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Random Errors in Kinetic Data from a Catalytic Flow Reactor

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Kinetic measurements of cyclohexanol dehydration on alumina at 200°C were conducted using a flow apparatus. The initial reaction rate approach was used to obtain data suitable for statistical evaluation of experimental error. The contribution of various error sources to the overall uncertainty of results was estimated either independently or by analysis of variance. Using the same procedure three sets of kinetic data from the work of other authors were also evaluated and information was obtained concerning the influence of minor changes of experimental technique on precision. The significance of errors found in dependent and independent variables is discussed and recommendations for improvement of experimental design are given.

NOMENCLATURE

F_i	feed rate of component i into the apparatus (mole/hr)
l	number of experimental points in a x-(W/F) dependence
m	number of product samples in a kinetic run
n	number of determinations of composition of a product sample
p_i	partial pressure of the component i (atm)
p_i^0	partial pressure of the component i in the feed (atm)
P	atmospheric pressure (atm)
r	reaction rate (mole/hr kg)
r^0	initial reaction rate (mole/hr kg)
T	temperature (°K)
$V(y)$	variance of the variable y
W	weight of the catalyst sample (kg)
x	conversion
Indices	
A	starting compound
I	inert diluent
j	level in the hierarchic scheme

INTRODUCTION

Precision and accuracy of rate measurements in heterogeneous catalysis and the influence of the resulting uncertainty on the correlation of kinetic data has received only occasional attention. Usually only some special problem has been analysed. Schneider and co-workers (*1–3*) have studied the effect of a systematic error in the determination of conversion on the selection of a suitable rate equation of the Langmuir–Hinshelwood type. Kraus (*4*) and Massaldi and Maymó (*5*) have dealt with the error which is introduced into the rate data by assuming the flow apparatus to operate as a pseudodifferential reactor. The most detailed study has been published by Pozzi and Rase (*6*) who have compared the precision of various types of laboratory reactor. They included in their studies an exothermic reaction (propylene hydrogenation) and proposed some rules for judging the accuracy of the results.

A critical estimation of the reliability of kinetic data seems very desirable in the light of the increasing use of computers and the recent development of nonlinear regression methods for rate equations (cf. (*7*) and (*8–11*)). In spite of the sophistication of these methods, their use in selecting the best rate model diminishes rapidly with the experimental error and the question arises whether, in general, a great computing effort is justified when data of unknown quality are available.

The purpose of the present work is to analyse various sources of error in dependent and independent variables when a continuous flow differential catalytic reactor is used and the general approach to kinetic measurements corresponds to the initial rate method (*12*, *13*). Both of these features appear in a number of kinetic studies of heterogeneous catalytic gas-phase reactions. In contrast to Pozzi and Rase (*6*), a slightly endothermic reaction, viz., dehydration of cyclohexanol on alumina, was chosen for the purpose of the work reported in this paper. Such a reaction has the advantage of small temperature gradients in the catalyst bed and, as a consequence, it is easier to discriminate among other sources of error. Only random errors were considered since the evaluation of systematic errors requires a different approach.

EXPERIMENTAL

Materials. Cyclohexanol (Lachema, Brno) was purified by double rectification through a laboratory column which has 35 theoretical plates. Its purity was checked by gas chromatography and by refractive index, $n_D^{25} = 1.4646$. Nitrogen and hydrogen were high-purity compressed gases.

Catalyst. Three preparations of aluminium hydroxide (catalyst precursors) made by precipitation of sodium aluminate solution with nitric acid under controlled conditions were obtained through the courtesy of Dr. H. Kostková (*14*). The hydroxides were transformed into the oxides by heating at 800 ± 10°C in a crucible placed in an electric oven for 8 hr. After cooling, crushing, and sieving, the aluminas obtained (catalyst lots) were used for kinetic measurements. The catalysts showed constant activity after use for only a short initial period; the constancy was checked by standard runs. As the result of experimenting with various fractions a catalyst particle size of 0.2–0.3 mm was chosen as the size which eliminated intraparticle diffusion effects. Similarly, a region of flow rates was found where the influence of mass transfer from the bulk phase does not influence the results.

Apparatus. An all-glass flow apparatus (Fig. 1) was used for the experiments. The cyclohexanol feeder, 6, consisted of a glass syringe, the piston of which could be depressed by a synchronous motor through a set of interchangeable gears. The alcohol was fed to the system by a syringe whose needle was in contact with the wall of the evaporator tube, 7, thus preventing drop formation. The evaporation of cyclohexanol into the stream of nitrogen was smooth and the preheated mixture passed into the reactor, 8, which consisted of a pipette with a central thermocouple well, 9. The upper and lower parts of the reactor were filled with glass beads; the catalyst formed a layer around the tip of the well. The products from the reactor were passed into the condenser, 12, which was immersed in a mixture of ethanol and solid carbon

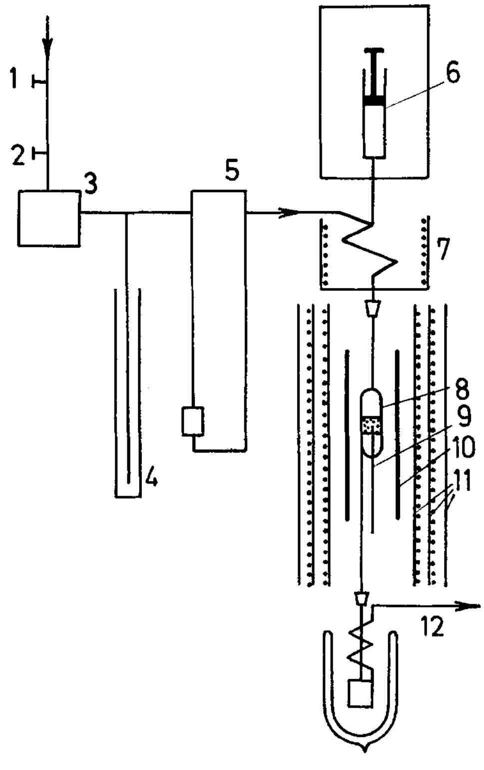

FIG. 1. Catalytic flow reactor. For an explanation of the numbers see the text.

dioxide. A constant flow rate of nitrogen was assured by means of a system of two needle valves, 1, 2, a mechanical manostat, 3, and a liquid manostat of the blowoff type, 4. The flow rate was measured by a differential pressure capillary flowmeter, 5, filled with oil. The reactor was inserted into an electrical oven with glass walls, 11, and two independent heating coils, the inner one giving approximately 90% of the necessary heat imput and adjusted to this level at the beginning of all experiments by adjusting the supply voltage. The outer heating coil was automatically switched on or off by a compensation regulator (ZPA, Prague) according to the temperature read by a platinum resistance thermometer. In order to minimize axial temperature gradients and to level out temperature fluctuations inside the oven, an iron tube, 10, was placed between the inner tube of the oven and the reactor. The temperature inside the catalyst bed was measured by an iron-constantan thermocouple.

Procedure. The catalyst sample was weighed, placed in the reactor and heated to 200°C in a stream of nitrogen. When the temperature inside the catalyst bed was constant, the cyclohexanol feed was started and the flow rate of nitrogen was adjusted. The first portion of the product (about 1g) was discarded and then two product samples amounting to 1–2 g were collected. Each product sample was analysed in duplicate.

Analysis. The composition of the liquid product was determined by gas chromatography using a thermal conductivity detector, and a column packed with polyethyleneglycol on celite (15%), operating at 170°C. The flow rate of the carrier gas (hydrogen) was 60 ml/min. The analysis of reaction products was performed by ensuring that the microsyringe always delivered the same quantity of sample into the chromatograph and then evaluating the amounts of the various fractions from the ratio of the peak heights. Based on calibration with synthetic mixtures corresponding to various degrees of completion of the reaction, the peak height ratio was directly transformed to the conversion value by means of a nomogram (*15*).

Statistical procedures. Standard methods described in texts (*16–19*) were used. All testing was conducted at 95% significance level.

RESULTS

The catalytic isothermal flow reactor yields kinetic data in the form of values of conversion at different ratios of W/F_A, partial pressures of the reactants p_i and temperatures T. If the reactor is operated at a low conversion level, the conservation equation for the reactor may be written as a differential equation and reaction rates r may be calculated thus:

$$r = \Delta x/\Delta(W/F)|_{T=\text{const},p_i=\text{const}}. \qquad (1)$$

Usually the r values are considered as belonging to the concentration of reactants entering the reactor (p_i^0) and are, therefore, denoted as initial rates, r^0 (*4*). The next step in the treatment of data is to find a suitable rate equation as a function of the partial pressures of reacting components and subsequently to evaluate the constants in such an equation.

$$r^0 = f(p_i^0)|_{T=\text{const}}. \qquad (2)$$

In order to evaluate the reliability of kinetic analysis conducted in this way, it is necessary to know the precision with which the quantities x, W, F_A, p_i^0, and r^0 were determined. Some of the sources of random variation in measured parameters may be estimated independently, e.g., the analytical error, but most of them are inherent in the experimental technique used and must be found from repeated, suitably arranged experiments by means of statistical procedures. Rarely is it possible to compare the precision of a quantity evaluated by both methods.

Errors in Independent Variables

According to Eqs. (1) and (2) the independent variables are W, F, p_i^0 (and T). Accuracy of adjustment and stability of their values can be ascertained independently of the experimental technique applied.

For the work described in this paper, catalyst samples were weighed with a maximum error of $\pm 5 \times 10^{-4}$ g. Assuming a normal distribution function and a maximum error corresponding to three times the standard deviation, the variance $V(W)$ was estimated as 2.77×10^{-14} kg². Similarly, the variance $V(T)$ in temperature was estimated as 1.3×10^{-2} deg² from an error of ±0.35°C. The value ±0.35°C represents the sum of actual fluctuations of the temperature inside the oven measured by a mercury thermometer (±0.15°C) and the uncertainty in reading the voltage of the thermocouple (±0.2°C).

However, in the catalyst bed small temperature gradients may be present which may cause additional error. These gradients and the corresponding error depend on the flow velocity of the gases and on the geometry of the bed and its position in the temperature field created by the oven. The gradients as well as the temperature fluctuations influence the measured conversions, so their random effect is included in the value of $V_2(x)$ (see below).

The variance $V(F_A)$ was obtained from ten measurements of the feed rate by weighing the amount of cyclohexanol expelled from the syringe during one time unit. It was estimated to be 5.7×10^{-7} kg², and does not depend on the feed rate. Since the actual independent variable is W/F_A, its variance $V(W/F_A)$ was calculated from the expression

$$V(W/F_A) = \frac{1}{F_A^2} V(W) + \frac{W^2}{F_A^4} V(F_A), \quad (3)$$

derived from the general equation for the sum of random errors. For typical values of W and F the calculated $V(W/F)$ values were of the order of 10^{-7}–10^{-9} and for further use the value 1×10^{-8} (kg hr/mole)² was selected.

The initial partial pressure of the reactant $p_A{}^0$ was calculated from the flow velocities of the alcohol F_A and of the inert gas F_I using the relation

$$p_A{}^0 = PF_A/(F_A + F_I), \quad (4)$$

where P represents the total pressure, in this case atmospheric.

The corresponding equation for the calculation of variance has the form

$$V(p_A{}^0) = \left[\frac{PF_I}{(F_A + F_I)^2}\right]^2 V(F_A) + \left[\frac{PF_I}{(F_A + F_I)^2}\right]^2 V(F_I) + \left[\frac{F_A}{F_A + F_I}\right]^2 V(P). \quad (5)$$

Since atmospheric pressure was measured with high precision by means of a mercury manometer, the last term may be omitted. In order to obtain low values for $V(F_I)$ it was necessary to correct the readings of the capillary differential flowmeter to standard temperature and pressure. Thus, the parallactic error in reading the pressure difference, which was estimated to be at most ±1 mm of oil, remains the main source of fluctuations. From this a mean value of $V(F_I)$ was calculated as 1.70×10^{-6} (mole/hr)². Hence the value of $V(p_A{}^0)$ could be calculated using equation (5); $V(p_A{}^0)$ depended to some extent on the experimental conditions (i.e., on $p_I{}^0$ and W/F_A values). However, 6.2×10^{-6} atm² was accepted as the mean value for further considerations.

Errors in Dependent Variables

For estimation of various error sources in the dependent variable x the analysis of variance technique (*15–18*) was employed and this is based on the hierarchic scheme presented in Fig. 2. The numerical values deduced for $V_1(x)$–$V_3(x)$ are summarized in Table 1.

The variance of the analytical procedure, $V_1(x)$, is caused by fluctuations in the functioning of the gas chromatograph and by irregularities in the size of the injected sample. Its value was estimated in two ways. First, the results of repeated analyses of synthetic mixtures (used for the construction of calibration graphs) were employed. Each mixture was analysed five–ten times. The variances of these sets were subjected to a χ^2 test and extremely large values were excluded. No dependence of variance on mixture composition was observed. Therefore, all remaining sets were

TABLE 1
ESTIMATED VARIANCES OF VARIOUS PARAMETERS FOR DEHYDRATION OF CYCLOHEXANOL

Variance	Level of the parameter or conditions	Value	Units	Degree of freedom
$V(T)$	473°K	1.3×10^{-2}	deg^2	—
$V(W)$	0.5–1.5×10^{-3} kg	2.8×10^{-14}	kg^2	—
$V(F_A)$	0.034–0.068 mole/hr	5.7×10^{-7}	(mole/hr)^2	9
$V(W/F_A)$	0.010–0.035 kg hr/mole	1×10^{-8}	(kg hr/mole)^2	—
$V(F_I)$	0.10–0.60 mole/hr	1.7×10^{-6}	(mole/hr)^2	—
$V(p_A{}^0)$	0.1–0.3 atm	6.2×10^{-6}	atm^2	—
$V'_1(x)$	0.03–0.10	1.1×10^{-6}	—	157
$V''_1(x)$		1.5×10^{-6}	—	16
$V_1(x)$		1.3×10^{-6}	—	173
$V'_2(x)$		2.1×10^{-5}	—	7
$V''_2(x)$		1.9×10^{-5}	—	18
$V_2(x)$		2.0×10^{-5}	—	25
$V_3(x)$		Not significant	—	12
$V_{res}(x)$		1.7×10^{-5}	—	94
$V_3(r^0)$	0.1 atm	1.4×10^{-2}	(mole/hr kg)^2	8
	0.2 atm	2.0×10^{-2}		8
	0.3 atm	2.1×10^{-2}		8
$V'_3(r^0)$	0.1 atm	1.0×10^{-2}		32
	0.2 atm	1.9×10^{-2}		32
	0.3 atm	2.8×10^{-2}		32
$V_4(r^0)$	0.1 atm	6.5×10^{-1}		8
	0.2 atm	1.2		8
	0.3 atm	1.7		8

considered to belong to the same population and a mean variance $V'_1(x)$ was calculated. The second estimate, $V''_1(x)$, was obtained from determinations in triplicate of eight product samples from a kinetic run at $W/F_A = 0.0116$ kg hr/mole and $p_A{}^0 = 0.2$ atm. The set of 24 values of x was subjected to a variance analysis and $V''_1(x)$ and $V'_2(x)$ thus estimated. An F test showed no difference between $V'_1(x)$ and

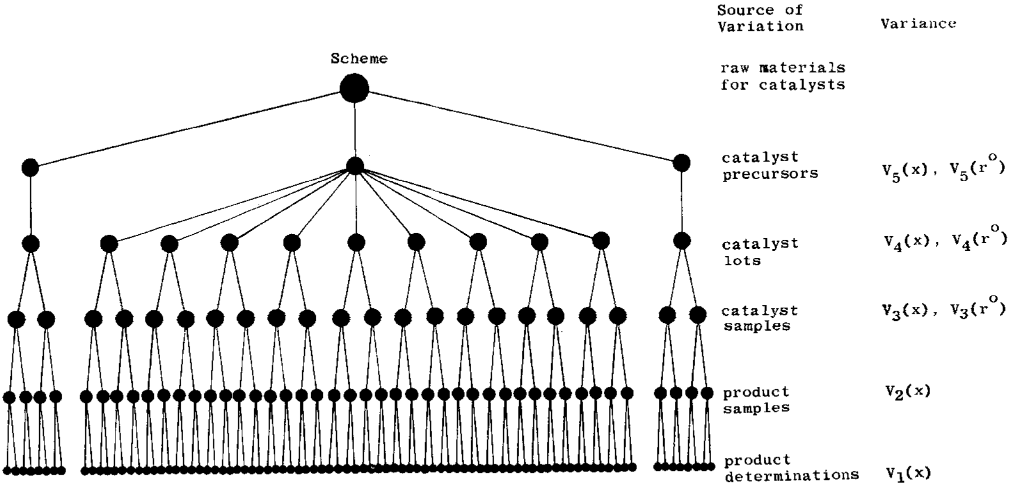

FIG. 2. Hierarchic scheme for cyclohexanol dehydration.

$V''_1(x)$ values. Subsequently a mean value, denoted $V_1(x)$, was employed.

Two independent values of variance $V_2(x)$ were also available. One was mentioned in the preceding paragraph; the second value, $V''_2(x)$, was obtained together with $V_3(x)$ from six sets of product samples consisting of three members, each set being prepared under the same conditions with different catalyst samples. A variance analysis yielded the required values and an F test again showed no difference between $V'_2(x)$ and $V''_2(x)$. For further work a combination of these two values, denotes as $V_2(x)$, was used (Table 1).

$V_3(x)$ does not contribute significantly to the total sum of squares. In our case, the use of different catalyst samples for individual kinetic runs does not increase the overall error. This is not surprising, since alumina, once it has been activated above 650°C, catalyses the dehydration of alcohols in a reproducible manner for quite long periods.

An attempt to estimate the variance $V_4(x)$ between catalyst lots prepared by separate heating of a single preparation of the catalyst precursor (aluminium hydroxide) to 800°C was unsuccessful because each lot exhibited a different catalytic activity. Hence it was not possible to obtain kinetic measurements at the same range of space velocities and partial pressures at low conversions. For this reason, the experimental x values were transformed into reaction rates r^0 by means of Eq. (1) and the comparison between lots was based on corresponding $V_3(r^0)$ and $V_4(r^0)$ values. The $V_j(r^0)$ values were determined for nine catalyst lots at three initial partial pressures (Fig. 2). Application of the F test revealed no significant difference between $V_3(r^0)$ or $V_4(r^0)$ determined at different partial pressures even though an increase of values with increasing pressure was observed (Table 1). Measurement over a broader pressure range would probably confirm the reality of this trend. Nevertheless, the $V_4(r^0)$ values are significantly higher than the $V_3(r^0)$ values at all pressure levels; a plausible interpretation is that the formation of active catalyst lots from catalyst precursors (activation step) is a source of major variation in kinetic measurements.

The last variance in the hierarchic scheme in Fig. 2, namely $V_5(x)$ (or the corresponding $V_5(r^0)$) could not be estimated because the mean activities of the catalysts prepared from the three catalyst precursors differed so much that kinetic measurements at the same temperature were not possible. This finding can be interpreted qualitatively as evidence of very large variance in different catalyst precursors. In fact, the preparations contained various amounts of silica (*14*).

The change from variance based on conversion $V_j(x)$ to that based on reaction rate $V_j(r^0)$ may be accomplished in the following way: The variance $V_3(r^0)$ of reaction rates found on the same catalyst sample is also the variance of the straight line described by Eq. (1) whose value can be calculated by the expression

$$V_3'(r^0) = V_{\mathrm{res}}(x)/\sum_i (W/F_{\mathrm{A}})^2, \qquad (6)$$

where the subscript res denotes residual variance around the line $\Delta x = r^0\Delta\ (W/F_{\mathrm{A}})$. For the arrangement of experiments according to the hierarchic scheme in Fig. 2, the value of $V_{\mathrm{res}}(x)$ is given by

$$V_{\mathrm{res}}(x) = \frac{V_2(x)}{m} + \frac{V_1(x)}{mn}. \qquad (7)$$

The residual variances, around 51 lines, were investigated and extremely large variances were excluded from this set using a χ^2 test. The mean residual variance had a value 1.69×10^{-5} (94° of freedom). The corresponding value calculated by means of Eq. (7) from $V_2(x)$ and $V_1(x)$ was found to be 1.03×10^{-5} (25° of freedom). By subjecting these to an F test it was found that both values are coincident. The next step was to calculate $V'_3(r^0)$ by means of Eq. (6) for all x-(W/F_{A}) dependences, combine them for each pressure and compare with $V_3(r^0)$ values obtained previously (Table 1). An F test revealed no significant difference between $V_3(r^0)$ and $V'_3(r^0)$ values and this confirms the correctness of the trans-

TABLE 2
Estimated Variances for Dehydration of 1-Phenylethanol

Variance	Level of the parameter	Value	Units	Degrees of freedom
$V(W)$	0.3–0.6 × 10^{-3} kg	1.1×10^{-13}	kg²	—
$V(F_A)$	0.004–0.050 mole/hr	1.8×10^{-7}	mole/hr²	—
$V(W/F_A)$		4.5×10^{-7} [a]	kg hr/mole²	—
		5.6×10^{-9} [b]	kg hr/mole²	—
$V(F_I)$	0.004–0.60 mole/hr	4.0×10^{-7}	mole/hr²	—
$V(p_A{}^0)$	0.08–0.85 atm	1.8×10^{-5}	atm²	—
$V_1(x)$	0.03–0.20	3.4×10^{-4}	—	26
$V_{res}(x)$	0.03–0.20	2.1×10^{-4}	—	32
$V_3(r^0)$		0.4	mole/hr kg²	30

[a] At 0.082 atm.
[b] At 0.825 atm.

formation from $V_j(x)$ to $V_j(r^0)$ in the upper part of the hierarchic scheme in Fig. 2.

Treatment of Other Data

The estimates, obtained from various sources of error, enabled us to conduct similar analyses with sets of data available in this Laboratory concerning actual kinetic measurements. These results have already been published (*20–22*). The experimental procedure employed during these investigations differed only in detail from that used in the present work. However, these differences provided an opportunity to estimate the influence of minor changes in technique on the precision of results. In some instances, lack of data did not permit estimation of a particular variance; in such cases the value based on our own experiments was accepted.

The first set of data refers to the dehydration of 1-phenylethanol on alumina (*20*). Instead of nitrogen, toluene was used as diluent for lowering the partial pressure of the reactant which was fed into the apparatus as a solution in hydrocarbon. The second difference was in the determination of product composition; a titration method based on acetylation of the unreacted alcohol was applied. Table 2 summarizes the estimated variances of independent and dependent variables. As the difference between the analytical variance $V_1(x)$ and $V_{res}(x)$ is insignificant, the contributions of $V_2(x)$ and $V_3(x)$ must be negligible. So, the most important source of error remaining is the determination of the unreacted alcohol. Because of the relatively simpler procedure used in this work (hierarchic scheme A on Fig. 3), it was not possible to estimate

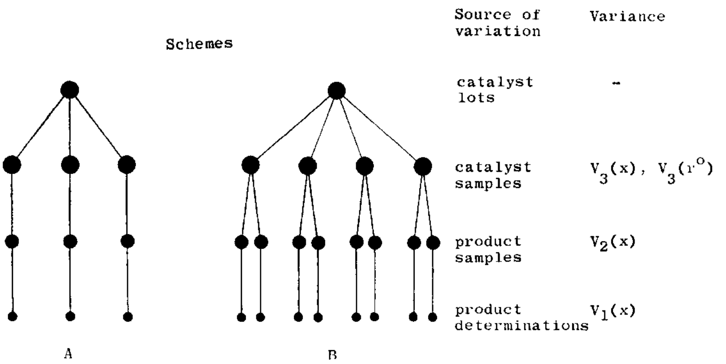

Fig. 3. Hierarchic scheme for 1-phenylethanol dehydration (A) and 2-propanol dehydrogenation (B).

$V_2(x)$ and $V_3(x)$ independently. Nevertheless, some conclusions may be drawn from a comparison of the values in Tables 1 and 2. The variance in feed rate of the inert $V(F_I)$ is one order of magnitude lower if a liquid is used instead of gas because the mechanical feeding device is more reliable than the measurement with a gas flowmeter. However, the low-precision analytical determination (see $V_1(x)$ values) is the weak point of the whole procedure.

In the second case, two procedures used by Kochloefl and co-workers (*21, 22*) in studying the dehydrogenation of 2-propanol on copper and platinum catalysts were compared. In general, their technique was very similar to ours and the procedure is described by the hierarchic scheme B and in Fig. 3. Their catalysts, however, were activated by reduction of each sample with hydrogen in situ. The reproducibility of this step of active catalyst preparation was low, as with the formation of alumina from aluminium hydroxide. With copper (*21*) as catalyst, the authors considered the experimental error tolerable and tabulated the measured conversions without any correction. With platinum (*22*), the reproducibility was lower and therefore they started each kinetic run with a measurement at standard conditions. The observed conversion was divided by the conversion obtained on the catalyst sample chosen as standard, and the conversions measured at other conditions were corrected by application of this simple factor. Hence the large error introduced through catalyst sample preparation was substituted by the smaller sum of errors in conversion determinations. The estimated values of variances are summarized in Table 3. An F test confirmed the significance of the difference between $V_3(r^0)$ values for the copper and platinum catalysts.

TABLE 3

ESTIMATED VARIANCES FOR DEHYDROGENATION OF 2-PROPANOL OVER COPPER AND PLATINUM CATALYSTS

Variance	Level of the parameter	Value	Units	Degrees of freedom
$V(W)$	0.07×10^{-3}–$0.15\ 10^{-3}$ kg	2.8×10^{-14}	kg^2	—
$V(F_A)$	0.05–0.30 mol/hr	1.6×10^{-6}	(mole/hr)^2	9
$V(W/F_A)$	1.5–18.0 10^{-4} kg mole/hr	1×10^{-11}	(kg hr mole)^2	—
$V(p_A{}^0)$	0.1–1.0 atm	1.1×10^{-6}	atm^2	—
$V_1(x) + V_2(x)$	0.02–0.11	5.0×10^{-6}	—	—
$V_{res}(x)$ Cu		9.8×10^{-5}	—	24
$V_{res}(x)$ Pt		1.6×10^{-5}	—	26
$V_3(r^0)$ Cu		47	(mole/hr kg)^2	24
$V_3(r^0)$ Pt		3.3	(mole/hr kg)^2	28

DISCUSSION

The more comprehensive relative errors in variables which appear in Eqs. (1) and (2) were calculated to provide a basis for comparison. Mean values of these variables and standard deviations based on variances from Tables 1–3 were applied; the results are given in Table 4. The error in reciprocal space velocity is, in all four cases, approximately one order of magnitude lower than the error in conversion. Therefore a simple least-squares procedures for calculation of r^0 values by means of Eq. (1) may be used, considering only the independent variable to be in error. However, with a small number of experimental points relating to the dependent variable x-(W/F), the least-squares method is hardly justified. We have checked, it does not give results differing from simpler procedures such as plotting a graph and reading the slope or calculating a mean r^0 value from r^0 found for each x-(W/F) pair by means of Eq. (1).

There is a less favourable situation with the variables of Eq. (2), the errors of which

TABLE 4
ERRORS OF SOME VARIABLES

Variable	Mean value	Standard deviation	Relative error (%)
Dehydration of cyclohexanol on Al_2O_3			
W/F_A	0.020	1.0×10^{-4}	0.5
x	0.055	4.1×10^{-3}	7.4
p_A^0	0.20	6.5×10^{-3}	3.2
r^0	3.0	1.3×10^{-1}	4.3
Dehydration of 1-Phenylethanol on Al_2O_3			
W/F_A	0.021	3.2×10^{-4}	1.5
x	0.117	1.4×10^{-1}	12.2
p_A^0	0.44	4.3×10^{-3}	1.0
r^0	7.4	6.3×10^{-1}	8.6
Dehydrogenation of 2-Propanol on Cu			
W/F_A	0.0036	3.2×10^{-6}	0.9
x	0.056	9.8×10^{-3}	17.4
p_A^0	—	—	2
r^0	154	6.8	4.4
Dehydrogenation of 2-Propanol on Pt			
W/F_A	0.00098	3.2×10^{-6}	0.9
x	0.053	4.0×10^{-3}	7.4
p_A^0	—	—	2
r^0	55	1.8	3.2

are of the same order of magnitude. However, published linear and nonlinear methods for estimation of the form of the functional dependence in Eq. (2) and its constants (*7–11*) are based on the assumption that only r^0 is subject to error. It is rather difficult to judge the correctness of this assumption in any particular case since the authors usually do not give enough details about precision of their experimental procedure. We suspect that in most cases the situation has not been better than in the present work. It might even be worse when the experiments have been conducted at superatmospheric pressure where the precision and accuracy of pressure measurement, especially with Bourdon-type gauges, are lower. Therefore, it seems reasonable to appeal for a further refinement of nonlinear estimation methods applicable to rate equations that would take into account the errors involved in the independent variables.

An alternative approach would be to reduce the experimental error of all variables. One obvious way of achieving this goal is to improve the measuring devices. However, in this paper, we only investigated the effect of the arrangement of experiments.

The variance $V_3(r^0)$ is actually a measure of the precision of our reaction-rate determinations. According to Eqs. (6) and (7), its value depends on the space velocity, the precision of analysis, the reproducibility of kinetic runs and the number of runs, product samples and product determinations, respectively. The first three factors are determined and fixed by the catalyst activity and the available apparatus. Thus, we can seek ways for lowering $V_3(r^0)$ by repeating some of the experimental operations. However, the effectiveness of doubling or trebling the number of experiments depends on the contribution which each operation makes to the overall error. In our case (see Fig. 2 and Table 1), $m = 2$, $n = 2$ and the contribution of the analytical error to $V_{\text{res}}(x)$ is only 2.5%, the balance (97.5%) being the contribution of the variation in product samples (i.e., of the error originating in kinetic runs). Therefore, it would be more effective to increase the number of product samples in one run than to repeat the determinations.

As the value of $V_3(r^0)$ depends inversely on the sum of space velocities, Eq. (6), we can improve the precision by experimenting at the highest possible level of this factor. [Note that a restriction is imposed by the necessity of keeping the conversion low (*4*, *5*)] and by increasing the number l of measured conversions. The effect of repeating the operation is thus straightforward.

In cases where the catalyst cannot be activated in sufficient lots in advance of experiments and kept in an activated state for the necessary time, the correction of conversions to values corresponding to standard activity, as used by Kochloefl and co-workers (*21*, *22*), is strongly recommended.

However, it should be pointed out that the optimum experimental design for the lowest overall error depends, in a particular case, on the relative contributions of individual sources of error. It is necessary to estimate these at typical conditions before systematic rate measurements are commenced.

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