$17 < N_{Re} < 450,\ \ 250 < N_{Sc}$ or N_{Pr}

$$N_{Sh} \text{ or } N_{Nu} = 2 + 0.4\, N_{Re}^{1/2}\, (N_{Sc} \text{ or } N_{Pr})^{0.42} \qquad (4)$$

$450 < N_{Re} < 10{,}000,\ \ N_{Sc}$ or $N_{Pr} < 250$

$$N_{Sh} \text{ or } N_{Nu} = 2 + 0.27\, N_{Re}^{0.62}\, (N_{Sc} \text{ or } N_{Pr})^{1/3} \qquad (5)$$

$450 < N_{Re} < 10{,}000,\ \ 250 < N_{Sc}$

$$N_{Sh} = 2 + 0.175\, N_{Re}^{0.62}\, N_{Sc}^{0.42} \qquad (6)$$

Table 1 shows the average absolute deviation and the standard deviation between experimental transfer coefficients and coefficients calculated from the equations.

Hammerton and Garner (9) obtained data for carbon dioxide bubbles in glycerine. Two of these data points could be expected to represent rigid sphere mass transfer. Extrapolation of Equation (3) shows an average absolute deviation of 27% for these data which represent a Schmidt number of 1.78×10^7.

SUMMARY

Smoothed heat and mass transfer data for rigid spheres have been plotted to investigate the exponents of the Reynolds and Schmidt numbers for Equation (1). The results indicate that the exponent for the Schmidt number increases with the Reynolds number and that the exponent for the Reynolds number indicates an eddy contribution from the wake at Reynolds numbers greater than 450.

NOTATION

C_p = specific heat, B.t.u./lb.$_m$ °F.
D_p = diameter of rigid sphere, ft.
$\mathfrak{D}$ = diffusivity, sq.ft./sec.
h = heat transfer coefficient, B.t.u./sec./sq.ft. °F.
k = thermal conductivity, B.t.u./sec./sq.ft.°F./ft.
k_c = mass transfer coefficient, ft./sec.
N_{Nu} = $h\, D_p/k$, Nusselt number
N_{Pr} = $C_p\, \mu/k$, Prandtl number
N_{Re} = $D_p\, V/\nu$, Reynolds number
N_{Sc} = $\nu/\mathfrak{D}$, Schmidt number
N_{Sh} = $k_c\, D_p/\mathfrak{D}$, Sherwood number
V = slip velocity, ft./sec.
μ = viscosity, lb.$_m$/ft./sec.
ν = kinematic viscosity, sq.ft./sec.

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Catalytic Hydrogenation of Olefins

D. N. SAWYER

University of Wisconsin, Madison, Wisconsin

REIJI MEZAKI

Yale University, New Haven, Connecticut

Hougen and co-workers (*1*) proposed the competitive-noncompetitive reaction rate model to correlate the data for the catalytic hydrogenation of propylene and isobutylene. Assuming that all of the catalytic sites are available to the smaller molecules, but that the larger molecules tend to exclude one another from adjacent sites through steric hindrance, and assuming that the reaction is surface reaction rate controlling, the kinetic analysis gives rise to a rate expression consisting of two terms, called the competitive and the noncompetitive terms which are as follows:

$$r = \frac{A K_H K_U \left(p_H p_U - \dfrac{p_S}{K} \right)}{(1 + K_H p_H + K_U p_U + K_S p_S)^2} + \frac{B K_H K_U \left(p_H p_U - \dfrac{p_S}{K} \right)}{(1 + K_H p_H)(1 + K_H p_H + K_U p_U + K_S p_S)} \qquad (1)$$

For the hydrogenation of olefins, the equilibrium constant is large, and as long as the product concentration is

TABLE 1. RATE AND ADSORPTION CONSTANTS FOR THE CATALYTIC HYDROGENATION OF PROPYLENE

		Isothermal Data*	Nonisothermal Data***
A†	ΔH	15,629	18,300
	ΔS	55	64
B†	ΔH	13,144	14,050
	ΔS	42	45
K_H††	ΔH	4,208	5,350
	ΔS	16	20
K_U††	ΔH	9,022	3,600
	ΔS	23	5
Residual mean squares of rates		3.0×10^{-4}	6.1×10^{-5}

† $\ln (A \text{ or } B) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$.

†† $\ln K = \frac{\Delta H}{RT} - \frac{\Delta S}{R}$.

* reported in reference 1.

** reexamined through nonlinear least squares.

TABLE 2. RATE AND ADSORPTION CONSTANTS FOR THE CATALYTIC HYDROGENATION OF ISOBUTYLENE

		Isothermal Data*	Nonisothermal Data**
A†	ΔH	7,150	17,450
	ΔS	24	56
B†	ΔH	14,840	13,960
	ΔS	47	43
K_H††	ΔH	1,283	5,000
	ΔS	5(20 to 35°C)	15
K_U††	ΔH	7,083	18,250
	ΔS	15(20 to 35°C)	48
Residual mean squares of rates		1.1×10^{-3}	8.0×10^{-4}

* reported in reference 1.

** reexamined through nonlinear least squares.

far from the equilibrium concentration, the term p_S/K can safely be neglected. These experimenters (*1*) used pure olefin and hydrogen feed to a differential reactor. Under these conditions the term $K_S p_S$ is negligible, so Equation (1) becomes

$$r = \frac{A K_H K_U p_H p_U}{(1 + K_H p_H + K_U p_U)^2} + \frac{B K_H K_U p_H p_U}{(1 + K_H p_H)(1 + K_H p_H + K_U p_U)} \tag{2}$$

In this communication the rate and adsorption constants of the hydrogenation reactions of propylene and isobutylene are reexamined and the existing hydrogenation data of two other olefins are correlated by the competitive-noncompetitive model. A simple method is suggested as an initial step to determine if the competitive-noncompetitive model is at all feasible.

RATE AND ADSORPTION CONSTANTS FOR HYDROGENATION OF OLEFINS

In an earlier paper (*1*), the catalytic hydrogenation reactions of propylene and isobutylene over platinum-alumina catalyst were investigated. The reaction temperatures were 1.4° to 34.3°C. for propylene and 20° to 50°C. for isobutylene. In an attempt to estimate enthalpy and entropy changes of the rate and adsorption constants and to utilize all of the nonisothermally obtained data, Equation (2) was written in the following form:

$$r = \frac{\exp\left(-\frac{\Delta H_A}{RT} + \frac{\Delta S_A}{R}\right) \cdot \exp\left(\frac{\Delta H_H}{RT} - \frac{\Delta S_H}{RT}\right) \cdot \exp\left(\frac{\Delta H_U}{RT} - \frac{\Delta S_U}{R}\right) \cdot p_H p_U}{\left[1 + p_H \cdot \exp\left(\frac{\Delta H_H}{RT} - \frac{\Delta S_H}{R}\right) + p_U \cdot \exp\left(\frac{\Delta H_U}{RT} - \frac{\Delta S_U}{R}\right)\right]^2} + \frac{\exp\left(-\frac{\Delta H_B}{RT} + \frac{\Delta S_B}{R}\right) \cdot \exp\left(\frac{\Delta H_H}{RT} - \frac{\Delta S_H}{R}\right) \cdot \exp\left(\frac{\Delta H_U}{RT} - \frac{\Delta S_U}{R}\right) \cdot p_H p_U}{\left[1 + p_H \cdot \exp\left(\frac{\Delta H_H}{RT} - \frac{\Delta S_H}{R}\right)\right]\left[1 + p_H \cdot \exp\left(\frac{\Delta H_H}{RT} - \frac{\Delta S_H}{R}\right) + p_U \cdot \exp\left(\frac{\Delta H_U}{RT} - \frac{\Delta S_U}{R}\right)\right]} \tag{3}$$

A nonlinear estimation procedure (*2*) was applied to estimate these constants of Equation (3). The results are tabulated in Tables 1 and 2. In the values of residual mean squares, some differences are noticeable between the results from isothermal data and those from nonisothermal data. For adsorption equilibrium constants of isobutylene and hydrogen, the nonisothermal data gave an appropriate Arrhenius type correlation without sacrificing the goodness of fit. The point estimates of ΔH and ΔS of propylene for K_U were rather low. For these two parameters, therefore, the approximate 95% confidence regions were investigated, setting all other parameters at the values shown in Table 1. The resulting regions were, respectively, 15,000 ~ 30,000 cal./g.-mole and 3 ~ 45 cal./(g.-mole) (°K.). In order to obtain more precise estimates of these parameters, a sequential design technique developed by Box and Hunter (*3*) should be employed. No test was performed on adequacy of competitive-noncompetitive model, partly because the earlier paper (*1*) stated that no single conventional equation such as those proposed by Hougen and Watson fitted the experimental data, and partly because replicated runs, which would give an estimate of experimental errors, were not available.

The data of the catalytic hydrogenation of ethylene (*4*) on alumina-supported nickel catalyst were correlated similarly. Concerning the catalytic hydrogenation of ethylene over metals and supported-metal catalysts, the results of numerous investigations are summarized by Eley (*5*), Schuit and van Reijen (*6*), and Bond (*7*). Most of these investigations were conducted in nonflow systems and not much consideration was given to the diffusional and heat transfer effect to the hydrogenation reaction rate. For this reason the data collected from nonflow systems were not directly usable for the investigation of plausible mechanistic reaction models of hydrogenation reaction. It appears that a study of Pauls and co-workers (*4*) is an investigation which was conducted in a flow system and supplied usable data. Therefore these data were employed for the analysis. As reported in the article (*4*), the activity decay of the catalyst, due to the formation of acetylenic residue, was experienced. However, the experimenters pre-

TABLE 3. RATE AND ADSORPTION CONSTANTS FOR THE CATALYTIC HYDROGENATION OF ETHYLENE

		Nonisothermal Data
A†	ΔH	18,300
	ΔS	60
B†	ΔH	611,700
	ΔS	17
K_H††	ΔH	567
	ΔS	17
K_U††	ΔH	15,070
	ΔS	48
Residual mean squares of rates		1.9×10^{-6}

treated the catalyst and obtained the stabilized activity. One set of reaction data which were obtained by the same procedure of pretreatment was selected from the tabular material deposited with A.D.I. The experimental conditions of these data were ranged from 30° to 80°C. in reaction temperature and from 1 to 4.8 atm. in pressure.

It is true that the decay of catalyst activity causes considerable difficulty in the accurate analysis of reaction data. In many cases the true mechanism of activity change is not completely known. For the catalytic hydrogenation of ethylene Beeck (*8*) and Jenkins (*9, 10*) postulated a mechanism of the formation of the acetylenic complex which was proposed to be mainly responsible for the decay of the catalyst activity. As described by Pauls (*4*), if the activity of the catalyst is stabilized due to the slow removal rate of the carbide residue which may be produced by dehydrogenation of acetylene complex, it may be considered that a part of active sites are constantly available for the hydrogenation reaction and furthermore the concentration of available active sites remains constant in the steady state operation of the reactor.

For the hydrogenation of ethylene the best parameter estimates of the competitive-noncompetitive model are presented in Table 3. Residual mean squares are also shown. As a comparison, residual mean squares were calculated to be 8.3×10^{-6} by utilizing a power function model given by Pauls et al. (*4*) and the rate data collected at 70°C. These values are comparable. The approximate 95% confidence regions of point estimates of ΔH and ΔS of K_H were examined. They were 500 ~ 4,200 cal./g.-mole and 1 ~ 22 cal./(g.-mole)(°K.), respectively. The lack-of-fit test was not conducted owing to the lack of replicated runs. However, the residuals of rate were randomly distributed and showed no systematic correlation with any of the dependent and independent variables.

Hougen and co-workers (*11*) in an earlier study investigated the catalytic hydrogenation of mixed iso-octenes over a nickel catalyst. The range of experimental conditions for this study was: temperature, 200° to 325°C.; pressure, 1 to 3.5 atm. The reaction rate model selected as best by these investigators was

$$r = \frac{kK_HK_Up_Hp_U}{(1 + K_Hp_H + K_Up_U + K_Sp_S)^2} \tag{4}$$

Rate Equation (4) describes a typical competitive model. We reestimated the values of the rate parameters, using the competitive-noncompetitive model. The equation used was

$$r = \frac{AK_HK_Up_Hp_U}{(1 + K_Hp_H + K_Up_U + K_Sp_S)^2} + \frac{BK_HK_Up_Hp_U}{(1 + K_Hp_H)(1 + K_Hp_H + K_Up_U + K_Sp_S)} \tag{5}$$

TABLE 4. RATE AND ADSORPTION CONSTANTS FOR THE CATALYTIC HYDROGENATION OF MIXED ISO-OCTENES

		Isothermal Data*	Nonisothermal Data**
A†	ΔH	1,740	4,770
	ΔS	2.85	7
B†	ΔH	3,110	2,670
	ΔS	8.49	1
K_H††	ΔH	3,110	5,730
	ΔS	8.49	13
K_U††	ΔH	940	10,160
	ΔS	3.08	18
K_S††	ΔH	13,700	19,800
	ΔS	30.46	38
Residual mean squares of rates		2.4×10^{-5}	7.0×10^{-6}

* reported in reference 11.
** reexamined through nonlinear least squares.

Equation (5) was put into the same form as Equation (3), and the constants were estimated using all of the nonisothermal data. The results are presented in Table 4. The computed residual mean squares for isothermal and nonisothermal data indicate the superiority of the competitive-noncompetitive model over the competitive model. The point estimates of ΔH and ΔS for two forward rate constants are considerably lower than those of the other olefins analyzed. The confidence regions of ΔH of both rate constants were examined to be rather large, ranging respectively 2,000 ~ 16,000 and 1,200 ~ 15,000 cal./g.-mole. In order to obtain more precise estimates of these parameters, one should use the experimental design technique developed by Box and Hunter (*3*).

In this communication the physico-chemical significance of the point estimates tabulated in Tables 1 through 4 is not fully interpreted. It is a general observation that the heat of adsorption obtained from kinetic data is different from the value obtained from adsorption experiment. The heats of adsorption of some gases which are discussed here are reported by Bond (*7*) and Trapnell (*12*) and these values are summarized in Table 5. To find a definite correlation between these values obviously more information should be needed on surface coverage, the physical and chemical properties of the metals, and the effect of the presence of foreign gases on adsorption.

Bond (*7*) pointed out that if both competitive and noncompetitive adsorption are occurring and contributing to the rate of reaction in the manner assumed in the derivation of this equation, then as the size of the olefin molecule increases, the relative contribution of the noncompetitive term to the total rate should increase. The ratio of the noncompetitive rate constant B to the competitive rate

TABLE 5. HEAT OF ADSORPTION

Gases	Metals	Heat of adsorption Kcal/mole
H_2	Ni	25-30
H_2	Supported Pt	28
Ethylene	Ni	58

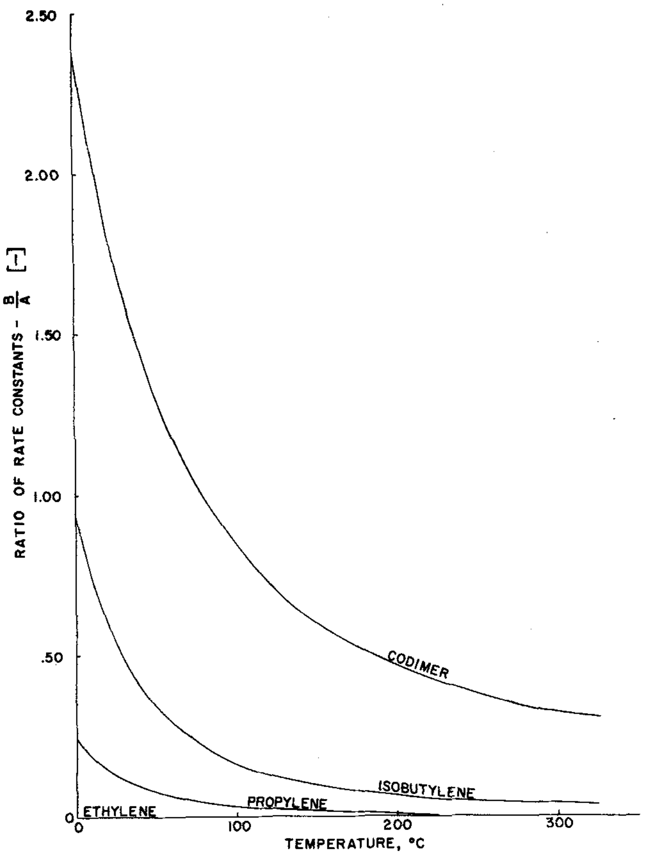

Fig. 1. The ratio of noncompetitive to competitive rate constant and reaction temperature.

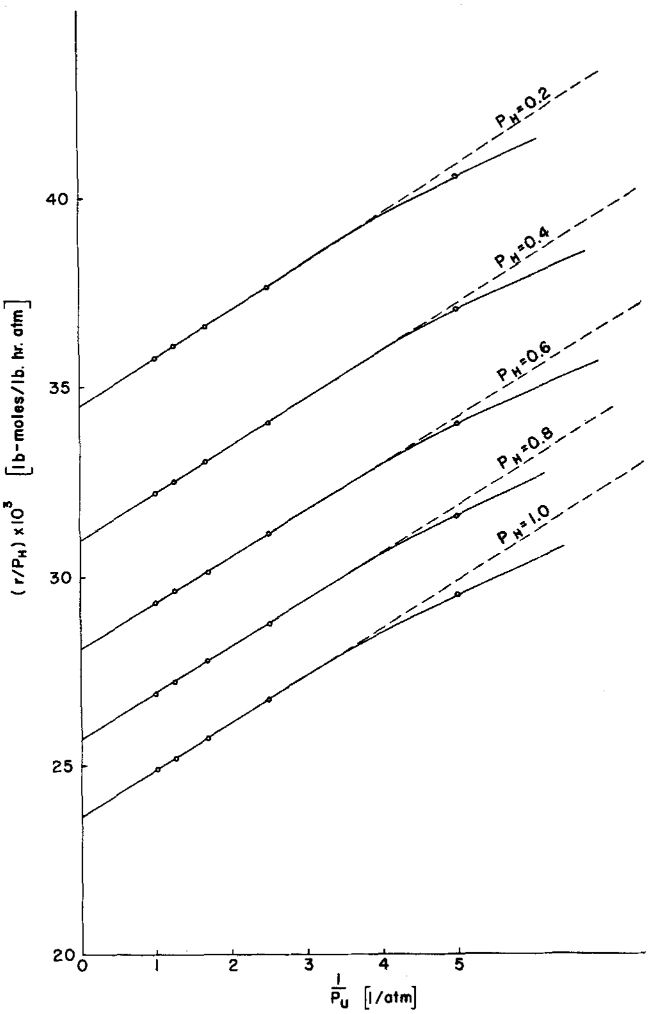

Fig. 2. Relationship between r/p_H and $1/p_U$ for propylene (1.4°C.).

constant A gives some indication of the importance of the noncompetitive term. The larger the ratio the less important the competitive term becomes. In fact, the ratio of the noncompetitive rate r_2 to the competitive rate r_1 is given by

$$\frac{r_2}{r_1} = \frac{B}{A} \cdot \frac{1 + K_H p_H + K_U p_U}{1 + K_H p_H} \tag{6}$$

According to Equation (6), the ratio r_2/r_1 is always larger than the ratio B/A. From the value of the ratio B/A, therefore, the relative importance of noncompetitive reaction may be approximately found. The use of the ratio B/A always results in a conservative estimation of the relative importance. Figure 1 presents the correlation between the ratio B/A and reaction temperature. Rate constants A and B were calculated from the values tabulated in Tables 1 to 4. Notice that this ratio for ethylene is essentially zero over the wide range of reaction temperature so that the contribution of the noncompetitive reaction would be negligible. This indicates that the ethylene molecule is small enough and that the active sites are spaced such that all active sites are available to both hydrogen and ethylene. On the contrary, the ratio B/A for codimer hydrogenation is large.

DISCRIMINATION METHOD

Because of the nonlinearizability of the rate equation, the parameters in the competitive-noncompetitive model must be estimated by nonlinear least squares. This computing procedure requires some effort to find good initial estimates for the parameters and often requires long computing time. Hence, it would be desirable to have some initial indication of whether or not this type of model is feasible before beginning the long process of parameter estimation. If the surface reaction model is found to be controlling, a simple indication of rejection of the competitive model is the deviation from linearity of the relationship between $(p_H p_U/r)^{1/2}$ and p_U, holding p_H constant. This test, however, is not sufficient to rule out the competitive-noncompetitive model, since this model may have a chance to show the same behavior as the competitive model under the circumstances shown below. In the case of olefin hydrogenation it is known that hydrogen is only weakly adsorbed, while the olefin is strongly adsorbed. Therefore if experimental conditions can be selected such that $K_U p_U >> K_H p_H$ and $K_U p_U >> 1$, the competitive-noncompetitive model will reduce to

$$r = \frac{AK_H p_H}{K_U p_U} + \frac{BK_H p_H}{(1 + K_H p_H)} \tag{7}$$

or

$$\frac{r}{p_H} = (AK_H/K_U)(1/p_U) + BK_H/(1 + K_H p_H)$$

Thus a linear plot with nonzero intercept should result if

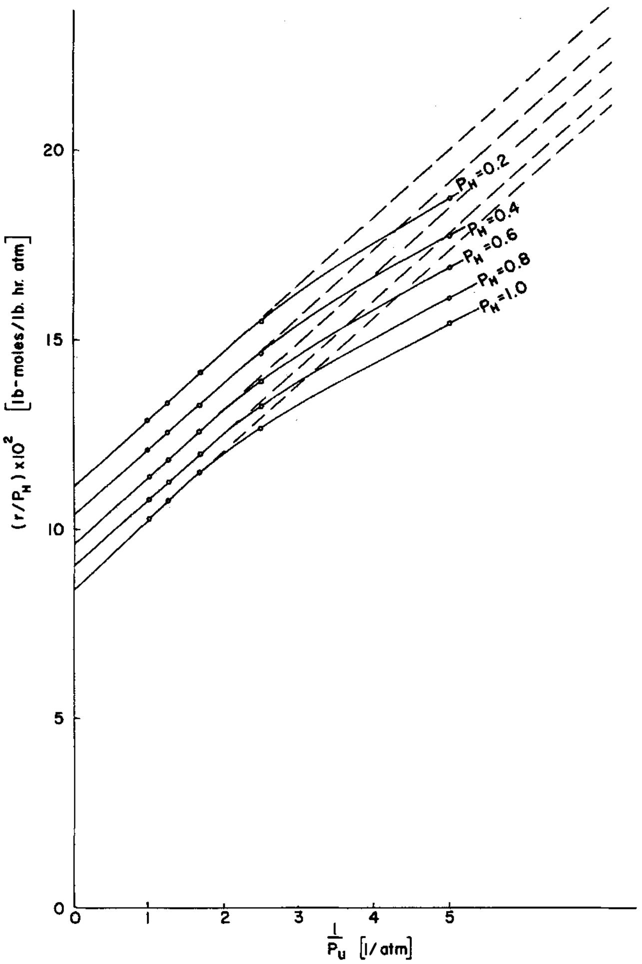

Fig. 3. Relationship between r/p_H and $1/p_U$ for propylene (21°C.).

r/p_H is plotted vs. $1/p_U$. Values of rate, r, were calculated at different temperatures for several values of p_H and p_U, using the competitive-noncompetitive model. The plots of r/p_H vs. $1/p_U$ for propylene (1.4°, 21°, 34.3°C.) and isobutylene (20°, 35°, 50°) are presented in Figures 2 to 7.[*] In these figures the circles denote the calculated values of r/p_H and the dotted lines are their asymptotes. These figures indicate that at lower temperatures and high mole fractions of the larger molecule the plots will be linear. For a purely competitive model, on the other hand, a linear plot with zero intercept should result by plotting r/p_H vs. $1/p_U$. For discrimination between the two models, a few preliminary runs at as low a temperature and as high a mole fraction of the larger molecules as possible should be taken at constant partial pressures of the smaller molecules. Needless to say, this discrimination technique is based upon the assumptions made. Furthermore, it appears that nonzero and zero intercept may be the most usable discrimination criterion for these models. If the value of nonzero intercept AK_H/K_U is very small, the method becomes insensitive. However, when investigating a solid catalyzed reaction between a component of large size and one of small size, the competitive-noncompetitive model should be given consideration.

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NOTATION

A = rate constant for competitive reaction rate, lb.-moles/(lb.)(hr.)
B = rate constant for noncompetitive reaction, lb.-moles/(lb.)(hr.)
ΔH_A, ΔH_B = enthalpy change for reaction rate, cal./g.-mole
ΔH_H, ΔH_U, ΔH_S = enthalpy change for adsorption, cal./g.-mole
k = forward rate constant, lb.-moles/(lb.)(hr.)
K = thermodynamic equilibrium constant, atm.$^{-1}$
K_H = adsorption constant for hydrogen or smaller molecule, atm.$^{-1}$
K_U = adsorption constant for olefin or larger molecule, atm.$^{-1}$
K_S = adsorption constant for saturated product, atm.$^{-1}$
p_H = partial pressure of hydrogen or smaller molecule, atm.
p_U = partial pressure of olefin or larger molecule, atm.
p_S = partial pressure of saturated product, atm.
r = reaction rate, lb.-moles/(lb.)(hr.)
r_1 = competitive reaction rate, lb.-moles/(lb.)(hr.)
r_2 = noncompetitive reaction rate, lb.-moles/(lb.)(hr.)
R = gas constant, 1.987 cal./(g.-mole)(°K.)
ΔS_A, ΔS_B = entropy change for reaction rate, cal./(g.-mole)(°K.)
ΔS_H, ΔS_U, ΔS_S = entropy change for adsorption, cal./(g.-mole)(°K.)
T = reaction temperature, °K.

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[*] Figures 4 to 7 have been deposited as document 9695 with the American Documentation Service, Library of Congress, Washington, D. C. 20402, and may be obtained for $1.25 for photo prints or 35-mm. microfilm.