Rate Factors in a Heterogeneous Catalytic System in a Stirred Reactor

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Optimum design and performance of chemical plants can be facilitated by an understanding of the kinetics of the chemical reaction systems involved. The rate behavior of multiphase catalytic systems may be influenced by several transport and kinetic processes (*11*). Each of these rate processes has been the subject of considerable research; some of these processes, chemisorption (*14*) for example, may consist of several elementary mechanisms. A quantitative evaluation by the direct experimental means of the role of each of these processes as it occurs in the total operating system is beyond reach for most cases at the present time. Many noteworthy investigations into the detailed mechanisms of catalytic reactions have resulted from examining these systems under conditions for which one step is rate controlling.

The purpose of this study was to explore the possibility of arriving at useful overall rate equations for systems in which more than one process step is important. Such equations could be employed for design and optimization studies for cases in which there is no single rate controlling step throughout the range of process variables pertinent to the problem. The method involves evaluating various models developed from relatively simple concepts and rate functions for each of several postulated process steps. Data were obtained for a common type of catalytic system, hydrogenation in a stirred reactor. A digital computer was used to evaluate the constants in the implicit nonlinear functions which describe the rate in terms of overall concentration values. A method for interpreting the rate behavior in terms of the relative importance or resistance of each step is suggested as a useful development and design tool.

DEVELOPMENT OF OVERALL RATE EQUATION

Research on the hydrogenation of fatty acids and esters has been reported by many investigators; only a few references which are related to this work will be mentioned here. The combined influence of diffusional and kinetic factors has long been recognized (*15*). Davis and Crandall (*5*) include resistance terms for the hydrogen solution and diffusion steps for the liquid phase catalytic hydrogenation of olefins. Gol'danskii and Elovitch (*8*) studied the hydrogenation of oleic acid in a rocking autoclave and considered diffusional and kinetic processes. Gol'danskii (*7*) gave a theoretical treatment for such systems. Albright and co-workers (*2, 6, 19*) were interested in chemical mechanisms in the hydrogenation of cotton-seed oil in a stirred reactor and employed high agitation rates to minimize mass transfer effects. Johnson, Saito, Polejes, and Hougen (*12*) studied the hydrogenation of α-methylstyrene in the region where mass transfer of hydrogen through the liquid is the rate controlling step.

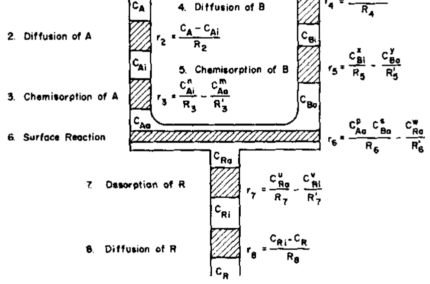

Fig. 1. Schematic diagram of rate processes for a gas-liquid-solid catalytic system.

This study deals with the hydrogenation of ethyl oleate to the saturated ester, ethyl stearate, with a finely divided nickel catalyst. It is postulated that the system consists of eight steps with simplified rate equations as shown in Figure 1. In general the transport processes have been considered to follow a relationship of the type

$$r = \frac{\Delta C}{R} \tag{1}$$

and the surface phenomena were considered to be chemical in nature with the rate represented by

$$r = \frac{C_A{}^a\, C_B{}^b}{R} - \frac{C_R{}^r}{R'} \tag{2}$$

As a first approximation therefore very simple rate equations were used, and temperature and concentration gradients within the particles were not taken into account. Thus bulk and pore diffusion mechanisms were treated as one diffusional step; chemisorption and surface reaction rate equations were based upon some average concentration for the catalyst particle.

If accumulation effects are neglected, then rates for all steps are equal, and the eight equations in Figure 1 can be written as one overall rate in terms of measurable bulk concentrations:

$$r = \frac{1}{R_6} \left[\frac{(P_A - (R_1 + HR_2)r)^n - R_3 H^n r}{H^n (R_3/R_3')} \right]^{p/m} \left[\frac{(C_B - R_4 r)^x - R_5 r}{R_5/R_5'} \right]^{s/y} - \frac{1}{R_6'} \left[\frac{(C_R + R_8 r)^v + R_7' r}{R_7'/R_7} \right]^{w/u} \tag{3}$$

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Thus, even when these simplified rate expressions are used for each of the eight steps;* the overall rate equation becomes quite cumbersome. Furthermore the above equation is implicit in r, which makes the solution and interpretation even more difficult. The kinetic resistance factors R_6, R_6', R_3, R_3', R_5, R_5', R_7, and R_7' would be expected to be functions of temperature and amount of catalyst since they represent rate constants for chemical changes. The transport resistance factors R_1, R_2, R_4, and R_8 would depend upon the above factors as well as the physical environment such as the type and degree of agitation, and other properties of the system.

KINETIC RESISTANCE CONCEPT

The analysis of complex systems involving several steps is simplified if the behavior can be interpreted in terms of the significance or the relative importance of each step. Expressing these effects in terms of resistances is a well-known concept for the analysis of heat and mass transport processes. In general chemical reaction systems cannot be treated in the same way because the rate equations may be nonlinear and there is difficulty in defining a fundamental potential which is applicable to all chemical species. For the special case of a first-order surface reaction Hurt (*11*) has applied the resistance concept in defining a height of a reactor unit.

In the development of the overall rate Equation (3) it is postulated that the system can be described in terms of a combination of individual steps each containing a step resistance as shown in Equations (1) and (2). A quantitative measure of the influence of any of m individual step resistances on overall systems performance for some value of the driving function $\Psi(P, T, C_i, \text{etc.})$ and at some time θ is the rate of change of reaction rate with respect to the step resistance, R_s:

$$\left(\frac{\partial r}{\partial R_s}\right)_{R_i,\,\theta,\,\psi} \qquad \begin{array}{l} i = 1, 2, \ldots m \\ i \neq s \end{array}$$

For purposes of comparison the relative effect expressed in terms of fractional changes is more useful. Thus for step resistance R_s, let ϕ_s be defined as

$$\phi_s = \frac{R_s}{r}\left(-\frac{\partial r}{\partial R_s}\right) \tag{4}$$

If the overall resistance R of the system is taken as that quantity which relates the reaction rate r with the driving function Ψ such that

$$R = \frac{\Psi}{r} \tag{5}$$

it follows that ϕ_s may likewise be expressed as

$$\phi_s = \frac{R_s}{R}\left(\frac{\partial R}{\partial R_s}\right) \tag{6}$$

To facilitate interpretation Equation (6) can be rewritten as

$$\phi_s \cong \frac{\left(\dfrac{\Delta R}{R}\right)}{\left(\dfrac{\Delta R_s}{R_s}\right)} \tag{7}$$

Thus ϕ_s may be viewed as the fractional change in the total resistance per unit fractional change in step resistance R_s.

An important property of ϕ is (1)

$$\phi = \Sigma\,\phi_i = 1 \tag{8}$$

Hence in view of Equations (7) and (8) ϕ_s may be regarded as an equivalent fractional resistance.

The definition of ϕ_s involves no assumption regarding the nature of the system, and hence ϕ_s retains its fundamental significance regardless of the relationship between total resistance and individual step resistances. For the special case of a series system

$$\phi_s = \frac{R_s}{\Sigma\,R_i} = \frac{R_s}{R} \tag{9}$$

and for a parallel system

$$\phi_s = \frac{1}{R_s\,\Sigma(1/R_i)} = \frac{R}{R_s} \tag{10}$$

and it is seen that ϕ_s is identical to the usual definition for fractional resistance.

The magnitude of ϕ_s is therefore a measure of the relative sensitivity of the entire system to a fractional change in a particular system parameter R_s. Therefore if a quantitative relationship between the design variables (pressure, temperature, agitation, etc.) and the resistances were available, ϕ_s values would be a valuable guide to permit an assessment of the change in performance of the system for a change in one of the design variables. Even if the above quantitative relationship is not available, a qualitative relationship is generally known, and therefore the ϕ_s values provide an indication as to which of the design variables have the greatest significance in determining the rate under a particular set of conditions. For example where ϕ_s for the chemical surface reaction is 0.95, it would be apparent that increased agitation would accomplish little to improve the rate. On the other hand if ϕ_s for the gas solution step were 0.5, it is evident that improved gas-liquid contact by changing equipment design or increasing agitator speed could increase the rate considerably.

KINETIC TIME CONTRIBUTION

The equivalent fractional resistance in a dynamic system is an instantaneous value which depends upon reaction rate which in turn is a function of design variables and system parameters. The instantaneous reaction rate may be defined by the relation

$$r = -\frac{dC}{d\theta} \tag{11}$$

Since ϕ equals unity, one may write Equation (11) as

$$-\,d\theta = \frac{dC}{r}(\phi_{1(r)} + \phi_{2(r)} + \ldots + \phi_{n(r)}) \tag{12}$$

Expanding and integrating (12) one obtains

$$\int_{\theta_0}^{\theta} d\theta = \int_{C}^{C_0} \frac{\phi_{1(r)}\,dC}{r} + \int_{C}^{C_0} \frac{\phi_{2(r)}\,dC}{r} + \ldots + \int_{C}^{C_0} \frac{\phi_{n(r)}\,dC}{r} \tag{13}$$

Thus

$$\theta_t = \theta_1 + \theta_2 + \ldots + \theta_i \ldots + \theta_n \tag{14}$$

where the individual θ_i's are regarded as the time contribution due to the *i*th resistance. The time contributions can be normalized by dividing by θ_t to yield the *NTC*, normalized time contribution. For a small change in concentration $NTC_s = \phi_s$; for larger changes NTC_s provides an average value for the relative retarding influence of resistance R_s during the change. Mathematically

$$NTC_s = \frac{\displaystyle\int_2^1 \frac{\phi_{s(r)}\,dC}{r}}{\displaystyle\int_2^1 \frac{dC}{r}} \tag{15}$$

where NTC_s is the fraction of the total time required to proceed from condition 1 to condition 2 that is attributable to step *s*.

For flow systems other averaging criteria based upon residence time, reactor volume, reactor length, etc. can be derived in a manner analogous to that above. For example it is readily shown that in a flow system the quantity evaluated above as NTC_s may be interpreted as fractional reactor length.

PARAMETER DETERMINATION

Certain of the parameters in the kinetic model, for example step resistances, are considered arbitrary in the sense that the values for these parameters are dependent upon the particular set of kinetic data to which the model is being fitted and upon the type of fit (error criterion) desired. Box and Coutie (*4*), Peterson (*17*), and Williams (*18*) have presented methods for the selection and evaluation of kinetic models with the aid of computers. Marquardt (*16*) discussed least-squares fitting of nonlinear models to experimental data. A fully developed nonlinear estimation program has been made available by Booth and Peterson (*3*). Other related work such as that of Hartley (*9*) is also available. The procedure used in this work employs the method of least-squares and the Taylor series expansion which have been widely used and discussed by others in connection with nonlinear estimation methods (*3, 4, 16, 17*). Following is a brief description of the computer implemented procedure used in this study.

A second-order Taylor expansion was used to approximate the kinetic model at some point in the parameter space. The least-squares normal equations derived using this approximation were, of course, nonlinear functions of the parameters expressed in terms of displacement from the base point. By maintaining displacements sufficiently small, a reasonable approximation is achieved by retention of the linear terms only. This process of linearization causes second partial derivatives to be retained in the normal equations. If, instead, linearization was accomplished by employing a first-order Taylor expansion of the function, only first partial derivatives would be involved. The inclusion of the second derivatives is done at considerable computational cost; more work is needed to determine if, and under what circumstances, the additional complexity is justified by improved efficiency.

Determination of values for the parameters in the kinetic model which suitably minimized the error function was done as follows. Beginning with a set of initial values for the parameters, the linearized normal equations were solved to yield a set of values for the increments which are to be used to adjust the parameters to define a new base point. If one of the increments exceeded an allowable magnitude, it was set equal to its limit and treated as a constant and the reduced set of normal equations was solved again. This process was repeated until values of permissible magnitude were obtained for all increments. The entire process was repeated and the parameters adjusted in this stepwise fashion until a satisfactory fit was indicated by a negligible change in the error criterion per iteration. It should be noted that if the numerical values for the parameters are of prime importance, as for example in optimization studies, it would be necessary to explore the response surface in the vicinity of the optimum in greater detail than was deemed necessary for the present purpose.

EXPERIMENTAL

The hydrogenation studies (*13*) were carried out in a jacketed, well-stirred, autoclave under constant conditions of temperature, hydrogen pressure, and agitation during each run. The reactor was designed for a high degree of gas-liquid-solid contact. The gas dispersing element near the liquid level include a turbine impeller inside a baffled hood ring with draft tube. The lower impeller provided additional mixing to prevent catalyst from settling to the bottom. The liquid capacity of the reactor at a level ½ in. above the hood ring was 2820 cc. and the total volume was 4,200 cc. A variable speed hydraulic drive provided agitator speeds from 400 to 3,600 rev./min. The reactor and all exposed parts were of stainless steel. Temperature control was accomplished by maintaining a boiling liquid in the jacket.

Hydrogen was fed from a calibrated accumulator which was insulated to minimize temperature variations. Temperature and pressure measurements of the accumulator provided an accurate method for determining the amount of hydrogen fed to the system. The pressure on the system following the accumulator was maintained constant by means of a pressure regulating valve. The rate of feed of hydrogen was measured by a calibrated rotameter; purification was accomplished by passing the hydrogen through a Deoxo unit followed by a drying unit. The purified hydrogen was heated to reaction temperature by means of a small electric preheater adjacent to the reactor. In order to minimize the effect of possible accumulation of inert gases in the reactor a small bleed was provided from the top of the reactor and was metered through a wet test meter. Great care was taken to prevent leaks from the system.

Materials

Ethyl Oleate. The ethyl oleate used in this investigation was prepared by esterifying a high grade commercial oleic acid. For the purpose of this investigation the ester was considered to have the composition shown in Table 1. These values are based on a $C_{17}H_nCO_2C_2H_5$ molecule, when for the saturated ester $n = 35$, for ethyl oleate $n = 33$, for an ester containing two double bonds per molecule $n = 31$, and so on.

Catalyst. The catalyst used in this investigation was prepared by modifying a commercially available hydrogenation catalyst to give a completely reduced form that could be handled in air conveniently. The starting catalyst was a nickel hydrogenation catalyst which was in the form of ⅛ × ⅛ in. cylindrical pellets of activated nickel supported on keiselguhr. This catalyst was mixed with melted hydrogenated vegetable oil, wet ground in a high-speed blender, and the resulting slurry hydrogenated to completion. The resultant hard solid mass was crushed and screened to 8 to 40 mesh and stored under a nitrogen atmosphere. The modified catalyst contained 28.69% nickel by weight. Microscopic analysis of the catalyst particles after the protective fat was removed indicated a size distribution of from 0.2 to 70 μ.

TABLE 1. COMPOSITION OF UNSATURATED ESTER

Type ester	Mole %
Diene	3.7
Triene	0.8
Mono-ene	87.4
Saturated	8.1

Chemical Analysis

The course of the reaction was followed by analyzing a sample from the reactor at suitable time intervals. The amount of hydrogen used as the reaction proceeded served as a convenient means for interpolation between samples taken for chemical analysis. The analytical method was used for determining the amount of unsaturate was the standard iodometric procedure. Index of refraction measurements also provided a rapid method for some samples.

Experimental Data

This study deals primarily with the effect of temperature, pressure, and concentration of reaction rate at an intermediate level of agitation and makes use of concentration-time data obtained from seven runs conducted as described above. These were made with a catalyst concentration of 0.44 lb./cu.ft. and an agitator speed of 1,200 rev./min. The temperature and pressure conditions for each run are presented in Table 2.

The data for values of concentration below 0.1 lb.-mole/cu.ft. are shown in Figure 2; numerical values can be found in reference *1*. The time axis has been translated so that a concentration of 0.1 corresponds to zero time. From analysis of other data (*13*) a concentration of 0.1 lb.-mole/cu.ft. represents a level where it is believed that polyunsaturated species have been hydrogenated and only monounsaturated compounds remain.

The temperature rise during a run was approximately 1°C. for the low temperature runs and a maximum of four degrees for the high temperature experiments. The values listed in Table 2 are time averaged temperatures. The pressure was maintained constant to within ± 0.05 atm. by a regulator in the hydrogen feed line.

Considerable care was taken in preparing and storing the catalyst and the oleate as well as in maintaining uniform experimental procedures. Based upon a series of runs in which catalyst concentration was varied (*13*) it was shown that a certain amount of catalyst poisoning took place; these data suggest that poisoning occurred rapidly from contaminants in the ethyl oleate and did not progress further during a run. It appeared in effect that a specific amount of the catalyst charged was

TABLE 2. TEMPERATURE AND PRESSURE CONDITIONS FOR EMPIRICAL DATA

Run no.	1	2	3	4	5	6	7
Temperature, °C.	121	121	121	165	165	167	199
Pressure, atm.	1.6	3.3	6.2	1.6	2.2	3.3	1.6

deactivated in cleaning up the feed and the remainder functioned without further deactivation. With reference to reproducibility of results comparison of data for duplicate runs (*13*) showed an average deviation in rates of approximately 10% over the concentration range mentioned above.

EVALUATION OF REACTION RATES

In checking the consistency of the original data via a semilog plot it was observed that the resulting curves very closely approximated conic sections. Accordingly a least-squares fit of the concentration-time data was attempted with the function

$$C = \exp\left[a_0 + a_1\theta + a_2\theta^2\right] \qquad (16)$$

This expression was able to represent the data from the seven runs with an average standard deviation of only 0.001. Since the analytical expression fit the integral (C, θ) data so well, the authors decided to obtain rate data by differentiation of (16); however since a few of the original data points were evidently out of line, the constants in (16) were redetermined from graphically smoothed (C, θ) data. Thus nine smoothed data points, ranging from a concentration of 0.10 to 0.02, were obtained for each run from plots of the original data. The good fit of Equation (16) to the original data can be seen in Figure 2, where the curves represent the calculated C vs. θ relationship. The experimental points in Figure 3 show the calculated rates obtained by differentiation of Equation (16).

SELECTION AND EVALUATION OF KINETIC MODEL

One of the primary criteria to be evaluated in determining the relative merit of different kinetic models is the degree of concordance between calculated and experimental results, viewed in relation to the complexity of the model. For the most part a more complex model would be chosen over a simpler one only if it does a significantly better job of correlating the results, and/or because the assumptions made in the model development appear more plausible.

The models discussed below represent special cases of the general rate equation developed earlier. Thermodynamic estimates of the equilibrium constant as well as experimental evidence of high conversion show that the reverse reaction in the total system is very small (*13*); on this basis it is postulated that the surface reaction step is irreversible so that R_6' of Equation (3) may be considered very large and the associated term of the equation dropped. Combining R_1 and HR_2 the solution and mass transfer steps for hydrogen and replacing R_3H^n with R_3'', one may write Equation (3) as

$$r = \frac{1}{A_1}\left[(P_A - R_Hr)^n - R_3''r\right]^{p/m}$$

$$\left[(C_B - R_4r)^x - R_5r\right]^{s/y} \qquad (17)$$

where

$$A_1 = R_6\left[H^n(R_3/R_3')\right]^{p/m}\left[R_5/R_5'\right]^{s/y}$$

The procedure used for the selection of appropriate models was to start with the simplest then proceed to the more complex forms of Equation (17) and compare the degree of fit with the data.

Preliminary graphical analysis of the rate behavior showed that it could not be represented by simplifying Equation (17) to the extent of eliminating the factors R_3'', R_5, R_H, etc. and using simple overall equations of the zero fractional, first, or second order types with respect to hydrogen pressure and unsaturate concentration. Accordingly several forms of Equation (17) were then evaluated for values of unity and ½ for the exponents with the computer-based method described above.

Agreement with experimental results was measured in terms of the value of the error criterion:

$$Q = \Sigma\,(R_i - r_i)^2/R_i \qquad (18)$$

This error criterion was selected over a straight least squares to force a better fit for low values of rate. Note that dividing by R_i^2 instead of R_i would have given a least-squares fit in terms of fractional error; hence the selected criterion is a compromise between straight least squares and an error criterion based upon percentage deviation.

Adjustable parameters in the kinetic models were regarded as being functions of temperature but independent of pressure and concentration. All temperature dependencies were assumed to be of the Arrhenius form:

$$R = ae^{b/T} \qquad (19)$$

Thus each temperature dependent parameter in the kinetic model was expressed in terms of two constants which then became the actual constants manipulated by the computer in the search for the best overall fit of all data at all temperatures. Note that Equation (19) permits the procedure used herein to treat rate data obtained under nonisothermal conditions.

Model I

Model I, the first and simplest model attempted, was derived from Equation (17) by assuming all exponents equal unity and then combining the two resistance terms in each of the brackets into a single term to obtain the equation

$$r = \frac{1}{A_1}\,(P - R'_Hr)\,(C - R_Ur) \qquad (20)$$

The resistance terms were found to be

$$A_1 = 2.25 \times 10^{-4} \exp{(5{,}296/T)}$$
$$R'_H = 71.9 \exp{(833/T)}$$
$$R_U = 1.28 \times 10^{-4} \exp{(4{,}805/T)}$$

In spite of its simplicity this equation fits the data within the estimated precision of the derived rate data. Nevertheless additional models were

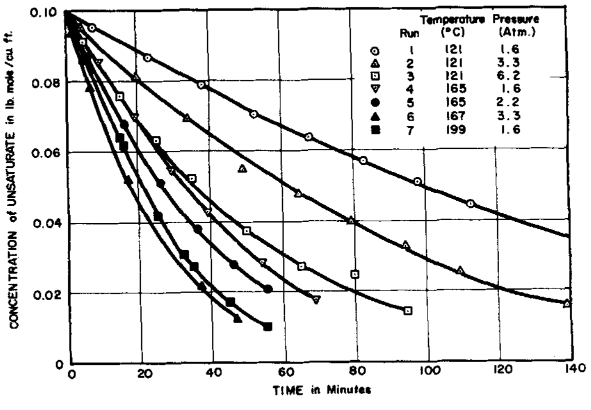

Fig. 2. Concentration-time values derived from Equation (16) (curves) compared with experimental data (points).

evaluated in an attempt to find an improved correlation and to gain experience with the techniques involved.

Model II

Experience with Model I suggested that the fit could be improved by employing a fractional power for the hydrogen pressure. Exploratory evaluation of the rate equation for various combinations of values of 1 and 1/2 for the exponents in the hydrogen adsorption equation led to Model II for which $n = m = 1/2$. With other exponents considered to be unity Equation (17) becomes

$$r = \frac{1}{A_1} [(P - R_H r)^{1/2} - R_3'' \mathrm{r}]^2 (C - R_4 r - R_5 r) \qquad (21)$$

It would be desirable to include both R_4 and R_5 because the temperature dependence of the two terms, one representing a physical resistance and the other a chemical resistance, should be different. However since representation of these two resistance terms by an Arrhenius expression involves four constants, it would not be possible to determine a unique set of values for the constants with data at only three temperature levels. Consequently R_4 and R_5 were combined, and the total resistance for mass transfer and chemisorption of unsaturate were expressed as R_U.

The temperature dependence term of R_H was found to be small. Since R_H includes both solution and mass transfer of hydrogen, it was thought that the low temperature dependence was possibly due to an opposing effect resulting from a negative coefficient for the solution step and a positive coefficient for the mass transfer step. Introduction of two terms for R_H and fixing the temperature coefficient of the mass transfer term at 1,500 resulted in a coefficient of − 900 for the solution step. This elaboration of the rate equation however did not provide a sufficient improvement in the fit over an R_H with zero temperature dependence to justify the increased complexity. Hence with these two modifications, namely combining R_4 and R_5 and setting the temperature dependence of R_H equal to zero, (21) becomes

$$r = \frac{1}{A_1} [(P - R_H r)^{1/2} - R_3'' r]^2 (C - R_U r) \qquad (22)$$

where

$$A_1 = 6.76 \times 10^{-4} \exp (4{,}851/T)$$
$$R_H = 381$$
$$R_3'' = 4.47 \times 10^{-6} \exp (6{,}977/T)$$
$$R_U = 1.49 \times 10^{-5} \exp (5{,}563/T)$$

Model III

Several other forms similar to Model II were cursorily evaluated. Work was terminated when it was judged that the probable final fit would not be appreciably better than that obtained for Models I and II.

In a departure from using specific fractional or integral exponents the equation

$$r = \frac{1}{A_1} (P - R_H' r)^m (C - R_U r)^n \qquad (23)$$

was tried. After approximately twenty iterations, with m and n initially unity, m had dropped to 0.7 and n was slightly less than 1.1. Since n was so close to unity, the selection of the first-order equation with respect to oleate adsorption and surface reaction seemed justified, and it was decided to fix n at unity and leave m variable. Further fitting showed that the temperature coefficient of R_H' was essentially zero. Equation (23) thus became

$$r = \frac{1}{A_1} (P - R_H' r)^m (C - R_U r) \qquad (24)$$

where

$$A_1 = 2.14 \times 10^{-4} \exp (5{,}370/T)$$
$$R_H' = 467$$
$$R_U = 2.18 \times 10^{-5} \exp (4{,}830/T)$$
$$m = 0.756$$

Selected Model

Table 3 presents a comparison of the three models discussed above. Models I and III are about equivalent; Model II is consistently better, but the degree of improvement is not large. All three models fit the data within the average experimental error. Exploration of more complex forms of Equation (17) was considered to be unwarranted.

Model I contains only three arbitrary constants, while Models II and III each contain four. However since some of the constants were permitted to vary with temperature (in a prescribed manner), the models actually have a greater degree of freedom than is indicated by the number of constants. The total number of parameters adjusted by the computer was six, seven, and six for Models I, II, and III, respectively.

Since the kinetic model must account for a fourfold variation of hydrogen pressure, permitting the model to choose its own exponent for the hydrogen term provided flexibility with respect to a key variable. This particular flexibility however tends to classify Model III as more empirical than Model I and Model II.

Although the choice of one of these models over the others is somewhat arbitrary, Model II is chosen because it gives a somewhat better fit than Models I and III (the average error is about 10% less), it is less empirical than Model III, and it presents a somewhat more detailed description of the system since it separates the step for chemisorption of hydrogen from the solution and diffusion steps. The correspondence of Model II with the experimental data is shown in Figures 3*a* and 3*b*.

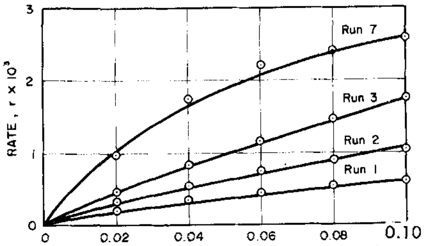

Fig. 3*a*. Comparison of Model II with experimental rate data.

INTERPRETATION OF SYSTEM BEHAVIOR BASED ON KINETIC MODEL

The following analysis of the rate behavior of the system based on Model II is made with full awareness of the speculative nature of these interpretations, since the model can be only an approximation to the actual complex system. It is the purpose of this discussion to point out the correspondence of the rate behavior with knowledge of the behavior of the individual steps and to demonstrate the application of the fractional resistance concept to the analysis of systems in which the relative importance of the several steps is evaluated in terms of the model.

Although agitation studies were not a part of this investigation, a few exploratory runs at different agitator speeds were made. These results show that 1,200 rev./min. is slightly above the minimum to keep all the catalyst

TABLE 3. COMPARISON OF CALCULATED RATES WITH EMPIRICAL RATES

	Model I	Model II	Model III
Standard deviation ($\times 10^5$)	7.4	6.9	7.3
Q^* ($\times 10^4$)	3.0	2.6	2.9
Average deviation (%)	6.3	5.7	6.3

* See Equation (18).

suspended and that increased speeds give substantially greater rates (at 165°C.) indicating that the mass transfer steps must be of some importance. The hydrogen solution and diffusion resistance (R_H) in Model II should be highly dependent upon agitation; ϕ_H is 0.38 at high concentrations (38% of the total resistance is in this step). If increased agitation could reduce this resistance to a very small value, the rate calculated from the model equation should increase more than 50% at these conditions. Since R_U also contains a diffusion resistance, the increase could be somewhat greater. Increasing the agitator speed to 1,600 and 2,400 rev./min. gave rates in the range of 20 to 50% higher than at 1,200 rev./min. This indicates that the model accounts for this behavior at least to a semiquantitative degree when extrapolating considerably beyond the conditions upon which the correlation is based. More data are needed to establish relationship between agitation and the agitation sensitive parameters.

Temperature Dependence of Resistances

For the Model II correlation the temperature dependence of the resistance parameters was considered to follow an Arrhenius form which placed some restriction on the correlation. The other alternative was to find the best values for the resistances at each temperature and then determine a suitable empirical function for the temperature dependence. This of course gives a closer fit but may offer less from the standpoint of interpretation.

It was necessary to combine the two resistance terms for the solution and diffusion of hydrogen. The temperature dependence of the combined term was found to be very small, perhaps smaller than would be expected. If the temperature dependence of the chemical steps is viewed in terms of an Arrhenius activation energy, the value for the hydrogen chemisorption step is about 13,900 cal./g. mole and for the unsaturate chemisorption and diffusion 11,100 cal./g. mole. The constant A_1 [Equation (4)] is a product of several parameters and has a temperature dependence corresponding to 9,600 cal./g. mole. In a qualitative sense these results seem to agree with expected values for the chemical and physical phenomena they represent in the model.

Equivalent Fractional Resistances

Figures 4*a* and 4*b* show the equivalent fractional resistances for different levels of concentration, pressure, and temperature. In the development of Equation (17) the term A_1 is a product of the surface reaction resistance (the inverse of surface reaction velocity constant), ratios of the chemisorption resistances for hydrogen and unsaturate, and the solubility constant H. All of these except H are related to catalytic surface phenomena, and for purposes of identification and discussion this resistance will be called *surface reaction resistance.*

It is observed that the fractional resistances for the surface reaction ϕ_{A_1} and the unsaturate diffusion and adsorption ϕ_{R_U} increase with decreasing concentration of unsaturate, while the hydrogen adsorption term ϕ_{R_3} and the diffusion and solution term ϕ_{R_H} decrease to zero. This is the expected trend, since in this system the hydrogen pressure is maintained constant and therefore fractional resistance terms associated with hydrogen steps must decrease with decreasing rate.

For the low temperature series, Figure 4*a*, the dominant resistance is the surface reaction. At this temperature system behavior is governed largely by chemical processes. At high concentrations and 200°C. ϕ_{R_H} represents about 60% of the total resistance which is significantly greater than any of the other resistances (surface reaction is 34%). Toward the end of the reaction at low concentrations the hydrogen resistance becomes negligible, and the system is again largely controlled by chemical phenomena.

In view of these results this model shows that this system has no single rate controlling step. At low temperature and near the end of the reaction the rate is largely controlled by chemical processes. At high temperature and near the beginning of the reaction where the rates are high the relative importance of the mass transfer of hydrogen is a major factor.

Kinetic Time Contributions

A measure of the relative influence of each of the process steps on the total reaction time is given by the normalized time contribution *NTC*. Figure 5 illustrates the effect of pressure and temperature on *NTC* for a change in concentration of 0.10 to 0.01 lb. moles/cu. ft. Note that at the lowest temperature and pressure the surface reaction accounts for about 73% of the time, while at the highest values for these variables the surface reaction accounts for about 52% of the time. The time contribution for the surface reaction increases with increased conversion since the surface reaction resistance becomes the predominant factor near the end of the reaction.

SUMMARY

A method has been proposed for dealing with kinetic systems for which a single rate process is not controlling. Experimental data are presented for the hydrogenation of ethyl oleate with a nickel catalyst in a stirred reactor. An empirical equation was found which fitted the concentration-time

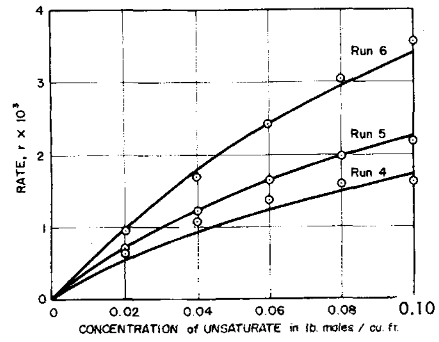

Fig. 3*b*. Comparison of Model II with experimental rate data.

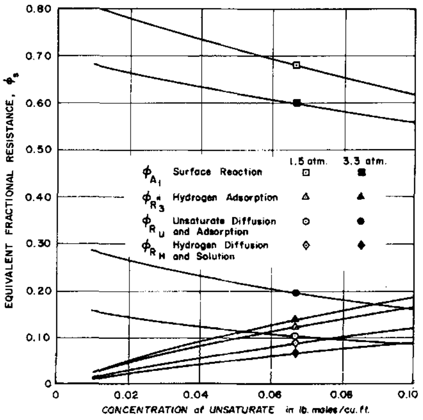

Fig. 4*a*. Equivalent fractional resistances at 120°C.

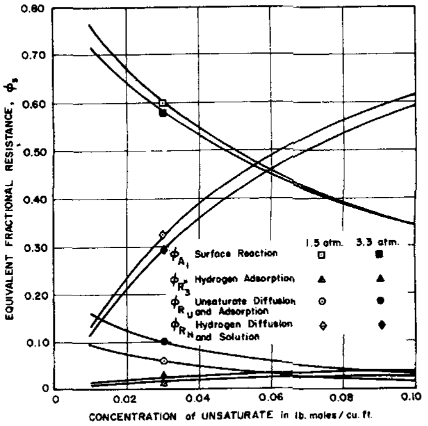

Fig. 4*b*. Equivalent fractional resistances at 200°C.

data well and was used to determine reaction rates by an analytical method. A kinetic model for this type of system is proposed, and several models employing certain simplifications were evaluated.

Model evaluation was accomplished by means of a computer-based nonlinear estimation procedure with a weighted least-squares criterion. A model was devised that described the behavior of the system within the bounds and accuracy of the data.

Concepts of equivalent fractional resistance and kinetic time contribution were proposed to facilitate interpretation of the rate behavior of the system. Analysis based on the selected model indicates that the rate is governed largely by chemical phenomena of adsorption and surface reaction at 120°C. At 200°C. and at the early stages of the reaction the mass transfer of hydrogen is the dominant rate factor.

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NOTATION

a = constant

b = constant

c = magnitude constraint value

C = concentration, lb. moles/cu.ft.

H = coefficient for relating equivalent pressure of a dissolved gas to concentration

P = pressure, atm.

r = rate, lb. moles/(min.)(cu.ft.)

R = resistance (or empirical rate value)

T = temperature, °K.

θ = time, min.

ϕ = equivalent fraction resistance

Ψ = driving function

Subscripts

A = reactant

a = absorbed on surface

B = reactant

H = hydrogen

i = region adjacent to catalyst surface (or summation index)

j = summation index

l = summation index

k = summation index

o = initial conditions

R = reaction product

s = process step

t = total

U = unsaturate (ethyl oleate)

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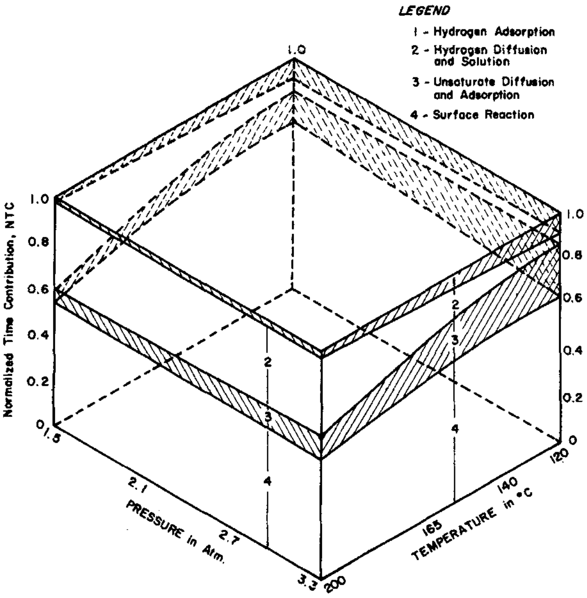

Fig. 5. Normalized time contribution for unsaturate concentration change of 0.10 to 0.01 lb. moles/cu. ft.