Temperatures and Partial Pressures at the Surfaces of Catalyst Particles

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Numerical and graphical methods are presented for estimating the temperatures and partial pressures at the surfaces of catalyst particles for gaseous reactions in flow systems. The errors resulting in the interpretation of catalytic reaction-rate data, where surface conditions are assumed to be those of the ambient gas stream, are presented. A numerical method of evaluating the reaction model with nonisothermal surface conditions is indicated.

In kinetic studies dealing with fluid reactions catalyzed by solid particles the interpretation of experimental data is greatly facilitated by operating at sufficiently high velocities and small particle sizes so as to maintain the composition and temperature of the fluid in contact with the catalyst surface nearly the same as in the ambient main stream. Under these favorable conditions resistances to mass and heat transfers from particle to ambient stream become negligible, and point reaction rates become independent of fluid velocity. Such high velocities are encountered in industrial reactors but are often not realized in laboratory scale reactors. Many examples appear in the literature where large drops of temperature and partial pressure from catalyst to ambient gas stream have been neglected with consequent erroneous interpretation of the reaction model.

This paper deals with the calculation of the temperatures and partial pressures of gases at the surface of catalyst particles for flow reactions taking place in fixed beds; the errors involved in the correlation of rate data in terms of the ambient gas stream when high resistances to mass and heat transfer are ignored; and the interpretation of experimental data where large drops of temperature and partial pressure from catalyst to the ambient stream prevail.

Another serious error arising in the interpretation of rate data is the neglect of gradients of temperature and partial pressures inside catalyst pellets. The methods employed in this paper still apply to the calculation of surface conditions despite these internal gradients, but for the correlation of reaction rate constants the internal gradients of temperature and composition should also be known. The mathematical procedures for calculating the internal gradients are reported in literature (*8*, *9*) and are considered in this paper where a reaction model is sought.

MASS TRANSFER DATA AT LOW REYNOLDS NUMBERS

Flow reactions in catalyst beds frequently take place at low Reynolds number where insufficient mass and heat transfer data have been available until recently. The data of Wakao, Oshima, and Yagi (*1*) now give the required reliability to mass transfer coefficients at low Reynolds numbers. These data were obtained from the rate of dissolution of betanaphthol by water flowing over spheres and cylinders of betanaphthol where the water stream completely filled the external void space of the bed. The betanaphthol particles were mixed with glass beads to reduce the attainment of saturation in the exit stream of thin beds. The data of Wilke and Hougen (*2*) were obtained from rates of evaporation of water from celite pellets to an air stream flowing through the bed. Both sets of data were recorrelated in terms of the j_D factor, as defined by Chilton and Colburn (*3*).

For gases

$$j_D = \frac{k_{GA}\, p_{fA}}{G_M} \left(\frac{\mu}{\rho D} \right)_f^{2/3} \qquad (1)$$

The exponent 2/3 on the Schmidt number was used in the correlation of experimental data and is acceptable at low Reynolds numbers encountered in experimental reactors.

The Reynolds number adopted in the present correlation is defined as

$$Re = \frac{G}{a_v\, \phi\, \mu} \qquad (2)$$

For spheres $\phi = 1.0$; for cylinders $\phi = 0.91$; for flakes $\phi = 0.81$; for irregular granules $\phi = 0.90$ (assumed).

DERIVATION OF REYNOLDS NUMBER

In the derivation of an appropriate form for the Reynolds number a unit cube of packed bed is considered with the fluid flowing through the bed normal to two opposite faces of the cube. The wetted area of the fluid channel available for mass transfer per unit volume of bed is equal to ϕa_v and the cross section of the channel is equal to the void fraction ϵ. The hydraulic radius is equal to $\epsilon / a_v \phi$, and the actual mass velocity is equal to G/ϵ. Hence

$$Re = \frac{R_h G'}{\mu} = \frac{\epsilon}{\phi\, a_v} \frac{G}{\epsilon} / \mu = \frac{G}{a_v \phi \mu} \qquad (3)$$

The term ϕa_v should then also be used in equations for mass and heat transfer. Thus for the rate of transfer of component *A* per unit volume of bed

$$r_{vA} = k_{GA}\, a_v\, \phi\, (p_A - p_{Ai}) \qquad (4)$$

or on the basis of unit mass of particles

$$r_{mA} = k_{GA}\, a_m\, \phi\, (p_A - p_{Ai}) \qquad (5)$$

The term ϕ is retained to permit data obtained on spheres ($\phi = 1$) to be extended to other shapes.

RECORRELATION OF j_D AT LOW REYNOLDS NUMBERS

By recorrelation of the data of Wilke and Hougen (*2*); Gamson, Thodos, and Hougen (*5*); and Wakao, Oshima, and Yagi (*1*) a smooth continuous curve of j_D values against values of *Re* was obtained on a logarithmic plot. For convenience without appreciable loss in accuracy the correlations were divided into two parts as follows:

For $0.01 < Re < 50$

$$j_D = 0.84\, Re^{-0.51} \qquad (6)$$

For $50 < Re < 1{,}000$

$$j_D = 0.57\, Re^{-0.41} \qquad (7)$$

No significance is attached to the intersection of these two equations at $Re = 50$.

PRESSURE FACTOR p_f

For diffusion through a stagnant film in binary gas mixtures the pressure factor p_f is the logarithmic mean value of the partial pressure of the non-

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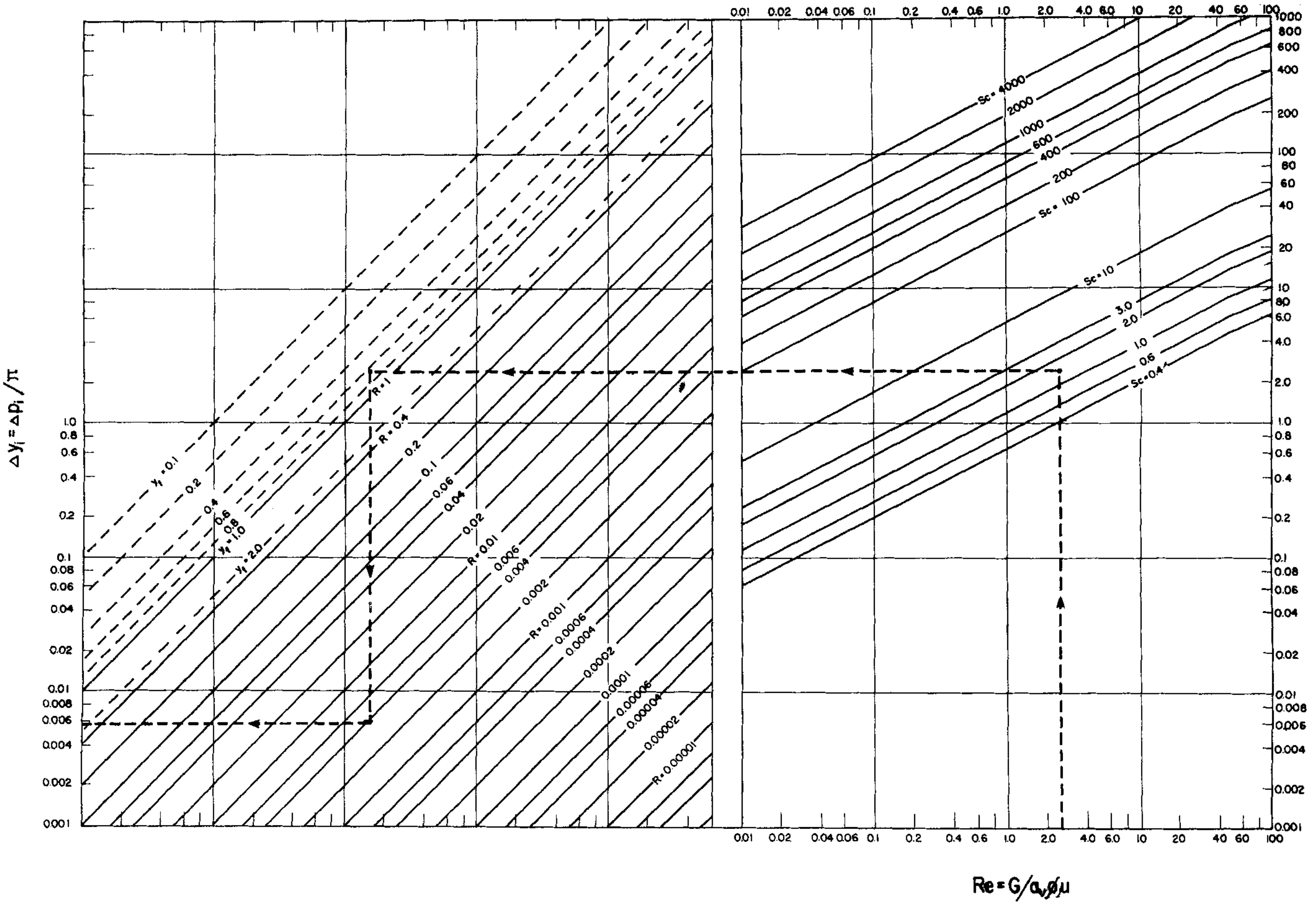

Fig. 1. Evaluation of partial pressure gradients between a flowing fluid and the exterior surface of catalyst particles in a packed bed.

diffusing gas between the interface and the main ambient stream. In case of equimolal diffusion the fluid has zero molar velocity with respect to fixed coordinates normal to the stream. The diffusion of a component normal to the stream is the same relative to the bulk of the fluid or to fixed coordinates. In general however the rate of transfer across the stream is affected by bulk flux as well as by diffusion through the fluid. Where a bulk flux of fluid occurs in the direction of diffusion, an additional transfer of *A* occurs in this direction.

The effective diffusion coefficient D_{mA} of component *A* in a multicomponent gaseous mixture is defined thus:

$$I_A = -\frac{D_{mA}}{RT}\frac{\partial p_A}{\partial x} \qquad (8)$$

For a general gaseous reaction $aA + bB \rightarrow rR + sS$ catalyzed by a solid surface the bulk flux F of the gaseous mixture relative to fixed coordinates is the algebraic sum of the bulk fluxes N_A, N_B, . . . of the separate components; thus

$$F = N_A + N_B - N_R - N_S = N_A\frac{(a+b-r-s)}{a} \qquad (9)$$

The total transfer N_A of A with respect *to fixed coordinates* becomes

$$N_A = I_A + y_A F = -\frac{D_{mA}}{RT}\frac{\partial p_A}{\partial x} + y_A N_A \frac{(a+b-r-s)}{a} \qquad (10)$$

From Equation (10)

$$N_A = -\frac{\pi}{\pi - p_A\left(\frac{a+b-r-s}{a}\right)}\frac{D_{mA}}{RT}\frac{\partial p_A}{\partial x} \qquad (11)$$

Application of Equation (11) to the transfer of *A* through a binary stagnant film gives

$$N_A = -\frac{D_{AB}}{(1-y_A)}\frac{\partial p_A}{RT\,\partial x} = -\frac{D_{AB}\,\pi}{p_f\,RT}\frac{\partial p_A}{\partial x} \qquad (12)$$

For diffusion in a multicomponent mixture

$$p_{fA} = \pi - p_A\left(\frac{a+b-r-s}{a}\right) \qquad (13)$$

or dividing by π gives

$$y_{fA} = 1 - y_A\left(\frac{a+b-r-s}{a}\right) \qquad (14)$$

where $y_A = p_A/\pi$. The rate of diffusion of *A* through a multicomponent mixture then becomes

$$N_A = -\frac{D_{mA}\,\pi\,\partial p_A}{p_f\,RT\,\partial x} = -\frac{D_{mA}}{y_{fA}\,RT}\frac{\partial p_A}{\partial x} \qquad (15)$$

For a fluid film of thickness Δx an integrated form of Equation (15), with D_{mA} assumed constant across the film, gives

$$N_A = -\frac{D_{mA}\,\pi}{(p_{fA})_{lm}\,RT}\frac{\Delta p_A}{\Delta x} = -\frac{D_{mA}\,\Delta p_A}{(y_{fA})_{lm}\,RT\,\Delta x} = \frac{r_{mA}}{a_m} \qquad (16)$$

The necessity of using the pressure factor term p_f arises because the reported correlations of j_D were obtained from experiments in stagnant films where p_f was used to allow for bulk flow in the direction of diffusion.

EFFECTIVE DIFFUSIVITY OF MULTICOMPONENT MIXTURES

In the molecular diffusion of *A* through a gaseous of *B*, *R*, *S*, . . . the partial pressure gradient of *A* is given by the Stefan-Maxwell equation as

$$\frac{\partial p_A}{\partial x} = \frac{RT}{D_{AB}\pi}(p_B N_A - p_A N_B) + \frac{RT}{D_{AR}\pi}(p_R N_A - p_A N_R) + \cdots \qquad (17)$$

From Equations (15) and (17) Stewart (*6*) developed the following for the effective diffusion coefficient of component *A* in a multicomponent mixture:

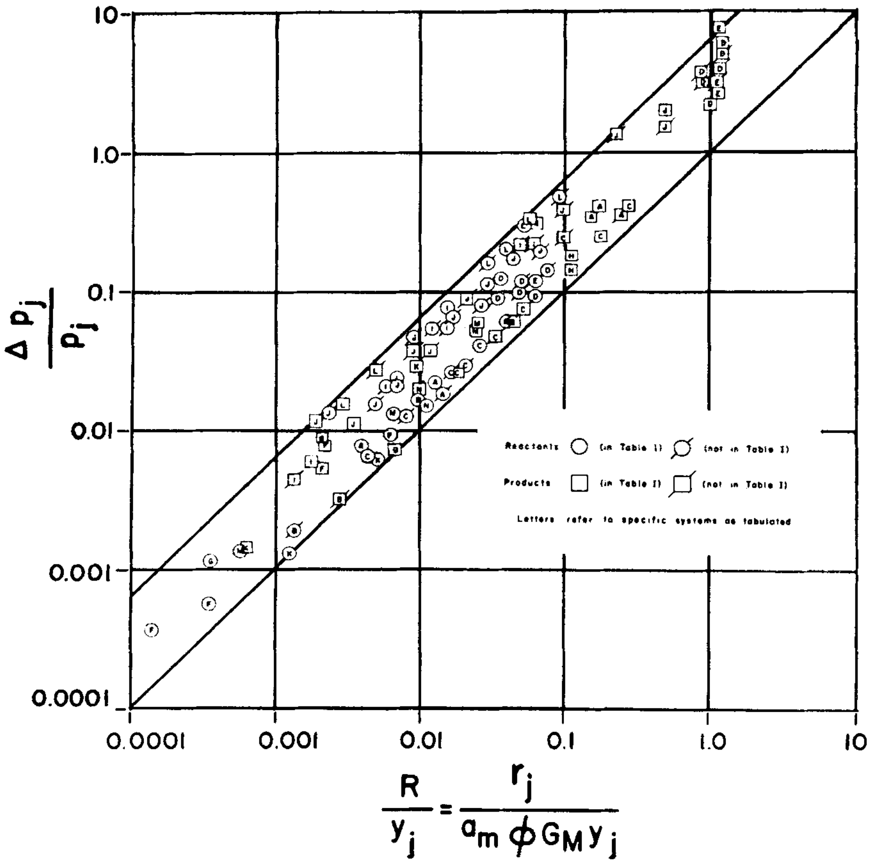

Fig. 2. Experimental range of $\Delta p_j/p_j$ between gases and catalytic particles in packed beds.

$$\frac{y_{fA}}{D_{mA}} = \frac{1}{D_{AB}}\left(y_B - y_A \frac{N_B}{N_A}\right) + \frac{1}{D_{AR}}\left(y_R - y_A \frac{N_R}{N_A}\right) + ---- \quad (18)$$

or in general

$$D_{mA} = \sum_{j=1}^{n} \frac{y_{fA}}{\frac{1}{D_{Aj}}\left(y_j - y_A \frac{N_j}{N_A}\right)} \quad (19)$$

Equation (17) can be used directly to obtain N_A for given values of Δx and Δp without requiring values of either p_{fA} or D_{mA}. The terms p_{fA} and D_{mA} become necessary however where Δx and Δp are unknown. Evaluation of D_{mA} requires a trial-and-error procedure because values of y_j for each component must be calculated from values averaged over the film thickness.

For a given chemical reaction the ratios N_j/N_A are stoichiometric. For the general case as in gas absorption combined with evaporation these ratios should be established independently.

CALCULATION OF PARTIAL PRESSURE DROPS

The partial pressure drops of component A between the main stream and the catalyst surface may be calculated from Equations (1) and (5); thus

$$\Delta p_A = \frac{r_m}{a_m \phi k_{GA}} = R\ (j_D)^{-1} p_{fA} \left(\frac{\mu}{\rho D_{mA}}\right)^{2/3} \quad (20)$$

or in terms of ratios

$$\Delta y_A = R\ (j_D)^{-1} y_{fA} \left(\frac{\mu}{\rho D_{mA}}\right)^{2/3} \quad (21)$$

where R is $(r_{mA}/a_m \phi G_M)$. All groups in Equation (21) are dimensionless.

The terms p_{fA} and y_{fA} should be calculated by Equations (13) and (14), and D_{mA} should be calculated by Equation (19). Actually trial-and-error procedures are required, since p_{fA}, y_{fA}, and D_{mA} require average values over the film. The boundary values of p_{fA} and y_{fA} are not known until values of Δp and Δy are established. For calculating binary diffusivities in lieu of experimental values the equation of Hirschfelder, Bird, and Spotz (7) was used.

The surface area a_v of particles per unit volume of packed bed can be readily calculated for geometric shapes of uniform size and shape if the void fraction or number of particles per unit volume are known. For estimating the surface area of irregular shaped granules the following relation applies:

$$a_v = \frac{6(1-\epsilon)}{SD_p} = a_m \rho_s \quad (22)$$

Values of partial pressure drops Δp_j from ambient gas stream to catalyst particle for component j may be calculated from Equation (20). These values can be more readily obtained by use of Figure 1, based upon Equation (21), wherein Δy_j and R are dimensionless coordinates and lines are drawn for various values of the parameter R, Schmidt number, and y_f factor.

In a gaseous system the Schmidt number is limited to a narrow range from 0.5 to 2.0; for liquid systems a wide range of Schmidt numbers is encountered from 2 to 4,000. In industrial reactions values of the Reynolds number above 100 are encountered, but in the experimental systems reported in the literature the Reynolds numbers vary from 1 to 100. Experimental values of y_f cover a narrow range from 0.5 to 1.2. However values of R cover an extremely wide range from 4 × 10^{-5} to 2,000 × 10^{-5}. The

TABLE 1. SOURCES OF EXPERIMENTAL DATA

Reaction	Catalyst	Size of catalyst	References*
Ammonia synthesis	Iron oxide	5- to 6-mesh granules	A, *14*
Water-gas shift reaction	Iron oxide	3-mm. × 1.75-mm. pellets	B, *15*
Methane synthesis from CO_2 and H_2	Nickel on kieselguhr	⅛-in. tablets	C, *16*
Hydrogenation of propylene	Nickel on kieselguhr	⅛-in. pellets	D, *10*
Hydrogenation of propylene	Palladium on alumina	12- to 16-mesh granules	H, *19*
Hydrogenation of isobutylene	Nickel on kieselguhr	⅛-in. pellets	E, *10*
Vapor phase esterifications			
Acetic acid and methyl alcohol	Silica gel	6- to 8-mesh granules	F, *17*
Acetic acid and propyl alcohol	Silica gel	6- to 8-mesh granules	G, *18*
Oxidation of nitric oxide	Activated carbon	11- to 20-mesh granules	I, *20*
Oxidation of nitric oxide	Activated carbon	4- to 6-mesh granules	L, 23
Isomerization of butylene	Alumina	3/32-in. pellets	M, *24*
Hydrogenation of isooctene	Nickel on kieselguhr	⅛-in. pellets	N, *25*
Oxidation of sulfur dioxide	Platinum on alumina	⅛-in. cylindrical pellets	J, *21*
Phosgene formation	Activated carbon	3.3-mm. granules	K, *22*

* The letters in Table 1 refer to points in Figures 2 and 4.

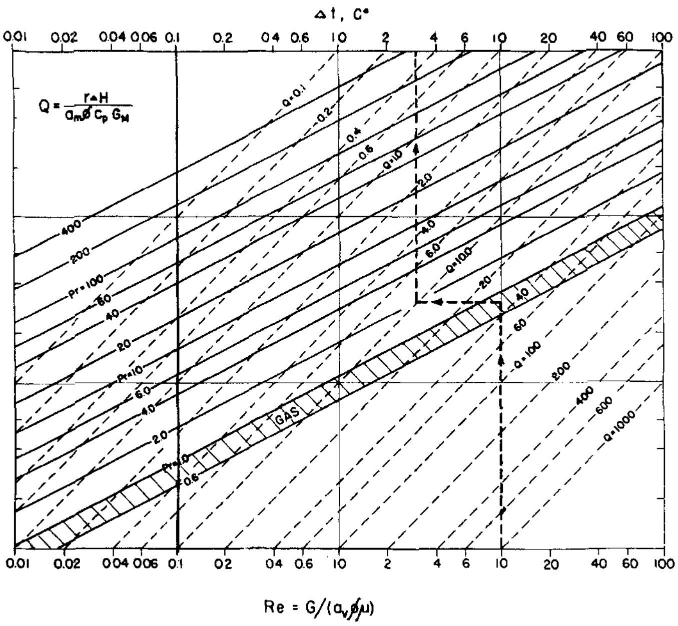

Fig. 3. Evaluation of temperature drop between a flowing fluid and the exterior surface of catalyst particles.

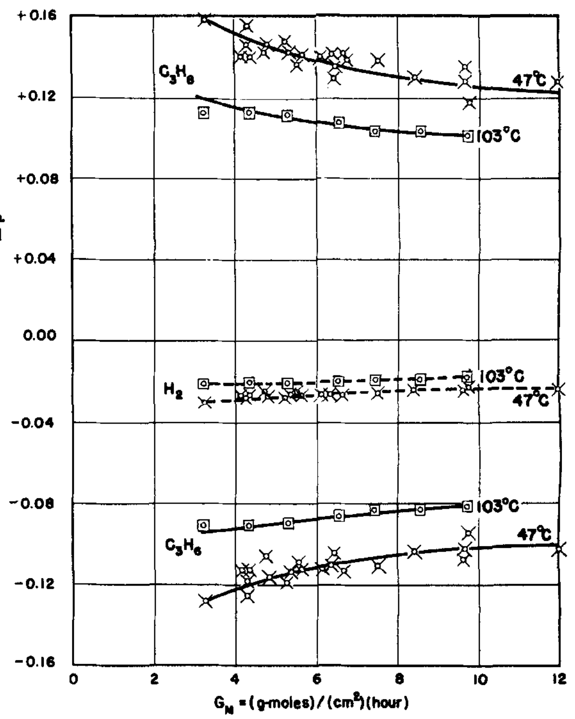

Fig. 5. Pressure drops from catalyst surface to ambient gas stream in the hydrogenation of propylene at 1-atm. pressure. Ambient gas stream $p_{C_3H_6} = 0.33$; $p_{H_2} = 0.67$ atm.

magnitude of R is by far the most important variable controlling the partial pressure drop from catalyst particle to ambient stream.

RANGE OF Δy_A VALUES IN EXPERIMENTAL REACTORS

Values of $[\Delta p_j/p_j]$ were calculated for the separate reactants and products from representative experimental data reported in the literature for fourteen gaseous reactions catalyzed by solids in fixed beds as given in Table 1. These values range from 0.0005 to 8.0. The calculated values of $[\Delta p_j/p_j]$ are plotted vs. $[R_j/y_j]$ in Figure 2. Both coordinates are dimensionless. For reactants the ratio $[\Delta p_j/p_j]$ can never exceed unity; the maximum value encountered was 0.5. However for products this ratio may exceed unity manifold. The maximum value encountered was 8.0. Hence neglect of partial pressure drop for the products in correlation of rate data may result in serious error in establishing the kinetic adsorption constants. Partial pressure drops should approach zero for correlation of rate data in terms of ambient conditions. It may be observed from Figure 2 that the points for all systems fall in a fairly narrow band. The ratio $[\Delta p_j/p_j]/[R_j/y_j]$ in the fourteen investigations varies only from 1 to 6.5, whereas values of $[\Delta p_j/p_j]$ vary 10,000 fold. The width of the band is due to variations of y_f, j_D, and Schmidt numbers which were purposely neglected in this plot to emphasize that R_j is the most significant factor in controlling partial pressure drops. Figure 2 serves as a rough guide in estimating the relative magnitudes of partial pressure drops without requiring the data on viscosities and diffusivities. A precise correlation of pressure drop data is shown in Figure 1. It will be observed from Figure 2 that for eight of the fourteen investigations the values of $[\Delta p_j/p_j]$ were less than 0.1; for two investigations the values of this ratio for products were greater than 1.0

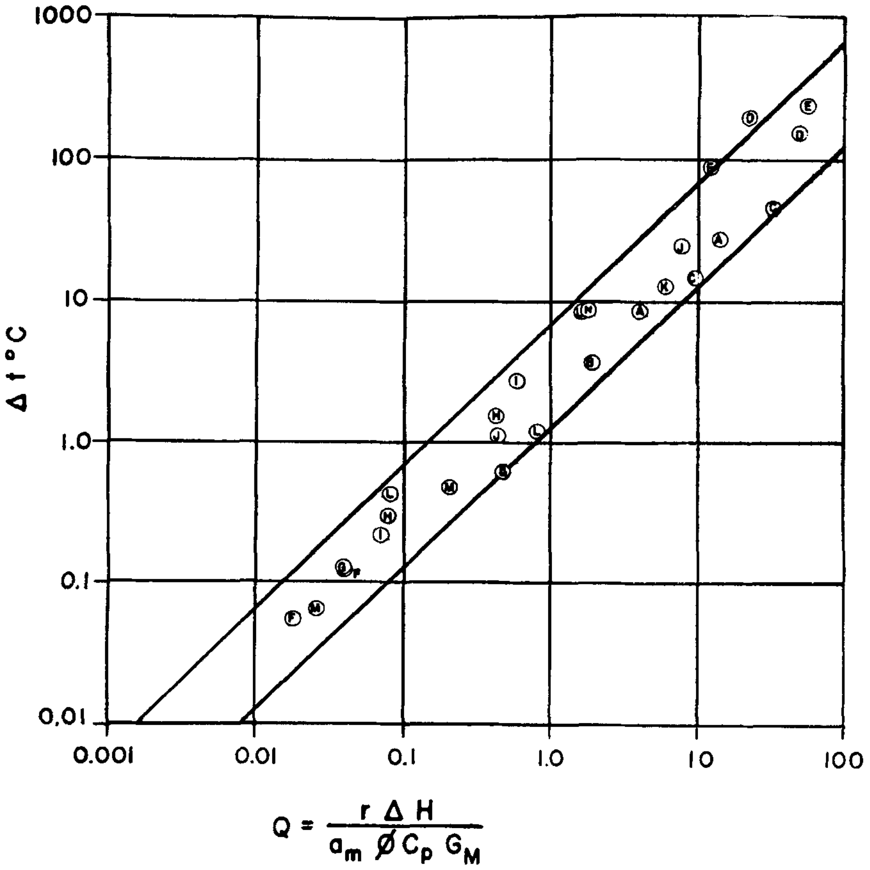

Fig. 4. Experimental range Δ ± between gases and catalytic particles in packed beds.

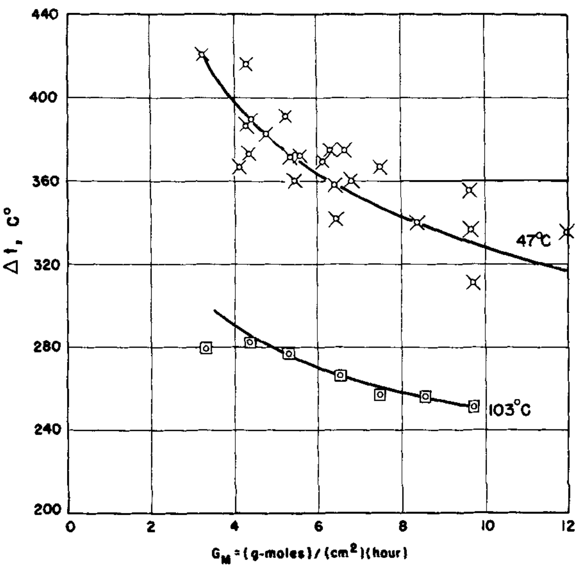

Fig. 6. Temperature drops from catalyst surface to ambient gas stream in the hydrogenation of propylene at 1-atm. pressure.

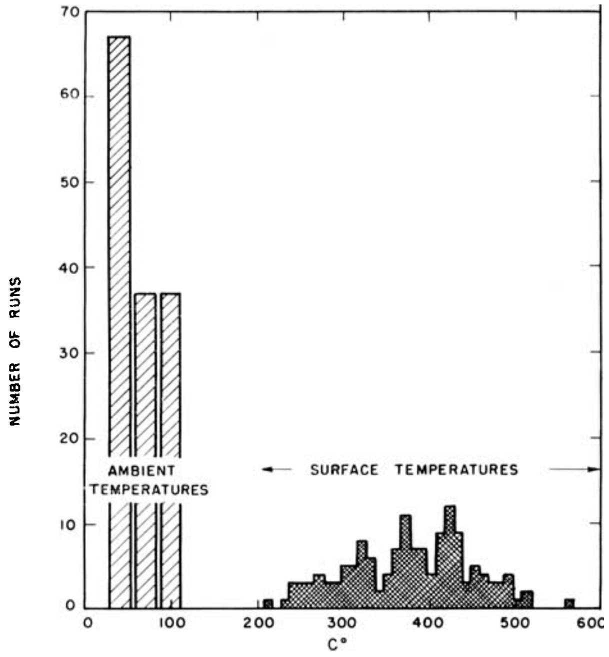

Fig. 7. Number of runs at given temperature levels (catalytic hydrogenation of propylene).

CALCULATION OF TEMPERATURE DROP FROM CATALYST PARTICLE TO AMBIENT GAS STREAM

The temperature drop from a catalyst surface to ambient fluid stream may be estimated from the relation $j_H = 1.076\ j_D$. This relation is still subject to some uncertainty. The j_H factor for heat transfer is defined by Chilton and Colburn (3) as

$$j_H = \frac{h_G}{C_p G}\left(\frac{C_p\mu}{k}\right)_f^{2/3} \qquad (23)$$

The temperature drop Δt from catalyst surface to the ambient stream may then be obtained from the following relation:

$$\Delta t = \frac{r_{mA}\,\Delta H_A}{a_m\,\phi\,h_G} \qquad (24)$$

Combining Equations (23) and (24) one gets

$$\Delta t = \frac{r_{mA}\,\Delta H_A}{a_m\,\phi\,c_p\,G_M}\,(j_H)^{-1}\,(P_r)_f^{2/3} = Q\,j_H^{-1}\,(P_r)_f^{2/3} \qquad (25)$$

where $Q = (r_{mA}\,\Delta H_A)/(a_m\,\phi\,c_p\,G_M)$

The terms Q and Δt have the dimensions of temperature; the other terms are dimensionless. The variations of j_H and the Prandtl number are small compared with values of Q. For gaseous systems the range of Prandtl numbers is from 0.6 to 1.0 and for liquid systems from 2 to 400. Thus Q is the most significant factor in controlling temperature drop just as R is the most significant factor in controlling the pressure drop ratio.

Values of Δt may be calculated from Equation (25) or obtained more readily from Figure 3. Values of ΔH at reaction temperatures were obtained from standard heats of reaction at 298°K. combined with heat capacity data for the separate components.

For the same system and runs previously used in calculating values of $[\Delta p_j/p_j]$ values of Δt were calculated and plotted vs. Q on logarithmic coordinates in Figure 4. This chart serves as a rough guide and indicates that temperature drop Δt is determined largely by Q and to a minor extent by the Prandtl and j_H numbers. Thus the dimensionless ratio $\Delta t/Q$ varies from 1.3 to 6.4 within the variations of viscosity and thermal conductivity of gases. The actual values of Δt obtained in all the experimental runs cover a wide range from 0.07° to 246°C., the latter value occurred in the hydrogenation of butylene. Even if the main gas stream in a catalyzed reaction is kept isothermal, the reaction taking place at the surface will not be isothermal.

For all calculations of Δp_j and Δt an IBM-650 computer and data processing machine were used.

SPECIFIC ILLUSTRATION OF PARTIAL PRESSURE DROPS AND TEMPERATURE DROP

A specific case will be illustrated for an extremely rapid reaction, namely the catalytic hydrogenation of propylene. This illustration is based upon the excellent thesis of Fair, and with the permission from Rase, his major professor. The partial pressure drops of the component gases from the ambient stream to the catalyst particle as a function of mass velocity are shown in Figure 5 for a feed mole fraction of hydrogen = 0.67 and propylene = 0.33 at atmospheric pressure, and ambient temperatures of 47° and 103°C. with a nickel catalyst supported on keiselguhr, ⅛ × ⅛ in. cylindrical pellets. The partial pressure of propane at the catalyst surface is significant even though negligible quantity appears in bulk stream. In this case the adsorption term for propane is negligible, and hence no adsorption term for propane need appear even though propane is present at the interface.

The corresponding temperature drops across the gas film are shown in Figure 6 for the catalytic hydrogenation of propylene. It will be observed that for the high rates of these reactions temperature drops of several hundred degrees across the gas film may occur at low mass velocities and that it may become experimentally difficult to render this drop negligible.

CORRELATION OF REACTION RATE DATA WHERE RESISTANCES TO MASS AND HEAT TRANSFER ARE SIGNIFICANT

Where experimental data on reaction rates are obtained under conditions of significant resistances to mass and heat transfer, reaction rate equations expressed in terms of ambient conditions become dependent on mass velocity as well as on temperature and partial pressures. Neglecting the effect of velocity may lead to the postulation of a false reaction model and to constants inconsistent with the correct model. These errors can be avoided by calculating the surface conditions and establishing the kinetic model and reaction rate constants from surface conditions. This method is extremely tedious and should be avoided if possible by eliminating experimentally these transfer resistances. The method of calculating the surface reaction rate and the reaction model where high transfer resistances prevail will be illustrated for the catalytic hydrogenation of propylene and butylene.

In the study of the hydrogenation of olefins over a nickel-on-kieselguhr catalyst Fair (*10*) recognized the high drop of temperature and partial pressures across the gas film. His observations led Perkins and Rase (*11*) to develop a high velocity flow reactor to make these drops negligible.

The thesis data of Fair was recorrelated in terms of the conditions at the surface of the catalyst. Surface temperatures and partial pressures were calculated for all runs by methods previously described.

The original data expressed in terms of the temperature of the bulk stream were reported at three temperature levels, 40°, 71°, and 97°C. respectively for a total of 141 runs. When rearranged in terms of surface temperatures the experimental runs spread over a much wider and higher range, namely from 200° to 525°C. (as shown in Figure 7) with many levels of surface temperatures.

Representative drops of temperature and partial pressures have been shown previously in Figures 6 and 5. The number of runs at any level of surface temperatures now become so few that correlation at isothermal levels was no longer possible without eliminating 60% of the experimental data. To use all the data required the acceptance of temperature as a simultaneous variable along with partial pressures.

The maximum possible temperature drops inside the catalyst pellets were estimated by the method of Schilson (*8*) for all the 141 runs. In the extreme case the maximum value encountered was 12°C. compared with 325°C. for the corresponding external drop, giving a ratio of 0.037. The average internal temperature drop for all the runs was 4.5°C., giving a ratio of only 0.015 compared with the average external drop. It may be concluded that internal gradients were negligible for the hydrogenation of propylene.

Two reaction models were accepted as representing the catalytic hydrogenation of propylene and isobutylene, namely a surface reaction between chemisorbed hydrogen and chemisorbed olefin with no adsorption of the product. The two models differ in considering hydrogen chemisorbed as molecules or as atoms. The latter model is generally accepted, although the distinction is difficult to establish from rate data alone.

The treatment of the experimental data will be illustrated with respect to the second model, where the rate equation in terms of surface conditions becomes

$$r = \frac{p_H\, p_U \exp\left(-\frac{A_1}{RT}+\frac{B_1}{R}\right)}{\left(1+\sqrt{p_H \exp\left(-\frac{A_2}{RT}+\frac{B_2}{R}\right)}+p_U \exp\left(-\frac{A_3}{RT}+\frac{B_3}{R}\right)+p_S \exp\left(-\frac{A_4}{RT}+\frac{A_4}{R}\right)\right)^3} \tag{26}$$

As a first approximation Equation (26) is expanded into a linear first-order Taylor series; thus

$$r = f(T,\ p_H,\ p_U,\ p_S,\ \theta_1,\ \theta_2,\ \theta_3,\ \theta_4,\ \theta_5,\ \theta_6,\ \theta_7,\ \theta_8) \tag{27}$$

where $\theta_1, \ldots, \theta_8$ are substituted for the $(A_1)/(R)$, $(-B_1)/(R)$, $(A_2)/(R)$, $(-B_2)/(R)$, $(A_3)/(R)$, $(-B_3)/(R)$, $(A_4)/(R)$, $(-B_4)/(R)$ in Equation (26). A first approximation in accordance with Taylor's theorem gives

$$r_1 = f(T, p_H, p_U, p_S, \theta_1^\circ, \ldots, \theta_8^\circ) + \Delta\theta_1' \frac{\partial f}{\partial \theta_1}(T, p_H, p_U, p_S, \theta_1^\circ, \ldots, \theta_8^\circ) + \ldots\ldots + \Delta\theta_8' \frac{\partial f}{\partial \theta_8}(T, p_H, p_U, p_S, \theta_1^\circ, \ldots, \theta_8^\circ) \tag{28}$$

where $\theta_1^\circ, \theta_2^\circ, \ldots, \theta_8^\circ$ are the initial guess values for $\theta_1, \theta, \ldots, \theta_8$, and $\Delta\theta_1' = \theta_1 - \theta_1^\circ, \ldots, \Delta\theta_8' = \theta_8 - \theta_8^\circ$. Equation (28) is linear in $\Delta\theta_1', \Delta\theta_2' \ldots, \Delta\theta_8'$. The coefficients, $\Delta\theta_1', \Delta\theta_2', \ldots, \Delta\theta_8'$ are estimated by multiple regression. The partial derivatives $(\partial f/\partial\theta_1), \ldots, (\partial f/\partial\theta_8)$ are approximated by difference quotients, $(\Delta f/\Delta\theta_1), \ldots, (\Delta f/\Delta\theta_8)$, where

$$\frac{\Delta f}{\Delta\theta_1} = \frac{f(T, p_H, p_U, p_S, \theta_1 + \Delta\theta_1, \ldots, \theta_8) - F(T, p_H, p_U, p_S\, \theta_1, \ldots, \theta_8)}{\Delta\theta_1}$$

From the estimated values of $\Delta\theta_1', \Delta\theta_2', \ldots, \Delta\theta_8'$ best approximations for $\theta_1, \theta_2, \ldots, \theta_8$ are obtained. The next approximation is obtained by replacing the previous guess values in the right-hand members of Equation (28) by those currently obtained. The feedback process is repeated until the input and output of a cycle agree within a specified tolerance (0.1) of the relative change in each parameter; that is

$$\text{for } 1 \leqq j \leqq 8 \left| \frac{\theta_j^{i+1} - \theta_j^{i}}{\theta_j^{i}} \right| \leqq 0.1$$

In general this iteration may or may not converge, depending on the guess values. In the present case the functional relationship is highly nonlinear. An optional feature of this program, the Lagrangian interpolation, gave the best choice of parameters in each iteration with rapid convergence.

In these calculations nonlinear estimation program written by Booth and Peterson (*13*) for the IBM-704 was used. The details of the computer programs for the various calculations mentioned earlier are reported by Ramaswami (*26*).

The final correlations are given in Table 2 and the constants are compared with those based upon ambient rather than surface conditions.

In the use of ambient conditions the correlations do not support the reaction model in three defaults high chemisorption is shown for both propane and isobutane, whereas the adsorption of these products is negligible; a negative value is obtained for the energy of activation of isobutylene $\Delta H^{\ddagger}$ (ambient) = −1,547; and the heat of adsorption of isobutylene is endothermic (ambient) = 1,364. With the use of surface conditions the results are consistent throughout; $\Delta H^{\ddagger}$ (surface) = 1,431 and ΔH_u (surface) = −4,295.

TABLE 2

	Hydrogenation of propylene		Hydrogenation of isobutylene	
	Model 2 using surface conditions	Model 2 using ambient conditions	Model 2 using surface conditions	Model 2 using ambient conditions
A_1	+2,324.0	+8,607	+1,430.8	−1,547 (should be +)
B_1	8.8705	36.5	6.2245	−1.32
A_2	−2,562.0	−11,610	−6,555.1	−3,112
B_2	0.8419	−38.1	−7.5504	−2.66
A_3	−5,193.2	−1,217	−4,295.3	+1,364 (should be −)
B_3	−4.2497	−3.42	−5.4129	7.17
A_4	no adsorption	−525.0	no adsorption	−1,062 (should show no adsorption
B_4	no adsorption	4.61	no adsorption	0.525 of isobutane)

ACKNOWLEDGMENT

Credit is acknowledged to Dr. H. F. Rase and Dr. J. R. Fair for permission to use the thesis data of Dr. Fair, to G. W. Struble, Project Supervisor of the Numerical Analysis Laboratory, University of Wisconsin, for providing necessary facilities in carrying out computer calculations; and to the Wisconsin Alumni Research Foundation for financial support.

NOTATION

$A_1 \ldots A_4$ = constants related to corresponding entropies
a = number of moles of A
a_m = area of particle per unit mass
a_v = area of particle per unit volume of bed
B = component
$B_1 \ldots$ = constants: enthalpies
b = number of moles of B
C_{fA} = concentration factor for component A
C_p = heat capacity per unit mass at constant pressure
c_p = molal heat capacity at constant pressure
D = diffusion coefficient
D_{AB}, D_{AR} = diffusion coefficients in binary system
D_{mA} = mean diffusion coefficient of component A in a multicomponent system
D_p = effective particle diameter
F = bulk flux in moles per unit volume
G = mass velocity of gas based on total cross section of bed
G' = G/ϵ
G_M = molal mass velocity of gas based on total cross section of bed
ΔH_A = molal heat of reaction of component A
$\Delta H^{\ddagger}$ = molal enthalpy of activation
$\Delta H_H, \Delta H_U, \Delta H_S$ = molal enthalpies of adsorption of hydrogen, unsaturated and saturated hydrocarbons, respectively
h_G = heat transfer coefficient in gas phase
I_A = transfer rate of component A by diffusion
j_D = mass transfer number
j_H = heat transfer number
K_H, K_U, K_S = equilibrium adsorption for hydrogen, unsaturated and saturated hydrocarbons, respectively
k = thermal conductivity
k_G, k_{GA} = mass transfer coefficient in gas phase, of component A
k_{LA} = mass transfer coefficient in liquid phase of component A
L = mass velocity of liquid based on total cross section of bed
L_M = molal mass velocity of liquid based on total cross section of bed
N_A, N_B, N_R, N_S = molal rates of transfer of components A, B, R, S, respectively
Pr = $(C_p \mu)/k$ = Prandtl number
p_A = partial pressure of component A in ambient fluid
p_{Ai} = partial pressure of component A at catalyst surface
p_f, p_{fA} = pressure factor and for component A
p_H, p_U, p_S = partial pressures of hydrogen, unsaturated and saturated component, respectively
Q = $(r_{mA} \Delta H_A)/(a_m \phi c_p G_M)$
R = gas constant
R = component R
R = $r_{mA}/(a_m \phi G_M)$
Re = Reynolds number = $G/(a_v \phi \mu)$
R_h = hydraulic radius = $\epsilon/(a_v \phi)$
r = reaction rate per unit mass of bed
r = number of moles of R
r_{mA} = molal reaction rate of component A per unit mass of catalyst
r_{vA} = molal reaction rate of component A per unit volume of bed
r_j = molal reaction rate of component j per unit mass of catalyst particles
S = component S
S = sphericity
Sc = Schmidt number = $(\mu/\rho D)$
$\Delta S_H, \Delta S_U, \Delta S_S$ = molal entropy of adsorption of hydrogen, unsaturated and saturated hydrocarbons, respectively
s = number of moles of S
T = temperature, °K.
t = temperature, °C.
x = direction of mass transfer
y, y_A = mole fraction of pressure factor
y_{fA} = mole fraction of pressure factor for component A

Greek Letters

Δ = difference
δ = partial differential operator
ϵ = void fraction
μ = viscosity of fluid
π = total pressure
ρ = density of fluid
Σ = summation
ϕ = shape factor
$\theta_1, \ldots, \theta_8$ = constants
$\theta_1^\circ, \ldots, \theta_8^\circ$ = constants (initial guess values for $\theta_1, \ldots, \theta_8$)

Subscripts

A,B,R,S = components
D = diffusion
f = film
G = gas
H = hydrogen
H = heat transfer
i = surface of the particles
j = component
L = liquid
M = moles
m = mean
m = unit mass of catalyst particles
p = constant pressure
p = particle
S = saturated compound: paraffin
u = unsaturated compound: olefin
v = unit volume

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Manuscript received January 12, 1961; revision received June 19, 1961; paper accepted June 19, 1961. Paper presented at A.I.Ch.E. Washington meeting.