Catalytic Hydrogenation of Propylene and Isobutylene over Platinum. Effect of Noncompetitive Adsorption

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A mathematical and kinetics model is presented for reactions catalyzed by solid surfaces where both competitive and noncompetitive adsorption take place, a situation that may be general in reactions between large and small molecules catalyzed by solid surfaces.

In the adsorption of large molecules steric hindrance or multiple site adsorption cause maximum surface coverage of such molecules before all sites are occupied. This does not, however, preclude further adsorption of small molecules on the remaining isolated vacant sites nor does it preclude further surface reaction. The overall reaction model for such conditions may be expressed as

$$r = r_1 + r_2 = \underset{\text{(competitive adsorption)}}{\frac{\alpha K_1 K_2 p_1 p_2}{(1 + K_1p_1 + K_2p_2)^2}} + \underset{\text{(noncompetitive adsorption of hydrogen)}}{\frac{\beta K_1 K_1 p_1 p_2}{(1 + K_1p_1)(1 + K_1p_1 + K_2p_2)}} \quad (12)$$

This particular model has been evaluated for the catalytic hydrogenation of propylene and isobutylene with the expectation that it may be useful in reactions that are of industrial importance. A reaction model based on either competitive adsorption or noncompetitive adsorption alone fails to correlate the experimental data.

In these two reactions maximum rates occur at olefin concentrations below 5 mole % and the catalytic adsorption constants for the olefins are a hundredfold greater than for hydrogen. This reaction model is similar to that proposed by Bond and Turkevich (*15*), who have further demonstrated through the deuteration of propylene that the actual mechanism of the reaction is much more complicated.

In this paper are presented the results of a study of the kinetics of the hydrogenation of propylene and isobutylene gases over a commercial supported platinum catalyst. This study was undertaken to obtain reliable kinetic data on the hydrogenation of olefins and from these to select a mathematical model of use in correlating the rates of similar reactions of commercial importance. These studies are apparently the first published on the hydrogenation of propylene and isobutylene catalyzed by platinum in a flow type of reactor.

PREVIOUS WORK

Although the catalytic hydrogenation of light olefins, ethylene in particular, has been widely studied, there still exists considerable uncertainty as to the best kinetic model for the reaction. The desired kinetic model is a mathematical expression of the reaction rate suitable for design purposes, even though it represents an oversimplification of the actual molecular mechanism involved.

Part of the uncertainty in obtaining a reliable model is due to the difficulty of obtaining rate data under isothermal conditions. The hydrogenation of olefins is highly exothermic and when catalyzed by the Group VIII metals (nickel, platinum, palladium, rhodium, and ruthenium) the reaction rate becomes exceedingly rapid. As a result mass and heat transfer resistances at the catalytic surface obscure and complicate the interpretation of the experimental data. For the hydrogenation of ethylene gas over nickel in a stirred fixed volume reactor it has been shown (*1*) that the reaction rate depends strongly on the degree of agitation of the gaseous system. An analysis of heat and mass transfer effects in the hydrogenation of propylene over nickel in a fixed-bed reactor (*2*) shows that the temperature of the catalyst surface may become several hundred degrees higher than the temperature of the ambient bulk gas stream. Another problem in the interpretation of ethylene hydrogenation data is the observed poisoning of the catalyst surface by dissociatively adsorbed ethylene (the acetylenic complex) which does not itself enter into the hydrogenation reaction. Beeck (*3*) found that about 80% of the surface of an evaporated nickel film used in ethylene hydrogenation was covered with this complex. In comparison the poisoning effect of dissociated ethylene on the more catalytically active members of Group VIII, such as platinum and rhodium, was not appreciable, and the adsorbed hydrocarbons could be quickly and completely removed by hydrogen. Formation of analogous hydrogen-deficient complexes with the higher olefins has not been reported.

In the hydrogenation of ethylene over nickel several investigators (see reference *4* for bibliography) have proposed that the reaction rate can be represented by a rate expression of the form

$$r = \frac{Ap_1p_2}{1 + Bp_2} \quad (1)$$

where A and B are temperature-dependent constants. At temperatures less than about 100°C. where $Bp_2 >> 1$ Equation (1) reduces to

$$r = (Ap_1/B) \quad (2)$$

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Beeck (*3*) hydrogenated ethylene over evaporated films of nickel, platinum, palladium, and rhodium and found in each case behavior given by Equation (2). As a result some workers (*1, 3, 5*) have concluded that ethylene hydrogenation involves the reaction of one of the components directly from the gas phase since Equation (1) can be derived on that basis.

Other investigators have obtained olefin hydrogenation data which are not in agreement with Equation (1), and indicate that the reaction occurs between competitively adsorbed olefin and hydrogen. Schuit and van Reijen (*6*) conducted ethylene hydrogenation experiments with Group VIII metals following the procedure of Beeck, except that they used supported catalysts instead of evaporated films. Their data were correlated with the relation

$$r = Ap_1^m p_2^n \tag{3}$$

where m was found to be positive but less than unity and n was negative for most of the metals studied. Studies of the hydrogenation of propylene (*7*), isobutylene (*8*), and mixed iso-octenes (*9*) over nickel have given results in agreement with the relation

$$r = \frac{\alpha K_1 K_2 p_1 p_2}{(1 + K_1 p_1 + K_2 p_2)^2} \tag{4}$$

It has been shown that if p_1 is held constant the hydrogenation rate of ethylene over platinized platinum (*10, 11*) and of iso-butylene over nickel (*12*) increases as p_2 decreases. This behavior can be explained by Equation (4) but not by Equation (1).

Bond and Turkevich (*13*) made a thorough investigation of the deuteration of propylene over a pumice-supported platinum catalyst. Although their chief goal was to study the exchange of hydrogen and deuterium at all bonds in the hydrocarbon molecule, kinetic data were also obtained. Experiments were carried out in an unagitated constant-volume reactor with the catalyst resting on the bottom of the reactor. The rate of change of total pressure was measured. The simplified reaction model was postulated to consist of two simultaneous rate-controlling surface reactions between adsorbed hydrogen and adsorbed propylene. One reaction was postulated to occur between hydrogen and olefin adsorbed competitively, while the second involved hydrogen adsorbed noncompetitively on catalytic sites not accessible to the olefin. The overall rate of reaction, expressed in terms of the drop of total pressure in mm. Hg per minute, was given as

$$-\frac{dP}{dt} = \frac{abp_1p_2}{(p_1 + bp_2)^2} + \frac{afbb'p_1p_2}{(p_1 + bp_2)(1 + b'p_1)} \tag{5}$$

The values of constants at 180°C. were reported as $a = 120$, $b = 11$, $f = 0.04$, and $b' =$ "large," that is, $b'p_1 >> 1$. The experiments of Bond and Turkevich were conducted in a batch reactor with the catalyst resting in the bottom of the vessel. Flow patterns were unknown and hence no correction could be made for resistances to heat and mass transfer. Rates were expressed in terms of the drop in total pressure and not rates of reaction per unit mass of catalyst. Under these conditions the constants in Equation (5) are not applicable to a flow reactor such as described in this present paper.

Many published reports show that the saturated hydrocarbons resulting from the hydrogenation of light olefins are not adsorbed to an appreciable extent in the presence of hydrogen and act only as diluents as far as adsorption is concerned.

Complete summaries of published hydrogenation studies are given by Eley (*14*) and more recently by Bond (*4*).

EXPERIMENTAL PRECAUTIONS

Due to the rapidity of reaction and high evolution of heat in the hydrogenation of olefins, stringent experimental precautions must be taken in order to obtain resolvable kinetic data. It is desirable that both temperature and composition gradients be negligible both within the catalyst pellet and from the exterior surface of the catalyst to the ambient fluid. In addition, temperature gradients within the catalyst bed should be kept small by operating at low conversions and by effective radial cooling in the reaction zone. To approach these conditions, it was decided to use small catalyst particles having an effectiveness factor of nearly unity and to distribute the catalyst in several small beds along the length of the reactor thus providing space for effective intercooling between beds. A long, small diameter reactor was chosen so that high mass velocities could be realized at a reasonable total flow rate.

Gas chromatography supplied an accurate means of product analysis even at very low conversion levels. As a result, differential rate data could be obtained and thereby analysis and correlation were facilitated.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A flow diagram of the experimental equipment is shown in Figure 1. The reactor body consisted of ⅜ in. O.D. (0.277 in. I.D.) stainless steel tubing 6 ft long, through which the reactant gases could be passed at mass velocities up to 3,000 lb./(hr.) (sq.ft.); Brass Swagelok ⅜ in. tees were used at the top and bottom of the reactor for introduction and removal of the gases and to allow insertion of the thermocouples. Figure 2 gives details of the closure at one end of the reactor. The reactant gases entered and left through the sides of the respective tees. Two calibrated iron-constantan thermocouples (30 B and S gauge) were enclosed in ⅛ in. O.D. stainless steel tubes 12¾ in. long, and made entry into the top and bottom of the reactor through drilled Teflon beads placed in the tees. These beads made it possible to adjust easily the vertical position of the ⅛ in. tubes. For improved temperature measurements, the bare thermocouple junction projected about ⅛ in. past the open end of the tube. The outer end of the ⅛ in. tube was closed by a brass fitting equipped with a smaller drilled Teflon bead.

Five small catalyst beds were spaced along the length of the reactor at 12 in. intervals to provide for intercooling of the flowing gases. A 16 in. preheating section was provided at the entrance to the reactor. A steel wool plug ¾ in. thick was used to support each catalyst bed. These plugs gripped the reactor wall tightly and provided an excellent support for the −45+50 mesh catalyst. The steel wool showed no catalytic activity and produced a negligible pressure drop. In order to avoid fluidization of the small catalyst particles, the gas mixture was passed downflow through the reactor. The thermocouple junctions were located directly above the top bed and directly below the bottom bed. Axial temperature profile measurements showed that at typical reaction conditions intercooling between the beds was complete.

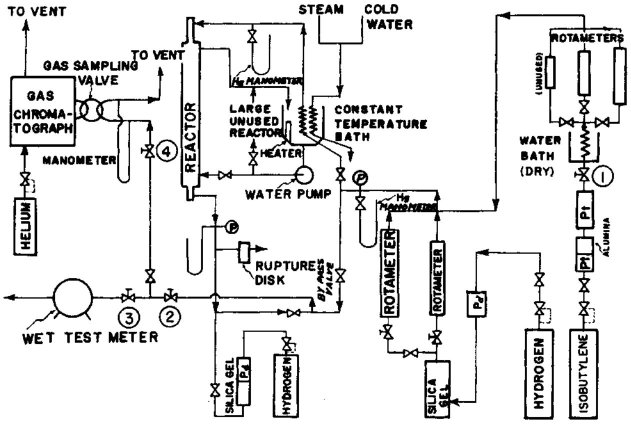

Fig. 1. Flow system during reactor operation.

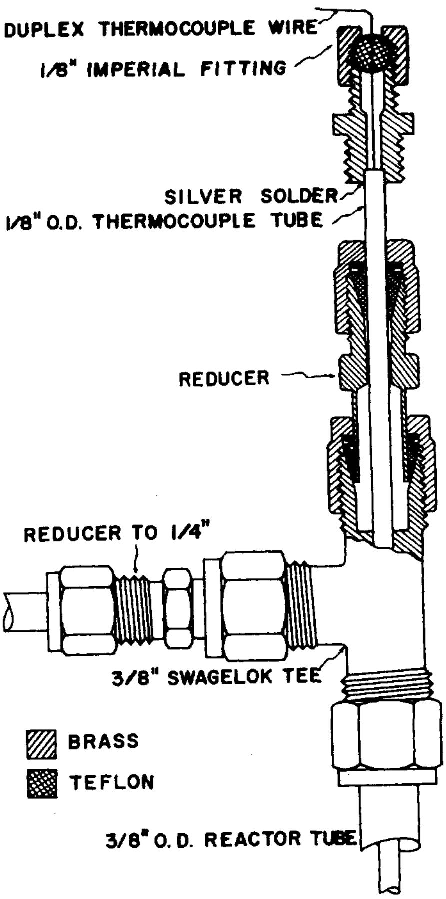

Fig. 2. Details of reactor top.

A ⅝ in. O.D. copper tube, 63½ in. long, enveloping the reactor served as a jacket through which water from a 15 gal. constant-temperature bath was circulated at the rate of ½ gal./min. At this flow rate difference between inlet and outlet water temperatures was negligible. The water bath contained a 20-ft. coil of ¼ in. O.D. stainless steel tubing through which the reactant gases were passed for preheating. The bath was heated by a 1,000 w. bayonet type of immersion heater controlled by a mercury thermoregulator. The bath temperature could be maintained constant within an accuracy of ± 0.15°C. For runs near 0°C. the water reservoir was filled with crushed ice; the water from the melting ice circulated through the reactor water jacket. Temperatures were measured by iron-constantan thermocouples connected to a Leeds and Northrup precision portable potentiometer.

Electrolytic hydrogen from a standard 200 cu. ft. cylinder was passed through a bed of palladium-on-alumina catalyst for removal of oxygen and then through a bed of silica gel to remove the water formed. The flow rate of the purified hydrogen was controlled by a Hoke needle valve and was measured by a calibrated rotameter. Chemically pure olefin (99% minimum purity) was found to contain a trace impurity (probably a sulfur compound) which poisoned the platinum catalyst. To remove this impurity, the olefin was passed through a clean-up bed containing a mixture of silica gel and 2% platinum-on-alumina catalyst. The olefin flow rate was controlled by a Hoke needle valve and measured by one of a battery of three differently sized calibrated rotameters.

The hydrogen and olefin streams were mixed and passed downflow through the reactor. Pressures at both the inlet and outlet of the reactor were measured by mercury manometers or calibrated Bourdon gauges. A Hoke needle valve in the product gas line was used to control the reactor pressure. Part of the product gas was continuously bypassed to an on-line gas chromatograph. The remainder of the gas was passed through a wet test meter and then exhausted.

A Perkin-Elmer Model 154B Vapor Fractometer using helium as the carrier gas was employed for product analysis. Twenty-five cc. samples of the product gas were analyzed for the saturated hydrocarbon (propane or isobutane) by the peak height method. The column packings used were silica gel for the propylene experiments and dimethylsulfolane on diatomaceous earth for the isobutylene. Most of the product gas samples contained between 0.10 and 0.80 mole % saturated hydrocarbon. At this concentration, the content of saturated product could be determined to a percentage accuracy of ± 2%. In order to insure accurate analysis, the instrument was calibrated daily by analyzing known mixtures of the appropriate saturated hydrocarbon mixed with nitrogen and hydrogen.

REACTANTS USED

Propylene and Isobutylene

Chemically pure grade olefins having a minimum purity of 99% were used. Propylene was supplied by Matheson and isobutylene by Matheson and Phillips. The chief impurity was found from chromatographic analysis to be the corresponding saturated hydrocarbon. Since reaction rates were calculated from the amount of propane or isobutane produced, the content of saturated hydrocarbons in a given cylinder was checked periodically. A trace impurity which poisoned the platinum catalyst was also present. This impurity was removed by a clean-up bed of platinum catalyst as previously described.

Hydrogen

Electrolytic hydrogen was supplied in 200 cu. ft. cylinders. This gas contained about 0.5% oxygen which was removed in the purification system previously described.

THE CATALYST AND ITS HANDLING

A commercial reforming catalyst, Sinclair-Baker RD-150, was used as supplied by the Sinclair Research Laboratories of Harvey, Illinois. It consisted of an alumina support in which 0.6 wt. % of platinum was uniformly dispersed. Typical properties are:

Size	1/16 in. diameter, 1/8 in. long (extruded)
Surface area	500 sq. meters/g.
Bulk density	0.79 g./cc.
Pore volume	0.56 cc./g.

This highly hygroscopic catalyst was crushed and screened to —45 +50 mesh in a nitrogen dry box. The catalyst charged to the reactor varied between 0.06 and 1.0 g., depending on the reaction rate expected. Sufficient —45 +50 mesh inert alumina (crushed Harshaw Al-0104 T-⅛ in. dried for 24 hr. at 400°C.) was mixed with the active catalyst to bring each bed to a thickness of about ¼ in. During catalyst loading the reactor was kept filled with dry nitrogen to prevent moisture pickup. After loading the entire flow system was flushed with dry nitrogen.

Catalyst Pretreatment

Before a fresh catalyst was used it was exposed to an atmosphere of stagnant hydrogen for at least 2 hr. A preliminary test showed that if a fresh catalyst charge were stored under nitrogen its initial catalytic activity was very low. However, after exposure to a hydrogen-olefin mixture for a few hours its activity was restored to its normal value. Between experimental runs the reactor and catalyst were placed under stagnant hydrogen 3 lb./sq.in. gauge.

PRELIMINARY TESTS

Blank Runs

In the absence of the catalyst, runs made with the alumina inerts and steel wool catalyst supports in place showed no measurable conversion. Thus it was established that all measurable conversion was due to the platinum catalyst.

Heat Transfer Effects

For a given reactant gas composition, it was found that the gas flow rate had no appreciable effect on the reaction rate above a certain rather sharply defined low value. Below this low value heating effects caused the reaction rate to increase rapidly as the gas velocity was decreased. The data used for correlation were taken at gas rates much above this low value. The greatest overall heat effect was encountered while hydrogenating a 15 mole % propylene–85 mole % hydrogen mixture at 34.3°C. and 1.13 atm. At a total flow rate of 6,019 cc./min. (STP) and a measured reaction rate of 0.2722 lb.-moles propane/(lb.-catalyst)(hr.) the calculated adiabatic temperature rise per bed was 1.02°C. Calculations from j_h factor indicated a temperature rise of only 0.19°C. from the ambient gas to the catalyst surface. Thus in the most extreme case the catalyst surface temperature was about 1.2°C. above that of the entering gas stream. Most data reported were obtained under conditions where temperature rises were much smaller and negligible.

Mass Transfer Effects

Mass Transfer Exterior to the Catalyst. By using the method of Yang and Hougen (*22*) for the highest reaction rates, it was determined that partial pressure drops of the reactants between the gas stream and exterior of the catalyst particle did not exceed 0.1% of their ambient values.

Diffusion Inside the Catalyst. For the small size catalyst (—45 +50 mesh) used in this investigation, calculations indicated that the value of the effectiveness factor was nearly unity and greater than 95% even at the fastest reaction rates.

Catalyst Activity Corrections

Activity of the platinum catalyst was found to decline slowly with use even with highly purified olefin. This activity decline was found to be nearly linear with time and independent of the composition of the reactant gas. In order to correct all data to the same level of activity standard reference runs were performed periodically. With a standard correction technique, duplicate runs made at different times very nearly reproduced the same corrected reaction rates. For both propylene and isobutylene duplicate runs checked within ± 3%.

EXPERIMENTAL DATA

A condensed summary of experimental data is plotted in Figures 3 to 8 for the catalytic hydrogenation of propylene and isobutylene. These data have been adjusted to constant catalyst activity and average values are given for duplicate runs.* Detailed tabulations of the uncorrected data and duplicate runs are given in the original sources (*15, 16*).

As shown in Figures 3, 4, and 5 for propylene, and in Figures 6, 7, and 8 for isobutylene, the reaction rates increase parabolically with total pressure within the experimental range. The most characteristic feature of these reactions is that at a constant pressure the maximum rate occurs at very low olefin concentrations for all experimental temperatures and pressures.

PRELIMINARY CORRELATIONS

No single conventional equation such as those proposed by Hougen and Watson (*17, 18*) fitted the experimental data. For a particular surface reaction between competitively adsorbed reactants such an equation gives

$$r = \frac{\alpha K_1 K_2 p_1 p_2}{(1 + K_1 p_1 + K_2 p_2)^2} \qquad (6)$$

If the constants in Equation (6) are adjusted to fit the data at low olefin levels, the calculated rates are only about one-third the experimental values at 45 mole % olefin.

Laidler (*19*) considered that hydrogenation proceeds with stepwise addition of two hydrogen atoms, and obtained

$$r = \frac{A(1 + Bp_2 - \sqrt{1 + 2\,Bp_2})^2\, p_1}{(Bp_2)^3} \qquad (7)$$

A nonlinear least squares fit of the data to this model gave a poorer fit than with Equation (6).

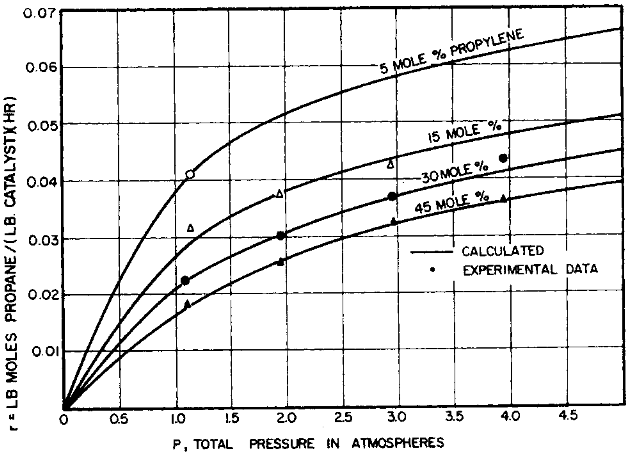

Fig. 3. Effect of total pressure on the rate of hydrogenation of propylene (at 14°C. and different compositions).

Equations (6) and (7) are based on the assumption that the catalytic adsorption constants do not vary with surface coverage. It should be noted that the authors distinguish between adsorption constants obtained from kinetic experiments from those obtained from separate adsorption experiments where total adsorption constants are obtained. According to the Temkin isotherm heats of adsorption decrease linearly with coverage where coverage is represented by the relation

$$\theta_2 = A \ln (Bp_2) \qquad (8)$$

If it is assumed that hydrogen is adsorbed according to the Langmuir isotherm while the olefin obeys the Temkin adsorption isotherm, the following relationship results where the olefin is adsorbed much more strongly than hydrogen:

$$r = \frac{\alpha K_1 p_1}{1 + K_1\, p_1} (1 - A \ln Bp_2)(A \ln Bp_2) \qquad (9)$$

According to the Freundlich isotherm heats of adsorption vary logarithmically with coverage and the reaction rate becomes

$$r = \frac{\alpha\, K_H p_H}{1 + K_H p_H} (1 - Cp_2{}^{1/n})(Cp_2{}^{1/n}) \qquad (10)$$

The best values for the constants in Equations (9) and (10) gave rates much too low at low olefin concentrations.

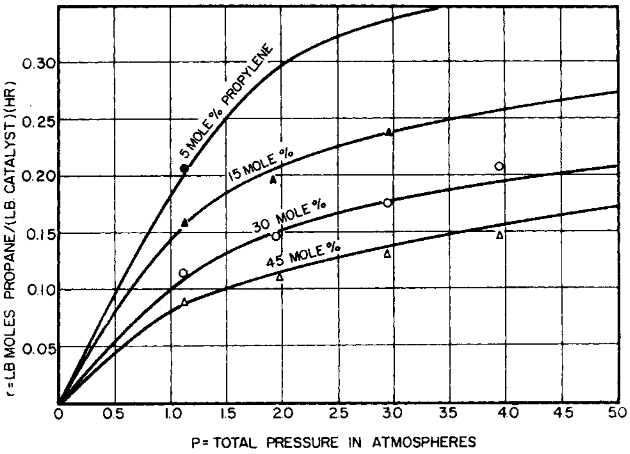

Fig. 4. Effect of total pressure on the rate of hydrogenation of propylene (at 21°C. and different compositions).

Summarized tables of experimental data have been deposited as document 8703 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.

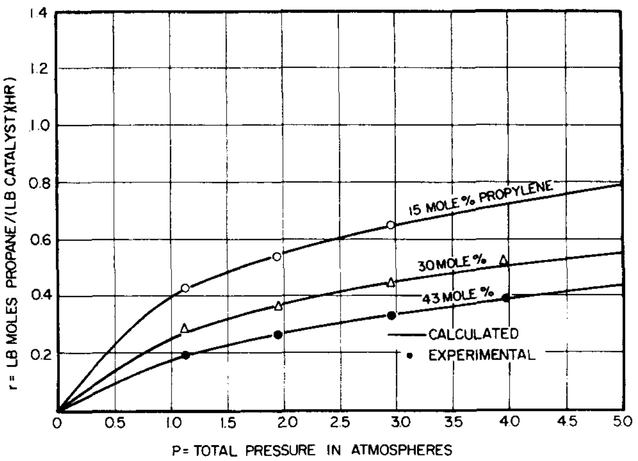

Fig. 5. Effect of total pressure on the rate of hydrogenation of propylene (at 34.3°C. and different compositions).

THE PROPOSED MODEL AND CORRELATION OF DATA

In constructing a reaction rate model involving competitive adsorption it is usually assumed the $\theta_A \to 1$ as $p_A \to \infty$, where A is one of the reactants. For the adsorption of light olefins there are several reasons why this assumption may break down.

First, it has been shown (*4*) that on metals of the platinum family, an adsorbed ethylene molecule is large enough to hinder adsorption of another ethylene on certain of the neighboring sites. Larger molecules such as propylene and isobutylene would show an even greater steric effect.

Second, it is very possible that olefin adsorption occurs with the formation of two metal-carbon bonds per molecule. If such an adsorption produces an immobile layer, Roberts (*20*) has shown that even with small molecules only about 92% of the surface sites can be occupied. The remaining isolated single sites are not usable for two-point adsorption. Thus, in the hydrogenation of propylene and isobutylene, two similar surface reactions may proceed simultaneously, one where competitive adsorption of the olefin and hydrogen occurs, and one which involves hydrogen adsorbed noncompetitively on sites not available to the olefin.

For a catalyst surface largely covered by olefin, the initial rate expression may be written as

$$r = r_1 + r_2 = \alpha\,\theta_1'\theta_2' + \beta\,\theta_1'\theta_2' \qquad (11)$$

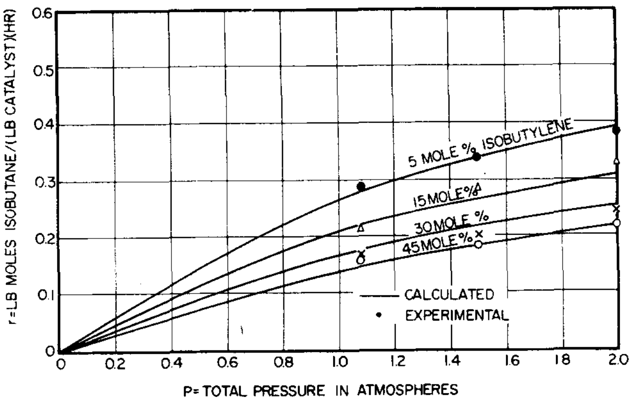

Fig. 7. Effect of pressure on the rate of hydrogenation of isobutylene (at 35°C. and different compositions).

In terms of partial pressures and adsorption constants, Equation (11) becomes

$$r = r_1 + r_2 = \frac{\alpha K_1 K_2 p_1 p_2}{(1 + K_1 p_1 + K_2 p_2)^2} + \frac{\beta K_1 K_2 p_1 p_2}{(1 + K_1 p_1)(1 + K_1 p_1 + K_2 p_2)} \qquad (12)$$

Correlation of Data

Evaluation of the four constants in Equation (12) at different temperature levels was achieved by the ALIN computer program which is based upon the transformation of parameters in nonlinear equations by the statistical procedures of Marquardt (*22*) which permit acceleration of convergence in iterative calculations. The method of transforming independent variables as used in this program is aimed at fitting experimental data with a simple functional form of the transformed variable as described by Box and Tidwell (*23*) and applied by Guttman and Meter (*24*). The convergent values in these iterative calculations are least mean square values. Values of the constants α, β, K_1, and K_2 in Equation (12) were obtained for each set of isothermal data and for each olefin. Results are tabulated in Tables 1 and 2 and plotted as a function of reciprocal temperatures in Figures 9 and 10. The values of A in Tables 1 and 2 are the pre-exponential terms in equations of the type $\log n = \log A - \dfrac{\Delta H}{4.576\,T}$ where n represents β, α, K_1, or K_2. Experimental values of rates r with calculated values in Figures 3 to 8. In Figures 11 and 12 reaction rates are plotted against composition at

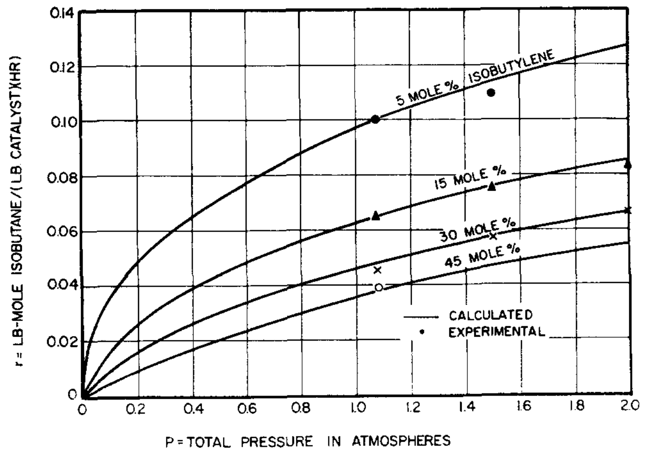

Fig. 6. Effect of pressure on the rate of hydrogenation of isobutylene (at 20°C. and different compositions).

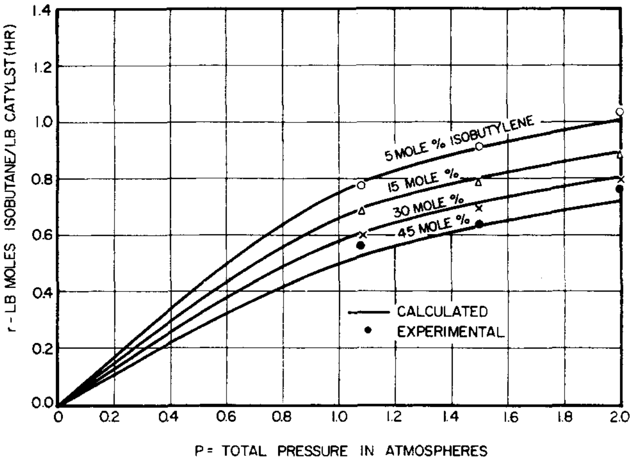

Fig. 8. Effect of total pressure on the rate of hydrogenation of isobutylene (at 50°C. and different compositions).

nearly atmospheric pressure at three temperature levels for each olefin.

Figures 13 and 14 show calculated reaction rates r_1 and r_2 and total reaction rates r for propylene and isobutylene at nearly the same conditions. For the hydrogenation of propylene at 21°C. and at 1.114 atm. (Figure 13), the calculated r_1 curve shows a maximum value of 0.1544 at 4 mole % propylene then declines sharply to 0.0225 at 50 mole % propylene; r_2 has a maximum value of 0.0639 at 20 mole % propylene then declines slowly to 0.0496 at 50 mole % propylene. The total rate r is the sum of these two with a maximum rate of 0.1991 at 4.5 mole % propylene declining to 0.0721 at 50 mole % propylene. The experimental data fit the top curve r in agreement with this interpretation. Isobutylene hydrogenation at nearly the same conditions (Figure 14) shows similar behavior. For each olefin the competitive rate r_1 shows a maximum at a very low olefin concentration, while the maximum in r_2 occurs at a much higher olefin concentration.

A tabular comparison of the calculated rate follows:

	at 21°C., 1.114 atm. Propylene	at 20°C., 1.08 atm. Isobutylene
r_1 maximum rate	0.1544	0.1012
at mole % olefin	4%	1%
rate at 50 mole % olefin	0.0225	0.00482
r_2 maximum rate	0.0639	0.0408
at mole % olefin	20%	10%
rate at 50 mole % olefin	0.0496	0.0295
$r = r_1 + r_2$ maximum rate	0.1991	0.1253
at mole % olefin	4.5%	1.5%
rate at 50 mole % olefin	0.0721	0.00343

TEMPERATURE DEPENDENCE OF CONSTANTS

As shown in Figure 9, all constants obtained for propylene hydrogenation follow Arrhenius behavior. The rate constants α and β increase uniformly with temperature, while the adsorption constants K_1 and K_2 decrease with increasing temperature as expected for adsorption.

The rate constants α and β for isobutylene plotted in Figure 10 follow Arrhenius behavior. The values of K_1 and K_2 for isobutylene hydrogenation at 50°C. are abnormally high even if runs at 45 mole % isobutylene are omitted. It is recommended that additional experimental runs be made at temperatures above 35°C. to define better the temperature trends.

TABLE 1. CONSTANTS IN RATE EQUATION (13) FOR THE CATALYTIC HYDROGENATION OF PROPYLENE

	1.4°C.	21°C.	34.3°C.
α	0.3585	1.973	7.938
β	0.0597	0.2761	0.7901
K_1	0.6510	0.4261	0.2811
K_2	144.5	32.80	26.27
Average percentage deviation	2.6%	3.1%	1.7%

For α:
$A = 0.922 \times 10^{12}$
$\Delta H_1^{\neq} = 15.629$ kcal./g.-mole (endothermic)

For β:
$A = 1.671 \times 10^{9}$
$\Delta H_2^{\neq} = 13.144$ kcal./g.-mole (endothermic)

For K_1:
$A = 2.997 \times 10^{-4}$
$\Delta H_{a1} = -4.208$ kcal./g.-mole (exothermic)

For K_2:
$A = 8.634 \times 10^{-6}$
$\Delta H_{a2} = -9.022$ kcal./g.-mole (exothermic)

COMPARISON OF ADSORPTION CONSTANTS FOR THE TWO OLEFINS

A comparison of the adsorption constants for the two olefins at nearly the same temperatures is as follows:

	Propylene hydrogenation	Isobutylene hydrogenation
K_1 (hydrogen)	0.4261 (21°C.)	0.5649 (20°C.)
	0.2811 (34.3°C.)	0.5093 (35°C.)
K_2 (olefin)	32.80 (21°C.)	122.2 (20°C.)
	26.27 (34.3°C.)	67.39 (35°C.)

The catalytic adsorption constants for propylene are nearly a hundred times larger than the hydrogen values and for isobutylene nearly two hundred times higher. The catalytic adsorption constants for hydrogen for each system are of the same magnitude, indicating that the adsorption constant of hydrogen is only slightly influenced by the olefin being hydrogenated.

A comparison of the calculated energies of activation and heats of catalytic adsorption is as follows expressed in kcalories per gram-mole:

	Propylene hydrogenation	Isobutylene hydrogenation
$\Delta H_1^{\neq}$ (reaction 1)	15.629	7.150
$\Delta H_2^{\neq}$ (reaction 2)	13.144	14.840
ΔH_{a1} (adsorption of hydrogen)	—4.208	—1.283
ΔH_{a2} (adsorption of olefin)	—9.022	—7.083

For isobutylene the values of ΔH_a are for the range 20° to 35°C. only.

CALCULATED RATIOS OF r_1/r_2 FOR THE TWO OLEFINS

The ratios r_1/r_2 of the two calculated rates at about 1 atm. pressure and at different temperature levels are plot-

TABLE 2. CONSTANTS IN RATE EQUATION (13) FOR THE CATALYTIC HYDROGENATION OF ISOBUTYLENE

	20°C.	35°C.	50°C.
α	1.085	2.043	3.391
β	0.1285	0.5543	1.361
K_1	0.5649	0.5093	0.883
K_2	122.2	67.39	115.7
Average deviation	3.1%	4.8%	2.8%

For α:
$A = 2.340 \times 10^{5}$
$\Delta H_1^{\neq} = 7.150$ kcal./g.-mole (endothermic)

For β:
$A = 1.600 \times 10^{10}$
$\Delta H_2^{\neq} = +14.840$ kcal./g.-mole (exothermic)

For K_1 (20° to 35°C.):
$A = 0.0680$
$\Delta H_{a1} = -1.283$ kcal./g.-mole (exothermic)

For K_2 (20° to 35°C.):
$A = 6.420 \times 10^{-4}$
$\Delta H_{a2} = -7.083$ kcal./g.-mole isobutylene (exothermic)

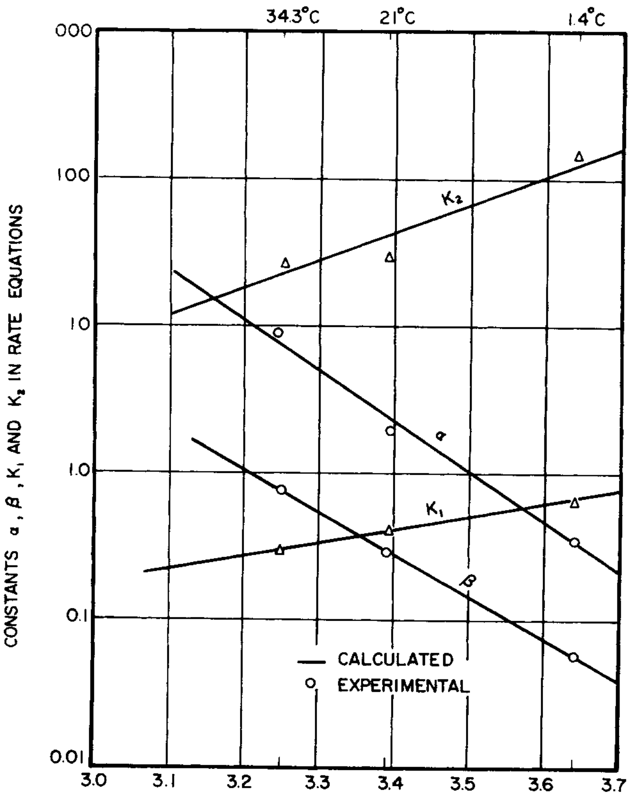

Fig. 9. Constants in rate equations as a function of reciprocal temperature for the catalytic hydrogenation of propylene.

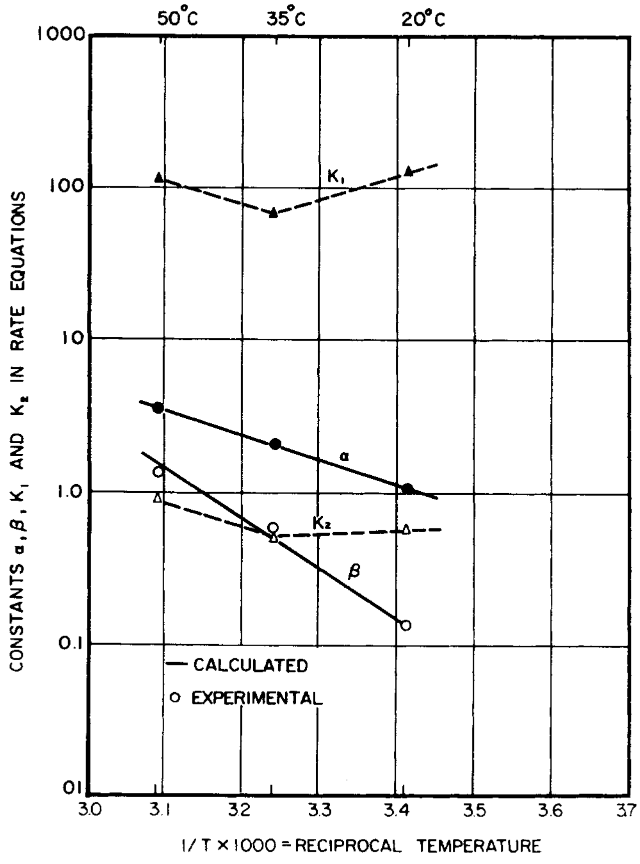

Fig. 10. Effect of reciprocal temperature on constants in rate equations in the catalytic hydrogenation of isobutylene.

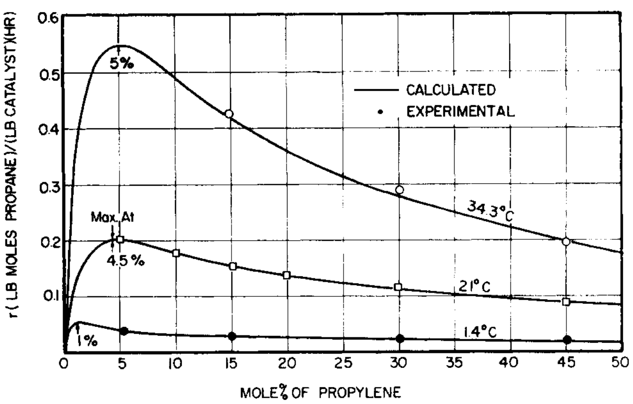

Fig. 11. Effect of gas composition in the rate of hydrogenation of propylene (at 1.114 atm. and different temperatures).

ted as a function of olefin concentration in Figure 15. At ratios exceeding unity olefin concentrations calculated are as follows:

Temperature	at 1.114 atm., propylene	at 1.08 atm., isobutylene
1.4°C.	5%	
20°C.		9.0%
21°C.	24%	
34.3°C.	37%	
35°C.		5.7%
50°C.		2.2%

For propylene the increase in r_1/r_2 with increase in temperature is consistent with a decrease in surface coverage with increased temperature as expected for exothermic chemisorption. The lower concentration for predominance of r_1 over r_2 for isobutylene is consistent with its larger size and greater steric hindrance. The contradictory temperature effect in the ratio r_1/r_2 for isobutylene is related to the anomalous temperature dependence of the adsorption constants K_1 and K_2 at 50°C. as discussed previously. (The ratio lines for isobutylene at 35°C. nearly coincide with the line for propylene at 1.4°C. For the sake of legibility the 35°C. line is omitted in Figure 13.)

APPLICATION OF MODEL TO PUBLISHED DATA

The kinetic model represented by Equation (12) seems capable of reconciling some of the conflicting interpretations of olefin hydrogenation kinetics published elsewhere.

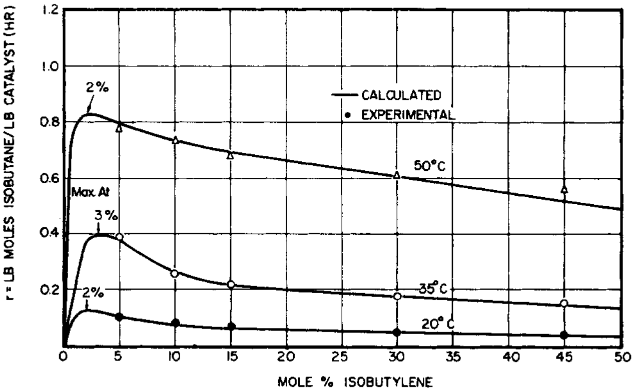

Fig. 12. Effect of gas composition in the rate of hydrogenation of isobutylene (at 1.080 atm. and different temperatures).

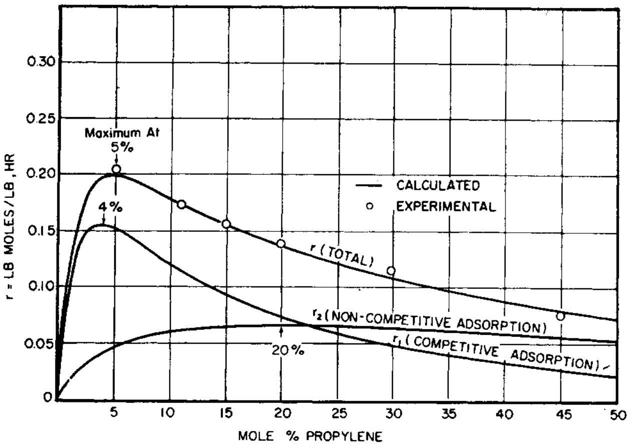

Fig. 13. Reaction model for the catalytic hydrogenation of propylene (at 21°C. and 1.114 atm. pressure).

If hydrogenation reactions are carried out over an extremely clean surface having a high heat of adsorption [for example, evaporated metal films as studied by Beeck (*3*)], the contribution of r_1 to the overall rate will be small and at low pressures where $K_1p_1 << 1$, r_2 reduces to

$$r_2 = \frac{\beta K_1 K_2 p_1 p_2}{(1 + K_2p_2)} \qquad (13)$$

in agreement with Equation (1). For the same metals when supported as in the experiments of Schuit and van Reijen (*6*) r_1 becomes a significant part of the total observed rate, and the reaction exhibits behavior in agreement with Equation (4).

The heat of adsorption for hydrogen on metals (*4*) decreases in the order Ni > Pt > Pd > Rh; a similar trend has been reported for the adsorption of ethylene (*3*). Assuming that the same order holds for kinetically determined adsorption constants, an interpretation can be made of the reaction rates of Schuit and van Reijen (*6*) wherein the value of n the ethylene exponent in Equation (3) became progressively more negative in going from nickel to rhodium in the above series. For nickel where the surface attains nearly maximum coverage by ethylene, the rate becomes nearly zero order with respect to p_2. In comparison rhodium at the same value of p_2 shows lower ethylene coverage; as a result an increase in p_2 would have a much more pronounced rate inhibiting effect than with nickel and a more negative value of n would result.

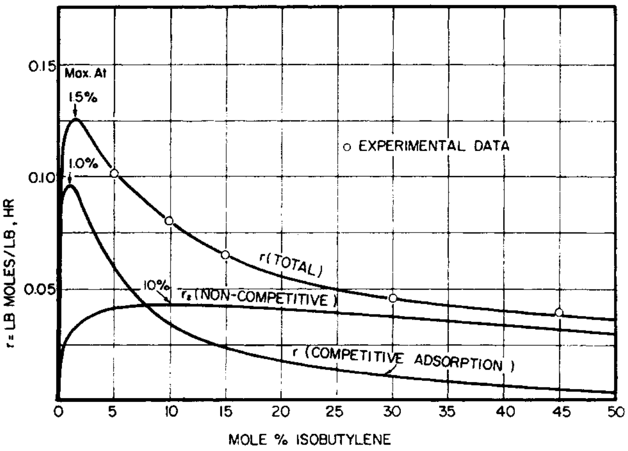

Fig. 14. Reaction model for the catalytic hydrogenation of isobutylene (at 20°C., 1.08 atm. pressure).

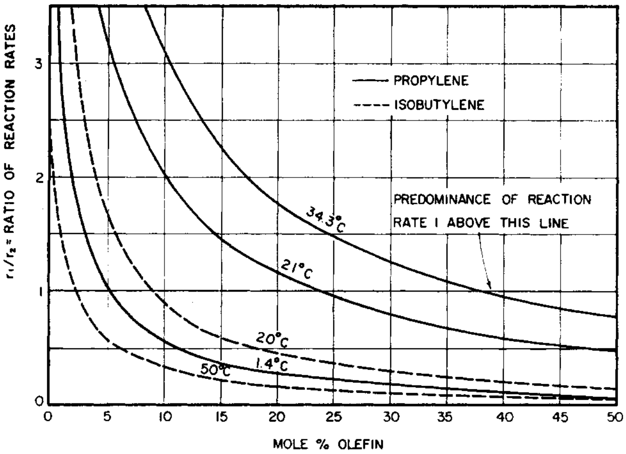

Fig. 15. Ratio of reaction rates involving competitive and non-competitive adsorption in the catalytic hydrogenation of propylene and isobutylene (at 1.1 atm. pressure and different temperatures).

CONCLUSIONS

The results of this study indicate that for reactions in which large molecules are strongly adsorbed account must be taken of steric hindrance on the catalyst surface. Although the hydrogenation of light olefins, per se, is not a commercial process the same model becomes of value for reactions between large and small molecules which are of commercial importance. The rate data given in this investigation show that over platinum propylene and isobutylene are adsorbed much more strongly than hydrogen and that isobutylene shows a greater steric hindrance than propylene.

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NOTATION

A = arbitrary constant or pre-exponential factor in Arrhenius expression
b = adsorption constant for hydrogen, Equation (5)
b' = adsorption constant for propylene relative to hydrogen, Equation (5)
B = arbitrary constant
C = arbitrary constant
f = fraction of total sites available only to hydrogen, Equation (5)
ΔH_a = heat of adsorption per mole
$\Delta H^{\neq}$ = energy of activation per mole
K_1 = kinetic adsorption constant for hydrogen
K_2 = kinetic adsorption constant for olefin
m = arbitrary constant
n = arbitrary constant
P = total pressure
p_1 = partial pressure of hydrogen
p_2 = partial pressure of olefin
r = reaction rate, moles/(unit time)(unit mass of catalyst)
r_1 = that portion of the total reaction rate due to reaction between competitively adsorbed hydrogen and olefin
r_2 = that portion of the total reaction rate involving reaction of olefin with noncompetitively adsorbed hydrogen
R = gas constant

T = absolute temperature, °K.
t = time

Greek Letters

α = rate constant
β = rate constant
θ_i = fraction of catalytic surface covered by component i
θ_1' = fraction of the sites available for competitive adsorption which are covered by hydrogen
θ_1'' = fraction of the noncompetitive sites which are covered by hydrogen
θ_2' = fraction of the sites available for competitive adsorption which are covered by olefin

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The Prediction of Liquid Mixture Enthalpies from Pure Component Properties

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The paper presents a procedure for calculating liquid mixture enthalpies, whereby a liquid heat of mixing is added to the molal average of the pure liquid enthalpies. The heat of mixing for the mixture is calculated from the heats of mixing of the binary systems at infinite dilution, which in turn are determined with a proposed molecular model for liquid mixing, and a *postulate of acceptance*. The two cases where the solute in the binary system is more volatile and less volatile than the solvent are treated separately. The case is also considered where a component of the liquid mixture is above its critical temperature; a pure liquid enthalpy is defined and justified for such pseudo liquids, and heats of mixing are then calculated as for actual liquids. Results are compared for four nonpolar binary systems, three with experimental data, and one with data calculated by other means. Data for a number of gases dissolved in water are also considered. The agreement in all cases is excellent.

An increasing amount of work is being done on the problem of predicting the enthalpy of liquid mixtures, and the need for better liquid mixture enthalpy calculation procedures becomes more urgent, particularly in the light of the complete absence of data for most systems, and the relative complexity of obtaining experimental mixture enthalpy data. The cost to the petroleum industry alone of the lack of good liquid enthalpy data was discussed in a recent article by Findlay (*1*).

Methods of calculating liquid mixture enthalpies fall into three categories: intermolecular theory, correlatory equations, and equations of state. Prigogine's (*2*) work has formed the basis of the first category, but the state of art is such that intermolecular theory has met with little success in predicting liquid nonideality. In a recent paper, Pierotti (*3*) developed a theory which appears to calculate very well the excess thermodynamic properties of the inert gases, but it breaks down when handling molecules that cannot be considered as rigid spheres. Correlatory equations all require some binary enthalpy data with which to derive empirical constants, and thence the equations may be used to extend the data over a wider temperature range, or to predict ternary or multicomponent

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