

Dynamics of H₂ production by steam reforming

P. Beckhaus^a, A. Heinzel^{a,b}, J. Mathiak^{a,*}, J. Roes^b

^a Zentrum für BrennstoffzellenTechnik GmbH, Carl-Benz-Str. 201, 47058 Duisburg, Germany

^b Department of Energy Technology, University of Duisburg, 47048 Duisburg, Germany

Abstract

The determining step for the dynamics of a fuel cell system including a hydrogen processor is the gas process itself. A simulative approach is presented to calculate the step response of a complete steam reformer system including heat exchangers and shift reactors. This tool enables the prediction of load- and time-depending pressure drop and mole flow. Additional simulations were carried out concerning chemical kinetics. Thermodynamic equilibrium, reaction rate and local temperatures are considered in this model and partial load gas compositions can be calculated. The comparison of the simulative results to experimentally taken data of a manufactured prototype show a reasonable accuracy.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Steam reforming; Dynamics; Hydrogen; Fuel cell; Simulation

1. Introduction

In traditional steam reforming plants (e.g. applications in refineries and petroleum industry) dynamic behaviour has not been a matter of interest. While reactor sizes decrease and hydrogen generation tends to decentralize for residential power supply on CHP-basis in the power range of 1–10 kW_{el}, the transient reaction of chemical reactors reach higher importance [1]. Especially if combined with fuel cells the dynamic potential of the electrochemical electricity source should be utilized to satisfy rapid load change demand. Therefore investigations into transient reaction of chemical reactors or plants are necessary. If tools for simulating the dynamic behaviour are available, successful prototyping would not be a time consuming task.

The design of the steam reforming process is explained referring to Fig. 1 where the main reactions of each conversion are subscribed. First, natural gas is desulphurized in, e.g. impregnated active carbon at room temperature from natural sulphur and odorizers. After blended with water in a molar ratio of 3 the mixture reacts over a catalyst at 800 °C. The dry composition of the reformat gas is about 77% hydrogen, 15% carbon monoxide and 8% carbon dioxide. Methane can be reduced to 0.4%. During the following water–gas-shift reactions the CO-contents can be converted to less than 1% before the residual catalyst-poison

is removed in a preferential oxidation unit consuming a stoichiometric air-ratio of 2. Afterwards, useful energy in form of power and heat is produced in a PEM fuel cell.

Generally two different aspects of non-steady-state operation have to be distinguished: cold startup and load change. Both phenomena are determined by different influences and thus must be investigated separately. This article focuses on load change reaction. Variation of load is accompanied by a change of pressure drop caused by varied volume flow described in Section 2, and a change of concentration due to a different space velocity (Section 3). Fluid dynamics and kinetics are investigated individually.

2. Fluid dynamics

The fluid dynamic step response of one chemical reactor can be calculated with tools of control engineering. A reactor can be simulated as a free volume followed by a flow resistance according to Fig. 2.

The volume V accounts for the pressure capacity and flow inertia, respectively. Corresponding to the thermodynamics of ideal gases the following equation can be applied:

$$p = \frac{nRT}{V} \Rightarrow \frac{\partial p}{\partial t} = \frac{(\dot{n}_{in} - \dot{n}_{out})RT}{V} \quad (1)$$

The nozzle in Fig. 2 represents a flow resistance K , which is proportional to the square of mole flow (e.g. friction in

* Corresponding author.

E-mail address: j.mathiak@zbt-duisburg.de (J. Mathiak).

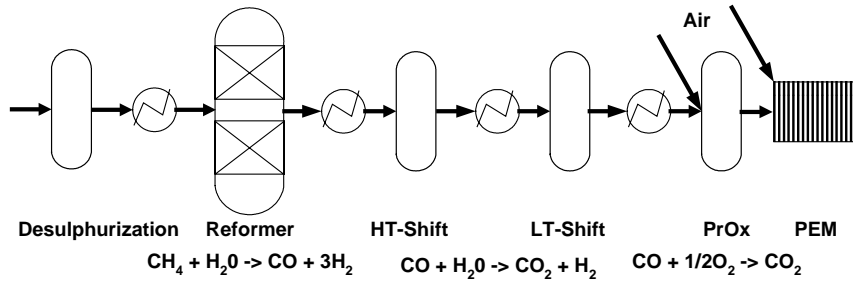


Fig. 1. Principle scheme of a steam reforming process.

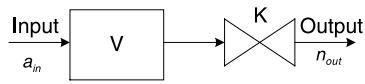


Fig. 2. Model of fluid dynamic simulation of chemical reactors.

pipes, change of cross-section area) [2]:

$$\ddot{A}p = K\dot{n}_{out}^2 \tag{2}$$

Hence, the equations build a set of two differential equations, but its solution is fairly complex. Commonly, this problem is solved by linearising the function at the operation level [3]. This procedure should not be applied, if the

research target is a wide range of scaling as in the considered objective. So simulation tools are required; in this case MATLAB and Simulink were used. Fig. 3 shows the setup of a fluid dynamic model according to Fig. 2 and Eqs. (1) and (2) and represents one chemical reactor or heat exchanger.

The input mole flow reduced by the output mole flow (which is the net input) is multiplied by the factor RT/V in accordance with Eq. (1). After integration the resulting pressure is divided by the flow resistance K and the root of this is the output mole flow (see Eq. (2)). Each reactor has a specific volume V_i and flow resistance K_i , which could either be estimated or measured.

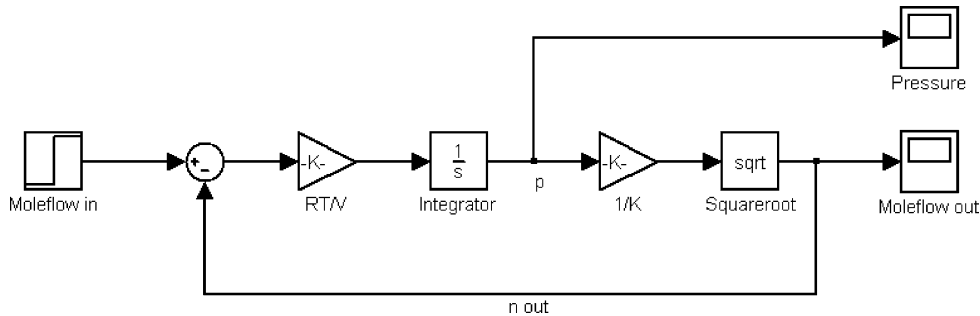


Fig. 3. Model of fluid dynamic simulation in MATLAB and Simulink.

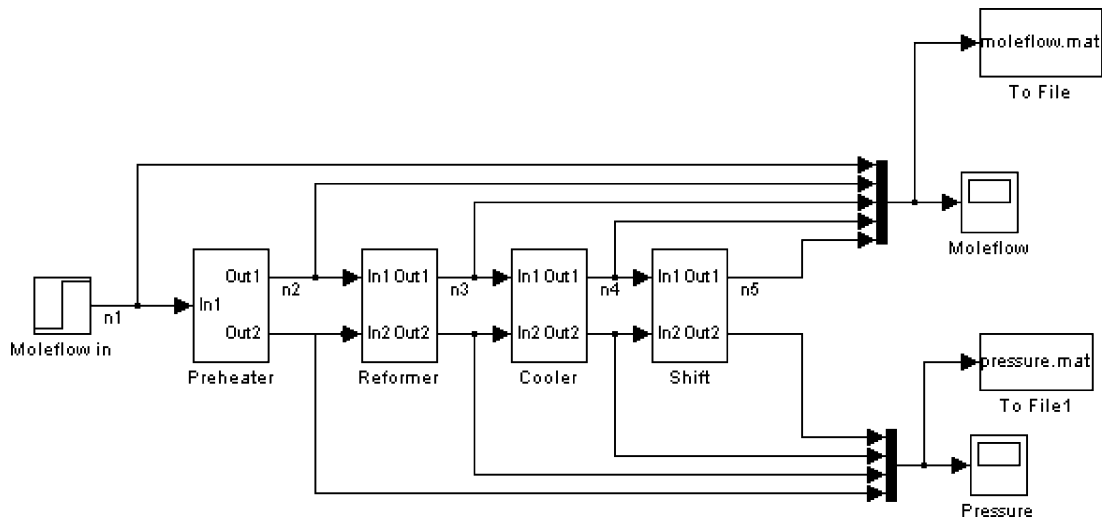


Fig. 4. Model of fluid dynamic simulation of a complete steam reformer system.

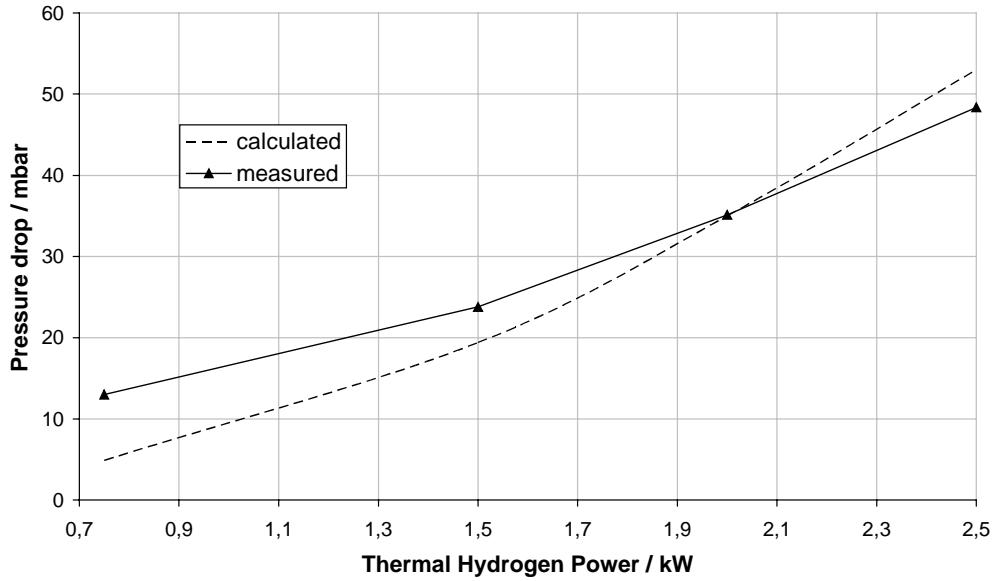


Fig. 5. Measurement and simulation of pressure drop.

The interaction of reactors and heat exchangers forming a complete steam reforming system is simply the sequential connection of several single simulations described above and the step response of one component is the input of the following. The fluid dynamic scheme of a steam reformer is shown in Fig. 4.

Important to notify is the mole flow increase inside the reformer due to molar multiplication according to the chemical reaction of the steam reforming process forming CO and 3H₂ from CH₄ and H₂O. With this calculation a prediction of the load-dependent and the time-dependent pressure drop downstream the plant is possible. Both have been calculated

and measured at a manufactured reformer with a rated load of 2.5 kW thermal hydrogen power output (Figs. 5 and 6). In Fig. 5 the pressure drop of the steam reformer in dependence of the load is presented.

Due to the fact, that volumes and flow resistances of the single components were estimated on the basis of engineering drawings the differences between simulation and experimental data are negligible and show reasonable accuracy.

Additionally, the transient pressure drop and volume flow of each reactor or heat exchanger can be examined from the same simulation shown in Fig. 4. As an example, Fig. 6

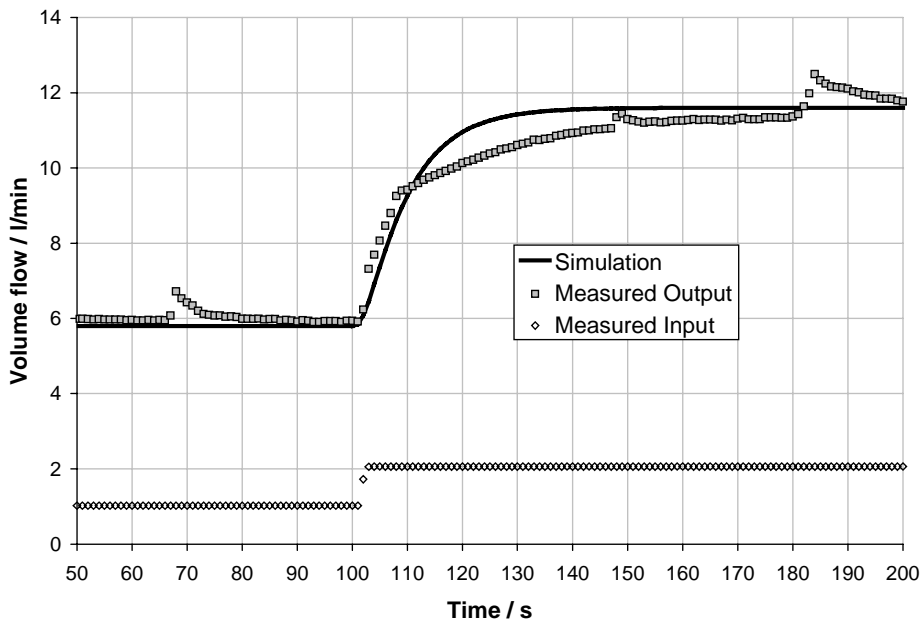


Fig. 6. Measurement and simulation of transient volume flow.

shows a load change reaction from 0.75 kW_{th} thermal hydrogen power to 1.5 kW_{th}.

In the shown experiment and in the related simulation the inlet volume flow was increased after 100 s. Also the

simulated step response corresponds well to the measurements and reveals real effects. Both data demonstrate a quick response on a load change and no time delay can be identified.

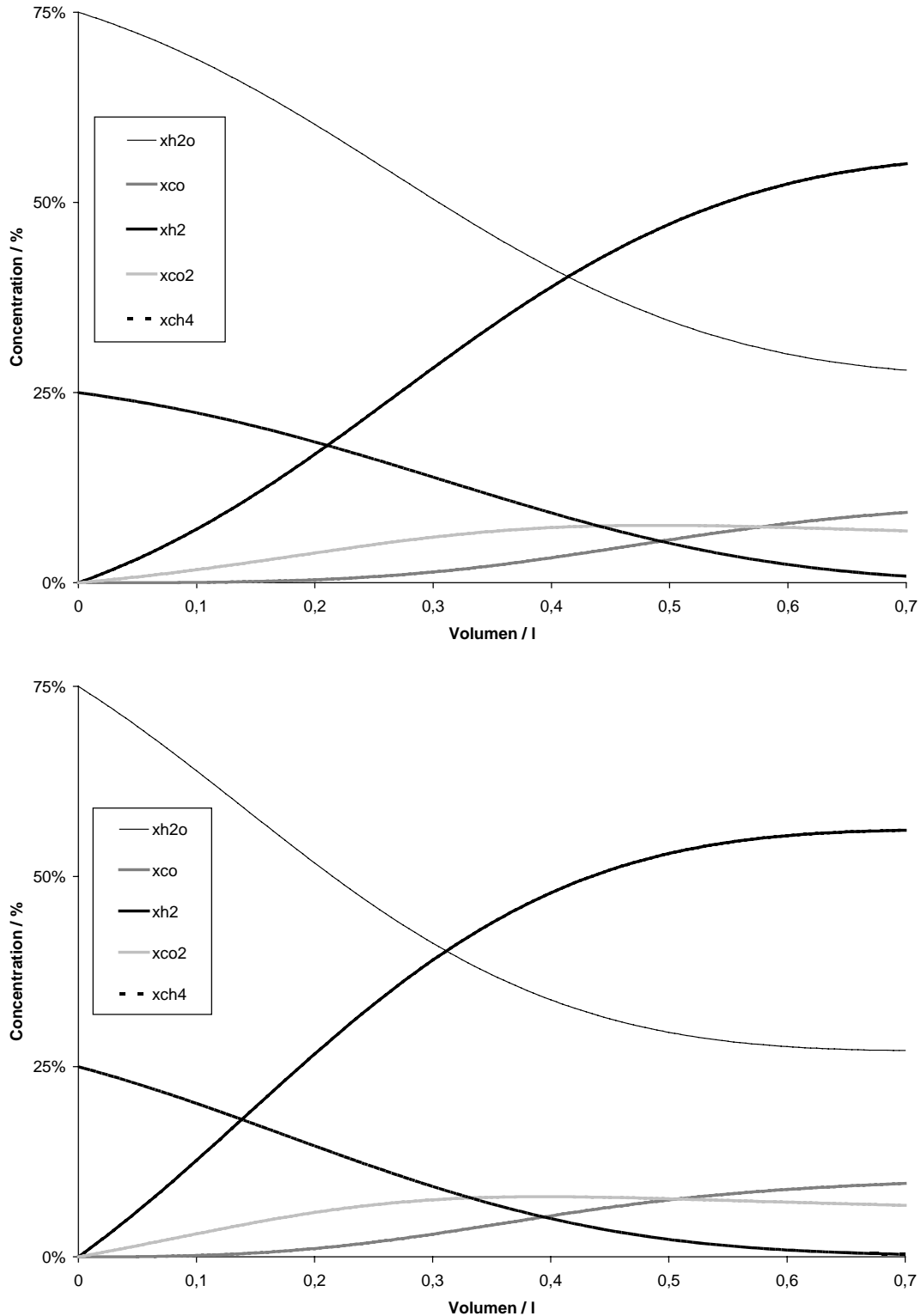


Fig. 7. Calculated reaction proceeding in the reforming section: rated load (top diagram) and 50% partial load (bottom diagram).

3. Kinetics

Partial load leads to lower space velocities and hence to other gas compositions under steady-state conditions. If the kinetics of the incorporated catalysts are known, the load-dependent gas composition can be forecast by applying the kinetic model, e.g. the Arrhenius equation. It is necessary to substitute the partial pressure of relevant components by the difference of the partial pressure to the thermodynamic equilibrium [4]. Otherwise complete conversion would occur. As an example, the reaction rate for steam reforming as a simple power law equation is

$$r = k_0 e^{-\frac{E_a}{RT}} (x_{\text{CH}_4} - x_{\text{CH}_4, \text{Eq}}(T)) \quad (3)$$

In addition, the parallel executed shift-conversion is assumed to be in thermodynamic equilibrium immediately due to a much higher reaction rate compared to the methane steam reforming. As an example, Fig. 7 presents the results of the calculated reaction proceeding at rated load (top diagram) and at 50% partial load operation. The calculations are based on a constant pressure of 1 bar, a steam to carbon ratio of 3 and a temperature profile from 500 °C at the inlet and 700 °C at the outlet.

In comparison the methane conversion is higher in partial load (second diagram) because of lower space velocity and higher residence time, respectively. The residual methane concentration of this calculation is compared to measurements in Fig. 8.

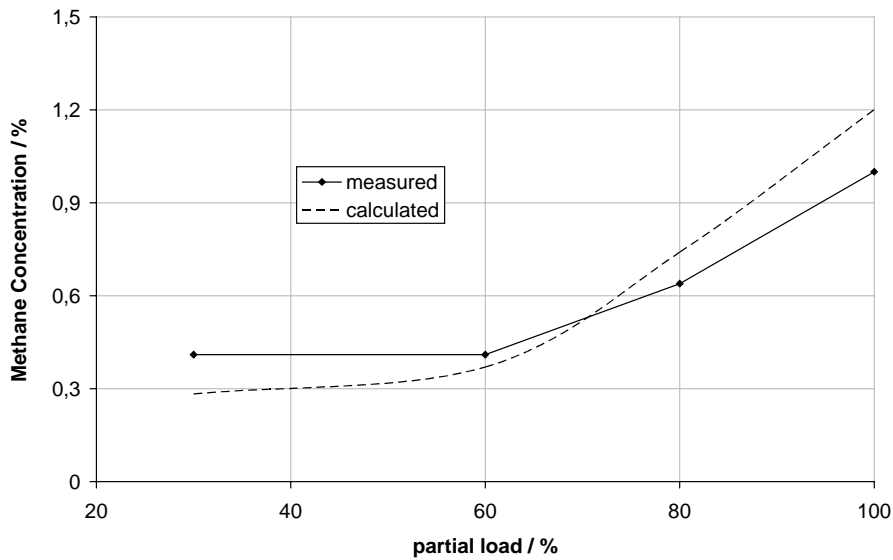


Fig. 8. Measured and calculated methane concentration.

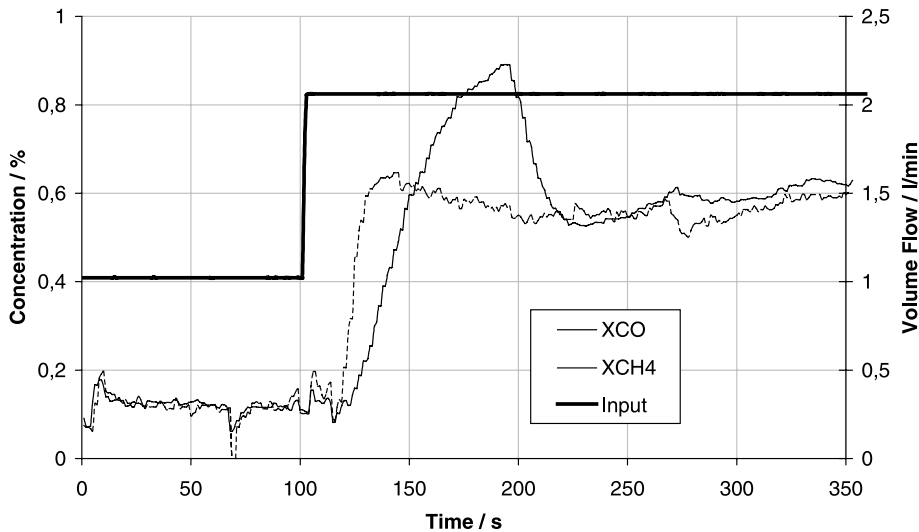


Fig. 9. Measurement of transient methane and carbon monoxide concentration.

A method to estimate the time-dependent concentration under load change condition has not yet been found. Several load change reactions have been carried out experimentally. Fig. 9 shows an example of a load change reaction.

The methane and carbon monoxide concentrations change their steady-state levels from about 0.2 to 0.6% with a time delay that is caused by the gas analysis and not by the steam reformer system. The carbon monoxide curve shows a slight overshoot, while methane concentration changes its steady-state operation points rapidly.

4. Results and discussion

A method of describing and calculating the time- and load-dependent pressure drop has been presented. Its application enables the prediction of expected flow resistances and fluid dynamic step response for partial load and under load change conditions. Possible accuracy has been proven by measurements at a manufactured steam reformer

designed for residential power supply by a PEM fuel cell. Hence, specification of peripheral components (e.g. pumps), system optimization and dynamic investigations are possible.

Gas compositions at partial load can simply be calculated by use of a suitable kinetic model. Although common kinetic models describe elementary reactions they can be applied if the concentrations as driving forces are substituted by the difference between the considered concentration and concentration at thermodynamic equilibrium.

References

- [1] K. Ledjeff (Ed.), Brennstoffzellen: Entwicklung, Technologie, Anwendung, second ed., Müller-Verlag, Heidelberg, 2001.
- [2] W. Beitz, K.-H. Küttner, *Dubbel—Taschenbuch für den Maschinenbau*, 20th ed., Springer-Verlag, Berlin, 2001.
- [3] W. Oppelt, *Kleines Handbuch Technischer Regelvorgänge*, fifth ed., Verlag-Chemie, Weinheim, 1972.
- [4] J.R. Andersen, M. Boudart (Eds.), *Catalysis—Science and Technology*, vol. 5, Springer-Verlag, Berlin, 1984.