Catalytic Dehydrogenation of Cyclohexane: a Transport Controlled Model

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Experimental data and a mathematical model for the dehydrogenation of cyclohexane on a platinum-on-alumina catalyst in the presence of excess hydrogen are presented. Differential rate data were obtained by using a fixed bed flow reactor over a temperature range of 400° to 500°C., and a pressure range of 21.3 to 41.8 atm. at modified Reynold's numbers of 20 to 65. Cyclohexane concentration was varied from 16 to 25 mole %. In the development of the basic model, complete transport control of the overall reaction rate with equilibrium at the fluid external surface interface is assumed. The average deviation between experimentally determined and basic model calculated rates was 5.65%.

Modification of the model by replacing the equilibrium assumption by a crude surface rate expression resulted in a reduction in average deviation to 4.3% and the maximum deviation was reduced from 22 to 12%.

The dehydrogenation of cycloparaffins to form aromatics is of considerable commercial interest due to the importance of these reactions in the reforming of petroleum naphthas. As a specific example of this class of reactions, the dehydrogenation of cyclohexane over a platinum-on-alumina catalyst has been studied by various investigators (*1, 7, 10*). Each of these studies revealed the catalyst to be very active for this reaction at temperatures above 372°C. Heinemann, et al. (*7*) made a pilot plant yield study at 527°C. and found that near equilibrium conversions were easily obtainable. Khoobair, et al. (*10*) obtained integral reactor data from which Chambers and Boudart (*3*) interpreted the reaction rate to be severely limited by diffusional resistances. Barnett, et al. (*1*) using a catalyst with 280 sq. meter/g. surface area and operating at relatively low pressure and temperature found the reaction to be uninfluenced by external diffusional resistance. They found that for the small conversions studied the reaction was pseudo first-order. These investigators also reported that internal mass transfer rates, that is, mass transfer within the catalyst pore structure, greatly influenced the overall reaction rate at temperatures in excess of 370°C.

In studies involving solid catalysts, the influence of temperature and concentration gradients between the bulk stream and the catalyst surface must be ascertained before meaningful kinetic results can be obtained. Due to the relatively fast overall reaction rate reported for the dehydrogenation of cyclohexane over supported platinum and also to the large endothermic heat of reaction (52 kcal./g. mole), the influence of external gradients could be very great for this reaction. This system was studied in order to establish the effects of the independent variables temperature, pressure, concentration, and flow rate on the rate of conversion. The range for each of the independent variables was extended over a wide region. Bulk stream temperature was varied between 399° and 499°C.; system pressure ranged from 21.3 to 41.8 atm, cyclohexane concentration from 16 to 25 mole %, and modified Reynold's number from 20 to 65.

EQUIPMENT

The apparatus used in this study was an isothermal, fixed bed, flow reactor packed with a mixture of stainless steel pellets and catalyst pellets (platinum supported on γ alumina). The catalyst was a relatively low surface area hydrogenation-dehydrogenation type commercially manufactured by Englehard Industries, Inc. Platinum content was 0.5% by weight, pellet size was 1/8 in. × 1/8 in. (cylinders), and surface area by nitrogen adsorption was 90 sq. meter/g.

The feed system was capable of precision metering of gases and liquids since small errors in the flow quantities could cause relatively large errors in the experimental results. A positive displacement, metal diaphram pump was used for pumping the liquid feed from a calibrated feed burette. The gaseous hydrogen (supplied from commercial cylinders) was passed through a catalytic deoxygenating unit, a dehydrating unit, a filter, a mass flow transducer, and then through a precision needle valve which was used for setting the flow rate.

The two reagent streams were mixed and then conducted into a combination vaporizer-preheater coil in which the mixed feed stream was brought to reaction temperature. Following the vaporizer was a glass packed mixing chamber used to insure a homogeneous feed to the reactor. The vaporized and preheated feed was then passed through a second coil of tubing submerged within the electrically heated lead bath surrounding the reactor before entering the reaction chamber. The reactor itself consisted of a 24 in. section of 1 in. sch. 80, type 347 stainless steel pipe fitted with inlet and outlet connections for downward flow through the bed. One thermowell (1/4 in. O.D.) ran down the center of the reactor to a point immediately above a stainless steel screen used for mechanical support of the catalyst bed. After the catalyst bed was in place, a second thermowell was inserted through the opening used for charging and removing catalyst. Three thermowells were placed in the lead bath surrounding the reactor and two thermowells were placed in the lead bath surrounding the preheater. Iron constantan thermocouples which were mobile within the thermowells were used to monitor the system temperatures.

After leaving the reactor, the product gases passed through a water cooled condenser and into a vapor-liquid separator. The phase separation was made at the pressure of the system (21 to 41 atm) and at a temperature of about 21°C. Following phase separation the gaseous portion of the product stream passed through a filter and a pneumatically operated pressure control valve. The gas was metered using a wet test meter and then vented. The liquid product from the phase separator passed through a manual pressure reduction valve and into a collection reservoir from which it was periodically removed for analysis.

All metal surfaces contacted by the reactants were stainless steel, either type 316 or 347. A more detailed description of the equipment and procedure is given elsewhere (*6*).

PROCEDURE AND ANALYSIS

The reactor was charged with 0.3571 g. of catalyst (8 pellets) mixed with 650 g. of stainless steel pellets, after which the catalyst was reduced for three hours at 525°C. under a hydrogen pressure of 40 atm. Reduction was necessary only after initially charging the catalyst since the system was maintained under a hydrogen pressure for the remainder of the study. While several catalyst loadings were used in the preliminary work for establishing the mass of catalyst and other conditions required to give meaningful experimental data, one catalyst charge was used in obtaining all experimental data reported herein.

In making a run, the temperatures of the lead baths around the preheater and the reactor were brought to the desired point and maintained by manual adjustment of the voltage supplied to the resistance heaters. The reactor lead bath temperature was maintained within 1°C. of the set point during each experimental run. Upon approaching the temperature set point, the hydrogen flow rate was set using both the mass flow meter and the wet test meter for measurement. The pump was then started and set to give the required flow of cyclohexane.

Liquid product was removed and measured volumetrically at approximately ten minute intervals. Due to the high pressure at which the phase separation was made, the hydrocarbon recovery in the liquid phase averaged 96% by weight. During a run the rate of gas evolution was periodically determined from wet test meter readings.

Liquid product samples were analyzed using a gas chromatograph equipped with a thermal conductivity detector assembly. Vapor samples were not quantitatively analyzed since it was found that the hydrocarbon composition of the vapor did not differ sufficiently from the liquid phase composition to affect the overall analysis. The chromatographic column was a 6 ft. × ¼ in. tube packed with 10% di-isodecylphthalate on 60 to 80 mesh fire brick operated at 134°C. using helium as a carrier gas.

EXPERIMENTAL RESULTS

An initial investigation for the presence of a system catalytic effect or of thermal reaction showed only a very small thermal isomerization of cyclohexane to methylcyclopentane (MCP) at the lower flow rates and higher temperatures. The maximum conversion to MCP was approximately 1% at 499°C. The catalyst was found to be very specific for the conversion of cyclohexane to benzene with essentially no other reaction being catalyzed under the conditions of this study. A periodic repetition of chosen runs was made for precision analysis and to monitor catalyst activity. From these repeated runs the 95% confidence range for a single rate measurement was found to be $r \pm 0.013$ mole/(hr.) (g. of catalyst). The largest contributor to the variation was found to be the product analysis. There was no indication of catalyst deactivation during the course of the study. Experimental results are shown in Table 1.

TABLE 1. EXPERIMENTAL DATA

Run	p Atm.	T_B °C	$G \times 10^3$ g. (sec.) (sq.cm.)	X' mole %
18	21.3	399	10.5	3.53
2	21.3	427	10.5	6.15
3	21.3	427	27.5	3.02
13	21.3	471	10.8	9.43
16	21.3	471	27.6	4.83
20	21.3	471	27.5	4.88
21	21.3	499	27.5	5.93
19	28.1	399	10.3	2.63
10	28.1	427	10.4	5.16
17	28.1	427	27.8	2.47
1	28.1	471	10.5	8.92
6	28.1	471	10.5	8.97
14	28.1	471	10.5	8.83
5	28.1	471	15.0	7.16
4	28.1	471	27.5	4.74
8	28.1	471	27.3	4.73
12**	28.1	471	27.4	4.65
9	41.8	471	10.3	7.27
11	41.8	471	13.5	6.32
15	41.8	471	27.6	3.93
22	41.8	499	25.5	5.50
	All above runs $\frac{H_2}{C_6H_{12}} = 3$			
7*	28.1	471	10.9	9.00

* $\frac{H_2}{C_6H_{12}} = 5$

** Hydrocarbon feed contained 4.48% benzene

Reaction rates were calculated using the conventional expression for differential conversion data.

$$r = \frac{F}{W} x' \tag{1}$$

This expression was applicable since cyclohexane conversions were below 9.4% (mole) for all experimental runs.

As may be seen by reference to Figure 1, the reaction rate increased with increasing mass flow rate at conditions of constant bulk temperature, pressure, and feed composition. The fact that reaction rate and mass flow rate were not independent for the differential reactor was highly important since it indicated that significant gradients of

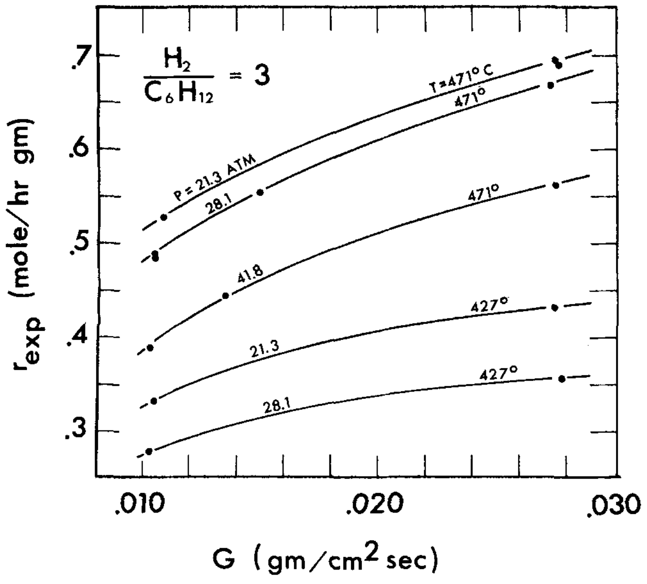

Fig. 1. The effect of mass velocity on reaction rate.

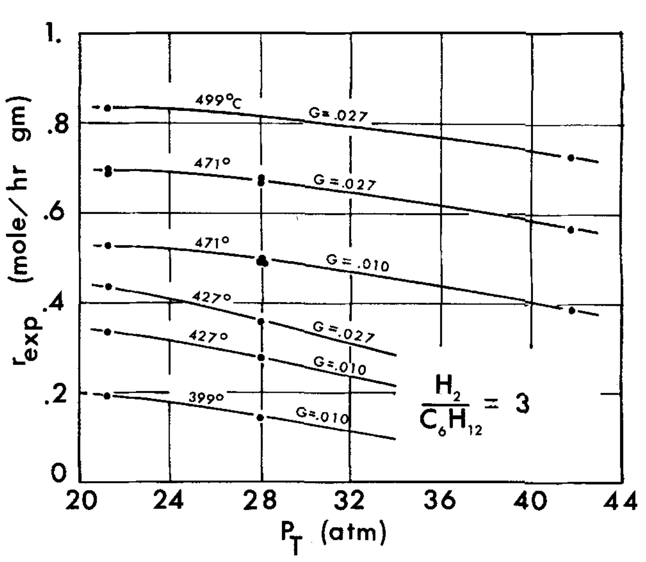

Fig. 2. The effect of pressure on reaction rate.

either temperature and/or concentration were present between the surface of the catalyst pellet and the ambient stream.

Shown in Figure 2 is the response of the reaction rate to changes in total system pressure at conditions of constant bulk temperature, mass flow rate, and feed composition. In all cases the reaction rate was diminished as the system pressure was increased. Since for small conversions most reactions are pseudo first-order, the fact that the rate decreased with increased pressure indicated that the reverse reaction was important. As the reverse reaction would appear to be insignificant at the bulk concentrations (less than 1.6% benzene), significant external gradients of temperature and/or concentration were indicated. The bulk stream properties were taken as arithmetic averages of inlet and outlet values.

MODEL DEVELOPMENT

Examination of the experimental results indicates three principal facts:

1. The overall reaction is rapid.
2. The rate of conversion is influenced by external concentration and/or temperature gradients.
3. The reverse reaction is important.

Since each of these observations suggests a large diffusional resistance, a mathematical model of the reaction was developed based on the assumption that the surface reaction rate was sufficiently fast to maintain equilibrium concentrations of each component at the catalyst interface. A very low catalyst effectiveness factor is implicit in the equilibrium assumption. Rate data developed on the basis of this assumption would represent the maximum possible reaction rate for any catalyst with the same external geometry at the same conditions of bulk temperature, pressure, composition, and flow rate.

Since equilibrium is assumed, the compositions at the surface would be related by the equilibrium constant

$$K_{\text{equil}} = \frac{\phi^3_H \, \phi_B}{\phi_C} \frac{P^3_{SH} \, P_{SB}}{P_{SC}} \qquad (2)$$

The fugacity coefficients for benzene (ϕ_B) and cyclohexane (ϕ_C) are almost identical and the fugacity coefficient for hydrogen (ϕ_H) is about unity at the conditions of this study. Thus equation (2) may be simplified to

$$K_{\text{equil}} = \frac{P^3_{SH} \, P_{SB}}{P_{SC}} \qquad (3)$$

The surface partial pressures (P_{SH}, P_{SB}, P_{SC}) are related to the bulk partial pressures by the familiar correlations for mass transfer.

$$N_H = k_{GH} \, (P_{SH} - P_H) \qquad (4)$$

$$N_B = k_{GB} \, (P_{SB} - P_B) \qquad (5)$$

$$N_C = k_{GC} \, (P_C - P_{SC}) \qquad (6)$$

If the rate of reaction at the catalyst surface is designated by r' (moles/sec./sq. cm. of external catalyst surface) then from the stoichiometry of the reaction at a condition of system steady state

$$N_H = 3\,r'$$
$$N_B = N_C = r'$$

Substituting r' into Equations (4), (5), (6) and solving for the surface partial pressures

$$P_{SH} = \frac{3\,r' + k_{GH} \, P_H}{k_{GH}} \qquad (7)$$

$$P_{SB} = \frac{r' + k_{GB} \, P_B}{k_{GB}} \qquad (8)$$

$$P_{SC} = \frac{-\,r' + k_{GC} \, P_C}{k_{GC}} \qquad (9)$$

Substituting Equations (8) and (9) into Equation (3) and solving for the reaction rate

$$r' = \frac{(k_{GC} \, K_{\text{equil}} \, P_C) - (k_{GC} \, P_B \, P^3_{SH})}{\left(\frac{k_{GC} \, P^3_{SH}}{k_{GB}}\right) + K_{\text{equil}}} \qquad (10)$$

The expression relating r and r' is

$$r = r' \times 3600 \, \frac{\text{sec.}}{\text{hr.}} \times 10.65 \, \frac{\text{sq. cm. external area}}{\text{g. catalyst}}$$

When the standard state of each substance is taken as the pure component at the temperature of the system and at unit fugacity, then the temperature dependence of the equilibrium constant is given by

$$\frac{d \ln K_{\text{equil}}}{d\,T_S} = \frac{\Delta H_R}{R\,T_S^2} \qquad (11)$$

The surface temperature of the catalyst (T_S) must be used in Equation (11) since it is at this point that the chemical equilibrium is assumed to be established. Since the heat of the reaction for this reaction is almost constant with respect to temperature over the temperature range of interest, then integration of Equation (11) yields

$$\ln K_{\text{equil}} = \frac{-\,\Delta H_R}{R\,T_S} + C \qquad (12)$$

Application of an overall heat transfer equation to the catalyst pellets yields the relationship between the bulk temperature (T_B) and the surface temperature.

$$r' \, \Delta H_R = h_G (T_B - T_S) \qquad (13)$$

Based on the assumptions made in the course of the development, the reaction rate can then be modeled by simultaneous solution of the following equations provided that thermodynamic data and heat and mass transfer coefficients can be obtained for the system:

$$T_S = \frac{h_G \, T_B - r' \, \Delta H_R}{h_G} \qquad (14)$$

$$K_{\text{equil}} = \exp\left[\frac{-\,\Delta H_R}{R\,T_S} + C\right] \qquad (15)$$

$$P_{SH} = \frac{3r' + k_{GH} \, P_H}{k_{GH}} \qquad (16)$$

$$r' = \frac{(k_{GC} \, K_{\text{equil}} \, P_C) - (k_{GC} \, P_B \, P^3_{SH})}{\left(\frac{k_{GC} \, P^3_{SH}}{k_{GB}}\right) + K_{\text{equil}}} \qquad (17)$$

HEAT AND MASS TRANSFER COEFFICIENTS

In order to successfully use the equations discussed above, accurate correlations for the prediction of heat and mass transfer coefficients must be available. Chilton and Colburn (*4*) suggested as a basis of correlation of mass transfer the equation

$$j_d = \left[\frac{k_{Gi} \, P_{fi}}{G_M}\right] \left[\frac{\mu}{\rho \, D_{mi}}\right]^{2/3}_{\text{film}} \qquad (18)$$

and of heat transfer

$$j_h = \left[\frac{h_G}{C_{p_{\text{mix}}} G_M}\right]\left[\frac{C_p \mu}{k}\right]_{\text{film}}$$

DeAcetis and Thodos (5) presented a correlation of simultaneous heat and mass transfer in which j_d was given by

$$j_d = \frac{0.725}{(N_{Re}{}^{0.41} - 1.5)}$$

and j_h by

$$j_h = 1.51\, j_d$$

These correlations are reported to be valid over a modified Reynolds number range of 10 to 2,000, where the Reynolds number is defined by $N_{Re} = (d_p\, G/\mu_{\text{Mix}})$. A discussion of the above mentioned approach to heat and mass transfer coefficients is given by Satterfield and Sherwood (*13*).

The diffusivity (D_{mi}) required to evaluate the Schmidt number ($\mu/\rho\, D_{mi}$) in Equation (18) must be the effective diffusivity of component i in the multicomponent mixture under conditions of molar flux of each component. Stewart (*2*) gives the following relationship for the effective diffusivity in terms of the various binary diffusivities

$$D_{mA} = \sum_{i=1}^{n} \frac{\left(\dfrac{P_{fA}}{P_T}\right)}{\left(\dfrac{1}{D_{Ai}}\right)\left(y_i - y_A \dfrac{N_i}{N_A}\right)} \tag{19}$$

For a chemical reaction the flux ratios (N_i/N_A) become equal to the ratios of the stoichiometric coefficients. The pressure factor (*9*) for each component was calculated from the expression $P_{fA} = P_T - P_A\ [(1 - 1 - 3)/a]$ where a is the stoichiometric coefficient of component A in the overall reaction.

Reid and Sherwood (*11*) present estimation and extrapolation procedures for transport properties of pure components, and they also present mixing rules for estimation of mixture properties. Holmes and Baerns (*8*) have presented a useful Fortran program for the prediction and estimation of transport properties. Many of the features of their program were utilized in this study for calculating the physical properties needed to evaluate the heat and mass transfer coefficients. The thermodynamic data from API project 44 (*12*) was used for calculating heat capacities and equilibrium constants.

MODEL TEST

In order to test the hypothesis of complete diffusional control of the reaction rate, the experimentally determined reaction rates were compared to rates generated by the simultaneous solution of Equations (14), (15), (16), and (17). The solution of the equations was achieved by an iterative procedure of incrementing r'. The calculations for this comparison were made using a IBM 7040 digital computer and a program described in detail elsewhere (*6*). Incorporated within the program were the equations for calculating physical properties as discussed by Holmes and Baerns (*8*) and the heat and mass transfer correlations of DeAcetis and Thodos (*5*). Since the physical

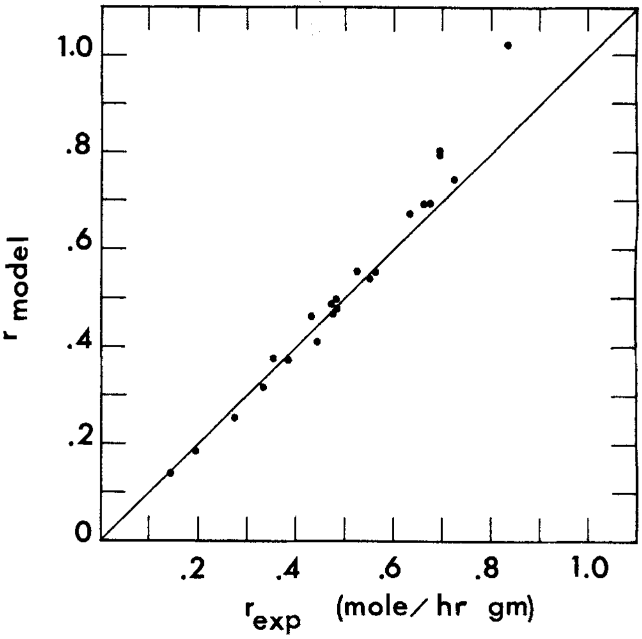

Fig. 3. Comparison of basic model and experimental reaction rates.

TABLE 2. CALCULATED DATA

Run	T_S °C	h_G cal./(sec.) (sq.cm.)(°k.)	k_{GH}	k_{GB}	k_{GC}	r_{exp}	r_{model}	
			[mole/(sq.cm.)(sec.)(atm.)] × 10^5				Equilibrium	Equation 21
18	370	0.0091	6.45	0.862	0.602	0.193	0.189	0.181
2	378	0.0094	6.60	0.890	0.620	0.334	0.312	0.297
3	383	0.0135	9.41	1.268	0.883	0.431	0.461	0.429
13	399	0.0100	7.02	0.961	0.666	0.527	0.553	0.523
16	404	0.0141	9.80	1.341	0.929	0.694	0.800	0.736
20	404	0.0141	9.84	1.343	0.931	0.696	0.799	0.735
21	420	0.0144	9.97	1.378	0.951	0.834	1.02	0.935
19	378	0.0090	4.85	0.646	0.452	0.141	0.140	0.136
10	386	0.0093	5.01	0.673	0.469	0.277	0.253	0.245
17	391	0.0135	7.20	0.968	0.674	0.356	0.378	0.362
1	404	0.0099	5.28	0.720	0.500	0.489	0.478	0.462
6	404	0.0099	5.28	0.720	0.499	0.489	0.477	0.462
14	405	0.0099	5.26	0.718	0.498	0.479	0.477	0.462
5	403	0.0111	5.89	0.804	0.557	0.553	0.541	0.521
4	406	0.0141	7.42	1.013	0.702	0.677	0.696	0.665
8	406	0.0140	7.39	1.008	0.699	0.669	0.693	0.661
12	410	0.0142	7.58	1.041	0.720	0.634	0.672	0.641
9	417	0.0098	3.51	0.477	0.331	0.387	0.374	0.368
11	415	0.0107	3.81	0.518	0.360	0.443	0.410	0.444
15	417	0.0142	5.00	0.679	0.472	0.564	0.552	0.542
22	431	0.0145	5.37	0.710	0.498	0.724	0.741	0.726
7	415	0.0118	8.62	0.947	0.706	0.486	0.498	0.475

properties required by the model were those of the film between the catalyst surface and the bulk stream, a first trial was made using the bulk values alone. The surface temperature and composition obtained from this trial were then averaged with the bulk values and a second calculation was made.

The mathematical model proved very successful in predicting the experimental rate (see Table 2 and Figure 3). The average deviation (Deviation = $|r_{\text{model}} - r_{\text{exp}}|/r_{\text{exp}}$) between the experimentally determined rate and the model calculated rate was 5.65% and elimination of three experimental points lowered the average deviation to 3.75%. The maximum deviation was 22.9%.

Of the experimental conditions tested, the model was least effective at the combined condition of low pressure, high mass flow rate, and high temperature. Under these conditions the reaction model consistenly gave higher rates than were measured experimentally. This trend is shown in Figure 4. In each case where the model failed to give accurate reaction rates, the ratio of the surface partial pressures (calculated using the experimental reaction rate) of hydrogen, benzene and cyclohexane was less than the calculated surface equilibrium constant

$$\frac{P^3_{SH}\,P_{SB}}{P_{SC}} < K_{\text{equil}}\ (\text{at}\ T_S)$$

These calculations would indicate that the reaction was not rapid enough to maintain chemical equilibrium at the catalyst surface under the above mentioned conditions.

For irreversible chemical reaction it is well known that the reaction rate increases rapidly with temperature while the increase in the heat and mass transfer coefficients with temperature is much less pronounced. Therefore the statement is commonly made that if a reaction is diffusion controlled at one temperature it should be diffusion controlled at higher temperatures.

In order to further investigate this apparent contradiction, the temperature response of the model was calculated at a constant bulk composition and mass flow rate. This response is shown in Figure 5. By assuming a rate expression of the form $r_{\text{model}} = \overline{A}\ exp\ [-E/RT_S]P_{SC}$ and fitting this expression to the constant pressure lines of Figure 5, it is found that the surface temperature response of the model is equivalent to an activation energy of 57 to 59 kcal./mole and is essentially independent of pressure. The activation energy of the forward rate constant for this reaction with a similar catalyst was reported by Barnett, et al. to be 41.6 kcal./mole or less depending on the degree of internal diffusional resistance. Thus due to the requirement set forth as a basis of the analysis that chemical equilibrium exists at the gas-solid interface, the increased deviation at 21.8 atm, and 499°C. is understandable. Because of the large endothermic heat of reaction the value of K_{equil} changes drastically with temperature. At a combined condition of higher temperature and lower pressure the reaction rate necessary to meet the equilibrium requirement is so large that surface kinetic and internal diffusion resistances become significant.

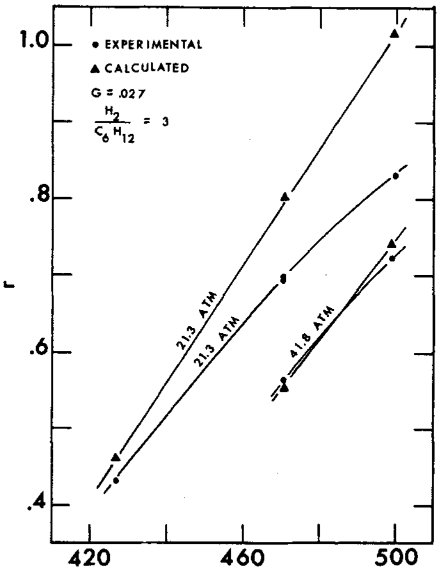

Fig. 4. Comparison of basic model and experimental reaction rates at higher bulk temperatures and higher mass flow rates.

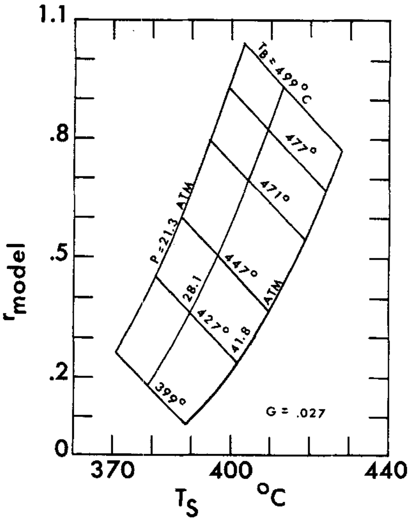

Fig. 5. Basic model temperature response.

Since kinetic resistances were believed to be significant at the combined extreme conditions, the assumption of surface equilibrium was relaxed by modification of the basic model to include a crude surface rate term. If Equation (3) is replaced by the following surface rate expression

$$r'A = k_f\,P_{SC} - \frac{k_f}{K_{\text{equil}}}\,P_{SB}\,P^3_{SH} \tag{20}$$

and Equations (8) and (9) are substituted for P_{SC} and P_{SB} the result after rearrangement is

$$r' = \frac{(k_{GC}\,K_{\text{equil}}\,P_C) - (k_{GC}\,P_B\,P^3_{SH})}{\left[\dfrac{P^3_{SH}\,k_{GC}}{k_{GB}}\right] + K_{\text{equil}}\left[1 + \dfrac{k_{GC}\,A}{k_f}\right]} \tag{21}$$

Comparison of Equations (10) and (21) reveals that the only difference between the two is that in Equation (10)

$$\frac{k_{GC}\,A}{k_f} \approx 0$$

Simultaneously solving Equations (14), (15), (16), and (20) for the reaction rate revealed that a small but significant reduction in the deviation between experimental and calculated reaction rates could be achieved. When k_f was taken to be 554 exp $(-\ 20{,}000/RT_S)$ the average deviation was 4.3% and the maximum was 12% (see Table 2). Because of the near equilibrium situation the calculated reaction rate was insensitive to variation in k_f. Values of 2.36×10^9 exp $[-40{,}000/RT_S]$ gave only slightly different calculated rates.

The improvement in model fit by incorporation of the surface kinetic term was insignificant except at conditions of highest rate where surface equilibrium is most difficult to maintain. While the average deviation was reduced only from 5.65 to 4.3%, the reduction in the maximum deviation from 22 to 12% illustrates the utility of this approach in the near equilibrium situation. The insensitivity of the overall model to variations in k_f permits the use of inexact surface rate expressions with good results under such conditions.

As previously noted the assumption of equilibrium or near equilibrium concentrations at the external catalyst surface implies a very low catalyst effectiveness factor. While the near equilibrium experimental data can not yield rate constants of sufficient accuracy for the precise calculation of effectiveness factors, they may be roughly estimated using reasonable values of k_f. The equation of Smith and Amundson (*14*) for calculation of the Thiele modulus (ϕ_s) for the first order isothermal reversible reaction $A \leftrightarrows B$ is

$$\phi_s = 3L\sqrt{\frac{k'_f\,(K_{\text{equil}} + 1)}{D_{\text{eff}}\,K_{\text{equil}}}} \qquad (22)$$

and the effectiveness factor (η) is given by

$$\eta = \frac{3}{\phi_s}\left[\frac{1}{\tanh\phi_s} - \frac{1}{\phi_s}\right] \qquad (23)$$

For the reaction under consideration the hydrogen is present in large excess and its diffusivity is much higher than that of the other components, making the hydrogen concentration very nearly constant. It was assumed to be so within the catalyst pellets, and Equation (22) was used in the following form

$$\phi_s = 3L\sqrt{\frac{k'_f\left(\dfrac{K_{\text{equil}}}{P^3{}_{SH}} + 1\right)}{D_{\text{eff}}\left(\dfrac{K_{\text{equil}}}{P^3{}_{SH}}\right)}} \qquad (24)$$

Using these equations and the value for k_f of $k_f = 554$ $(-\,20{,}000/RT_S)$ the calculated effectiveness factor ranged from a low of .025 to a high of .068. These extremely low effectiveness factors are therefore consistent with the original assumption of surface equilibrium.

The engineering implications of the results of this work are considerable in view of the fact that the reaction is typical of an important commercial process. Analysis of the data on the basis of boundary layer heat and mass transfer with only external catalyst area active resulted in good agreement between calculated and experimental rates of reaction. Even better agreement was obtained by incorporation of a crude surface kinetic term into the system of equations. For reaction systems in which the reaction is fast, catalyst geometry is well defined and accurate thermodynamic data are available, the method of analysis used herein should be quite promising in the development of descriptive process models. For such systems, accurate surface kinetic models are not only difficult to develop, they add little to the effectiveness of the overall model in describing the effect of process variables on the reaction rate.

Certainly for reactions in which significant external heat and mass transfer effects are expected, calculation of maximum possible rates of reaction should be made in the initial stages of model development.

CONCLUSIONS

As demonstrated by the work reported here, the influence of diffusional resistances may be very great for some catalytic reactions. Furthermore these resistances, which are often neglected in kinetic studies, are readily treatable by available methods and correlations. When the reaction system was modeled using an assumption of surface equilibrium it was found that agreement between calculated and experimental results was very good except at a combined condition of high temperature and low pressure where reaction rate was fastest.

By modifying the model to include an approximate surface rate equation rather than the assumption of surface equilibrium, a small but significant improvement resulted. The average deviation of only 4.3% between calculated and experimental results tends to encourage confidence in the analysis of the reaction.

ACKNOWLEDGMENT

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NOTATION

A = external area of catalyst = 10.65 sq. cm./g.
$\overline{A}$ = frequency-factor constant in Arrhenius equation
C = constant of integration
C_p = heat capacity, cal./mole °C.
D_{eff} = effective diffusion coefficient for a porous solid, based on total cross section normal to direction of diffusion, sq. cm./sec.
D_{ij} = binary diffusivity, sq. cm./sec.
D_{mi} = effective diffusivity of component i in mixture, sq. cm./sec.
d_p = effective diameter of packing, cm.
E = activation energy, cal./mole
F = flow rate of cyclohexane, mole/hr.
G = superficial mass velocity based on total cross section of reactor, g./(sec.)(sq. cm.)
G_M = superficial molar velocity based on total cross section of reactor, mole/(sec.) (sq. cm.)
ΔH_R = heat of reaction, cal./mole
h_G = heat transfer coefficient based on external pellet area, cal./(sec.) (sq. cm.) (°K.)
j_d = mass transfer factor
j_h = heat transfer factor
k = thermal conductivity, cal./(hr.) (cm.) (°K.)
K_{equil} = equilibrium constant
k_f = forward rate constant, mole/(sec.) (atm.) (g. of catalyst)
k'_f = intrinsic forward rate constant/unit volume of catalyst pellet, sec.$^{-1}$
k_{Gi} = mass transfer coefficient for component i, moles/(sec.) (sq. cm.) (atm.)
L = length parameter in Thiele modulus; L is the ratio of catalyst volume to outside surface area, cm.
N_i = molar flux of component i, moles/(sec.) (sq. cm.)
P_i, P_{si} = partial pressure of component i bulk and surface, atm.
P_{fi} = pressure factor, atm.
P_T = total system pressure, atm.
R = gas constant
$r_{\text{exp}}, r_{\text{model}}$ = reaction rate, experimentally measured and calculated respectively, moles/(hr.) (g. of catalyst)
r' = reaction rate, moles/(sec.) (sq. cm. of catalyst external area)
T_B = bulk temperature °K.
T_S = catalyst surface temp °K.
W = weight of catalyst. g.
x' = conversion, fraction of cyclohexane converted
y_i = mole fraction of component i

Greek Letters

η = catalyst effectiveness factor
μ = viscosity
ρ = density, g./cc.
ϕ = fugacity coefficient
ϕ_s = Thiele modulus

LITERATURE CITED

1. Barnett, L. G., R. E. C. Weaver, and M. M. Gilkeson, *AIChE J.*, 7, 211 (1961).
2. Bird, R. B., W. E. Steward, and E. N. Lightfoot, "Transport Phenomena," John Wiley, New York (1960).
3. Chambers, R. P., and M. Boudart, *J. Catalysis*, 3, 141 (1966).
4. Chilton, T. H., and A. P. Colburn, *Ind. Eng. Chem.*, 26, 1183 (1934).
5. DeAcetis, J., and G. Thodos, *ibid.*, 52, 1003 (1960).
6. Graham, R. R., MS thesis, Texas Tech., Lubbock (1967).
7. Heinemann, H., G. A. Mills, J. B. Hattman, and F. W. Kirsch, *Ind. Eng. Chem.* 45, 130 (1953).
8. Holmes, J. T., and M. G. Baerns, *U. S. Atomic Energy Commission Report ANL-6951*, Argonne Nat. Lab., Argonne, Ill. (1964).
9. Hougen, O. A., and K. M. Watson, "Chemical Process Principles, III." Wiley, New York (1947).
10. Khoobiar, S., R. R. Peck, and B. J. Reitzer, *Proc. Intern. Congr. Catalysis, 3rd*, Amsterdam (1964).
11. Reid, R. C., and T. K. Sherwood, "The Properties of Gases and Liquids," McGraw-Hill, New York (1958).
12. Rossini, F. D., et al. *Am. Petrol. Inst.*, Project 44, 4 (1953).
13. Satterfield, C. N., and T. K. Sherwood, "The Role of Diffusion in Catalysis," Addison-Wesley, Palo Alto, California (1963).
14. Smith, N. L., and N. R. Amundson, *Ind. Eng. Chem.*, 43, 2156 (1951).

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A Generalized B-W-R Equation of State

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The Benedict-Webb-Rubin Equation of State has been generalized by expressing the eight constants as functions of critical pressure, critical temperature, and acentric factor. An evaluation of the resulting generalization against the observed P-V-T data of thirteen hydrocarbons and carbon dioxide shows 0.3 to 2.0% average deviations of the calculated pressures from the observed, as compared with 0.2 to 1.4% when using the individual (that is, nongeneralized constants for each component. Standard errors of estimate for 1,464 experimental data points were 0.0089 for the proposed generalization vs. 0.0084 for the original B-W-R Equation.

As originally developed and applied to the computation of thermodynamic properties of hydrocarbons and their mixtures, the Benedict-Webb-Rubin (*7, 8*) Equation of State employed a set of eight individual constants for each hydrocarbon. These eight constants were derived empirically by fitting the equation to experimental P-V-T data.

Efforts to develop generalizations for the prediction of these constants have had only limited success (*9, 13, 17, 28*). Canjar, et al. (*9*), correlated the constants with critical temperature. Hansen (*13*) used critical temperature to correlate generalized constants reduced with critical volume. Opfell, et al. (*17*), used critical temperature, critical pressure, critical volume and acentric factor (*19*) in their generalization. Su and Viswanath (*28*) used the critical temperature and critical pressure in a generalization similar to the Su-Chang (*27*) treatment of the Beattie-Bridgeman Equation.

These three generalizations employed one, two, and four properties of the components. In the generalization study reported here, three of these properties, the critical temperature, the critical pressure, and the acentric factor, have been employed in the development of reduced constant relationships for the B-W-R Equation.

CRITICAL TEMPERATURE AND PRESSURE EFFECTS

The first step in the study was to replace the pressure, temperature and density parameters of the original B-W-R Equation with reduced parameters. This was done in the way suggested by Su, et al. (*27, 28*), starting with the original specific form of the B-W-R, namely:

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^3}{T^2}(1 + \gamma d^2)\exp(-\gamma d^2) \quad (1)$$