

Errors Due to Bed-Temperature Gradients in Catalytic Kinetic Studies

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The error introduced by bed-temperature gradients on kinetic data obtained from real differential packed-bed catalytic reactors is considered. Results are presented as upper bounds for such error, which result from considering simplified forms of the differential energy balance in the reactor. These bounds may help in designing proper experimental conditions to achieve practically isothermal operation in catalytic kinetic studies. An illustrative example is given.

INTRODUCTION

The advantages of differential reactors in kinetic studies have been largely recognized, mainly because of the easy handling of their rate data to establish a rate equation.

One of the most serious limitations of these reactors is, however, that working at very low conversion levels, the accuracy of the rate measurements usually decreases, while large conversions may lead to severe variations of the local reaction rate within the reactor, which invalidate the "differential" character of the subsequent analysis.

It is then convenient to develop some criteria to see how much the conversion level may be increased without a significant loss of accuracy in the treatment of the rate data.

The variation of local reaction rate arises from two coupled effects: composition and temperature changes within the reactor volume. These changes may occur at the level of particle dimensions (intraparticle composition and temperature gradients) and at the level of reactor dimensions (bed composition and temperature gradients). This note is concerned *only with bed composition and temperature gradients*, since

satisfactory criteria have been developed and largely used to avoid mass and heat transfer problems at the level of particle dimensions (5).

Since mass and energy balances in the bed are interrelated to each other, the exact solution of the problem implies the simultaneous solution of heat and mass differential equations, although, the complexity of the problem and the high number of variables involved would lead to solutions of no generality and of little use from a practical point of view. Another approach which seems more convenient for our purpose consists in a separated analysis of the effect of composition changes, assuming constancy of temperature, and the effect of temperature gradients, assuming constant composition on the systematic error due to local variations of reaction rate, introduced when giving differential treatment to the data.

Of course, the results obtained by the proposed method are valid *only* if the analysis leads to the conclusion that *both* composition and temperature gradients are not important.

The effect of composition changes on the error, under isothermal conditions, has been partially considered by Pauls (1), who estimated the influence of conversion on the

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error introduced by giving differential treatment to his data for the catalytic hydrogenation of ethylene. More recently, Kraus (2) and Massaldi and Maymó (3) have extended this analysis to most of the rate expressions frequently found in engineering kinetic studies. Their results indicate that, under isothermal conditions, conversions of the order of 10–15% may usually be used for irreversible reactions, without a significant loss of accuracy.

These relatively large conversions may, however, give place to considerable temperature differences within the reactor volume and, in fact, these temperature differences, more than the composition change, may be in many cases the controlling factor on the systematic error, when the reaction is highly exo or endothermic and concentration of reactants in the feed is relatively large.

This paper considers this part of the problem, and develops a simple criteria to estimate the magnitude of the error introduced by *bed-temperature gradients* in the kinetic treatment of rate data from real differential reactors.

THE SYSTEMATIC ERROR

To evaluate this error, a similar criteria to that used in reference (3) is used here. Equation (1) represents the true kinetic relationship between reaction rate, composition, and temperature. This relation holds at any point in the reactor, but since composition and temperature change in some extent along the reactor volume, r is not a constant but varies from point to point; the measured value \bar{r} , is an average value for the whole reactor.

$$r = f(C, T). \quad (1)$$

In the analysis of the rate data by the differential method in order to obtain a rate equation, a reference composition, \dot{C} , and temperature, \dot{T} , are assigned to each measured value of \bar{r} , and generally the true kinetic relationship given by Eq. (1) does not hold between \bar{r} , \dot{C} , and \dot{T} , and a systematic error is introduced by this fact, which is given by Eq. (2) as follows:

$$(\text{SE}) = (\bar{r} - \dot{r})/\dot{r} = (\bar{r}/\dot{r}) - 1, \quad (2)$$

where \dot{r} is the reaction rate that would be observed if the whole reactor volume operates at the reference composition and temperature, i.e., $\dot{r} = f(\dot{C}, \dot{T})$ and

$$(\bar{r}/\dot{r}) = (1/V_R) \int_0^{V_R} (r/\dot{r}) dV_R. \quad (3)$$

For the sake of simplicity, the following assumptions are considered:

1. Packed bed tubular catalytic reactor, with wall held at constant and uniform temperature T_0 . Long preheating and calming sections are provided so that fluid reaches the catalyst zone at temperature T_0 ;
2. Plug flow of fluid and steady-state operation;
3. Temperature effect on reaction rate can be properly accounted for by the Arrhenius law, within the small range of temperatures occurring in the catalyst bed;
4. Composition changes along the reactor are not important;
5. Bed-(reactor wall) heat transfer resistance is not significant (not a severe restriction for large ratios of reactor/particle diameter);
6. T_0 is chosen as reference temperature ($\dot{T} = T_0$). The convenience of other values for the reference temperature will be briefly discussed below.

Because of assumptions 3, 4, and 6, $(r/\dot{r}) = \exp(A - A/\theta)$, where $A = \text{Arrhenius number} = E/(R_g T_0)$ and $\theta = T/T_0$. Then, Eq. (2) becomes

$$(\text{SE}) = (1/V_R) \int_0^{V_R} \exp(A - A/\theta) dV_R - 1. \quad (4)$$

Evaluation of (SE) by Eq. (4) requires the knowledge of the temperature field in the catalytic zone of the reactor. This can be done by integration of the dimensionless partial differential Eq. (5), which results from setting up a differential energy balance in the reactor.

$$\exp(A - A/\theta) = \frac{1}{\phi_f} \frac{\partial \theta}{\partial z} + \frac{(-1)}{\phi_r x} \frac{\partial}{\partial x} \left(x \frac{\partial \theta}{\partial x} \right) + \frac{(-1)}{\phi_a} \frac{\partial^2 \theta}{\partial z^2} \quad (5)$$

heat source by chemical reaction
 heat dissipation by flow
 heat dissipation by radial conduction
 heat dissipation by axial conduction

where

$$\phi_a = (-\Delta H)L^2 r_0 / (k_a T_0), \quad (6)$$

$$\phi_f = (-\Delta H)L r_0 / (GC_p T_0), \quad (7)$$

and

$$\phi_r = (-\Delta H)R^2 r_0 / (k_r T_0). \quad (8)$$

Solution of Eq. (5) is too involved to be useful from a practical point of view. A great simplification of the problem can be done, however, to obtain upper bounds for the absolute value of (SE). In fact, the three terms of the right side of Eq. (5) can be regarded as parallel paths of heat dissipation; and *under the boundary conditions implicit in assumption 1* (see Fig. 1), all these three terms have equal sign. Hence, dropping any pair of them lead to simplified differential equations *which will give*

higher values for the temperature gradients than those corresponding to the real situation. These simplified equations can be used to predict upper bounds for the absolute value of (SE) for the general case where the three mechanisms of heat dissipation may be significant.

Simplification I. Only heat dissipation by radial conduction is considered:

$$\exp(A - A/\theta) = \frac{(-1)}{\phi_r x} \frac{d}{dx} \left(x \frac{d\theta}{dx} \right),$$

$$\theta = 1 \text{ at } x = 1 \text{ and } (d\theta/dx) = 0 \text{ at } x = 0. \quad (9)$$

Equation (9) was numerically integrated by standard methods to obtain the θ field; and this result is introduced into Eq. (4), which for this case reduces to (10) in order to compute an upper bound for (SE).

$$(SE)_r = 2 \int_0^1 \exp(A - A/\theta) x dx - 1 = f(A, \phi_r) \quad (10)$$

An analytic asymptotic solution for $(SE)_r$ is obtained by linear expansion of the exponential term: $\exp(A - A/\theta) \cong 1 + A(\theta - 1)$ in Eq. (9), which becomes a Bessel's equation and in Eq. (10) to give

$$\theta \cong 1 + \frac{\frac{\phi_r(1-x^2)}{4} - \frac{(A\phi_r)(1-x^4)}{64A} + \dots}{1 - \frac{(A\phi_r)}{4} + \frac{(A\phi_r)^2}{64} - \dots} \quad (11)$$

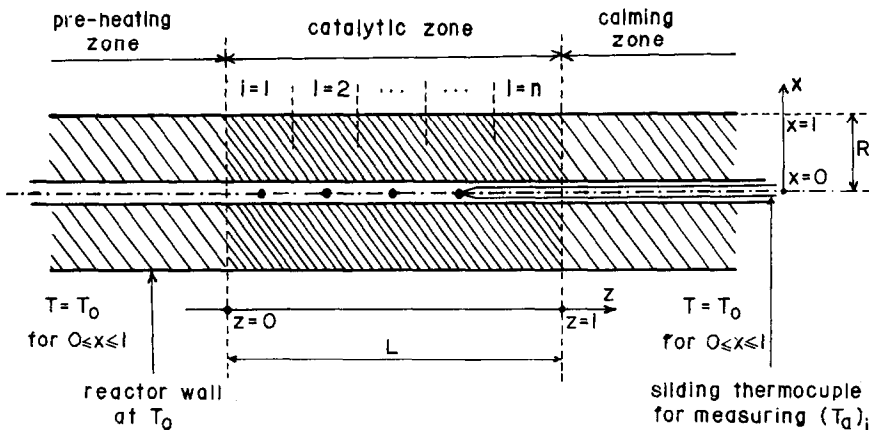


FIG. 1. Scheme of reactor.

$$(SE)_r \cong \frac{\frac{(A\phi_r)}{8} - \frac{(A\phi_r)^2}{86} + \dots}{1 - \frac{(A\phi_r)}{4} + \frac{(A\phi_r)^2}{64} - \dots} \cong (A\phi_r)/8. \quad (12)$$

Equation (12) shows that, as $(SE)_r$ becomes small, it becomes a function of the single parameter $(A\phi_r)$.

Simplification 2. Only heat dissipation by flow is considered:

$$\exp(A - A/\theta) = (1/\phi_f)(d\theta/dz), \quad \theta = 1 \text{ at } z = 0. \quad (13)$$

Equation (13) was integrated to give the temperature field, and this result introduced into Eq. (4), which for this case transforms into Eq. (14), to compute an upper bound for (SE) .

$$(SE)_f = \int_0^1 \exp(A - A/\theta) dz - 1 = f(A, \phi_f). \quad (14)$$

Again an asymptotic solution can be obtained by linear expansion of the exponential term in Eqs. (13) and (14) to give

$$1 + A(\theta - 1) \cong \exp(A\phi_f z) \quad (15)$$

and

$$(SE)_f \cong \frac{\exp(A\phi_f) - 1}{(A\phi_f)} - 1. \quad (16)$$

Since Eq. (16) only applies for small values of $(A\phi_f)$, the exponential can be expanded in series to give

$$(SE)_f \cong \frac{(A\phi_f)}{2} + \frac{(A\phi_f)^2}{6} + \dots \cong (A\phi_f)/2. \quad (17)$$

This asymptotic solution also shows that as $(SE)_f$ becomes small; it can be represented as a function of a single parameter: $(A\phi_f)$.

Simplification 3. Only heat dissipation by axial heat conduction from the reaction zone: This case seems far from representing any real situation, and would lead to a too conservative upper bound for (SE) to be useful. For this reason is not considered here.

RESULTS

The computed results for $(SE)_r$ and $(SE)_f$ vs the parameters $(A\phi_r)$ and $(A\phi_f)$, respectively, are presented in Figs. 2 and 3. Since usually the value of A ranges between 5 and 50, most of the results fall within the shadowy regions. The asymptotic solutions (Eqs. (12) and (17)) give a good representation of these results for values of $(SE)_r$ and $(SE)_f$ up to about 10%.

The use of ϕ_r and ϕ_f have the disadvantage of requiring the value of r_0 (which is not a measured value) in their calculation. It is then convenient to define the modified parameters $\bar{\phi}_r$ and $\bar{\phi}_f$:

$$\bar{\phi}_f = \frac{(-\Delta H)L\bar{r}}{GC_p T_0} = \frac{(-\Delta H)y_{B_0} X_{B_f}}{C_p T_0} = (1 + (SE))\phi_f \quad (18)$$

and

$$\bar{\phi}_r = \frac{(-\Delta H)R^2\bar{r}}{k_r T_0} = \frac{(-\Delta H)F_{B_0} X_{B_f}}{\pi L k_r T_0} = (1 + (SE))\phi_r. \quad (19)$$

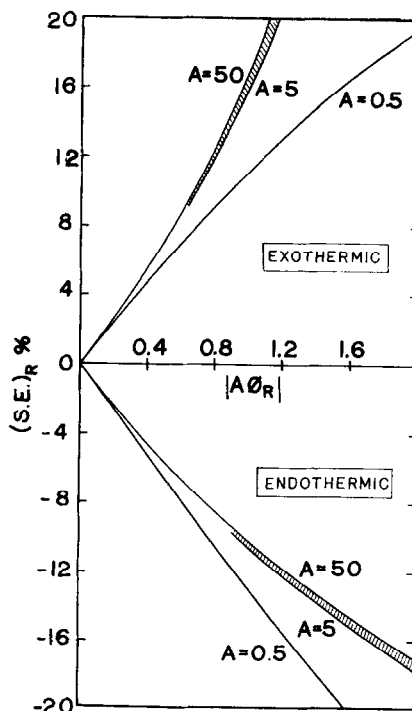
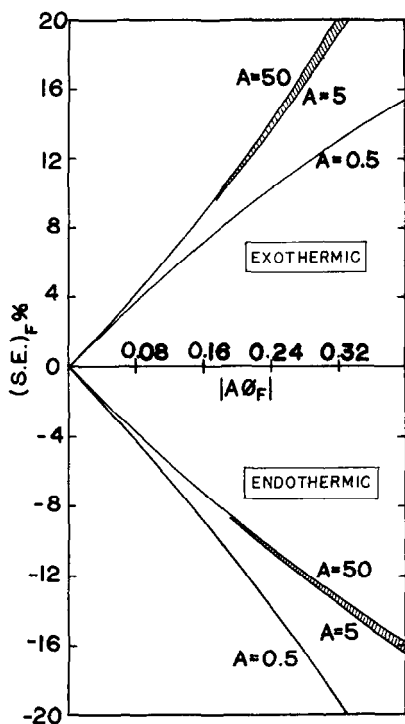


FIG. 2. $(SE)_r$ vs $(A\phi_r)$.

FIG. 3. $(SE)_f$ vs $(A\bar{\phi}_f)$.

Figures 4 and 5 are plots of the results obtained for $(SE)_r$ and $(SE)_f$ in terms of the modified parameters $(A\bar{\phi}_r)$ and $(A\bar{\phi}_f)$. For small values of (SE) , these results are closely given by Eqs. (20) and (21):

$$(SE)_r \cong (A\bar{\phi}_r)/8 \quad (20)$$

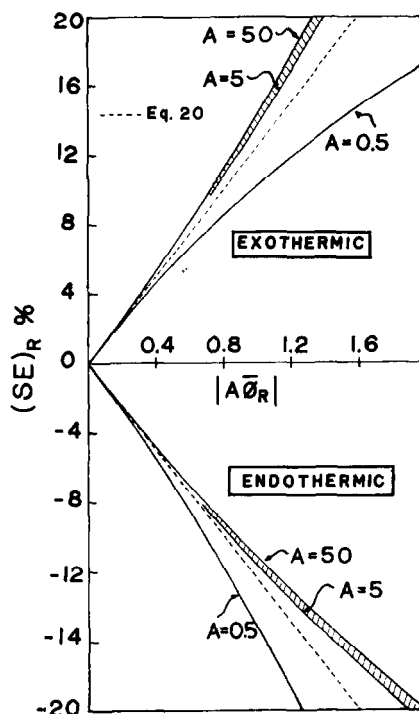
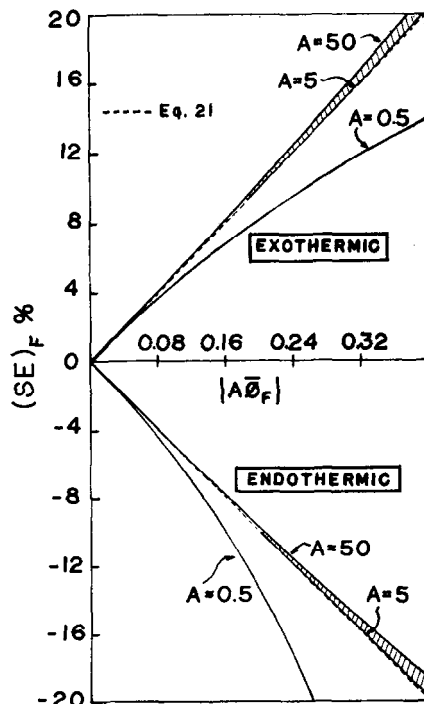
and

$$(SE)_f \cong (A\bar{\phi}_f)/2. \quad (21)$$

These equations can be used to estimate the order of magnitude of the systematic error due to bed-temperature gradients in fixed-bed catalytic studies. So, in order to assure that (SE) is below 1% will suffice that either $(A\bar{\phi}_r)/8 \leq 0.01$ or $(A\bar{\phi}_f)/2 \leq 0.01$ (since both $(SE)_r$ and $(SE)_f$ must be upper bounds for (SE)). This can be accomplished by proper design of reactor dimensions, by limiting the extent of conversion and by dilution of the catalyst with inert particles to reduce \bar{r} .

Reference Temperature other than T_0

Sometimes the reactor setup allows the measurement of bed temperatures in posi-

FIG. 4. $(SE)_r$ vs $(A\bar{\phi}_r)$. The dotted line corresponds to the asymptotic solution: $(SE)_r = (A\bar{\phi}_r)/8$.FIG. 5. $(SE)_f$ vs $(A\bar{\phi}_f)$. The dotted line corresponds to the asymptotic solution $(SE)_f = (A\bar{\phi}_f)/2$.

tions other than the reactor wall; in particular along the reactor axis by means of a sliding thermocouple. In such cases it is more convenient to use a temperature other than T_0 as reference temperature. The best choice of this temperature, usually a mean value, depends on the relative importance of the three terms of heat dissipation in Eq. (5). If radial heat conduction is predominant: $(SE)_r \ll (SE)_f$, a mean temperature calculated under the assumption of parabolic radial temperature profile is recommended for \dot{T} (Eq. (22)). If heat dissipation by flow is predominant: $(SE)_r \gg (SE)_f$, a mean value obtained assuming flat radial temperature profile for each value of z is the best choice for \dot{T} (Eq. (23)). If $(SE)_r$ and $(SE)_f$ are of comparable order of magnitude, perhaps an average between the previous values (Eq. (24)) will be a suitable choice for \dot{T} .

$$\dot{T} = (1/2n) \sum_{i=1}^{i=n} (T_a + T_0)_i;$$

recommended for $(SE)_r \ll (SE)_f$. (22)

$$\dot{T} = (1/n) \sum_{i=1}^{i=n} (T_a)_i;$$

recommended for $(SE)_r \gg (SE)_f$. (23)

$$\dot{T} = (1/4n) \sum_{i=1}^{i=n} (3T_a + T_0)_i;$$

recommended for $(SE)_r \cong (SE)_f$. (24)

If one of the three paths of heat dissipation is largely predominant, then the use of a proper value for \dot{T} drastically reduces the extent of (SE), as shown by Table 1. It should be emphasized, however, that this strong reduction in (SE) will occur if only one of the mechanisms of heat dissipation is significant in the real situation. If that is the case, the small remaining value for (SE) arises from the nonlinearity of reaction rate upon temperature.

ILLUSTRATIVE EXAMPLE

Maymó and Smith (4) have studied the kinetics of the hydrogen-oxygen reaction over platinum-alumina catalyst. Their particle runs were carried out in a fixed-bed

TABLE 1
TYPICAL COMPUTED VALUES OF (SE) FOR
DIFFERENT CHOICES OF REFERENCE
TEMPERATURE \dot{T}

Case where only heat dissipation by radial heat conduction is important ($A\phi_f \cong 0$; $A\phi_a \cong 0$)				
(SE)				
$(A\phi_r)$	A	$(A\bar{\phi}_r)$	Computed for $\dot{T} = T_0$	Computed for \dot{T} given by Eq. (22)
0.825	50.0	0.935	13.22%	-0.05%
0.835	5.0	0.942	12.86%	-0.10%
-1.21	50.0	-1.07	-11.79%	-0.01%
-3.02	5.0	-2.30	-23.55%	-0.53%
Case where only heat dissipation by flow is important ($A\phi_r \cong 0$; $A\phi_a \cong 0$)				
(SE)				
$(A\phi_f)$	A	$(A\bar{\phi}_f)$	Computed for $\dot{T} = T_0$	Computed for \dot{T} given by Eq. (23)
0.200	50.0	0.223	11.53%	0.22%
0.200	5.0	0.222	11.19%	0.11%
-0.200	50.0	-0.182	-8.86%	0.15%
-0.200	5.0	-0.182	-9.04%	0.09%

reactor which closely approached the boundary conditions stated in this paper. It is desirable to estimate the error due to bed-temperature gradients in their data.

Data from Their Run No. 47

Reactor internal radius: $R = 0.45$ cm;

Length of catalyst bed: $L = 3.5$ cm;

Heat of reaction: $(-\Delta H) = 57\ 800$ cal/(mole of H_2O);

Total feed rate: 5.67×10^{-5} mole/sec;

Mass of catalyst: 0.01801 g (catalyst was strongly diluted with glass beads to reduce bed-temperature gradients);

Reaction rate per unit mass of catalyst: 59.2×10^{-6} (mole of H_2O)/(sec) (g-catalyst);

Reaction rate per unit volume of catalytic bed: $\bar{r} = 0.48 \times 10^{-6}$ (mole of H_2O)/(sec) (cm^3 of bed);

Temperature of reactor wall: $T_0 = 100.1^\circ\text{C} = 373.3^\circ\text{K}$;

Activation energy: $E = 5\,230$ cal/mole;

Mass velocity: $G = 8.9 \times 10^{-5}$ (mole)/(sec) (cm^2);

Heat capacity of fluid: $C_p = 7.1$ cal/(mole) ($^\circ\text{K}$);

Effective radial thermalconductivity: $k_r = 2 \times 10^{-3}$ (cal)/(cm) (sec) ($^\circ\text{K}$), (estimated value), where

$$A = E/(R_0 T_0) = 5\,230/(1.987 \times 373.3) = 7.05,$$

$$\begin{aligned} \bar{\phi}_r &= (-\Delta H)R^2\bar{r}/(k_r T_0) \\ &= (57\,800 \times 0.45^2 \times 0.48 \times 10^{-6})/ \\ &\quad (0.002 \times 373.3) \\ &= 0.0075, \end{aligned}$$

$$\begin{aligned} \bar{\phi}_f &= (-\Delta H)L\bar{r}/(GC_p T_0) \\ &= (57\,800 \times 3.5 \times 0.48 \times 10^{-6})/ \\ &\quad (8.9 \times 10^{-5} \times 7.1 \times 373.3) = 0.41, \end{aligned}$$

$$\begin{aligned} (\text{SE})_r &= (A\bar{\phi}_r) = (7.05 \times 0.0075)/8 \\ &= 0.0066 \end{aligned}$$

and

$$(\text{SE})_f = (A\bar{\phi}_f) = (7.05 \times 0.41)/2 = 1.45.$$

These two values are upper bounds for (SE). Hence, if for such run the temperature T_0 is assigned to the measured reaction rate, the systematic error due to bed-temperature gradients would be smaller than 0.0066 (0.66%). The fact that $(\text{SE})_r$ is in this case much smaller than $(\text{SE})_f$ merely means that under the experimental conditions of this run, the mechanism of heat dissipation by radial conduction was much more important than the heat dissipation by flow; and $(\text{SE})_r$ will be quite close to (SE). On the other hand, $(\text{SE})_f$ is a too conservative upper bound for (SE), of little value. These results support the use of an average temperature estimated assuming a parabolic radial profile instead of T_0 as the reference temperature. Such average temperature was estimated to be 100.5°C for the considered run (from mea-

surement of reactor wall temperature and axis temperature), which was the reference temperature used in that work.

NOMENCLATURE

A	Arrhenius group: $E/R_0 T_0$
B	reference reactant
C	composition (appropriate units)
\bar{C}	reference composition (appropriate units)
C_p	molar heat capacity of fluid (cal/mole $^\circ\text{K}$)
E	activation energy (cal/mole)
F_{B_0}	feed rate of reactant B (mole/sec)
G	mass velocity (mole/ cm^2 sec)
k_r	radial effective thermal conductivity (cal/cm sec $^\circ\text{K}$)
k_a	axial effective thermal conductivity (cal/cm sec $^\circ\text{K}$)
L	length of catalytic bed (cm)
r	volumetric reaction rate (mole of B)/(sec) (cm^3 of catalytic bed)
\hat{r}	reaction rate at reference temperature and composition (mole of B)/(sec) (cm^3 of catalytic bed)
\bar{r}	average reaction rate (mole of B)/(sec) (cm^3 of catalytic bed)
R	radius of catalytic bed (cm)
R_0	gas constant (cal/mole $^\circ\text{K}$)
(SE)	systematic error, defined by Eq. (2)
(SE) _r	upper limit of (SE) given by Simplification 1
(SE) _f	upper limit of (SE) given by Simplification 2
T	temperature ($^\circ\text{K}$)
T_0	temperature at reactor wall ($^\circ\text{K}$)
T_a	temperature at axis position ($^\circ\text{K}$)
\bar{T}	reference temperature ($^\circ\text{K}$)
V_R	volume of catalytic bed (cm^3)
x	dimensionless radial position
X_{B_f}	exit conversion of reactant B
y_{B_0}	mole fraction of B in the feed
z	dimensionless axial position

Greek Symbols:

ΔH	heat of reaction (cal/mole of reactant B)
$\phi_a, \phi_r, \phi_f, \bar{\phi}_r, \bar{\phi}_f$	dimensionless groups, defined by Eqs. (6), (8), (7), (19) and (18)
θ	dimensionless temperature: T/T_0

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