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Nonlinear Evaluation of Kinetic Data of Heterogeneous Catalytic Reactions

Application to the Hydrogenation of Phenol and of Cyclohexanone

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A method of evaluation of kinetic data for heterogeneous catalytic reactions is described which consists of a combination of linear regression of transformed rate data and nonlinear regression of the measured rate data by the grid search method. By this procedure it is possible to obtain the most probable estimates of kinetic constants and, if necessary, to determine their range of reliability, as well as to exclude unsuitable kinetic models on the basis of approximate statistical considerations, which is not possible when the evaluation is based on linear regression only. The procedure is illustrated by the treatment of kinetic data for the hydrogenation of phenol and of cyclohexanone, on a platinum catalyst, considering 26 kinetic models of the Langmuir-Hinshelwood type for competitive and noncompetitive adsorption of reactants and the power-law rate equation.

The procedure usually adopted in the treatment of kinetic data is that the assumed rate equation (which is for heterogeneous catalytic reactions usually nonlinear with respect to the parameters) is transformed to a linear form [see refs. (*1*, *2*), for example]. By the method of linear regression, estimates of the constants of the linearized equation are then obtained, and the suitability of different kinetic models for representing the experimental data expressed as variables of the linearized rate equation is then assessed. Finally, the parameters of the original rate equation are calculated from the estimates of the constants of the linearized equation. This procedure has lately been criticized several times in the literature (*3–8*) from the standpoint of statistical methods. The main argument against the procedure outlined is that by transforming the experimental data into variables of the linearized equation the normal distribution of the error of the dependent variable is distorted, and this invalidates the basic assumption of the regression analysis applied. When this assumption is not fulfilled, the application of the least-squares method may yield incorrect estimates of the kinetic constants and can lead to the establishment of an inappropriate order of suitability of the different kinetic models, with the possible result that a particular model may erroneously be rejected [see also refs. (*6*, *9*)]. As is suggested in the cited papers, these insufficiencies can be obviated by using nonlinear regression in which the optimum values of the parameters of the model assumed are determined, for example, by applying the criterion of minimum sum of squares of deviations between the experimentally determined and calculated values of the kinetic variables (reaction rate, conversion, etc.), i.e., without the prior transformation (linearization) of the experimental results.

The authors of the above-mentioned papers have used nonlinear regression (*4–7*, *10–12*) for reevaluating some older data on heterogeneous catalytic reactions. The procedure is not described by them in detail; usually it consisted in the combination of the Gauss-Newton (*13–15*) and steepest descent (*16*) methods, as developed by Marquardt (*17*). Like all other iterative procedures, it requires at the start an approximate estimate of the parameters to be determined. Kittrell, Mezaki, and Watson (*5*) mention some methods for obtaining such first estimates; among others they mention the grid search method, which consists in the calculation of the sum of squares of deviations of the measured and calculated values of the kinetic quantity for certain combinations of values of the parameters which are systematically varied over a sufficiently large range [see also refs. (*4*, *18*)]. The combination for which the sum of squares of deviations is smallest is used as the first estimate for the nonlinear optimization procedure. It appeared to us suitable to develop this method as an iterative procedure which would, similarly to Marquardt's method, itself be able to lead to the optimum values of the parameters of the nonlinear relation, and which would be suitable for evaluating a large number of rate equations. In the present work we shall give a description of this method and of its application to the evaluation of kinetic data for the hydrogenation of phenol and of cyclohexanone on a platinum catalyst at 150°C studied in connection with another work (*19*). Although the choice of the first estimate of the parameters desired is to some extent arbitrary, we have used as the starting values estimates obtained by linear regression of transformed rate data. Because the possibility of discrimination among the Langmuir-Hinshelwood type models is small (*4*, *7*, *9*, *20*), we have finally applied an approximate statistical criterion for the elimination of unsuitable models.

LIST OF SYMBOLS

A	Phenol, molecule of phenol
B	Hydrogen, molecule of hydrogen
C	Cyclohexanone, molecule of cyclohexanone
D	Cyclohexanol, molecule of cyclohexanol
$F(p,N-p,\alpha)$	Fisher's F
K_{I}	Adsorption coefficient of substance I (atm^{-1})
$K'_1 - K'_3$	Equilibrium constants of surface reactions
k	Rate constant of surface reaction or of power-law kinetic equation
k_{ads}	Rate constant of adsorption (mole $\mathrm{kg}^{-1}\,\mathrm{hr}^{-1}\,\mathrm{atm}^{-1}$)
k_{des}	Rate constant of desorption (mole $\mathrm{kg}^{-1}\,\mathrm{hr}^{-1}$)
M	Cyclohexadienol, nondesorbing intermediary product
N	Number of experiments
p	Number of unknown parameters
p_{I}	Initial partial pressure of substance I (atm)
$Q(\kappa)$	Sum of squares of deviations as a function of the parameters κ
$Q(\kappa)_{\mathrm{crit}}$	Critical value of $Q(\kappa)$
$Q(\hat{\kappa})$	Value of the sum of squares of deviations at the minimum value of the function $Q(\kappa)$
r_{I}	Initial reaction rate of hydrogenation of phenol (mole $\mathrm{kg}^{-1}\,\mathrm{hr}^{-1}$)
r_{II}	Initial reaction rate of hydrogenation of cyclohexanone (mole $\mathrm{kg}^{-1}\,\mathrm{hr}^{-1}$)
r_i	Experimentally determined initial reaction rate in ith experiment (mole $\mathrm{kg}^{-1}\,\mathrm{hr}^{-1}$)
$r(\kappa)$	Initial reaction rate as a function of the parameters κ (mole $\mathrm{kg}^{-1}\,\mathrm{hr}^{-1}$)
$r(\kappa)_i$	Initial reaction rate calculated for the parameters κ and the independent variables for the ith experiment (mole $\mathrm{kg}^{-1}\,\mathrm{hr}^{-1}$)
u, v	Exponents in power-law kinetic equation
U, V, X, Y	Hypothetical substances
α	Significance level
κ	Ordered set of p parameters
$\hat{\kappa}$	Ordered set of p parameters defining the minimum value of $Q(\kappa)$

EXPERIMENTAL

The substances used, the flow-type apparatus, and the methods by which the hydrogenation products of phenol and cyclohexanone were analyzed are all described elsewhere (*19*). The values of the initial reaction rates were determined as slopes of the found dependencies of the reactants conversion on the reciprocal space velocity. Over the range of conversions employed (up to 10%), these dependencies were linear. The overall pressure of the reactants was either atmospheric or reduced by diluting the reaction mixture with nitrogen. The initial partial pressure of phenol was varied from 0.015 to 0.5 atm, of cyclohexanone from 0.05 to 0.75 atm, and of hydrogen from 0.05 to 0.985 atm. By comparing conversions attained on a powdered catalyst and on a granular sample of 0.2–0.25 mm particle size it was found that the reaction rate is not influenced by intraparticle diffusion. Further, it was found that the reaction rate is independent of mass rate of feed higher than 0.01 kg m^{-2} sec^{-1}, which shows that the results are not influenced by external diffusion. Over a certain range of lower mass rates higher reaction rates were found. This rather surprising increase in the reaction rate can hardly be due to temperature effects, because the temperature was at all mass velocities maintained constant with the same accuracy of ±0.5°C. From a theoretical analysis (*21*), however, it follows that in some bimolecular catalytic reactions, even those without a thermal effect, the reaction rate can be enhanced by external diffusion. In the kinetic region we have determined 28 values of initial reaction rates of phenol hydrogenation $(r_I = f_I(p_A,p_B))$, and 21 values of initial reaction rates of cyclohexanone hydrogenation $[r_{II} = f_{II}(p_C,p_B)]$. These results are plotted as points in Figs. 1 and 2.

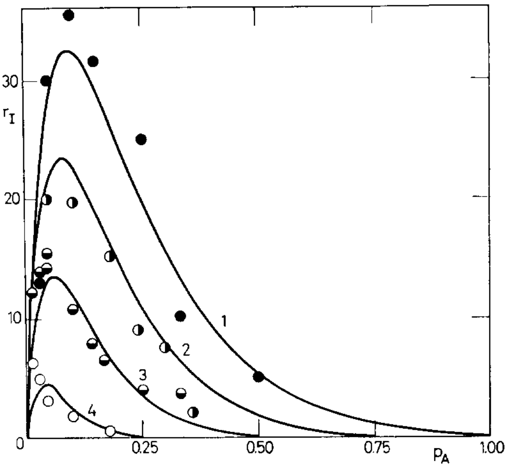

FIG. 1. Dependence of initial rate r_I (mole kg^{-1} hr^{-1}) of hydrogenation of phenol on its initial partial pressure p_A(atm) at constant total pressures of reactants; 1, total pressure of reactants 1 atm; 2, total pressure of reactants 0.75 atm; 3, total pressure of reactants 0.5 atm; 4, total pressure of reactants 0.25 atm. The curves were calculated from Eq. (8); the points represent experimental values for the following total pressures of reactants: ●, 1 atm; ◑, 0.75 atm; ◒, 0.5 atm; ○, 0.25 atm.

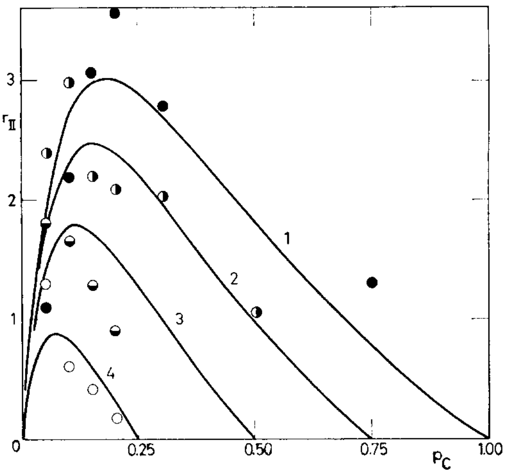

FIG. 2. Dependence of initial rate r_{II} (mole kg^{-1} hr^{-1}) of hydrogenation of cyclohexanone on its initial partial pressure p_C (atm) at constant total pressure of reactants; 1, total pressure of reactants 1 atm; 2, total pressure of reactants 0.75 atm; 3, total pressure of reactants 0.5 atm; 4, total pressure of reactants 0.25 atm. The curves were calculated from Eq. (15), the points represent experimental values for the following total pressures of reactants: ●, 1 atm; ◑, 0.75 atm; ◒, 0.5 atm; ○, 0.25 atm.

RESULTS

Derivation of Rate Equations

In the derivation of rate equations, it was assumed that each of the reactions has only one rate determining step (adsorption, surface reaction, or desorption, respectively). Our analysis of the hydrogenation of phenol was based on information published in the literature (*22–25*), namely, that this is a consecutive reaction, irreversible at 150°C, in which first cyclohexanone is formed and then in the next step converted to cyclohexanol. From preliminary experiments it was estimated that the difference in the rates of the slowest steps of the first and second reactions (hydrogenation of phenol and hydrogenation of cyclohexanone) does not exceed one order of magnitude (*19*). For example, at p_A (or p_C) = 0.1 atm and p_B = 0.4 atm the rate of the first reaction is 6.5 times higher than that of the second reaction; the maximum concentration of the intermediate product (cyclohexanone) was about 70%, and up to 40% conversion of phenol it was not possible to determine cyclohexanol in the product (i.e., its concentration did not exceed 1%). This result was subsequently confirmed by calculation. It follows from this (a) that we have confirmed that the hydrogenation of phenol on the catalyst used is a consecutive reaction, and (b) that the desorption of cyclohexanone is not the slowest step of the first reaction. The measured rate of consumption of phenol can therefore be controlled only by the rate of its conversion to cyclohexanone (i.e., by the adsorption of either phenol or hydrogen, or by a surface reaction) and not by the parallel formation of cyclohexanone and cyclohexanol. The second reaction—hydrogenation of cyclohexanone—can be studied separately and independently of the first one; its rate can be controlled either by the adsorption of the reactants, by a surface reaction, or by the desorption of cyclohexanol.

In the derivation of rate equations we have applied Langmuir and Hinshelwood's concepts, which have been further developed by Hougen and Watson (*1*). In addition to equations assuming competitive adsorption of reaction components on the catalyst surface we have also derived equations based on the concept of noncompetitive adsorption of the reactants. It was also assumed that the organic substance, i.e., phenol or cyclohexanone, respectively, is adsorbed without dissociation, and that hydrogen can be adsorbed with or without dissociation, or that it may react directly from the gaseous phase. Further we assumed that the hydrogenation of phenol to cyclohexanone can proceed in one of two ways: (1) cyclohexanone is formed by a direct reaction of a molecule of phenol with two molecules of hydrogen i.e.,

$$\mathrm{A} + 2\mathrm{B} = \mathrm{C} \tag{a}$$

(2) cyclohexanone is formed by the successive addition of two molecules of hydrogen; the intermediate product of this reaction is a nondesorbing dienol M which, because of its instability, is rapidly converted to cyclohexanone C

$$\mathrm{A} + \mathrm{B} = \mathrm{M} \tag{b}$$

$$\mathrm{M} + \mathrm{B} = \mathrm{C} \tag{c}$$

The hydrogenation of cyclohexanone to cyclohexanol is formally of the same type as the reaction (b). The method of derivation of the rate equations is described in the literature (*1*, *2*). The resulting equations for the initial rates of both types of reaction are listed in Table 1. As a matter of interest we have also included a power-law kinetic equation (27) for interpreting the data.

Description of the Procedure Used

The nonlinear least-squares method consists in finding such parameters of the kinetic equation which satisfy the condition (28)

$$Q(\hat{\kappa}) = \min \sum_{i=1}^{N} [r_i - r(\kappa)_i]^2 \tag{28}$$

i.e., parameters κ which correspond to the minimum possible value of $Q(\kappa)$. If, simultaneously, the condition is fulfilled that the error of the reaction rate is distributed normally with the same (unknown) variance, then the parameters $\hat{\kappa}$ found are also the most probable ones. In the grid search method, the dependence of the function $Q(\kappa)$ on the values of the parameters κ is investigated so that $Q(\kappa)$ is calculated for certain, in the interval chosen systematically varied combinations of values of the parameters. In our case the combinations were represented by the points of intersection of a rectangular grid of the parameter space. From the set of values of $Q(\kappa)$ calculated in this way the smallest one was chosen, and in the vicinity of the values of κ which corre-

TABLE 1

EQUATIONS FOR KINETIC MODELS ASSUMED

Number of equation	Mode of adsorption[a] of V	Rate-determining step[b]	Number of centers	Right side of rate equation for initial conditions $r = f(\mathrm{U}p_{\mathrm{U}}, \mathrm{V}p_{\mathrm{V}})$	Square of correlation coefficient from linear regression for hydrogenation of —	
					phenol	cyclohexanone
(1)	0	ads-U	1	$k_{\mathrm{ads}}p_{\mathrm{U}}$	0.08	0.12
(2)	1	ads-U	1	$k_{\mathrm{ads}}p_{\mathrm{U}}/(1 + K_{\mathrm{V}}p_{\mathrm{V}})$	0.19	0.40
(3)	2	ads-U	1	$k_{\mathrm{ads}}p_{\mathrm{U}}/[1 + (K_{\mathrm{V}}p_{\mathrm{V}})^{1/2}]$	0.27	0.49
(4)	1	ads-V	1	$k_{\mathrm{ads}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}})$	0.16	0.09
(5)	2	ads-V	2	$k_{\mathrm{ads}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}})^2$	0.19	0.11
(6)	0	sr-U2V	1	$kK_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}}^2/(1 + K_{\mathrm{U}}p_{\mathrm{U}})$	0.67	—
(7)	0	sr-U2V	2	$kK_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}}^2/(1 + K_{\mathrm{U}}p_{\mathrm{U}})^2$	0.81	—
(8)	1	sr-U2V	3	$kK_{\mathrm{U}}p_{\mathrm{U}}(K_{\mathrm{V}}p_{\mathrm{V}})^2/(1 + K_{\mathrm{U}}p_{\mathrm{U}} + K_{\mathrm{V}}p_{\mathrm{V}})^3$	0.88	—
(9)	1	sr-U2V	4	$kK_{\mathrm{U}}p_{\mathrm{U}}(K_{\mathrm{V}}p_{\mathrm{V}})^2/(1 + K_{\mathrm{U}}p_{\mathrm{U}} + K_{\mathrm{V}}p_{\mathrm{V}})^4$	0.89	—
(10)	2	sr-U2V	5	$kK_{\mathrm{U}}p_{\mathrm{U}}(K_{\mathrm{V}}p_{\mathrm{V}})^2/[1 + K_{\mathrm{U}}p_{\mathrm{U}} + (K_{\mathrm{V}}p_{\mathrm{V}})^{1/2}]^5$	0.89	—
(11)	0	sr-UV	1	$kK_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}})$	0.60	0.92
(12)	0	sr-UV	2	$kK_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}})^2$	0.76	0.82
(13)	0	sr-UV	3	$kK_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}})^3$	0.79	0.77
(14)	0	sr-UV	4	$kK_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}})^4$	0.80	0.74
(15)	1	sr-UV	2	$kK_{\mathrm{U}}p_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}} + K_{\mathrm{V}}p_{\mathrm{V}})^2$	0.79	0.83
(16)	1	sr-UV	3	$kK_{\mathrm{U}}p_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}} + K_{\mathrm{V}}p_{\mathrm{V}})^3$	0.83	0.79
(17)	1	sr-UV	4	$kK_{\mathrm{U}}p_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}} + K_{\mathrm{V}}p_{\mathrm{V}})^4$	0.63	0.76
(18)	2	sr-UV	3	$kK_{\mathrm{U}}p_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{V}}/[(1 + K_{\mathrm{U}}p_{\mathrm{U}} + (K_{\mathrm{V}}p_{\mathrm{V}})^{1/2}]^3$	0.80	0.78
(19)	2	sr-UV	4	$kK_{\mathrm{U}}p_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{V}}/[(1 + K_{\mathrm{U}}p_{\mathrm{U}} + (K_{\mathrm{V}}p_{\mathrm{V}})^{1/2}]^4$	0.64	0.75
(20)	0	des-Y	1	$k_{\mathrm{des}}K_1'K_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}} + K_1'K_{\mathrm{U}}p_{\mathrm{U}}p_{\mathrm{V}})$	—	0.10
(21)	1	des-Y	1	$k_{\mathrm{des}}K'_2K_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{U}}p_{\mathrm{V}}/(1 + K_{\mathrm{U}}p_{\mathrm{U}} + K_{\mathrm{V}}p_{\mathrm{V}} + K'_2K_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{U}}p_{\mathrm{V}})$	—	0.12
(22)	2	des-Y	1	$k_{\mathrm{des}}K_3'K_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{U}}p_{\mathrm{V}}/[1 + K_{\mathrm{U}}p_{\mathrm{U}} + (K_{\mathrm{V}}p_{\mathrm{V}})^{1/2} + K_3'K_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{U}}p_{\mathrm{V}}]$	—	0.11
(23)	1[c]	sr-U2V	1 + 2	$kK_{\mathrm{U}}K_{\mathrm{V}}^2p_{\mathrm{U}}p_{\mathrm{V}}^2/[(1 + K_{\mathrm{U}}p_{\mathrm{U}})(1 + K_{\mathrm{V}}p_{\mathrm{V}})^2]$	[d]	—
(24)	2[c]	sr-U2V	1 + 4	$kK_{\mathrm{U}}K_{\mathrm{V}}^2p_{\mathrm{U}}p_{\mathrm{V}}^2/\{(1 + K_{\mathrm{U}}p_{\mathrm{U}})[1 + (K_{\mathrm{V}}p_{\mathrm{V}})^{1/2}]^4\}$	[d]	—
(25)	1[c]	sr-UV	1 + 1	$kK_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{U}}p_{\mathrm{V}}/[(1 + K_{\mathrm{U}}p_{\mathrm{U}})(1 + K_{\mathrm{V}}p_{\mathrm{V}})]$	[d]	[d]
(26)	2[c]	sr-UV	1 + 2	$kK_{\mathrm{U}}K_{\mathrm{V}}p_{\mathrm{U}}p_{\mathrm{V}}/\{(1 + K_{\mathrm{U}}p_{\mathrm{U}})[1 + (K_{\mathrm{V}}p_{\mathrm{V}})^{1/2}]^2\}$	[d]	[d]
(27)	Power-law kinetic equation			$kp_{\mathrm{U}}^{u}p_{\mathrm{V}}^{v}$	0.81	0.83

[a] The symbols in this column denote; 0, nonadsorbing; 1, adsorption without dissociation; 2, adsorption with dissociation.

[b] The symbols in this column denote: ads-U, rate determined by adsorption of U; ads-V, rate determined by adsorption of V; sr-U2V, rate determined by surface reaction of U with two molecules of V according to the equation U + 2V = X (cannot be considered for hydrogenation of cyclohexanone); sr-UV, rate determined by surface reaction of U with one molecule of V according to equation U + V = Y; des-Y, rate determined by desorption of product of the reaction U + V = Y (derived for hydrogenation of cyclohexanone). For the hydrogenation of phenol to cyclohexanone U denotes phenol (substance A), for the hydrogenation of cyclohexanone to cyclohexanol U denotes cyclohexanone (substance C), V denotes in both reactions hydrogen (substance B).

[c] Substance is adsorbed on another type of active centers than U.

[d] These relations have not been linearized.

sponded to it a new grid was formed. The density of the new grid depended on whether the last found, tentatively best values of the parameters were well within the region investigated in the preceding iteration or at its boundary. In the former case the region of investigation was reduced and the grid density was therefore increased; if the value of any one of the parameters was at the boundary, the region was increased and consequently the grid density was decreased. In all cases the number of points at which the function $Q(\kappa)$ was investigated was the same. The next trial was carried out in a similar manner, and the entire procedure was repeated until the difference between two successive values of $Q(\kappa)$ was sufficiently small. The method also allowed finding the minimum value of the function $Q(\kappa)$ in cases when the first estimate was so far from the minimum to be found that it was not contained in the initially investigated region of values of the parameters. It leads to the correct result—to the true minimum of the function $Q(\kappa)$—when this function is well behaved at least in the neighborhood of the true minimum, and if there are no local minima in the first chosen region of values of the parameters or between this region and the true minimum.

When the minimum of the function $Q(\kappa)$ and the optimum values of the parameters of the given rate equation are found, the procedure can be repeated for further equations; it is very simple to incorporate into the program an arbitrary number of various kinetic models. In order to reduce the number of trials and more reliably to determine the optimum values of the parameters we have combined in the evaluation of experimental data this nonlinear method with linear regression, so that we used the results of linear regression as starting values of the parameters for the nonlinear procedure.

By this basically very simple procedure it is possible to evaluate a number of rate equations for the models assumed, and to arrange them in the order of increasing values of the sum of squares of deviations. In this way we can obtain the kinetic equation and its parameters with the least sum of squares of deviations. Because the set of data investigated is always subject to random experimental error, the equation found in this way need not necessarily give the "best" description of the actual kinetics of the reaction represented by an infinite set of data. The model best representing the actual kinetics may be one expressed by another of the equations evaluated. Only in the case of a set of data entirely free of experimental error could we be certain that the best-fitting model expresses the actual kinetics of the reaction (the sum of squares of deviations being in this case zero). In practical cases, however, we must expect that the experimental data will be fitted approximately equally well by more than one equation [e. g. refs. (*4, 7, 9, 20*)] and that the degree of discrimination between them will be the less the lower the accuracy of measurement and the less the difference in the mathematical formulation of different kinetic models. However, in order to be more certain that we have included among the equations treated the one which really expresses the kinetics of the reaction, we must consider a large number of kinetic models, including very complex ones, many of which are very similar. In such a case, however, even with experimental data subject to only a small error we do not arrive at a conclusive result even when the true model is included among those considered. Moreover, considering the complexity of heterogeneous catalytic reactions we can never be quite certain that the true model has been included. We must therefore accept the fact that relations obtained by a kinetic analysis of heterogeneous catalytic reactions will, as a rule, express the reaction mechanism only approximately.

In order to be able to select from the models treated those which have to be further considered, we can employ approximate statistical considerations for determining the limits in which discrimination between the different models is possible, and in this way we can reject unsuitable models, if necessary. We have employed for this the principle of a procedure proposed by Beale (*26*) for finding the confidence limits of the parameters of a nonlinear relation and which has also been used by Mezaki and Kittrell (*12*). The procedure consists in finding the critical value of the sum of squares of deviations on a certain significance level. This value is approximately given by the relation (29)

$$Q(\kappa)_{\mathrm{crit}} = Q(\hat{\;})\{1 + [p/(N - p)]F(p,N-p,\alpha)\} \qquad (29)$$

and it can therefore be determined from the known value of the function $Q(\kappa)$ at its minimum point for the kinetic model under consideration $[Q(\hat{\kappa})]$. According to Beale (*26*) we may claim on a 100α % significance level that the correct combination of parameters is one of those for which $Q(\kappa)$ is less then $Q(\kappa)_{\mathrm{crit}}$ calculated from Eq. (29). We must therefore consider all combinations which fulfill this condition.

We believe that the treatment can be extended also to the case of comparing a larger number of models (rate equations) with the model which best represents the set of experimental data. It may then be claimed that those rate equations for which the sum of squares of deviations is less than $Q(\kappa)_{\mathrm{crit}}$ calculated on the basis of $Q(\hat{\kappa})$ for the rate equation with the least sum of squares of deviations cannot be rejected at the significance level chosen. Those models whose sums of squares of deviations are higher can be excluded from further consideration.

Treatment of Data

For the first selection from the models considered we have used linear regression and the square values of the correlation coefficients (Table 1). The relations (23)–(26), which were derived on the assumption of noncompetitive adsorption of the reactants, were not linearized, so that for them the square of the correlation coefficient is not given in Table 1. In order to make certain that by this first selection we shall not exclude any of the relations which correlate well, we have included for further treatment, for the case of the hydrogenation of phenol, all the mechanisms for which the square of the correlation coefficient was higher than 0.8. For the hydrogenation of cyclohexanone, for which fewer experimental results were obtained, we chose the critical value of 0.5. All the rate equations satisfying these conditions were further investigated by nonlinear regression—by the grid search method; the results of this evaluation are given in Tables 2 and 3. In these tables the rate equations are arranged in the order of increasing values of the sum of squares of deviations.* The goodness of fit of the relations $r_{\mathrm{I}} = f_{\mathrm{I}}(p_{\mathrm{A}})$ and $r_{\mathrm{II}} = f_{\mathrm{II}}(p_{\mathrm{C}})$ calculated on the basis of Eqs. (8) or (15), which are first on the lists, can be seen from Figs. 1 and 2.

For deciding which of the remaining relations can be definitely rejected we applied the criterion (29). It was found that for the hydrogenation of phenol the situation is relatively simple. For the rate equation (8) as the starting equation, and on a 95% probability level, the critical value $Q(\kappa)_{\mathrm{crit}}$ is 36% higher than $Q(\hat{\kappa})$ for Eq. (8), and amounts to 322. Therefore all the relations given in Table 2 can be excluded, excepting the first three, one of which should represent the correct model. For the hydrogenation of cyclohexanone the critical value of the sum of squares of deviations is rather high, apparently because the set of experimental data treated was smaller. For this case $Q(\kappa)_{\mathrm{crit}}$ is 53% higher than $Q(\hat{\kappa})$ for Eq. (15) and amounts to 5.63. Therefore any of the models given in Table 3 could be suitable for expressing the hydrogenation of cyclohexanone.

DISCUSSION

From the approximate statistical analysis it follows that although we are able to select the most probable rate equation, its priority is not pronounced. It is of interest, however, to note some of the properties of the models considered. Of the 10 best equations in Table

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* It is not possible definitely to decide whethe these sums are the actual minima of the function $Q(\kappa)$ for individual mechanisms. However, if the conditions for the application of the method are fulfilled, then we should arrive at the same combination of parameters, and the same minimum value of the sums of squares of deviations, regardless of the first estimate used (i.e., not only when the first estimate is based on results of regression of the linearized data). This condition was verified for several cases and invariably it was fulfilled.

TABLE 2

ORDER OF CORRELATING RELATIONS FOR HYDROGENATION OF PHENOL IN THE INITIAL REGION

Order of suitability according to sum of squares of deviations	Number of relation in Table 1	Mode of adsorption[a] of B	Rate-determining step[b]	Number of centers	Square of correlation coefficient from linear regression	Sum of squares of deviations $[Q(\hat{k})]$ $[\text{mole kg}^{-1}\ \text{hr}^{-1}]^2$
1	(8)	1	sr-A2B	3	0.88	236.4
2	(9)	1	sr-A2B	4	0.89	249.9
3	(10)	1	sr-A2B	5	0.89	279.3
4	(16)	1	sr-AB	3	0.83	419.3
5	(7)	0	sr-A2B	2	0.81	514.4
6	(23)	1[c]	sr-A2B	$1+2$	[d]	649.1
7	(24)	2[c]	sr-A2B	$1+4$	[d]	689.0
8	(27)	Power-law kinetic equation			0.81	722.7
9	(25)	1[c]	sr-AB	$1+1$	[d]	1137.2
10	(26)	2[c]	sr-AB	$1+2$	[d]	1526.3

[a–d] See footnotes to Table 1.

2 and of the 12 best equations in Table 3 all (with the exception of the empirical power-law equation, which, however, is eighth in both Tables 2 and 3) correspond to models for which the rate-determining step is a surface reaction. It can therefore fairly definitely be concluded, without going into more detailed considerations of the reaction mechanism, that the adsorption or desorption of reaction components is not the rate-determining step of the reactions studied. A further point worth noting is that the two models found as most probable [Eq. (8) for the hydrogenation of phenol, and Eq. (15) for the hydrogenation of cyclohexanone] are derived on the basis of the simplest concept: both the organic substance and hydrogen are adsorbed without dissociation on active centers of the same kind, and the order of the reaction with respect to surface concentrations equals their molecularity. A further interesting fact is that for this pair of most probable models we have also obtained the best agreement between the values of the adsorption coefficient of hydrogen, which is a reagent common to both reactions. (Their respective values are 1.1 and 0.91 atm^{-1}, which for kinetics of heterogeneous catalytic reactions can be considered as a very good agreement.)

The results of the kinetic analysis presented enable us to examine to what extent

TABLE 3

ORDER OF CORRELATING RELATIONS FOR HYDROGENATION OF CYCLOHEXANONE IN THE INITIAL REGION

Order of suitability according to sum of squares of deviations	Number of relation in Table 1	Mode of adsorption[a] of B	Rate-determining step[b]	Number of centers	Square of correlation coefficient from linear regression	Sum of squares of deviations $[Q(\hat{k})]$ $[\text{mole kg}^{-1}\ \text{hr}^{-1}]^2$
1	(15)	1	sr-CB	2	0.83	3.68
2	(16)	1	sr-CB	3	0.79	4.18
3	(26)	2[c]	sr-CB	$1+2$	[d]	4.20
4	(25)	1[c]	sr-CB	$1+1$	[d]	4.46
5	(17)	1	sr-CB	4	0.76	4.48
6	(19)	2	sr-CB	4	0.75	4.59
7	(18)	2	sr-CB	3	0.78	4.62
8	(27)	Power-law kinetic equation			0.83	4.70
9	(11)	0	sr-CB	1	0.92	4.91
10	(12)	0	sr-CB	2	0.82	5.19
11	(13)	0	sr-CB	3	0.77	5.43
12	(14)	0	sr-CB	4	0.74	5.58

[a–d] See footnotes to Table 1.

TABLE 4

COMPARISON OF VALUES OF CONSTANTS AND SUMS OF SQUARES $Q(\kappa)$ OBTAINED BY LINEARIZATION AND BY THE GRID SEARCH METHOD FOR THE THREE BEST MODELS AND FOR THE POWER-LAW KINETIC EQUATION

Equation	Method	Estimates of parameters k (mole kg^{-1} hr^{-1})	 K_A or K_C (atm^{-1})	 K_B (atm^{-1})	Sum of squares of deviations $Q(\kappa)$ (mole^2 kg^{-2} hr^{-2})
		Hydrogenation of phenol (A)			
(8)	Linearization	640	10.9	1.39	285.3
	Grid search	876.6	9.2	1.1	236.6
(9)	Linearization	3145	5.2	0.71	271.3
	Grid search	4501	4.6	0.53	249.9
(10)	Linearization	7516	4.1	0.59	1424.9
	Grid search	5063	5.1	1.4	279.3
(27)	Linearization	28.3	−0.0255[a]	1.47[b]	775.0
	Grid search	35	0.0560[a]	1.42[b]	722.7
		Hydrogenation of cyclohexanone (C)			
(15)	Linearization	74.7	6.56	0.81	4.70
	Grid search	28.7	7.7	0.91	3.68
(16)	Linearization	221.2	1.8	0.18	4.96
	Grid search	126.6	2.8	0.34	4.18
(17)	Linearization	440.4	1.22	0.13	5.17
	Grid search	263.0	1.8	0.23	4.48
(27)	Linearization	4.2	0.13[c]	0.87[b]	5.41
	Grid search	5.1	0.24[c]	0.79[b]	4.70

[a] Represents the exponent over the partial pressure of A (phenol).

[b] Represents the exponent over the partial pressure of B (hydrogen).

[c] Represents the exponent over the partial pressure of C (cyclohexanone).

the nonlinear grid search method is more reliable than linear regression. From Table 4 it follows that the kinetic constants obtained by the grid search method lead to a better agreement between the calculated and experimental dependencies than those obtained by linear regression. The differences in the values of the constants obtained by the two methods are in some cases considerable. Similar results were obtained for the evaluation of rate data for the hydrogenolysis of indane (*9*). A comparison of values of constants following from linear and nonlinear regression is also given in the work of Blakemore and Hoerl (*4*), Kittrell, Hunter, and Watson (*5, 6*), and Peterson and Lapidus (*11*). The nonlinear procedure enables one more reliably than linear regression to arrange the rate equations according to their ability to describe the experimental data and to choose from them the most suitable relation. As is apparent from Tables 2 and 3, the order of arrangement of the equations in accordance with the squares of the correlation coefficient following from linear regression would be different, and it could easily occur that a badly correlating model would be selected as the best one [see, for example, Eq. (11) which is ninth in Table 3)], or, as has been shown elsewhere (*9*), some suitable models would be rejected. By the nonlinear method it is also possible to find the confidence limits of the constants determined, which it is not possible to determine exactly when linear regression is used. The nonlinear method also enables one to employ a modification of Beale's method and thereby to reject, on a chosen significance level, unsuitable rate equations. The use of the nonlinear method also obviates the ambiguity of the results following from the possibility of different ways in which a particular equation can be linearized; this possibility has been pointed out, for example, by Kokotov (*27*). Since because of the complexity of heterogeneous catalytic reactions a large number of kinetic models must be considered for their evaluation in order to be more certain that the correct kinetic model will even be included, it is suitable to employ the combination of the nonlinear grid search method with preliminary linear regression; the procedure is sufficiently rapid, and in addition to the present work it has also been used in some other work carried out in our laboratory (*9*, *28*, *29*).

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