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THE APPLICATION OF IDEAL REACTORS TO STUDIES IN ATMOSPHERIC CHEMISTRY

J. M. Hales, J. O. Wilkes and J. L. York

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THE APPLICATION OF IDEAL REACTORS TO STUDIES IN ATMOSPHERIC CHEMISTRY

Jeremy M. Hales,[1] James O. Wilkes,[2] and J. Louis York[3]

ABSTRACT

Mass-transfer effects and surface reactions may severely obscure the observation of homogeneous chemical reaction rates from experimental reactor data. Such problems are particularly pertinent to studies in the atmospheric sciences, owing to the tendency for increased surface-reaction interference at the low concentrations usually of interest.

The present work provides criteria for ideal behavior in three basic types of experimental reactors. Under conditions satisfying these criteria the effects of competing surface reactions can be accounted for quantitatively, allowing the true homogeneous effect to be observed. Data from tubular reactors can be analyzed accurately even under some nonideal conditions. The available solutions to tubular reactor models useful for this purpose have been compiled and tabulated herein.

The material presented in this paper will be useful in providing more systematic bases for experimental reactor design and the analysis of future reaction-rate data.

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INTRODUCTION

The "empirical-phenomenological" era of chemical kinetics, beginning in the late 1800's (cf. van Krevelin (1958), was characterized primarily by the advent of systematic reaction-rate experiments using simple "ideal" chemical reactors. Since this early period, significant advances in analytical technique and experimental methodology have occurred. Moreover, the field of experimental reaction-rate studies has expanded to cover an extremely broad scope. This has ranged from highly specific mechanistic studies of relatively simple reactions to the more general reaction-rate evaluations of complex systems, which include smog-chamber studies and industrial process evaluations as well as a host of other applications.

Throughout this evolution, ideal reactors have continued to play a prominent underlying role. They have been incorporated with modern analytical systems, and continue to contribute to the influx of reaction-rate and kinetics data appearing in the modern literature. Unfortunately, however, some rather critical factors in reactor design are sometimes ignored by experimentalists in constructing experimental equipment and interpreting the resulting data. The primary purpose of this report is to review some of these factors to provide a practical aid in this respect, especially as it pertains to problems in atmospheric chemistry.

At the outset it is important to draw attention to the difference between "reaction-rate" and "kinetics" experimentation. Depending on the complexity of the reaction and the reactor design, data obtained from a given experiment may be rather unspecific with regard to the mechanism of the reaction being studied--even though it represents valid reaction-rate information that is potentially valuable for a host of applications. Thus some applications of ideal reactors tend to provide a convenient means for assessing the empirical "rate" of a reaction, but do not furnish information sufficiently specific to elucidate its "kinetics," in the mechanistic sense of the word. Such reactors (smog chambers, for example) play an important role in advancing the state of knowledge in various areas of

research. They are constrained primarily, however, to analyses of the verification of postulated mechanistic behavior in complex, mixed systems, and the production of empirical rate data where basic mechanistic determinations are considered impractical. This second area usually forces the expression of reaction-rate behavior in terms of empirical rate equations, a subject that is discussed in detail by Weller (1956).

Obviously there is no clear demarkation between reaction-rate and kinetics experimentation. Because of past tendencies to "over-interpret," however, it is extremely important for the experimentalist to recognize the limitations of technique, so as not to draw unwarranted or false conclusions pertaining to mechanism from unspecific experimental results (cf. Margerison, 1969).

Conversion in chemical reactors occurs by virtue of two separate rate processes--mixing of the reactants, i.e., mass transfer, and chemical reaction (cf. Frank-Kamenetskii, 1969). To measure chemical reaction rates accurately, the reactor must be designed such that the mass-transfer step is negligible, or can be accounted for quantitatively. Reactors such as the batch, backmix, and flat concentration-profile tubular reactors conveniently eliminate mass transfer considerations and are referred to, therefore, as "ideal" reactors. Reaction-rate analysis using ideal reactors is dealt with in many textbooks on the subject, including the works of Denbigh (1965), Kramers and Westerterp (1963), and Levenspiel (1964), and will not be considered explicitly here. This report, rather, is addressed to the task of identifying the conditions for reactor ideality and investigating the consequences of deviation from such ideal behavior.

Both surface and bulk (homogeneous) reactions are considered. Often one is confronted with the possibility of competing surface reactions, and must verify their absence, or account for their presence appropriately. Note at the outset that the simultaneous existence of homogeneous and heterogeneous reactions is not a peculiar situation, and should always be suspected for a particular experimental system until proven otherwise.

Whenever a gas is in contact with a solid a certain amount of sorption will occur, and it is natural to expect that a reaction occurring in the gas phase might also tend to proceed on the surface; the decomposition of hydrogen peroxide, the combination of hydrogen and iodine, and the spontaneous decay of ozone are well-known examples.

The problem of simultaneous wall and bulk reactions, however, is especially significant in the context of atmospheric chemistry. At normal concentrations the ratio of free to sorbed molecules is usually very large, and the homogeneous reaction may mask any heterogeneous effects. However, as concentrations fall to those normally experienced in the atmosphere, the ratio of free to sorbed molecules may fall markedly, and any wall reaction will tend to become much more significant. The problem of competing surface bulk reactions will be dealt with generally in the following sections, and will be discussed specifically prior to the conclusion of this report.

IDEAL BATCH REACTORS

Ideal batch reactors are the simplest of chemical reactors, and have been used extensively in the measurement of reaction rates. Such reactors depend upon the absence of any spatial variation in concentration of the reacting components, thus eliminating any complications from mass-transfer effects in their analysis. Providing that the reactants can be mixed adequately when the reaction is initiated, this situation is satisfied easily in most isothermal, homogeneously reacting systems. When surface reactions are present, however, fluid mixing must be adequate to eliminate any appreciable concentration gradients created by virtue of these reactions.

The basic equation describing the ideal batch reactor is

$$dc/dt = r_b + (s/v)r_s \quad , \tag{1}$$

with the initial conditions

$$c = c_0 \quad \text{at} \quad t = 0 \quad . \tag{1a}$$

Here, c is the concentration of a reacting species in the reactor at any time t, and r_b and r_s are the bulk and surface reaction rates, respectively; s/v denotes the ratio of surface area to volume. Thus, simultaneous surface and bulk reactions can be measured simply by performing measurements with two or more ideal batch reactors of different s/v ratios and solving the resulting simultaneous equations (e.g., Melvile and Gowenlock, 1964).

For cases wherein reaction rates can be represented by simple expressions of the forms $r_b = -k_b c^{\alpha}$ and $r_s = -k_s c^{\beta}$, equations (1) lead to the integrated form

$$\int_{c}^{c_0} \frac{dc}{k_b c^{\alpha} + (s/v) k_s c^{\beta}} = t \quad . \tag{2}$$

It is of interest to examine the conditions for which fluid mixing is sufficient to satisfy ideal batch conditions under circumstances involving surface reactions. This can be accomplished for unstirred systems by comparing reaction rates predicted by equations (1) or (2) with those given by the more general equations of continuity. Consider, for example, the case of a spherical, unstirred reactor of radius r_0 with a first-order surface reaction. Here, the reactant must migrate to the reactor wall by molecular diffusion, and subsequently undergo the prescribed conversion. The appropriate continuity equation for a single reacting component in dilute solution (Bird, et al., 1960) reduces to

$$\frac{\partial c}{\partial t} = D_A \left(\frac{2}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial r^2}\right) \quad , \tag{3}$$

$$c = c_0 \quad \text{at} \quad t = 0 \quad , \tag{3a}$$

$$\frac{\partial c}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad , \tag{3b}$$

$$\frac{\partial c}{\partial r} = -\frac{k_s}{D_A} c \quad \text{at} \quad r = r_0 \quad , \tag{3c}$$

where D_A is the diffusion coefficient of the reacting substance in the mixture. Also for these conditions, equation (2) reduces to

$$k_{s(ideal)} = -(v/st) \ln c/c_0 \quad . \tag{4}$$

Comparison of equation (4) with published solutions to equation (3) (Carslaw and Jaeger, 1959) indicates that the percentage error in determining k_s by assuming ideal conditions to exist,

$$E = 100 \frac{k - k_{(ideal)}}{k} \tag{5}$$

($k = k_s$ at present), depends upon the dimensionless groups $r_0 k_s/D_A$ and $D_A t/r_0^2$. Analysis of these solutions shows that E is less than 1% for all values of $D_A t/r_0^2$ whenever*

$$\frac{r_0 k_s}{D_A} < 0.05 \quad . \tag{6}$$

The dimensionless group in inequality (6) is known as the "heterogeneous Damkohler group of the second type". It represents the ratio of removal rates of reactant by reaction and diffusion. Criteria similar to (6) can be derived for systems of other geometries and reaction orders. This inequality, however, should generally be useful for order-of-magnitude estimates, upon linearizing rate expressions and choosing appropriate characteristic lengths to substitute for the radius r_0. For example, consider surface reactions in a short cylindrical spectrophotometer cell used as a batch reactor; their ideality can be evaluated roughly by linearizing the surface-reaction expression and employing the cell diameter as an appropriate equivalent to r_0.

---

*Criterion (6) is based on the assumption that the concentrations measured in the hypothetical experimental reactor are the true mixed-mean values.

It is obvious that stirring of batch reactors will help to induce ideal behavior, although such a measure adds the potential problem of introducing reactions that occur on the surfaces of the impeller, baffles, and associated equipment. In addition, it is difficult to determine *a priori* whether or not a given amount of stirring will induce ideal behavior, because of the complexity of the mixing process and the variety of geometries that can be employed.

The effect of stirring on inducing ideality in batch reactors with surface reactions can be demonstrated by referring to Figure 1. Here a batch reactor contains an average concentration c_b of reactant which drops, because of the surface reaction, to the value c_s in the vicinity of the wall. Assuming that the bulk concentration is nearly uniform throughout the interior of the reactor, one may apply equation (1) to obtain

$$\frac{dc_b}{dt} \cong -k_b c_b^{\alpha} - (s/v) k_s c_s^{\beta} \quad . \tag{7}$$

For ideal operation, stirring must be sufficiently rapid to enable the value of c_s to approach that of c_b; that is, the rate of transport of material to the surface must be rapid compared to the rate of depletion by the wall reaction.

The rate of material transport to the reactor wall may be described in terms of a mass-transfer coefficient,

$$k_y = \frac{(\text{molar flux of reactant to surface})\ c_T}{c_b - c_s} \quad , \tag{8}$$

where c_T is the total molar concentration of gas in the reactor. Thus c_s can be expressed (implicitly) in terms of k_y.

$$c_s^{\beta}\left(\frac{k_s c_T}{k_y}\right) + c_s = c_b \quad . \tag{9}$$

Equation (9) shows that ideal conditions, ($c_s = c_b$), will be approached only under conditions wherein the mass-transfer coefficient is large. And

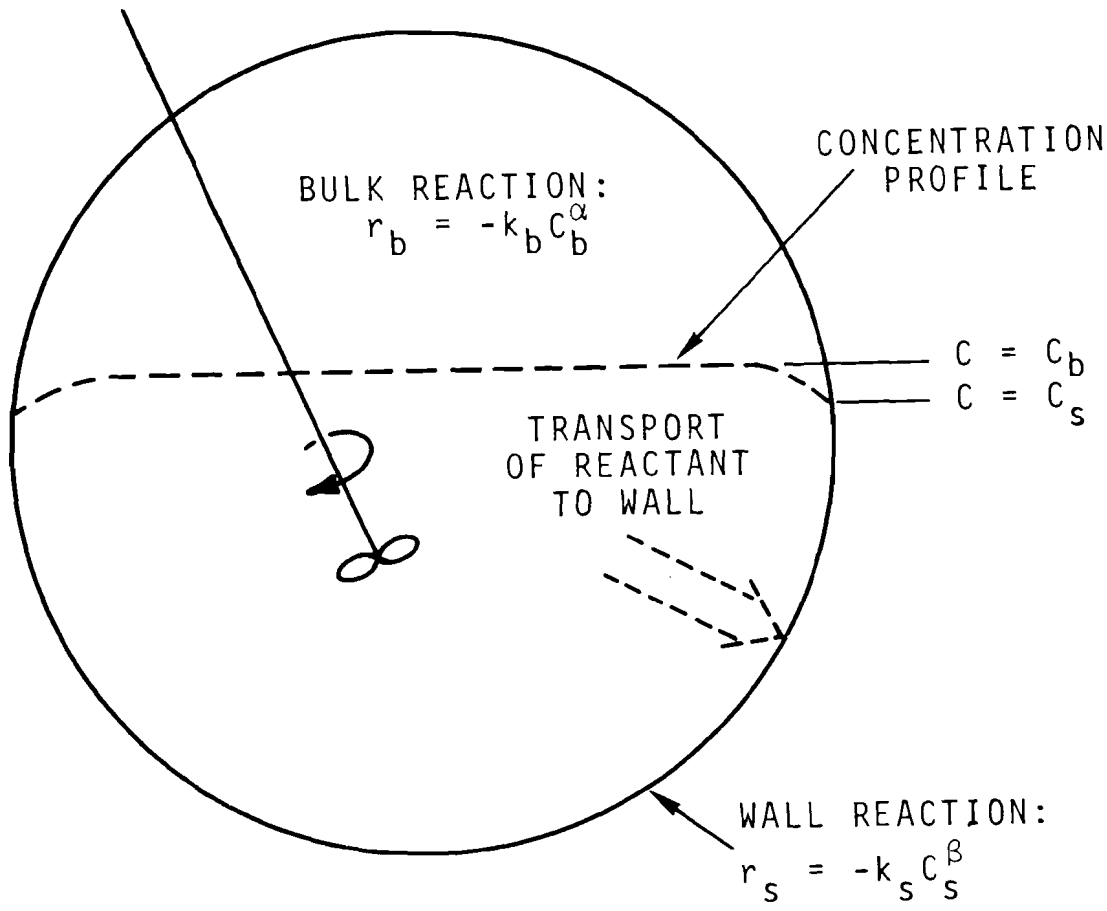

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FIGURE 1

SCHEMATIC OF STIRRED BATCH REACTOR

provided the mass-transfer coefficient is indeed sufficiently large, its value is of no further significance to the analysis. k_y can be increased either by more vigorous mixing or by good vessel design; values of k_y for a given mixing situation often can be estimated using results from the literature. It is usually more practical however, to measure conversion from a reactor operating under set conditions and increasing degrees of agitation. As soon as conversion no longer changes with agitation rate, then k_y is sufficiently large to provide ideal behavior. If the system cannot be stirred rapidly enough to achieve these conditions, then another system should be chosen to perform the required measurements.

IDEAL BACKMIX REACTORS

Ideal backmix reactors share with ideal batch reactors the characteristic lack of spatial variations in concentration. Their basic equation is given by the (steady-state) form

$$c = c_0 + (\frac{v}{w})[r_b + (\frac{s}{v})r_s] \quad , \tag{10}$$

w being the volumetric rate of flow through the reactor. Steady-state backmix reactors offer some advantage over batch reactors because they maintain constant concentrations in time and thus allow direct observation of rates, even if mechanistic changes occur over the concentration ranges of interest. Also, they frequently allow the investigation of reactions faster than those observable in batch reactors, because of the more convenient means of initiating the reaction. As indicated by equation (10), simultaneous surface and bulk reactions can be investigated conveniently with ideal backmix reactors, again by employing two or more reactors of different s/v ratios.

Deviations from ideality in backmix reactors can occur for both bulk and surface reactions. Owing to the variety of inlet conditions and geometries possible, the errors arising from incomplete mixing in such reactors are difficult to analyze. A rather conservative criterion for the approach to ideality for homogeneous reactions in unstirred backmix reactors can be

obtained by visualizing the hypothetical cylindrical reactor shown in Figure 2. The velocity profile throughout the reactor is assumed to be flat (plug flow), so that one-dimensionality exists. The binary continuity equation for a first-order homogeneous reaction then reduces to

$$\frac{d^2c}{dz^2} - \left(\frac{v_o}{D_A}\right)\frac{dc}{dz} - \frac{k_b c}{D_A} = 0 \quad , \tag{11}$$

with the boundary conditions

$$c = c_0 \quad \text{at} \quad z = 0 \quad , \tag{11a}$$

and

$$c = 0 \quad \text{at} \quad z = \infty \quad . \tag{11b}$$

The solution to equations (11) is

$$\frac{c}{c_0} = \exp\left\{\frac{1 - \sqrt{1 + 4k_b D_A/v_o^2}}{2}\left(\frac{zv_o}{D_A}\right)\right\} \quad , \tag{12}$$

which, combined with the corresponding equation for an ideal homogeneous backmix reactor [equation (10)], provides the following approximate (and conservative) expression for the percentage error arising from the neglect of non-ideal behavior in unstirred, homogeneously-reacting backmix systems:

$$E = 100\left\{1 + \frac{1 - c_0/c}{\left[\left(1 - \frac{2D_A \ln c/c_0}{zv_o}\right)^2 - 1\right]\frac{v_o^2\tau}{4D_A}}\right\} \quad , \tag{13}$$

$\tau = v/w$ being the average residence time in the reactor.

Criteria for conditions under which unstirred backmix reactors involving <u>surface reactions</u> may be considered ideal, may be estimated from inequality (6) using τ as the appropriate measure of reaction time.

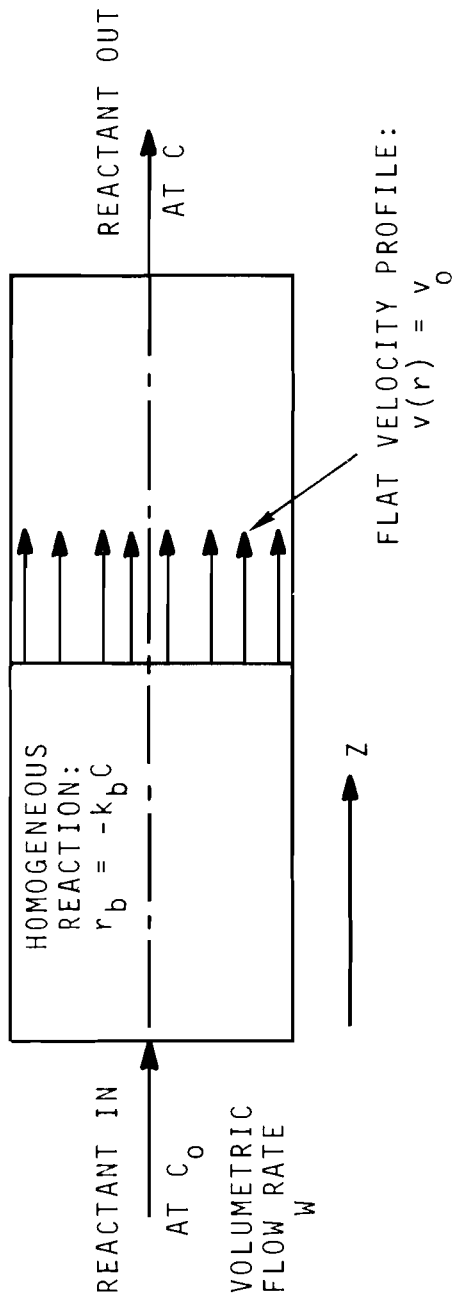

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FIGURE 2

SCHEMATIC OF IDEALIZED REACTOR

Stirred backmix reactors may be analyzed by employing a mass-transfer analysis similar to that used previously for stirred batch reactors. Again, however, it is usually more expedient to approach the problem empirically by increasing stirring rates until a situation of negligible mass-transfer resistance is approached.

LAMINAR-FLOW TUBULAR REACTORS

Laminar-flow tubular reactors offer a number of advantages for reaction-rate measurements involving trace gases. In addition to exhibiting rather simple ideal behavior under appropriate circumstances, these reactors are characterized by flow patterns which are sufficiently uncomplex to enable analysis even under nonlimiting conditions. Also, tubular reactors require no stirring, thereby eliminating any problems associated with extraneous reactions on the surface of impellers and associated equipment. Multiple tubular reactors can be utilized to evaluate simultaneous surface and bulk reaction behavior under both limiting and nonlimiting conditions (Hales, 1968).

For an isothermal fluid with constant transport properties and negligible entrance effects, the tubular reactor may be described by the steady-state multicomponent continuity equations for trace molecular species $i = A, B, \ldots, n$ in solution with a Newtonian diluent (cf., Bird et al., 1960).

$$D_i\left(\frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r}\frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2}\right) - 2\left(1 - \frac{r^2}{r_0^2}\right)v_{avg}\frac{\partial c_i}{\partial z} = -r_i(c_A, c_B, \ldots, c_n) \quad ; \quad (14)$$

$$i = A, B, \ldots, n \quad .$$

The associated boundary conditions are: (with $i = A, B, \ldots, n$ throughout)

$$\frac{\partial c_i}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad \text{for all} \quad z \quad ; \qquad (14a)$$

$$c_i = c_{i0} \quad \text{at} \quad z = -\infty \quad \text{for} \quad 0 \le r \le r_0 \quad ; \qquad (14b)$$

$$c_i = c_{i(\text{equilibrium})} \quad \text{at} \quad z = \infty \quad \text{for} \quad 0 \le r \le r_0 \quad ; \qquad (14c)$$

and

$$D_i \frac{\partial c_i}{\partial r} = r_{is}(c_A, c_B, \ldots, c_n) \quad \text{for} \quad z \geq 0 \quad . \tag{14d}$$

Equations (14) are too complex to be of much use for reaction-rate measurement except under rather specialized circumstances, such as when only one of the components changes significantly in concentration during its passage through the reactor. Such conditions will be realized for monomolecular reactions or when all reactants except one are present in excess. For these conditions (i = A, for example) the simultaneous set of equations reduce simply to a single set of equations.

Frequently, longitudinal diffusion is negligible, and the equations are simplified further by dropping the associated term $\partial^2 c_A/\partial z^2$. This results in the second order partial differential equation

$$D_A\left(\frac{\partial^2 c_A}{\partial r^2} + \frac{1}{r}\frac{\partial c_A}{\partial r}\right) - 2\left(1 - \frac{r^2}{r_0^2}\right) v_{avg} \frac{\partial c_A}{\partial z} = -r_A(c_A) \quad , \tag{15}$$

with the boundary conditions

$$\frac{\partial c_A}{\partial r} = 0 \quad \text{at} \quad r = 0 \quad \text{for all} \quad z \quad ; \tag{15a}$$

$$c_A = 0 \quad \text{at} \quad z = 0 \quad \text{for} \quad 0 \leq r \leq r_0 \quad ; \tag{15b}$$

$$\frac{D_A \partial c_A}{\partial r} = r_{As}(c_A) \quad \text{at} \quad r = r_0 \quad \text{for} \quad z > 0 \quad . \tag{15c}$$

Alternatively, in dimensionless form:

$$\frac{\partial^2 C_A}{\partial R^2} + \frac{1}{R}\frac{\partial C_A}{\partial r} - (1 - R^2)\frac{\partial C_A}{\partial Z} = \theta C_A^{\alpha} \quad ; \tag{16}$$

$$\frac{\partial C_A}{\partial R} = 0 \quad \text{at} \quad R = 0 \quad \text{for all} \quad Z \quad ; \tag{16a}$$

$$C_A = 0 \quad \text{at} \quad Z = 0 \quad \text{for} \quad 0 \le R \le 1 \quad ; \tag{16b}$$

$$\frac{\partial C_A}{\partial R} = -\Gamma C_A^{\beta} \quad \text{at} \quad R = 1 \quad \text{for} \quad Z \ge 0 \quad . \tag{16c}$$

Here, the reaction rates in the bulk and at the wall have been expressed in terms of the reaction orders α and β, respectively. Definitions and physical significances of the dimensionless groups are given in Table III.

Mathematical solutions to equations (16) for various types of reactions have been obtained by a number of authors, and are summarized in Table II. These solutions are of potential value for the analysis of experimental reaction-rate data. They also are valuable in assessing conditions under which the more convenient "ideal" tubular reactor equations are valid. Such conditions will be analyzed in detail upon first examining the general applicability of equations (16) to real physical systems.

There are two major areas where the applicability of equations (16) to real tubular reactors might be questioned: (a) when longitudinal diffusion is neglected as mentioned previously, and (b) when entrance effects are neglected, that is, the demand of equations (16) that the reactants be mixed instantaneously at the entrance in a manner such that the laminar velocity pattern remains undisturbed--an obvious impossibility in a majority of cases.

Positive testing of the assumption of negligible longitudinal diffusion requires a comparison of solutions to equations (14) for $i = A$, with corresponding solutions to the restricted equations (16). This is difficult to accomplish satisfactorily, however, owing to the complexity of equations (14), which has limited the extent of their solutions available in the literature.

Among the few investigators that have considered this problem are Hsu (1967) and Verhoff (1967), who have examined the particular case of a zero-order wall reaction (by analogy to constant-flux heat transfer).

These authors' results indicate that errors from ignoring longitudinal diffusion approach zero with distance down the tube, and with increasing values of the Peclet number:

$$Pe = \frac{v_{avg} r_0}{D_A} \quad . \tag{17}$$

For most practical situations these results show that axial diffusion can be ignored whenever

$$Pe > 25 \quad . \tag{18}$$

Jones (1971) and Singh (1958) have performed corresponding calculations for the case of diffusion-controlled wall reactions, again by analogy to heat transfer, with comparable results. Jones' calculations show that the error from neglect of axial diffusion decreases with increasing Z and Pe; for Z greater than 0.1 axial diffusion can be neglected whenever criterion (18) is satisfied.

Tan and Hsu (1970) provide an analytical solution for the special case involving a diffusion-controlled wall reaction with simultaneous generation in the bulk. These authors have produced curves which show that one can safely neglect axial diffusion under criterior (18) for values of Z as small as 0.1. Cohen and Rippin (1967) have obtained corresponding solutions for cases involving second-order homogeneous reactions; however, their solutions are not sufficiently extensive to be used for comparison.

Other authors have provided additional insight in this area by solving approximations to equations (14) or by considering mixing phenomena in non-reacting flows. The most noteworthy of these works was published by Taylor (1953) in his cornerstone investigation of the mechanisms of longitudinal dispersion in laminar tube-flow. Taylor's analysis showed mainly that, under most conditions, the primary mechanism for longitudinal dispersion was not longitudinal molecular diffusion, but the action of radial diffusion over the parabolic velocity profile. This mechanism, which can be visualized by observing the trajectories of the hypothetical molecules

shown in Figure 3, was shown to predominate over longitudinal molecular diffusion whenever

$$Pe \gg \sqrt{48} \quad . \tag{19}$$

This also can be used as a criterion for the neglect of axial molecular diffusion in laminar reactors--one which agrees reasonably well with that based upon the total solutions by the previously mentioned authors.

Criteria for the neglect of axial molecular diffusion based on other approximations to equation (14) have been reviewed elsewhere (Hales, 1968). In general these do not disagree with (18) and (19); if anything they tend to be more lenient in their limits for the allowable neglect of this component of dispersion; hence, these equations represent conservative limits for application of equations (16) to the analysis of experimental reactors.

The second question of applicability of equations (16), regarding entrance effects, obviously depends upon the arrangement of the particular reactor in question. The mathematical requirements are met well in specific cases, for instance, that of a heterogeneous reactor whose catalytic surface (and therefore the chemical reaction) begins exactly at $Z = 0$ with no mixing of reactants required. Normal homogeneously reacting systems, as discussed previously, must be mixed in as non-disruptive a manner as possible so as to allow re-establishment of laminar flow at a minimal distance downstream from the inlet.

The most pertinent examination of entrance effects that exists in the present literature is that of Ulrichson and Schmitz (1965), who investigated the effect of a normal transition from a flat to a parabolic velocity profile on the response of both homogeneous and heterogeneous reactors. Their results show that such a transition will be insignificant in its effect on reactor response whenever

$$\frac{\theta}{Sc} = \frac{k_b r_0^2}{\nu} < 4, \text{ for homogeneous (bulk) reaction;} \tag{20}$$

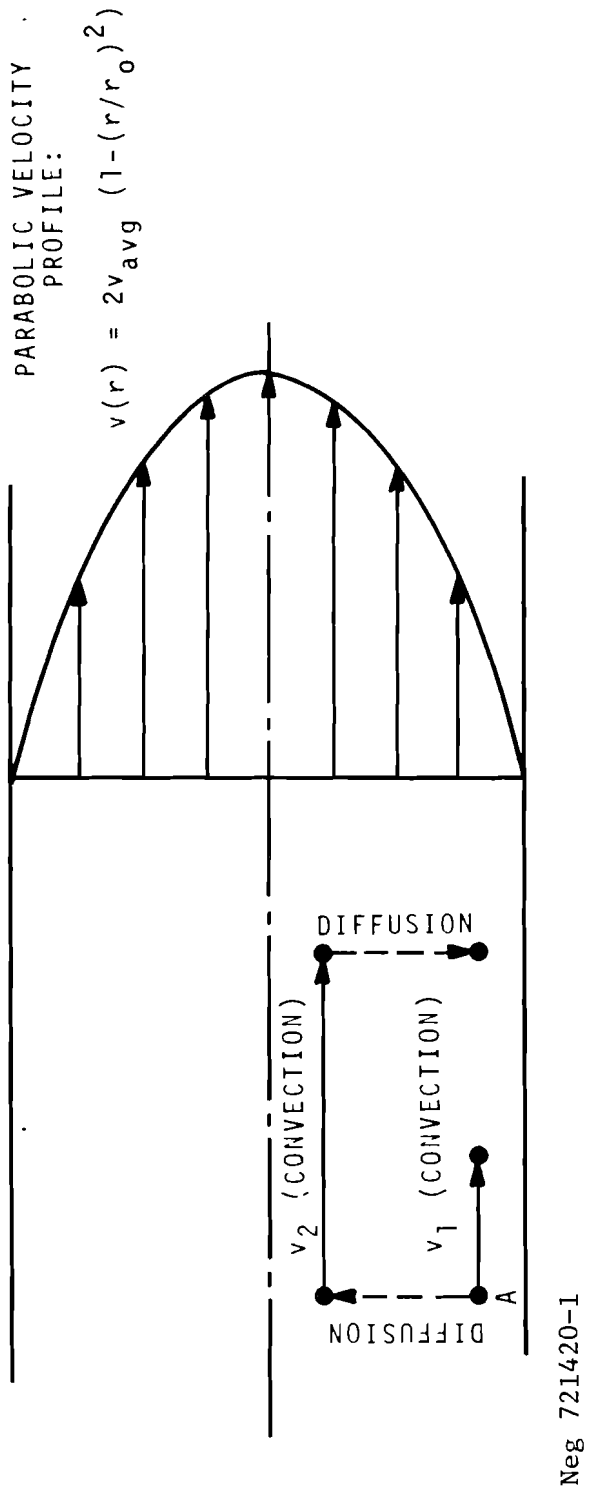

FIGURE 3

PICTORIAL REPRESENTATION OF TAYLOR DISPERSION

$$\frac{\Gamma}{Sc} = \frac{k_s r_0}{\nu} < 4, \text{ for heterogeneous (wall) reaction.} \tag{21}$$

Here, ν and Sc are, respectively, the kinematic viscosity of the fluid and the Schmidt number (see Table III). With suitable linearizations, these inequalities can be used as approximate criteria for reactions of other orders. These criteria, while pertaining to the specific case of flat-to-parabolic transitions should be useful in providing guidelines for transitions from other types of flow.

A final, almost trivial constraint on the applicability of equations (16) is the conditions required for the existence of laminar flow. These are established in the well known Reynolds-number criterion,

$$Re = \frac{2v_{avg} r_0}{\nu} < 2300 \quad . \tag{22}$$

Experimental reactors should be operated well within this limit. The criteria for applicability of the reactor design equations (16) are summarized in Table I.

TABLE I.

SUMMARY OF CRITERIA FOR APPLICABILITY OF TUBULAR-REACTOR EQUATION

Neglect of Longitudinal Diffusion	Neglect of Entrance Effects	Laminar Flow
$\frac{r_0 v_{avg}}{D_A} > 25$	$\frac{k_b r_0^2}{\nu} < 4$ (homogeneous)	$\frac{2 r_0 v_{avg}}{\nu} < 2300$
	$\frac{k_s r_0}{\nu} < 4$ (heterogeneous)	

IDEAL TUBULAR REACTORS

Under special circumstances the solutions to equations (16) approach those of simplified limiting equations. This simplicity provides considerable incentive to design experimental systems to conform to limiting behavior if possible. The present section is addressed to the task of examining

the conditions under which such "ideal" behavior is approached, and in pointing out some of the advantages of these limiting types of reactors.

The most well known limiting model of tubular reactor behavior is the flat concentration-profile, zero-backmixing (FCPZB) reactor, which obeys the basic equations

$$v_{avg} \frac{dc}{dz} = \frac{2}{r_0} r_s + r_b \quad , \tag{23}$$

$$c = c_0 \quad \text{at} \quad z = 0 \quad . \tag{23a}$$

This model essentially requires all fluid particles to have identical residence times. Also, as implied by the name, the concentration is invariant with radial position throughout the reactor. In spite of the implied anomaly of large radial molecular diffusion but negligible longitudinal molecular diffusion, the solutions of the associated equations approach one another sufficiently to enable considerable practical utilization of this model.

The difference between this limiting model and "plug flow" models described elsewhere throughout the literature should be emphasized. "Plug flow" normally indicates a flat velocity-profile situation, although some authors have used this terminology to describe the situation envisioned in the present sense. To avoid confusion, the term "plug flow" will not be used further here.

For the special conditions wherein the bulk and wall reactions obey simple n-th order laws, equations (23) may be integrated to yield the (dimensionless) form

$$\int_1^C \frac{dC}{4\Gamma Z C^{\beta} + 2\Theta Z C^{\alpha}} = -1 \quad , \tag{24}$$

where α and β are the bulk and wall reaction orders, and the dimensionless quantities retain their usual significance as defined in Table III.

The question of primary importance concerns the errors in measured reaction rate constants that will arise if this limiting model is employed rather than the more exact equations (16). Defining this error E by equation (5) and comparing predictions of equations (16) and (24) for first-order reactions, it is found [Hales (1968)] that E increases rapidly with Θ (or Γ) and is nearly invariant with the extent of conversion over ranges of practical importance. E is less than 1% if

$$\Theta < 0.4 \quad , \tag{25}$$

and

$$\Gamma < 0.01 \quad . \tag{26}$$

Semiquantitative evaluations can also be performed for other reaction orders using these criteria upon providing suitable linearizations.

In contrast, homogeneous tubular reactors wherein diffusion is negligibly small, constitute another type of limiting model. Equations corresponding to this model were first set forth by Bosworth and Groden (1962). In dimensionless form these reduce to

$$\frac{c_{Ab}}{c_m} = \frac{2(\alpha - 1)^3(\Theta Z)^2}{[1 + 2(\alpha - 1)\Theta Z]^{-1/(\alpha-1)}} \int_0^{[1+(\alpha-1)\Theta Z]^{-1/(\alpha-1)}} \frac{z^{2\alpha-2}}{(1 - z^{\alpha-1}\ 3} \quad , \tag{27}$$

for $\alpha = 1$, and

$$\frac{c_{Ab}}{c_m} = e^{\Theta Z}[1 - (\Theta Z)^2 + (\Theta Z)^2 e^{\Theta Z}\ Ei(\Theta Z)] \quad , \tag{28}$$

for $\alpha = 1$. Here, c_{Ab}/c_m is the ratio of the mixed-mean reactor outlet concentration predicted by this model to that predicted by equation (24), and Ei denotes the exponential integral

$$Ei(x) = \int_x^{\infty} \frac{e^{-u}}{u}\, du \quad , \tag{29}$$

which is tabulated elsewhere (Abramowitz and Stegun, 1964).

Comparison with computed results [Hales (1968)] shows that the errors in predicting rate constants using this zero-diffusion model of reactor behavior rather than equations (16) decrease with Θ and again are essentially invariant with the extent of conversion. The corresponding criterion for $E < 1\%$ is, approximately,

$$\Theta > 500 \quad . \tag{30}$$

Because of entrance-effect considerations (cf. Table I) this zero-diffusion model is useful only for large Schmidt numbers, precluding its use for atmospheric sciences studies except, conceivably, for systems involving aerosols, or for investigation of liquid-phase reactions in studies of precipitation chemistry.

Besides being attractive for their relative simplicity, the models represented by equations (24), (27), and (28) share the advantage of not being restricted to systems wherein only one of the reacting components varies appreciably. This quality provides a marked experimental convenience and a distinct incentive to design experiments so as to attain such ideal behavior.

Since surface reactions can occur only in conjunction with diffusional transport to the reactor wall, a zero-diffusion model cannot be applied to situations involving heterogeneous reactions. A corresponding model, however, can be constructed by visualizing a situation wherein the wall reaction-rate constant becomes infinitely large, thereby rendering diffusion the sole rate-influencing step of the process. This case, described by equations (16) with infinite k_s, has been solved by a number of authors for the analogous case of diffusion-controlled heat transfer. Subsequent authors (cf., Table II) have discussed various aspects of this problem. This model is of little value to reaction-rate studies, since it is based on diffusion-limited behavior. It has found considerable use, however, in diffusion-tube studies of aerosol behavior; a particularly interesting

application of this technique has been described by Smith, *et al.* (1968) in conjunction with their studies of gas-aerosol sorption interactions.

In addition to the limiting models described above, a variety of other simplified models of tubular-reactor performance have appeared in the literature. Some of these models may find limited application in the analysis of data from experimental reactors. Boundary-layer analyses (cf. Table II), for example, may be particularly useful for situations involving wall reactions near the reactor entrance region. In general, however, these other simplified models are not sufficiently reliable to be useful for experimental purposes.

The majority of these additional models have been based upon the assumption of a flat velocity profile. The numerous attempts that have been made to compensate for this assumption by adding an axial diffusion component to account for Taylor dispersion have met with fair success; others have been found to agree so poorly with true behavior as to earn the title "fictitious models."

Many of the above models were developed in the past to avoid computational difficulties posed by equations such as (16). Computers, however, have facilitated solutions to equations (16) now published for most practical conditions. Therefore, the use of the above simplified, nonlimiting models for analysis of experimental reactors is no longer really justified.

The variety of simplifying assumptions that can be made regarding tubular-reactor performance has resulted in a large number of related publications, and it is useful to possess a compilation of these works, both to provide convenient access to mathematical solutions and to prevent confusion from related publications that are not usable for the purpose at hand. Such a compilation is given in Table II, which is a listing of works pertaining to tubular reactors operating with isothermal, Newtonian fluids in the absence of entrance effects. Because of the large number of related publications, the construction of a complete list for reactors operating

outside of these restrictions would be virtually impossible; Melville's (1948) observation that "any human thing supposed to be complete must for that very reason infallibly be faulty" applies with certainty here. This listing, however, is felt to cover rather completely the associated works of relevance to reaction-rate studies in the atmospheric sciences. The compilation is ordered according to restrictions on axial and radial diffusion, a criterion which seems to be the most logical basis for classification. Some of the previous authors listed in the table have reviewed limited portions of the material appearing here.

FURTHER CONSIDERATIONS OF SIMULTANEOUS SURFACE AND BULK REACTIONS

The previous sections have noted the potential importance of surface reactions in influencing gas-phase reaction-rate measurements, and have suggested techniques, using ideal reactors, to evaluate this influence quantitatively. This section deals briefly with the problem of surface reactions in general and discusses some alternative measures that may be utilized when they are encountered.

A literature survey indicates that there are three classes of techniques dealing with unwanted surface reactions:

1. Techniques that define the surface reaction quantitatively, thus allowing for its effect to be separated from the homogeneous reaction.
2. Techniques that attempt to prevent contact of the material from the vessel walls.
3. Techniques involving removal of the active surface, or effective inactivation of the surface by changing operating conditions.

Techniques of the first type, involving changes of the s/v ratio, have been discussed previously in the context of ideal reactors. Additional ways of varying the s/v ratio include changing the vessel geometry (cf., Batt and Benson, 1968) or by packing it with smaller pieces of the material of interest (cf., Frost and Pearson, 1964). In their treatise on gas-phase reaction-rate measurement, Melville and Gowenlock (1964) suggest packing

a reactor in such a manner, plotting conversion versus the s/v ratio, and extrapolating to zero to find the homogeneous contribution. These authors point out that the method is reliable only if the packing material has had the same heat-treating and cleaning history as that of the vessel.

The main objection to techniques of the first type is that they tend to disregard the previously discussed importance of mass transfer as a rate-influencing step in the overall process. These techniques are valid for cases where slow reaction rates and rapid mass transfer are encountered, but unfortunately, one is seldom certain of what the true situation really is for other than the simplest of geometries.

Variations of the simple tubular reactor have been employed to isolate reacting gases from the wall. Satterfield *et al.* (1963) attempted to accomplish this using a porous-walled reactor. Reactant flowing axially through this system was swept away from the reactor surface by inert gas permeating inward radially through the walls; however, the practical problems of excessive flow rates and poor stability limited the usefulness of this technique.

Isolation from the walls of a tubular reactor using a coaxial jet system has been reported by Wood (1964). Seider (1966) has subsequently published a numerical solution of the corresponding flow equations. In a preliminary experimental investigation, however, Seider found the coaxial jet system too unstable to be used as a practical means for measurement. Moderate success has been attained with a related technique which involves introduction of reactant as a "point source" in the center of a tubular reactor through which inert gas is flowing, [Walker and Westenberg (1958)]. A recent application of this "point source technique" has been described by Frazier and Kooyman (1968).

Perhaps the most simple and obvious means of isolating the true homogeneous reaction is to change the reactor wall material to one that is inert for the heterogeneous reaction. Indeed, the wall material and its past history

are extremely important factors. Even the more inert substances sometimes exhibit variations. For example, the heterogeneous decomposition of hydrogen iodide will occur in Pyrex vessels, but not in Silica vessels [cf. Laidler (1965)].

Melville and Gowenlock emphasize the importance of cleaning the vessel in reducing wall effects and suggest cleaning techniques. These authors cite numerous examples of the influence of heat treating and cleaning. Wood (1922), for example, found that the recombination of hydrogen atoms in an electric discharge is catalyzed by broken glass but not by fire-polished glass. Hoare (1953) has shown that the formation of devitrified layers on the surfaces of silica vessels produces a change in catalytic activity as aging occurs; an effect that has also been observed with Pyrex [Minkoff and Tipper (1962)].

In addition to proper cleaning of the vessel and changing its material, an inert wall coating may be applied successfully in the investigation of several gas-phase reactions, and coating methods are described in the literature [Melville and Gowenlock (1964)].

One additional technique that should be mentioned in this context involves heating the reaction vessel [Satterfield and Yeung (1965)]. Since activation energies for gas-phase reactions are generally higher than those for corresponding wall reactions, one may be able to create conditions at higher temperatures where the bulk reaction will predominate. The value of this method is limited because it usually involves an extrapolation back to the temperatures of interest.

Another technique of this general nature can be applied when the order of the wall reaction differs from that in the bulk [Smith (1943)]. This method simply involves changing the concentrations of the reactants so that one of the reactions predominates by virtue of its unique concentration dependence.

The main difficulty with all of these techniques is that it takes a considerable amount of experimental work to ascertain whether or not the wall reaction has indeed been eliminated. This difficulty is compounded by the increased importance of surface reactions at low reactant concentrations. Such difficulties emphasize the importance of accounting for mass-transfer phenomena in relation to chemical kinetics, and the utility of the dual ideal-reactor approach to account for extraneous surface reactions in homogeneous reaction-rate studies.

CONCLUSIONS

In the final analysis it is apparent that mass-transfer effects may be highly important in obscuring and even "falsifying" chemical reaction phenomena, depending upon reaction kinetics and experimental reaction design. Experimental reactors therefore must be designed so as to render mass-transfer effects negligible, or to account quantitatively for their influence. This problem is especially pertinent whenever surface reactions are involved, owing to the increased importance of mass-transfer as a rate-influencing step under these circumstances.

Modern mathematical techniques have served to alleviate this problem somewhat, especially for the case of tubular reactors. The large number of solutions that presently exist for tubular-reactor models can be used for reactor data analysis, even under some non-ideal circumstances. The compilation of these solutions in Table II presents a useful reference to these works, both for use in the analysis of rate data and as a means of avoiding confusion with inappropriate models.

The approximate criteria for reactor ideality presented in this report should be useful in providing a more systematic basis for experimental reactor design, and the analysis of future rate data.

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TABLE II.

SUMMARY OF AVAILABLE SOLUTIONS TO TUBULAR REACTOR MODELS INVOLVING ISOTHERMAL NEWTONIAN FLUIDS WITH CONSTANT TRANSPORT PROPERTIES AND NEGLIGIBLE ENTRANCE EFFECTS

DESCRIPTION OF MODEL	REACTION TYPE	TYPE OF SOLUTION	AUTHOR(S)
— PART I: MODELS BASED UPON PARABOLIC VELOCITY PROFILE WITH FINITE AXIAL AND RADIAL DIFFUSION —			
SINGLE TRACE COMPONENT REACTING IN BULK, AS DESCRIBED BY EQUATIONS (14) WITH $r_{is} = 0$	FIRST ORDER	APPROXIMATION TO ANALYTICAL SOLUTION	DAMKOHLER (1937)
		APPROXIMATE ANALYTICAL	WISSLER (1969)
	SECOND ORDER	NUMERICAL	COHEN AND RIPPIN (1967)
SINGLE TRACE COMPONENT REACTING AT WALL, AS DESCRIBED BY EQUATIONS (14) WITH $r_i = 0$	ZERO ORDER	ANALYTICAL (EIGENFUNCTION EXPANSION, FROM HEAT-TRANSFER ANALOGY)	HSU (1967) SCHNEIDER (1957)
		NUMERICAL (FROM HEAT-TRANSFER ANALOGY)	VERHOFF (1967)
	TOTAL SINK AT WALL	ANALYTICAL (LAPLACE TRANSFORMATION, FROM HEAT-TRANSFER ANALOGY)	JONES (1971)
		ANALYTICAL (EIGENFUNCTION EXPANSION, FROM HEAT-TRANSFER ANALOGY)	SINGH (1958)
SINGLE TRACE COMPONENT REACTING BOTH IN BULK AND AT WALL, AS DESCRIBED BY EQUATIONS (14)	FIRST-ORDER AT WALL AND IN BULK	ANALYTICAL-VALID ASYMPTOTICALLY FOR LARGE VALUES OF Z	WALKER (1961)
	ZERO-ORDER GENERATION IN BULK AND TOTAL SINK AT WALL	ANALYTICAL (EIGENFUNCTION EXPANSION)	TAN (1969) TAN AND HSU (1970)
— PART II: MODELS BASED ON PARABOLIC VELOCITY PROFILE WITH FINITE RADIAL DIFFUSION, BUT ZERO AXIAL DIFFUSION —			
SINGLE TRACE COMPONENT REACTING IN BULK, AS DESCRIBED BY EQUATIONS (16) WITH $\Gamma = 0$	FIRST ORDER	ANALYTICAL (EIGENFUNCTION EXPANSION)	LAUWERIER (1959) WISSLER AND SCHECHTER (1961)
		ANALYTICAL (BOUNDARY-LAYER APPROXIMATION)	ACRIVOS (1953)
		NUMERICAL	CLELAND AND WILHELM (1956) HSU (1965) LAPIDUS (1962)
	FIRST-ORDER CONSECUTIVE $A \rightarrow B \rightarrow C$	ANALYTICAL	WISSLER AND SCHECHTER (1961)
	FIRST-ORDER REVERSIBLE	ANALYTICAL	SCHECHTER (1967)
	SECOND ORDER	NUMERICAL	VIGNES AND TRAMBOUZE (1962)
SINGLE TRACE COMPONENT REACTING AT WALL, AS DESCRIBED BY EQUATIONS (16) WITH $\Theta = 0$	ZERO ORDER	ANALYTICAL (EIGENFUNCTION EXPANSION, FROM HEAT-TRANSFEP ANALOGY)	SIEGEL, et al. (1958)
		ANALYTICAL (ASYMPTOTIC FOR LARGE Z)	BIRD, et al. (1960)
		ANALYTICAL (ASYMPTOTIC FOR SMALL Z)	KRAMERS AND KREYGER (1959)
	FIRST ORDER	ANALYTICAL	FALQUE (1968) SCHENK AND DUNMORE (1954) SIDEMAN, et al. (1965) TOWNSEND (1899)
	GENERALIZED KINETICS OR TOTAL SINK AT WALL	ANALYTICAL (EIGENFUNCTION EXPANSION, SOME ARE FROM HEAT-TRANSFER ANALOGY)	BROWN (1960) GORMLEY AND KENNEDY (1949) GRAETZ (1883) KNUDSEN AND KATZ (1958) NUSSELT (1910) SELLARS, et al (1956) SINGH (1958) TOWNSEND (1899)
		ANALYTICAL (BOUNDARY-LAYER APPROXIMATION, SOME FROM HEAT-TRANSFER ANALOGY)	CHAMBRÉ (1956) CHAMBRÉ AND ACRIVOS (1956) COWHERD AND HOELSCHER (1965) LEVEQUE (1928) ROSNER (1969)
SINGLE TRACE COMPONENT REACTING IN BULK AND AT WALL AS DESCRIBED BY EQUATIONS (16)	FIRST ORDER AT WALL, FIRST ORDER IN BULK	ANALYTICAL (GALERKIN'S METHOD)	SOLOMON AND HUDSON (1967)
		NUMERICAL	HALES (1968)
	FIRST ORDER AT WALL, SECOND ORDER IN BULK	NUMERICAL	HALES (1968) KRONGELB AND STRANDBERG (1959)
		ANALYTICAL (BOUNDARY-LAYER APPROXIMATION)	KLATT AND BLADEL (1966, 1968)
	SECOND ORDER AT WALL FIRST ORDER IN BULK	NUMERICAL	HALES (1968)

TABLE II. CONTINUED

DESCRIPTION OF MODEL	REACTION TYPE	TYPE OF SOLUTION	AUTHOR(S)
—PART II: MODELS BASED ON PARABOLIC VELOCITY PROFILE WITH FINITE RADIAL DIFFUSION, BUT ZERO AXIAL DIFFUSION (CONT'D) —			
	SECOND ORDER AT WALL, SECOND ORDER IN BULK	NUMERICAL	HALES (1968)
	GENERALIZED KINETICS	ANALYTICAL - EXPRESSES REACTION RATES AS INHOMOGENEOUS TERMS AND APPLIES GREEN'S - FUNCTION TECHNIQUE	GIDASPOW (1971)
MULTIPLE COMPONENTS REACTING IN BULK AND AT WALL	LINEARIZED REACTION EXPRESSIONS IN NEIGHBORHOOD OF CHEMICAL EQUILIBRIUM	ANALYTICAL APPROXIMATION (GALERKIN'S METHOD)	SOLOMON AND HUDSON (1971)
MULTIPLE COMPONENTS REACTING AT WALL	LINEARIZED REACTION EXPRESSIONS FOR NONEQUILIBRIUM SYSTEMS	ANALYTICAL APPROXIMATION (GALERKIN'S METHOD)	SOLOMON AND HUDSON (1971)
—PART III: MODELS BASED ON PARABOLIC VELOCITY PROFILE WITH ZERO AXIAL AND RADIAL DIFFUSION —			
ONE OR MORE COMPONENTS REACTING IN BULK	GENERAL ORDER	ANALYTICAL	BOSWORTH AND GRODEN (1962) DENBIGH (1951) JOHNSON (1970) WILDE (1957)
— PART IV: MODELS ASSUMING COMPLETE RADIAL MIXING BUT FINITE AXIAL MIXING —			
SINGLE TRACE COMPONENTS REACTING IN BULK OR AT WALL, FLAT VELOCITY PROFILE	FIRST ORDER	ANALYTICAL	BURGHARDT (1967) BISCHOFF (1968) COSTE, et al. (1961) CORRIGAN AND DEAN (1969) DANCKWERTS (1953) DICKENS, et al. (1960) FORSTER AND GEIB (1934) HULBURT (1944, 1945) LEVENSPIEL AND BISCHOFF (1959) PEARSON (1959) TICHACEK (1963) WEHNER AND WILHELM (1956)
	SECOND ORDER	NUMERICAL	LEVENSPIEL AND BISCHOFF (1959)
	GENERAL ORDER	ANALYTICAL	LANGMUIR (1908)
		ANALYTICAL (PERTURBATION TECHNIQUES)	BURGHARDT (1967) BURGHARDT AND ZALESKI (1968) HORN AND PARISH (1967) PASQUON AND DENTE (1962)
		ANALYTICAL (VARIATIONAL TECHNIQUES)	SCHECHTER (1967) GROTCH (1969)
		NUMERICAL	FAN AND BALIE (1960) FAN AND AHN (1968)
		ANALOG	HOFMANN AND ASTHEIMER (1963)
	CONSECUTIVE $A \rightarrow B \rightarrow C$	ANALYTICAL (PERTURBATION TECHNIQUES)	KIPP AND DAVIS (1968)
SINGLE TRACE COMPONENT REACTING IN BULK AND AT WALL, FLAT VELOCITY PROFILE	FIRST ORDER IN BULK AND AT WALL	ANALYTICAL	WALKER (1961)
— PART V: MODELS ASSUMING A FLAT VELOCITY PROFILE WITH NONZERO AND FINITE RADIAL DIFFUSION —			
SINGLE TRACE COMPONENT REACTING AT WALL	FIRST ORDER	ANALYTICAL	FALQUE (1968) HULBURT (1945) KATZ (1959)
	CONSECUTIVE $A \rightarrow X_1B \rightarrow X_2C$	NUMERICAL	HUDSON (1965)
— PART VI: MODELS ASSUMING A FLAT VELOCITY PROFILE WITH FINITE RADIAL AND AXIAL DIFFUSION —			
SINGLE TRACE COMPONENT REACTING AT WALL	FIRST ORDER	ANALYTICAL	BARON, et al. (1952) DAMKOHLER (1937) HOELSCHER (1954) PANETH AND HERTZFELD (1931)
— PART VII: MODEL ASSUMING ZERO AXIAL DIFFUSION AND COMPLETE RADIAL MIXING —			
FLAT CONCENTRATION-PROFILE, ZERO BACK-MIXING MODEL	GENERAL	ANALYTICAL	TEXTBOOK CASE, CF. EQ (24)

TABLE III.

DEFINITIONS OF DIMENSIONLESS GROUPS

Group	Definition	Name	Physical Significance
c_A	c_A/c_{A0}	--	dimensionless concentration
Pe	$\frac{v_{avg} r_0}{\upsilon}$	Peclet Group	$\frac{\text{axial transport by flow}}{\text{radial transport by diffusion}}$
R	r/r_0	--	dimensionless radial position
Re	$\frac{2v_{avg} r_0}{\upsilon}$	Reynolds Group	$\frac{\text{inertial forces}}{\text{viscous forces}}$
Sc	$\frac{\upsilon}{D_A}$	Schmidt Group	$\frac{\text{diffusivity of momentum}}{\text{diffusivity of mass}}$
Z	$\frac{D_A z}{2v_{avg} r_0^2}$	Bodenstein Group	dimensionless axial position (z/zr_0Pe)
α	--	--	homogeneous reaction order
β	--	--	heterogeneous reaction order
Γ	$\frac{r_0 k_s c_0^{\beta-1}}{D_A}$	heterogeneous Damkohler Group II	$\frac{\text{removal by wall reaction}}{\text{removal by radial diffusion}}$
Θ	$\frac{r_0^2 k_b c_0^{\alpha-1}}{D_A}$	homogeneous Damkohler Group II	$\frac{\text{removal by bulk reaction}}{\text{removal by radial diffusion}}$
ΓZ	$\frac{k_s z c_0^{\beta-1}}{2v_{avg} r_0}$	heterogeneous Damkohler Group I	$\frac{\text{removal by wall reaction}}{\text{removal by axial flow}}$
ΘZ	$\frac{k_b z c_0^{\alpha-1}}{2v_{avg}}$	homogeneous Damkohler Group I	$\frac{\text{removal by bulk reaction}}{\text{removal by axial flow}}$

NOMENCLATURE

c_A	concentration
c_{Ab}	bulk-mean concentration
c_{A0}	reactor entrance concentration
D_A	Fick's-law diffusion coefficient
k_b	homogeneous reaction-rate constant
k_s	heterogeneous reaction-rate constant
k_y	mass-transfer coefficient
r	radial position
r_b	homogeneous reaction rate
r_0	tube radius
r_s	heterogeneous reaction rate
s	surface area
t	time
u	integration variable
v_{avg}	average axial flow velocity
v	reaction volume
v_o	axial flow velocity
w	volumetric flow rate
z	axial position
τ	average space-time in reactor

The following main dimensionless quantities are defined in Table III:

C_A, Pe, R, Re, Sc, Z, α, β, Γ, Θ.

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