

## DIFFUSION AND SURFACE REACTION IN HETEROGENEOUS CATALYSIS

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**T**HE INTERACTIONS between mass transfer and chemical reaction in heterogeneous catalysis are described in many textbooks on chemical reaction engineering. However, few laboratory experiments are known that permit the student to apply his theoretical knowledge [1]. This is certainly due to the fact that it is difficult to find suitable easy-to-handle heterogeneous reaction systems. Furthermore, a rigorous quantitative determination of the chemical reaction rate on the catalyst surface is not possible in most cases since boundary conditions that permit a solution of the differential equations describing mass transfer are too complicated.

Now, the ethylene hydrogenation on a platinum catalyst, electrolytically applied to a tube wall, proved to be a good system for the study of the interactions between diffusion and surface reaction in heterogeneous catalysis. Boundary conditions are well defined and by varying the temperature from room temperature to 180°C, the transition between surface reaction control and mass transfer control can be well observed. Since the differential mass balance can be integrated numerically for this laminar flow system, an exact value of the surface reaction rate constant may be obtained.

In a previous publication [2], some aspects of the 4th year ChE laboratory program at the Swiss Federal Institute of Technology (ETH) have been described. This experiment is part of that course and has been developed in recent years in order to combine transport phenomena and heterogeneous catalysis and to bring at the same time the FORSIM computer simulation program [3] into

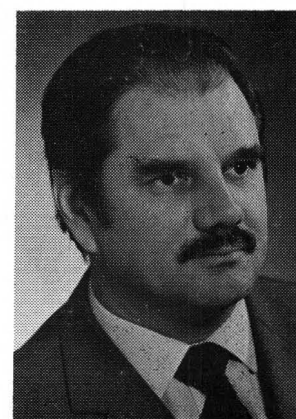
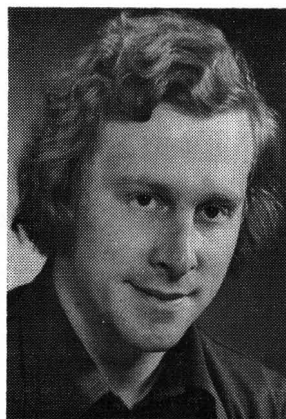
ChE laboratory. Its application permits the student to integrate the differential mass balance and helps to take away some of the magic still associated with partial differential equations.

In fact, the laminar flow system used has a simple geometry (tube) so that the differential mass balance is easily established and boundary conditions can be precisely stated. After transformation of the partial differential equations to dimensionless form as described by Bräuer [4], the numerical integration by the FORSIM program is straightforward and rapid.

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## THEORETICAL BACKGROUND

IT HAS BEEN SHOWN that the ethylene hydrogenation is 1<sup>st</sup> order with respect to ethylene (gas mixture: 98% H<sub>2</sub>, 2% C<sub>2</sub>H<sub>4</sub>). Thus the global reaction rate can be defined as:

$$r_G = -k_{\text{eff}} \bar{c}(x) \quad (1)$$

The average ethylene concentration at the exit of the reactor is therefore:

$$\bar{c}(L) = c_0 \exp(-k_{\text{eff}} \tau) \quad (2)$$

The surface reaction rate is given by:

$$r_s = -k_s c(R, x) \quad (3)$$

The influence of diffusion can be seen by comparing the global and surface reaction rates. However, for this comparison  $k_{\text{eff}}$  has to be multiplied by  $V_R/S$ . The surface reaction rate is determined by integrating the differential mass balance over the cross section and length of the reactor.

We assume that

- we have a constant volume reaction (in fact,  $\epsilon \leq .02$ )
- the reaction is conducted isothermally
- the flow is steady-state and the laminar velocity profile is fully developed
- axial diffusion is negligible as compared to the transport by bulk flow.

Therefore we have the following mass balance:

$$D \left[ \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r} \right] - 2\bar{v}_x \left[ 1 - \left( \frac{r}{R} \right)^2 \right] \frac{\partial c}{\partial x} = 0 \quad (4)$$

For the system described in Figure 1 the boundary conditions are:

$$c(r, 0) = c_0 \quad (5)$$

$$\frac{\partial c(0, x)}{\partial r} = 0 \quad (6)$$

$$D \frac{\partial c(R, x)}{\partial r} = -k_s c(R, x) \quad (7)$$

Bräuer [4] integrated equation (4) numerically after transformation to dimensionless form by introducing the numbers given in Table 1.

Thus equations (4) to (7) become:

$$\frac{\partial^2 f}{\partial \rho^2} + \frac{1}{\rho} \frac{\partial f}{\partial \rho} - 2[1 - \rho^2] \frac{\partial f}{\partial \theta} = 0 \quad (8)$$

$$f(\rho, 0) = 1 \quad (9)$$

$$\frac{\partial f(0, \theta)}{\partial \rho} = 0 \quad (10)$$

$$\frac{\partial f(1, \theta)}{\partial \rho} = -Da f(1, \theta) \quad (11)$$

The mean concentration  $\bar{f}(\theta)$  at the exit of the reactor is calculated by integrating  $f(\rho, \theta)$  over the cross section:

$$\bar{f}(\theta) = \frac{\int_0^1 \rho(1 - \rho^2) f(\rho, \theta) d\rho}{\int_0^1 \rho(1 - \rho^2) d\rho} \quad (12)$$

The results of the numerical integration by the FORSIM-program are given in Figure 2. For all important parameters the programs default values

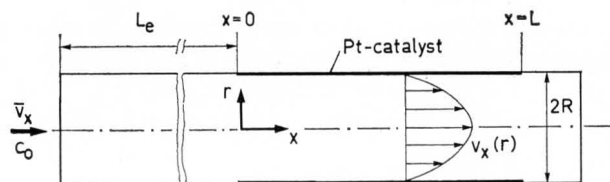


FIGURE 1. Notations for the ethylene hydrogenation system

can be used (Runge-Kutta-integration, eleven spatial points, three-point difference formulae). Equation (12) is integrated by the Simpson-method. For the evaluation of the experimental

As a whole, this experiment proved to be a very helpful tool for a better understanding of the influence of diffusion on heterogeneous chemical reactions.

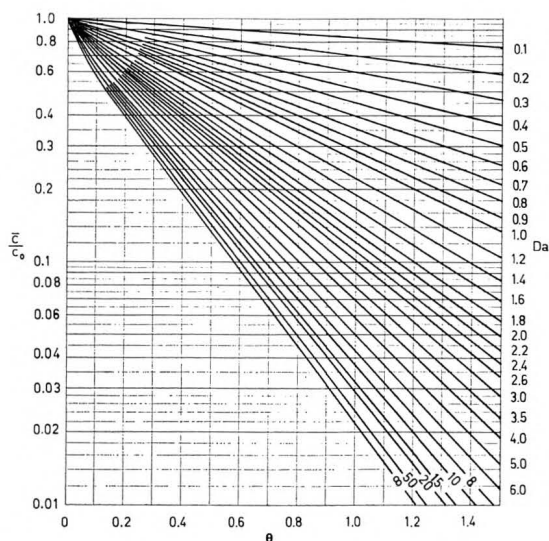


FIGURE 2.  $\bar{c}/c_0$  as a function of  $Da$  and  $\theta$

results i.e. the determination of the surface reaction constant, the graph as given in Figure 2 is most useful. The diffusion coefficients needed can be estimated e.g. by the Wilke-Lee-method [5].

#### APPARATUS

A SCHEMATIC DIAGRAM of the experimental system is given in Figure 3. It consists essentially of two gas cylinders containing pure  $H_2$  and the premixed 98%  $H_2/2\%$   $C_2H_4$ , a gas metering valve, the thermostated reactor tube, a gas meter and a gas chromatograph.

In our setup we use an automatic sampling valve, but sample taking with a gas syringe is equally good, only a bit more tiresome.

A simple gas chromatograph is sufficient; we

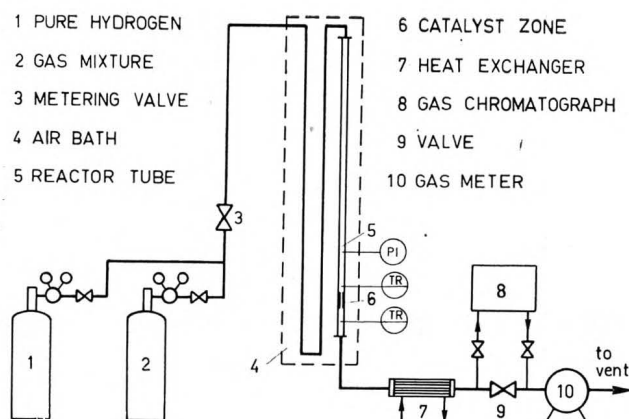


FIGURE 3. Flow diagram of experimental reactor system

use a GowMac 69-552. Column: Poropak s, length 1.7 m, inner diameter 0.005 m. Column temperature:  $55^\circ C$ . Detector: HW. Analysis time: 4 min.

Reactor and piping are made of stainless steel. The reactor tube is heated in an air bath and has the following dimensions: inner diameter 0.02 m, length 1.4 m. Gas temperature is measured before and after the reaction zone with NiCr/Ni thermoelements enabling one to verify that the reaction is conducted isothermally. The platinum catalyst is not directly applied to the tube wall but to a thin tubular nickel support consisting of two separate halves, put together by means of two O-rings (see Fig. 4).

After electrolysis, the support is put together and introduced into the reactor. The catalyst zone length is 0.1 m. If the zone is longer, the reaction

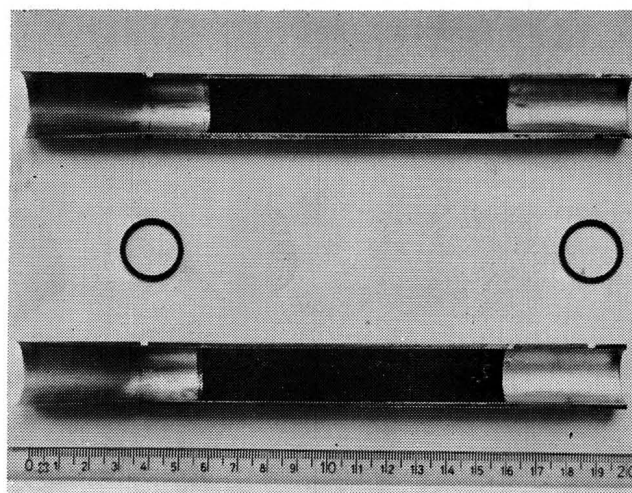


FIGURE 4. Catalyst support

can not be conducted isothermally. The entrance length is 1.2 m.

#### PROCEDURE

IN ORDER TO HAVE high and constant activity, fresh catalyst is prepared for each series of measurements (old catalyst is easily wiped off the nickel support). For the electrolysis, each half of the nickel support is treated separately in a 3% aqueous solution of  $H_2(Pt_6Cl_6) \cdot 6H_2O$ . At a current of 0.4 A ( $750 A/m^2$ ) electrolysis time is 3 minutes. The catalytic surface is then rinsed with distilled water. The catalyst is introduced into the reactor tube and heated to the highest desired temperature in a pure hydrogen atmosphere in order to avoid catalyst poisoning. At a given temperature, measurements are made at several gas flow rates vary-

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ing from 0.001 to 0.006 m<sup>3</sup>/min. Steady state is always quickly achieved (less than the time necessary for product gas analysis). Usually the measurements are carried out going from the lowest to the highest temperature.

### STUDENT PERFORMANCE

**T**HIRTY HOURS LABORATORY TIME during 3 weeks are provided for this experiment. The students usually need about a day for the theoretical preparation of the experiment and to get acquainted with the apparatus. Some difficulty arises from the fact that a change of flow rate in the reactor has to be made with valves 3 and 9 simultaneously in order to maintain the pressure at a given value. The experiments should be run in one day in order to have constant catalytic activity. Invariably, good results are obtained. Evaluation of the measurements are rapid,  $k_{eff}$  is calculated from equation (2),  $k_s$  is determined from the Damköhler group by means of the graph given in Figure 2. Some typical results are given in Figure 5.

In addition, for some of their experiments the students have to calculate axial and radial concentration profiles in the reactor by means of the FORSIM-program. Previously we discuss the physical situation with the students. Their uncertainty clearly shows the need for this exercise. As a whole, this experiment proved to be a very helpful tool for a better understanding of the influence of diffusion on heterogeneous chemical reactions.

TABLE 1. Dimensionless groups

DEFINITION	SIGNIFICANCE
$Da = \frac{k_s R}{D}$	$\frac{\text{chemical reaction rate}}{\text{diffusion rate}}$
$\theta = \frac{D L}{R^2 v_x}$	$\frac{\text{mean residence time}}{\text{diffusion time from tube center to wall}}$
$\rho = \frac{r}{R}$	$\frac{\text{radius (variable)}}{\text{tube radius}}$
$f = \frac{c}{c_0}$	$\frac{\text{concentration (variable)}}{\text{concentration at reactor entrance}}$

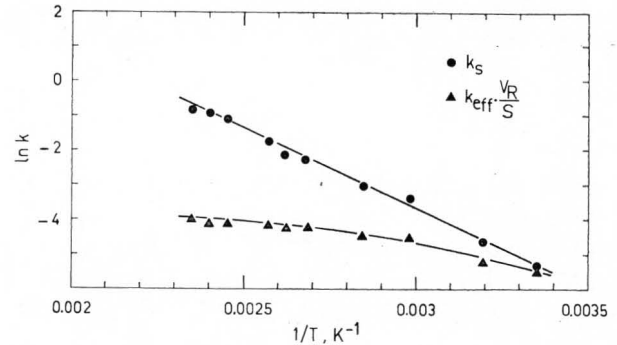


FIGURE 5. Arrhenius plot of reaction rate constants

### ACKNOWLEDGMENT

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### NOMENCLATURE

$c$	concentration, mole/m <sup>3</sup>
$c_0$	initial concentration, mole/m <sup>3</sup>
$\bar{c}$	mean concentration, mole/m <sup>3</sup>
$D$	diffusion coefficient, m <sup>2</sup> /s
$Da$	Damköhler
$k_{eff}$	effective reaction rate constant, s <sup>-1</sup>
$k_s$	surface reaction rate constant, m/s
$L$	catalyst zone length, m
$r$	radius (variable), m
$R$	tube radius, m
$r_G$	global reaction rate, mole/m <sup>3</sup> ·s
$r_s$	surface reaction rate, mole/m <sup>2</sup> ·s
$S$	catalyst surface, m <sup>2</sup>
$\bar{v}_x$	mean flow rate, m/s
$V_R$	volume of catalyst zone, m <sup>3</sup>
$\epsilon$	fractional volume change
$\tau$	mean residence time, s

### REFERENCES

1. J. B. Anderson, *Chem. Eng. Ed.* 1, 78 (1971) and *Chem. Eng. Ed.* 2, 130 (1971).
2. J. Dunn, J. E. Prenosil, J. Ingham, *Chem. Eng. Ed.* 1, 23 (1976).
3. M. B. Carver, FORSIM: a Fortran-oriented Simulation Package, Atomic Energy of Canada Limited report AECL-4844 (1974).
4. W. Bräuer, F. Fetting, *Chem. Ing. Techn.* 38, 30 (1966).
5. C. R. Wilke and C. Y. Lee, *Ind. Eng. Chem.* 47, 1253 (1955).