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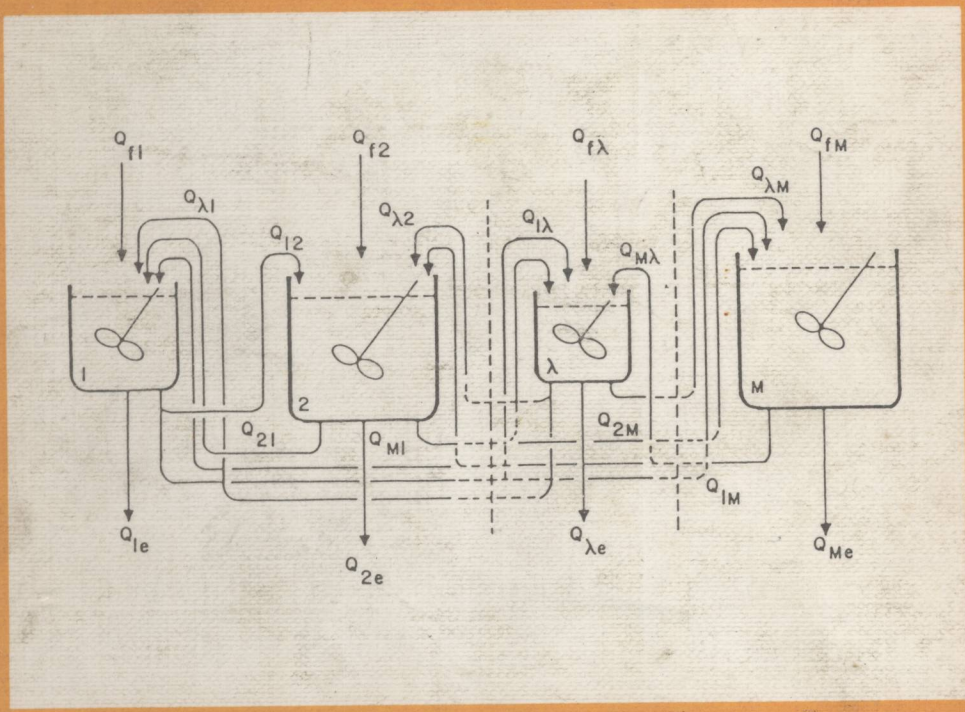
ISCRE 8

The Eighth International Symposium on

CHEMICAL REACTION ENGINEERING



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ISCRE 8

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Organised by the Institution of Chemical Engineers on behalf of the EFCE Working Party on Chemical Reaction Engineering, and held at the University of Edinburgh, 10-13 September 1984.

Symposium Co-Chairmen

Prof. G.S.G. Beveridge *(The University of Strathclyde)*

Prof. P.N. Rowe *(University College London)*

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PREFACE

ISCRE8 is the latest in a series of symposia on Chemical Reaction Engineering held every two years, alternating between the USA and Europe. ISCRE7 was held in Boston, USA, in October 1982 and ISCRE6 in Nice, France, in March 1980.

The conference aims to bring together experts in chemical reaction engineering from all over the world to provide a forum for discussion on developments in all aspects of the field, both academic and industrial.

ERRATUM

In paper 2.3 the text on page 687 should precede that on page 686.

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PLENARY LECTURES

THE PROBLEM OF DIFFUSIONAL TRANSPORT IN THE PERFORMANCE OF SUPPORTED LIQUID PHASE CATALYSTS

E. Wicke* and D. Hesse*

In SLP catalysts the liquid loading q of the porous carrier material occupies part of the pore space and thereby diminishes the permeability of the pore system. A study of the diffusion as a function of gas pressure yields detailed information on the distribution of the liquid within the porous framework. This is demonstrated by means of two types of support, with mono- and bi-disperse pore structures. The blocking effect can be described by a simple model equation that yields the effectiveness factor of the catalyst solution and explains the maximum of the reaction rate usually observed at $q \approx 0.5$.

INTRODUCTION

Two methods are currently being studied for the heterogenization of homogeneously catalyzed reactions: "supported solid phase catalysts", SSPC, or "supported liquid phase catalysts", SLPC. In SSP catalysts the catalytically active transition metal complex is chemically bound by reactive groups to the internal surface of an inert porous support, whereas SLP catalysts are prepared by impregnating a porous support with the catalyst solution using a solvent with low vapor pressure. In these SLP catalysts blocking of pore space by the catalyst solution deserves special attention [1]. This effect lengthens the transport ways of pore diffusion, and diminishes the exchange area between the open pore space and the catalyst solution. The yield in such catalyst systems is determined by two opposing effects: with ascending grade q of filling up the pore system with catalyst solution the amount of catalyst in the support increases; simultaneously, however, this causes a decrease of gas-liquid exchange area. Thus a maximum should be observed in the course of reaction rate with the loading q of the support. Indeed this has been found by earlier workers in the field [2-4]. Fig. 1 presents an example obtained by L. Heinrich [5] in our group.
For understanding the blocking effect in detail it is necessary to determine not only the pore diffusion resistance but also the mean value of the pore radii open for gas diffusion, and their change with increasing loading of the support framework. In order to get these informations the pressure dependence of the gas diffusion resistance has to be measured down to about 10^{-2} bar. Most suitable for such investigations is the method of counter-current

* Institut für Physikalische Chemie, Univ. Münster, F.R.G.

diffusion in a diffusion-reaction-cell [6] where use is made of the o-H_2/p-H_2 conversion. Measurements with this method are presented that have been made on two model pore systems impregnated with squalan [7]. The data obtained from an investigation like this on the blocking of the pore system can then be used to predict the optimal value of the support loading q of a given SLP catalyst.

PRESSURE DEPENDENCE OF GAS DIFFUSION THROUGH IMPREGNATED POR SYSTEMS

The ortho-para hydrogen method, principle and evaluation

The porous sample with the shape of a flat disk of thickness d and cross sectional area A separates in the measuring cell (DRC in Fig. 2) the reaction chamber R from the mixing chamber M. The reaction chamber contains a highly active platinum catalyst that establishes the equilibrium ratio o-H_2/p-H_2= 3/1 very quickly at room temperature. A constant flow Q of hydrogen, with about equal amounts of the two species is fed into the mixing chamber by means of a piston device AC. Part of the p-H_2 that enters the mixing chamber with the molar fraction x_E (see Fig. 2) diffuses through the porous wall (molar flux j_D) and is transformed in the reaction chamber to o-H_2 down to the equilibrium mole fraction x_{eq}. The rest of the p-H_2 leaves the mixing chamber with the exhaust (molar fraction x_A). Under steady state conditions the following p-H_2 balance for the mixing chamber holds:

$$Q \cdot c(x_E - x_A) = A \cdot j_D \qquad (1)$$

where c is the overall molar gas concentration. With

$$j_D = D_{eff} \cdot c \cdot \frac{x_A - x_{eq}}{d} \qquad (2)$$

it follows from equation (1) that

$$D_{eff} = \frac{d \cdot Q}{A} \cdot \frac{x_E - x_A}{x_A - x_{eq}} \qquad (3)$$

This equation yields the coefficient D_{eff} of the countercurrent o-H_2/p-H_2 diffusion through the porous sample from the geometrical data of the sample, the flow velocity, and the molar fractions of the p-H_2. These were determined by means of a thermal conductivity cell (TCC in Fig. 2) at the temperature of liquid nitrogen. A series of measurements at normal temperature and different total pressures p yields the wanted function $D_{eff} = D_{eff}(p)$.
For a successful application of the method it is necessary that in the pressure range of the measurements the diffusion resistance is determined by gas-gas as well as by gas-wall collisions. With pore radii of the order 1 to 10 µm this happens with pressures in the range $10^{-2} \leq p \leq 1$ bar, as they were applied here. In this socalled transition range the overall diffusion resistance is to be taken as the sum of the resistances of normal gas diffusion and of Knudsen flow (Bosanquet-formula, see for instance [8]):

$$1/D_{eff} = 1/D^G_{eff} + 1/D^K_{eff} \qquad (4)$$

The resistance of normal gas diffusion can be expressed by: