

# Practical Problems in the Modelling of Chemical Reactions in Fixed Bed Reactors

Praktische Probleme bei der Beschreibung von chemischen Reaktionen in Festbettreaktoren

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## Abstract

Establishing a reaction rate model consists of the following steps: experimental design, evaluation of experimental results, choice of main components and main reaction steps, choice of a mathematical model for the test reactor and the rate equations and parameter identification. It will be shown that each of the above steps requires a number of decisions and assumptions which limit the general validity and extrapolability of the resulting model. In particular there is a strong interrelation of the rate equation and the underlying model of the reactor in which the kinetic experiments are performed.

The restricted extrapolability requires discrimination between two different ways of using mathematical models. For design purposes, models are required which have the character of interpolations between experiments rather than that of extrapolations. In the second category models are used for speculative extrapolations to gain a better qualitative understanding of the complex interactions of transport and reaction. This in turn provides a base for decisions among rival options in chemical reaction engineering research and development.

## Zusammenfassung

Die Ermittlung eines Reaktionsgeschwindigkeitsmodells erfordert folgende Schritte: Planung und Auswertung von Versuchen, Auswahl von Schlüsselkomponenten und Hauptreaktionsschritten, Wahl eines mathematischen Modells für den Versuchsreaktor sowie eines Ansatzes für die Reaktionsgeschwindigkeiten und schliesslich Bestimmung der offenen Parameter durch Anpassungsrechnungen. Es soll gezeigt werden, dass jeder der genannten Schritte Annahmen und Entscheidungen zwischen möglichen Optionen erfordert, die die Allgemeingültigkeit und die Extrapolierbarkeit des erhaltenen Modells einschränken. Insbesondere gibt es starke Wechselwirkungen zwischen den resultierenden Reaktionsgeschwindigkeitsausdrücken und dem Reaktormodell, mit dem die Versuche ausgewertet werden.

Die eingeschränkte Extrapolierbarkeit führt dazu, dass man zwischen zwei verschiedenen Anwendungsmöglichkeiten mathematischer Modelle unterscheiden sollte. Für Auslegungszwecke werden Modelle benötigt, die mehr der Interpolation zwischen verschiedenen Versuchen dienen als der Extrapolation aus dem Versuchsrahmen heraus. Der zweite Anwendungsbereich umfasst die spekulative Vorausberechnung, durch die ein besseres qualitatives Verständnis für die komplexen Wechselwirkungen zwischen Transportvorgängen und chemischer Reaktion erreicht werden kann. Solange andere Kriterien fehlen, bieten solche Abschätzungsrechnungen eine rationale Grundlage für Entscheidungen zwischen unterschiedlichen reaktionstechnischen Alternativen in Forschung und Entwicklung.

## Introduction

The design of chemical reactors and the simulation of their behavior by means of mathematical models is of ever growing practical importance. This paper deals with the basis of such mathematical models, the reaction rate expression, and the problems and difficulties associated with its experimental determination. The following steps will be considered as being the most important ones in leading to a macrokinetic or formal reaction rate expression:

- Choice of the test reactor and design of the experiments.
- Evaluation and balancing of the experimental results.
- Choice of the main reaction steps and the main reaction components.
- Choice of a suitable mathematical structure for the rate expression.
- Choice of a mathematical model for the test reactor.
- Parameter identification.

It is not the intention of this paper to give a comprehensive review of methods to be used in the determination

of rate equations (see ref. 1) but to discuss major practical problems encountered in each of the above steps.

The discussion will be limited to reactions in fixed-bed reactors but most of the problems mentioned can also be found in analysing reactions in other reactor types.

The basis for the discussion is that of industrial application, where, with a limited amount of time and money, results are required that lead to an improved design and/or operation of the reactor.

The restricted resources for the determination of the rate model are to some extent compensated in practice by the fact that the required range of validity of the model is also restricted by the specific task. This is of great practical importance since it reduces the problem considerably and in many cases provides the only way to arrive at a solution at all. On the other hand the rate models thus derived can—at best—be considered a formal or overall image of the true or intrinsic kinetics within a limited range of operating conditions.

### Test reactor and experimental set-up

The first important questions are raised in connection with the choice of a suitable test reactor and the measurement technique. In heterogeneously catalyzed reactions the differential loop reactor has been strongly promoted as "kinetic reactor" in recent years (see ref. 2 for a survey). However, its behavior is in many aspects different from the behavior of industrial reactors of either the fixed-bed, fluidized-bed or moving-bed type. Loop reactor kinetics can therefore only be used successfully in models of industrial reactors if the following conditions are fulfilled: (i) the loop reactor kinetics are not disguised by non-kinetic effects, (ii) a model for the industrial reactor is available which reliably distinguishes between the kinetic influence and the influence of transport processes such as flow profile, mixing characteristics and heat transport.

It is the author's belief that in most cases at least one of these two requirements is not fulfilled and that the few papers which claim a successful transfer of loop reactor kinetics to the modelling of fixed-bed reactors are the exception rather than the rule.

A reliable model for an industrial reactor is of course much more difficult to obtain than unequivocal (formal) kinetics from loop reactor experiments. But even this seemingly easier task has a number of pitfalls which will briefly be mentioned below:

- In complex reactions a careful design of experiments is necessary to discriminate between purely kinetic effects and effects brought about by the well-mixed environment.
- Reaction conditions with very low concentrations of certain reaction components (as at the entrance of an integral reactor for products or at the exit of an integral reactor at high conversions for feed components) are difficult to realize in loop reactor experiments. The latter may lead to a poor description of the reaction rate in the important range of high conversions.

- In the common types of loop reactors the ratio of void volume to catalyst volume is at least three times as great as in fixed-bed reactors. This means that homogeneous side reactions in the voids may influence the experimental results. Typical examples are partial oxidation reactions of hydrocarbons where it has been well established that some of the undesired side reactions towards total combustion take place in the gas phase as so-called "cool flames" [3]. A complete description of the kinetics therefore would require a separate formulation of the catalyst kinetics and the homogeneous kinetics. However, differentiation between the two effects by suitable measurements in empty reactors seems impossible since some of the necessary components needed for the homogeneous reaction (aldehydes and hydroperoxides) will be formed on the catalyst, so that without catalyst no, or only a minor, homogeneous reaction takes place.
- A similar objection is in order if the reaction is partly catalyzed on the reactor walls.
- A further difference between the behavior of the (differential) loop reactor and that of the (integral) fixed-bed reactor is the effect of catalyst deactivation. The kind of deactivation (front to end, end to front or uniform deactivation) can be decisive for the reactor design and its operation. Because of the complete backmixing only uniform deactivation is observed in loop reactors.

The uncertainties in the transfer of loop reactor results to the operation of fixed-bed reactors therefore require further experiments in integral fixed-bed reactors. The question can then be asked whether loop reactor experiments are necessary at all or whether the experimentation can be confined to integral test reactors. The latter has been common industrial practice, especially in the scale-up of multitube fixed-bed reactors, which up to now has often been performed empirically without the aid of formal kinetics and mathematical models.

Attention is focussed below on the extraction of reaction rate models from integral reactor data. A typical experimental configuration is given in Fig. 1. The reactor tube dimensions are such that either isothermal operation can safely be assumed or a temperature measurement along the length of the reactor is required. Composition measurements would be strongly desirable not only at

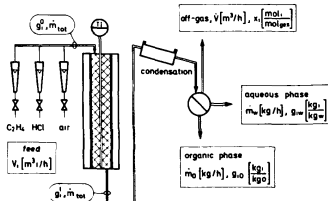


Fig. 1. Integral test reactor set-up for the oxychlorination reaction. (▭) possible measurements, (○) desired information.

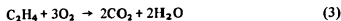
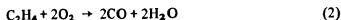
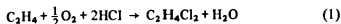
the exit but also at different points over the length of the reactor but usually this information is not available. The amount of feed and exit composition analysis depends upon the requirements of the evaluation and the balancing of the experiments and will be discussed in this context later.

### Design of experiments

Formal planning of the experiments in the sense of a statistical experimental design [1] is frequently claimed to be a requirement in deriving reaction rate models. In practice, however, experimental difficulties and unexpected results usually prevent a formal experimental design at an early stage. Only after the questions of main reaction components, main reaction steps and reasonable mathematical forms of the reaction rate expressions have been more or less settled, can the tool of formal experimental design be used reasonably. In the case of complex kinetics this can be a very powerful tool since it requires measurements at points where the sensitivity of the system to a given question is at a maximum. In many cases, however, the range of strong sensitivity is quite obvious and statistical experimental design never is a substitute for intuition and careful interpretation and evaluation of experimental results.

### Evaluation of experimental results

The feed and the exit composition required for modelling the test reactor cannot usually be measured directly but have to be calculated from a number of different measurements. Figure 1 gives an example for the oxychlorination of ethene to 1,2-dichloroethane with the main reaction steps



The reaction products will be found in two liquid phases (organic and aqueous) and in the gas phase. If the feed consists of a mixture of the pure components  $C_2H_4$ ,  $HCl$  and air, knowledge of the mass of the aqueous and organic phases as well as the compositions of the two liquid phases and the gas phase would be sufficient to calculate the reactor mass-flow rate and the feed and exit composition. The necessary additional information is taken from the element balances for C, Cl,  $H_2$  and  $O_2$ .

Usually more than this minimum set of measurements is available. In our case, for example, the flow rates of the different feed gases and of the off-gas can also be measured. In practice, every measurement is subject to measurement errors. This means that the calculated feed and exit concentrations vary, depending on the set of measurements that are used for its determination. A simple way of avoiding disagreement between redundant measurements is to restrict the measurements to

the minimum. However, this removes an effective means of detecting measurement errors.

The simplest means of detecting measurement errors using redundant measurements is to calculate the differences in the element balances between reactor entrance and exit. Frequently additional "balancing" of the measurements is performed, the measurements being corrected in such a way that the element balances and additional stoichiometric relations are fulfilled. The fulfillment of the element balances seems necessary for the later step of comparison between the mathematical model and the experimental results because otherwise it is not clear whether a bad fit is due to inconsistent measurements or due to the wrong model. However, in some cases such a balancing procedure has a negative effect in that it only slightly improves wrong measurements while good measurements are impaired. An example will be discussed briefly.

The process of balancing measurements is based upon the supposition that measurement errors are statistically distributed and that each measurement can be weighted with respect to its assumed mean deviation. In practice, however, a (known) statistical error distribution is of minor importance as compared to (unknown) systematic errors, such as leakages, drift, wrong calibration, etc. During the balancing procedure a systematic error is distributed more or less evenly over all measurements. Thus, good measurements are impaired while a wrong measurement is only slightly improved. Table I gives a simple example with two systematic errors. As can be expected, the error in the entrance mass flow rate  $\dot{m}^0$  is evenly distributed over the entrance and exit mass flow rates,  $\dot{m}^0$  and  $\dot{m}^1$ . However the systematic error in one of

TABLE I. Example of the balancing procedure in the presence of two systematic errors (weight fractions  $g_i$  and mass flow rate  $\dot{m}^i$ )\*

	Exact value	Measurement error	Correction through balancing procedure	
			abs.	rel.
$\frac{g_1^0}{\dot{m}^0}$	0.144	0	-0.0014	-1%
$\frac{g_2^0}{\dot{m}^0}$	0.378	0	0	
.				
$\frac{g_5^0}{\dot{m}^0}$	0	0	0	
$\frac{g_6^0}{\dot{m}^0}$	1.	+1.5%	-0.075	-7.5%
$\frac{g_1^1}{\dot{m}^1}$	0.01	0	0.0039	+39%
$\frac{g_2^1}{\dot{m}^1}$	0.192	0	0.0024	+1%
.				
$\frac{g_5^1}{\dot{m}^1}$	0.197	-10%	0.0037	+2%
$\frac{g_6^1}{\dot{m}^1}$	0.0092	0	0.0041	+45%
$\frac{\dot{m}^1}{\dot{m}^0}$	1.	0	0.075	+7.5%

\*The data of Table I kindly have been furnished by Dr. K. Maurer.

the exit concentrations,  $g_5^1$ , leads to only a minor correction in the wrong concentration but to serious deviations from the correct measurements  $g_1^1$  and  $g_6^1$ .

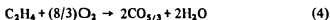
Tracing and eliminating the most serious systematic errors is usually the most important and the most time-consuming part of the evaluation of experimental results. Unfortunately this problem has elicited only weak resonance in the literature. An obvious procedure is an automated search for systematic errors during which one measurement after another is skipped in the balancing procedure and the total error is monitored [4]. The method works well if only one serious systematic error is present but it fails if several systematic errors tend to compensate each other.

In addition to diligence, the elimination of systematic errors requires a certain amount of intuition since the possibility for measurement errors or wrong interpretations is almost unlimited.

A valuable aid for tracing measurement errors is a sensitivity analysis of the evaluation procedure. Even in complex reactions only a few characteristics, like conversion and selectivity of the main products, are of practical importance. Knowledge of the dependence of these quantities upon measurement errors allows critical measurements to be located and their accuracy improved or, if impossible, the evaluation procedure to be changed.

### Choice of main reaction components and main reaction steps

In simple reactions like the ammonia synthesis from  $N_2$  and  $H_2$ , the stoichiometry and reaction components are quite obvious. The picture changes substantially, however, if complex reactions with a broad spectrum of products have to be considered. Here the first step is a reduction in the number of components by choosing a few main components and lumping the side products together as pseudo-components. The conditions are simple, if in the range of importance, the side products are produced in a fairly constant ratio to each other. If, e.g. in the oxychlorination example, CO and  $CO_2$  are generated in a molar ratio of 1:2, the combustion reactions (2) and (3) can be condensed into a single step with the pseudo-component  $\frac{1}{3}(CO + 2CO_2) = CO_{5/3}$ :



"Lumping" to pseudo-components is indispensable if a large number of insufficiently characterized components take part in the reaction. Typical examples can be found in crude oil processing steps, like cracking and hydrogenation, and in polymerization reactions. As an example, the work of Jaffe [5] should be mentioned, who found that the catalytic hydrogenation of different mixtures of paraffins, olefins, aromatics and naphthenes can be characterized by only four reaction steps if the three kinds of carbon-carbon bonds are used as pseudo-components. Further examples of successful lumping procedures can be found in ref. 6.

Efforts have been made to create a systematic scientific basis for the process of lumping reaction

components, but, except for trivial cases, the results have not been encouraging [6]. Therefore, choice of main components and main reaction steps remains basically a matter of experience and of trial and error.

### Reaction rate expressions

The choice of the reaction rate expression is closely related to the choice of the main reaction steps. In the case of clearly defined "simple" reaction steps, theory offers a number of different ways of arriving at a suitable rate expression. If the heterogeneously catalyzed surface reaction being considered is not disguised by transport limitations between the active surface and the bulk gas, the Langmuir-Hinshelwood-type chemisorption-reaction sequence is frequently used as the basis. However this basis is often not as sound as it seems [7, 8]. First, the chemisorption step is seldom sufficiently well described by the simple Langmuir theory; second, the postulation of the different surface reaction steps is arbitrary since surface compositions cannot usually be measured; and third, the Langmuir-Hinshelwood procedure requires the choice of one rate-determining step while all the other surface reaction steps have to be in equilibrium or at least in quasi steady state. Otherwise no explicit reaction rate expression can be obtained [9]. In the case of an integral reactor with conversion ranging from zero at the entrance to close to 100% at the exit the last assumption is more than questionable.

Similar objections apply to modifications of the Langmuir-Hinshelwood procedure by using Freundlich or Temkin adsorption models or Eley-Rideal reaction steps.

Nevertheless the theory provides us with a reasonable qualitative picture of the possible causes of reactant or product inhibition and ways how this can be taken into account in terms of a suitable reaction rate equation. The "hyperbolic" rate equations thus derived are indeed much more powerful and flexible than the common power rate laws. For practical purposes, however, the theory is certainly overstressed if one attempts to determine the rate constants in the denominator by means of separate adsorption/desorption experiments. A useful heuristic approach for the construction of an appropriate hyperbolic rate law is given by Cropley [10].

### Heat and mass transfer limitations

It is well known that heat and mass transfer limitation, either inside the catalyst pellet (internal problem) or through the stagnant film between the pellet surface and the flowing gas (external problem), may lead to differences in composition and temperature between the flowing gas and the gas in the catalyst pores. The actual reaction rates and hence the conversion and selectivities of the reactor may therefore differ substantially with and without transport limitations.

Under industrial operating conditions the gas flow rate is usually that large that the external heat and mass transfer is not restricted. Also, since the pellet conduc-

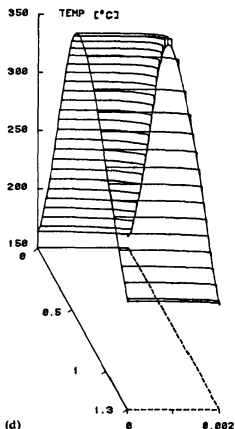
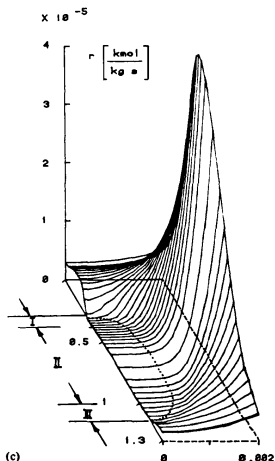
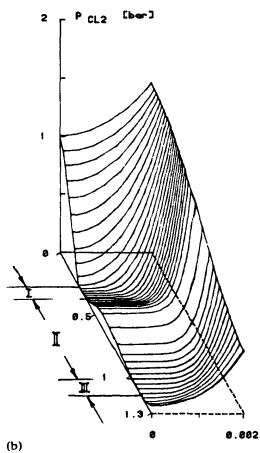
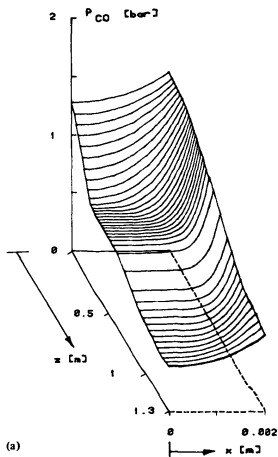
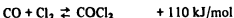


Fig. 2. Concentration-, reaction rate- and temperature-profiles for the phosgene synthesis over the reactor length ( $z$ ) and the catalyst pellet radius ( $r$ ). (Pellet center at  $r = 0$ , flowing gas at  $r = 0.002$  m.)

tivity is relatively large, the temperature within a catalyst particle can be assumed to be uniform. So the only transport limitation of importance is the diffusional resistance within the catalyst pores. Bulk diffusion, Knudsen diffusion, surface diffusion and, where a number of moles change by reaction, viscous flow, are known to contribute to the mass transport in the catalyst pellet. Only recently has a comprehensive theory of diffusion and reaction in catalysts been presented (Jackson [11]), which permits a more soundly based treatment of the subject than by using the concept of the common effectiveness factor.

To give an impression of how the apparent reaction rate can be influenced by pore diffusion, two examples will be discussed. In the first example simulation results for the phosgene synthesis in a wall-cooled tubular reactor will be considered. Phosgene is produced from a stoichiometric mixture of CO and Cl<sub>2</sub> on activated carbon in a very rapid and strongly exothermic reaction almost without side-products via



The reaction starts below 100 °C; above 300 °C the reverse reaction is of importance. Figure 2 shows the profiles for reactant concentrations, temperature and reaction rate over the length of the reactor ( $z$ -coordinate) and over the radius of the pellet. In spite of the fact that the feed is almost stoichiometric, the reactant concentration in the pellet is far from stoichiometry due to the greater diffusivity of CO as compared with chlorine. The region of zero reaction rate in the middle of the pellet is caused by two different effects. Near the entrance of the reactor, the reaction is so rapid that Cl<sub>2</sub> is completely consumed some distance from the pellet center (region I). Further downstream the reactor, the temperature is so high that the reaction near the pellet center is in equilibrium (Cl<sub>2</sub> starts to rise with  $z$  at  $x=0$ —region II) and, as the temperature drops, Cl<sub>2</sub> is again rate limiting (region III). It is obvious that it may be difficult to incorporate these intrinsic effects into an overall (formal) rate expression.

Even the reaction sequence can be disguised by pore diffusion. This will be shown in the next example where a partial oxidation reaction, comparable to oxychlorination, eqns. (1)–(3), will be considered. Here it is often a question whether the total oxidation takes place in a parallel or a consecutive reaction, i.e. whether mechanism (4) or (5) predominates (A = reactant, P = desired product):



Looking at the concentration profiles of Fig. 3 for a quasi-homogeneous reaction in an isothermal fixed-bed reactor, it is obvious that an appreciable amount of CO<sub>2</sub> must have been formed directly from A via mechanism (5) because in the case of mechanism (4) the slope of C<sub>CO<sub>2</sub></sub> at  $z=0$  would be zero. However, the gas phase

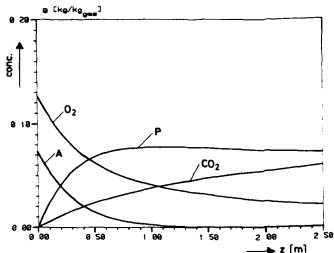


Fig. 3. Concentration profiles over the reactor length  $z$  for the isothermal partial oxidation  $A \rightarrow P$  with  $\text{CO}_2$  as by-product.

concentrations of Fig. 3 have been calculated by a model using only mechanism (4) but including diffusion and reaction in the pores. The resulting profiles over the pellet radius and the reactor length are given in Fig. 4. Since even in the pores of the first pellet at  $z=0$  an appreciable amount of  $\text{CO}_2$  is formed via the consecutive mechanism (decrease of the intermediate P towards the pellet center), the gas phase concentration of  $\text{CO}_2$  starts to rise with non-zero slope at  $z=0$ .

This means that two different mechanisms have to be considered, depending upon whether the reaction will be treated as quasi-homogeneous (rates depending only upon gas phase conditions) or whether a heterogeneous model including diffusion and reaction in the pores is to be used. It is obvious that the simple effectiveness factor concept is not applicable to this example unless rather sophisticated transformations are used [12].

## Reactor model

Reaction rate equations, however formal or sophisticated they may be, can only be evaluated as part of the reactor model that is used to describe the experimental results. So the question has to be posed whether deficiencies of the test-reactor model may be transferred into the rate equations during the process of model evaluation. This problem has already been mentioned above for test reactors of the differential loop reactor type. If an integral fixed-bed reactor, cooled or heated through the reactor wall, is used as test reactor, the question of appropriate reactor modelling is even more serious.

It has been common practice to use a spatially one- or two-dimensional quasi-homogeneous plug-flow model for fixed-bed reactor simulation [13], where the reaction rates are effective rate expressions, depending upon the concentrations of the flowing gas and upon a mean temperature between gas and catalyst. In addition, it is usually assumed that the radial conductivity of the packed bed and the wall heat-transfer coefficient can be taken from heat-transfer experiments without reaction

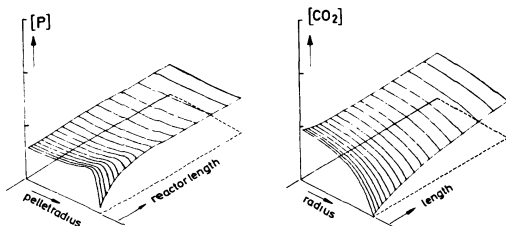


Fig. 4. Detailed calculation results for the partial oxidation reaction  $A \rightarrow P \rightarrow CO_2$ .

and that they can be considered constant along the length of the reactor.

Among the objections to the above model, particularly the plug flow assumption has often been questioned. It is well established that the void fraction varies over the tube radius, having a maximum at the reactor wall [14]. Since the mean flow rate is proportional to the void area, the flow rate will also exhibit a maximum near the wall. A recently published method (Vortmeyer [15]) permits radial flow profiles to be calculated on the basis of the measured void distribution. The following simulation results give an impression of how the refined flow profile changes the behavior of the reactor model. A single exothermic reaction is considered, with reaction and transport parameters and operating conditions reflecting typical industrial operation of partial oxidation reactions. A two-dimensional quasi-homogeneous model with the above assumptions has been used. The only differences between the two simulation results are the radial flow profile and the value of the wall heat-transfer coefficient. The two flow profiles are given in Fig. 5. The wall heat-transfer coefficient  $h_w$  of the plug flow model was calculated from standard correlations [16,

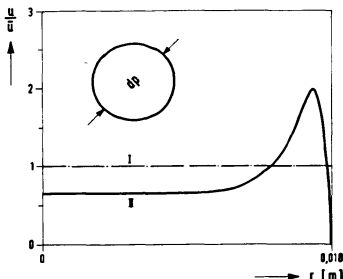


Fig. 5. Profile of the axial flow velocity after Vortmeyer [15] and plug flow profile over the radius of a fixed bed reactor ( $d_p$  = catalyst pellet diameter).

17] whereas the wall heat transfer with a radially varying flow rate was adjusted so that the mean temperature increase in the preheating section ( $0 \leq z < 0.5$  m) was the same in both models (equal wall heat transfer without reaction). Since in the second case most of the gas flows close to the wall, it is easier to transfer heat from the wall to the gas or *vice versa* and hence the apparent  $h_{wII}$  value has to be smaller than under plug flow conditions ( $h_{wI} = 95 \text{ W m}^{-2} \text{ K}^{-1}$ ,  $h_{wII} = 80 \text{ W m}^{-2} \text{ K}^{-1}$ ).

The simulation results, Fig. 6, reveal that under these conditions the radial flow profile II leads to a peak temperature which is about  $70^\circ \text{C}$  above the plug flow example and hence substantial differences in total conversion result. The reasons for the more rapid reaction in the second case are twofold: one is the smaller  $h_w$  value, the second is the fact that the residence time has a maximum in the tube centre, leading to higher conversions and hence more heat generation in a region remote from the cool walls.

If we say that flow profile II is closer to reality than profile I, this means that in the common plug flow model a deficient flow description has to be compensated by modifications of the rate constants and the activation

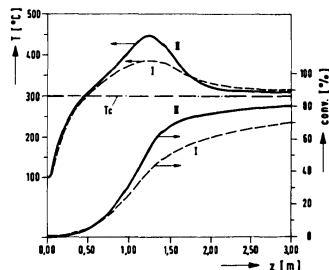


Fig. 6. Axial temperature and total conversion for a second order exothermic reaction using the flow profiles of Fig. 5.

energies of the rate expression to ensure a suitable overall description of the reactor behavior. Other model deficiencies will have to be compensated in a similar way. This leads to the conclusion that a formal rate expression is strictly valid only in connection with the reactor model on which it is based. The transfer to a reactor with substantially different residence time and heat transport behavior is always risky and requires a close examination of the specific circumstances.

### Parameter estimation

After a reactor model including the stoichiometry of the reaction and the structure of the rate equations has been chosen, the unknown model parameters have to be determined by parameter estimation. Equilibrium constants, reaction enthalpies and transport parameters (diffusion coefficients, heat conductivities and heat-transfer coefficients) can either be measured separately or calculated from standard correlations. It is our practice however to include the heat-transfer coefficient between packed bed and reactor wall,  $h_w$ , in the parameter adaptation procedure, since  $h_w$  values calculated from literature correlations tend to differ from adapted  $h_w$  values by a factor of two or more.

If the reactor model were appropriate and the experimental results against which the model will be tested were free from errors, the parameter adaptation procedure could easily be handled by the computer. Unfortunately, at least one of the two requirements is often not fulfilled. It is therefore our experience that the computer programs for parameter adaptation run nicely with "artificial" data from simulated experiments but break down easily if they are fed with "real life" data. Three causes for this frequently experienced failure of computerized parameter estimation will briefly be discussed below.

The first example concerns the influence of systematic errors in the experiments and the occurrence of side

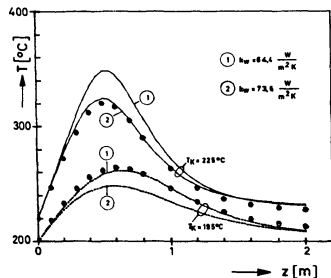


Fig. 7. Temperature "measurements" (circles) and two different model approximations with different wall heat transfer coefficients  $k_w$ .

optima. Two sets of temperature "measurements" (circles) are given in Fig. 7. They have been calculated with the same model and two different cooling temperatures. It was assumed that the measured cooling temperature was subject to systematic errors, i.e.  $T_K = 225$  K was measured instead of 230 K and 195 K instead of 190 K. Only the heat-transfer parameter  $k_w$  was changed to adapt the model to the "measurements". Figure 8 shows the performance index (sum of absolute values of temperature deviations at measurement points) over  $k_w$ . It can be seen that in each of the two minima, one measured profile is well represented. The example shows that side optima can be caused by systematic errors in the experiments if a few erroneous measurements are well represented by a specific parameter combination. Common parameter-estimation procedures are not able to distinguish between local and global optima.

The correct choice of the performance index, i.e. the valuation of the differences between model and experiment, is a second, frequently encountered problem in parameter estimation. In the above example, for instance, a performance index using the squares of the temperature deviations instead of the absolute values would give a single minimum with  $k_w$  close to its exact value ( $k_w = 70$ ).

A problem that is often encountered during the adaptation of temperature or concentration profiles is represented in Fig. 9. The measured temperatures  $T_{exp}$  can be represented by two rival models  $T_1$  and  $T_2$ . It is obvious that profile  $T_1$ , shifted slightly to the left is a very good approximation of the measurements. However the sum of the temperature deviations at the measurement points (either quadratic or absolute values) is substantially lower for  $T_2$  than for  $T_1$ , hence the worse approximation  $T_2$  is preferred by the computer program. This is a typical example of the fact that it can be rather difficult to transfer the valuation criteria of an experienced experimenter into a computer code.

A third problem which is often encountered during parameter estimation for industrial problems is the fact

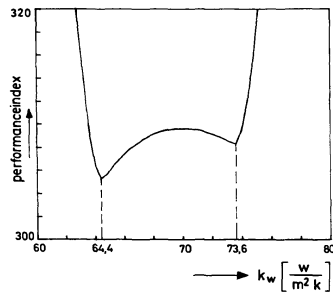


Fig. 8. Performance index over wall heat transfer coefficient  $k_w$  of Fig. 7.



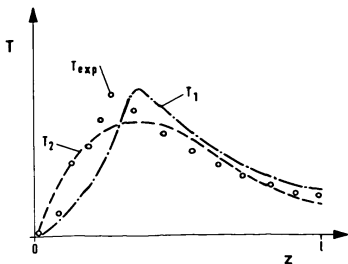


Fig. 9. Temperature measurements (circles) and two different temperature profile approximations.

that the variations between measurements are not sufficient to allow for an unequivocal determination of the unknown parameters. The result is a flat minimum of the performance index and a drift of the estimated parameters. Significance tests can be performed to investigate what measurements are necessary to determine the particular parameters with the required accuracy; often, however, these measurements are impossible in practice (e.g. concentrations of radicals or surface intermediates).

It has been assumed up to now in this Section that the model structure is appropriate and only the model parameters have to be adjusted. As mentioned earlier, however, this is seldom the case. The process of parameter estimation therefore will frequently be interrupted by returns to modify the main reaction steps, the structure of the rate equations or the reactor model. This means that total computerization of the process of model adaptation does not seem feasible.

It is our experience that an interactive procedure is a reasonable compromise. Here the computer is used to adjust only a few parameters at a time by simple, derivative-free optimization algorithms while the model adaptation procedure is controlled and modified via terminal dialog. The best man for this procedure is certainly the experimenter himself, since he has full knowledge of the significance and accuracy of his experimental results. An additional and necessary prerequisite for this job is the knowledge of the problems and pitfalls that have been mentioned in the preceding sections.

## Discussion

It has been shown that establishing reaction rate models requires a number of more or less arbitrary assumptions which may hamper the usefulness and applicability of the particular models for the solution of industrial problems.

To discuss this question, two different kinds of use of mathematical models in chemical reaction engineering

should be distinguished. The first category consists of design problems where a fairly accurate prediction of the reactor behavior in a specified range is required. To cope with these problems it is necessary for the results of the model calculations to have the character of interpolations rather than extrapolations, i.e. the underlying experiments have to cover the specified range of operating conditions. Typical examples are the choice of proper tube dimensions (length and diameter) for multitube fixed-bed reactors or the influence of means that change heat generation or heat transport within a reactor. It is our experience that this kind of problem can be solved by model simulations as long as the catalyst and the feed composition remain about the same.

A simple example is the design of an appropriate catalyst dilution strategy for an exothermic reaction. Calderbank *et al.* [18] proposed the method of diluting a catalyst bed with inert particles in order to reduce the hot spot temperature. In the following example, the reactor model was based upon experiments where the bed activity increased linearly over the length of the reactor (activity = volume ratio of active catalyst to catalyst plus inert material) and the question was how the activity profile has to be changed to limit the excess temperature ( $T - T^0$ ) to 70 °C. Figure 10(a) shows simulation results and Fig. 10(b) an experimental verification. The model used was a simple one-dimensional quasi-homogeneous plug-flow model where the rate parameters were adapted to experiments with only slightly different operating conditions.

Similar accuracy of simulation results can be expected for problems where changes in the heat transfer to or from the reaction tubes are considered, as for example the use of multiple cooling sections or the influence of different coolant flow patterns in multitubular reactors [19].

A second category comprises problems where either extrapolation to areas not covered by experiments is required or the model results are based upon unproved model assumptions. Typical examples are the design of fluidized-bed reactors with reaction models extracted from fixed-bed experiments, simulation of catalyst deactivation under different operating conditions and catalyst design problems. In these cases the simulation results represent reality only with a certain degree of probability. They are "speculative extrapolations" in the sense of Schoenemann [20] but as compared with our common mental speculations these extrapolations have the advantage of being quantified and they obey at least some basic physicochemical laws. The calculated pellet concentration profiles (Fig. 2) for the phosgene synthesis serve as an example. Apart from the question whether the underlying dusty gas model is really appropriate, the assumed spherical symmetry and the representation of the interconnected macro/micropore diffusion and reaction by means of a single tortuosity factor is certainly doubtful. Nevertheless it is obvious that due to the greater diffusivity of  $\text{CO}_2$ , the  $\text{Cl}_2$  concentration in the pores is below stoichiometric and may go to zero at the pellet centre. Similarly, equilibrium conditions will be reached in the pellet well before the gas phase is at equilibrium, thus reducing the overall

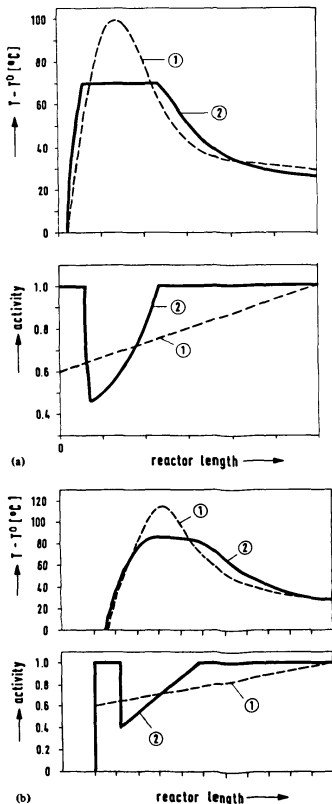


Fig. 10. (a) Temperature profiles of a partial oxidation reaction with "isothermal" activity profile (model calculations); (b) experimental verification of the different catalyst dilution strategies.

reaction rate at an early stage. Speculative extrapolations can thus help to gain a better understanding of intrinsic details of heterogeneous reactions which, in turn, may result in an improved catalyst design.

## Summary

The purpose of this paper was to provide a critical review of the different steps that lead to the formulation of a reaction rate model. It was shown that each step forces a number of assumptions and decisions and this limits the general validity and extrapolability of the resulting rate model. In particular, the strong interrelations of the rate equation and the underlying reactor model are pointed out. This means that reliable simulation results can only be expected if the rate model has been determined in the same kind of reactor that is to be simulated and if the simulation results have the character of interpolations between the underlying experiments rather than extrapolations.

However, even in ranges where the model results have the character of speculative extrapolations, modelling has proven an important tool in reaction engineering. Since the model results are quantified and fulfil at least the basic laws of heat and mass conservation, they can serve as guidelines for the complex interrelations of heat and mass transport and reaction in industrial reactors. It is with these guidelines at hand that decisions about alternative options for research and development in chemical reaction engineering can be put on a sound base.

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