LITERATURE CITED

1. Lee, E. S., *Ind. Eng. Chem. Fundamentals,* 3, 373 (1964).
2. Bellman, R., and S. E. Dreyfus, "Applied Dynamic Programming," Princeton Univ. Press, New Jersey (1962).
3. Fan, L. T., "The Continuous Maximum Principle," John Wiley, New York (1966).
4. Courant, R., *Bull. Am. Math. Soc.,* 49, 1 (1943).
5. Tompkins, C. B., "Methods of Steep descent," *Modern Mathematics for the Engineer,* E. F. Beckenbach, ed., Chap. 18, McGraw-Hill, New York (1956).
6. Box, G. E. P., and K. B. Wilson, *J. Roy. Statist. Soc. Ser.,* B13, 1 (1951).
7. Fletcher, R., and C. M. Reeves, *Computer J.,* 7, 149 (1964).
8. Arrow, K. J., L. Hurwicz, and H. Uzawa, "Studies in Linear and Nonlinear Programming," Stanford Univ. Press, Stanford, Calif. (1958).
9. Wolfe, P., "Methods of Nonlinear Programming," *Recent Advances in Mathematical Programming,* R. L. Graves and P. Wolfe, ed., McGraw-Hill, New York (1963).
10. Rosen, J. B., *J. Soc. Ind. Appl. Math.,* 8, 181 (1960), 9, 514 (1961).
11. Hestenes, M. R. and E. Stiefel, *J. Res. Natl. Bur. Std.,* 49, 409 (1952).
12. Kelley, H. J., *Am. Rocket Soc. J.,* 30, 947 (1960).
13. ———, "Methods of Gradients," *Optimization Techniques,* G. Leitman, ed., Academic Press, New York (1962).
14. Bryson, A. E. and W. F. Denham, *J. Appl. Mech.,* 29, 247 (1962).
15. Bliss, G. A., "Lectures on the Calculus of Variations," Univ. of Chicago Press, Illinois (1946).
16. Aris, R., A. L. Nemhauser, and D. J. Wilde, *AIChE J.,* 10, 913 (1964).
17. Niederlinski, A., *ibid.,* 12, 805 (1966).

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The Effects of Internal Mass Transfer on the Hydrogenation of Benzene Over Nickel-Alumina Catalyst

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The influence of mass transfer on reaction kinetics, within the porous structure of a catalyst, was investigated during the hydrogenation of benzene. The temperature range for a nickel catalyst at atmospheric pressure was 99 to 160°C. The rate equation and the apparent activation energy on a cylindrical catalyst pellet (4.5 mm. in diameter and 5.5 mm. in height) and on the catalyst particles (0.5 to 0.63 mm. in diameter) were evaluated.

The effect of internal diffusion on the dependence of the reaction rate, on the temperature, and on the partial pressures of benzene and hydrogen was satisfactorily explained by means of theoretical relations. The values of the effective diffusion coefficient of benzene were compared by calculating the kinetic data and temperature difference in the cylindrical pellet.

Many papers have been published relating to the theoretical effect of internal diffusion on the rate of a catalytic reaction. Few papers, however, aim at verifying such theories. The object of this paper (*4*) is to verify the theory of mass transfer effect on the reaction order within the porous structure of a catalyst, that is, on the rate equation and on the temperature dependence of the catalytic reaction rate. Furthermore, a kinetic measurement was made of the effective diffusion coefficient of a reaction component in the porous structure and its value was compared with that of the temperature difference in a catalyst pellet.

EXPERIMENTAL PROCEDURE

Reaction Used

The reaction chosen for this study was the hydrogenation of benzene on a nickel catalyst in the benzene-hydrogen-nitrogen mixture at atmospheric pressure and 99 to 160°C. The partial pressure in the inlet stream varied from 22 to 93 Torr for benzene and 100 to 700 Torr for hydrogen. The conversion of benzene to cyclohexane in the outlet stream varied from 5 to 95%.

Catalyst

An industrial nickel-alumina catalyst was used containing 49% nickel and 4.3% graphite by weight (*1*). The specific area per unit mass was 256 sq.m./g., the apparent pellet density was 1.17 g./cc., the mean solid density was 3.84 g./cc., the micropore volume (pore size below 150 Å.) was 0.308 cc./g., the macropore volume (pore size above 150 Å.) was 0.288 cc./g., and the thermal conductivity was 3.9×10^{-4} cal./(cm.)(sec.)(°C.). A mean pore radius of 50Å. was determined from the specific surface, the apparent pellet density, and the mean density of a solid phase catalyst.

Before carrying out the measurements, the catalyst was activated by heating it in a hydrogen stream (20 liters/hr.) to 180°C. for 3 hr. The effective thermal conductivity of the catalyst pellet was determined experimentally as described by Masamune and Smith (*6*).

Apparatus

A schematic diagram of the experimental apparatus is shown in Figure 1. Kinetic measurements were carried out in a recycle reactor. The hydrogen and nitrogen were metered by flow meters (*2*), the mixed and combined feed streams were purified in a series of columns. The first column was purified by phosphoric acid on a kieselguhr to absorb alkaline impurities, in the second column a copper catalyst was used

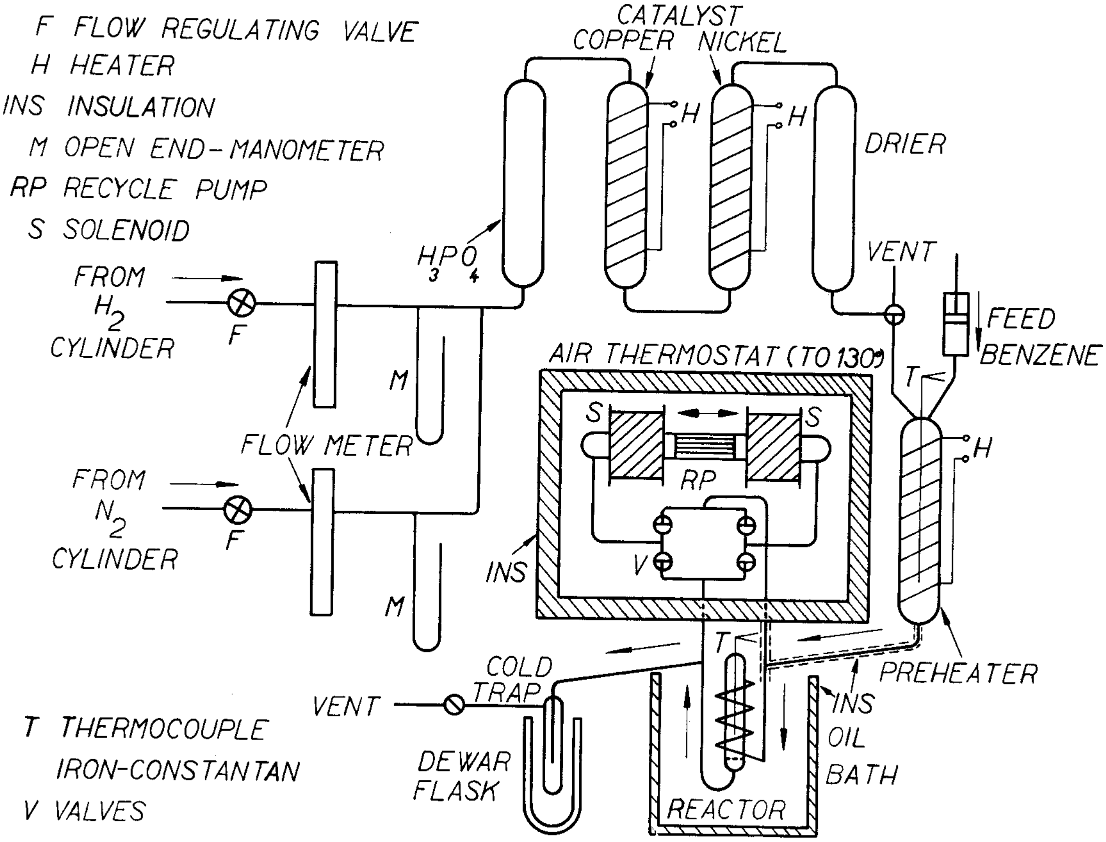

Fig. 1. Schematic diagram of experimental apparatus.

to convert traces of oxygen to water, the third column had a nickel catalyst to adsorb catalytic poisons, and in the fourth column a molecular sieve was used to adsorb water.

Benzene was fed into the reactor by a special apparatus consisting of a hypodermic syringe pressed by a servomotor. The reaction mixture was circulated by means of a magnetic circulating pump having a capacity of 1,000 liters/hr. The pump was heated in an air thermostat to 130°C. The reactor consisted of a preheating section and a 1.68 cm. diameter section containing the catalyst. The arrangement of the catalyst in the reactor is shown in Figure 2.

In order to maintain the desired reaction temperature, the reactor was surrounded by a heated silicon oil bath. The oil in the bath was heated electrically and the temperature was controlled automatically up to ± 0.5°C. The temperature of the reaction mixture was measured by iron-constantan thermocouples in a glass well located on the reactor axis. The outlet gas stream was cooled to —78°C. the condensed benzene and cyclohexane mixtures were analyzed by determining their refractive indexes. These indexes were measured by means of an Abbe refractometer with a precision of ±0.1% error in conversion.

Temperature Difference Determination

The temperature differences within the catalyst pellets were measured by thermistors having inlet cables 0.01 cm. in diameter (see Figure 3). One thermistor was placed in a 0.1 cm. diameter cylindrical hole which was bored into the catalyst pellet in an axial direction. The hole was filled with a mixture of asbestos powder and water glass. Another thermistor was in the stream of circulating gases. The temperature differences between the surface of the catalyst pellet and the volume of the stream were assumed to be negligible. The resistances of the thermistors were measured by a Wheatstone Bridge Metra.

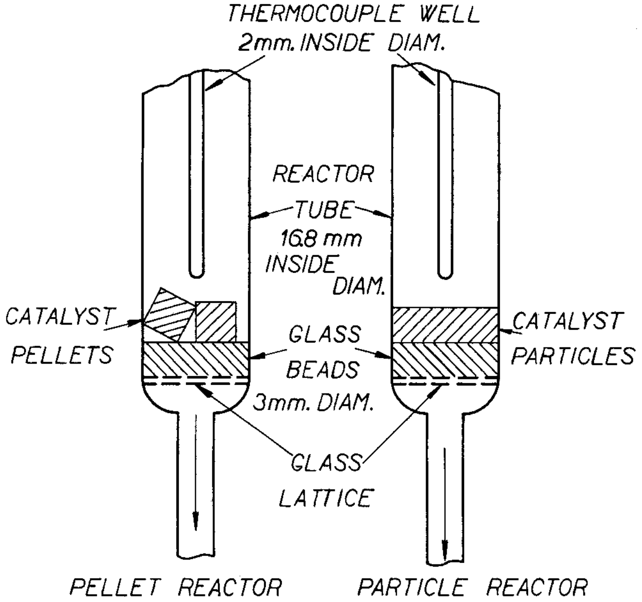

Fig. 2. Arrangement of the catalyst in the reactor.

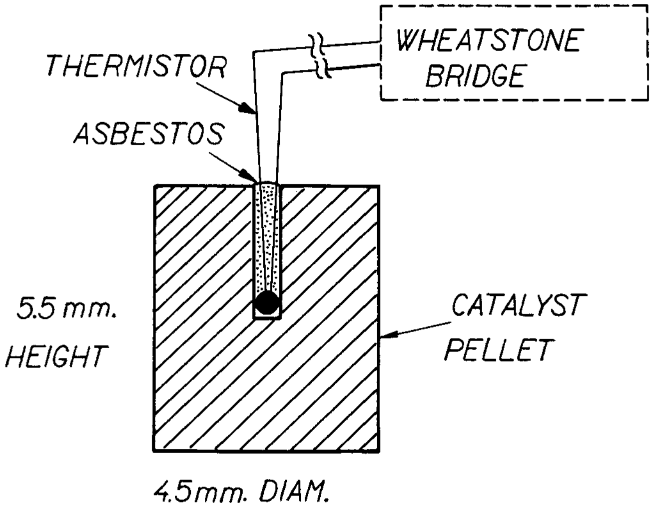

Fig. 3. Arrangement of the temperature difference measurements.

RESULTS AND DISCUSSION

Effect of Internal Diffusion on Reaction Order and Apparent Activation Energy

The hydrogenation of benzene on two types of catalyst grains was investigated to determine the effect of internal diffusion on the reaction order and on the apparent activation energy; that is, the particles of a cylindrical catalyst (4.5 mm. in diameter and 5.5 mm. in height) on which the course of the reaction was strongly effected by the internal diffusion, and the particles of an irregular shape catalyst (0.5 to 0.63 mm.) prepared by crushing the cylinder, on which the influence of the internal diffusion was negligible.

The stated particle sizes were chosen after preliminary experiments in which the effectiveness factor was fixed for a broad range of catalyst grains.

Two types of equations were used to correlate the kinetic data: the kinetic equation of power [Equation (1)] and the kinetic equation of Langmuir-Hinshelwood/Hougen-Watson.

The parameters in the kinetic equation of power were evaluated by using the weighed linear-multiple regression. The values of the constants at 122°C. are given in Table 1. It has been found that in the temperature range of 122 to 160°C. the order of reaction is about 0.6 for benzene and about 1.0 for hydrogen. These data are in agreement with the results published in the literature for similar types of catalysts. Snogovskij, et al. (*10*) found the reaction to be 0.22 to 0.43 for benzene and 0.89 to 1.19 for hydrogen on a nickel-chromium catalyst, whereas Germain, Maurel, and Bourgeois (3) found the reaction to be 0.25 to 0.48 for benzene and 1.0 to 1.3 for hydrogen on a nickel-alumina catalyst, and Nicolai, Martin, and Jungers (7) found the reaction to be 0.4 for benzene and 0.9 for hydrogen on a nickel-kieselguhr catalyst.

$$r = k_0 \exp\left(-\frac{E}{R_g T}\right) p_H^{\alpha} p_B^{\beta} p_C^{\alpha} \qquad (1)$$

where r is the reaction rate of a unit of catalyst weight, k_0 is the frequency factor of the Arrhenius equation, T is the absolute temperature, R is the gas constant, E is the apparent activation energy, p_H, p_B, and p_C is the partial pressure of hydrogen, benzene, and cyclohexane, α, β, γ denote the reaction order with respect to hydrogen, benzene, and cyclohexane.

In order to choose a suitable type of Langmuir-Hinshelwood kinetic equation we tested fourteen. The parameters in these equations were evaluated by the nonlinear regression method. The nonlinear least squares technique used here is from Margardt (5) and is a combination of steepest descent and Gaussian procedures. The starting values of the parameters for the nonlinear regression were estimated by the linear least squares method. To compare the kinetic equations, the residual sums of squares were used as a criterion of validity of an equation. The residual sum of squares, S_o, is defined as

$$S_o = \sum_{j=1}^{N} (r_{\exp-j} - r_{\mathrm{calc}-j})^2 \qquad (2)$$

$r_{\exp-j}$ being the experimental value of the reaction rate, $r_{\mathrm{calc}-j}$ the corresponding value of the reaction rate, calculated from the tested kinetic equation, and N the number of experimental points used.

TABLE 1. CONSTANTS OF KINETIC EQUATION OF POWER [EQUATION (1)] AT 122°C.

Diameter of catalyst particles mm.	k_o moles/ $(\text{g.})_{\text{cat.}}(\text{hr.})(\text{torr.})^{\alpha+\beta+\gamma}$	E cal./ g.-mole	α	β	γ
Cylinder 4.5 × 5.5	6.26×10^{-2}	4,300	0.31	0.78	0
0.50 to 0.63	0.6525	8,700	1.06	0.66	0

The residual sum of squares was found to be less for

$$r = k \frac{K_B\, p_{Bo}\, p_{Ho}}{(1 + K_B\, p_{Bo})^2} \qquad (3)$$

where k is the rate constant of a catalytic reaction referring to the unit volume of a catalyst, K_B is the adsorption coefficient of benzene.

The values of the parameters at 122°C. for the kinetic region are k = 1297.5 moles benzene/$(1_{\text{cat.}})$(hr.)(atm.) and K_B = 3.168 (atm.)$^{-1}$. In comparing the suitability of Equation (1) and (3) it was proved that both types of equations agree with the experimental data within ±5% relatively.

The influence of the internal diffusion on the reaction order and on the apparent activation energy is dealt with in Equation (1). The changes of the reaction order caused by the internal diffusion can be theoretically explained. The simplified theoretical relations were rendered possible only due to accepting a number of estimations. To begin with, the real geometric form of the catalyst particles was approximated by spherical form. The catalyst particle is regarded as isothermic, also the effective diffusion coefficient is assumed constant in the whole particle volume. The influence of chemical equilibrium and of the change in the number of moles at the reaction may be negligible on account of the reaction conditions used. As there is a large surplus of hydrogen in the reaction mixture it may be assumed that the partial pressure of hydrogen at the reaction is constant and can be comprised in a kinetic equation into the rate constant of a catalytic reaction:

$$r = k_0 \exp\left(-\frac{E}{R_g T}\right) p_H^{1.06}\, p_B^{0.66} = k_g p_B^{0.66} \qquad (4)$$

Thiele's modulus for reaction of n-order and for a spherical catalyst particle is defined in the term (*8*):

$$h_n = R_p \sqrt{\frac{k_g\, \rho_p\, p_{oi}^{(n-1)}}{D_{ei}}} \qquad (5)$$

where R_p is the radius of a spherical catalyst particle, p_{oi} is the partial pressure of reaction component i at the external surface of a particle, ρ_p is the apparent pellet density and D_{ei} is the effective diffusion coefficient of reaction component i in the porous structure of a catalyst.

In the region of strong diffusion retardation the effectiveness factor is indirect in proportion to Thiele's modulus and stands for $\eta = 3/h_n$. The effectiveness factor is given by the reaction rate ratio taking a strong hold upon the internal diffusion r_D and upon the reaction rate in the kinetic region r_k:

$$\eta = r_D/r_k = 3/h_n \qquad (6)$$

By employing Equations (4) and (5) for the reaction rate, strongly influenced by the internal diffusion, it follows that:

$$r_D = r_k \frac{3}{h_n} = \frac{3\, k_g\, \rho_p\, p_B^{0.66}}{R_p \sqrt{\dfrac{k_g\, \rho_p\, p_B^{(0.66-1)}}{D_{eB}}}}$$

$$= K \exp\left(-\frac{4350}{R_g\, T}\right) p_H^{0.53}\, p_B^{0.83} \qquad (7)$$

where K is constant

$$K = \frac{3\sqrt{D_{eB}\, \rho_p\, k_0}}{R_p}$$

The dependence of the reaction rate on temperature and on the partial pressures of hydrogen and benzene, expressed in relation (7) is in good agreement with the dependence determined experimentally (see Table 1).

Determination of the Effective Diffusion Coefficient of Benzene in the Porous Structure of a Catalyst

Another objective of this investigation was to compare two methods of determining the effective diffusion coefficient. One method was to determine the dependence of the effectiveness factor on the reaction mixture composition of a cylindrical catalyst pellet, for which we used the calculation procedure suggested by Schneider and Mitschka (9), and the second method was to determine the temperature difference in a cylindrical pellet. For the above calculation we used the Langmuir-Hinshelwood type of equation which is valid at a reaction temperature of 122°C. for the kinetic region [Equation (3)]. This equation was converted to the dimensionless form:

$$r(y) = A\frac{(1+B)^2}{(1+By)^2}\,y\,\frac{(y+C)}{(1+C)} \tag{8}$$

introducing the dimensionless partial pressure of benzene $y = p_B/p_{Bo}$, constant A and dimensionless parameters B, C according to the relations:

$$A = K'_{24}\frac{(1+C)\,p_{Bo}{}^2}{(1+K_B\,p_{Bo})^2} \tag{9}$$

$$B = K_B\,p_{Bo} \tag{9a}$$

$$C = K'_{14}/(K'_{24}\,p_{Bo}) \tag{9b}$$

where

$$K'_{14} = k\,K_B(p_{Ho} - \delta_H\,p_{Bo}) \tag{10}$$

$$K'_{24} = k\,K_B\,\delta_H \tag{10a}$$

and p_{Ho}, p_{Bo} is the partial pressure of hydrogen and benzene at the external surface of the catalyst particle. The dimensionless diffusion parameter δ_H is defined by

$$\delta_H = \left(\frac{a_H}{a_B}\right)\left(\frac{D_{eB}}{D_{eH}}\right) \tag{11}$$

where a_H, a_B are the stoichiometric coefficient and D_{eH}, D_{eB} are the effective diffusion coefficient of hydrogen and benzene in multicomponent mixture.

Equation (8) was employed to balance the equation which describes the change in the concentration of chemical reaction of the catalyst particle when influenced by internal diffusion. The resulting equation was transferred into dimensionless form by introducing dimensionless distance x

$$x = (R_p - z)/R_p \tag{12}$$

R_p is the particle radius and z is the distance from the center of the particle perpendicular to the external surface (at steady state)

$$\frac{d^2y}{dx^2} - \frac{2}{(1-x)}\frac{dy}{dx} = M_R{}^2\frac{(1+B)^2}{(1+By)^2}\,y\,\frac{(y+C)}{(1+C)} \tag{13}$$

The corresponding boundary conditions are as follows:

$x = 0 \quad y = 1$

$x = 1 \quad (dy/dx) = 0$ (condition of symmetry)

M_R is the analogy for Thiele's modulus

$$M_R = R_p\sqrt{\frac{R_g\,T\,A}{D_{eB}\,p_{Bo}}} \tag{14}$$

It is evident that for the effectiveness factor:

$$\eta = -\,3(dy/dx)|_{x=0}/M_R{}^2 \tag{15}$$

Therefore, to determine the effectiveness factor it is necessary to know the magnitude of the gradient of the dimensionless partial pressure of benzene at the external surface of the catalyst particle $(dy/dx)|_{x=0}$. This value was obtained by solving Equation (13) on a digital computer. The method proposed by Weisz and Hicks (*11*) for the problem of simultaneous heat and mass transfer in a porous catalyst was used, and for the numerical integration Merson's modification of the Runge-Kutta method was used. The values of the dimensionless partial pressure of benzene in the center of the particle y_c were chosen in such a way that the resulting value of the effectiveness factor is in agreement with the value determined experimentally. By using the modulus M_R that corresponds with the determined value of the effectiveness factor, we were able to fix the effective diffusion coefficient of benzene.

In the calculations it was necessary to know the ratio of the effective diffusion coefficient of benzene to that of hydrogen [Equation (11)]. Since this ratio was not known, the values of the modulus M_R were calculated for two limit cases, that is, for the ratio corresponding to pure Knudsen diffusion and for the ratio corresponding to pure bulk diffusion. In the former case the diffusion parameter δ_H is given by

$$\delta_H = \left(\frac{a_H}{a_B}\right)\sqrt{\frac{M_H}{M_B}} = 0.4818$$

in the latter case $\delta_H = 3$, since under the conditions used, the ratio of the diffusion coefficient of benzene to that of hydrogen in a multicomponent mixture can be assumed to be 1. We assume the right value of the parameter δ_H to be between these two limits. As a particle radius, R_p was used as an effective radius of the pellet. The effective radius is defined as the radius of a sphere having the same volume-surface ratio V_p/S_p as the cylindrical pellet. For the catalyst pellets used in the study the effective radius R_p was equal to 2.4 mm. The experimental values of the effectiveness factor were calculated from the experimental data using the relation:

$$\eta = r_{\text{exp}}/r_{\text{calc}} \tag{16}$$

where r_{exp} is the measure value of the reaction rate on a

TABLE 2. EXPERIMENTAL DATA USED FOR THE NUMERICAL INTEGRATION OF EQUATION (13) AND RESULTING VALUES

			$\delta_H = 0.4818$			$\delta_H = 3.0$		
p_{Ho} atm.	p_{Bo} atm.	η_{exp}	$y_c \times 10^3$	M_R	$D_{eB} \times 10^2$ sq.cm./sec.	$y_c \times 10^3$	M_R	$D_{eB} \times 10^2$ sq.cm./sec.
0.887	0.0871	0.32	0.38	8.96	1.45	2.2	8.47	1.62
0.887	0.1198	0.36	0.67	7.95	1.58	6.7	7.34	1.85
0.887	0.0442	0.31	0.83	9.07	1.44	1.9	8.77	1.89
0.887	0.0293	0.30	1.21	9.05	1.94	2.0	8.86	2.03
0.779	0.0871	0.35	0.96	8.59	1.41	5.4	7.73	1.71
0.608	0.0871	0.40	4.62	6.81	1.72	28.0	6.22	2.06
0.366	0.0871	0.58	82.80	4.12	2.83	290.0	3.46	4.01
The average values:					1.76			2.16

Final constants: T = 395°K, R_p = 0.24 cm., k = 1297.5 moles/(liter)$_{\text{cat}}$.(hr.) (atm.), K_B = 3.168 (atm.)$^{-1}$.

pellet, r_{calc} is the reaction rate on a powder catalyst at the same conditions, calculated from Equation (3).

The experimental data and the results of the calculations are given in Table 2.

A comparison of the values of the effective diffusion coefficients calculated from the experimental data by using different values of the parameter δ_H proved that the sensibility of the result towards this parameter is very low. The values of the effective diffusion coefficients for the limit values of this parameter (0.4818 and 3.0) are very close, the difference between them being within the limits of experimental error. Thus, to calculate the effective diffusion coefficient of benzene from the kinetic data it is not necessary to know the parameter δ_H with high accuracy. This low sensibility is a consequence of the excess of hydrogen in the reaction mixture. Because of this excess the concentration of hydrogen within the pellet is barely influenced by the internal diffusion.

The second procedure for determining the effective diffusion coefficient of benzene in a porous catalyst structure is to obtain the temperature difference in the cylindrical pellet.

The measurements of the temperature difference were carried out at 122°C. and the molar ratio of benzene to hydrogen in the initial reaction mixture was 1:9.6. The difference in temperature was 3.3 ± 0.3°C. The effective diffusion coefficient of benzene was determined from the expression drawn by Damköhler:

$$k_e(T_c - T_o) = (-\Delta H) D_{eB} (c_{Bo} - c_{Bc}) \qquad (17)$$

where $(T_c - T_o)$ is the temperature difference between the center and external surface of the cylindrical catalyst pellet, K_e is the effective thermal conductivity of the catalyst pellet, ΔH is the enthalpy change on reaction and c_{Bo}, c_{Bc} is the concentration of benzene at the external surface and the center of a catalyst pellet.

In the calculation it was assumed that the concentration of benzene at the center is zero. This assumption is acceptable in view of the dimensionless partial pressure values of benzene at the center of the cylindrical pellet (see Table 2). The effective diffusion coefficient of benzene fixed from relation (17) was 8.1×10^{-3} sq.cm./sec. This value is somewhat lower than the average values resulting from the kinetic data. The estimation of errors in both methods was very difficult and we were not in a position to determine whether the difference found can be considered as being within the range of experimental error. The investigations are being continued in this direction.

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NOTATION

a = stoichiometric coefficient of reactant
A = constant in Equation (8) defined by Equation (9), moles/($1_{cat.}$)(hr.)
B = dimensionless parameter defined by Equation (9*a*)
c = concentration of reactant, moles/cc.
C = dimensionless parameter defined by Equation (9*b*)
D_{ei} = effective diffusion coefficient of reactant-*i*, sq.cm./sec.
E = apparent activation energy, cal./g.-mole
ΔH = enthalpy change on reaction, cal./g.-mole
h_n = Thiele modulus for spherical catalyst particle defined by Equation (5)
j = a particular experimental run
k_e = effective thermal conductivity of catalyst particle, cal./(cm.)(sec.)(°C.)
k_g = reaction rate constant defined by Equation (4)
k_0 = Arrhenius frequency factor, moles/($g_{cat.}$)(hr.)(Torr.)$^{\alpha+\beta+\gamma}$
k = reaction rate constant, moles/($1_{cat.}$)(hr.)(atm.)
K_i = adsorption coefficient of reaction-*i*, (atm.)$^{-1}$
K'_{14}, K'_{24} = constants in rate equation [Equation (8)], defined by Equations (10) and (10*a*)
M_R = dimensionless modulus for spherical catalyst particle defined by Equation (14)
M_i = molecular weight of reactant-*i*
n = reaction order
N = number of experimental data
p_i = partial pressure of reactant-*i*, atm. or Torr.
r = reaction rate, moles benzene/($g_{cat.}$)(hr.) or moles benzene/($1_{cat.}$)(hr.)
R_g = gas constant
R_p = radius of spherical catalyst particle, cm.
S_o = residual sum of squares, defined by Equation (2)
S_p = area of external surface of catalyst particle
T = temperature, °K.
V_p = volume of catalyst particle
x = dimensionless coordinate defined by Equation (12)
y = dimensionless partial pressure of reactant
z = distance from center of catalyst particle in direction perpendicular to external surface, cm.

Greek Letters

α, β, γ = reaction orders for hydrogen, benzene and cyclohexane, respectively
δ_i = dimensionless diffusion parameter of reactant-*i*, defined by Equation (11)
η = effectiveness factor for spherical catalyst particle, defined by Equations (6) and (15)
ρ_p = apparent pellet density, g./cc.

Subscripts

B = benzene
c = conditions at the center of the particle
calc. = calculation
cat. = catalyst
C = cyclohexane
exp = experimental
H = hydrogen
o = conditions at the external surface of the particle

LITERATURE CITED

1. Blume, H., W. Naundor, and A. Wrubel, *Chem. Tech.*, **15**, 583 (1963).
2. Ergun, S., *Anal. Chem.*, **25**, 790 (1953).
3. Germain, J. E., R. Maurel, and Y. Bourgeois, *J. Chim. Phys.*, **60**, 1219, 1227 (1963).
4. Jirácek, F., Ph.D. thesis, Inst. Chem. Tech., Prague (1967).
5. Marquardt, D. W., *J. Soc. Ind. Appl. Math.*, **11**, 431 (1963).
6. Masamune, S., and J. M. Smith, *J. Chem. Eng. Data*, **8**, 54 (1963).
7. Nicolai, J., R. Martin, and J. C. Jungers, *Bull. Soc. Chim. Belge*, **57**, 555 (1948).
8. Satterfield, C. N., and T. K. Sherwood, "The Role of Diffusion in Catalysis," Addison Wesley, Cambridge, Mass. (1963).
9. Schneider, P., and P. Mitschka, *Chem. Eng. Sci.*, **21**, 455 (1966).
10. Snogovskij, J. S., G. D. Ljubarskij, and G. M. Ostrovskij, *Kinetika i kataliz*, **7**, 258 (1966).
11. Weisz, P. B., and J. S. Hicks, *Chem. Eng. Sci.*, **17**, 256 (1962).

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