Model Discrimination and Parameter Estimation in Heterogeneous Catalysis

After a brief discussion of the experimental aspects of a kinetic investigation, the paper reviews the methodology of kinetic analysis, for both single and complex reactions. The necessity of statistical testing of the results is emphasized. Special attention is given to methods for estimating parameters in algebraic and differential equations. Sequential methods for the design of an experimental program aiming at optimal discrimination between rival models and optimal parameter estimation are reviewed and illustrated by means of practical examples.

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SCOPE

The major fraction of large-tonnage production in the chemical industry is based on reactions catalyzed by solids. Kinetic studies of these reactions are the basis for more accurate reactor design and for progress in the understanding of the phenomenon of catalysis. This explains why the area of catalytic kinetics has always been one of the prominent areas in chemical engineering and why it will remain so as long as new catalysts are being developed or existing ones improved.

In a kinetic investigation the form of the rate equation (of the model) is not known *a priori*, although physicochemical insight and several formalisms limit the spectrum of possible models. Also unknown, of course, are the values of the rate coefficient and of the adsorption coefficients, or in other words the parameters of the model.

A kinetic investigation, therefore, consists mainly of two parts: model discrimination and parameter estimation. Both tasks are evidently based upon experimental data, and, since obtaining accurate experimental data is of prime importance, the first section of this paper will deal briefly with experimental reactors. The methodology of kinetic analysis, by both the differential and the integral method, will be illustrated in a second section. The estimation of the parameters will be discussed in detail, and, finally, recent methods for designing an optimal experimental program will be reviewed and illustrated.

CONCLUSIONS AND SIGNIFICANCE

In the experimental part of a kinetic investigation, many precautions have to be taken, some of which may be contradictory, to measure the true chemical reaction rate. If it is obscured by physical phenomena, the kinetic analysis becomes too cumbersome and involves too many parameters to lead to reliable results.

The rate equation should be based upon insight into the true physicochemical nature of the process, rather than upon purely empirical fitting.

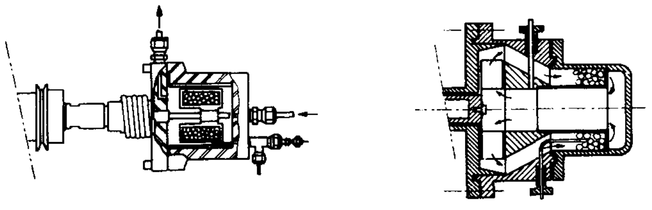
The methodology of kinetic analysis is illustrated, and it is stressed that the estimation of parameters should be accompanied by extensive statistical testing. In kinetic analysis the equations are often rearranged to permit estimation of the parameters by linear regression, a practice that violates some of the premises of the statistical analysis. Examples show that there is little influence on the estimates when accurate data are dealt with. But it is still not clear how important the deviations would be with less accurate data and whether they would lead to false conclusions in the model discrimination. On the other hand, with the increasing use of computers, the necessity for forcing the estimation into a linear problem has become far less stringent.

Substantial progress may be expected from the application of modern methods for parameter estimation in nonlinear algebraic equations and in differential equations. This is particularly true for the analysis of complex reactions, which is seriously lagging behind and is too often unnecessarily oversimplified, and for the analysis of the kinetics of catalyst deactivation. Accuracy of the experimental data is no guarantee of a successful kinetic analysis when the experimental program suffers from a lack of insight into the effect of the different variables and is poorly designed.

Recently introduced sequential methods for the design of an experimental program, aiming at optimal discrimination or optimal parameter estimation, enable substantial savings in experimentation, greater adequacy in modeling, and greater accuracy in estimation. These methods should be of particular importance for pilot scale experimentation, in which the number of experiments has to be limited. The methods reveal the importance of experimentation on the borders of the operability region, another challenge for the experimentalist.

EXPERIMENTAL REACTORS

Kinetic experiments concerning heterogeneous catalytic reactions with one fluid phase only are generally carried out in flow reactors usually of the tubular type, operated in single pass. To keep the interpretation as simple as possible, the flow is considered to be perfectly ordered, with uniform velocity (of the plug flow type). This requires a sufficiently high velocity and a tube-to-particle diameter ratio of at least ten to avoid too much channeling along the wall, where the void fraction is higher than in the core of the bed. The tube diameter should not be too large either to avoid radial gradients of temperature and concentration, which again lead to complications in the analysis of the data. When the heat effect of the reaction(s) is pronounced, it is probably more important to avoid radial gradients by allowing for a smaller ratio of



1a 1b

Fig. 1. Recycling and spinning basket reactors for kinetic studies (Tajbl, 1969; Luft, Römer and Röder), Chemie-Ingenieur-Technik, Vol. 45, 596 (1973). Reproduced by permission of Chemie-Ingenieur-Technik.

tube-to-particle diameter than to try to completely exclude channeling effects. This is substantiated by the results of Kondelik and Boyarinov (1966) who accounted for both effects in an analysis of a fixed bed reactor with a single fluid phase.

Temperature gradients in the longitudinal, that is, in the flow direction, should also be avoided. Although computers have coped with nonisothermal situations, up to a certain extent, determining the functional form of the rate equation is convenient only on the basis of isothermal data. Isothermal conditions are not easily achieved with reactions having important heat effects. Care should be taken to minimize heat transfer resistance at the outside wall (for very exothermic reactions, for example, through the use of molten salts). Ultimately, however, no further gain can be achieved, since the most important resistance then becomes that at the inside wall. This resistance cannot be decreased at will, tied as it is to the process conditions. If isothermality is still not achieved, the only remaining possibility is to dilute the catalyst bed. Excessive dilution has to be avoided as well; all the fluid streamlines should hit the same number of catalyst particles.

Plug flow tubular reactors are generally operated in an integral way, that is, with relatively large conversion. This is achieved by choosing an amount of catalyst, W(kg), which is rather large with respect to the flow rate of the reference component A at the inlet, F_{A_0}(kmole/hr). By varying the ratio W/F_{A_0}, a wide range of conversions, x, may be covered. To determine the reaction rate the conversion vs. W/F_{A_0} data pertaining to the same temperature have to be differentiated, as can be seen from the continuity equation for the reference component A in this type of reactor:

$$F_{A_0}\,dx = r_A\,dW$$

and over the whole reactor

$$\frac{W}{F_{A_0}} = \int_{x_1}^{x_2} \frac{dx}{r_A} \tag{1}$$

Plug flow reactors can also be operated in a differential way. In that case the amount of catalyst is relatively small, so that the conversion is limited and may be considered to occur at a nearly constant concentration of A. The continuity equation for A then becomes

$$F_{A_0}\,\Delta x = r_A\,W \tag{2}$$

and r_A follows directly from the measured conversion. Very accurate analytical methods are required in this case, of course. Further, it is always a matter of debate how small the conversion has to be to fulfill the requirements. In kinetic investigations, the reacting gases are sometimes recycled to come to a differential or gradientless way of operation without excessive consumption of reactants. The recycling may be internal too, as shown in Figure 1a (Tajbl, 1969). It is clear that in both cases it is possible to come to a uniform concentration of the reactant over the catalyst bed. These conditions correspond to those of complete mixing, and the rate is also derived from (2).

Another way of achieving complete mixing of the fluid is shown in Figure 1b (Luft et al., 1974). In this reactor the catalyst is inserted into a basket which spins inside a vessel. Recycle reactors or spinning basket reactors present serious challenges of mechanical nature when they have to operate at high temperatures and pressures, as is often required with petrochemical and petroleum refining processes. Problems with bearings are inevitable above 400°C; Bennett (1972) and Berty (1973) have described and compared several types of gradientless reactors which have proven to be reliable.

Recently, Weekman (1974) has thoroughly discussed the relative merits of various types of reactors used in kinetic investigations. Transport phenomena can seriously interfere with the reaction itself, and great care should be taken to eliminate these as much as possible in kinetic investigations (Carberry 1964, 1969).

Transfer resistances between the fluid and the solid may be eliminated by sufficient turbulence. With the tubular reactor this requires a sufficiently high flow velocity. This is not so simple to realize in laboratory equipment, since the catalyst weight is often restricted to avoid too high a consumption of reactant or to permit isothermal operation. With the spinning basket reactor the speed of rotation has to be high.

Transport resistances inside the particle can also obscure the true rate of reaction. Determining the kinetic equation of the reaction proper in the presence of this effect is a difficult task. Suffice it to say here that internal resistance can be decreased, for a given catalyst, by crushing the catalyst to reduce its dimensions. If the industrial reactor is to operate with a catalyst with which internal resistances are of importance, the laboratory investigation will involve experiments at several particle diameters. Catalysts with a bimodal pore size distribution may present pitfalls, however (Boudart, 1972).

The elimination of the various heat and mass transfer limitations in catalytic reactors, briefly mentioned above, has been reviewed in quantitative terms by Mears (1971), also for fixed bed reactors with two fluid phases. Finally, catalysts tend to deactivate through sintering, poisoning, or coke deposition, and this should not be overlooked in a kinetic investigation. If the deactivation is inevitable and associated with the ultimate industrial operation also, the phenomenon requires special attention and should be expressed quantitatively, as an inherent part of the kinetic study. This task will be discussed somewhat more in detail in a later section.

KINETIC ANALYSIS

The experimental data may be analyzed in two ways: by the differential method of kinetic analysis, based on the rates as such, or by the integral method, based upon the conversion vs. W/F_{A_0} data and Equation (1). The results obtained in an integral reactor may be analyzed by the differential method provided that the conversion vs. W/F_{A_0} curves are differentiated to yield the rates, as illustrated by Figure 2 (Froment, 1970). Both methods will be discussed and illustrated in what follows. Before that, however, it should be mentioned that the Langmuir-Hinschelwood or Hougen-Watson formalism will be adhered to in the derivation of the rate equations. Therefore, so-called adaptive model building techniques will not be considered here. Modeling should be related as closely as possible to the physicochemical phenomenon and not deviate into purely empirical fitting. Only then can we expect

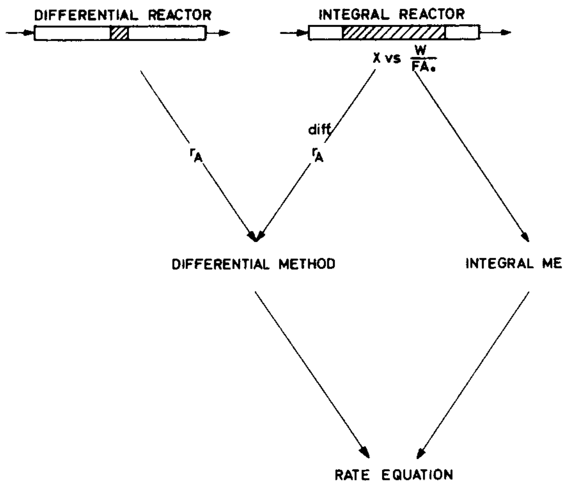


Fig. 2. Relation between differential and integral methods of kinetic analysis and differential and integral reactors.

to avoid a lot of superfluous computations, to arrive at general correlations, and to progress towards better understanding of catalysis.

Single Reactions

The differential method of kinetic analysis. A classical example of application of this method is the study of isooctene hydrogenation by Hougen and Watson (1947). By considering all possible mechanisms and rate determining steps they derived eighteen possible rate equations which were confronted with the experimental data. The discrimination was based upon the requirement that the kinetic and adsorption parameters had to be positive. Sixteen out of the eighteen possible models could be rejected on this basis. The choice between the seventeenth and eighteenth model was based on the goodness of fit. Many years later some aspects of their approach were criticized for lack of statistical tests and statistical rigor (Chou, 1958).

Since this is a well-known example, we will illustrate the methodology by means of the ethanol dehydrogenation data of Franckaerts and Froment (1964). Some 300 experiments were performed in an integral tubular reactor. In most of the experiments the feed consisted of the binary azeotrope ethanol-water, containing 13.5 mole % water. This was called *pure feed.* A certain number of experiments was carried out with so-called *mixed feed,* containing ethanol, water, and the reaction product acetaldehyde, for reasons which will become obvious from what follows. Conversion vs. W/F_{A_0} diagrams were set up at 1, 3, 4, 7, and 10 atm and temperatures ranging from 225° to 285°C, with both types of feed. The rates were obtained by numerical differentiation of these data by using Newton's interpolation formula. There was no appreciable side reaction. Three possible rate equations were considered:

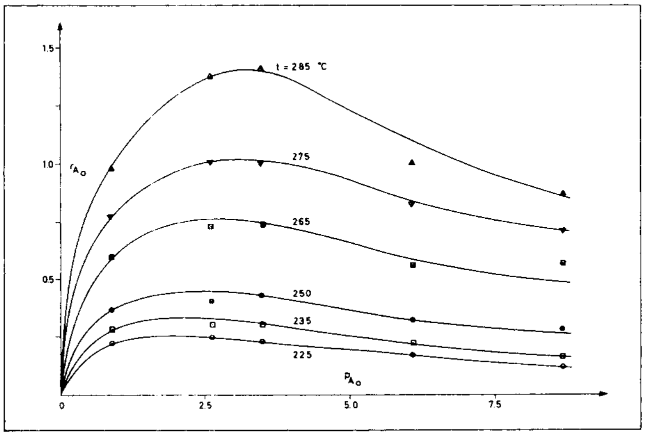


Fig. 3. Initial rate data. Dehydrogenation of ethanol.

$$r_A = \frac{k_A(p_A - p_R p_S/K)}{1 + \frac{K_A}{K} p_R p_S + K_R p_R + K_S p_S + K_W p_W} \tag{3}$$

$$r_A = \frac{k\,K_A(p_A - p_R p_S/K)}{(1 + K_A p_A + K_R p_R + K_S p_S + K_W p_W)^2} \tag{4}$$

$$r_A = \frac{k_R\,K\,K_R\left(\frac{p_A}{p_S} - \frac{p_R}{K}\right)}{1 + K_A p_A + K\,K_R \frac{p_A}{p_S} + K_S p_S + K_W p_W} \tag{5}$$

(A stands for ethanol, R for acetaldehyde, S for hydrogen and W for water). Equation (3) is the kinetic equation under the assumption that the adsorption of A takes place without dissociation, is of second order to the right, of first order to the left, and is the rate determining step. Equation (4) is the kinetic equation when the surface reaction on dual sites is the rate determining step. For reaction on a single site, the denominator would not be squared. Equation (5) is the kinetic equation when desorption determines the rate of the overall process. Note that the equations also account for the possible adsorption of water.

The discrimination between the rival models could have been based upon the requirement of positive parameters and the goodness of fit, supplemented with statistical tests. Yet, with the differential method a powerful tool for discrimination, proposed by Yang and Hougen (1950), is the total pressure dependence of the initial rate. Nowadays this is only one of the so-called *intrinsic parameter methods* (Kittrell, 1970). When pure A is fed to an integral reactor, for example, initial rates are observed at the inlet, where $p_R = p_S = 0$. Equations (3), (4), and (5) then simplify into

$$r_{A_0} = k_A\,p_{A_0} \tag{6}$$

$$r_{A_0} = \frac{k\,K_A\,p_{A_0}}{(1 + K_A p_{A_0})^2} \tag{7}$$

$$r_{A_0} = k_R \tag{8}$$

Clearly, these relations reveal by mere inspection which is the rate determining step, in other words which is the model corresponding to the experimental observations. It can be seen on Figure 3 that, for the data of Franckaerts and Froment, model (7) has to be retained. An even more critical test involves a rearrangement of (7):

$$\sqrt{\frac{p_{A_0}}{r_{A_0}}} = \frac{1}{\sqrt{kK_A}} + \frac{K_A}{\sqrt{kK_A}}\,p_{A_0} \tag{9}$$

which leads to a straight line in the plot of Figure 4. At this stage the discrimination is accomplished, although it is recommended to check it by means of all the data, not only those under initial conditions alone. Now the definitive estimation can be undertaken.

Obviously, k and K_A can be determined from the intercept and the slope of the straight line of Figure 4. It is preferable to use regression, however. Since in Equation (9) the retained rate equation is linear in the groups

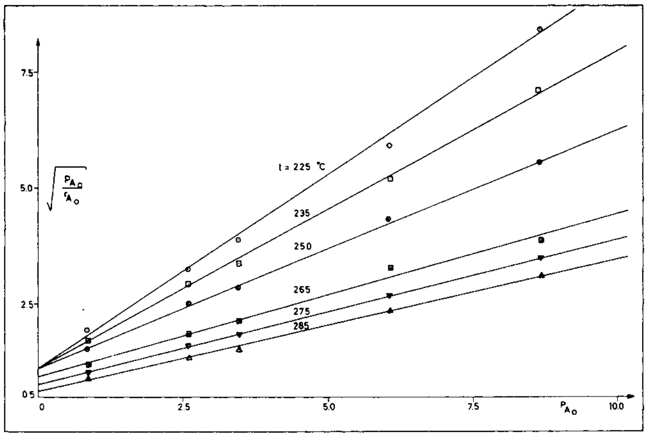


Fig. 4. Rearranged initial rate data. Dehydrogenation of ethanol.

$1/\sqrt{kK_A}$ and $K_A/\sqrt{kK_A}$, these can be determined by linear regression. The regression should be accompanied by statistical tests on the parameters and on the fit achieved by the equation. The other parameters K_R, K_S, and K_W, can be determined either from initial rate data obtained with feeds containing R or S or W besides A or directly from the data at all W/F_{A_0} and the complete Equation (4). In order to determine all the parameters in a simple way, (4) is rearranged in the same manner as (7) to give

$$\zeta = a + bp_A + cp_R + dp_S + ep_W \tag{10}$$

where

$$\zeta = \sqrt{\frac{p_A - \dfrac{p_R p_S}{K}}{r_A}} \quad a = \frac{1}{\sqrt{kK_A}} \quad b = \frac{K_A}{\sqrt{kK_A}}$$

$$c = \frac{K_R}{\sqrt{kK_A}} \quad d = \frac{K_S}{\sqrt{kK_A}} \quad e = \frac{K_W}{\sqrt{kK_A}}$$

Written in this form, which is linear in the groups a, b, c, d, and e, again linear regression can be applied to estimate these groups and therefore the parameters k, K_A, K_R . . . . When the error on ζ is normally distributed with zero mean and constant variance, exact confidence intervals on the groups may be obtained and the significance of the regression coefficients may be tested, for example, by means of a t test and the adequacy of the regression itself by means of an F test. When the variances on ζ are not constant, the regression should be based upon a weighted least-squares criterion. Franckaerts and Froment found K_W to be nonsignificant and small, so that it could be deleted from the equation without affecting the values of the remaining parameters. It is of interest to call attention to a pitfall which may be easily overlooked. If the experiments were limited to pure feeds, containing only A as reacting component, the stoichiometry would inevitably lead to $p_R = p_S$, so that the system of normal equations would contain two identical equations and have no solution. Obviously, to determine K_R and K_S individually requires results for which $p_R \neq p_S$, that is, mixed feeds containing A and either R or S, or both, in unequal amounts. The structure of the experimental program of Franckaerts and Froment (1964) and the potentials of each subset of data with regard to the kinetic analysis are shown in Table 1.

TABLE 1. STRUCTURE OF THE EXPERIMENTAL PROGRAM AND OF THE KINETIC ANALYSIS OF ETHANOL DEHYDROGENATION

Conversion vs. W/F_{A_0} data
↓
Initial rate data vs. p_t (or p_{A_0} for pure feed)
↓
Discrimination and Parameter estimation

Subset: pure feed	Subset: mixed feed
$\frac{W}{F_{A_0}} = 0 \rightarrow \mathrm{k}, \mathrm{K_A}$	$\frac{W}{F_{A_0}} = 0 \rightarrow k, K_A, K_R$
all $\frac{W}{F_{A_0}} \rightarrow k, K_A, K_R + K_S$	all $\frac{W}{F_{A_0}} \rightarrow k, K_A, K_R, K_S$

Statistically, the rearrangement of (7) into (9) or (4) into (10), with subsequent parameter estimation from the rearranged form, may be criticized. Indeed, what was minimized in the linear regression was the sum of squares of residuals between experimental and calculated ζ values. The calculation of the confidence intervals requires the error to be normally distributed with zero mean and constant variance. This condition may be fulfilled for the dependent variable r_A but not necessarily for the group

$$\zeta = \sqrt{\frac{p_A - p_R p_S/K}{r_A}}$$

This may, in principle, affect the values of k, K_A, K_R, K_S and yield erroneous confidence intervals for the parameter estimates. When, however, the rate equation is not rearranged, as done here, the regression is no longer linear, in general, and the minimization of the objective function, the sum of squares of residuals, becomes iterative. Search procedures are recommended for this, and these will be discussed in the next section.

Franckaerts and Froment analyzed the data per temperature and determined subsequently the activation energies from the Arrhenius law. This two-step procedure can be avoided by substituting directly the temperature dependence of the parameters into the rate Equation (10) and by performing the regression on all the data simultaneously at all temperatures (Blakemore and Hoerl, 1963). This, of course, strongly increases the nonlinear character of the equations. Further, to reduce the computational difficulties arising from the strong correlation between the frequency factor and the activation energy, the following reparameterization is often beneficial (Kittrell, 1970):

$$A\,e^{-\frac{E}{RT}} = A\,e^{-\frac{E}{R\overline{T}}}\,e^{-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{\overline{T}}\right)} = A^{*}\,e^{-\frac{E}{R}\left(\frac{1}{T}-\frac{1}{\overline{T}}\right)}$$

where $\overline{T}$ is the average temperature.

Some further aspects of the statistical analysis of rate data are illustrated in the review by Kittrell (1970), using data on ethanol dehydration (Kabel and Johanson, 1962), on ethanol dehydrogenation (Franckaerts and Froment, 1964), on isooctene hydrogenation (Hougen and Watson, 1947), and on pentane isomerization (Carr, 1960).

The integral method of kinetic analysis. The analytical integration of the rate equations leads to

$$\frac{W}{F_{A_0}} = f(x, p_t, k, K_A \ldots) \tag{11}$$

These equations are so complex that no simple dependence on the total pressure or on other intrinsic parameters can be detected. The discrimination between rival models, therefore, has to be based on the criteria already mentioned above: the requirement for the parameters to be positive and the goodness of fit. The estimation is simplest when the objective function, that is, the sum of

Table 2. Comparison of the Results Obtained by the Differential and Integral Methods of Kinetic Analysis

	k	K_A	K_R	K_S
Differential method with linear regression	1.66	0.40	2.23	0.49
Integral method with nonlinear regression	2.00	0.39	3.17	0.47

squares of residuals, is based on W/F_{A_0}. Even then the regression is generally nonlinear. It may be argued against this choice that W/F_{A_0} is an independent variable, generally measured with great accuracy, while x, the conversion, is the true dependent variable whose measurement is subject to larger and random error. Therefore, it is recommended to base the sum of squares of residuals on x, even when this complicates the calculations, since an implicit equation has to be solved in each iteration of the parameter vector.

Peterson and Lapidus (1966) applied the integral method with nonlinear regression to Franckaerts and Froment's data and found excellent agreement, as shown by Table 2. Such an agreement was also observed by Froment and Mezaki (1970) in their analysis of the data of Hosten and Froment (1971) on the isomerization of *n*-pentane.

The data indicated that the overall rate was independent of total pressure, indicating that the isomerization step was rate controlling. Within this step, three partial steps may be distinguished: surface reaction, adsorption, or desorption, each of which could be rate controlling. The first was rejected by Hosten and Froment because of significant negative parameter values. The adsorption and desorption rate determining expressions each contained two parameters. It should be noted that discrimination based on the Yang and Hougen initial rate criterion is impossible here, since both rate equations are independent of total pressure. Froment and Mezaki's estimation results are given in Table 3. In this table, *A* represents *n*-pentane, *B* *i*-pentane, H hydrogen, and Pt platinum. In this case the expression W/F_{A_0} vs. $f(x)$ was linear in two groups containing the parameters, so that linear regression was possible when the sum of squares of residuals on W/F_{A_0} was minimized. When the objective function was based on the conversion itself, an implicit equation had to be solved, and the regression was nonlinear. Only approximate confidence intervals can then be calculated from a linearization of the model equation in the vicinity of the minimum of the objective function.

The agreement between the results of linear regression and minimization of $\Sigma(W/F_{A_0} - W/F_{A_0})^2$ and nonlinear regression and minimization of $\Sigma(x - x)^2$ is excellent. This is probably due to the precision of the data. Poor data may give differences, but they probably do not deserve such a refined treatment, in any event.

So far the Hougen-Watson formalism has been applied almost exclusively under the assumption that the rate coefficients and equilibrium constants of the elementary steps take on such values that all but one of the driving forces are close to zero, so that one step is said to be rate limiting. Boudart has formulated three theorems which may serve as a guideline for the reduction of the kinetic complexity of reactions involving a large number of steps and which are derived under the simplifying assumptions of the existence of a rate determining step and of a most abundant surface intermediate (Boudart, 1968, 1972).

Table 3. Isomerization of *n*-Pentane. Parameter Estimation by Linear and Nonlinear Regression

$$n\text{-pentane} \xrightleftharpoons{\text{Pt}} n\text{-pentene} \xrightleftharpoons{\text{Al}_2\text{O}_2 + \text{Cl}_2} i\text{-pentene} \xrightleftharpoons{\text{Pt}} i\text{-pentane}$$

Integral method

Desorption rate controlling,

$$r = \frac{k\left(p_A - \dfrac{p_B}{K}\right)}{p_\text{H} + K_A p_A} \rightarrow \frac{W}{F_{A_o}} = \frac{1}{k}\left(\frac{a'}{\alpha} + \frac{b'}{\alpha} K_A\right)$$

Regression	Linear	Nonlinear
k	0.93 ± 0.21	$0.92 \pm 0.09^*$
K_A	2.20 ± 1.94	$2.28 \pm 0.95^*$
Sum of squares of residuals	1.05	1.25×10^{-3}
	$\left(\text{on}\ \dfrac{W}{F_{A_o}}\right)$	(on x)

Adsorption rate controlling,

$$r = \frac{k\left(p_A - \dfrac{p_B}{K}\right)}{p_\text{H} + K_B p_B} \rightarrow \frac{W}{F_{A_o}} = \frac{1}{k}\left(\frac{a'}{\alpha'} + \frac{c'}{\alpha'} K_B\right)$$

Regression	Linear	Nonlinear
k	0.89 ± 0.10	$0.89 \pm 0.07^*$
K_B	6.57 ± 3.47	$8.50 \pm 2.78^*$
Sum of squares of residuals	0.70	2.82×10^{-3}

* approximate 95% confidence interval.

The relaxation of the above restrictions leads to cumbersome equations containing a rather large number of parameters. With the present day computational facilities and mathematical tools, this should not be too serious a problem any more. What is lacking, however, to progress in this direction are accurate experimental results, gathered over a sufficiently wide range of the independent variables.

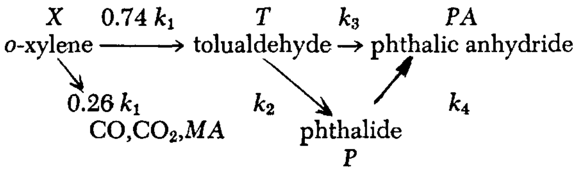
Thaller and Thodos (1960) explained some of their observations on butanol dehydrogenation by the gradual shift from the surface reaction step as single rate determining step to a situation in which the desorption too would be controlling. Their data analysis did not account for the occurrence of two rate controlling steps, however.

Bischoff and Froment (1962) have illustrated, starting from the above example, how difficult it would be to find out by mere visual inspection of the r_{A_0} vs. p_t data if more than one step is rate determining. When a dual site surface reaction is involved, the bell shape of the curve r_{A_0} vs. p_t is retained very far into the region in which desorption or adsorption are cocontrolling. The clear-cut characteristics implied in (7) and (9) would only be encountered in the limits: k_A or $k_D << k$. Evidently, upon kinetic analysis by using simplified rate equations, erroneous values of the parameters would be obtained. It is interesting to note, however, that this would not strongly affect the activation energies (Bischoff and Froment, 1962). Bradshaw and Davidson (1969) analyzed Franckaerts and Froment's ethanol dehydrogenation data under the relaxation of the assumption of a single rate determining step. The rate equation then contained seven parameters instead of four, but the data enabled these seven parameters to be significantly determined. The ratio between largest and smallest rate coefficient in their general model never exceeded seven. Yet, the parameter values determined by Franckaerts and Froment were only slightly affected: k differed by a factor of 4, K_A by a factor of 3, and K_R by a factor of 1½. Again, the activation energies were practically the same. Obviously, this is a matter which is not settled yet and which requires further careful experimental investigation.

Complex Reactions

The approach outlined for single reactions is easily extended to a network of reactions. The discrimination and estimation aspects have to be repeated for each step of the network. Prior to this, the structure of the network has to be determined, a difficult task in itself. There are very few examples of analysis of complex reactions in which the characteristics of the reaction between adsorbed species are retained, in other words, which are based upon the Hougen and Watson formalism, obviously because of the complexity and the large number of parameters.

The neat approach developed for networks of monomolecular reactions (Wei and Prater, 1962) is evidently of no help. Yet, Jungers and his co-workers (1958) have already dealt extensively with this problem from 1950 to 1960. The limited computational possibilities restrained the estimation part of this work, in particular also the statistical tests which are considered nowadays as a necessary ingredient of modeling. Mention should be made also of work by Beranek (1975). Recently, Vanhove and Froment (to be published) investigated the air oxidation of o-xylene on a V_2O_5 catalyst in a tubular reactor of the integral type. They derived the following reaction scheme for o-xylene conversions up to 98 to 99%:



One of the formalisms considered strictly followed the Hougen-Watson approach. The surface reactions on single sites of identical nature were assumed to be rate controlling in each step, and, to somewhat reduce the number of parameters, the adsorption equilibrium constants of all the reaction products were assumed to be identical: $K_T = K_P = K_{PA} = K_R$. The rates could then be written:

for the disappearance of o-xylene

$$r_X = \frac{k_1 K_a p_o^{1/2} p_X}{1 + K_X p_X + K_R p_R} \quad \text{parameters: } k_1, K_a, K_X, K_R \tag{12}$$

net rate of production of tolualdehyde

$$r_T = r_X \left[\frac{0.74\, k_1 p_X - (k_2 + k_3) p_T}{k_1 p_X} \right] \quad \text{parameters: id.} + k_2, k_3 \tag{13}$$

net rate of production of phthalide

$$r_P = r_X \left[\frac{k_2 p_T - k_4 p_P}{k_1 p_X} \right] \quad \text{parameters: id.} + k_2, k_4 \tag{14}$$

net rate of production of phthalic anhydride

$$r_{PA} = r_X \left[\frac{k_3 p_T + k_4 p_P}{k_1 p_X} \right] \quad \text{parameters: id.} + k_3, k_4 \tag{15}$$

With the differential method of kinetic analysis, the rates would have to be obtained by differentiation of the data $x = f(W/F_{X_o})$, $u = f(W/F_{X_o})$, etc., provided that the volume changes can be neglected. This is justified in this case, since the feed contains at most 1 mole % of xylene, the rest being air. Then, k_1, K_a, K_X, and K_R could be estimated from (12) by using $\Sigma(r_X - \hat{r}_X)^2$ as an objective function. Estimation based on (13) would lead to another set of k_1, K_a, K_X, K_R and in addition k_2 and k_3, etc. Obviously, the best approach would be to perform the estimation simultaneously on all the data, that is, on r_X, r_T, r_P, r_{PA}, and this would lead to a single set of parameters. The estimation would then involve the minimization of sums of squares of residuals on all the rates. By using the jargon of modern estimation, the estimation would become a multiresponse problem and the objective function would contain the sum of squares of residuals on the various responses r_X, r_T . . . . Generally, these rates are not measured with the same accuracy. To account for this, each sum of squares of residuals is then weighted by means of a factor which reflects the degree of accuracy of the measurements of the corresponding response. This weighted least-squares objective function will be taken up again in the next section, dealing more specifically with estimation.

Vanhove and Froment preferred to follow the integral method of kinetic analysis. Before the continuity equation for o-xylene (12) could be integrated, they needed

$$u = f(x), \quad \text{containing } \frac{k_2}{k_1} \text{ and } \frac{k_3}{k_1} \tag{16}$$

$$v = f(x) \quad \text{containing } \frac{k_2}{k_1}, \frac{k_3}{k_1} \text{ and } \frac{k_4}{k_1} \tag{17}$$

$$z = f(x) \quad \text{containing } \frac{k_2}{k_1}, \frac{k_3}{k_1} \text{ and } \frac{k_4}{k_1} \tag{18}$$

These were obtained by dividing Equations (13), (14), and (15) by (12) and by integrating analytically. They are the so-called selectivity relations. Equations (16), (17), and (18) could be used separately in a single-response analysis or simultaneously in a multiresponse approach to determine the ratios of the parameters indicated in Equations (16), (17), and (18). The latter approach was adopted by Vanhove and Froment, who used the Box-Draper determinant criterion, to be given further in this text, as an objective function.

The next step was the integration of Equation (12). With single site mechanisms the equations are such that Equation (12) could be integrated analytically, with the help of the (16), (17), and (18), to yield an implicit equation in x:

$$\frac{W}{F_{X_o}} = f(x), \quad \text{containing } k_1, K_a, K_R, K_X \tag{19}$$

From this the remaining parameters k_1, K_a, K_R, and K_X could be obtained through a single-response treatment, minimizing an objective function consisting of only $\Sigma(x - \hat{x})^2$. Another approach would be to consider (19) simultaneously with the selectivity relations (16), (17), and (18) in a multiresponse analysis with weighted sums of squares of residuals on the conversions. Still another approach would be to use (19) in conjunction with the analogous equations $W/F_{X_o} = f(u)$, etc., but this would be more complicated, since all the equations would be implicit with respect to the conversions.

Often, the number of data points concerning the product selectivities does not equal the number of data points of the type $x = f(W/F_{X_o})$. The application of the determinant criterion requires each response, u, v . . ., to be measured in all the experiments. To avoid having to discard some of the data points W/F_{X_0} vs. x, Vanhove and Froment first estimated the ratios given in Equations (16), (17), and (18) by a multiresponse analysis, kept these ratios fixed in (19), and proceeded along a single-response analysis of these data to estimate the complete set of parameters.

When the analytical integration of the continuity equations is impossible, the problem is even more complicated, as will be clear from the next section.

Previously, it was mentioned that the deactivation of the catalyst by sintering, poisoning, or coke deposition is frequently encountered in industrial processes and that it should be accounted for in the kinetic study. The logical approach is to determine, whenever possible, the kinetics in the absence of deactivation first and to account for the deactivation afterwards. Variations on this approach may be required, depending upon the nature of the deactivation.

In the case of poisoning, the use of pure feed components allows the first part of the problem to be readily solved. A rigorous solution to the second part requires the addition of continuity equations for the poison in the fluid phase and on the catalyst to those for the reacting components. With an integral tubular reactor the former equation is a partial differential equation in time and axial position. The adsorbed poison concentration has to enter in one way or another into the rate equation(s) for the main reaction(s), for example, as a term in the denominator or as part of a deactivation function multiplying the rate coefficient at zero poison concentration. Often, the deactivation function is expressed in terms of time instead of adsorbed poison concentration, which is a less satisfactory approach since time is not the true variable in the deactivation.

Sintering is a slow phenomenon, at least with catalysts used in practice and under normal conditions, so that the rate equation can easily be determined under conditions of initial catalyst activity by means of short runs. The deactivation is generally expressed as an empirical function of time and operating conditions.

Coke deposition is generally initiated from a reaction partner through side reactions and is often relatively fast, so that the two-stage approach outlined for poisoning and sintering is not so readily applied in this case. One way out is to extrapolate the measured response(s) to zero coke content or zero time, but this may be a hazardous procedure. The hard way is to couple a coking rate equation to that (or those) for the main reaction(s) and to account for the effect of coke on the rate(s) of the main reaction(s) as outlined for the deactivation by poisons. An example of such an approach is given by Depauw and Froment (1975). The area of catalyst deactivation has been reviewed by Butt (1972) and by Froment (1975). Weekman and Nace (1970), Levenspiel (1972), Hegedus and Petersen (1973), John et al. (1974), and Rückenstein and Pulvermacher (1973), among others, have addressed themselves to specific kinetic problems in the presence of deactivation.

ESTIMATION METHODS

The preceding section mainly focused on the methodology of kinetic analysis and did not enter into the details of the parameter estimation, obviously the main item of the data treatment. Estimation in algebraic equations which are linear in the parameters is well known, and elementary computer packages contain all the associated statistical tests. Estimation in algebraic equations which are nonlinear in the parameters and in differential equations was recently reviewed, with particular emphasis on its application in kinetics, by Seinfeld (1970), by Bard and Lapidus (1968), and by Froment (1974). An extensive treatment of the estimation problem may be found in the books by Draper and Smith (1966) and by Bard (1974). Some items of these texts will be taken up again here. They are dealt with in a somewhat general form to include the treatment of multiresponse problems. These arise with complex reactions, when more than one rate or more than one exit conversion have to be measured. Inclusion of the residuals on each dependent variable into the objective function presumably leads to better estimates. It is believed that the availability of powerful computers and the application of more sophisticated estimation techniques could lead to a real breakthrough in the kinetic analysis of complex reaction systems. The area could benefit from some of the techniques developed in aerospace and process control fields.

Objective Functions

Any estimation starts with the definition of a suitable objective function. Let the model equation be represented by

$$\mathbf{y} = \mathbf{f}(\mathbf{c}, \mathbf{k}) \tag{20}$$

where y represents the m vector of dependent variables, **c** the n vector of independent variables (also called *states*) like concentration, temperature, or W/F_{A_0}, and **k** the p vector of unknown parameters. R experiments are carried out, and y is measured for known **c**, with certain random experimental errors. If the difference between the model prediction and the data is called *residual*

$$\mathbf{e}_r(\mathbf{k}) = \mathbf{y}_r - \mathbf{f}(\mathbf{c}_r, \mathbf{k}) \tag{21}$$

and the moment matrix of the residuals is given by

$$\mathbf{M}(\mathbf{k}) = \sum_{r=1}^{R} \mathbf{e}_r(\mathbf{k})\, \mathbf{e}_r(\mathbf{k})^T \tag{22}$$

then the estimation aims at minimizing some function of this moment matrix, generally called *objective function*, by the suitable choice of **k**.

The most common objective function is the weighted least-square definition

$$S = \text{Trace}[\mathbf{Q}\,\mathbf{M}\,(\mathbf{k})] \tag{23}$$

where **Q** is an $m \times m$ weighting matrix, whose elements are selected to reflect the knowledge about the relative precision of the residuals. **Q** is a diagonal matrix when only sums of squares of residuals are considered and a full matrix when the sums of cross products are also taken into account. For single-response models, Equation (23) reduces to the sum of squares of residuals encountered previously.

The objective function can also be based upon the maximum likelihood principle. The likelihood function is the conditional probability relating the dependent variable y (also called *output*) to the parameters **k**. When the the variance-covariance matrix of the responses **V** is is known, maximizing the likelihood is equivalent to minimizing

$$S = \text{Trace}[\mathbf{V}^{-1}\,\mathbf{M}\,(\mathbf{k})] \tag{24}$$

When **Q** in Equation (23) equals $\mathbf{V}^{-1}$, the weighted least-squares estimates are also the maximum likelihood estimates. When the variance-covariance matrix of the responses is unknown, it turns out, from a Bayesian analysis, that the maximum likelihood estimates are obtained from the minimization, with respect to the parameters, of

$$S = \det \mathbf{M}\,(\mathbf{k})$$

TABLE 4. CHARACTERISTICS OF BASIC METHODS OF THREE CATEGORIES OF HILL DESCENDING PROCEDURES (HOFFMANN AND HOFMANN, 1971)

Category	Required	Basic procedure	Iteration cycle
Function	S	Univariable	$\mathbf{k}^{(i+1)} = \mathbf{k}^{(i)} + \sum_{j=1}^{p} \lambda_j^* e_j$
Gradient	S and $\frac{\partial S}{\partial k}$	Steepest descent	$\mathbf{k}^{(i+1)} = \mathbf{k}^{(i)} - \lambda_i^* \left(\frac{\partial S}{\partial \mathbf{k}}\right)_{\mathbf{k}^{(i)}}$
Newton	S, $\frac{\partial S}{\partial k}$ and $\frac{\partial^2 S}{\partial k^2}$	Newton-Raphson	$\mathbf{k}^{(i+1)} = \mathbf{k}^{(i)} - \left[\left(\frac{\partial^2 S}{\partial \mathbf{k}^2}\right)_{\mathbf{k}^{(i)}}\right]^{-1} \left(\frac{\partial S}{\partial \mathbf{k}}\right)_{\mathbf{k}^{(i)}}$

This objective function has been derived and applied to synthetic examples by Box and Draper (1965).

Estimation in Algebraic Equations

As mentioned already, estimation in algebraic equations which are nonlinear in the parameters generally requires extensive iteration involving some hill descending procedure. The numerous procedures which have been proposed can be classified into three categories. The first category could be called *function* methods, the second is well known under the name *gradient* methods, and the third groups the *Newton* methods. The basic procedures in these categories are, respectively, the univariable, the steepest descent, and the Newton-Raphson method. The principal characteristics of these three basic methods are shown in Table 4.

In the univariable procedure, the search directions are parallel to the axes. λ_j^* is the value of the scalar λ_j corresponding to the minimum of S in the j direction in the cycle leading from $\mathbf{k}^{(i)}$ to the next approximation $\mathbf{k}^{(i+1)}$. The steepest descent procedure calculates S in the opposite direction of the gradient and changes direction when a minimum is attained. λ_i^* is the value of λ corresponding to the minimum of S in the direction followed between the i^{th} and $(i+1)^{\text{th}}$ iteration.

The Newton-Raphson procedure develops the objective function $S[\mathbf{k}^{(i+1)}]$ in a Taylor series around a starting value $\mathbf{k}^{(i)}$ which contains no terms beyond second order. $S[\mathbf{k}^{(i+1)}]$ is then considered as the minimum of the objective function, so that a system of p linear equations is obtained, from which $\mathbf{k}^{(i+1)}$ is easily calculated. The method generates simultaneously the search direction and the distance in that direction. The method converges quite rapidly in the vicinity of the minimum of S, but it is more complicated, since it requires the calculation of second-order derivatives and inversion of matrices. For quadratic objective functions, this method leads to the minimum of S in one single step.

The univariable and steepest descent methods do not account for information gathered in previous steps and therefore may converge slowly. For this reason more elaborate methods have been developed. Some of the better known are the Hooke-Jeeves method, which is based on pattern search that progresses in the successful direction and has ridge following properties; Rosenbrock's method, which involves rotation and orthogonalization of search directions by the Gram-Schmidt method; the Powell methods, which search along conjugated directions; the simplicial method which proceeds over regular simplexes produced by reflection; and the Nelder-Mead method, which allows expansion and contraction of the simplexes. More efficient gradient methods have been developed to avoid oscillation in the vicinity of the minimum, to account for past information, and to take advantage of the fact that many objective functions are approximately quadratic in the vicinity of the minimum. The idea of the Fletcher-Powell and Fletcher-Reeves methods is that the minimum of an n dimensional quadratic function is found by n one-dimensional searches along conjugated directions. The Fletcher-Powell method has also been called the method of deflected gradients and progressively transfers from the steepest descent to the Newton method. The algorithm can be represented as

$$\mathbf{k}^{(i+1)} = \mathbf{k}^{(i)} + \lambda_i \mathbf{R}_i \left(\frac{\partial S}{\partial K}\right)_{K^{(i)}}$$

where λ_i is a scalar and $\mathbf{R}_i$ is an approximation to $-\mathbf{H}_i^{-1}$, which is the Hessian matrix of second derivatives of S. The Fletcher-Reeves method proceeds along conjugated directions after starting in the opposite direction of the gradient. With nonquadratic objective functions, the method switches after $p+1$ one-dimensional searches along conjugated directions, again to an initial search opposite to the gradient. For the special case frequently encountered in kinetic analysis, that the objective function S is a sum of squares of R nonlinear functions $Z(\mathbf{k})$, special methods have been devised which are more efficient than the improved gradient techniques. Some of the best known are listed in Table 5.

The algorithm of the Newton-Gauss method is derived from a quadratic approximation of the objective function; $Z_r(\mathbf{k})$ is developed in a Taylor series, neglecting all derivatives of second and higher order. This linearization may lead to $\Delta \mathbf{k}$ which are too large, so that the method becomes unstable. To overcome this, Levenberg and later

TABLE 5. ALGORITHM OF METHODS FOR MINIMIZING OBJECTIVE FUNCTIONS THAT ARE OF THE SUM OF SQUARES TYPE (HOFFMANN AND HOFMANN, 1971)

Method	Algorithm
Gauss-Newton	$\mathbf{k}^{(i+1)} = \mathbf{k}^{(i)} - [\mathbf{J}^T(\mathbf{k}^{(i)})\,\mathbf{J}(\mathbf{k}^{(i)})]^{-1}\,\mathbf{J}^T[\mathbf{k}^{(i)}]\,\mathbf{Z}[\mathbf{k}^{(i)}]$
Levenberg-Marquardt	$= \mathbf{k}^{(i)} - [\mathbf{J}^T(\mathbf{k}^{(i)})\,\mathbf{J}(\mathbf{k}^{(i)}) + \lambda^{(i)}\,\mathbf{D}^{(i)}]^{-1}\,\mathbf{J}^T[\mathbf{k}^{(i)}]\,\mathbf{Z}[\mathbf{k}^{(i)}]$
Powell	$= \mathbf{k}^{(i)} + \lambda_i^*\,\mathbf{U}^{(i)}\,[\overline{\mathbf{\Gamma}}^T(\mathbf{k}^{(i)})\,\overline{\mathbf{\Gamma}}(\mathbf{k}^{(i)})]^{-1}\,\overline{\mathbf{\Gamma}}^T[\mathbf{k}^{(i)}]\,\mathbf{Z}[\mathbf{k}^{(i)}]$

Marquardt developed very similar modifications of the method. The algorithm is derived from a constrained application of the Newton-Gauss approximation. λ is a Lagrangian multiplier, restricting the step length and continuously adjusting the search direction. At the start, λ has to be large, and the direction of search is close to that of the steepest descent. λ is gradually decreased until, in the vicinity of the minimum, the constraint upon the Newton-Gauss procedure is no longer necessary, and λ is set equal to zero. In Levenberg's derivation $\mathbf{D}$ is a diagonal matrix of positive constants, although in practice $\mathbf{D}$ is taken to be an identity matrix, as in Marquardt's modification.

The Powell method is a function method which does not make use of gradients, except at the start. $\overline{\mathbf{U}}^{(i)}$ is the matrix of the normalized search directions. At the start, these coincide with the coordinate axes. $\overline{\mathbf{\Gamma}}$ is the matrix of the normalized derivatives of the $Z(\mathbf{k})$ with respect to the parameters. This matrix is updated continuously, without really recalculating the derivatives.

The efficiency of various methods for solving nonlinear parameter estimation problems has been compared by several authors (McKeown, 1973; Hensley and Himmelblau, 1973; Box, 1965; Hoffmann and Hofmann, 1971).

Estimation of Parameters in Ordinary Differential Equations

There are cases in which the continuity equations cannot be integrated analytically, but only numerically, in particular when several reactions are occurring simultaneously. The parameter estimation remains possible, although it is complicated by the numerical integration of the differential equations in each iteration of the parameter vector. One positive aspect of the numerical integration is that it yields the conversions directly, but this does not compensate for the increase in computing effort with respect to that required for the solution of an implicit algebraic equation. It is clear that when several models are in competition, the computational labor may become overwhelming.

Let the model equations be represented by

$$\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}, \mathbf{k})$$

$$\mathbf{x}(o) = \mathbf{x}_o \qquad (25)$$

$\dot{\mathbf{x}}$ represents differentiation with respect to W/F_{A_0}, $\mathbf{x}$ is an n dimensional state vector (for example, of partial pressures or temperatures), and $\mathbf{k}$ is a p dimensional parameter vector. The output of the system is the m dimensional vector y, measured at $(W/F_{A_0})_1 \ldots (W/F_{A_0})_2 \ldots$ and related to the states through:

$$\mathbf{y}_r = \mathbf{h}\left\{ \mathbf{x}\left[\left(\frac{W}{F_{A_0}}\right)_r\right]\right\} + \boldsymbol{\varepsilon}_r \qquad (26)$$

$\mathbf{k}$ has to be determined in such way that the model fits the measurements $\mathbf{y}_r$.

When the p parameters are time invariant and all the state variables and their derivatives are accessible, the problem is reduced to estimation in algebraic equations. This would be the case if the differential method of kinetic analysis were applied to the data. A sophisticated method following this approach was recently proposed by Van den Bosch and Hellinckx (1974) and applied by Depauw and Froment (1975) to the parameter estimation in the isomerization of pentane subject to coking. Since the data were obtained in an integral reactor, the rates could have been obtained by a fit of the experimental partial pressure profiles followed by analytical differentiation. A more direct and simpler way was to express the experimental rates in terms of the partial pressures by means of collocation. The multiresponse objective function was also evaluated in the collocation points. Generally, the collocation points do not correspond with the experimental.

In the general case, however, neither the derivatives nor the state variables themselves are available. Then there are two possibilities for tackling the problem. The first is the so-called *direct* method and consists of estimating the parameters through minimization of the objective function itself. The most obvious way of applying the direct method is to numerically integrate the differential equations in each iteration of the parameter vector. Various techniques discussed in the section on estimation in algebraic equations may be used to optimize the iteration. Another approach is to transform the problem into a boundary-value problem by considering the parameters as states and adjoining the p equations

$$\dot{\mathbf{k}} = 0$$

to the model equations. The augmented $n + p$ state vector $\mathbf{z}$ and the vector $\mathbf{g}$ are defined as

$$\mathbf{z} = \begin{bmatrix} \mathbf{x} \\ \mathbf{k} \end{bmatrix} \quad \mathbf{g} = \begin{bmatrix} \mathbf{f} \\ \mathbf{o} \end{bmatrix}$$

Equation (25) then becomes

$$\dot{\mathbf{z}} = \mathbf{g}(\mathbf{z})$$

with

$$z_i(o) = x_{io} \quad i = 1, 2 \ldots n$$

$$z_i(o) = ? \quad i = n + 1, \ldots n + p$$

The problem is now to determine the initial conditions $z_i(o)$ with $i = n + 1, \ldots n + p$ in such way that an objective functional, for example, a least-squares criterion, is minimized:

$$S = \sum_{r=1}^{R} \left\| \mathbf{y}_r - \mathbf{h}\left\{ \mathbf{z}\left[\left(\frac{W}{F_{A_0}}\right)_r\right]\right\}\right\|^2_{\mathbf{Q}_r}$$

Again, $\mathbf{Q}_r$ is an $m \times m$ weighting matrix. The parameter estimation is now written in the form of a nonlinear boundary-value problem, often encountered in chemical engineering, for example, in optimal control theory. A powerful method for solving such a problem is quasilinearization, which converts the nonlinear problem into a series of linear boundary-values problems. Emig and Köppner (1974) recently investigated the application of this technique to parameter estimation in methanol oxidation in a tubular reactor. The system of equations consisted of two continuity equations and one energy equation and contained eight parameters. Nieman and Fisher (1972) also applied this technique, in combination with linear programming, to an example of chemical kinetics. An analogous problem, the determination of the kinetic parameters in the isomerization of pentane subject to coking and therefore time dependent, was handled in a more conventional way by Lambrecht et al. (1972).

The second possibility for tackling the problem is the so-called *indirect* approach that sets up the necessary conditions for optimality of the objective functional and then attempts to determine the parameter estimates which satisfy these conditions (Ray and Szekely, 1973).

As process computers become more popular, there is a growing interest for online estimation of parameters. Again, this implies that the discrimination has been achieved, so that the kinetic equation is available. An example would be estimation in a rapidly deactivating system. In such a situation it is convenient to have a so-called *recursive* or *sequential* solution, that is, to have a method for updating the estimates based upon a time interval $t_1 \leq t \leq t_R$, given a new observation at time t_{R+1}, without having to store all past observation. Such a sequential solution is called a filter. Filters, however, are much more effective for true

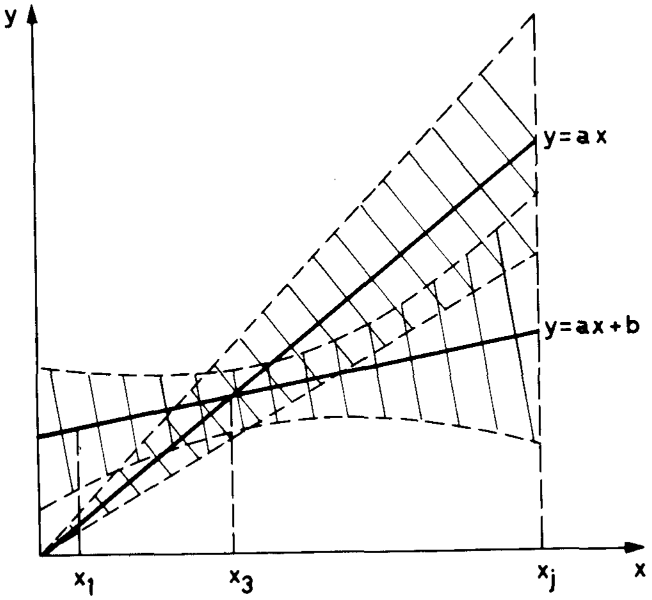


Fig. 5. Discrimination between two linear models.

state estimation in the presence of error than for parameter estimation, so that so far their greatest value was in the computer implementation of control algorithms. Progress may be expected in this area in the coming years. Finally it should be mentioned that the statistical reliability of the parameter estimates can be obtained in the way outlined in the book of Rosenbrock and Storey (1966).

SEQUENTIAL METHODS FOR OPTIMAL DESIGN OF EXPERIMENTS

Mechanistic model studies of the type discussed here have not always been convincing. Often the data were too scanty or not sufficiently precise but even more often the design was poor, so that the variables were not varied over a sufficient range. There is no fitting technique which can compensate for a poor experimental design. In the design of experiments, much is just common sense. Mere visual inspection of the rate equations may already reveal regions of optimal experimentation. With complex multivariable models, however, a rigorous, systematic approach may be required to achieve maximum efficiency.

Until recently, most design was of the factorial, that is, of the a priori type. During the last few years, however, sequential methods have been proposed which design an experiment taking advantage of the information and insight obtained from the previous experiments. Two types of sequential methods for optimal design have been proposed: for optimal discrimination and for optimal estimation.

Optimal Sequential Discrimination

Suppose one has to discriminate between two models $y^{(1)} = ax + b$ and $y^{(2)} = ax$, where y is a dependent variable which can be a conversion or a rate. At first sight it is logical to design an experiment where a maximum difference or divergence can be expected. It can be seen from Figure 5 that for the given example this would be for values of the independent variable x close to zero and x_j, but surely not in the vicinity of x_3.

Suppose $n - 1$ experiments have been performed at $n - 1$ settings of x, so that estimates for a and b can be obtained. To design the n^{th} experiment, the region of interest (operability region) on the x axis is divided into a certain number of intervals. The grid points are numbered i. Then the estimates $\hat{y}^{(1)}$ and $\hat{y}^{(2)}$ are computed for each grid point. Further, the divergence between the estimates of the function y for each of the two models

$$D_{i,n} = [\hat{y}_i^{(1)} - \hat{y}_i^{(2)}]^2 \tag{27}$$

is calculated, and the n^{th} experiment is performed with settings corresponding to the grid point on the x axis where $D_{i,n}$ is maximum (Hunter and Reiner, 1965). The criterion is easily extended to more than two models, for example

$$D_{i,n} = \sum_{k=1}^{m} \sum_{l=k+1}^{m} [\hat{y}_i^{(k)} - \hat{y}_i^{(l)}]^2 \tag{28}$$

where k and l stand for the models and the index i for the grid point. The double summation ensures that each model is taken consecutively as a reference.

Box and Hill (1967) argued that the criterion would have to account for the uncertainties associated with the model predictions, that is, the variances σ_j^2, since the divergences might be obscured by eventual large uncertainties in the model predictions in a given range of the settings. Starting from information theory, Box and Hill derived the following expression for the divergence between two rival models:

$$D_{i,n} = \pi_{1,n-1}\,\pi_{2,n-1} \left[\frac{(\sigma_2^2 - \sigma_1^2)^2}{(\sigma^2 + \sigma_1^2)(\sigma^2 + \sigma_2^2)} + [\hat{y}_i^{(1)} - \hat{y}_i^{(2)}]^2 \left(\frac{1}{\sigma^2 + \sigma_1^2} + \frac{1}{\sigma^2 + \sigma_2^2} \right) \right] \tag{29}$$

σ^2 is the variance of the observations y and σ_1^2, respectively, σ_2^2 is the variance of the estimated value of the dependent variable for the i^{th} grid point under model 1, respectively, model 2. $\pi_{1,n-1}$ is the prior probability of the model 1 after $n - 1$ experiments. The product $\pi_{1,n-1}$ $\pi_{2,n-1}$ is a factor which gives a greater weight to the model with the greatest probability after $n - 1$ experiments. After the n^{th} experiment has been performed at the settings of the independent variables, where $D_{i,n}$ is a maximum, the adequacy of each of the models remains to be tested. Box and Hill (1967) and Box and Henson (1969) expressed the adequacy in terms of the posterior probabilities. These will serve as prior probabilities in the design of the $n + 1^{\text{th}}$ experiment. When the probability of one of the models has reached a value of one, the discrimination is terminated. Examples of application of this method to real data, (Hunter and Mezaki 1967), may be found in the literature (Froment and Mezaki, 1970). The designed experiments were all found to lie on the border of the operability region. The procedure led to a substantial saving in experiments.

The model probabilities of Box and Hill do not account for the parameter distributions. Therefore, Hsiang and Reilly (1971) proposed an extension of the theory, where for each model a certain number of combinations of discrete parameter values is considered and a numerical value, expressing their degree of plausibility, is assigned to each of these. Each time an experiment has been completed, both model probability and parameter distributions are updated according to Bayes' rule. Hosten (1976) proposed a test for the model adequacy that makes use of elementary statistical principles only. The underlying idea is that the minimum sum of squares of residuals divided by the appropriate number of degrees of freedom is an unbiased estimate of the experimental error variance for the correct mathematical model only. For all other models this quantity is biased owing to a lack of fit of the model. The criterion for adequacy therefore consists of testing the homogeneity of the estimates of the experimental error variance obtained from each of the rival models. This is done by means of Bartlett's χ_c^2:

$$\chi_c^2 = \frac{(\ln \bar{s}^2) \sum_{i=1}^{m} (\text{D.F.})_i - \sum_{i=1}^{m} (\text{D.F.})_i \ln s_i^2}{1 + \frac{1}{3(m-1)} \left[\sum_{i=1}^{m} \frac{1}{(\text{D.F.})_i} - \frac{1}{\sum_{i=1}^{m} (\text{D.F.})_i} \right]} \tag{30}$$

Whenever χ_c^2 exceeds the tabulated value, the model corresponding to the largest estimate of error variance is discarded, and χ_c^2 is recalculated. Another model may be discarded when χ_c^2 exceeds the tabulated value, and so on. The application of statistics, no matter which, to nonlinear models requires the model to be locally linear. For the particular application considered here, this means that the residual mean-square distribution is approximated to a reasonable extent by the χ^2 distribution. Furthermore, care has to be taken with outliers, since χ^2 appears to be rather sensitive to departures of the data from normality. In the example given below, this was taken care of by starting the elimination from the beginning again after each experiment. Finally, the theory requires the variance estimates which are tested upon homogeneity to be statistically independent. It is hard to say how far this restriction is fulfilled. From the examples tested so far, which have a widely different character, it would seem that the procedure is efficient and reliable.

Dumez and Froment (1976) studied the dehydrogenation of n-butene to butadiene on a chromium-aluminium-oxide catalyst in a differential reactor. This work is probably one of the first in which the experimental program was actually and uniquely based upon a sequential discrimination procedure. The following mechanisms were considered to be plausible: atomic dehydrogenation, surface recombination of hydrogen; atomic dehydrogenation, gas phase hydrogen recombination; molecular dehydrogenation; atomic dehydrogenation, intermediate complex with short lifetime, surface recombination of hydrogen; atomic dehydrogenation, intermediate complex with short lifetime, gas phase recombination of hydrogen. For each of these mechanisms, several rate equations may be deduced, depending upon the rate determining step which is postulated. Fifteen possible rate equations were retained. Four rate equations a_1 to a_4 were derived from the first mechanism, four rate equations b_1 to b_4 from the second, three c_1 to c_3 from the third, two d_1 to d_2 from the fourth, and two e_1 to e_2 from the fifth. By way of example, only the finally retained equation c_2 is given here:

$$r = \frac{k_1 K_1 C_t^2 \left(p_B - \frac{p_H p_D}{K} \right)}{(1 + p_D/K_3 + K_1 p_B + p_H/K_4)^2}$$

The discrimination was based upon the divergence criterion (28), in which y is replaced by r, and upon Hosten's model adequacy criterion. Since the experiments were performed in a differential reactor, the independent variables were the partial pressure of butene p_B, butadiene p_D, and hydrogen p_H. The operability region for the experiments at 525°C was limited by: p_H, 0 to 0.1; p_B, 0 to 0.2; p_D, 0 to 0.1; and by the equilibrium surface in the tridimensional space. Experimental settings too close to the equilibrium were avoided, for obvious reasons.

Table 6. Evolution of Sequential Model Discrimination. Butene Dehydrogenation

Number of designed experiments		0	1	2	3	4	5	6	7
Total number of experiments		7	8	9	10	11	12	13	14
Settings of variables, atm		⑧	⑨	⑩	⑪	⑫ ≡ ⑨	⑬ ≡ ⑨	⑭ ≡ ⑧	
p_H		0.1	0.025	0	0				
p_B		0.2	0.2	0.2	0.05				
p_D		0	0	0	0				
	$(\chi^2)_{tab}$				χ_c^2				
	23.68	50.59	68.80	85.31	84.80	98.38	114.14	129.44	139.13
eliminated model (EM)		a3	a3	a3	a3	a3	a3	a3	a3
	22.36	43.66	58.78	72.61	69.55	80.84	93.82	106.40	113.60
(EM)		b3	b3	b3	b3	b3	b3	b3	b3
	21.03	32.50	42.19	50.55	43.37	50.86	58.81	66.39	69.17
(EM)		a4	a4	a4	a4	a4	a4	a4	a4
	19.68	27.36	35.44	42.47	36.67	43.81	50.87	57.58	59.70
(EM)		b4	b4	b4	b4	b4	b4	b4	b4
	18.31	20.18	25.82	30.72	28.03	34.75	40.40	45.75	46.92
(EM)		c3	c3	c3	c3	c3	c3	c3	c3
	16.92	1.91	3.37	4.56	14.04	20.59	23.74	26.66	26.39
(EM)						a1	a1	a1	a1
	15.51					18.83	21.79	24.53	24.39
(EM)						b1	b1	b1	b1
	14.07					16.59	19.20	21.78	21.45
(EM)						d1	d1	d1	d1
	12.59					13.95	16.23	18.32	18.18
(EM)						e1	e1	e1	e1
	11.07					9.38	10.97	12.42	12.06
(EM)								c1	c1
	9.49							0.44	1.28

TABLE 7. SEQUENTIAL DESIGN FOR OPTIMUM DISCRIMINATION IN THE DEHYDROGENATION OF ETHANOL INTO ACETALDEHYDE, WITH INTEGRAL REACTOR DATA USED AS SUCH

Nr. exp.	W/F_{A_0}	p_t	x	χ_c^2	χ^2_{tab}	Delete model
1	0.2	4	0.14			
2	1.6	4	0.32			
3	0.88	7	0.214			
4	0.2	10	0.1			
5	1.6	10	0.229	2.81	5.99	
6	0.88	1	0.339	5.83		
7	0.2	1	0.118	2.0		
8	0.2	3	0.14	3.75		
9	0.2	3	0.14	5.40		
10	2.66	1	0.524	7.59	5.99	Adsorption
				2.01	3.84	
11	0.6	1	0.262	3.07		
12	1.6	3	0.332	3.42		
13	0.4	10	0.148	3.64		
14	0.2	3	0.14	4.60	3.84	Desorption

The maximum number of parameters in the possible models is six, so at least seven preliminary experiments are required to estimate the parameters and start the discrimination procedure with Equation (28). As can be seen from Table 6, after these seven preliminary experiments, the models a_3, b_3, b_4, and c_3 may be eliminated. The eighth experiment, which is the first of the designed ones, is carried out at the conditions represented by ⑧ in Table 6. Then the model adequacies are recalculated. Note that after each experiment the elimination was started from the beginning again to avoid discarding a model on the basis of one or more experiments with a biased error, especially in the early stages of discrimination. After seven designed experiments, or after a total of fourteen experiments, no further discrimination was possible between the dual site rate determining models a_2, b_2, c_2, d_2, and e_2, since the differences between these models were smaller than the experimental error. The models a_2, b_2, and d_2 were then eliminated because they contained at least one parameter that was not significantly different from zero at the 95% confidence level.

It is interesting to note that ⑫ and ⑬ are replicates of ⑨, while ⑭ is a duplicate of ⑧. Further, all the designed experiments, except ⑪, are on the limit of the operability region, while none of the designed feed compositions contains butadiene. The latter observation may be related to the nature of the design criterion itself. Indeed, from the preliminary experiments already, it followed that butadiene is strongly adsorbed. Consequently, it strongly reduces the rate of reaction and therefore the divergence corresponding to such experimental settings.

Finally, it should be stressed how efficient sequential design procedures are for model discrimination. A classical experimental program, less conscious of the ultimate goal, would no doubt have involved a much more extensive experimental program. It is true that at first sight the limited number of experiments provides less feeling for the influence of the process variables on the rate or conversion, for example, which is of course of great importance for practical application. Such information is easily generated a posteriori, however; the detailed response surface can be obtained by means of the computer, starting from the retained model. The above example dealt with the design of an experimental program carried out in a differential reactor. When the data are obtained in an integral reactor, it is more convenient, of course, to deal with the integrated form of the rate equation. As mentioned already, Franckaerts and Froment, in their study of the dehydrogenation of ethanol in an integral reactor, discriminated between three rival models, Equations (3), (4), and (5), on the basis of an extensive, classical experimental program, using a criterion involving initial rates. By using their data a posteriori, a sequentially designed experimental program could have looked as follows. The operability region at 275°C in the W/F_{A_0}-p_t plane is shown in Figure 6. Since the models contain 4 parameters, at least 5 preliminary runs have to be performed. Then the parameters are estimated by nonlinear regression, minimizing the sum of squares of the residuals on the conversion. Next, the first experiment is designed by using Equation (28) in which y now stands for the conversion x. Then the model adequacy criterion Equation (30), is applied. The design is given in Table 7, from which it follows that the surface reaction is the rate determining step. Again, the experiments are located on the border of the operability region.

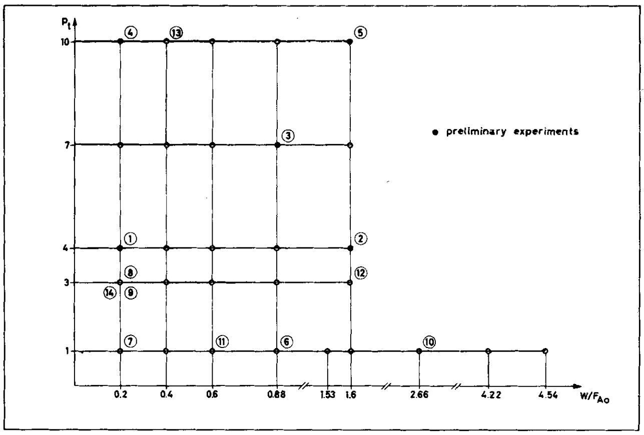


Fig. 6. Experimental grid for optimal sequential discrimination. Dehydrogenation of ethanol.

It is to be noted that the design procedure for sequential discrimination is applicable even when the continuity equation cannot be integrated analytically, but only numerically. This problem is quite often encountered when dealing with complex reactions. Hill and Hunter (1966) have extended the Box-Hill criterion to multiresponse cases.

Sequential Design Procedures for Optimal Parameter Estimation

Even if model discrimination has been accomplished and one test model has been selected as being adequate, it is frequently necessary to obtain more precise estimates of the parameters than those determined from the discrimination procedure. Or the model may be given, from previous experience, so that only estimation is required. Box and Lucas (1959) developed a sequential design procedure for decreasing the amount of uncertainty associated with estimates of parameters. It aims at reducing the joint confidence volume associated with the estimates. An example of such a joint confidence region is shown in Figure 7 for a rate equation with three parameters (Kittrell, 1970). If the model is linear in the parameters, each point on the surface of this volume, that is, each set of parameter values corresponding to a point on the surface, will lead to the same sum of squares of residuals. The example given in the figure is typical for rate equations of the Hougen and Watson type. The long, narrow shape results primarily from important covariance terms, that is, a high degree of correlation among the various parameter estimates. Widely varying values of the estimates will lead to the same overall fit of the equation to the data. The problem is now to

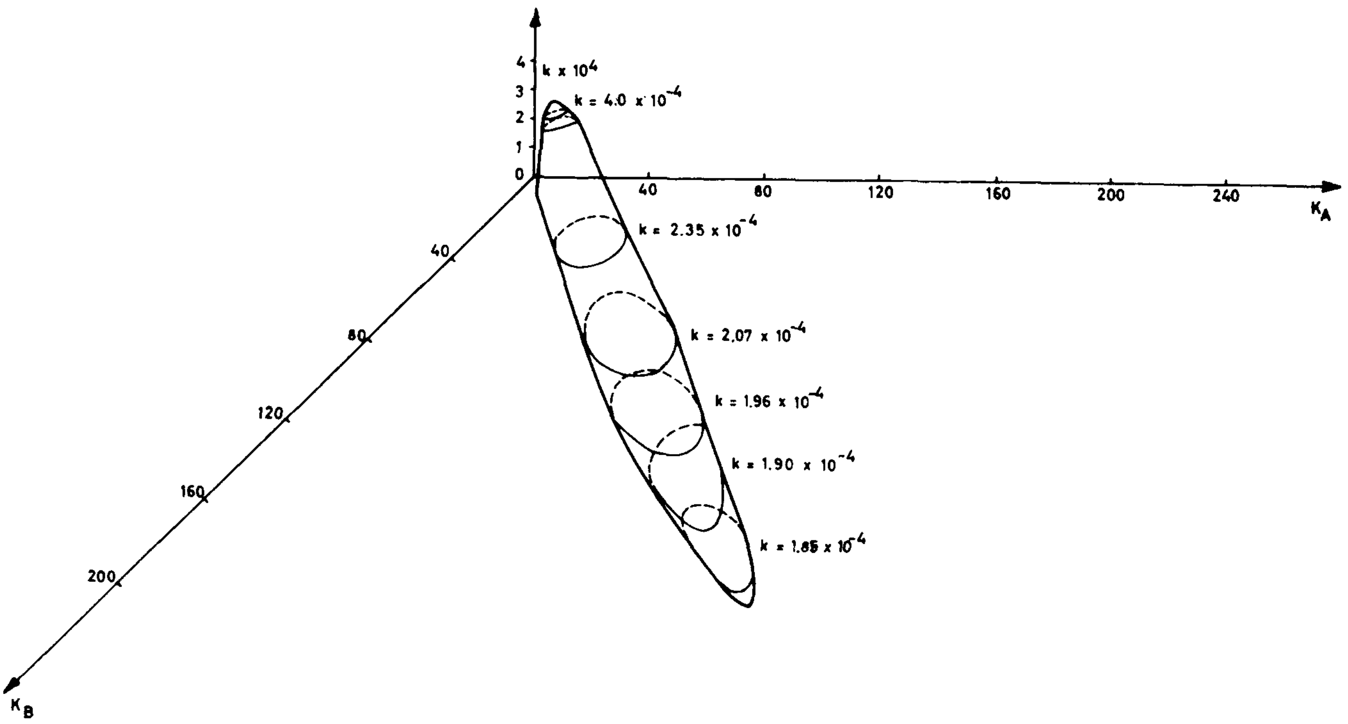


Fig. 7. Joint confidence volume for the parameters of a Hougen-Watson type of rate equation (Kittrell, 1970).

choose the experimental settings in such a way that the volume of the confidence region is minimized by a minimum number of experiments. Let the rate be given by

$$r = g(p_A, p_B, p_S, \ldots; k, K_A, K_B, \ldots)$$

or more compactly

$$r = g(\mathbf{p}, \mathbf{k})$$

Let the partial derivatives of g with respect to any parameter k_i, evaluated at the u^{th} set of experimental conditions and taken at some set of parameter values $\mathbf{k}_o$, be given by $g_{u,i}$. Then

$$g_{u,i} = \frac{\partial g(\mathbf{p}_u, \mathbf{k})}{\partial k_i} \Bigg|_{\mathbf{k} = \mathbf{k}_o}$$

After $n - 1$ experiments, the matrix of these derivatives G contains $n - 1$ rows and p columns (p parameters). When G^T is the transpose matrix of G, the product $G^T \cdot G$ is a $p \times p$ matrix. Box and Lucas (1959) have shown that under certain plausible assumptions, a choice of experimental settings for the n^{th} experiment which maximizes the determinant of G^TG will minimize the volume of the joint confidence region of the parameter estimates. The matrix G, used in the planning of the n^{th} experiment, contains n rows. The n^{th} row is different for each of the grid points of the operability region. The n^{th} experiment has to be carried out in that experimental setting where the determinant G^TG is maximum. Then, the parameters are reestimated. If the experimenter is not satisfied with the confidence volume, another experiment is designed.

The method is illustrated for the adsorption rate controlling model for n-pentane isomerization (Froment and Mezaki, 1970). This rate equation contains two independent variables, p_A and p_{H_2}, or the n-pentane conversion and the ratio hydrogen/n-pentane. In reality, these experiments were not planned according to this criterion. Thirteen experiments were carried out which are shown in Figure 8. This figure shows the limits on the experimental settings, that is, the so-called *operability* region. A grid is chosen through, or close to, the experimental settings to make use of the experimental results. Three preliminary, unplanned experiments are performed to calculate first estimates for the parameters. Then the fourth experiments is designed. The value of $|G^TG|$ is calculated in each point of the grid. The fourth experiment is performed at these values of the independent variables, where the determinant is maximum. The results are shown in Table 8 for three cases. The preliminary experiments for each case were chosen in a somewhat arbitrary manner in an attempt to investigate the sensitivity of the experimental design to the settings of the preliminary runs, that is, the parameter estimates obtained from these runs. It can be seen that the designed experiments always fall on either of the two settings 105 and 114, both on the limits of the operability region. The design seems to be insensitive to

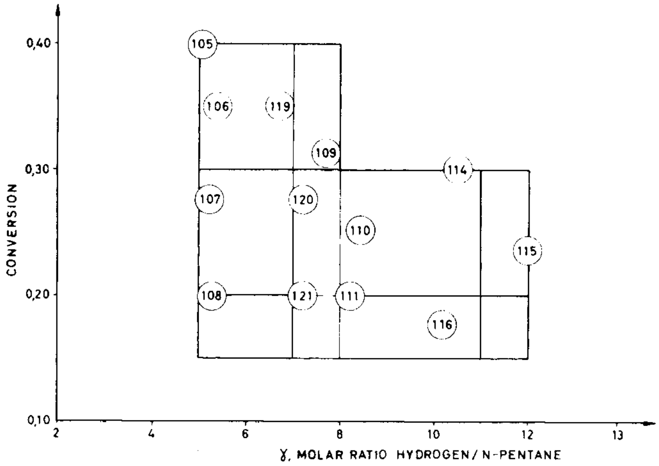


Fig. 8. Experimental grid for precise parameter estimation. Isomerization of *n*-pentane.

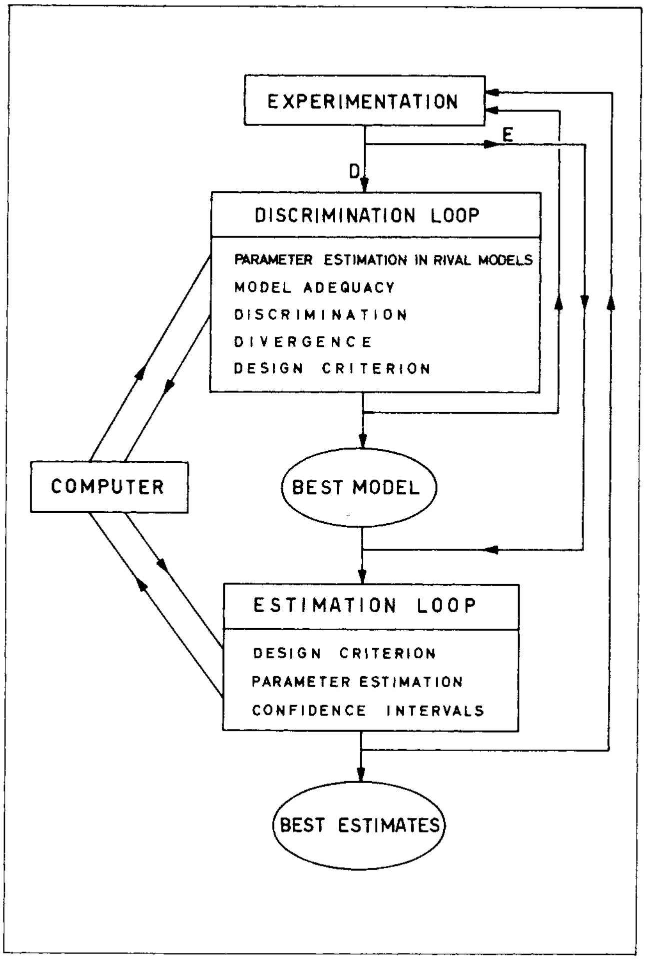


Fig. 9. Sequential procedure for optimal design of experiments.

the choice of the preliminary runs and consequently to the preliminary estimates of the parameters. Also, it is shown that only three designed experiments suffice to reduce the standard deviation of the parameter estimates to that based on all thirteen experiments of Figure 8. The drop in the standard deviations experienced in Case 1 after only one designed experiment is really spectacular. This is due to the poor choice of the preliminary runs, of course. Juusola et al. (1972) applied this procedure to the design of experiments on *o*-xylene oxidation in a differential reactor.

Hosten (1974) recently proposed a different criterion. Instead of minimizing the volume of the joint confidence volume associated with the estimates, he aimed at a more spherical shape for this confidence volume by influencing the length of the principal axes of the confidence hyperellipsoid. When both criteria were applied to the design of twenty-three experiments for the kinetic study of saccharose hydrolysis, it was found that the ultimate volume of the joint confidence region obtained with the minimum volume design was about 3.7 times smaller than with the

TABLE 8. SEQUENTIAL EXPERIMENTAL DESIGN FOR OPTIMAL PARAMETER DETERMINATION *n*-PENTANE ISOMERIZATION ADSORPTION MODEL (FROMENT AND MEZAKI, 1970)

Case	Preliminary runs	Planned	k	$2s(k)$	K_B	$2s(K_B)$	$\lvert G^T \cdot G \rvert$
	108						
1	121						
	111		0.79	0.39	3.35	27.57	$3.87\ 10^{-3}$
		105	0.82	0.08	6.15	2.99	$4.09\ 10^{-1}$
		114	0.89	0.08	8.20	3.55	$8.15\ 10^{-1}$
		105	0.89	0.07	8.21	2.54	1.62
		114					
	106						
2	120						
	116		0.79	0.18	2.39	7.62	$2.54\ 10^{-1}$
		105	0.87	0.19	6.32	6.92	$5.98\ 10^{-1}$
		114	0.89	0.12	7.31	4.78	1.27
		105					
	106						
3	120						
	116						
	109						
	103		0.82	0.14	5.33	5.10	2.80
		114	0.87	0.12	6.96	5.01	1.85
		105	0.87	0.10	7.36	5.90	3.02
		114	0.87	0.08	7.86	3.42	4.11

13 unplanned experiments:
k: 0.20; $2s(k)$: 0, 10
K_B: 6.57; $2s(K_B)$: 3.47

shape design. This was achieved, however, at the expense of superfluous contractions of some axes of the hyperellipsoid which were already much smaller than the longest at early stages of the design. Owing to its specific action, the shape criterion arrives at a longest axis which is about two-thirds that obtained by the minimum volume criterion. In addition, in this example at least, the correlation between the parameters was much smaller with the shape criterion.

The examples given above are all related to algebraic equations. Hosten and Emig (1975) have applied sequential design methods for optimal parameter estimation in differential equations that cannot be analytically integrated.

To summarize, the approach followed on optimal sequential design is illustrated in Figure 9 by means of a kind of flow diagram (Froment, 1974).

Hill, Hunter and Wichern (1968) have combined model discrimination and parameter estimation design procedures which gradually switch from the first to the second task as experiments are being performed.

In conclusion, it may be said that the sequential methods for the design of an experimental program permit a substantial saving in experimental effort for equal significance or a greater significance for comparable experimental effort, with respect to classical procedures. Automatic application of these methods, no matter how powerful they are, should not be substituted for sound judgment.

NOTATION

a', b', c' = functions of the conversion and molar ratio H_2/C_5 in the isomerization of *n*-pentane
A = preexponential factor in the temperature dependence of the parameters
A^* = reparameterized preexponential factor
C_t = total concentration of active sites
$D_{i,n}$ = measure of divergence in the i^{th} grid point
$(D.F.)_i$ = number of degrees of freedom associated with s_i^2
E = activation energy
F_{J_o} = molar flow rate of reactant J at the inlet of the reactor
$k, k_A, k_R, \ldots,$ $k_1, k_2, \ldots$ = rate coefficients
K_J = adsorption equilibrium constant of component J
K_α = equilibrium constant of the α^{th} elementary step
K = equilibrium constant of the overall chemical reaction
m = number of rival models, or number of measured responses
n = number of state equations
p = number of parameters
p_t = total pressure
p_J = partial pressure of component J
r_A = rate of reaction of component A
R = gas constant
S = objective function
s_i^2 = estimate of error variance under model i
$\overline{s}^2$ = pooled estimate of error variance
t = time
T = temperature
$\overline{T}$ = mean temperature
u, v, z = conversions of *o*-xylene into tolualdehyde, phthalide, and phthalic anhydride
W = weight of catalyst
x = conversion of reactant
y = dependent variable
$Z(k)$ = component of the sum of squares objective function

Vectors and Matrices

$\mathbf{c}$ = n vector of independent variables
$\mathbf{e}_r(\mathbf{k})$ = m vector of residuals of the r^{th} experiment
$\mathbf{k}$ = p vector of parameters
$\mathbf{p}$ = vector of independent variables
$\mathbf{x}$ = n vector of state variables
$\mathbf{y}$ = m vector of dependent variables
$\mathbf{D}$ = diagonal matrix of constants (Levenberg-Marquardt algorithms)
$\mathbf{G}$ = matrix of numerical values of partial derivatives $g_{u,i}$
$\mathbf{H}$ = Hessian matrix of second-order partial derivatives
$\mathbf{J}$ = matrix of partial derivatives of model equation with respect to the parameters
$\mathbf{M}$ = $m \times m$ moment matrix of residuals
$\mathbf{Q}$ = $m \times m$ weighting matrix
$\mathbf{R}_i$ = i^{th} approximation of $\mathbf{H}$
$\overline{\mathbf{U}}$ = matrix of normalized search directions (Powell methods)
$\mathbf{V}$ = $m \times m$ covariance matrix of responses
$\mathbf{Z}$ = vector of residuals
$\boldsymbol{\varepsilon}$ = m vector of unobservable experimental errors
$\overline{\mathbf{\Gamma}}$ = matrix of normalized derivatives of $\mathbf{Z}(\mathbf{k})$ with respect to the parameters (Powell methods)

Greek Letters

α, α' = constants in integrated continuity equations of *n*-pentane isomerization
ζ = transformed dependent variable defined by (10)
λ = scalar determining the step length in parameter estimation algorithms
χ_c^2 = corrected calculated χ^2 value used in Bartlett's χ^2 test
σ^2 = error variance
σ_i^2 = variance of predicted value of dependent variable under model i
$\pi_{i,n-1}$ = probability of model i after $n - 1$ experiments

Superscripts

$\wedge$ = calculated value
— = mean value
T = transpose
= derivative with respect to the independent variable

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Membrane Ultrafiltration of a Nonionic Surfactant and Inorganic Salts from Complex Aqueous Suspensions: Design for Water Reuse

Complex aqueous suspensions containing a nonionic surfactant, phosphates, silicate, hypochlorite, oil, and kaolinite particulates are subjected to continuous flow membrane ultrafiltration with noncellulosic membranes. The ultrafiltrate water flux and the rejections by the Millipore PSAL membrane of total organic carbon, surfactant, and total phosphate are related by stepwise, multiple linear regression analysis (logarithmic model) to transmembrane pressure difference, thin channel velocity, membrane resistance, and feed solution concentration. The variables are adjusted to eliminate gel polarization and to minimize concentration polarization.

The data are extended, by the development and use of a computer simulation scale-up procedure, to a 1 000 cm^3/s (23 000 gal/day) laundry waste treatment and water recovery unit. The procedure considers banks of modules in series, banks in parallel, and a parallel-series-tapered arrangement. Membrane area requirements per unit ultrafiltrate water flux and solute rejections are predicted for water recoveries up to 95% of the inlet flow rate.

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SCOPE

Membrane ultrafiltration has been used successfully as an effective process for the treatment of a large number of industrial wastes. The process is appropriate for applications requiring water recycle and reuse and particularly for systems in which the very high rejection of low-molecular-weight solutes is not warranted. Ultrafiltration is a pressure-activated process and is generally carried out at low pressures of 10^5 to 10^6 N/m^2. The use of ultrafiltration for the separation of low-molecular-weight ionic solutes with charged membranes (Bhattacharyya et al., 1974*a*), modest-molecular-weight (size) organic solutes (Grieves et al., 1973; Bhattacharyya et al., 1974*b*), and organic macromolecules and colloids (Porter and Nelsen, 1972) has been reported in the literature. Some of the water reuse applications involving ultrafiltration include electrodeposition primers (Goldsmith et al., 1970), oil-water separation in metal cutting operations (Goldsmith, 1974), and the renovation of sewage effluents (Witmer, 1974). Porter and Nelsen (1972) have reviewed applications of ultrafiltration in the chemical, food processing, and pharmaceutical industries. High-pressure membrane processes such as reverse osmosis and hyperfiltration with dynamic membranes have also been utilized in many water reuse and solute recovery systems (Okey, 1972; Rozelle et al., 1973; Brandon et al., 1972).

Excellent discussions and mathematical formulations of the ultrafiltration process, including considerable detail on concentration polarization, have been presented by Michaels et al. (1971), Porter (1972) and de Filippi and Goldsmith (1970). The concentration polarization caused