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Studies in Catalytic Reactions

I. Theory

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The theoretical implications behind the derivation and application of Hougen-Watson rate equations to catalytic reactions are discussed. For reactions which possess an order higher than one, there may be numerous complex Hougen-Watson rate equations and the task of selecting the particular one which fits the data most satisfactorily becomes exceedingly difficult. It is shown that in the examination of such complex equations the choice of the data to which they are applied is of paramount importance, while the sophistication of the method of fitting an equation to a set of data is of secondary importance. Thus it is found that integral reactor data are preferable to differential data, and that in certain situations the analysis of differential data is intractable. The use of a complex and statistically sophisticated nonlinear least-squares technique is found to be no more successful than a simple linear least-squares curve-fitting procedure.

SYMBOLS

A	Initial oxygen concentration (mole fraction), this symbol is also used to refer generally to oxygen
a	Stoichiometric coefficient
B	Initial fuel concentration (mole fraction), this symbol is also used to refer generally to fuel
b_1 to b_p	Regression coefficients
D	Dissociated fuel
F	Total volume flow rate to reactor (ml/min)
K	Adsorption equilibrium constant (atm^{-1})
k	Rate constant
k_1,k_2	Constants in rate conversion equation
M	Initial product concentration (mole fraction), this symbol is also used to refer generally to a product
m	Stoichiometric coefficient
p	Partial pressure, with subscript
p	Number of terms in polynomial regression equation
r	Reaction rate (moles fuel/min)
V_m	Molar volume at entry conditions to reactor (ml/mole)
x	Fractional conversion
θ	Fractional surface coverage, with subscript
ϕ	Variable to allow integration of rate conversion equation, defined by $\sin^2\phi = (A - aB)/(A - aBx)$
π	Total pressure (atm)

Subscripts

A	Oxygen
B	Fuel
D	Dissociated fuel
i	Interface
g	Gas phase
M	Product

HOUGEN-WATSON RATE EQUATIONS—THEIR DERIVATION AND MEANING

Gas reactions which are catalyzed by solids actually occur on the surface of the solids between atoms or molecules of reactants which are chemically adsorbed at points of high chemical activity. These points are termed "active centers." The catalyst increases the rate of reaction through its ability to adsorb the reactants in such a form that the activation energy for reaction is reduced below its value for the uncatalyzed reaction. Thus the rate of the surface reaction will be proportional to the surface concentration of the adsorbed species on active centers.

The Langmuir adsorption theory enables these surface concentrations to be determined, and from them equations connecting the rate of reaction with the gas-phase partial pressure of the reactants can be devised. These equations are known as Hougen-Watson rate equations.

The derivation of these equations is best illustrated by a simple example. Consider the irreversible decomposition

$$\mathrm{A} \rightarrow \mathrm{B}$$

taking place on a nonporous catalyst where the "slowest" or rate-controlling step is the surface reaction of A.

The rates of the various steps in this reaction are

(1) Diffusion of A to the catalyst surface:

$$r_1 = k_1(P_{\mathrm{A_g}} - P_{\mathrm{A_i}})$$

(2) Activated adsorption of A:

$$r_2 = k_2[p_{\mathrm{A_i}}\theta_{\mathrm{v}} - (\theta_{\mathrm{A}}/K_{\mathrm{A}})]$$

(3) The surface reaction (this is the rate-controlling step in the example being considered):

$$r_3 = k_3\theta_{\mathrm{A}}$$

(4) Activated desorption of B:

$$r_4 = k_4[(\theta_{\mathrm{B}}/K_{\mathrm{B}}) - p_{\mathrm{B_i}}\theta_{\mathrm{v}}]$$

(5) Diffusion of B from the catalyst surface:

$$r_5 = k_5(p_{\mathrm{B_i}} - p_{\mathrm{B_g}})$$

Under steady state conditions the rates of all these steps must be equal, i.e.,

$$r_1 = r_2 = r_3 = r_4 = r_5 = r$$

Hougen-Watson rate equations are obtained by assuming that one of these steps is rate-controlling. The other four steps are all intrinsically capable of going much faster than this rate-controlling step, but their rates and the rate of the overall reaction are governed by that of the slowest. The inherent speed of these four steps will be reflected in the high values of their rate constants (k_1, k_2, k_4, k_5) when compared with the rate of the overall reaction. It is thus permissible to consider that

$$\frac{r}{k_1} \sim \frac{r}{k_2} \sim \frac{r}{k_4} \sim \frac{r}{k_5} \sim 0$$

Thus step (1) gives

$$P_{\mathrm{A_i}} = P_{\mathrm{A_g}} \tag{1}$$

(i.e., the partial pressure of A in the gas phase is the same as its partial pressure at the interface).

Step (2) gives

$$P_{\mathrm{A_i}}\theta_{\mathrm{v}} = \theta_{\mathrm{A}}/K_{\mathrm{A}} \tag{2}$$

Step (4) gives

$$\theta_{\mathrm{B}}/K_{\mathrm{B}} = p_{\mathrm{B_i}}\theta_{\mathrm{v}} \tag{3}$$

Step (5) gives

$$p_{\mathrm{B_i}} = p_{\mathrm{B_g}} \tag{4}$$

Substituting $\theta_{\mathrm{v}} = 1 - \theta_{\mathrm{A}} - \theta_{\mathrm{B}}$, solving Eqs. (2) and (3) first for θ_{A} and then for θ_{B}, and putting $p_{\mathrm{A_i}} = p_{\mathrm{A_g}}$ and $p_{\mathrm{B_i}} = p_{\mathrm{B_g}}$ produces the familiar equations:

$$\theta_{\mathrm{A}} = \frac{K_{\mathrm{A}}p_{\mathrm{A_g}}}{1 + K_{\mathrm{A}}p_{\mathrm{A_g}} + K_{\mathrm{B}}p_{\mathrm{B_g}}}$$

$$\theta_{\mathrm{B}} = \frac{K_{\mathrm{B}}p_{\mathrm{B_g}}}{1 + K_{\mathrm{A}}p_{\mathrm{A_g}} + K_{\mathrm{B}}p_{\mathrm{B_g}}}$$

which are the Langmuir isotherms when two adsorbents are present on the surface.*

Substituting the Langmuir isotherm for θ_{A} into the equation for the rate of step (3) (the rate-controlling step) then produces a typical Hougen-Watson rate equation:

$$r = \frac{k_3K_{\mathrm{A}}p_{\mathrm{A_g}}}{1 + K_{\mathrm{A}}p_{\mathrm{A_g}} + K_{\mathrm{B}}p_{\mathrm{B_g}}}$$

In a similar way it is possible to construct Hougen-Watson rate equations for every conceivable situation. This is fairly easy to do for the simple example quoted above where the total number of possible rate equations is small. However, in the case of a reaction such as

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{M}$$

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* The adsorption constants K_{A} and K_{B} may be functions of surface coverage, and it is a limitation of this approach that they are assumed independent of coverage.

there is a very large number of possible rate equations and a logical and systematic method of generating them must be adopted.

It has been found that the most suitable way of doing this is to construct a table comprising all possible adsorbed species and rate-controlling steps. This has been carried out for a hydrocarbon oxidation reaction

$$\underset{\text{Hydrocarbon}}{B} + \underset{\text{Oxygen}}{O_2} \rightarrow \underset{\text{Product}}{M}$$

Generally in hydrocarbon oxidation, desorption is not rate-controlling and so in this particular case the number of possible mechanisms is reduced. The reason for this is that the adsorption of products such as water, carbon dioxide, or carbon monoxide on noble metal catalysts is either nonexistent or weak in comparison the adsorption of oxygen or hydrocarbons (*1*, *2*). Desorption will certainly be unimportant in this study since the hydrocarbon concentration was deliberately kept low (< 1%), the conversions were usually less than 0.5, and thus the product concentrations were always much less than 1%.

Furthermore, the Hougen-Watson rate equations are simplified somewhat since the reaction is irreversible.

When oxidation is occurring over a noble metal catalyst the possible adsorbed species include

(i) B, the hydrocarbon
(ii) D, the dissociated hydrocarbon
(i.e., B = D + H)
(iii) O_2, molecular oxygen
(iv) O, atomic oxygen

The need for a systematic method of developing Hougen-Watson rate equations becomes apparent when it is realized that any combination of these adsorbed species may exist on the surface and for each of these combinations several controlling mechanisms may be possible. The possible rate-controlling steps and their rates are listed in Table 1. Table 2 shows the matrix of adsorbed reactant species and rate-controlling steps. The adsorption system number in this table is indicative of the adsorbed species present on the surface.

TABLE 1

POSSIBLE RATE-CONTROLLING STEPS AND THEIR RATES

Rate-controlling step	Rate of rate-controlling steps
Adsorption controlling	
1. Adsorption O_2	$r = k\theta_v p_{O_2}$
2. Adsorption O	$r = k\theta_v^2 p_{O_2}$
3. Dissociation $\underset{*}{O_2} \rightarrow \underset{*}{O}$	$r = k\theta_v \theta_{O_2}$
4. Adsorption of fuel (B)	$r = k\theta_v p_B$
5. Adsorption of D	$r = k\theta_v^2 p_B$
6. Dissociation $\underset{*}{B} \rightarrow \underset{*}{D} + \underset{*}{H}$	$r = k\theta_v \theta_B$
Surface reaction controlling	
7. Reaction $B + \underset{*}{O_2}$	$r = k\theta_{O_2} p_B$
8. Reaction $B + \underset{*}{O}$	$r = k\theta_O p_B$
9. Reaction $B + \underset{*}{2O}$	$r = k\theta_O^2 p_B$
10. Reaction $\underset{*}{B} + O_2$	$r = k\theta_B p_{O_2}$
11. Reaction $\underset{*}{B} + \underset{*}{O_2}$	$r = k\theta_B \theta_{O_2}$
12. Reaction $\underset{*}{B} + \underset{*}{O}$	$r = k\theta_B \theta_O$
13. Reaction $\underset{*}{B} + \underset{*}{2O}$	$r = k\theta_B \theta_O^2$
14. Reaction $\underset{*}{D} + \underset{*}{O_2}$	$r = k\theta_D \theta_{O_2}$
15. Reaction $\underset{*}{D} + \underset{*}{O}$	$r = k\theta_D \theta_O$
16. Reaction $\underset{*}{D} + \underset{*}{2O}$	$r = k\theta_D \theta_O^2$
17. Reaction $\underset{*}{D} + O_2$	$r = k\theta_D p_{O_2}$

Adsorbed species

Molecular oxygen	$\underset{*}{O_2}$	Fuel	$\underset{*}{B}$
Atomic oxygen	$\underset{*}{O}$	Dissociated fuel	$\underset{*}{D}$

Coverages

θ_v	Fraction of surface vacant	θ_B	Fraction of surface covered by fuel
θ_{O_2}	Fraction of surface covered by molecular oxygen	θ_D	Fraction of surface covered by dissociated fuel
θ	Fraction of surface covered by atomic oxygen		

A combination of an adsorption system

TABLE 2

Adsorbed Species and Controlling Mechanisms

Adsorption system number	Adsorbed species[a]				Possible rate-controlling steps
	D	B	O_2	O	
0	—	—	—	—	
i	—	*	—	—	4, 10
ii	—	—	*	—	1, 7
iii	—	—	*	*	1, 2, 3, 7, 8, 9
iv	—	*	*	—	1, 4, 7, 10, 11
v	—	*	—	*	2, 4, 8, 9, 10, 12, 13
vi	—	*	*	*	1, 2, 3, 4, 7, 8, 9, 10, 11, 12, 13
vii	—	—	—	*	2, 8, 9
viii	*	—	—	—	5, 17
ix	*	*	—	—	4, 5, 6, 10, 17
x	*	—	*	—	1, 5, 7, 14, 17
xi	*	—	*	*	1, 2, 3, 5, 7, 8, 9, 14, 15, 16, 17
xii	*	*	*	—	1, 4, 5, 6, 7, 10, 11, 14, 17
xiii	*	*	—	*	2, 4, 5, 6, 8, 9, 10, 12, 13, 15, 16, 17
xiv	*	*	*	*	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17
xv	*	—	—	*	2, 5, 8, 9, 15, 16, 17

[a] *, Adsorbed; —, not adsorbed.

number and a rate-controlling step leads to a Hougen-Watson rate equation and, in the present case there are 104 possible rate equations. Each rate-controlling step can give rise to several Hougen-Watson rate equations because the form of the Langmuir isotherm for the coverage by a particular reactant depends on the other adsorbed species present. Thus step 1, the adsorption of oxygen, may be rate-controlling in several situations; for example, when molecular oxygen alone is chemisorbed (adsorption system ii) the Hougen-Watson rate equation is

$$r = kp_{O_2}/(1 + K_M p_M) \tag{5}$$

yet if the fuel (B) is also adsorbed [adsorption system (iv)], the Hougen-Watson rate equation becomes

$$r = \frac{kp_{O_2}}{1 + K_{O_2}p_{O_2} + K_M p_M} \tag{6}$$

(the term $K_M p_M$ in the denominator arises because these equations allow for the possible adsorption of a product M).

Analysis of Data from Catalytic Reactors Using Hougen-Watson Rate Equations

In the analysis of catalytic data the object is to decide which Hougen-Watson equation best describes the data and thereby decide on the reaction mechanism. There are two criteria on which to base this decision:

(i) The rate and adsorption constants (k, K_{O_2}, K_B) must be positive.

(ii) The statistical fit of the equations to the data should be good.

In order to make a satisfactory choice, it is necessary to obtain an accurate estimate of the rate and adsorption constants, but the complexity of the Hougen-Watson rate equations makes this very difficult.

Before discussing the application of these rate equations to experimental measurements, it is first necessary to describe briefly the types of reactor and data that may be used.

Both static and flow reactors may be used in the study of catalytic reactors. Most work has, however, been performed using flow reactors; one of the reasons for this is that it is easier to eliminate diffusion effects in a reactor of this type.

In a flow reactor, the relationship between flow rate and conversion is given by (*3*)

$$\left(\frac{V_m}{B}\right)\left(\frac{1}{F}\right) = \int_0^x \frac{dx}{r} \tag{7}$$

and the reaction rate is then given by differentiating Eq. (7)

$$r = \left(\frac{B}{V_m}\right)\frac{dx}{d(1/F)} \tag{8}$$

Thus in order to measure the reaction rate a series of runs is required measuring conversion as a function of flow rate. The reaction rate is then given by the gradient of the graph of conversion (x) vs. reciprocal flow-rate ($1/F$).

Alternatively, the rate may be measured in a differential reactor. Here, the reactor bed is small and the conversion very low, so that the rate may be assumed to be constant

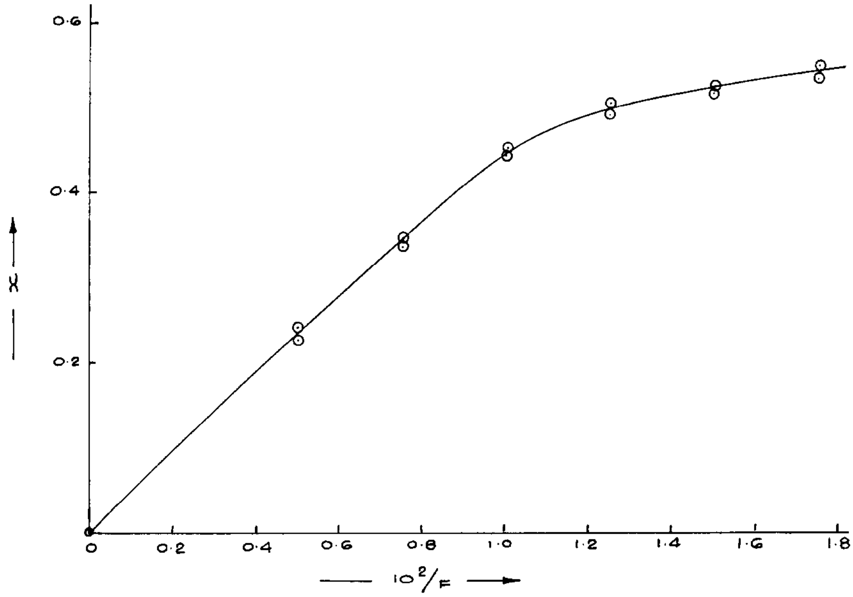

FIG. 1. Integral data: conversion as a function of reciprocal flow rate for combustion of benzene over a silica-supported platinum catalyst. $A = 0.2$; $B = 6.74 \times 10^{-3}$; $\pi = 1$ atm; temperature 313°C.

Through the bed. The rate is then given by

$$r = \frac{BF}{V_m} \Delta x \tag{9}$$

Two kinds of data are thus available for analysis. The first type, integral data, is illustrated in Fig. 1 for the oxidation of benzene over a platinum on silica gel catalyst. A complete set of integral data consists of several such plots at varying initial reactant conditions. The second type of data, differential data, comprises a set of measurements of reaction rate at various partial pressures of the reactants. A typical set of differential data for the same reaction is shown on Fig. 2.

To date, most catalytic work involving Hougen-Watson rate equations has been concerned with the analysis of differential data, since these may be obtained more easily and quickly than integral data. However, this economy proves to be false when an attempt is made to analyze differential data using complex rate equations.

This has commonly involved the rearrangement or "linearization" of equations such as (10)*

$$r = \frac{kK_{O_2}K_B p_{O_2} p_B}{(1 + K_{O_2}p_{O_2} + K_B p_B + K_M p_M)^2} \tag{10}$$

to give:

$$1 + K_{O_2}p_{O_2} + K_B p_B + K_M p_M = (kK_{O_2}K_B)^{1/2}(p_{O_2}p_B/r)^{1/2} \tag{11}$$

Values of $[p_{O_2}p_B/r]^{\frac{1}{2}}$ are computed from the sets of measurements of r as a function of firstly p_{O_2} and secondly p_B. These values are then fitted by the linear least-squares technique to equations such as (11) to give the regression constants K_{O_2}, K_B, and $(kK_{O_2}K_B)^{\frac{1}{2}}$. (The term $K_M p_M$ disappears in this case since measurements have been made under initial conditions where $p_M = 0$.)

Thus, when the data are slightly scattered, and when the curvature of the plot of rate against partial pressure of reactant is very gradual, then this analysis is found to be unreliable. The graphs of r against p_{O_2} in the experimentally accessible region were, in fact, close to straight lines.

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* Equation (10) is derived from the model system in which fuel and oxygen are molecularly adsorbed (adsorption system number iv in Table 2) and the rate-controlling step is the surface reaction between the two (step 11 in Table 1).

These difficulties have also been noted by Kitrell *et al.* (*4*) and by Blakemore and Hoerl (*5*), who suggested that a more accurate estimate of the rate and adsorption equilibrium constants will be obtained if a nonlinear least-squares technique using Eq. (10) in its nonlinear form is employed. However, although this method of treating Eq. (10) is certainly superior to the simpler linearization technique from a statistical viewpoint, it still involves the fundamentally unsound application of a complex rate equation to ill-designed data. Thus an examination of the results obtained by these workers (*4*, *5*) in an analysis of data by both linear and nonlinear techniques suggests that there is little advantage in using the nonlinear technique.

Certainly, if a large number of rate equations have to be handled, the complexity of this technique renders its use prohibitively time-consuming.

Upon reflection, it would appear more fruitful to attempt to measure the reaction rate (r) in regions of concentration (p_{O_2} and p_B) where K_{O_2} and K_B can be most accurately calculated. A method of deciding on such regions of concentration (i.e., an experimental design) for nonlinear equations such as Eq. (11) has been described by Box and Lucas (*6*) and applied in a hypothetical situation by Kittrell *et al.* (*7*). It involves the calculation and minimization of the confidence volume, a measure of the total error in the estimated rate parameters [k, K_{O_2}, K_B in Eq. (11)]. But as Box and Lucas (*6*) point out, the experimental conditions which an experimental design shows would be most fruitful often prove unworkable, in practice. For example, under conditions of temperature or concentration which are statistically ideal for the calculation of the rate constants, it may be impossible to measure the rate of reaction.

This was indeed found to be the case in experiments concerned with the oxidation of benzene over a platinum catalyst. An examination was therefore made of data collected from an integral reactor. These were found to be more attractive for the

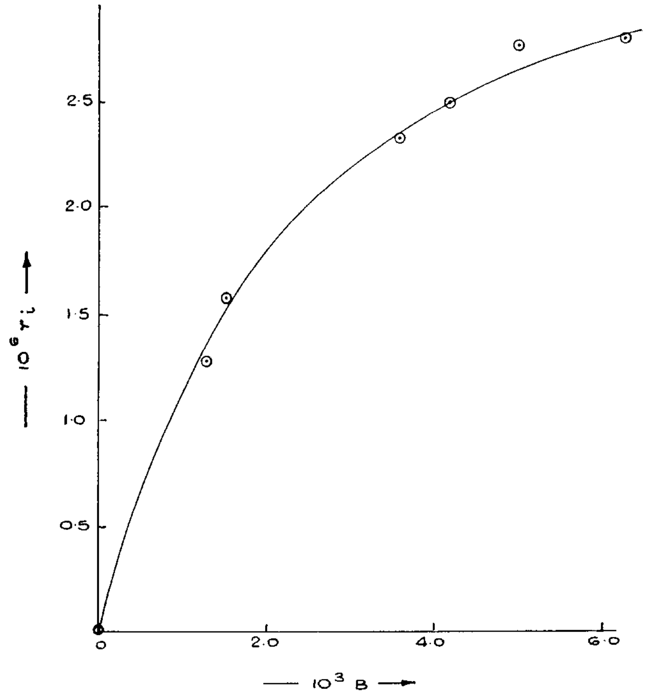

FIG. 2. Differential data: reaction rate as a function of initial benzene concentration. $A = 0.25$; temperature 267°C; $\pi = 1$ atm; catalyst 0.043 g platinum on silica.

following reasons: It is possible to make measurements more accurately and the accuracy does not decrease with conversion, as it does with differential data, but rather increases since at higher conversions concentration changes are more accurately measured. Furthermore, the effect of the products on the reaction as they are formed is easily noted; this introduces an additional constraint which must help in the selection of the correct rate equation.

Relatively little use has been made of integral data, because its analysis is complex. For example, as early as 1947, Hougen and Watson (*3*) showed that if the rate (r) was expressed as an explicit function of the conversion (x) then it was possible to integrate Eq. (8) to give an equation of the form

$$1/F = f(k, K_{O_2}, K_B, x) \qquad (12)$$

The fitting of Eq. (12) to integral data (x vs. $1/F$) then gives the constants (k, K_{O_2}, K_B). Objections to this technique are that firstly, in only a few cases is it possible to integrate the Hougen-Watson rate equations analytically, and secondly, if this integration is achieved the resulting equation (12) is so complex that the use of complex nonlinear least-squares techniques is required. However, this method has been used to examine a few relatively simple Hougen-Watson rate equations in a study of the catalytic oxidation of methane on palladium (*8*). It was found that very complex nonlinear techniques were required to fit the integrated equations to the data. The value of integral data has also been stressed by Peterson and Lapidus (*9*), who also point out that discrimination among alternative models may be due in large part to the experimental design in certain circumstances.

In view of the fact that integral data can be measured accurately, a method of analysis was sought which would use this data and yet was free from the mathematical objection discussed above. This method of analysis has to be relatively simple so that it can be applied to a large number of equations. One method described in this paper (Method B) utilizes equations which are developed from the equations suggested by Hougen and Watson (*3*) in which the rate is expressed as an explicit function of the conversion, the so-called "rate-conversion equation."

However, an even simpler method of fitting these equations to integral data has been devised (Method A). This involves fitting a polynomial to the conversion vs. reciprocal flow rate data, thereby effectively smoothing the curve. Differentiation of this polynomial then enables a set of empirical rate vs. conversion data to be generated, to which the equation connecting the rate explicitly with the conversion may be fitted. This method will now be discussed in more detail.

THE APPLICATION OF HOUGEN-WATSON RATE EQUATIONS TO INTEGRAL DATA

In this particular study, since the volume change is very small, it is possible to simplify the Hougen-Watson rate equations somewhat by expressing the partial pressures in terms of the initial mole fractions of the reactants. However, the procedure could be easily adapted to reactions in which a large volume change takes place.

Thus for the hydrocarbon oxidation reaction

$$B + aO_2 \rightarrow mM$$

taking place at very low hydrocarbon concentrations (<1% by volume) it is permissible to write

$$p_{O_2} = (A - aBx)\pi$$
$$p_B = (1 - x)B\pi$$
$$p_M = (M + mBx)\pi$$

In the example previously considered, viz., surface reaction between molecularly adsorbed fuel and oxygen, then substitution of these values into Eq. (11) gives

$$r = \frac{(A - aBx)(1 - x)}{(k_1 + k_2 x)^2} \qquad \mathbf{(13)}$$

where

$$k_1 = \frac{1 + AK_{O_2}\pi + BK_B\pi + MK_M\pi}{(kK_{O_2}K_B B\pi^2)^{1/2}} \qquad (14)$$

$$k_2 = \frac{(mK_M - aK_{O_2} - K_B)B\pi}{(kK_{O_2}K_B B\pi^2)^{1/2}} \qquad (15)$$

The problem is now reduced to finding the constants k_1 and k_2 in rate-conversion equations such as (13), given a set of integral data [conversion (x) vs. reciprocal flowrate ($1/F$)].

METHOD A

This method of calculating k_1 and k_2 involves fitting a polynomial of the form of Eq. (16) to the x vs. $1/F$ data.

$$\left(\frac{V_m}{B}\right)\left(\frac{1}{F}\right) = b_1x + b_2x^2 + \cdots + b_px^p \quad (16)$$

where $b_1,b_2, \ldots b_p$ are regression coefficients and p is the number of terms in Eq. (16).

This polynomial is then differentiated to give

$$\left(\frac{V_m}{B}\right)\frac{d(1/F)}{dx} = b_1 + 2b_2x + 3b_3x^2 + \cdots + pb_px^{p-1} \quad (17)$$

Equation (8) indicates that

$$\left(\frac{V_m}{B}\right)\frac{d(1/F)}{dx} = \frac{1}{r}$$

thus by substitution of suitable values of conversion into Eq. (17) it is possible to generate a set of $1/r$ vs. x data (within the range of experimental measurements) to which a rearranged form of Eq. (13), namely Eq. (18) may be fitted.

$$\left(\frac{1}{r}\right)^{1/2} = k_1\left\{\frac{1}{(A - aBx)(1 - x)}\right\}^{1/2} + k_2\left\{\frac{x^2}{(A - aBx)(1 - x)}\right\}^{1/2} \quad (18)$$

This is the form

$$y = k_1w + k_2z \quad (19)$$

where

$$y = \left(\frac{1}{r}\right)^{1/2}$$

$$w = \left\{\frac{1}{(A - aBx)(1 - x)}\right\}^{1/2}$$

$$z = \left\{\frac{x^2}{(A - aBx)(1 - x)}\right\}^{1/2}$$

It is apparent that the functions y,w, and z are easily calculated from the empirical r vs. x data and then fitted by a straightforward multilinear least-squares procedure to Eq. (19) to give the constants k_1 and k_2.

Having calculated k_1 and k_2 for several sets of integral data at different initial reactant concentrations (i.e., different values of A and B). k, K_{O_2}, K_B, and K_M may easily be calculated from the simultaneous equations obtained by substitution of the values of k_1, k_2, A, and B into Eqs. (14) and (15).

The advantages of this procedure are that the equations being handled are relatively simple and linear in k_1 and k_2, thus allowing a linear least-squares curve fitting procedure to be employed. The development of a linear least-squares curve-fitting routine on a computer which will fit any linear equation of any functional form has enabled a large number of equations to be handled.

METHOD B

Integration of Eq. (13), followed by fitting it directly to conversion vs. reciprocal flow rate data gives k_1 and k_2. These values can be compared with those obtained by Method A.

The integration of Eq. (13) yields

$$1/F = k_1^2f_1(x) + k_1k_2f_2(x) + k_2^2f_3(x) \quad (20)$$

where

$$f_1(x) = \frac{-2\log\cos\phi_L}{A - aB}$$

$$f_2(x) = -\left\{\frac{4}{A - aB}\frac{A}{aB}\log\cos\phi_L + \frac{4}{aB}\log\tan\phi_L\right\}$$

$$f_3(x) = -\left\{\left(\frac{A}{aB}\right)^2\frac{2\log\cos\phi_L}{A - aB} + \frac{2(A + aB)}{(aB)^2}\log\tan\phi_L + \frac{A - aB}{(aB)^2}\cdot\frac{1}{\sin^2\phi_L}\right\}$$

and

$$\log\cos\phi_L = \log\cos\phi - \log\cos\phi_0$$
$$\log\cos\phi_L = \log\tan\phi - \log\tan\phi_0$$
$$\frac{1}{\sin^2\phi_L} = \frac{1}{\sin^2\phi} - \frac{1}{\sin^2\phi_0}$$

ϕ_0 is the value of ϕ at $x = 0$ (the lower limit of integration) and ϕ is defined by

TABLE 3
COMPARISON OF VALUES OF k_1 AND k_2 OBTAINED FOR EQ. (13) BY METHOD A (LINEAR LEAST-SQUARES) AND METHOD B (NONLINEAR LEAST-SQUARES)

	k_1		k_2	
Run	Method A	Method B	Method A	Method B
802	1.92×10^2	1.91×10^2	-1.22×10^2	-1.18×10^2
8031	2.09×10^2	2.09×10^2	-1.17×10^2	-1.16×10^2
8032	2.06×10^2	2.04×10^2	-1.09×10^2	-1.10×10^2
804	1.76×10^2	1.80×10^2	-8.95×10	-9.80×10

$$\sin^2 \phi = \frac{A - aB}{A - aBx}$$

Equation (20) is thus quite complex and nonlinear. It must be fitted to the x vs. $1/F$ data using nonlinear least-squares and this involves the use of the Newton-Raphson iteration procedure. The range of application of this procedure is therefore limited by (a) the complexity of the curve fitting procedure and (b) the fact that only a few of the simpler equations can be integrated.

The results obtained by both methods of analysis are compared in Table 3 for some data obtained for the oxidation of benzene on palladium on glass.

From these and some similar results obtained for other simpler Hougen-Watson rate equations it was concluded that the linear least-squares curve fitting (Method A) provides an adequate method of accurately calculating the constants k_1 and k_2. Thus the mathematical sophistication of the analysis is of relatively little importance when compared with the type and accuracy of the data used. This conclusion was also reached (see discussion above on differential data) when the results obtained by an analysis of differential data by both linear and nonlinear techniques were examined (*3*, *4*).

Briefly summarizing the procedure, Table 2 leads to a total of 104 Hougen-Watson rate equations. When the partial pressures in these rate equations are replaced by the initial mole fractions and conversion a total of 28 distinct rate equations results. Equation (13) is one such equation. These 28 rate-conversion equations are now fitted to the integral conversion vs. reciprocal flow rate data, using the relatively simple linear least-squares method, to give the constants k_1 and k_2. Having calculated k_1 and k_2 for all the rate conversion equations, the selection of the correct Hougen-Watson rate equation and hence the reaction mechanism is a simple procedure. Equations (14) and (15) show that for the rate and adsorption equilibrium constants to be positive then k_1 must be positive, and furthermore, k_1 and k_2 must vary in a particular way with the initial mole fraction of the reactants. Thus by observing the effect of initial concentrations on k_1 and k_2 it is possible to select the correct mechanism and calculate the rate and adsorption equilibrium constants (k, K_{O_2}, K_B, K_M). A further check is provided by the statistical fit of the rate-conversion equations to the data, as indicated by the variance of the fitted curves. In the reactions investigated in this work it has been found that only one Hougen Watson equation out of a possible 104 is able to satisfy the two conditions, namely that the constants k_1 and k_2 should vary in a particular way with initial concentration and that the equation provides the best statistical fit to the data (*10*).

In conclusion, it is worthwhile considering why an analysis of integral data should yield more accurate results than an analysis of differential data.

The first reason is simply an experimental one. It is difficult to measure the differential rate accurately, whereas it is fairly easy to measure accurate integral data collected at higher conversions. Furthermore, it has been found that an analysis of integral data, when the whole of the conversion vs. reciprocal flow rate graph is utilized, yields more accurate results than an analysis utilizing only part of this graph. For example, the most accurate method of measuring the differential rate is by determing the gradient of the tangent at the origin of the graph conversion vs. reciprocal flow rate. This was done for two duplicate runs measured under the same experimental conditions and it was found that the rates differed by 11%. Yet when Eq. (13) was fitted to the whole of the conversion vs. reciprocal flow rate graph the values of k_1 (a quantity dependent on the rate at zero conversion—see below) for the two runs differed by only 1.5%.

This accuracy is further illustrated by an examination of some results obtained on benzene and cyclohexane oxidation on palladium on glass (*10*). It was found that the rate equations derived from integral data were capable of predicting the initial rate within the error limits involved in the measurement of this rate. Yet an attempt to derive these rate equations from the initial rate failed due to the errors in the initial rate in the experimental region in which the data was measured.

The second advantage to be gained in using integral data is the selectivity of the method of analysis. For example, four catalytic systems were studied (*10*) and it was found in each case that only one out of 104 mechanisms was capable of satisfying the conditions imposed.

Upon reflection, it would seem that the accuracy and selectivity which results from the analysis of integral data is due to the fact that a particular rate equation is required to satisfy more rigid and accurate conditions than are required in the analysis of differential data. Firstly, it is required to fit a set of conversion vs. reciprocal flow rate data (effectively rate vs. time of reaction data) and secondly, the constants obtained from this curve fitting must vary in a particular way with reactant concentrations (effectively rate vs. initial concentration data). On the other hand, in an analysis of differential data an equation only has to fit the observed variation of the rate with initial concentration.

This becomes apparent if one examines the physical significance of the constants k_1 and k_2 in a typical case, e.g., Eq. (13). Since the initial rate (r_i) is the rate at zero conversion ($x = 0$), putting $x = 0$ in Eq. (14) and rearranging gives

$$k_1 = (A/r_i)^{1/2}$$

furthermore by differentiating Eq. (13), rearranging, and putting $x = 0$

$$k_2 = -\frac{1}{2A}\left\{k_1^3\left(\frac{dr}{dx}\right)_i + k_1(A + aB)\right\}$$

Thus k_1 is a quantity dependent on the initial rate (r_i) while k_2 is dependent on the initial rate of change of the rate with conversion. This is confirmed by an examination of Eqs. (14) and (15), which indicates that k_1 is only dependent on the initial concentrations. Equation (15) however, contains the stoichiometric coefficients a and m and thus k_2 will depend on the rate of disappearance of the reactants and formation of products. Therefore in order to measure it accurately, it is necessary to work at high conversions. This has been experimentally confirmed.

Thus the earlier conclusion that an analysis of integral data is more accurate and selective than analysis of differential data because it requires a prospective rate equation to satisfy two conditions rather than one is justified.

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