparation and characterization of ceramic membranes made of corundum and γ -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 [Ref. 5]. Permeation method for the characterization of supports and the first supported layer was developed [Refs. 11, 12, 22].

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 [Ref. 19] and sea buckthorn with dense carbon dioxide was investigated. Mass transfer model including the efficiency of grinding and solvent flow inhomogeneity was developed [Refs. 8, 9, 32, 33] and used to describe the changes of extract composition during the extraction of black pepper oleoresin. [see Department of Analytical Chemistry: Refs. 8, 13]

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

(V. Staněk; supported by GA CR)

An experimental set-up has been built consisting of a 200 mm in diameter column equipped with sensitive pressure transducers and a strain gauge capable of monitoring instantaneous values of the pressure profile, apparent liquid hold up and the degree of flooding of the column operated in a quasi-stationary regime [Ref. 30]. The research has been aimed at construction of physical models of complex multiphase systems [Ref. 34].

Transient states of trickle-bed catalytic reactor

(V. Staněk; joint project with ICTP; supported by Ministry of Education CR)

Variety of states of a trickle bed reactor on transition between various hydrodynamic regimes have been experimentally observed and monitored by computing data logger. The obtained profiles were interpreted in terms of simple first-order physical models and deviations from the simplified model explained on the basis of additional qualitative concepts of the flow. The work served as practical training for students with specialized organic technology curriculum.

Participation in project "Supercritical fluid extraction - experiment and modelling" (see E. Hála Laboratory of Thermodynamics) [Ref. 10].

International cooperations

Institut für Thermische Verfahrenstechnik und Umwelttechnik, TU Graz, Austria: Liquid-liquid extraction

University of Padua, Italy: Polymer catalysts

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

Visits abroad

K. Jeřábek: Polymer Institute, Nankai University, Tianjin; Dalian Institute of Chemical Physics, Dalian, China

J. Procházka: Institut für Thermische Verfahrenstechnik und Umwelttechnik, TU Graz, Austria

P. Uchytíl: Institute of Chemistry Beijing, Research Centre for Eco-Environmental Sciences, Beijing; Fudan University, Shanghai; Dalian Institute of Chemical Physics, Dalian, China

Teaching

K. Jeřábek: ICTP, postgraduate course "Preparation and evaluation of heterogeneous catalysts"

V. Jiříčný: ICTP, laboratory training on "Hydrodynamics of packed columns"

Publications

Papers

1. Jeřábek K., Hanková L., Prokop Z.: Post-crosslinked polymer adsorbents and their properties for separation of furfural from aqueous solutions. *React. Polym.* 23, 107-112 (1994).
2. Jiříčný V., Staněk V.: Production of D-arabinose in a pilot-plant fluidized bed electrochemical reactor. *J. Appl. Electrochem.* 24, 930-935 (1994).
3. Nguyen X. Q., Brož Z., Vašák F., Nguyen Q. T.: Manometric techniques for determination of gas transport parameters in membranes. Application to the study of dense and asymmetric poly(vinyltrimethylsilane) membranes. *J. Membr. Sci.* 91, 65-76 (1994).
4. Procházka J., Heyberger A., Bízek V., Koušová M., Volaufová E.: Amine extraction of hydroxycarboxylic acids. 2. Comparison of equilibria for lactic, malic and citric acids. *Ind. Chem. Eng. Res.* 33(6), 1565-1573 (1994).
5. Roček J., Uchytíl P.: Evaluation of selected methods for characterization of ceramic membranes. *J. Membr. Sci.* 89, 119-129 (1994).
6. Schneider P., Uchytíl P.: Liquid expulsion permporometry for characterization of porous membranes. *J. Membr. Sci.* 95, 29 (1994).
7. Sovová H., Komers R., Kučera J., Jež J.: Supercritical carbon dioxide extraction of caraway essential oil. *Chem. Eng. Sci.* 49(15), 2499-2505 (1994).
8. Sovová H., Kučera J., Jež J.: Rate of the vegetable oil extraction with supercritical CO₂. II. Extraction of grape oil. *Chem. Eng. Sci.* 49, 3, 415-420 (1994).
9. Sovová H.: Rate of the vegetable oil extraction with supercritical CO₂. I. Modelling of extraction curves. *Chem. Eng. Sci.* 49, 3, 409-414 (1994).
10. Sovová H., Jež J.: Solubility of menthol in supercritical carbon dioxide. *J. Chem. Eng. Data* 39(4), 840-841 (1994).
11. Uchytíl P.: Gas permeation in ceramic membranes. Part I. Theory and testing of ceramic membranes. *J. Membr. Sci.* 97, 139-144 (1994).
12. Uchytíl P., Brož Z.: Gas permeation in ceramic membranes. Part II. Modeling of gas permeation through ceramic membrane with one supported layer. *J. Membr. Sci.* 97, 145-153 (1994).
13. Vašák F., Brož Z.: Removal of volatile substances from water. *J. Hazard. Mater.* 37(1), 153-164 (1994).

14. 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. Am. Chem. Soc.* 117(5), 1603-1606 (1995).
15. Jeřábek K., Hanková L., Revillon A.: Functional polymers prepared from styrene sulphochloride as the functional monomer. *Ind. Eng. Chem. Res.* (in press).
16. Jeřábek K., Hanková L., Strikowsky A. G., Warshawsky A.: Solvent impregnated resins: Relation between impregnation process and polymer support morphology: I. di-(2-ethylhexyl)dithiophosphoric acid. *React. Polym.* (in press).
17. Jiříčný V., Staněk V.: Preparation of D-arabinose in a laboratory fluidized bed electrode cell. *Collect. Czech. Chem. Commun.* (in press).
18. Nguyen X. Q., Nguyen Q. T., Clement R., Uchytíl P.: Gas-sweeping pervaporation: A method for studying the transport of solvents in polymers. Part 2: Separation of methanol and 1-propanol mixture by cellulose triacetate membrane. *J. Appl. Polym. Sci.* (in press).
19. Sovová H., Jež J., Bártlová M., Šťastová J.: Supercritical carbon dioxide extraction of black pepper. *J. Supercrit. Fluids* (in press).
20. Strikowsky 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.* (in press).
21. Uchytíl P., Essamri A., Nguyen Q. T., Clement R.: Diffusion of acetic acid and water through poly(vinyl alcohol) membranes. Coupling effects. *J. Appl. Polym. Sci.* (in press).
22. 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.* (in press).

Monographs

23. Biffis A., Corain B., Zecca M., Corvaja C., Jeřábek K.: Microporous polymer supports: physico-chemical investigations related to macromolecular structure and molecular accessibility. In: *Syntheses and Methodologies in Inorganic Chemistry "New Compounds and Materials"*, Vol. III, p. 335, S. Daolio, E. Tondello, P. A. Vigato (Eds.), Photograph, Padova (1994).
24. Procházka J., Sovová H., Baird M. H. I., Rama Rao N. V.: *Reciprocating-plate columns. Liquid-liquid extraction equipment*, J. Wiley & Sons (1994).
25. Staněk V.: *Fixed bed operations. Flow distribution and efficiency*. Ellis Horwood series in Chemical Engineering. Ellis Horwood, New York (1994).

Conferences

26. García A., Sovová H., Álvarez A., Kučera J.: Supercritical extraction of lipids from sugar cane by-products. *Symposium on Supercritical Fluids, Strasbourg, 17.-19. 10.* (1994).
27. Jeřábek K.: Polymeric sulphonic acids as catalysts. Invited lecture, Autumn meeting of The Royal Society of Chemistry, Glasgow, Great Britain, September 6-10 (1994).
28. Jeřábek K.: Influence of skeleton structure on application properties of polymer catalysts and adsorbents. Plenary lecture, International Conference on Reactive Polymers, Xi'an, China, October 8-11 (1994).
29. Jeřábek K., Hanková L., Prokop Z.: Post-crosslinked polymer adsorbents and their properties for separation of furfural from aqueous solutions. *POC'94 6th International Conference on Polymer Supported Reactions in Organic Chemistry, Venice, Italy, June 19-23* (1994).

30. Jiříčný V., Staněk V.: Hydrodynamics of packed bed column under unsteady conditions. Konference Řízení procesů 1994, Horní Bečva, ČR, 30. 5.-2. 6. 1994, Conf. Proceedings pp. 183-86, University of Pardubice (1994).
31. Roček J., Syslová V., Vavříčka P., Uchytíl P.: Determination of pore size distribution of membrane support using permeation method. Engineering of membrane processes II. II Ciocco, Italy, April 26.-28. (1994).
32. Sovová H.: Modelling the CO₂ extraction from plant materials. Symposium on Supercritical Fluids, Strasbourg 17.-19. 10. (1994).
33. Sovová H.: Extrakce superkritickým CO₂ v potravinářství-kmín, pepř, oleje. (in Czech) Extraction with supercritical CO₂ in food industry - caraway, pepper, fatty oils. Sborník 21. Konference Slovenské společnosti chem. inženýrství, Proceedings pp. 44-47, Vyhne, 23.-27. 6. (1994).
34. Staněk V.: Mathematical model of cupola. Int. Cupola Conference, Chicago, USA, March 1.-3. (1994).
35. Strnad M., Jiříčný V., Jakeš B., Staněk V.: Comparison of the mathematical models of packed bed column transients. Konference Řízení procesů 1994, Horní Bečva, ČR, 30. 5.-2. 6. 1994, Conference Proceedings pp. 395-98, University of Pardubice (1994).
36. Uchytíl P., Wagner Z., Roček J., Brož Z.: Possibility of pore size determination in separation layer of ceramic membrane using permeation method. Engineering of membrane processes II. II Ciocco, Italy, April 26.-28. (1994).

E. Hála Laboratory of Thermodynamics

Head: I. Wichterle
Deputy: K. Aim
Research Staff: O. Drábek, J. Fárková, J. Kolafa, J. Linek, I. Nezbeda, J. Pavlíček, M. Strnad,
Z. Wagner,
Part time: T. Boublík
Technical Staff: S. Bernatová, J. Wolfová

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 the modelling of supercritical fluid extraction
- Thermodynamic modelling and statistical treatment of experimental thermodynamic data
- Molecular simulations on model fluids
- Formulation of approximate theories of fluids, leading to derivation of bulk thermodynamic models
- Examination of the applicability of the 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 methylacetamide
- Computerized bibliography of vapour-liquid equilibrium data

Research projects

Molecular theory-based equations of state for real fluids

(K. Aim, supported by GA ASCR)

A base of the computer-simulated pseudoexperimental data on the Lennard-Jones fluid has been supplemented and an accurate theoretically based equation of state has been formulated. A semiempirical method improving pure-compound phase equilibrium calculations from pressure-explicit equations of state has been developed. Critically evaluated properties of a series of compounds along their vapour-liquid coexistence locus have been compiled for the evaluation of parameters of intermolecular potentials of the model fluids. [Refs. 6, 25, 34, 35]

Behaviour of fluids of nonspherical liquid molecules

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

The second virial coefficients of the 2-,3-, and 4-centre Lennard-Jones fluids have been evaluated and correlated. A new equation with two geometric parameters accounting for the nonsphericity of a molecule has been developed, allowing simple calculation of the third virial coefficient of prolate and oblate spherocylinders over a wide range of nonsphericity. Promising results for the thermodynamic properties of binary mixtures of n-alkanes calculated from the perturbation theory of the anisotropic molecule fluid have been obtained. [Refs.: 2, 3, 4, 42, 46]

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

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

Experimental set-up for the measurement of saturated vapour pressures by a comparative ebulliometric method has been modified so as to allow experiments (i) over an extended range of temperatures (up to 500 K) and (ii) for substances which are solids at room conditions. Accurate vapour pressures of isomeric chlorobenzonitriles have been determined. Critically evaluated vapour pressure data for selected classes of compounds, important from the environmental viewpoint, have been compiled. [Refs. 1, 15, 16, 36]

Molecular theory of phase behaviour of aqueous solutions and its application

(I. Nezbeda; supported by GA ASCR)

An extended primitive model of water (primitive model with a mean field term) in the mixture with a van der Waals fluid has been used to determine the global phase diagram of aqueous mixtures of nonpolar fluids. The model has been shown to give, without any adjustable parameter, the correct prediction of the phase behaviour of real aqueous mixtures of inert gases and n-alkanes, including the presence/absence of pressure or temperature extreme on critical lines [Refs. 9, 26, 40, 41].

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; a general methodology of computer simulations has been developed, (3) a new theoretically-based and most accurate equation of state to date of the Lennard-Jones fluid has been derived [Refs. 6, 24, 27, 28, 38, 43].

Supercritical fluid extraction - experiment and modelling

(I. Wichterle; supported by GA ASCR)

Gas-liquid equilibrium data for the CO₂ + (ethyl or propyl) ethanoate systems were measured at pressures up to 100 bar and along 3 isotherms. Solubility of menthol in supercritical CO₂ was determined; then, the influence of entrainer on solubility of glycerine, dinonyl phthalate, and squalane was investigated in a newly constructed equipment with extractor. The correlation procedure for fluid phase equilibrium data was generalized for arbitrary analytical equation of state (e.g., the RKS EOS with Kvak-Mansoori mixing rules) [Refs. 14, 30, 31, 45, see Department of Diffusion and Separation Processes, Ref. 10].

Phase equilibria and state behaviour of fluid systems

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

Experiments: Systematic investigation of vapour-liquid equilibria and excess molar volumes in series of systems (alkane + alkanol, naphthene + alkanolate) has been carried out. Data processing: The DISQUAC prediction method was extended by the evaluation of disperse and quasichemical contributions for halogen-carboxyl interaction. Data base: Vapour-liquid equilibrium data bibliography was supplemented by the end of 1993 and published as the book with diskette [Refs. 5, 7, 8, 17-20, 22, 23, 32, 33, 37, 39].

International cooperations

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

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

Visits abroad

O. Drábek: McGill University, Montreal, Canada (4 months, continued)

J. Kolafa: University of Odense, Odense, Denmark (5 months, continued)

I. Nezbeda: Visiting Professor, University of Guelph, Guelph, Canada (8 weeks)

Visitors

A. Dahmani: Université de Science et Technologie in Alger, Alger (2 months, continued)

E. Rezanova: St. Petersburg University, St. Petersburg, Russia (1 month)

H. Vörtler: University of Leipzig, Leipzig, FRG (3 weeks)

Teaching

K. Aim: ICTP, postgraduate course "Applied statistical analysis and data processing"

T. Boublík: CU, courses "Basic physical chemistry", "Advanced chemical thermodynamics", and "Statistical thermodynamics"

I. Nezbeda: CU, courses "Selected topics in theoretical physics", and "Computer simulation - principles and applications"

Publications

Papers

1. Aim K.: A modified ebulliometric method for high-boiling substances: vapour pressures of 2-chlorobenzonitrile and 4-chlorobenzonitrile from 380 K to 490 K. *J. Chem. Thermodyn.* 26, 977-986 (1994).
2. Aim K.: Saturated vapor pressure measurements on isomeric mononitrotoluenes at temperatures between 380 and 460 K. *J. Chem. Eng. Data* 39(3), 591-594 (1994).
3. Boublík T.: Second virial coefficient of the 2cLJ, 3cLJ and 4cLJ molecules. *Collect. Czech. Chem. Commun.* 59 (4), 756-767 (1994).
4. Boublík T.: Third virial coefficient and hard convex body equation of state. *Molec. Phys.* 83, 1285-1297 (1994).
5. 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 (1994).
6. Kolafa J., Nezbeda I.: The Lennard-Jones fluid: An accurate analytic and theoretically-based equation of state. *Fluid Phase Equilib.* 100, 1-34 (1994).
7. 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 (1994).
8. Linek J.: Excess volume of binary liquid mixtures containing ethers, alcohols, esters and alkanes. *ELDATA: Int. Electron. J. Phys.-Chem. Data* 1, 43-52 (1994).
9. Nezbeda I., Smith W. R., Kolafa J.: Molecular theory of phase equilibria in model associated mixtures. I. Binary mixtures of water and a simple fluid. *J. Chem. Phys.* 100, 2191 (1994).
10. Ponec R., Strnad M.: The least motion principle, concertedness and the mechanisms of pericyclic reactions. A similarity approach. *Collect. Czech. Chem. Commun.* 59(1), 75-88 (1994).
11. Ponec R., Strnad M.: On the role of Fermi and Coulomb correlation in pericyclic reactions. *Chem. Papers* 48(2), 72-78 (1994).
12. Ponec R., Strnad M.: Population analysis of pair densities. A link between quantum chemical and classical picture of bonding. *Int. J. Quant. Chem.* 50, 43 (1994).
13. Strnad M., Ponec R.: Novel approach to molecular similarity. 2nd order similarity indices from geminal expansion of pair densities. *Int. J. Quant. Chem.* 49, 35 (1994).
14. Wagner Z., Pavlíček J.: Vapor-liquid equilibrium in the carbon dioxide-ethyl acetate system at high pressure. *Fluid Phase Equilib.* 97, 119-126 (1994).
15. Aim K.: Vapor pressures of 2-chlorotoluene and 4-chlorotoluene and relative volatility in their binary system. *Thermochim. Acta* (in press).
16. Aim K.: Vapour pressures of some linear and branched dialkyl ethers. *Fluid Phase Equilib.* (in press).
17. Bernatová S., Linek J., Wichterle I.: Vapor-liquid equilibria of cyclohexane or methylcyclohexane + alkyl alkanoate systems. *ELDATA: Int. Electron. J. Phys.-Chem. Data* (in press).
18. Fárková J., Linek J., Wichterle I.: Vapor-liquid equilibria of methanol + ether systems. *ELDATA: Int. Electron. J. Phys.-Chem. Data* (in press).
19. Fárková J., Linek J., Wichterle I.: Isothermal vapour-liquid equilibria in the methanol-aliphatic ether systems. *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., Nezbeda I.: The hard tetrahedron fluid: A model for the structure of water? *Molec. Phys.* (in press).

22. Linek J., Wichterle I., Marsh K. N.: Vapor-liquid equilibria in systems containing N-methyl-2-pyrrolidone. *AIChE Symp. Ser.* (in press).
23. Linek J., Wichterle I., Marsh K. N.: Vapor-liquid equilibria in the water-diacetone alcohol, ethyl methanoate-water, and ethyl methanoate-phenol systems. *AIChE Symp. Ser.* (in press).
24. Nezbeda I., Kolafa J.: The use of control quantities in computer simulation experiments: Application to the exp-6 potential fluid. *Mol. Simul.* (in press).
25. Nezbeda I., Aim K.: A general method improving phase equilibrium calculations from pressure-explicit equations of state. *Fluid Phase Equilib.* (in press).
26. 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.* (in press).
27. Nezbeda I., Strnad M.: Monte Carlo simulations in the vicinity of the critical point: vapor-liquid coexistence curve. *J. Chem. Phys.* (in press).
28. Strnad M., Nezbeda I.: Equation of state and chemical potential of ternary mixtures of hard spheres and heteronuclear diatomics. *Molec. Phys.* (in press).
29. 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.* (in press).
30. Wagner Z.: Vapour-liquid equilibrium at high pressure in the system containing carbon dioxide and propyl acetate. *Fluid Phase Equilib.* (in press).
31. Wagner Z.: Vapour-liquid equilibrium in the system containing carbon dioxide and ethyl propanoate. *Fluid Phase Equilib.* (in press).
32. Wolfová J., Linek J., Wichterle I.: Vapor-liquid equilibria in various systems. *ELDATA: Int. Electron. J. Phys.-Chem. Data* (in press).

Monographs

33. Wichterle I., Linek J., Wagner Z., Kehiaian H. V.: Vapor-Liquid Equilibrium Mixtures and Solutions. *Bibliographic Database. Integrated Electronic Chemical Databases - Vol. II*, 140 pp., ELDATA SARL, Paris, 1994.
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39. Linek J.: Excess volumes of 1,1,2,2-tetrachloroethane + some n-alkyl n-alkanoates. 13th IUPAC Conf. Chem. Thermodyn., Clermont-Ferrand, France, Abstr. p. 74, July 18-22 (1994).
40. Nezbeda I., Smith W. R., Kolafa J.: Molecular theory of the phase equilibria in aqueous solutions. *AIChE 1994 Annual Meeting*. San Francisco, USA (1994).

41. Pavlíček J., Kolafa J., Nezbeda I., Smith W. R.: Molecular theory of the phase behavior of aqueous mixtures. 4th Liblice Conf. Statist. Mechanics Liquids, Milovy, CR June 6-10 (1994).
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46. Boublík T.: Hard body fluids: The 3rd virial coefficient and equations of state. 4th Liblice Conf. Statist. Mechanics Liquids, Milovy, CR June 6-10 (1994).

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. Jiráková, G. Južakov, L. Morávková, R. Ponec, H. Šnajdaufová, O. Šolcová, Z. Vít
Part time: D. Arnošt, L. Beránek, K. Klusáček, M. Kraus

Fields of research

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

Research projects

Diffusion of large molecules in porous glass

(P. Schneider; supported by GA ASCR)

Effective diffusion coefficients for perylene and vanadyl porphyrine in acetone and six polystyrenes with molecular weight in the range 1,200 - 19,000 g/mol in tetrahydrofuran were determined by flow method using column packed with porous glass. The effective diffusion coefficients are related to the bulk diffusivities of the solute - solvent pair [Ref. 7].

Dynamics of multicomponent gas transport in porous solids

(P. Schneider)

Dynamic transport of ternary mixtures was studied in the dynamic version of the Wicke-Kallenbach diffusion cell. It appeared that pulse response due to the step change in gas composition could be safely predicted by the mean transport pores model (MTPM) with parameters determined from measurements with binary gases [Refs. 1, 2].

Axial dispersion in single-pellet-string column

(P. Schneider)

Axial dispersion in single-pellet-string columns (SPSR) packed with cylindrical particles was studied. Fitting in time domain was used for extracting the axial dispersion coefficient, E_{TC} , from the column responses to square-wave input signals. From the results obtained with eight tracer -

carrier gas pairs, a distinct dependence of Bodenstein numbers on the Reynolds Schmidt product and on the Schmidt number of the gas pair could be seen [Ref. 22].

The dynamic model of water gas-shift reaction

(K. Klusáček)

The dynamic model of water gas-shift reaction system was derived on the basis of extensive data. Numerical modelling has shown good agreement of predicted and experimental unsteady system behaviour. It is the first experimentally verified model of a complex catalytic system published in engineering literature [Refs. 3, 4].

Sulphide catalysts for hydrodenitrogenation and hydrodesulphurization

(M. Zdražil; supported by GA ASCR)

The Mo/Al₂O₃ 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% MoO₃, respectively) and the activity of catalysts was the same as that of catalysts prepared by more complicated conventional impregnation with ammonium heptamolybdate [Refs. 25, 26].

Multiphase catalytic processes for environment protection

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

Parallel hydrodesulphurization of methylthiophene and hydrodechlorination of dichlorobenzene over Ni/C, Mo/C and Ni-Mo/C catalysts were studied as model reactions of the hydrogenolysis of organochlorinated pollutants in organic wastes contaminated with sulphur [Ref. 31].

Chemical applications and theoretical interpretation of pair density matrices

(R. Ponec)

The 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. 16-19, 39, 40].

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 SiO₂-CeO₂ support was studied. The catalysts have higher activities and the better C-N bond hydrogenolytic efficiency than alumina based catalyst [Ref. 32].

Catalytic combustion of methane

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

In the combustion of methane, the concentration of NO_x 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) supported on ceramic foams [Ref. 35].

International cooperations

Theoretische Chemie, Universität Hannover, Hannover, FRG: Theoretical analysis of reaction mechanism of selected organic reactions

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

Visits abroad

R. Ponec: Universität Hannover, Hannover, FRG (2 months)

K. JirátoVá: Institute of Isotopes, Budapest, Hungary (1 week)

Visitors

S. Cresswel: University of Greenwich, UK (3 months)

R. Kandiyoti: Imperial College of Science, Technology and Medicine, London, UK (4 days)

L. Paterson: University of Waterloo, Canada (18 months)

A. Spojakina: Institute of Catalysis, Sofia, Bulgaria (1 week)

Teaching

K. JirátoVá: ICTP, course "Preparation of heterogeneous catalysts"

M. Kraus: ICTP, course "Applied catalysis"

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

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

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

Publications

Papers

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2. Arnošt D., Schneider P.: Dynamics of gas transport in porous solids: The influence of non-isobaric transport and concentration. *Catal. Today* 20(3), 381-393 (1994).
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7. Hejtmánek V., Schneider P.: Diffusion of large molecules in porous glass. *Chem. Eng. Sci.* 49(16), 2575-2584 (1994).

8. Hillerová E., Vít Z., Zdražil M.: Magnesia supported Ni-Mo sulphide hydrodesulphurization and hydrodenitrogenation catalysts prepared by non-aqueous impregnation. *Appl. Catal. A* 118(2), 111-125 (1994).
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10. Klusáček K.: Zahraniční vědecké parky a technologická centra. II. Cambridge a Limerick. (in Czech) Foreign science parks and technology centres. II. Cambridge and Limerick. *Inovační podnikání a transfer technologií* 2(4), 9-10 (1994).
11. Klusáček K.: Česko-americká konference o komercializaci technologií. (in Czech) Czech-American conference on commercialization of technologies. *Inovační podnikání a transfer technologií* 2(3), 3-4 (1994).
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13. Pola J., Čukanová D., Ponec R., Stanczyk W.: Laser powered homogeneous decomposition of tetramethylcyclotetrasiloxane. A source for hydroxy(methyl)silylene. *J. Organomet. Chem.* 468, 49-53 (1994).
14. Ponec R., Strnad M.: The least motion principle, concertedness and the mechanisms of pericyclic reactions. A similarity approach. *Collect. Czech. Chem. Commun.* 59(1), 75-88 (1994).
15. Ponec R., Strnad M.: On the role of Fermi and Coulomb correlation in pericyclic reactions. *Chem. Papers* 48(2), 72-78 (1994).
16. Ponec R., Strnad M.: Population analysis of pair densities. A link between quantum chemical and classical picture of bonding. *Int. J. Quant. Chem.* 50, 43-53 (1994).
17. Ponec R.: From the wave function to structural formula. *Croat. Chim. Acta* 67, 55-66 (1994).
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19. Ponec R., Uhlík F.: Electron pairing and chemical bonds. Physical meaning of effective pairs. *Collect. Czech. Chem. Commun.* 59(12), 2567-3578 (1994).
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25. Zdražil M.: Preparation of alumina supported molybdenum catalysts by new slurry impregnation method: Mo/Al₂O₃ Sulphide hydrodesulphurization catalyst. *Catal. Letters* 27(3, 4), 337-344 (1994).
26. Zdražil M.: Preparation of molybdenum-based catalysts by new slurry impregnation method: active carbon supported molybdenum sulphide hydrodesulphurization catalyst. *Appl. Catal. A* 115, 285-298 (1994).
27. Arnošt D., Schneider P.: Dynamic transport of multicomponent mixtures of gases in porous solids. *Chem. Eng. J.* (in press).

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29. Čapka M., Czakoová M., Hillerová E., Petzold E., Oehme G.: 2-(3-trimethoxysilylthio) ethyldiphenylphosphine as a new agent for transition metals immobilization. *J. Mol. Catal.* (in press).
30. Damyanova S., Spojakina A., Jiráťová K.: Nickel-molybdenum hydrodesulphurization catalysts supported on titania-alumina. *Appl. Catal.* (in press).
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32. Gulková D., Vít Z.: Silica-ceria as support for the preparation of NiMo(P) hydrodesulphurization and hydrodenitrogenation catalysts. *Appl. Catal.* (in press).
33. Hillerová E., Zdražil M.: Effect of loading on hydrodesulphurization activity of Mo/Al₂O₃ and Mo/C sulphide catalysts prepared by slurry impregnation with molybdic acid. *Appl. Catal. A* (in press).
34. Jiráťová K., Paukshtis E. A.: Surface acidity of the La₂O₃/Al₂O₃ system. *React. Kinet. Catal. Lett.* (in press).
35. Jiráťová K., Morávková L., Malecha J., Koutský B.: Ceramic foam in the catalytic combustion of methane. *Collect. Czech. Chem. Commun.* (in press).
36. Jiráťová K., Morávková L., Círová A., Říčanek M.: Katalytické spalování těkavých organických látek. (in Czech) Catalytic combustion of VOC. *Chem. Prům.* (in press).
37. 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).
38. Klusáček K., Stuchlý V.: Increasing of carbon monoxide methanation rate by forced feed composition cycling. *Catal. Today* (in press).
39. Ponec R., Uhlík F., Cooper D. L.: Population analysis of pair densities. A study of basic set dependence. *Croat. Chim.* (in press).
40. Ponec R., Bochicchio R.: Nonlinear population analysis from geminal expansion of pair densities. *Int. J. Quant. Chem.* (in press).
41. Vít Z., Portefaix J. L., Zdražil M., Breyse M.: Ketones formation during ethylene hydroformylation over sulphided Rh, Ir and NiMo carbon supported catalysts. *Catal. Lett.* (in press).
42. Vít Z., Gulková D., Novák M.: Preparation of alumina supported Mo catalysts from Mo blue precursor. *React. Kinet. Catal. Lett.* (in press).

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43. Ponec R.: Podobnost v chemii. (in Czech) Similarity in chemistry. *Chem. Listy* 88(11), 680-685 (1994).

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44. Ponec R.: Overlap determinant method in the theory of pericyclic reactions. *Lecture Notes in Chemistry*, Springer Verlag, Heidelberg, 130 p. (1995).
45. Kraus M.: Substituent effects. Chapter 5. 3. 1. in *Handbook of Heterogeneous Catalysis*, Verlag Chemie, Weinheim (in press).
46. Kraus M.: Dehydrogenation of Alcohols. Chapter 4. 3. 3. in *Handbook of Heterogeneous Catalysis* (H. Knözinger, J. Weitkamp, J. Ertl), VCH, Weinheim (in press).

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48. Ponec R.: Molecular similarity and LFER. Molecular similarity and reactivity from quantum chemical to phenomenological approaches (Ed. R. Carbo), Kluwer (in press).
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50. Čapek P., Klusáček K.: Temperature programmed surface reaction as a tool for dynamic studies in catalysis: water-gas-shift reaction. Proceedings of the European Symposium on Catalysis in Multiphase Reactors, Lyon, France, 7.-9. 12. (1994).
51. Čapka M., Czakoová M., Hillerová E., Oehme G., Petzold E.: 2-(3-trimethoxysilylpropylthio) ethyldiphenylphosphine nové činidlo pro imobilizaci přechodových kovů. (in Czech). 2-(3-trimethoxysilylpropylthio) ethyldiphenylphosphine a new agent for transition metals immobilization. 21. Konf. Slov. spol. chem. inž., Vyhne, 23.-27. 5. (1994).
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53. Čapka M., Czakoová M., Hillerová E., Anderson C.: Catalytic activity of rhodium complexes immobilized to phosphinated poly(trimethylolpropane trimethacrylate). XVIth Int. Conf. Organometallic Chemistry, Abstr. P. 311, University Sussex, 1-15 July (1994).
54. Gulková D., Vít Z.: Silica-ceria as support for the preparation of Ni-Mo hydrotreating catalysts. 8th Roermond Conference on Catalysis "Catalysis 2000", Rolduc Kerkrade, The Netherlands 10.-15. July (1994).
55. Klusáček K., Čapek P.: Heterogenní katalýza za nestacionárních podmínek. (in Czech) Heterogeneous catalysis under unsteady state conditions. 21. Konference Slovenské společnosti chemického inženýrství, Conf. Proceedings p. 82, Vyhne, 23.-27. 5. (1994).
56. Kraus M.: Correlations in heterogeneous catalysis. Lecture, Ferien-Akademie, Universität Erlangen und TU München, Thema 7, Homogene und heterogene Katalyse, September (1994).
57. Ponec R., Uhlík F., Cooper D. L.: Population analysis of pair densities. A study of basis set dependence. 8th Internat. Congress of Quantum Chemistry, Prague, June 19-23 (1994).
58. Ponec R., Bochicchio R.: Nonlinear population analysis from geminal expansion of pair densities. 8th Internat. Congress of Quantum Chemistry, Prague, June 19-23 (1994).
59. Ponec R.: Molecular similarity and LFER. VIth Internat. Conference on Correlation Analysis in Organic Chemistry, Prague, September 5-9 (1994).
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61. Hillerová E., Zdražil M.: Preparation of molybdena catalysts by new slurry impregnation method: Mo/AL₂O₃ and Mo/C sulphide hydrotreating catalysts. XXVI. Symposium o katalýze, Praha, 7.-8. 11. (1994).
62. Vít Z., Gulková D.: Preparation of alumina supported Mo catalysts from molybdenum blue precursor. XXVI. Symposium o katalýze, Praha, 7.-8. 11. (1994).
63. Schneider P.: Dynamics of multicomponent gas transport in porous solids. Internat. symposium on Maxwell-Stefan approach to mass transport, Amsterdam, November 1994.

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

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

Utilization of low rank brown coal with pollution control

(J. Drahoš, joint project with Tokyo University; supported by Japanese Ministry of Education)

Removal of heavy metals from waste waters using calcium loaded brown coal brings a problem of subsequent processing of the sorbent. Therefore the combustion of coals loaded by heavy metals was studied in a pilot-plant fluidized bed. It was found that in a carefully conducted experiment, the metals can be quantitatively captured in the flying ash, bed ash and slug. Possibilities of inertization of these materials have been examined [Ref. 4].

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 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 a weak sign of deterministic chaos was diagnosed within a transition from plug to slug flow [Ref. 15].

Utilization of coal based materials for removal of heavy metals from waste solutions

(J. Drahoš; supported by GA Ministry of Environment CR)

Several types of the calcium loaded brown coals, peat and oxyhumolite were tested both in the batch and continuous modes with respect to their ability to remove various heavy metals (Cu, Zn, Pb, Cd, Co and Fe) from aqueous solutions. The results showed a high efficiency of extraction for concentrations of metals less than 10 mmol/l [Ref. 4].

Application of fuzzy sets for identification of fractal structures

(M. Punčochář)

The methodology of fuzzy analysis has been developed for time series arising by superposition (generally non-linear) of two signals. The time evolution of surfaces limited by fractal curves has been studied by using the theory of fuzzy sets [Ref. 14].

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 using 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.

Spraying of liquid film by gaseous jet in pneumatic atomizers

(O. Wein; supported by GA CR)

A large-scale experiment provides the design data for a special kind of two-phase nozzles. The project was completed.

Apparent wall slip in microdisperse liquids

(O. Wein, joint project with ICTP and 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 AWS effect [Ref. 32].

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 on the potential step) was successfully applied for testing propellers in high-speed centrifugal pumps [Ref. 23].

Determination of oxygen permeability in polymers

(K. Wichterle; supported by GA ASCR)

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 evaluation of the oxygen permeability in new biocompatible materials.

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

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

Dispersion efficiency of ejector distributors was studied in two basic working regimes, i. e., under conditions of free suction and forced gas supply to the ejector. The effect of ejector geometry on gas hold-up in the reactor was examined for the two different modes of ejector performance and the energy effectiveness of gas-liquid dispersion formation in both working regimes was compared. The forced-supply data yielded the maximum ratio of gas to liquid volumetric flow rates still allowing efficient gas dispersion in the ejector.

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).

An experimental study was aimed at linking the coalescence behaviour in aqueous electrolyte solutions with the character of bubble beds generated in bubble column reactors 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 [Ref. 26].

International cooperations

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

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

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, FRG: Shear stresses on rotating bodies

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

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

Visits abroad

J. Drahoš: University of Tokyo, Tokyo; Kyushu University, Fukuoka, Japan; University of Naples, Naples; University of Basilicata, Potenza, Italy; University of Hannover, Hannover, FRG

M. Růžicka: University of Birmingham, Birmingham, UK (4 months)

J. Zahradník: Drexel University, Philadelphia, PA, USA

V. Sobolík: Materialprüfungszenrum Freiburg, FRG; ENSIC Nancy; LEMTA Vandoeuvre, CNRS Paris; LEGI / IMG Grenoble, France

M. Punčochář: University of Tokyo, Tokyo; Kyushu University, Fukuoka, Japan

Visitors

T. Chiba: Hokkaido University, Sapporo, Japan

C. Serio, University of Basilicata, Potenza, Italy

V. Tovchigrechko: ITMO Minsk, Byelorussia (3 months)

N. H. Thomas: University of Birmingham, Birmingham, UK

P. Marty: LEGI / IMG Grenoble, France

B. Izrar: LEMTA Vandoeuvre, France
A. Sakalariou (IASTE): University of Athens, Greece
I. Koskinen (IASTE): University Helsinki, Finland
V. Denk, H. Nirschl: Technical University, Munich, FRG

Teaching

J. Drahoš: ICTP, courses "Applied statistical analysis and data processing" and "Time series analysis in reactor engineering"
K. Wichterle: ICTP, course "Convective heat transfer"
K. Wichterle: TU Ostrava, courses "Chemistry" and "Physical chemistry of combustion and explosion"
V. Sobolík: CTU, courses "Rheology" and "Thermodynamics"

Publications

Papers

1. Baleras F., Deslouis C., Tribollet B., Sobolík V.: A three-segment electrodiffusion probe in axisymmetric flow with stagnation and separation. *J. Appl. Electrochem.* 24, 676-684 (1994).
2. Ebner L., Fialová M.: On instabilities in horizontal two-phase flow. *Collect. Czech. Chem. Commun.* 59(12), 2595-2603 (1994).
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Monographs

27. Punčochář M., Drahoš J.: Geometric concept of flow over immersed body in non-laminar conditions. *Fractals in the Natural and Applied Sciences* (Ed. M. M. Novak), Elsevier, Amsterdam, pp. 305-311 (1994).

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28. Drahoš J.: Diagnostika hydrodynamického režimu dvoufázových reaktorů. Habilitační práce, VŠCHT Praha. (in Czech) Diagnostics of hydrodynamic regime of two-phase reactors., Thesis, Inst. Chem. Technol. Prague.(1994).

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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 dehalogenation with reducing agents and surface active inorganic compounds
- Synthesis of biodegradable surface active compounds of biological provenience
- Optical fibre sensors for chemical reactors, monitoring of water and soil pollution
- Microwave-induced chemical reactions
- Synthesis of new heterogenized and highly selective heterogeneous catalysts
- Immobilization of biocatalysts, development of new agents for their chemical bonding to inorganic supports
- Chiral LC phases - their synthesis and performance

Applied research

- New processes for detoxification of solid wastes containing PCBs, based on thermal chemical treatment under fluidized bed combustion conditions, pilot plant tests of their performance [Refs. 3, 13, 14].

Research projects

Materials for chromatographic separation of enantiomers

(M. Čapka; supported by GA CR)

Reaction of (3-isocyanatopropyl)triethoxysilane with amino groups of natural and synthetic optically active compounds was found to be a new and efficient method for immobilization of chiral selectors. The procedure not only allows the preparation of new chiral chromatographic

phases but it also preserves optical purity of the starting selectors [Ref. 23].

Poly(methacrylates) with oligosiloxane groups

(M. Čapka, joint project with Inst. Macromolecular Chemistry ASCR; supported by GA ASCR)

A new hydrosilylation catalyst immobilized on inorganic supports has been developed for the synthesis of the title polymers, using the adduct of (3-mercaptopropyl)triethoxysilane with vinyl-diphenylphosphine as a functionalizing agent [Refs. 33, 34].

New heterogenized and heterogeneous catalysts bonded to inorganic supports

(M. Čapka; supported by GA ASCR)

A study of Diels-Alder self-addition of cyclopentadienyltriethoxysilane [Ref. 1] resulted in the synthesis of new catalysts immobilized via pentamethylcyclopentadienyl groups [Refs. 22, 36]. Phosphinated alkyl-ethoxyalkyl(alkoxy)silanes [Refs. 21, 33-35] were used to immobilize transition metal hydrodesulphurization catalysts [Ref. 21], the activity of which was higher than that of some commercial heterogeneous catalysts.

Microwave activation of chemical reactions

(M. Hájek; supported by GA CR)

In homogeneous addition reactions catalyzed by transition metal complexes, no activation of reactants and/or catalysts by microwaves has been detected. The rate enhancement observed was ascribed to a "superheating effect" due to the effective coupling of microwave irradiation with polar solvents. The microwave-induced solvent-free heterogeneously catalyzed alkylation of amines seemed to be more favourable on solid catalyst than in solution.

Transition metal catalysed addition reactions of halo compounds

(M. Hájek; supported by TEMPUS)

Courses for undergraduate and postgraduate students.

Laboratory of biotechnology and environmental biotechnology

(F. Kaštanek; supported by Ministry of Education CR)

Courses for undergraduate and postgraduate students.

Recycling of rare earth metals extracted from waste colour TV screens

(F. Kaštanek; supported by Ministry of Environment CR)

A method for selective separation of yttrium and europium from nitrate solutions after washing out luminophores was developed. It is based on controlled pH changes to remove general elements in the first step, followed by separation of yttrium from europium in the second one. A continuous extractive multistep separation in a continuous-flow mixer-settler extractor has been proposed.

Study of effect of polychlorinated biphenyls on selected technologically important fungi

(F. Kaštanek, joint project with ICTP; supported by Ministry of Education CR)

Accumulation of PCBs on selected types of food fungi of the strain *Penicillium* had been studied. The 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) [Ref. 24]. This points to the need of critical reevaluation of reported data.

Fundamentals of environmental engineering

(F. Kaštanek; supported by GA CR)

New results concerning biodegradation of persistent substances, extractions of heavy metals from wastes, sorptions of toxic pollutants (PCBs) on solid sorbents (activated carbon fibres, activated carbon, activated bentonite) and bioreactors for biotransformations of toxic substances in liquids (filled with hydrophilic gel with immobilized cells) were obtained and used in several technical applications [Refs. 5, 17, 31].

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

(F. Kaštánek; supported by AG 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.

Bioreactor technique of production of diagnostic monoclonal antibodies

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

A new type of bioreactor packed with a layer of the support of hybridoma cells and medium circulation was studied, using hybridoma 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 Institute of Organic Chemistry ASCR and with 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 as well as long-time and high efficiency in ground water decontamination [Refs. 27, 28].

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

(G. Kuncová; supported by GA CR)

A novel method for bioremediation of soils and ground waters contaminated with PCBs and oil pollutants was developed and applied with success in field experiments [Refs. 37, 40].

Ecology 2 - monitoring and optical fibre sensors

(G. Kuncová; supported by Ministry of Defence CR)

In developing optical fibre sensors of organophosphates with evanescent field detection, suitable enzymes were immobilized by sol-gel technique. Lipases and cholinesterases were immobilized 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. 18].

Dynamic behaviour of spatial one- and two-dimensional model chemical systems computer image processing and simulation

(F. Vašák, joint project with ICTP; supported by GA CR)

A software for interactive identification was developed and used to analyse states of particles and visualization of measurements in simulation of the movement of solid particles in a viscous liquid in a piping system [Ref. 30].

International cooperations

ENSIC, Caen, France: Synthesis of new chlorophosphonates
Kingston University, Kingston, UK: Stereoselective reactions of organic compounds
University of Rostock and Max Planck Gesellschaft Arbeitsgruppe Asymmetrische Katalyse, Rostock, FRG: Synthesis of new chiral phases
University Lund, Lund, Sweden: Synthesis of heterogenized catalysts bonded to poly-(methacrylates)
University of Pisa, Pisa, Italy: Complexes immobilized by cyclopentadienyl ligands
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
M. Hájek: University of Giessen (FRG); Institut Quimic de Sarría, Barcelona, Spain; Greenwich University, London, UK
F. Kaštánek: Cooper Union University, New York, USA; University Nice, Nice, France
M. Kotora: Institute of Molecular Science, Okazaki, Japan (6 months)
M. Kvičalová: University of Pisa, Pisa, Italy
G. Kuncová: University of Padova, Padova, Italy (2 months)

Visitors

J. P. Gorrichon: ENSC Toulouse, France
B. Ameduri: ENSC Montpellier, France
J. Texido: Institut Quimic de Sarría, Barcelona, Spain
S. Cresswell: Greenwich University, London, UK (3 months)
Y. Shabtai: Ben Gurion University, Beer-Sheva, Israel

Teaching

J. Hetflejš: ICTP, course "Organometallic Catalysis"
F. Kaštánek: University Pardubice, Pardubice and ICTP, courses "Bioengineering"

Publications

Papers

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10. Takahashi T., Kotora M., Kasai K., Suzuki N.: Copper catalyzed C-C bond formation reaction of allylzirconation products of alkynes. *Tetrahedron Lett.* 35(31), 5685-5688 (1994).
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14. Včelák J., Hetflejš J.: Dehalogenation of chloroarenes with sodium dihydridobis(2-methoxyethoxy)aluminate in the presence of transition metal compounds. *Collect. Czech. Chem. Commun.* 59(7), 1645-1653 (1994).
15. Včelák J., Šabata S., Hetflejš J.: Comparative study of biphasic reduction of carbonyl compounds catalyzed by homogeneous and water soluble Ru catalysts. NATO ASI series No. 350, pp. 137-140, Kluwer Academic Publ., Dordrecht (1994).
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26. Manseri A., Améduri B., Boutevin B., Kotora M., Hájek M., Caporiccio G.: Synthesis of telechelic dienes from fluorinated diiodoalkanes. Part I. Divinyl and diallyl derivatives from model I(C₂F₄)_nI compounds. *J. Fluorine Chem.* (in press).
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30. Vašák F., Bowen B. D., Chen C. Y., Kaštánek F., Epstein N.: Fine particle deposition in laminar and turbulent flows. *Can. J. Chem. Eng.* (in press).
31. Zahradník J., Fialová M., Kaštánek F., Green K. D., Thomas N. H.: The effect of electrolytes on bubble coalescence and gas holdup in bubble column reactors. *Chem. Eng. Res. Des.* (in press).

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32. Blechta V., Čermák J., Kvíčalová M., Schraml J.: Comparison of tert-butyldimethylsilyl and trimethylsilyl groups. XVIth International Conference on Organometallic Chemistry, Brighton, 10-15 July (1994).
33. Čapka M., Czakoová M., Hillerová E., Oehme G., Petzold E.: 2-(3-trimethoxysilylpropylthio)ethyldiphenylphosphine - nové činidlo pro imobilizaci přechodových kovů. (in Czech). 2-(3-trimethoxysilylpropylthio)ethyldiphenylphosphine a new agent for transition metals immobilization. 21. Konf. Slov. spol. chem. inž., Vyhne, 23.-27. 5. (1994).
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- indigenous bacteria. Int. Symposium Biosorption and Bioremediation, Madrid, Oct. 15-17 (1994).
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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
- Evaporation of droplets at low Reynolds numbers
- Experimental study of thermodiffusiophoresis in multicomponent mixtures
- Synthesis of nanoparticles via aerosol process

Applied research

- Know-how for the combustion of waste organic materials in fluidized bed [Ref. 42]

Research projects

Reactions in the systems with solid particles

(M. Hartman; supported by GA ASCR)

Increasing- and constant-temperature gravimetric methods were used to measure the thermal decomposition rates of $\text{Mg}(\text{OH})_2$ particles. Temperature, exposure time on surface area of the calcined particles and other effects of variables were explored. An integrated model is presented that considers the surface area generation by calcination and the simultaneous surface reduction caused by sintering of the measured oxide [Ref. 1].

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. 40].

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 on 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 greater than that of calcium oxide sintered under the same conditions [Refs. 2, 3].

Fuel reactivity and release of pollutants

(K. Svoboda; supported by the EC in the program COST: JOU II-CT 12-0037)

A unique experimental facility with a pressurized fluidized bed has been under construction [Ref. 54]. The dependence of the NO_x and N_2O emissions released by combustion in the pressurized fluidized bed will be explored on such factors as operating conditions (temperature, excess air, pressure) and types of functional bonds of nitrogen in the liquid or solid fuel.

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)

IR laser induced decomposition of the title compounds was studied at various parameters of laser radiation and found to yield polycarbosilane or α -SiC:H films. The technique is promising for low temperature chemical vapour deposition of SiC-based materials [Ref. 23].

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. 23, 31].

Laser thermolysis of pyridine for CVD of polypyridine films

(J. Pola; supported by GA CR)

CW CO_2 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. 35].

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 methoxy(methyl)germanes. The process represents the first successful approach to preparation of polyorganooxo-materials [Refs. 7, 25, 26].

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. 6, 8, 9, 14, 21, 24, 29].

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 CO₂ laser pyrolysis. The oxidation produced spherical nanoparticles of silica [Refs. 17, 33]. In the photolysis spherical particles of new phase Si/C/O were obtained.

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 will be devoted to the formation of ultrafine particles enriched by toxic elements. An interinstitutionary research was elaborated and submitted to GA CR. Main part of the measuring device was acquired and the experimental apparatus has been built up.

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 that includes mass transfer due to non-isothermal diffusion, radial efflux of vapour, and thermal diffusion [Refs. 18, 28]. The effect of individual contributions to the mass transfer was investigated during the evaporation of water and methanol droplets [Ref. 13].

Homogeneous nucleation in gaseous phase

(V. Ždímal, J. Smolík)

The project included the experimental study of homogeneous nucleation in supersaturated vapours of organic substances using static thermal diffusion chamber. The goals achieved were: a) testing of the newly developed method of measurement [Ref. 16], b) comparison with other experimental techniques, and c) testing of the existing nucleation theories.

International cooperations

University College London, London, UK: Settling of nonspherical particles
University of Connecticut, Storrs, USA: Reactivity of solids
University of Technology Delft, The Netherlands: Circulating fluidized beds
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: Sussex University, Brighton, UK (12 months)
R. Fajgar: Bergische Universität, Wuppertal, FRG (6 weeks)
J. Pola: Bhabha Atomic Research Centre, Bombay, India (2 weeks)
B. Tříška: Philipps University, Marburg, FRG (3 months)
J. Smolík: Tokyo Institute of Technology, Tokyo, Japan (2 weeks)

Visitors

M. Santos: Instituto de Estructura de la Materia, CSIC Madrid, Spain (2 weeks)
M. Senzlober: Bergische Universität, Wuppertal, FRG (6 weeks)
K. Haemeri: University of Helsinki, Helsinki, Finland (1 month)
P.E. Wagner: University of Vienna, Vienna, Austria
A. Laloef (IAESTE): University of Maine, France, 1.5 month
S.F. Ragona (IAESTE): Queens University, Kingstown, Canada, 1.5 month
J. Egami (IAESTE): Universidade Estadual de Campinas, Brasil, 3 months)

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4. Hartman M., Trnka O., Svoboda K.: Free-settling of nonspherical particles. *Ind. Eng. Chem. Res.* 33, 1979-1983 (1994).
5. Hartman M., Trnka O., Svoboda K., Veselý V.: Influence of particle shape on the drag coefficient for isometric particles. *Collect. Czech. Chem. Commun.* 59(12), 2583-2594 (1994).
6. Jakoubková M., Fajgar R., Tláskal J., Pola J.: Laser induced decomposition of 1,1-dichloro-1-silacyclobutane for gas-phase deposition of reactive solid polycarbosilane. *J. Organometal. Chem.* 466, 29-34 (1994).
7. Jakoubková M., Bastl Z., Fiedler P., Pola J.: IR laser thermolysis of tetramethylgermane for CVD of germanium. *Infrared Phys. Technol.* 35, 633-635 (1994).
8. Jakoubková M., Bastl Z., Šubrt J., Čukanová D., Fajgar R., Pola J.: CO₂ laser photosensitized decomposition of diethylsilane (DES) for deposition of SixC1-x coatings. *Proceedings ROMOPTO'94, Vol. Lasers in Optics*, p. 324 (1994).
9. Pola J., Čukanová D., Ponec R., Stanczyk W.: Laser powered homogeneous decomposition of tetramethylcyclotetrasiloxane. A source for hydroxy(methyl)silylene. *J. Organomet. Chem.* 468, 49-53 (1994).
10. Pola J., Taylor R.: Molecular decomposition of acetone. *Tetrahedron Lett.* 35(17), 2799 (1994).
11. Pola J., Taylor R.: Evidence for a role of charge-transfer complex and isotope-solvent effect in iodination of phenylsilane. *Polyhedron* 13, 2451-2453 (1994).
12. Schraml J., Jakoubková M., Kvíčalová M., Kasal A.: Steric effects on NMR chemical shifts controlled by solvent accessible surface. *J. Chem. Soc. Perkin Trans. 2* (1), 1-2 (1994).
13. Schwarz J., Smolík J.: Mass transfer from a drop-I. Experimental study and comparison with existing correlations. *Int. J. Heat Mass Transfer* 27(14), 2139-2143 (1994).
14. Siguenza C., Diaz L., Gonzalez-Diaz P. F., Bürger H., Beckers H., Pola J.: Single and double IR laser multiphoton decomposition of trifluoromethylsilane. *Spectrochim. Acta* 50A(6), 1207-1210 (1994).
15. Smith W. R., Tříška B.: The reaction ensemble method for the computer simulation of chemical and phase equilibria. I. Theory and basic examples. *J. Chem. Phys.* 100(4), 3019 (1994).
16. Smolík J., Ždímal V.: Condensation of a supersaturated vapors of dioctylphthalate(DOP). Homogeneous nucleation rate measurements. *Aerosol Sci. Technol.* 20, 127-134 (1994).
17. Smolík J., Moravec P.: Vapor phase synthesis of silica particles. *J. Aerosol Sci.* 25 S1, 45 (1994).
18. Smolík J., Kulmala M., Schwarz J., Vesala T.: Evaporation of a drop. A temperature dependent mass transfer correlation. *J. Aerosol Sci.* 25 S1, 99 (1994).
19. Svoboda K., Lin W., Hannes J., Korbee R., van den Bleek C. M.: Low-temperature flue gas desulphurization by alumina-CaO Regenerable Sorbents. *FUEL* 73, 1144 (1994).

20. Vašáková J., Smolík J.: Thermal diffusion factors for binary gas systems at low pressures: Estimation from theory. Report Series in Aerosol Science (Finnish Association for Aerosol Research) No. 25, 1 (1994).
21. Vitek J., Urbanová M., Bastl Z., Tláskal J., Pola J., Zeldin M., Fife W. K.: Laser-induced decomposition of 3-Pyridinyl(trimethyl)- and 3-Pyridinyl(triethoxy)silane. *J. Anal. Appl. Pyrol.* 28, 175-182 (1994).
22. Ždímal V., Smolík J., Meijer I. G. N.: Homogeneous nucleation in supersaturated vapors of n-nonane. *Collect. Czech. Chem. Commun.* 59(2), 253-261 (1994).
23. 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).
24. Dřínek V., Bastl Z., Šubrt J., Urbanová M., Pola J.: IR laser decomposition of tetravinylsilane for deposition of SixC1-x coatings. *Proceedings ROMOPTO'94, Vol. Lasers in Optics*, p. 300 (in press).
25. Fajgar R., Bastl Z., Tláskal J., Pola J.: Chemical vapour deposition of germanium-containing films by IR laser-induced decomposition of ethoxy(trimethyl)germane. *J. Mater. Chem.* (in press).
26. 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.* (in press).
27. Fajgar R., Vitek J., Pola J., Bastl Z., Tláskal J., Gregora I., McGhee L., Stevenson P. R., Winfield J. M.: IR laser degradation of some fluoro-polymers. *J. Fluor. Chem.* (in press).
28. 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* (in press).
29. Pola J., Parsons J. P., Taylor R.: ArF laser photolysis of tetraethyl- and tetravinylsilane. *J. Organometal. Chem.* (in press).
30. 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.* (in press).
31. 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.* (in press).
32. Smolík J., Tříška B., Ždímal V., Uchtmann H.: Thermodiffusiophoresis and droplet growth in ternary gaseous mixtures. *J. Aerosol Sci.* (in press).
33. Smolík J., Moravec P.: Gas phase synthesis of fine silica particles by oxidation of TEOS vapor. *J. Mater. Sci., Lett.* (in press).
34. Trnka O., Hartman M.: Solving unsteady-state models for the rapid gas sorption with nonlinear kinetics. *Chem. Eng. Sci.* (in press).
35. Urbanová M., Vitek J., Pola J.: Laser powered homogeneous decomposition of pyridine for CVD of polypyridine thin films. *J. Mater. Chem.* (in press).
36. Veselý V., Hartman M., Trnka O., Fetsch D.: Performance of the afterburner with a natural gas burner. *Fuel* (in press).
37. Ždímal V., Tříška B., Smolík J.: Experiments on thermodiffusiophoresis of droplets in gaseous mixtures. *Colloids Surf.* (in press).

Review papers

38. Dřínek V., Pola J.: Laser-induced chemical vapour deposition of silicon carbide. *Ceramics* 38, 37-43 (1994).

39. Pola J.: CO₂ laser-induced thermal chemical vapour deposition of polymers. *J. Anal. Appl. Pyrol.* 30, 73-90 (1994).
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42. Veselý V., Hartman M., Palán E., Videman K.: Zařízení pro přívod kapaliny do spalovacího prostoru kotle s fluidní vrstvou. (in Czech) Apparatus for introducing a liquid into the combustion chamber of a fluidized bed boiler. *Czech. Pat.* 278785 (Appl. 1813-92) (1994).

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43. Dřínek V., Bastl Z., Šubrt J., Urbanová M., Pola J.: IR laser decomposition of tetravinylsilane for deposition of Si₆C_{1-x} coatings. *Conf. Romopto'94*, Bucharest, Romania, September 5-8 (1994).
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45. Guselnikov L. E., Volnina E. A., Volkova V. V., Pola J.: Spontaneous polymerization of silenes and 1, 2-disilacyclobutanes. *Symposium on Silicon-containing Polymers*, Canterbury, July 6-8 (1994).
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47. Kulmala M., Vesala T., Schwarz J., Smolík J.: A new expression for the droplet Sherwood number in the intermediate Reynolds number range. *4th Internat. Aerosol Conf.*, Abstr. 5 P, Los Angeles, USA (1994).
48. Pola J.: Laser chemistry in the gas phase and CVD of some silicon-containing materials. *Invited Lectures. Internat. Conf. on Radiation and Photochemistry*, Bombay, January (1994).
49. Schwarz J., Smolík J., Kulmala M., Vesala T.: Mass transfer from a drop at elevated temperatures. *6th Internat. Conf. on Liquid Atomization and Spray Systems ICLASS 94*, Poster Abstracts P23, p. 59-60, Rouen, France, July 18-22 (1994).
50. Schwarz J., Smolík J.: Evaporation of a water drop into ternary gaseous mixture containing a condensable component. *6th Internat. Conf. on Liquid Atomization and Spray Systems ICLASS 94*, Poster Abstracts P22, p. 57-58, Rouen, France, July 18-22 (1994).
51. Smolík J.: Emission fluxes of heavy metals in the fluidized bed combustion of fossil fuels. *17th World Congress of the Czechoslovak Society of Arts and Sciences*, V F 111, Prague (1994).
52. Smolík J., Kulmala M., Schwarz J., Vesala T.: Evaporation of a drop. A temperature dependent mass transfer correlation. *European Aerosol Conference*, Abstr. 11 O 02, Blois, France (1994).
53. Smolík J., Moravec P.: Vapor phase synthesis of silica particles. *European Aerosol Conference*, Abstr. 05 O 06, Blois, France (1994).

54. Svoboda K.: Apparatus for pressurized fluidized bed combustion - study of NO_x and N₂O emissions. Lecture, Joule II Coordination Meeting-Working Party "Pressurized Powder Coal Combustion", Veldhoven, The Netherlands, 26.-28. 9. (1994).
55. Ždímal V., Smolík J.: Nucleation studies using thermal diffusion cloud chamber. Short Course II. Metastable Behaviour of Fluids and Critical Phenomena, Lecture Notes p. 89-91, Prague, Oct. 31-Nov. 2 (1994).

Research reports

56. 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. Progress report No. 2 covering period 1. 10. 1993-31. 7. 1994, Contract No. JOU2-CT92-0037. (1994).

Department of Analytical Chemistry

Head: J. Schraml
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Technical staff: J. Lněničková, V. Zimová

Fields of research

- NMR spectroscopy
- Removal of heavy metals

Applied research

- Analytical services to all 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, we improved the J-doubling method for estimation of spin-spin coupling constants [Refs. 1, 3, 10, 14].

NMR Spectroscopy of Sterically Demanding Silyl Groups

(J. Schraml; supported by GA CR)

A new mechanism of steric effect in ^{29}Si NMR spectroscopy was discovered and quantified [Refs. 5, 6]. 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 [Refs. 7, 12, 15].

Hydroxamic Acids Derivatives - Structure by NMR Spectroscopy, Properties, and Use

J. Schraml; supported by GA ASCR)

A number of derivatives of mono- and dihydroxamic acids were prepared and their NMR (^1H , ^{13}C , ^{15}N , and ^{29}Si) spectra measured and analysed. The results for dihydroxamic acid derivatives show a striking dependence on the separation of the two hydroxamic functions.

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

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

Using NMR techniques, partial structure of polymers prepared in the collaborating Institutes were determined.

Participation in project "Materials for chromatographic separation of enantiomers" (see Department of Biotechnology and Environmental Processes): New liquid chromatographic columns were tested for their ability to separate racemic mixtures of enantiomers in various solvents.

Participation in project "Utilization of coal based materials for removal of heavy metals from waste solutions" (see Department of Multiphase Reactors): Calcium loaded coal was used to remove heavy metals from waste waters. The following quantities were experimentally determined: calcium loading capacity for different coals, peat, and oxyhumolite; selectivity coefficients of Cu, Zn, Pb, Cd, Ni, Co, and Fe ions, influence of flow rate on the metal removal, and the height equivalent of the theoretical plate [Ref. 4].

Participation in project "Mass transfer during the supercritical fluid extraction of natural products from solids" (see Department of Diffusional and Separation Processes): Supercritical extraction of fats, essential oils, and some other volatile components of natural products was followed by reversed liquid chromatography [Refs. 8, 13].

International cooperations

University of Ghent, Belgium: Study of Neurotoxins as Food Contaminants. Model System: the Neurotoxin β -ODAP in Grass Pea

Visits abroad

J. Schraml: Invited lectures at University of Athens, Greece (2 weeks)

J. Schraml: Paderborn and Münster, FRG, DAAD fellowship (2 months)

Teaching

J. Schraml: CU, undergraduate course "NMR Spectroscopy"

R. Řeřicha: ICTP, course "Chemical Spectroscopy"

Publications

Papers

1. Blechta V., del Rio-Portilla F., Freeman R.: Long-range carbon-proton couplings in strychnine. *Magn. Reson. Chem.* 32, 134-137 (1994).

2. Čermák J., Kvičalová M., Schraml J., Čapka M.: Diels-Alder self-addition and retroaddition of (cyclopentadienylmethyl)triethoxysilane and synthesis of its permethylated analogue. *Collect. Czech. Chem. Commun.* 59(2), 453-456 (1994).
3. del Rio-Portilla F., Blechta V., Freeman R.: Measurement of poorly resolved splittings by J doubling in the frequency domain. *J. Magn. Reson. A* 111, 132-135 (1994).
4. Horáček J., Soukupová L., Punčochář M., Slezák J., Drahoš J., Yoshida K., Tsutsumi A.: Purification of waste waters containing low concentrations of heavy metals. *J. Hazard. Mater.* 37(1), 69-76 (1994).
5. Kasal A., Schraml J., Čermák J.: Steric effects induced by solvent association. ^{29}Si NMR chemical shifts in trimethylsilyloxysteroids controlled by solvent accessible surface. *Magn. Reson. Chem.* 32, 394-398 (1994).
6. Schraml J., Jakoubková M., Kvičalová M., Kasal A.: Steric effects on NMR chemical shifts controlled by solvent accessible surface. *J. Chem. Soc. Perkin Trans. 2* (1), 1-2 (1994).
7. Schraml J., Kvičalová M., Schwarzová I., Velíšek J.: ^{29}Si and ^{13}C NMR spectra of Trimethylsilylated Aminoacids. *Magn. Reson. Chem.* 32, 591-595 (1994).
8. Sovová H., Komers R., Kučera J., Jež J.: Supercritical carbon dioxide extraction of caraway essential oil. *Chem. Eng. Sci.* 49(15), 2499-2505 (1994).
9. Včelák J., Friesová A., Řeřicha R., Hetflejš J.: Dehalogenation of chlorobenzenes with sodium dihydridobis(2-methoxyethoxy)aluminate. *Collect. Czech. Chem. Commun.* 59(6), 1368-1383 (1994).
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11. Čermák J., Kvičalová M., Blechta V., Čapka M.: Preparation of polysiloxanes containing pentamethylcyclopentadienyl groups by a sol-gel procedure and catalytic activity of titanium complexes anchored on them. *J. Organomet. Chem.* (in press).
12. Kubec R., Velíšek J., Kvičalová M., Čermák J., Schraml J.: ^{29}Si and ^{13}C NMR spectra of t-butyl dimethylsilyl derivatives of amino acids. *Magn. Reson. Chem.* (in press).
13. Sovová H., Jež J., Bártlová M., Šťastová J.: Supercritical carbon dioxide extraction of black pepper. *J. Supercrit. Fluids* (in press).

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14. Blechta V., Schraml J.: Double-pulse on two spin system. 10th NMR Valtice, Abstr. P. 15, April 26-29 (1994).
15. Blechta V., Čermák J., Kvičalová M., Schraml J.: Comparison of tert-butyl dimethylsilyl and trimethylsilyl groups. XVIth International Conference on Organometallic Chemistry, Brighton, 10-15 July (1994).
16. Čermák J., Kvičalová M., Blechta V., Čapka M.: Tetramethylcyclopentadienylalkyl alkoxy silanes - new ligands for anchoring transition metal homogeneous catalysts. 9th International Symposium on Homogeneous Catalysis, Abstr. p. 311, Jerusalem, Aug. 21-26 (1994).
17. Ksandr Z., Schraml J.: The last 30 years of NMR in the world and in Bohemia. 10th NMR Valtice, Abstr. P. 20, April 26-29 (1994).
18. Řeřicha R.: Chemie a životní styl: vědomí souvislostí a smysl pro míru věcí. (in Czech) Chemistry and style of life: Knowledge of relationships and a sense for proper measures. 17th World Congress of the Czechoslovak Soc. of Arts and Sciences, Abstr. p. 97, Prague, June 26-29 (1994).

Miscellaneous

The Technological Innovation Centre originally within the ICPF was transformed to the Technological Park ASCR in May 1994.

The “4th Liblice conference on statistical mechanics of liquids” at Lake Milovy, (with 120 foreign participants) was organized by the Institute.