the data as in the case for carbon dioxide. However the excellent agreement with the work of Hirth (*11*), Leduc (*14*), Rayleigh (*19*), and Cawood and Patterson (*4*) substantiates the reliability of this investigation. The values of Bateucas (*1*) and Johnson (*12*) vary considerably from these data.

The actual maximum error of the reported compressibility factors is estimated to be less than ± 0.10%.

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Relationship Between Pellet Size and Performance of Catalysts

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The effect of mass transfer resistance in reducing the effectiveness of porous catalysts has been known since the publication of Thiele's classical paper in 1939. The variation in temperature caused by resistance to heat transfer may bring about equally significant changes in effectiveness in some cases. An extension of Thiele's treatment to take exact account of heat transfer resistance leads to a set of nonlinear differential equations that can only be solved numerically.

This paper presents an approximate treatment of the simultaneous effects of resistances to mass and heat transfer. With the limitations imposed by linearizing the equations the formulas derived give the activity and selectivity for any combination of reactions. The use of the results is illustrated by three examples. It is shown that the principal effects are associated with the variation of concentration within the pellet of catalyst and with the difference in temperature between the surface of the pellet and the bulk fluid.

PURPOSE AND SCOPE

The purpose of this paper is to extend the work of Thiele (*10*) on the relation between the size of catalyst pellets and the rate of the catalyzed reaction to take account of two additional effects. Thiele gave a quantitative theory for the diminution in average rate of reaction associated with resistance to diffusion through a porous catalyst, under the assumptions that the temperature is uniform within the pellet and that the composition at the surface of the pellet is the same as the composition in the bulk fluid. There is in addition the tacit assumption that the temperature at the surface of the pellet is the same as the temperature in the bulk fluid. These assumptions are removed from the basis of the present work.

The range of application of the results given below is restricted however by the assumption that the rates of all reactions involved vary linearly with concentrations and with temperature. Although the assumption with regard to concentration is by no means as strong as the assumption that all reactions are of first order, it certainly limits the magnitude of effects that can be described quantitatively. The analogous limitation on the range of temperature that can be covered applies to most reactions because it is rarely that one finds an approximately linear relation between rate and temperature. It must be understood that the ranges of concentration and temperature that are in question here are the ranges covered in the interval between the center of a pellet and the bulk fluid in the immediate neighborhood of that pellet, but not the ranges covered in the whole reactor.

A second restrictive assumption is that the flux of each substance is related to the gradient of its concentration by a constant diffusion coefficient. This assumption is justified if only two substances are present, if all substances present have about the same diffusivity and the reaction does not change the number of molecules, or if the concentrations of all reactants and products are small. A good example of a case in which this assumption is not justified is a gas-phase hydrogenation in which hydrogen and the other reactant are fed in comparable concentrations.

In one respect the results given in this paper greatly extend the scope of the theory. There is no limitation in principle on the number of reactions that are going on, or on the number of *concentrations that determine the rates* of these reactions. In practice the step from one to two reactions seriously increases the difficulty of calculating the average rates, and the step from two to three reactions reaches almost to the practical limit for desk computation.

The assumption that the pellet of catalyst is spherical is not seriously restrictive. A chemist or an engineer can probably guess an equivalent radius for a nonspherical particle as well as he can estimate the required transport coefficients.

The principal uses of this extension of the theory are then to give estimates of moderate effects on rates and to indicate when the effects are large enough to require calculation by direct numerical solution of the differential equations.

Some indication of the accuracy of the approximations involved is given by the numerical results obtained with three examples. The table shows the ratio of the average production rate of a substance in the catalyst pellet to what the production rate would be if the ambient conditions held throughout the pellet, as calculated in three ways: first by solving the complete set of differential equations numerically, second by the method given in this paper, and third by the isothermal theory.

		Numerical solution	This report	Isothermal
1		0.83	0.88	0.74
2		1.12	1.42	0.74
3	A_1	0.76	0.78	0.74
	A_2	−0.19	−0.13	0.24

The numerical solutions of the differential equations were carried out by Dr. R. D. Hawthorn, using a program coded by him for the Datatron. In the first two examples a single first-order reaction is going on, but in the third example A_1 is reacting to give A_2 which reacts in turn to an undesired product. As might be expected there is some improvement over the isothermal theory, but the effect of the change in temperature is exaggerated by the linear approximation, as is explained in the discussion of the examples.

DEVELOPMENT OF THE THEORY

Review of the Current Theory

The effect of the size of porous catalyst pellets on the apparent activity of the catalyst has been well known since 1939, when Thiele published his quantitative theory (*10*). Very little has been added to Thiele's work since that time. Wheeler's article (*11*) gives expressions for the selectivity in certain sets of first-order reactions, and the article by Weisz and Prater (*10*) shows how the over-all selectivity for successive first-order reactions may be calculated for an isothermal reactor. In all this work no variation of temperature is taken into account, although there are practically important cases where the effect is significant.

Frank-Kamenetsky (*5*) discussed the relation between mass and heat transfer from the surface of a catalytic particle and showed that there can be two steady states. Buben (*2*) realized the steady states experimentally and proposed to use the corresponding conditions to study the kinetics of reactions. Both these authors considered only impermeable pellets of catalyst.

Damköhler (*3*) calculated an upper limit on the rise in temperature within a spherical pellet and showed that for several practical catalysts this rise in temperature is insignificant. Pshezhetskii and Rubinstein (*9*), without referring to Damköhler's work, showed that the limiting rise does not depend *on the shape of the particle*. In addition they gave, in their Equation (30), an explicit expression for the functional dependence of the local rate on concentration and temperature, in terms of the average rate and its variation with concentration and temperature, with the restrictions that only one reaction is going on and that the depth of penetration of the reaction within the granule is small. Prater (*8*) has recently given an example in which the change in temperature is important, the dehydrogenation of cyclohexane with a supported platinum catalyst. Wicke (*13*) indicated the qualitative nature of the interaction between the change of temperature across a surface film and the change of concentration within the porous solid, but did not develop a quantitative relation.

A complete theory should take account of the changes in both composition and temperature encountered in going from the bulk fluid to the surface of the pellet and on into the pellet toward the center. Such a theory is possible only in the form of a set of differential equations that are to be solved numerically, both because the general diffusion equations are not linear and because the relations between rates of reaction and temperature are not linear. An analytic theory must be based on some simplifying assumptions.

Basis of the Theory

This paper describes the behavior within a spherical pellet in the linear approximation, that is in the case when the rate of reaction depends linearly on both concentration and temperature. Although the relation between the rate and the temperature is ordinarily far from linear, when the variation of temperature is small one can get a good estimate of it and of its effect on the rate. The other assumptions restricting the application of the theory are stated and discussed in the section on the purpose and scope of the report. Except for the assumption that one can neglect the effect of any change in the number of moles during the reaction, the same assumptions are involved in the usual applications of the Thiele theory and its extensions.

Theory for a Single Reaction

It is convenient to use as a reference point the condition of the fluid surrounding the pellet and to express the concentration and temperature as differences from their reference values. Consider first the case of a single reaction. The rate of reaction at any point is given in the form

$$R = R_o + ac + bt$$

where R_o is the rate that would hold if the concentration and temperature were uniform, c and t are the differences in concentration and temperature, and a and b are equal to $\partial R/\partial c$ and $\partial R/\partial t$ in the condition of the bulk fluid.

In a steady state the material balance at a point gives the equation

$$\frac{D}{r_1^2 r^2}\frac{d}{dr}\left(r^2\frac{dc}{dr}\right) + s\,(R_o + ac + bt) = 0$$

and the heat balance gives

$$\frac{\lambda}{r_1^2 r^2}\frac{d}{dr}\left(r^2\frac{dt}{dr}\right) + Q\,(R_o + ac + bt) = 0$$

In this equation, s gives the number of moles of the substance in question produced by the reaction, and Q is the heat produced.

The boundary conditions are

$$\frac{dc}{dr} = 0 \quad (r = 0)$$

$$\frac{dt}{dr} = 0 \quad (r = 0)$$

$$k_o\,c + (D/r_1)\,\frac{dc}{dr} = 0 \quad (r = 1)$$

and

$$ht + (\lambda/r_1)\,\frac{dt}{dr} = 0 \quad (r = 1)$$

From the solution of these equations one derives three quantities of interest. The most important of these is the effectiveness factor for the catalyst, that is the average rate divided by R_o. The expression is

$$\overline{R}/R_o = \frac{3(\varphi\coth\varphi - 1)}{\varphi^2 + \omega(\varphi\coth\varphi - 1)}$$

or, in a form that exhibits the separate resistance in transport to the surface

$$\overline{R}/R_o = \left[\frac{\varphi^2}{3(\varphi \coth \varphi - 1)} + \frac{\omega}{3} \right]^{-1}$$

φ is defined by

$$\varphi^2 = -r_1^2 \, (sa/D + bQ/\lambda)$$

ω denotes a dimensionless quantity involving the mass transfer and heat transfer coefficients defined as

$$\omega = -r_1 \, (sa/k_c + bQ/h)$$

The rise in temperature at the center of the pellet is given by the expression

$$t(0) = \frac{r_1^2 Q R_o}{\lambda} \left[\frac{1 + (\lambda/\mathrm{hr}_1)(\varphi \coth \varphi - 1) - \varphi/\sinh \varphi}{\varphi^2 + \omega(\varphi \coth \varphi - 1)} \right]$$

and the rise in concentration at the center is

$$c(0) = -\frac{r_1^2 R_o}{D} \left[\frac{1 + (D/k_c r_1)(\varphi \coth \varphi - 1) - \varphi/\sinh \varphi}{\varphi^2 + \omega(\varphi \coth \varphi - 1)} \right]$$

For completeness the forms appropriate when φ^2 is negative are added. In this case one defines ψ by

$$\psi = (-\varphi^2)^{1/2}$$

and finds

$$\overline{R}/R_o = \frac{3(1 - \psi \cot \psi)}{\psi^2 + \omega(1 - \psi \cot \psi)}$$

$$t(0) = \frac{r_1^2 Q R_o}{\lambda} \left[\frac{-1 + (\lambda/\mathrm{hr}_1)(1 - \psi \cot \psi) + \psi/\sin \psi}{\psi^2 + \omega\ (1 - \psi \cot \psi)} \right]$$

and

$$c(0) = -\frac{r_1^2 R_o}{D} \left[\frac{-1 + (D/k_c r_1)(1 - \psi \cot \psi) + \psi/\sin \psi}{\psi^2 + \omega\ (1 - \psi \cot \psi)} \right]$$

The derivations of these formulas are given in the Appendix, together with the modifications that are necessary when more than one reaction is going on.[*]

The estimation of thermal conductivity and molecular diffusivity through pellets presents a real problem. If the thermal conductivity has not been measured, a rough estimate can be formed by analogy with materials for which the conductivity is known. Diffusivities through catalyst supports have been reported in the range from 0.12 to 0.03 times their values in the absence of the solid (2, 3, 7) with no clear relation between the ratio and the structure of the solid. Apparently the only satisfactory course is to measure the effective diffusivity.

Figure 1 gives a convenient means for evaluating the ratio of the resistance to transport through the pellet to the chemical resistance. In other terms it gives the contribution made by transport through the pellet to the reciprocal of the effectiveness factor. One finds the reciprocal of the effectiveness factor by adding three quantities: $\omega/3$ for transport to the pellet, the quantity from the graph for transport through the pellet, and unity for the chemical process.

Theory for More Than One Reaction

The differential equation and rate expressions describing the system when more than one reaction is going on are the same as those given above for a single reaction, except that some of the symbols appearing are understood to represent matrices instead of simple quantities. R and Q become column matrices, having as their elements the rates and heats of the independent reactions. c is a row matrix representing the changes in the concentrations of the key substances used in describing the system. a is a square matrix, with elements $\partial R/\partial c$; b is a column matrix, with elements $\partial R/\partial t$, and s is a square matrix giving the amounts of the key substances produced by the independent reactions.

The derivation of the expressions for the average production rates of substances, and for the temperature and composition at the center of the pellet, follows the pattern that would be used for a single reaction but is somewhat complicated by the need for taking account of the order of multiplications. It is convenient to use the auxiliary quantities and matrices defined by the following formulas:

$K = D/k_c r_1$

$H = \lambda/\mathrm{hr}_1$

$f = -r_1^2 b' \, s/\lambda$

$q = -s^{-1} Q$

The generalization of the Thiele modulus that arises naturally from this treatment is a square matrix defined by the equation

$$\varphi^2 = -r_1^2 \left[\left(\frac{a}{D} \right)' + \frac{1}{\lambda} s^{-1} Q b' \right] s$$

The matrix (a/D) is formed by dividing the elements of a by the diffusivities of the corresponding substances.

Given these definitions one can write the expressions for the average production rates and for the temperature and concentrations at the center of the pellet:

$$\overline{R's} = R_o's \left\{ \frac{\varphi^2}{3(\varphi \coth \varphi - \mathrm{I})} + \frac{1}{3} [K\varphi^2(1 + f\varphi^{-2}q) - Hqf] \, (\mathrm{I} + f\varphi^{-2}q - \varphi^{-2}qf)^{-1} \right\}^{-1}$$

$t(0) =$

$$\frac{-r_1^2}{3\lambda} \overline{R's} \left(\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - \mathrm{I}} + H\mathrm{I} \right) q$$

and

$(DC)(0) =$

$$\frac{r_1^2}{3} \overline{R's} \left(\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - \mathrm{I}} + K\mathrm{I} \right)$$

$\overline{R's}$, the quantity that appears in the first of these expressions, is usually a more useful set of quantities than the set of rates of individual reactions. The average rates can be calculated from $\overline{R's}$ by

$$\overline{R} = [(\overline{R's}) \, s^{-1}]'$$

Examples

1. Consider a first-order reaction with a moderate heat of reaction and activation energy. The quantities required to characterize the system are set forth in the following tables.

Conditions around the pellet

T_o = 500 °K.

G = 0.449 g./sq. cm. sec.

N_o = 0.5

P = 10 bar

Properties of the gas

Average molecular weight = 104.7 g./mole

c_p = 2.45 j./g. deg.

λ_g = 6.55×10^{-4} j./cm. sec. deg.

η = 2.06×10^{-4} g./cm. sec.

D_g = 6.11×10^{-3} sq. cm./sec.

Properties of the catalyst

r_1 = 0.21 cm.

λ = 2.51×10^{-3} j./cm. sec. deg.

D = $0.16 \, D_g = 9.78 \times 10^{-4}$ sq. cm./sec.

Description of the chemical process

Q = 2.054×10^{5} j./mole

$$R = k(N_o\rho_n + c) \exp \left[\frac{E}{R_g} \left(\frac{1}{T_o} - \frac{1}{T} \right) \right] \text{ mole/cc. sec.}$$

where

k = 0.133 sec.$^{-1}$

ρ_n = $P/R_gT = 2.4054 \times 10^{-4}$ mole/cc.

E = 8×10^{4} j./mole

From these data one calculates the derived quantities

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[*] Material has been deposited as document 6624 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$2.50 for photoprints or \$1.75 for 35-mm. microfilm.

$N_{Pr} = c_p\eta/\lambda_g = 0.771$
$N_{Sc} = \eta/\rho D_g = 1.339$
$N_{Re} = Gd_p/\eta = 915$
$N_{Nu}N_{Pr}^{-1/3} = N_{Sh}N_{Sc}^{-1/3} = 60.3$
$N_{Nu} = 55.3$
$N_{Sh} = 66.5$
$h = N_{Nu}\lambda_g/d_p = 8.62 \times 10^{-2}$ j./sq. cm. sec. deg.
$k_c = N_{Sh}D_g/d_p = 0.967$ cm./sec.
$R_o = kN_o\rho_n = 1.600 \times 10^{-5}$ mole/cc. sec.
$a = k = 0.133$ sec.$^{-1}$
$b = R_oE/R_gT_o^2 = 6.16 \times 10^{-7}$ mole/cc. sec. deg.
$-sr_1^2a/D = 6.00$
$r_1^2bQ/\lambda = 2.22$
$\varphi = r_1(-sa/D - bQ/\lambda)^{1/2} = 1.944$

In the analysis of Thiele, one would use r_1^2a/D as the square of the modulus, giving a value of 2.449 for the modulus and 0.743 for the effectiveness factor. By taking account of the rise in temperature within the pellet one adjusts the modulus to 1.944, which corresponds to an effectiveness factor of 0.814. The effect at the surface has still to be taken into account. One finds

$-sa/k_c = 0.1376$ cm.$^{-1}$
$bQ/h = 1.467$ cm.$^{-1}$
$\omega = r_1(-sa/k_c - bQ/h) = -0.279$

This gives a figure of 0.881 for the effectiveness factor.

This result can be shown more clearly in terms of the separate resistances. Referring to the chemical resistance as unity one has for the diffusive resistance within the pellet

$$\varphi^2/3(\varphi \coth \varphi - 1) - 1 = 0.229$$

and for the resistance in transport to the surface

$$\omega/3 = -0.093$$

The sum of all the resistances is

$$1/E_A = 1 + 0.229 - 0.093$$
$$= 1.136$$

from which one finds that

$$E_A = 0.881$$

2. Exaggerate the thermal effect found in the first example. Take larger values for three quantities

$N_o = 0.75$
$E = 1.2 \times 10^5$ j./mole
$Q = 2.5675 \times 10^5$ j./mole

These changes have the effect of multiplying the product bQ by the factor 2.8125. Now $\varphi^2 = -0.2488$, so the expressions written for imaginary values of φ are

$$\psi = i\varphi = 0.499$$
$$\omega = -0.837$$
$$\psi^2/[3(1 - \psi \cot \psi)] - 1 = -0.0167$$
$$\omega/3 = -0.2791$$
$$1/E_A = 1 - 0.0167 - 0.2791 = 0.704$$
$$E_A = 1.42$$

In this rather extreme case one has negative resistances both within and at the surface of the pellet.

3. Study the selectivity of a catalyst for the first of two successive first-order reactions. The formulas that are required are given in the Appendix. The chemical equations are

$$A_1 = A_2$$
$$A_2 = A_3$$

or, in the desired form

$$0 = -A_1 + A_2$$
$$0 = -A_2 + A_3$$

with the rates

$$R_i = k_i(N_{io}\rho_n + c_i) \exp \left[\frac{E_i}{R_g}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right]$$

The coefficients of A_1 and A_2 in the chemical equations constitute the stoichiometric matrix. It should be remarked that although in this example the rate of each reaction depends only on the concentration of the substance that is being consumed in the reaction, the application of the theory is not restricted to this condition. The parameters of the reactions are

	1	2
Q(j/mole)	6×10^4	2×10^5
E(j/mole)	4×10^4	1.6×10^5
k(sec.$^{-1}$)	1.5	0.5

For the substances one has

	1	2
N_o	0.25	0.50
D(sq. cm./sec.)	10^{-2}	10^{-2}

The other data are

$T_o = 500$°K.
$P = 1$ bar
$r_1 = 0.2$ cm.
$\lambda = 2.5 \times 10^{-3}$ j./cm. sec. deg.
$k_c = 5$ cm./sec.
$h = 9 \times 10^{-2}$ j./sq. cm. sec. deg.

The data required in matrix form are

$$Q = 10^5 \begin{pmatrix} 0.6 \\ 2 \end{pmatrix} \text{j./mole}$$

$$R_o = 10^{-6} \begin{pmatrix} 9.02 \\ 6.01 \end{pmatrix} \text{mole/cc. sec.}$$

$$s = \begin{pmatrix} -1 & 1 \\ 0 & -1 \end{pmatrix}$$

$$R_o's = 10^{-6}(-9.02, 3.01) \text{mole/cc. sec.}$$

and

$$a = \begin{pmatrix} 1.5 & 0 \\ 0 & 0.5 \end{pmatrix} \text{sec.}^{-1}$$

The selectivity under the reference conditions is given by the ratio of the production rate for A_2 to the consumption rate for A_1, that is by the negative of the ratio of the two terms in $R_o's$ which is 0.33. This value is low enough to raise the question whether it is useful to continue to higher conversions.

The calculation proceeds as follows:

$$(a/D) = 10^2 \begin{pmatrix} 1.5 & 0 \\ 0 & 0.5 \end{pmatrix} \text{cm.}^{-2}$$

$$b = \begin{pmatrix} R_{o1}E_1/R_gT_o^2 \\ R_{o2}E_2/R_gT_o^2 \end{pmatrix} = 10^{-7} \begin{pmatrix} 1.736 \\ 4.629 \end{pmatrix} \text{mole/cc. sec. deg.}$$

$$f = -r_1^2b's/\lambda = -\frac{0.04}{2.5 \times 10^{-3}} (10^{-7}) (1.736, 4.629) \begin{pmatrix} -1 & 1 \\ 0 & -1 \end{pmatrix} \text{mole/j.}$$

$$= 10^{-6} (2.777, 4.629) \text{ mole/j.}$$

$$s^{-1} = \begin{pmatrix} -1 & -1 \\ 0 & -1 \end{pmatrix}$$

$$q = -s^{-1}Q$$

$$= \begin{pmatrix} 1 & 1 \\ 0 & 1 \end{pmatrix} 10^5 \begin{pmatrix} 0.6 \\ 2.0 \end{pmatrix} \text{j./mole}$$

$$= 10^5 \begin{pmatrix} 2.6 \\ 2.0 \end{pmatrix} \text{j./mole}$$

$$-r_1^2(a/D)'s = (0.04)(10^2) \begin{pmatrix} 1.5 & 0 \\ 0 & 0.5 \end{pmatrix} \begin{pmatrix} 1 & -1 \\ 0 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} 6 & -6 \\ 0 & 2 \end{pmatrix}$$

$$qf = 10^{-1} \begin{pmatrix} 2.6 \\ 2.0 \end{pmatrix} (2.777, 4.629)$$

$$= \begin{pmatrix} 0.7221 & 1.2035 \\ 0.5554 & 0.9257 \end{pmatrix}$$

$$\varphi^2 = -r_1^2(a/D)'s - qf$$

$$= \begin{pmatrix} 5.2779 & -7.2035 \\ -0.5554 & 1.0743 \end{pmatrix}$$

There is no need here to calculate the matrix φ because the functions of φ can be evaluated as easily from φ^2 as from φ. One must have the characteristic values of φ^2, given by the solutions for x of the determinantal equation

$$|\varphi^2 - x\mathrm{I}| = 0$$

or

$$x^2 - 6.3522x + 1.6687 = 0$$

The solutions are $x_1 = 6.078$ and $x_2 = 0.2746$. Now construct the auxiliary matrices

$$M_1 = (\varphi^2 - x_2\mathrm{I})/(x_1 - x_2)$$

and

$$M_2 = (\varphi^2 - x_1\mathrm{I})/(x_2 - x_1)$$

to be used with Sylvester's theorem (*6*) in computing functions of φ^2. One finds

$$M_1 = \begin{pmatrix} 0.8622 & -1.2413 \\ -0.0957 & 0.1378 \end{pmatrix}$$

and

$$M_2 = \begin{pmatrix} 0.1378 & 1.2413 \\ 0.0957 & 0.8622 \end{pmatrix}$$

Sylvester's formula for this case is

$$g(\varphi^2) = M_1 g(x_1) + M_2 g(x_2)$$

The first function needed is

$$\varphi^2/[3(\varphi \coth \varphi - \mathrm{I})]$$

so that for this function

$$g(x) = x/[3(x^{1/2} \coth x^{1/2} - 1)]$$

One finds $g(x_1) = 1.3495$ and $g(x_2) = 1.0182$, which gives for $g(\varphi^2)$

$$\varphi^2/[3(\varphi \coth \varphi - \mathrm{I})] = \begin{pmatrix} 1.3002 & -0.4114 \\ -0.0317 & 1.0638 \end{pmatrix}$$

Now one needs the quantity $f\varphi^{-2}q$, involving φ^{-2}, which is found more easily by the ordinary process of inversion than from Sylvester's theorem. One finds successively

$$\varphi^{-2} = \begin{pmatrix} 0.6438 & 4.3168 \\ 0.3329 & 3.1629 \end{pmatrix}$$

$$\varphi^{-2}q = 10^5 \begin{pmatrix} 10.3073 \\ 7.1912 \end{pmatrix}$$

$$f\varphi^{-2}q = 6.1912$$

$$\varphi^{-2}qf = \begin{pmatrix} 2.8626 & 4.7710 \\ 1.9971 & 3.3286 \end{pmatrix}$$

$$\mathrm{I} + f\varphi^{-2}q - \varphi^{-2}qf = \begin{pmatrix} 4.3286 & -4.7710 \\ -1.9971 & 3.8626 \end{pmatrix}$$

$$(\mathrm{I} + f\varphi^{-2}q - \varphi^{-2}qf)^{-1} = \begin{pmatrix} 0.5371 & 0.6634 \\ 0.2777 & 0.6019 \end{pmatrix}$$

and

$$K\varphi^2(\mathrm{I} + f\varphi^{-2}q) - Hqf = \begin{pmatrix} 0.2793 & -0.6852 \\ -0.1171 & -0.0513 \end{pmatrix}$$

using for the last result the expressions

$$K = D/k_c r_1 = 10^{-2}$$

and

$$H = \lambda/hr_1 = 0.1389$$

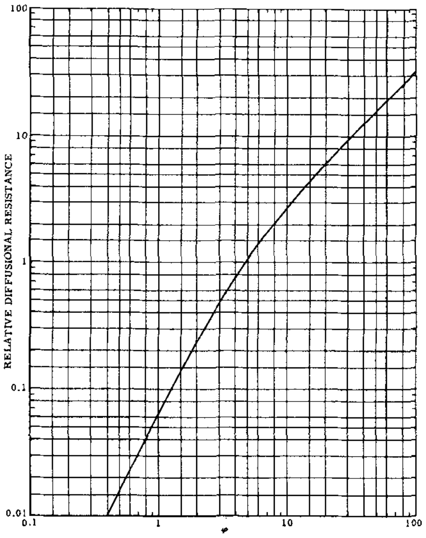

Fig. 1. Ratio of effective diffusional resistance to chemical resistance.

From these results one can calculate the relative resistance in transport to the surface of the pellet:

$$\frac{1}{3}[K\varphi^{-2}(1 + f\varphi^{-2}q) - Hqf](\mathrm{I} + f\varphi^{-2}q - \varphi^{-2}qf)^{-1} = \begin{pmatrix} -0.0134 & -0.0757 \\ -0.0257 & -0.0362 \end{pmatrix}$$

This term is added to the term for the sum of the chemical resistance and the resistance to diffusion through the pellet $\varphi^2/[3(\varphi \coth \varphi - \mathrm{I})]$ to give the ratio of the total resistance to the chemical resistance. The result is the matrix

$$\begin{pmatrix} 1.2868 & -0.4871 \\ -0.0574 & 1.0276 \end{pmatrix}$$

the reciprocal of which

$$\begin{pmatrix} 0.7916 & 0.3752 \\ 0.0442 & 0.9941 \end{pmatrix}$$

is premultiplied by the matrix of ideal production rates to get the average production rates. The product is

$$\overline{R's} = 10^{-6}\ (-7.008, -0.396)\ \text{mole/cc. sec.}$$

which is to be compared with the ideal value

$$R_o's = 10^{-6}\ (-9.020,\ 3.007)\ \text{mole/cc. sec.}$$

The selectivity for the pellet as a whole is actually negative, so it is obvious that the conversion is too high.

The matrix function

$$\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - \mathrm{I}}$$

is required in calculating the temperature and composition at the center of the pellet. From Sylvester's theorem one finds

$$\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - 1} = \begin{pmatrix} 0.3999 & 0.1344 \\ 0.0104 & 0.4783 \end{pmatrix}$$

and then

$$\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - \mathrm{I}} + H\mathrm{I} = \begin{pmatrix} 0.5388 & 0.1344 \\ 0.0104 & 0.6172 \end{pmatrix}$$

$$\frac{r_1^2}{3\lambda}\left(\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - \mathrm{I}} + H\mathrm{I}\right) q = 10^6 \begin{pmatrix} 0.8905 \\ 0.6727 \end{pmatrix} \text{cc. sec. deg./mole}$$

Finally from the expression

$$t(0) = \overline{R's}\ (10^6) \begin{pmatrix} 0.8905 \\ 0.6727 \end{pmatrix}$$

$$t(0) = 6.51 \text{ deg.}$$

In calculating the composition one has the steps

$$\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - \mathrm{I}} + K\mathrm{I} = \begin{pmatrix} 0.4099 & 0.1344 \\ 0.0104 & 0.4883 \end{pmatrix}$$

$$\frac{1}{3} r_1^2 \left(\frac{\mathrm{I} - \varphi/\sinh \varphi}{\varphi \coth \varphi - \mathrm{I}} + K\mathrm{I}\right) = 10^{-2} \begin{pmatrix} 0.5465 & 0.1792 \\ 0.0138 & 0.6511 \end{pmatrix} \text{sq. cm.}$$

and from the expression

$$(Dc)(0) = \overline{R's}(10^{-2}) \begin{pmatrix} 0.5465 & 0.1792 \\ 0.0138 & 0.6511 \end{pmatrix}$$

$$(Dc)(0) = 10^{-8}\ (-3.835, -1.513)\ \text{mole/cm. sec.}$$

From this one finds that

$$c(0) = 10^{-6}\ (-3.835, -1.513)$$

from which one can calculate the mole fractions at the center:

$$N_1(0) = 0.091 \text{ and } N_2(0) = 0.437$$

DISCUSSION OF EXAMPLES

Several significant features of the results calculated in the examples should be pointed out. One can get an idea how much the assumptions about the rate of reaction distort the results by testing the assumed form under the most extreme conditions, those obtaining at the center of the pellet. In the first example the calculated temperature and mole fraction of reactant at the center are 509.49°K. and 0.125. The corresponding rate calculated from the linear approximation is 9.8 x 10^{-6} mole/cc. sec., whereas the correct rate expression gives 5.7 x 10^{-6} mole/cc. sec. One sees that despite the unduly small variation of rate with temperature alone that is given by the linear form, the calculated rate is much too high. The explanation of this anamoly lies in the separation of the effects of concentration and of temperature, making it possible for the calculated rate to be large when the temperature is high even if the concentration is zero. One can improve the representation of the rate by giving it as a product of two factors, one linear in the temperature and the other linear in the concentration. In this example the rate would be expressed in the form $R = (1.6 \times 10^5)(1 + 8.31 \times 10^3 C)(1 + 3.85 \times 10^{-2} t)$ mole/cc. sec. the corresponding calculated rate 5.5×10^{-6} mole/sq. cm. sec., a much better result. But one cannot take advantage of the improvement because this description of the rate is not linear in the temperature and concentration taken together and so cannot be incorporated into the analysis.

In the section on the purpose and scope of the work two results from the third example were shown in the form of ratios of average production rates to their ideal values. One could also calculate the ratio of the average rate of each reaction to its ideal value, getting the results 0.78 and 1.23 for the two reactions. It may be seen that these numbers, even taken together, do not constitute an effectiveness factor. One might consider the matrix that is multiplied by R_0's, the set of ideal production rates, to give $\overline{R}$'s, the set of average production rates, as a sort of effectiveness factor; however it has no unique status since there is another matrix that converts the set of ideal reaction rates to the set of average reaction rates, which could just as well be taken as an effectiveness factor. One concludes that there is no uniquely defined effectiveness factor when more than one reaction is going on by observing that there is no unique matrix that transforms R_0 to $\overline{R}$.

The following table gives the comparison of the results obtained in example 3 with those from the exact calculation and from the isothermal theory.

		Exact	This report	Isothermal
$\overline{(R's)}_1$	μ mole/cc. sec.	−6.87	−7.01	−6.70
$\overline{(R's)}_2$	μ mole/cc. sec.	−0.57	−0.40	0.71
$\overline{R_1}$	μ mole/cc. sec.	6.87	7.01	6.70
$\overline{R_2}$	μ mole/cc. sec.	7.44	7.40	5.99
$t(O)$	deg.	5.94	6.51	–
$c_1(O)$	μ mole/cc.	−3.27	−3.84	−3.45
$c_2(O)$	μ mole/cc.	−1.68	−1.51	−0.49
Selectivity		−0.08	−0.06	0.11

Although the linear theory fails seriously in predicting the concentration of the primary reactant at the center of the pellet in this example, the general picture it gives is much better than what is found from the isothermal theory. The selectivity, the quantity of most interest, is much better approximated when the rise in temperature is taken into account.

NOTATION

The symbols that denote matrices when more than one reaction is involved are preceded by an asterisk. The dimensions are: M, mass; L, length; t, time; T, temperature; E, energy; n, number of moles.

$^*a$ = $\partial R/\partial c$ $\quad t^{-1}$
$^*b$ = $\partial R/\partial t$ $\quad n/L^3tT$
$^*c$ = excess concentration of key substance $\quad n/L^3$
c_p = heat capacity $\quad E/MT$
d_p = diameter of pellet $\quad L$
$^*f$ = $-r_1^2 b's/\lambda$ $\quad n/E$
h = heat transfer coefficient $\quad E/L^2tT$
k_c = mass transfer coefficient $\quad L/t$
m = index of a reaction, Appendix
n = index of a substance, Appendix
$^*q$ = $-s^{-1}Q$ $\quad E/n$
r = dimensionless radial variable
r_1 = radius of pellet $\quad L$
$^*s$ = stoichiometric coefficient
t = excess temperature $\quad T$
$^*u$ = rDc/r_1^2 $\quad n/L^3t$
v = $r\lambda t/r_1^2$ $\quad E/L^3t$
$^*w$ = production rate of a key substance $\quad n/L^3t$
x = characteristic value of a matrix
$^*y$ = flux of a key substance $\quad n/L^2t$
$^*z$ = flux of a virtual conversion $\quad n/L^2t$
$^*A$ = chemical symbol for a substance
$^*B$ = constant of integration [Equation (21)] $\quad n/L^3t$
$^*C$ = excess concentration
D = effective diffusivity through pellet $\quad L^2/t$
D_g = diffusivity in laminar boundary layer $\quad L^2/t$
E = activation energy for a reaction $\quad E/n$
E_A = effectiveness factor for catalyst pellet
G = superficial mass velocity $\quad M/L^2t$
H = $\lambda/h\, r_1$
I = unit matrix
K = $D/k_c r_1$
L = constant of integration [Equation (14)] $\quad E/L^3t$
M = auxiliary matrix, used in example 3
N = mole fraction
N_{Nu} = hd_p/λ_g, the Nusselt number
N_{Pr} = $c_p\eta/\lambda_g$, the Prandtl number
N_{Re} = Gd_p/η, the Reynolds number
N_{Sc} = $\eta/\rho D_g$, the Schmidt number
N_{Sh} = $k_c d_p/D_g$, the Sherwood number
P = pressure $\quad E/L^3$
$^*Q$ = heat of reaction $\quad E/n$
$^*R$ = rate of key reaction $\quad n/L^3$
R_g = ideal gas constant $\quad E/nT$
$^*S$ = complete matrix of stoichiometric coefficients
$^*S_r, S_c$ = submatrices of S, defined in Appendix
T = absolute temperature $\quad T$
$^*U$ = rDC/r_1^2 $\quad n/L^3t$
$^*W$ = production rate of a substance $\quad n/L^3t$
$^*Y$ = flux of a substance $\quad n/L^2t$

Greek Letters

$^*\alpha$ = $\partial\sigma/\partial C$ $\quad t^{-1}$
$^*\beta$ = $\partial\sigma/\partial t$ $\quad n/L^3tT$
η = viscosity $\quad M/Lt$
λ = thermal conductivity in pellet $\quad E/LtT$
λ_g = thermal conductivity in laminar boundary layer $\quad E/LtT$
ρ = density of fluid $\quad M/L^3$
ρ_n = molar density of fluid $\quad n/L^3$
$^*\sigma$ = rate of reaction $\quad n/L^3t$
$^*\varphi$ = generalized modulus, defined before Equation (20)
ψ = $(-\varphi^2)^{1/2}$ if $\varphi^2 < 0$, for a single reaction
$^*\omega$ = $r_1(a/k_c - bQ/h)$ for a single reaction, defined by Equation (30) for the general case

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