Influence of Volume Change on Gas-Phase Reactions in Porous Catalysts

VERN W. WEEKMAN, JR. AND ROBERT L. GORRING

From the Socony Mobil Oil Co., Inc.,
Research Department, Paulsboro, New Jersey

Quantitative relationships describing the influence of volume change on the kinetics of constant-pressure, isothermal reactions in porous catalysts have been obtained. The results are valid for gas-phase reactions in the ordinary diffusion regime. Volume-change effectiveness factors were shown to be functions only of the diffusional-kinetic modulus and a newly defined volume-change modulus. Asymptotic solutions, developed for zero, first, and second order reactions, yielded basic relationships describing the theoretical maximum effect of volume change, independent of particle shape. Effectiveness factors as a function of the diffusional-kinetic modulus and the volume-change modulus are presented for zero, first, and second order reactions in spherical catalyst particles.

I. INTRODUCTION

Chemical reactions occurring in porous catalysts become controlled by intraparticle diffusion at sufficiently high reaction rates. For such reactions, a basic understanding of the mode of coupling between diffusive and chemical factors is essential to a rational analysis of the over-all kinetics (*1, 2*). For reactions in which the number of moles of reactants and products are equal, the influence of diffusional restriction has been expressed in terms of the effectiveness factor concept (*1–9*). The effectiveness factor, η, represents the actual reaction rate divided by the rate which would occur if the intraparticle reactant concentration were everywhere identical to that at the pellet surface. For constant-volume reactions of fixed order, η is a function *only* of the diffusional-kinetic, or Thiele modulus, φ.

For example, for semi-infinite flat plates, the normalized intraparticle concentration and its gradient are (*3*),

$$y = \cosh \varphi r / \cosh \varphi \qquad (1)$$

$$\frac{dy}{dr} = \varphi \left[\frac{\sinh \varphi r}{\cosh \varphi} \right] = \varphi \left[\left(\frac{\cosh \varphi r}{\cosh \varphi} \right)^2 \right.$$
$$\left. - \left(\frac{1}{\cosh \varphi} \right)^2 \right]^{1/2} = \varphi [y^2 - y_0^2]^{1/2} \qquad (2)$$

For diffusionally restricted reactions at constant pressure in which the volume of reactant and product differs, and the transport mechanism is ordinary diffusion, the kinetics may be significantly affected relative to the constant volume cases just described, i.e. the η vs. φ relationship may be shifted. Such a reaction may be represented as:

$$A \rightarrow nB \qquad (3)$$

Thiele (*3*), using a graphical technique, computed the effect of volume expansion for a few cases of first order reaction in flat plate geometry. Hawthorn (*10*), using numerical methods, computed effectiveness factors for volume-change reactions under isothermal and nonisothermal conditions.

The present study has the objective of quantitatively assessing the effects of (1) volume change [value of n in Eq. (3)], (2) order of reaction, and (3) concentration of inert diluents on the kinetics of constant-pressure, isothermal reactions in porous catalysts when the mass transport mechanism is ordinary diffusion.

II. NOMENCLATURE

a Radius of sphere or half-thickness of plate (cm)

$\bar{A}$ Cross-sectional area normal to flow (cm²)

A   Reactant

B   Product

C Concentration of reactant A,(g moles/ cm³) $= yC_1$

C_1 Concentration of A at catalyst surface, (g moles/cm³)

C_T Total gas concentration (g moles/cm³)

D_e Effective gas diffusivity in catalyst (cm²/sec)

k Reaction rate constant [sec⁻¹ (g moles/ cm³)¹⁻ᵐ]

m Order of reaction

n Stoichiometric coefficient in reaction A → nB

p dy/dr

q_i Molar flux of component i (g moles/ cm² sec)

r ζ/a, normalized distance from center of sphere or flat plate

r_e Normalized extinction length; fractional distance from center where $y = 0$, for zero order reactions

S_x Exterior surface area of particle

V_p Volume of particle

x $yx_1 = C/C_T$, mole fraction of A in gas

x_i Mole fraction of component i in gas

y $x/x_1 = C/C_1$, normalized concentration of reactant A

Greek Symbols

∇ Divergence operator

ζ Distance from center of plate or sphere (cm)

η Effectiveness factor, constant-volume case

η' Effectiveness factor, volume-change case

θ $(n - 1)x_1$, volume-change modulus

λ Empirical constant

Λ $(V_p/S_x)(k/D_e)^{1/2}$, volume to surface diffusion-kinetic modulus

φ $a(kC_1^{m-1}/D_e)^{1/2}$, diffusional-kinetic (Thiele) modulus

φ' $(3V_p/S_V)(k/D_e)^{1/2}$

Subscripts

e Effective value of quantity

1   Exterior surface of flat plate or sphere

i,j Components i,j

0   Center of flat plate or sphere

Superscripts

Designates quantities for volume-change reactions

III. DEVELOPMENT OF BASIC DIFFERENTIAL EQUATIONS

The following derivation applies to porous catalyst particles in the form of flat plates or spheres at whose surface the reactant concentration is held constant. Complicating factors such as surface diffusion, adsorption kinetics and equilibria, and external diffusion are assumed to be absent. The diffusivity of any inert diluent in the feed is assumed to be the same with respect to both reactant A and product B. This condition is approximately realized in practice since all gases (except H₂ and He) have diffusivities lying in a reasonably narrow range. Thus, we work with a single diffusion coefficient in the catalyst pore space, D_e.

The basic relations describing species transport in ideal gas mixtures when convection and ordinary diffusion occur simultaneously are the Stephan-Maxwell equations,

$$\nabla x_i = \sum_j [(x_i \mathbf{q}_j - x_j \mathbf{q}_i)/C_T D_{ei,j}] \quad (4)$$

where the binary diffusivities $\mathfrak{D}_{ij}$ have been replaced by the effective diffusivities, $D_{ei,j}$, in the catalyst pores (11–13). In a binary system containing only A and B reacting according to Eq. (3), the following auxiliary relationships are applicable,

$$x_A + x_B = 1 \quad (5)$$

$$nq_A = -q_B \quad (6)$$

Substitution of Eqs. (5) and (6) into Eq. (4) yields,

$$q_A = \{D_e C_1/[1 + (n - 1)x_A]\}\nabla x_A \quad (7)$$

The material balance on a differential element of catalyst lying between ζ and $\zeta + d\zeta$ is, for mth order reaction

$$q_A \bar{A}|_\zeta - \left[q_A \bar{A}|_\zeta + \frac{d(q_A \bar{A})}{d\zeta} d\zeta \right] = kC^m \bar{A} d\zeta \quad (8)$$

(Input flux at ζ) − (Output flux at $\zeta + d\zeta$) = reaction rate in $d\zeta$. Substitution in Eq. (8) for q_A from Eq. (7), introduction of the

appropriate normalizing definitions, and simplification yield the basic differential equations.

For flat plates (mth order reaction)

$$\frac{d^2y}{dr^2} - \frac{\theta}{1 + \theta y}\left(\frac{dy}{dr}\right)^2 = \varphi^2 y^m(1 + \theta y) \quad (9)$$

For spheres (mth order reaction)

$$\frac{d^2y}{dr^2} - \frac{\theta}{1 + \theta y}\left(\frac{dy}{dr}\right)^2 \left[1 - \frac{2(1 + \theta y)}{r\theta(dy/dr)}\right]$$
$$= \varphi^2 y^m(1 + \theta y) \quad (10)$$

with boundary conditions:

1. $dy/dr = 0$ at $r = 0$
2. $y = 1$ at $r = 1$

Note that boundary condition 1 implies that $dy/dr = 0$ when $y = y_0$. Examination of Eqs. (9) and (10) shows that the influence of the volume expansion on the effectiveness factor is a function of only the *single modulus* θ, which will hereafter be called the *volume-change modulus*. The modulus $\theta = (n - 1)x_1$ is seen to be composed of an "expansion factor," $n - 1$, multiplied by a "dilution factor," x_1, which together give a measure of the net "intensity" of the volume-change effect. Thus, the effectiveness factor for volume-change reactions is a function *only* of the conventional diffusional-kinetic modulus φ and the volume-change modulus θ.

When no volume change occurs ($\theta = 0$), Eqs. (9) and (10) are seen to reduce to the conventional relationships which have been treated previously (1–9).

The effectiveness factor for mth order reaction with volume change in a spherical catalyst pellet is,

$$\eta' = \frac{4\pi a^2 q_A|_{r=a}}{(4\pi a^3/3)kC_1^m} = \frac{3(dy/dr)'_{r=1}}{\varphi^2(1 + \theta)} \quad (11)$$

The ratio of effectiveness factors for volume-change to non-volume-change reactions is,

$$\frac{\eta'}{\eta} = \frac{(dy/dr)'_{r=1}}{(1 + \theta)(dy/dr)_{r=1}} \quad (12)$$

IV. CALCULATION METHODS AND PRESENTATION OF RESULTS

In this section, previous solutions to Eqs. (9) and (10) are reviewed and new solutions

are presented. First, analytic solutions to non-volume-change cases are discussed in order to provide a frame of reference. Then, it is shown that an asymptotic solution for the volume-change case can be obtained. Finally, solutions for volume-change reaction in spherical geometry [Eq. (10)] are computed numerically and shown to be in close agreement with the asymptotic solutions.

A. Analytic Solutions

Certain important cases are amenable to analytic solution. With no volume expansion, zero and first order reactions yield closed form solutions for spherical, cylindrical, and flat plate geometry. Thiele (3) and Aris (5) present solutions for first order reactions while Wheeler (4) treated general mth order reactions with flat plate geometry.

For zero order reactions in spheres, without volume expansion (i.e., $m = 0$, $\theta = 0$) a closed form solution of Eq. (10) is possible. The boundary conditions are,

1. $y = 1$ at $r = 1$
2. $y = 0$ at $r = r_e$

The extinction radius, r_e, is the normalized radius at which the concentration of reactant becomes zero. This "reactant exhaustion phenomenon" is unique with zero order reactions and is a consequence of the independence of reaction rate and reactant concentration. The required solution of Eq. (10) for no volume expansion is given as follows:

$$y = 1 - (1 - r)\left\{\frac{\varphi^2}{6}(1 + r)\right.$$
$$\left. - \frac{r_e}{r}\left[\frac{\varphi^2(1 + r_e)}{6} - \frac{1}{1 - r_e}\right]\right\} \quad (13)$$

If the dimensionless concentration y is finite at $r = 0$, then r_e must also be zero and Eq. (13) becomes,

$$y = 1 - (\varphi^2/6)(1 - r^2) \quad (14)$$

Differentiation of Eq. (14) and substitution into Eq. (11) shows that $\eta = 1$ whenever the reactant concentration is finite at $r = 0$. Furthermore, the value of φ at which $y = 0$ at $r_e = 0$ can be obtained from Eq. (14) as $\sqrt{6}$. Thus with no volume expansion,

if $\varphi < \sqrt{6}$, then $\eta = 1.0$ for zero order reactions in spheres.

For $\varphi > \sqrt{6}$, the effectiveness factor can be obtained by differentiating Eq. (13) and substituting in Eq. (11). The result is

$$\eta = 1 - r_e \left[\frac{1 + r_e}{2} - \frac{3}{\varphi^2(1 - r_e)} \right] \quad (15)$$

The relationship between φ and r_e can be obtained from the condition that when $r = r_e$, $dy/dr = 0$. This relationship is:

$$\varphi^2 = \frac{3}{(1 - r_e)[\frac{1}{2}(1 + r_e) - r_e^2]} \quad (16)$$

Finally substitution of Eq. (16) into Eq. (15) gives the following form of the effectiveness factor:

$$\eta = 1 - r_e^3 \quad \text{for} \quad \varphi > \sqrt{6} \quad (17)$$

Thus the effectiveness factor is the ratio of the volume in the sphere where $y \neq 0$, to the total volume. Using Eqs. (16) and (17) the effectiveness factor for the zero volume expansion case is presented on Fig. 1. Thiele's results (3) were used for the $\theta = 0$ curve in Fig. 2 for first order reaction.

B. Asymptotic Solutions

The differential equation for spheres [Eq. (10)] is seen to differ from that for flat plates [Eq. (9)] by a single term. Examination of Eqs. (1) and (2) (no volume change) shows that, as the modulus φ increases, the greatest amount of reaction takes place near the pellet exterior. Also, the concentration gradient at the surface is seen to increase linearly with φ, when φ becomes large. These two factors indicate that, for sufficiently large values of the modulus φ,

$$\frac{2(1 + \theta y)}{r\theta(dy/dr)} \ll 1$$

in Eq. (10) and the equations for spheres and flat plates become identical. We thus seek a solution to Eq. (9) which, by virtue of the arguments cited above, will be valid for spherical geometry, provided the diffusional-kinetic modulus φ is sufficiently large. Criteria for the limiting values of φ will be subsequently developed.

Equation (9) does not contain the inde-

ZERO ORDER REACTIONS — SPHERICAL PARTICLES
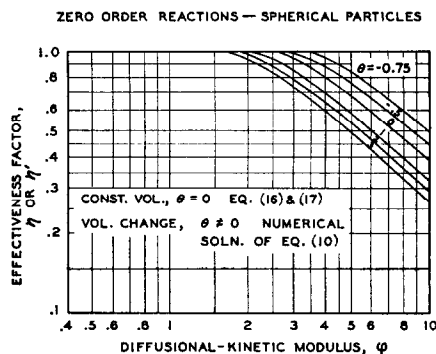
FIGS. 1–3. Influence of volume change on catalyst effectiveness.

FIG. 1. Zero order reactions—spherical particles.

FIRST ORDER REACTIONS— SPHERICAL PARTICLES
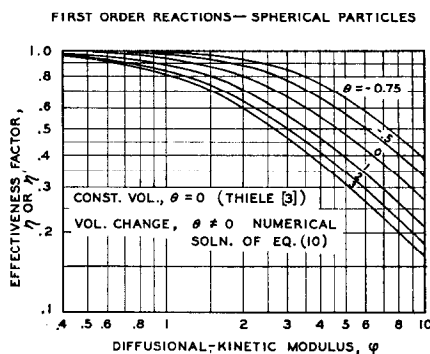
FIG. 2. First order reactions—spherical particles.

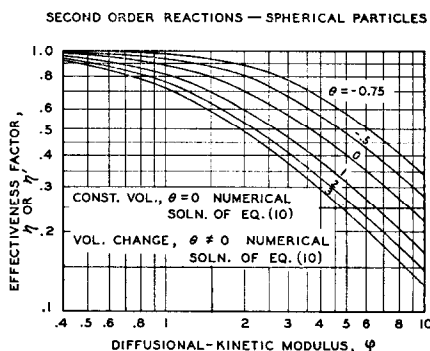SECOND ORDER REACTIONS — SPHERICAL PARTICLES

FIG. 3. Second order reactions—spherical particles.

pendent variable and can, therefore, be solved by conventional methods using the substitution $p = dy/dr$, yielding,

$$(dp^2/dy) - [2\theta/(1 + \theta y)]p^2 = 2\varphi^2 y^m (1 + \theta y) \quad (18)$$

Solution of Eq. (18) and application of the boundary condition $p = 0$ when $y = y_0$ yields

First order reaction $(m = 1)$

$$p = \frac{dy}{dr} = \varphi \sqrt{2}(1 + \theta y)\left[\frac{y}{\theta} - \frac{1}{\theta^2} \ln (1 + \theta y)\right.$$

$$\left. - \frac{y_0}{\theta} + \frac{1}{\theta^2} \ln (1 + \theta y_0)\right]^{1/2} \quad (19a)$$

*Zero order reaction** $(m = 0)$

$$p = \frac{dy}{dr} = \varphi \sqrt{2}(1 + \theta y)\left[\frac{1}{\theta} \ln (1 + \theta y)\right]^{1/2} \quad (19b)$$

Second order reaction $(m = 2)$

$$p = \frac{dy}{dr} = \varphi \sqrt{2}(1 + \theta y)\left[\frac{y^2}{2\theta} - \frac{y}{\theta^2} + \frac{1}{\theta^3}\right.$$

$$\left. \ln (1 + \theta y) - \frac{y_0^2}{2\theta} + \frac{y_0}{\theta^2} - \frac{1}{\theta^3} \ln (1 + \theta y_0)\right]^{1/2} \quad (19c)$$

Reference to Eq. (2) shows that, for constant-volume reactions in flat plates, the normalized concentration gradient at the pellet surface can be expressed as,

$$\left.\frac{dy}{dr}\right|_{r=1} \cong \varphi \left[\frac{\cosh \varphi r}{\cosh \varphi}\right]_{r=1} = \varphi[y(1)] = \varphi$$

$$\text{when } \varphi > 5 \quad (20a)$$

Similar developments lead to expressions for concentration gradients for zero and second order reactions (*3, 4*).

$$\left.\frac{dy}{dr}\right|_{r=1} = \varphi \sqrt{2} \text{ zero order}\dagger \ (\varphi > \sqrt{2}) \quad (20b)$$

$$\left.\frac{dy}{dr}\right|_{r=1} \cong \varphi \sqrt{\frac{2}{3}} \text{ second order } (\varphi > 5) \quad (20c)$$

Physically, Eqs. (20) state that for $\varphi > 5$, the reactant concentration at the pellet center, y_0, has been reduced to a sufficiently low value that it no longer has any influence on the concentration gradient at the surface. We argue that the same line of reasoning applies to the volume-change reactions and

* For finite extinction radius, $y_0 = dy(0)/dr = 0$. Hence there is no constant involving y_0 in Eq. (19b).

† This expression is exact for finite extinction radius.

that the terms in Eqs. (19) involving y_0 can also be dropped for sufficiently large φ. For example, the concentration gradient at the pellet exterior for first order reaction then becomes, from Eq. (19a)

$$\left.\frac{dy}{dr}\right|_{r=1} = \varphi \sqrt{2}(1 + \theta)\left[\frac{1}{\theta} - \frac{1}{\theta^2} \ln (1 + \theta)\right]^{1/2} \quad (21)$$

Similarly for the other reaction orders. Substitution from Eqs. (19) and (20) into Eq. (12) produces the asymptotic relations for the effectiveness factor ratio for flat plates.

First order reaction

$$\frac{\eta'}{\eta} = \sqrt{2}\left[\frac{1}{\theta} - \frac{1}{\theta^2} \ln (1 + \theta)\right]^{1/2} \quad (22a)$$

Zero order reaction

$$\frac{\eta'}{\eta} = \left[\frac{1}{\theta} \ln (1 + \theta)\right]^{1/2} \quad (22b)$$

Second order reaction

$$\frac{\eta}{\eta'} = \sqrt{3}\left[\frac{1}{2\theta} - \frac{1}{\theta^2} + \frac{1}{\theta^3} \ln (1 + \theta)\right]^{1/2} \quad (22c)$$

Equations (22) are valid only for $\varphi > \sim 5$. A significant conclusion which may be drawn from Eqs. (22) is that, for sufficiently large φ, the shift in η is a function *only* of θ. This conclusion is valid regardless of geometry. The shifts shown in Eqs. (22) are the *maximum attainable*. Equations (22) show that, for a given reaction order, all curves in the η–φ plane have identical slopes at sufficiently large φ. This is shown in Figs. 1–3.

The quantity η'/η from Eqs. (22) is shown plotted vs. θ in Figs. 4, 5, and 6 as the curves labeled $\varphi = \infty$.

C. Numerical Solutions

Since a closed form solution of Eq. (10) for $\theta \neq 0$ does not appear possible in terms of ordinary functions, numerical solutions were sought. The solution method employed was that of Nordsieck (*14*) adapted to the IBM 7040 computer by Hicks (*15*). This method provides stable solutions with automatic step-size adjustment based on a specified accuracy.

ZERO ORDER REACTIONS — SPHERICAL PARTICLES
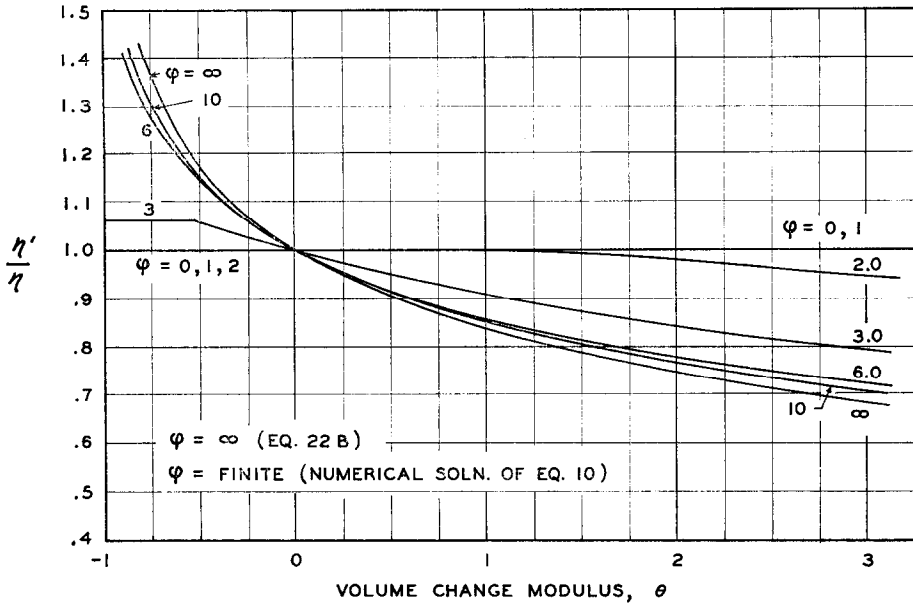
FIGS. 4–6. Effectiveness factor ratios for constant volume and volume change reactions versus volume change modulus.

FIG. 4. Zero order reactions—spherical particles.

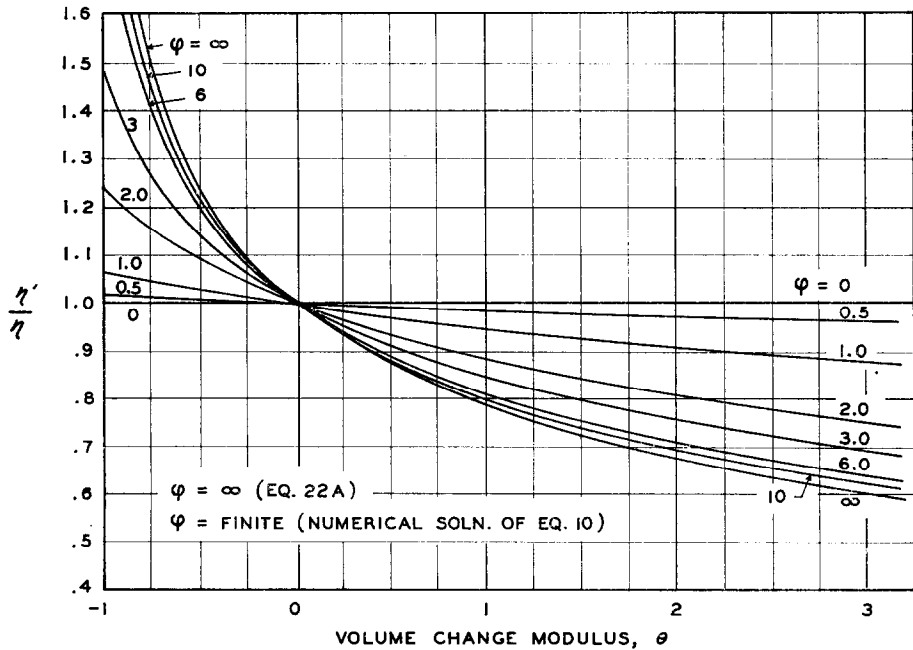FIRST ORDER REACTIONS — SPHERICAL PARTICLES

FIG. 5. First order reactions—spherical particles.
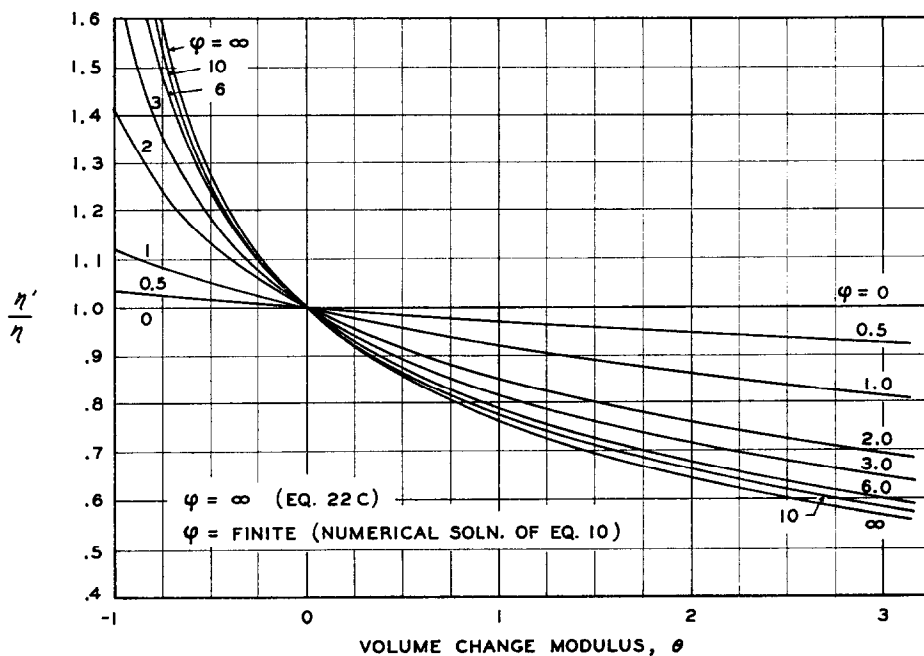
SECOND ORDER REACTIONS — SPHERICAL PARTICLES

FIG. 6. Second order reactions—spherical particles.

It should be noted that the required boundary conditions are split, that is one condition is given at $r = 0$ and the other at $r = 1$. The solution was begun by assuming the reactant concentration at the particle center $(r = 0)$ and the concentration was computed at $r = 1$ by the numerical technique. Convergence on the external concentration was required to be $y = 1.0 \pm 0.001$. A modified Newton technique was employed to speed convergence giving typical converged solutions in 5 min of machine time.

A check was made on the computer program by solving numerically the first order, non-volume-expansion case and comparing the result to the analytic solution. The numerical calculation checked the analytic to within 1 part in 10^7.

The results of the numerical calculations are presented in Figs. 1 through 6 and are also tabulated in Table 1. Figures 1, 2, and 3 present the effectiveness factor vs. φ with the parameter θ covering a fourfold range of volume expansion or contraction and values of φ ranging up to 10.

Figures 4, 5, and 6 present the ratio of the volume change to the nonvolume change effectiveness factors as functions of φ and θ. The limiting case of $\varphi = \infty$ was computed from the asymptotic solutions given by Eqs. (22). It is important to note that when φ is finite, the ratio η'/η is known exactly at the limiting value of $\theta = -1$ (i.e., complete volume contraction). The volume-change effectiveness factor (η') approaches 1 as θ approaches -1, since the increasing inward flow of molecules causes the reactant concentration in the pellet to everywhere approach the external concentration. Thus the following limit results:

$$\lim_{\theta \to -1} \frac{\eta'}{\eta} = \frac{1}{\eta} \; (\varphi \text{ finite})$$

For $\varphi = \infty$ the effectiveness factor ratio becomes infinite at $\theta = -1$. The limiting case of $\theta = -1$ can be attained only with pure feed streams $(x_1 = 1)$.

Examination of the asymptotic solutions (valid for large φ), given in Eq. (22), shows that η'/η approaches zero as θ becomes increasingly large. The same argument can be

TABLE 1

EFFECTIVENESS FACTORS FROM NUMERICAL SOLUTION OF EQ. (10)

	φ				
	0.5	1.0	3.0	6.0	10.0
m = 0					
−0.75	1.0	1.0	1.0	0.7498	0.5015
−0.50	1.0	1.0	0.9958	0.6738	0.4432
1.0	1.0	1.0	0.8550	0.5102	0.3253
2.0	1.0	1.0	0.7946	0.4619	0.2923
3.0	1.0	1.0	0.7486	0.4286	0.2698
m = 1					
−0.75	0.9966	0.9830	0.8487	0.5856	0.3917
−0.50	0.9917	0.9674	0.7684	0.5011	0.3927
1.0	0.9690	0.8915	0.5666	0.3366	0.2149
2.0	0.9537	0.8530	0.5046	0.2934	0.1861
3.0	0.9408	0.8193	0.4623	0.2647	0.1670
m = 2					
−0.75	0.9915	0.9673	0.7709	0.5104	0.3393
−0.50	0.9842	0.9392	0.6752	0.4250	0.2782
0	0.9683	0.8915	0.5703	0.3434	0.2210
1.0	0.9407	0.8196	0.4651	0.2696	0.1712
2.0	0.9156	0.7662	0.4068	0.2308	0.1459
3.0	0.8940	0.7241	0.3676	0.2060	0.1295

extended to situations involving finite φ by noting that increasingly large θ always reduces the particle center reactant concentration toward zero, i.e., to the asymptotic case.

V. DISCUSSION

The Stefan-Maxwell relations [Eq. (4)], from which the basic differential equations [Eqs. (9) and (10)] were derived, are strictly valid only for ideal mixtures of gases. However, the results of this study are expected also to apply to all fluid mixtures not deviating seriously from ideality.

The volume-change modulus,

$$\theta = (n - 1)x_1,$$

is directly proportional to the mole fraction of reactant in the feed. Thus, for fixed stoichiometry, the influence of diluents on the shift in reaction rates is quite significant, as shown in Figs. 1 to 6. In fact, volume-change effects are seen to be virtually absent in highly dilute solution, due to the ability of the inert gases to moderate the effect of the net molar flux.

Since the asymptotic solutions are valid when the concentration at the particle center is essentially zero, the numerical and asymptotic solutions should approach each other at large values of φ. Figure 7 gives an example of the excellent agreement of the asymptotic and numerical solutions for increasingly large φ. Figures 4–6 also show that as φ becomes larger the asymptotic and numerical solutions approach each other for all values of the volume-change modulus, θ. Numerical calculations were made up to $\varphi = 10$ (cf. Figs. 1–3). Figures 4–6 show that the asymptotic solution differs by less than about 2.5% from the $\varphi = 10$ curves for all θ. It is, therefore, recommended that the asymptotic solutions given in Eq. (22) be used for work in the range above $\varphi = 10$.

As noted earlier, zero order reactions give effectiveness factors of 1.0 when the center concentration is finite. Thus on Fig. 1 as the volume-change modulus θ decreases, the effectiveness factor becomes 1.0 at progressively higher values of the diffusional-kinetic modulus φ. This same effect is shown on Fig. 4.
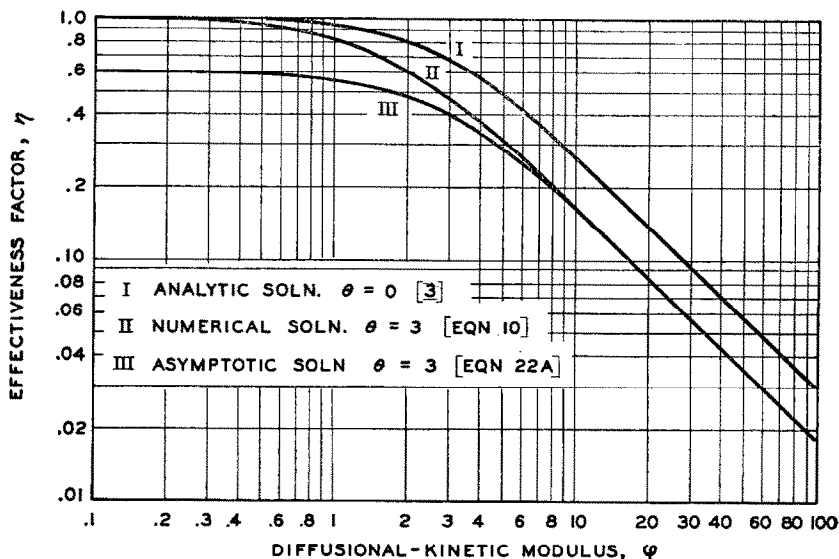
SPHERICAL PARTICLES — FIRST ORDER REACTIONS

FIG. 7. Convergence of asymptotic to numerical solution for volume-change reactions.

It is also shown on Fig. 4 that, for volume contraction (i.e., $\theta < 0$), the ratio of η'/η can become independent of θ for zero order reactions. This phenomena occurs because at a fixed φ, as θ is decreased, the center concentration will eventually become finite. Thus while $\eta' = 1.0$, $\eta \leq 1.0$, and a constant η'/η ratio results, since η is, by definition, independent of θ.

Figure 8 is a map of the φ and θ space for zero order reactions, defining the conditions under which the transition to unit effectiveness factor occurs. The line represents the locus of points fulfilling the criterion $y = 0$ at $r = 0$ when $r_e = 0$. These points were determined from the numerical solution of Eq. (10).

All numerical calculations were based on spherical geometry. However, Aris (5) has shown that by defining the diffusional-kinetic modulus as $\Lambda = (V_p/S_x)(k/D_e)^{1/2}$ (for first order reactions), cylinders, spheres, and flat plates can be approximated by a single line on an η vs. Λ plot. The maximum deviation was 16% between flat plates and spheres at $\Lambda = 2$.

The Aris approximation is essentially a shifting of the diffusional-kinetic modulus
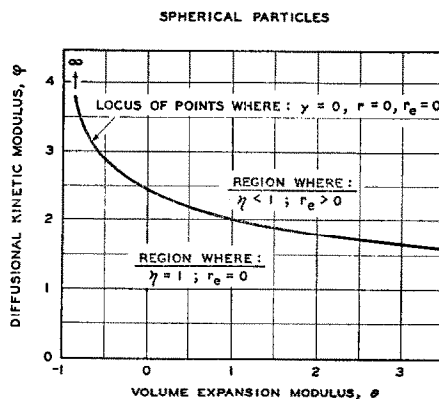
SPHERICAL PARTICLES

FIG. 8. Unit effectiveness factor region for zero-order reactions.

to give a common curve for all geometries. A similar shift for the volume expansion cases also appears to work equally as well. Thus Fig. 2 may be used for other shapes by employing a redefined value of φ, say φ', defined on the basis of the volume-to-surface ratio of the particle. This value of φ is

$$\varphi' = (3V_p/S_x)(k/D_e)^{1/2} \qquad (23)$$

Thus for flat plates, $\varphi' = 3a(k/D_e)^{1/2}$; for cylinders, $\varphi' = 2a(k/D_e)^{1/2}$, and for spheres,

$\varphi' = a(k/D_e)^{1/2}$. Table 2 shows a comparison of effectiveness factors computed in this way with some numerical calculations for flat plates obtained for $\theta = 1$ by Thiele (3). Table 2 shows that the use of φ' brings the effectiveness factor plots for spheres and flat plates into approximate agreement as was also observed for the nonvolume case (5).

TABLE 2
COMPARISON OF EFFECTIVENESS FACTORS WITH VOLUME AND CHANGE BASED ON SHAPE FACTOR APPROXIMATION

	First order reaction, $\theta = 1$		
	Flat plates $[\varphi' = 3a(k/D_e)^{1/2}]$	From Fig. 2	From Thiele's Fig. 1-IVa[a]
$a(k/D_e)^{1/2}$	φ'	η'	η'
10	30	0.08	0.08
5	15	0.15	0.16
3	9	0.24	0.25
2	6	0.34	0.37
1	3	0.56	0.64
0.3	0.9	0.90	0.92

[a] Reference 3.

From Fig. 2 it can be observed that the effect of volume change is a displacement of the $\theta = 0$ curve. This suggested a simple approximation for first order reactions which would be of considerable use in computer programs. The approximation for spheres, which can be used over the entire range of φ is a simple displacement of φ as follows:

$$\bar{\varphi} = \varphi(1 + \theta)^\lambda \quad (24)$$

where $\lambda = 0.4$ for volume expansion, $\lambda = 0.35$ for volume contraction.

This displaced value of φ may then be used in the analytic effectiveness factor expression for first order reactions ($\theta = 0$) as follows:

$$\eta' = \frac{3}{\bar{\varphi}} \left[\frac{1}{\tanh \bar{\varphi}} - \frac{1}{\bar{\varphi}} \right] \quad (25)$$

Comparison of the approximate method with the numerical solutions showed that the absolute error was less than 3% for volume expansion and less than 5% for contraction.

As shown earlier, the first order analysis

with volume expansion could be extended to other geometries by including a volume-to-surface term in the φ modulus. The displaced modulus to be used in Eq. (25), for all shaped particles and first order reactions with volume change, is as follows:

$$\bar{\varphi}' = (3V_p/S_x)(1 + \theta)^\lambda(k/D_e)^{1/2} \quad (26)$$

Results shown in Fig. 2 and also given by Eq. (24) agree with the empirical correlation developed by Hawthorn (Eq. 4.6 of ref. 10).

VI. CONCLUSIONS

1. Volume change may significantly affect the rate of diffusionally restricted reactions in porous catalysts.

2. The influence of volume change on effectiveness factors is dependent on a *single parameter θ*, designated as the *volume-change modulus; θ* is a function solely of the reaction stoichiometry and mole fraction of reactant in the feed mixture.

3. The shift in effectiveness factors due to volume change, relative to the constant-volume case, has an *upper bound* which is closely approached when φ becomes large. This upper limit is a function only of θ and is thus independent of the reaction rate constant and catalyst characteristics. The present work has shown that the upper bound to the effect of volume changes is a weak function of reaction order.

REFERENCES

1. ZELDOVICH, Y. B., *Acta Physicochim. URSS* 10, 583–597 (1939).
2. WEISZ, P. B., AND PRATER, C. D., *Advan. Catalysis* 6, 143–196 (1954).
3. THIELE, E. W., *Ind. Eng. Chem.* 31, 916–920 (1939).
4. WHEELER, A., *Advan. Catalysis* 3, 249–327 (1951).
5. ARIS, R., *Chem. Eng. Sci.* 6, 262–268 (1957).
6. WEISZ, P. B., AND SWEGLER, E. W., *J. Phys. Chem.* 59, 823–826 (1955).
7. WEISZ, P. B., *Science* 123, 887–888 (1956).
8. WEISZ, P. B., *Chem. Eng. Prog. Symp. Ser.,* No. 25 55, 29–36 (1959).
9. PRATER, C. D., AND LAGO, R. M., *Advan. Catalysis* 8, 293–339 (1956).

10. HAWTHORN, R. D., paper presented at National Meeting, AIChE, December 2–7, 1961, New York, N. Y.

11. WEISZ, P. B., Z. Physik. Chem. (Frankfurt) 11, 1–15 (1957).

12. WEISZ, P. B., AND SCHWARTZ, A. B., J. Catalysis 1, 399–406 (1962).

13. GORRING, R. L., AND DeROSSET, A. J., J. Catalysis 3, 341 (1964).

14. NORDSIECK, A., Mathematics of Computation 16 (No. 77), 22–49 (1962).

15. HICKS, J. S., Socony Mobil Central Research Division, private communication.