



Announcement

Two Issues of Fortschritt-Berichte VDI in honor of Professor Jürgen U. Keller:

No. 554: *Technische Sorptionprozesse* (in German)
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No. 555: *Adsorption by Porous Solids* (in English)
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Both are edited by Dr.-Ing. Reiner Staudt, Siegen.

These comprise the proceedings of a Festschrift, held in August 1998, in honor of Prof. Dr. sc. techn. Jürgen U. Keller, on the occasion of his 60th birthday. The Festschrift includes 33 articles by 79 authors.

Jürgen U. Keller is Professor of Thermodynamics at the Dept. of Mechanical Engineering, University of Siegen, Siegen, Germany. He graduated at the University of Graz in Mathematics, Physics and Chemistry, got a Doctoral Degree in 1963 at Technical University of Graz, Austria. After spending a couple of years as coworker of Prof. Meixner at RWTH Aachen and as Privatdozent at the Institute of H. Knapp at TU Berlin, he joined the Daimler-Benz Company as a research engineer. Thereafter, he became Full Professor of Thermodynamics in 1984 at the University of Siegen founded in 1972.

He has authored and coauthored more than 90 refereed papers in theoretical thermodynamics, stochastics, statistical physics, thermodynamics of irreversible processes, thermodynamics of adsorption, and thermophysical properties of multi-component gaseous and liquid mixtures. He is the author of a book on *Thermodynamics of Irreversible Processes* (de Gruyter, 1977) and on *Engineering Thermodynamics* (de Gruyter, 1979). Since 1976 he is also Editor-in-Chief of the *Journal of Non-Equilibrium Thermodynamics*, published by de Gruyter, Berlin, which in 1997 has been rated as No. 1 among 31 Journals in the field of Thermodynamics by the Institute of Scientific Information, Philadelphia. Prof. Keller holds several patents on new absorption working fluids and is cooperating with various companies on industrial projects in Germany and abroad.

He has been a Visiting Professor at several Universities, among them University of Michigan, Ann Arbor (1974), University of BC, Vancouver (1988, 1992), University of Queensland, Brisbane, Australia (1996, 1998), and others. In 1998 he has been elected as a member of the Board of Directors of the International Adsorption Society (IAS). His current research interests focus on gas adsorption equilibria where he is pursuing new measurement methods for both single- and multi-component systems. He may be contacted at: Professor Dr. J.U. Keller, Institute Fluid- and Thermo-dynamics, Mechanical Engineering, University of Siegen, D-57068 Siegen, Germany.

The following pages contain a synopsis of the papers that were presented in German, and the titles of the papers that were presented in English.

No. 554: Technische Sorptionprozesse (in German)

Remarks on the History of Adsorption, Erich Robens

This paper reviews many key events in the field since Biblical times, e.g., from 1550 BC to the 20th century AD. Key combinations were adsorption of air by charcoal, clay as a drying and bleaching agent, a carrier for paints, and for various medical purposes, charcoal as an antidote, charcoal for purification of cane sugar and of beet sugar. In addition, experimental techniques are covered, including the volumetric method, the apparatus of Brunauer, Emmett and Teller for surface area and porosity, the first gravimetric adsorption measuring instruments (hygrometers), an electronic beam microbalance, and a coil spring balance to investigate adsorption. Modern gravimetric instruments are based on the work of Gast.

Adsorption Data for Porous Systems and Their Standardization, Klaus Meyer and P. Lorenz

Adsorption and desorption of gases on highly dispersed or porous solids is used on the one hand for the determination of pore size parameters (adsorbent characterization) and on the other hand for the analysis of

the interaction between adsorbent and adsorbate. Both ways are distinguished by their specific approaches and their objectives. The determination of surface and pore size parameters, like specific surface area and pore size distribution, requires standardized procedures aiming at standardizing the substances. The usage of certified reference materials (CRM's) provides a significant foundation for the accuracy and for the reproducibility of the results. For gaining information concerning interaction between adsorbent and adsorbate in terms of thermodynamic parameters like heat of adsorption or entropy, modeling technical processes becomes important.

Remarks to the Henry's Law Region of Adsorptive Equilibria, Dr. U.v. Gemmingen

A volumetric concentration measurement method is presented detecting adsorptive equilibria at the Henry's law region down to partial pressures of $1.0\text{E-}08$ bar and fractional coverages of $1.0\text{E-}05$. Results with numerous components show not exactly the Henry's law linearity but a temperature dependent Freundlich exponent of 0.6–0.95. This reflects the energetic inhomogeneity originating from the individual binding of the adsorbates to the surfaces which may be characterized by the corresponding Boltzmann factor e/RT .

Some Ideas about the Development of Porous Materials, Erich Robens and Klaus K. Unger

The most important processes which cause porosity of materials are compression of powders, precipitation of gels, crystallization, calcination, pyrolysis, dissolution of components and swelling. By means of some examples (sand stone, cement, gypsum, asbestos, zeolites, bread, activated carbon, porous glass, minerals) the large variety of pore systems is demonstrated.

Adsorption on Carbon—The Early History of Activated Carbon, Dr. H.v. Kienle

Nowadays activated carbon is a material widely used in many different adsorption processes. Industrial production of activated carbon started at the beginning of 20th century based on patents applied by Raphael von Ostrejko, a Russian-German inventor. But already since 2000 B.C. we find written documents which show that diverse carbonaceous products were used for medical purposes and purification processes. Sometimes charcoal was used but also materials produced by carbonization of blood or bones. Bone char was a decolorisation material mainly used in sugar industry even still in the middle of our century.

Thermal Reactivation of Spent Activated Carbon, Klaus-Dirk Henning

The use of Activated Carbon for gas and water cleaning in industry and environmental if suitable processes for the regeneration of spent activated carbon are available. In the last 20 years the success of activated carbon in drinking water and waste water treatment has been due to the development of regenerable activated carbon types and the development of effective processes for the regeneration of the spent carbon.

Desorption of Toluene from Hydrophobic Zeolites using Steam, Küntzel, J.; Ham, R.; Melin, T.

Desorption using steam is a process that has been used for years in the case of active carbon. However for the regeneration of hydrophobic zeolites, which have recently been employed as adsorbents for the separation of volatile organic carbons from the gas phase, desorption with hot (inert) gas has been the only method of choice up until now. The experiments in this paper have shown that regeneration of hydrophobic zeolites with steam can also be effective.

Non-linear dynamics of PSA-processes at the example of oxygen-enrichment out of air, U. Hofmann, M. Straub, M. Loehr

Pressure-swing-adsorption (PSA) is increasingly gaining in significance as far as oxygen-enrichment from air is concerned. When calculating the adsorption process, the simulation program considers different connections with adsorbers, storage vessels, valves and machinery as for example compressors and vacuum pumps. The mathematical model comprises: material and energy balance, Ergun equation for the pressure drop, and linear driving force (LDF) kinetics, as well as the calculation of equilibrium according to different models. Comparisons of simulations with results from measurements at PSA-plants show that the simulation program calculates the plant product rate and yield with a maximum deviation of 5%.

Influence of Relative Air Humidity on the Adsorption of N-butane onto Activated Carbon, K.-H. Radeke, H. Schröder, P. Kussin, P. Brackner, F. Reichert

The entrance air of car passenger space is increasingly purified from petrolhydrocarbons by adsorption onto active carbon in thin-layer filters. In this work, some carbons are characterized by fixed-bed adsorption measurements of 80 ppm n-butane with different air humidity levels at 23° . From breakthrough curves of butane

the specific adsorption capacity of the different carbons is evaluated; the variation is discussed in terms of water vapor and nitrogen adsorption isotherms on the same adsorbents.

Gravimetric Measurements of Multicomponent Adsorption Equilibria with Chromatographic Analysis of the Sorbate Phase, U. Quesel und W. Kast
For the design of technical adsorption processes the knowledge of equilibria is an important pre-condition. Usually the adsorption gas is a multi-component mixture. Therefore the knowledge of single-gas isotherms is not sufficient in most cases. There have to be data about the multi-component system in addition. For the experimental determination of equilibria a gravimetric apparatus was employed with a continuous flow of adsorption gas under constant pressure. The composition of the sorbate phase was determined by chromatographic analysis. Therefore a desorption had to be carried out after equilibrium was obtained.

Volumetric-Gravimetric Measurement of High Pressure Co-adsorption Equilibria of CH₄/CO Mixtures on Activated Carbon, F. Dreisbach, H. Mueller, M. Loehr, A. Westkaemper
Adsorption equilibria of the gases CH₄ and CO and their binary mixtures on activated carbon Norit R1 Extra have been measured in the pressure range $0 \leq P \leq 10$ MPa at $T = 298$ K. Pure gas adsorption equilibria were measured gravimetrically. Co-adsorption data of three binary mixtures CH₄/CO were obtained by the volume-gravimetric method. First, the measuring method and procedure of measurement as well as the data handling procedure are presented. The resulting pure gas adsorption data are correlated using a generalized Langmuir isotherm. Measured mixture co-adsorption data can be predicted by this model using only pure component parameters with good accuracy.

Determination of Partial Loadings in the Adsorption of Gas Mixtures up to Higher Pressures, P. Harting, J. Germanus and S. Beutekamp
Experimental adsorption studies of pure gases and gas mixtures on micro-porous solids represent an important prerequisite of adsorption separation processes. The aim of this work is the determination of partial loadings in mixture adsorption by the example of gas mixtures consisting of nitrogen and methane at pressures of up to 15 MPa in the temperature range between 283 and 343 K. Activated coal of the type Norit

R1 was used as adsorbent. Adsorption isotherms were constructed from experimental data obtained by gravimetric adsorption measurements.

Measurement and Calculation of Ternary Adsorption Equilibria, Stefan Sander, Arnold Sehweer, Jürgen Gmehling

In this paper a method for the measurement of adsorption equilibria and two models for the prediction of these data are presented. For the measurement a flow type apparatus is used which allows the determination of pure, binary and ternary adsorption data. For the measurements de-aluminated Y-zeolites (DAY) with different silicon to aluminum ratio manufactured by Degussa AG. are used. As adsorptives the solvents 1-propanol, methylcyclohexane and toluene were investigated. For the prediction of the binary and ternary adsorption equilibria the Ideal Adsorbed Solution Theory of Myers and Prausnitz and the "Predictive Real Adsorbed Solution Theory" of Sakuth, which takes into account the real behavior are applied. Since the binary and ternary systems show real behavior, the prediction using the IAS-theory often leads to unsatisfying results when compared with the results of the PRAS-theory.

Impedance Spectroscopic Measurements of Pure and Mixed Gas Adsorption Equilibria on Activated Carbon and Zeolites, R. Staudt, M. Gummersbach, S. Kramer, S. Dohrmann

Physisorption equilibria of gases on inert porous solids like activated carbon or molecular sieves can be characterized by measuring the (frequency dependent) capacitance of a capacitor filled with a sample adsorbent. The aim of this work is to show for various pure gases and adsorbents that the change of the capacitance of an adsorption system is depending on the adsorbed mass. Therefore this effect can be used to measure gas adsorption equilibria. To check the state or the quality of industrial adsorbents on site if calibration measurements have been taken.

Technical Development and Works Engineering, Dr.-Ing. J. Ciprian and Dr.-Ing. U. Eiden

If a specialist subject area may be measured by its publications then liquid phase adsorption, with the exception of chromatographic separation processes, appears to play only a subordinate role by comparison with gas phase adsorption. Nevertheless, there is in reality a whole series of successfully operated liquid adsorption processes.

Oscillometric-Gravimetric Measurements of Pure Gas-Adsorption Equilibria on Activated Carbon,

H. Rave, K. Esch, D. Mathweis, M. Ohm

Resulting experimental data of either gravimetric or volumetric measurements of gas-adsorption equilibria only allow to calculate the difference $\Omega = m - \rho^f \bullet V^{\text{as}}$ between the net mass adsorbed m and the buoyancy related product of the volume V^{as} of the adsorbent/adsorbate system and the fluid's (adsorptive's) density ρ^f . To determine the adsorbed mass m from such experimental data, a model for the volume V^{as} must be introduced. In this work the information gained by combined oscillometric and gravimetric measurements is investigated.

Phase Equilibria in Adsorption from the Liquid Phase: A Highly Accurate Measurement Device,

Rolf Hirsch and Wolfgang Arlt

Adsorption as a unit operation and especially the adsorption out of the liquid phase gains more and more importance. The possibility to produce suitable stationary phases for any separation problem allows the separation more and more complex mixtures. For this the accurate description of the thermodynamic phase equilibrium is important. Here the adsorption excess is used to describe the adsorption out of the liquid phase. The fundamental equilibrium is formulated by the isofugacity relation. Thus, similar to g^E models, the multi component adsorption can be predicted by the usage of binary parameters. For the measurement of the adsorption excess a highly accurate apparatus is presented which has been especially optimized to minimize measurement errors. It is constructed for temperatures from 298.15 to 423.15 K and pressures from 0 to 20 bar. The comparison of test measurements with literature data showed a good qualitative agreement. The results could be described well with the proposed adsorption excess isotherms.

No. 555: Adsorption by Porous Solids (in English) (Table of Contents)

Physisorption of gases by microporous solids,
K. Sing

Molecular interaction energies of an N₂ molecule with micrographitic pore-wall by high pressure adsorption, K. Kaneko, K. Shimizu, N. Uekawa

Pore condensation and phase behavior of pure fluids in mesoporous materials, S. Groß, G.H. Findenegg

Mercury porosimetry measures the volume of micropores in activated carbon, Y. Zhou, H. Len

One-dimensional adsorption of Xenon on the (110) face of TiO₂, W.A. Steele

Quantitative analysis of TPD spectra from energetically heterogeneous solid surfaces based on employing the absolute rate theory approach, W. Rudzinski, T. Borowiecki, T. Panczyk, A. Dominko

Spreading of surfactant solutions over hydrophobic substrate, V.M. Starov, S.R. Kosvintsev, M.G. Velarde

Structure analysis of nanoporous materials by PFG NMR diffusion measurement, J. Kärger, C. Krause, H. Schäfer

Sorption of atmospheric gases on a faujasite-type zeolite, M. Bülow, D. Shen

Adsorption of vapour mixtures in active carbons described by the Myers-Prausnitz-Dubinin Method, F. Stoeckli, A. Lavanchy, D. Wintgens

A binary-UNILAN mode! for predicting binary mixture adsorption on energetically heterogeneous surfaces, S.U. Rege, R.T. Yang

The potential of energy saving by gas phase adsorption processes, A. Mersmann, B. Markwana, R. Hartmann

The hemoglobin connection, B. Ahlborn, S. Jacob