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Error in Handling Finite Conversion Reactor Data by the Differential Method

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The error introduced by using the differential method to handle reaction rate data from reactors operated at finite conversion in order to establish the rate equation is considered. A general method of evaluating this error is developed and several of the more typical kinetic models are analyzed. The results show that even for reversible reactions and for kinetics of the Langmuir-Hinshelwood type with strong adsorption of reactants or products the differential method can be used up to rather large conversions, about 15% for most cases.

Although the results are developed for plug-flow tubular reactors, they can easily be extended to batch systems.

INTRODUCTION

Differential reactors are frequently preferred in carrying out kinetic studies in flow systems because the differential method of handling reaction rate data is more simple, direct, and sensitive than the integral method (*1*, *2*). Strictly speaking, no real reactor is differential since it must be operated at finite conversion, so, "differential reactors" are only an approach to the concept of differential reactor.

Not too much attention has been given to the problem of getting a criterion to establish whether a reactor can be considered as differential from a practical point of view. There are two limiting situations: operation at relatively large conversions impairs the concept of differential reactor and so increases the systematic error introduced when the differential method is used to analyze the reaction rate data. On the other hand, decreasing conversion to very small values usually increases the experimental error to undesirable values. Then the necessity arises of setting a suitable range of conversions to operate in the experimental work, and it can be done by determining the systematic error as a function of conversion and taking into account the effect of conversion on the experimental error of measured reaction rates for a given system.

The magnitude of that systematic error has been considered by Pauls (*3*) for the rate equation for the hydrogenation of ethylene

$$r = \frac{kp_Ap_B}{1 + K_Bp_B}$$

De Tar and Day (*4*) studied this error but for rate models of little use in chemical engineering.

In the present paper, a general method of evaluation of the systematic error is developed and applied to several of the more typical kinetic models in chemical engineering.

Considering that it is impossible to carry out a completely quantitative treatment including the numerous variables involved, some restrictions are assumed, as pointed out below. Among them, isothermal operation is by far the most severe one. Due to the exponential effect of temperature on reaction rate, in many cases thermal effects can be a more restrictive criterion than conversion level in determining the errors involved in differential reactor operation and much care should be taken with respect to this point.

However, the magnitude of temperature

gradients inside laboratory tubular reactors is not fixed by conversion level only, and very often it can be reduced to reasonable values by using a small reactor diameter and proper dilution of reactants in the feed. For the case of heterogeneous gas–solid catalytic reactions, temperature gradients can also be reduced by strong dilution of the catalyst with particles of an inert solid, in order to make smaller the heat generation per unit volume of bed.

The following development was made to help to choose on a rational basis the range of conversions to operate in a real differential reactor. Although the development has been made for plug flow tubular reactors, the results can be extended to batch systems.

NOMENCLATURE

a, b, s	Stoichiometric coefficients for A, B, and S
A	Limiting reactant
C_A, C_B, C_S	Concentration of A, B, and S (mole/cm³)
$C_{A_0}, C_{B_0}, C_{S_0}$	Initial concentration of A, B, and S (mole/cm³)
$\bar{C}_A, \bar{C}_B, \bar{C}_S$	Arithmetic average composition of A, B, and S (mole/cm³)
F	Total flow rate (cm³/sec)
k	Rate constant $[(\text{cm}^3)^{n-1}/\text{sec mole}^{n-1}]$
K_A, K_S	Adsorption constant for A and S (cm³/mole)
M	C_{B_0}/C_{A_0}
n	Reaction order
r	Reaction rate (mole/cm³ sec)
$\bar{r}$	Average reaction rate for the reactor (mole/cm³ sec)
$\dot{r}$	Reaction rate at $x = 0.5x_e$ (mole/cm³ sec)
(S.E.)	Systematic error defined by Eq. (3)
V_R	Reactor volume (cm³)
W	Mass of catalyst (g)
x	Conversion, defined for the limiting reactant A
x_e	Exit conversion for reactant A
$x‡$	Maximum or equilibrium conversion for reactant A
x'_e	Relative conversion, $= x_e/x‡$

THE EXPRESSION OF THE SYSTEMATIC ERROR

When the differential method is used to find the rate equation, it is usual to correlate the measured reaction rate data with the arithmetic average composition between entrance and exit of reactor instead of initial composition because conversions, although small, are finite. On this basis, an expression for the systematic error is developed. The assumptions made in this development are as follows:

(1) The reactor operates isothermally.

(2) Plug flow is ideal.

(3) Flow rate is constant along the reactor.

(4) Products of reaction are not present in the feed. This restriction is not necessary where product concentrations do not appear in the rate equation.

(5) Stoichiometry is

$$a\text{A} + b\text{B} = s\text{S} + \cdots .$$

Equation (1) is used to represent the true kinetic relation between reaction rate and composition

$$r = f(C_A, C_B, C_S, \ldots) \qquad (1)$$

This relationship holds at any point in the reactor and, since composition changes from point to point, r is not constant but varies to some extent along the reactor. Then, the measured value of reaction rate $\bar{r}$, is an average value for the whole reactor; $\bar{r}$ is written in terms of the exit conversion as follows.

$$\bar{r} = \frac{\text{Number of moles converted per unit time}}{\text{Reactor volume}} = \frac{FC_{A_0}x_e}{V_R} \qquad (2)$$

In general, the true kinetic relationship given by Eq. (1) does not hold strictly between the average reaction rate $\bar{r}$ and the arithmetic average composition, and then a systematic error is introduced when the differential method is applied to analyze data from reactors operated at finite conversion. The systematic error can be evaluated by comparison of the average reaction rate $\bar{r}$ with the true local reaction rate $\dot{r}$ at the point where composition is just the arithmetic average value, where $x = x_e/2$.

$$(\text{S.E.}) = \frac{\bar{r} - \dot{r}}{\dot{r}} = \frac{\bar{r}}{\dot{r}} - 1 \qquad (3)$$

To compute (S.E.) according to Eq. (3), $\dot{r}$ is taken from Eq. (1) for $x = x_e/2$, and $\bar{r}$ from Eq. (2) with the aid of the design equation for plug-flow tubular reactors [Eq. (4)].

$$\frac{V_R}{FC_{A_0}} = \int_0^{x_e} \frac{dx}{r} = \int_0^{x_e} \frac{dx}{f(C_A, C_B, C_S, \ldots)} \qquad (4)$$

Then Eq. (3) becomes

$$(\text{S.E.}) = x_e \bigg/ \left[f(\bar{C}_A, \bar{C}_B, \bar{C}_S, \ldots) \int_0^{x_e} \frac{dx}{f(C_A, C_B, C_S, \ldots)} \right] - 1 \qquad (5)$$

where

$$\begin{aligned} \bar{C}_A &= C_{A_0}(1 - 0.5x_e); & C_A &= C_{A_0}(1 - x) \\ \bar{C}_B &= C_{B_0} - 0.5\frac{b}{a}x_e; & C_B &= C_{B_0} - \frac{b}{a}C_{A_0}x \\ \bar{C}_S &= C_{S_0} + 0.5\frac{s}{a}x_e; & C_S &= C_{S_0} + \frac{s}{a}C_{A_0}x \end{aligned} \qquad (6)$$

ILLUSTRATIVE EXAMPLE: For a rate model of the type $r = k(C_A)^n$, Eq. (5) becomes

$$\begin{aligned} (\text{S.E.}) &= x_e \bigg/ \left\{ k[C_{A_0}(1 - 0.5x_e)]^n \int_0^{x_e} \frac{dx}{k[C_{A_0}(1 - x)]^n} \right\} - 1 \\ &= \frac{x_e}{(1 - 0.5x_e)^n \ln[1/(1 - x_e)]} - 1 \qquad \text{when } n = 1 \\ &= \frac{x_e(1 - n)}{(1 - 0.5x_e)^n[1 - (1 - x_e)^{1-n}]} - 1 \qquad \text{when } n \neq 1 \end{aligned} \qquad (7)$$

Equation (5) is valid also for batch or heterogeneous catalytic tubular reactors, since the design equations for these systems are like Eq. (4) provided that reaction time or (W/F) is used instead of (V_R/F).

RESULTS AND DISCUSSION

Table 1 [which includes Eqs. (8)–(14)] summarizes results similar to Eq. (7) for different types of kinetic models, which are plotted on Figs. 1 to 5. Figure 1 shows that for rate equation $r = k(C_A)^n$, the error remains below 1% up to conversions of 15% to 20% for $n \leq 2$. For the case of rate equation of the type $r = kC_AC_B$ the error is not a function of conversion only, but depends also on the ratio $M = C_{B_0}/C_{A_0}$. As shown in Fig. 2 (S.E.) ranges between two limiting curves corresponding to $M = \infty$ and $M = 1$, which coincide with that for $n = 1$ and $n = 2$ in Fig. 1.

First and second order reversible kinetics have been considered; for the first order one (S.E.) is equivalent to that for the first order irreversible case but x'_e (conversion relative to equilibrium) appears instead of x_e.

For the case of the second order reversible reaction (S.E.) does not depend on relative conversion only, but also on the equilibrium conversion, $x‡$, itself, as shown by Eq. (11), and ranges between two limiting functions: as $x‡ \to 1$, (S.E.) obviously approaches that for second order irreversible case. On the other hand, as $x‡ \to 0$, Eq. (11) becomes

$$\lim_{x \to 0} (\text{S.E.}) = \left\{ 2x'_e \bigg/ [1 - (0.5x'_e)^2] \ln \frac{1 + x'_e}{1 - x'_e} \right\} - 1 \qquad (15)$$

Figure 3 shows that even for this case relative conversion can be as high as 15% without substantial error.

Equations (12), (13), and (14) give (S.E.)

TABLE 1

THE SYSTEMATIC ERROR FOR DIFFERENT RATE MODELS

Rate model	Stoichiometry	Expression for the systematic error [isolution of Eq. (5)]	
$r = k(C_A)^n$	$A + \cdots \rightarrow$ prod.	for $n = 1$ $(\text{S.E.}) = \dfrac{x_e}{(1 - 0.5x_e)\ln[1/(1 - x_e)]} - 1$ for $n \neq 1$ $(\text{S.E.}) = \dfrac{x_e}{(1 - 0.5x_e)^n[1 - (1 - x_e)^{1-n}]} - 1$	(8)
$r = kC_AC_B$	$A + B \rightarrow$ prod.	$(\text{S.E.}) = \dfrac{x_e(M - 1)}{(1 - 0.5x_e)(M - 0.5x_e)\ln[(M - x_e)/M(1 - x_e)]} - 1$ where $M = C_{B0}/C_{A0}$	(9)
$r = kC_A - k'C_S$	$A + \cdots \rightarrow S + \cdots$	$(\text{S.E.}) = \dfrac{x'_e}{(1 - 0.5x'_e)\ln[1/(1 - x'_e)]} - 1$ where $x'_e = x_e/x\ddagger$	(10)
$r = k(C_A)^2 - k'C_SC_R$	$2A + \cdots \rightarrow S + R$	$(\text{S.E.}) = \dfrac{2(1 - x\ddagger)x'_e}{\left[\left(\dfrac{2x\ddagger - 1}{4}\right)x'^2_e - x\ddagger x'_e + 1\right]\ln\dfrac{(2x\ddagger - 1)x'_e - 1}{x'_e - 1}} - 1$	(11)
$r = \dfrac{kC_A}{1 + K_AC_A}$	$A + \cdots \xrightarrow{\text{cat.}}$ prod.	$(\text{S.E.}) = \dfrac{[1 + (K_AC_{A0})(1 - 0.5x_e)]x_e}{(1 - 0.5x_e)\left[\ln\dfrac{1}{1 - x_e} + (K_AC_{A0})x_e\right]} - 1$	(12)
$r = \dfrac{kC_A}{1 + K_SC_S}$	$A + \cdots \xrightarrow{\text{cat.}} S + \cdots$	$(\text{S.E.}) = \dfrac{[1 + (K_SC_{A0})(0.5x_e)]x_e}{(1 - 0.5x_e)\left[\ln\dfrac{1}{1 - x_e} + (K_SC_{A0})\left(\ln\dfrac{1}{1 - x_e} - x_e\right)\right]} - 1$	(13)
$r = \dfrac{kC_A}{1 + K_AC_A + K_SC_S}$	$A + \cdots \xrightarrow{\text{cat.}} S + \cdots$	$(\text{S.E.}) = \dfrac{[1 + (K_AC_{A0})(1 - 0.5x_e) + (K_SC_{A0})(0.5x_e)]x_e}{(1 - 0.5x_e)\left[(1 + K_SC_{A0})\ln\dfrac{1}{1 - x_e} + (K_AC_{A0} - K_SC_{A0})x_e\right]} - 1$	(14)

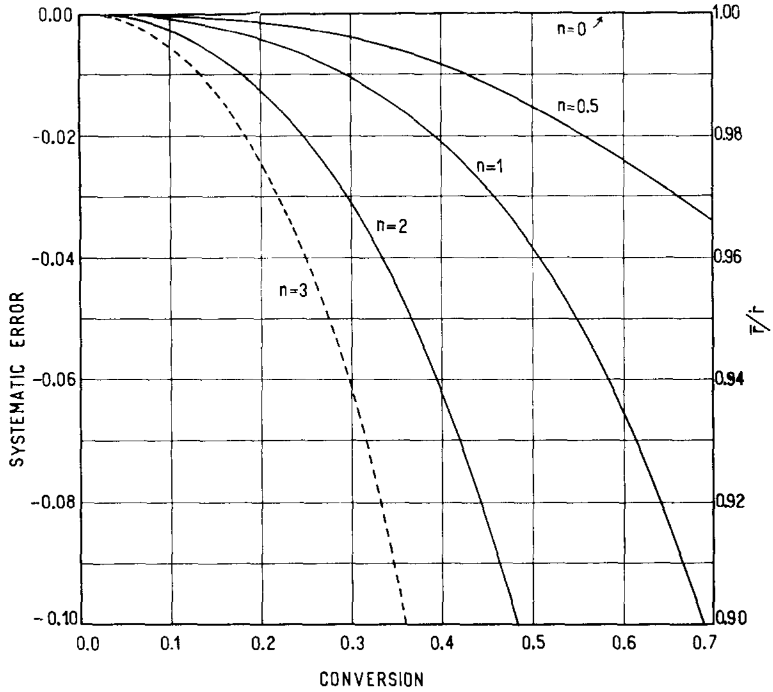

FIG. 1. Systematic error versus exit conversion for rate model: $r = k(C_A)^n$.

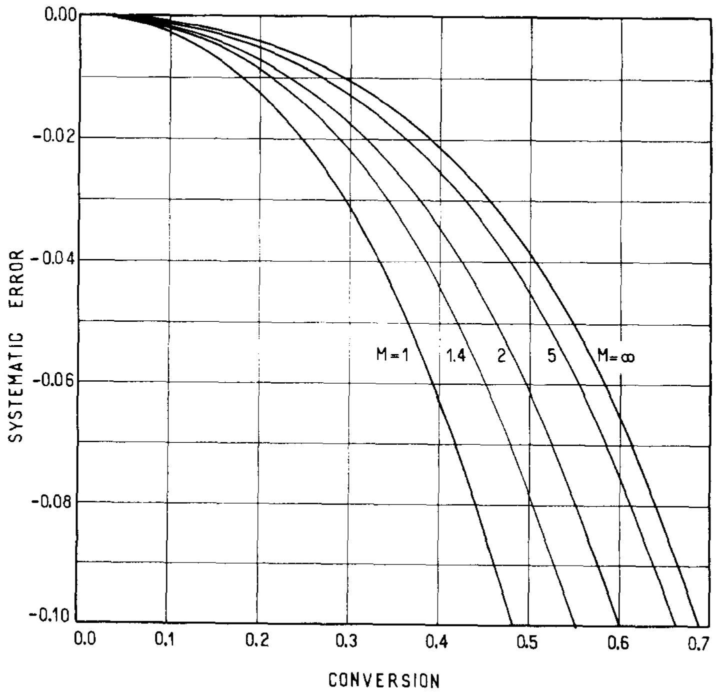

FIG. 2. Systematic error versus exit conversion for rate model: $r = kC_AC_B$.

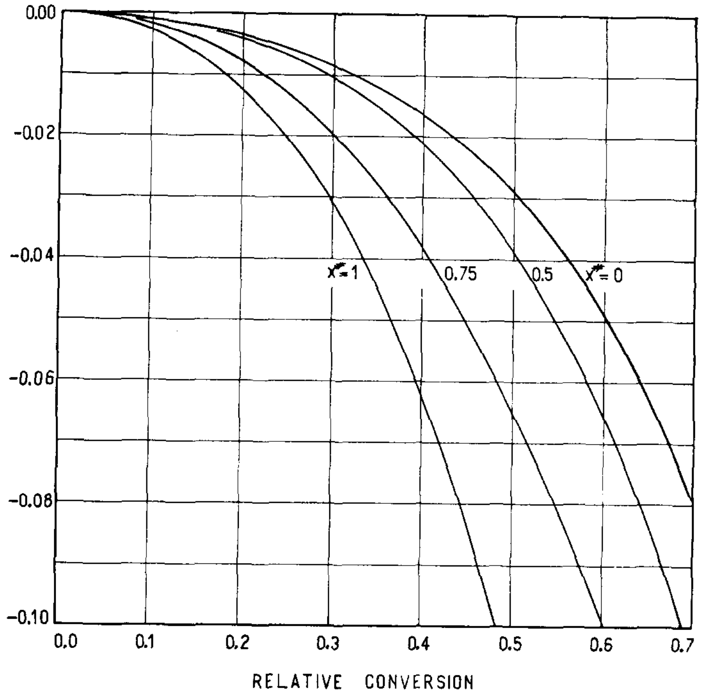

FIG. 3. Systematic error versus exit conversion for rate model: $r = k(C_A)^2 - k'C_RC_S$ ($C_{R_0} = C_{S_0} = 0$).

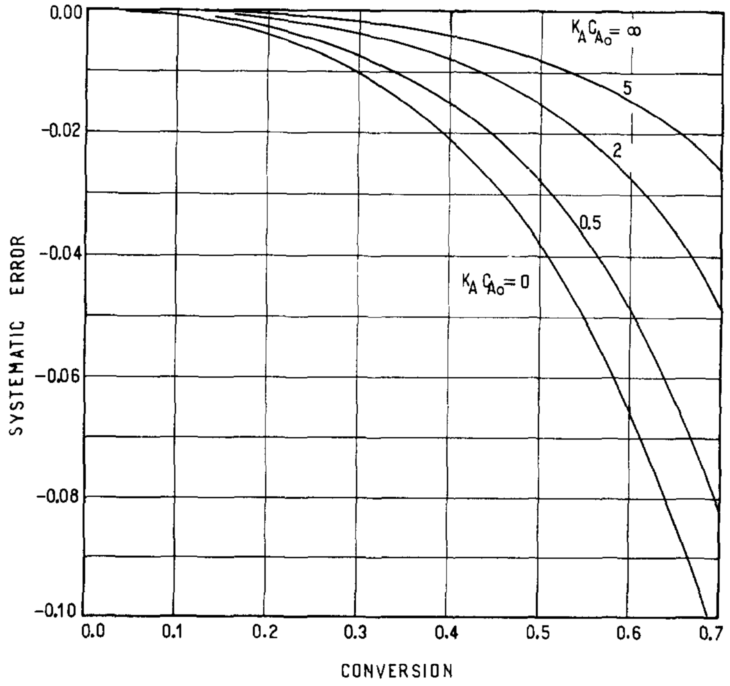

FIG. 4. Systematic error versus exit conversion for rate model: $r = kC_A/(1+K_AC_A)$.

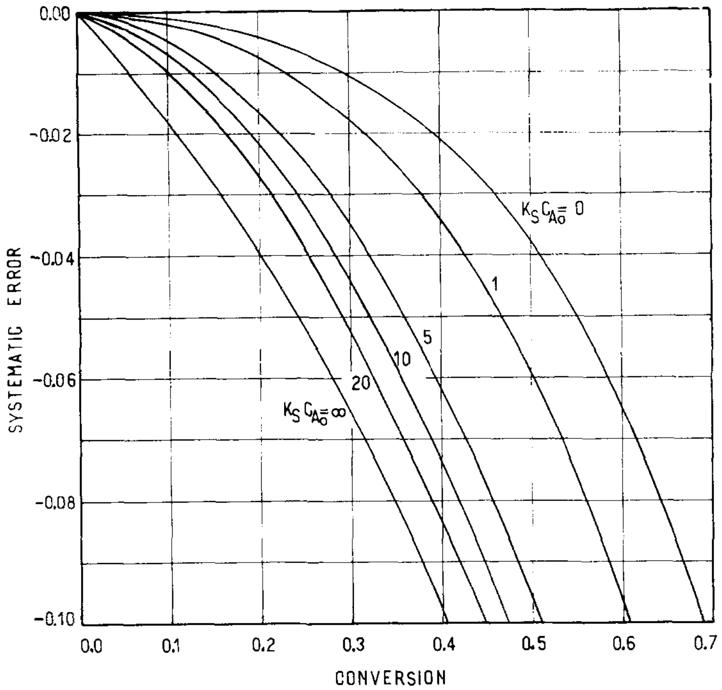

FIG. 5. Systematic error versus exit conversion for rate model: $r = kC_A/(1+K_S C_S)$ $(C_{S_0} = 0)$.

for several of the simplest and more representative models of the Langmuir Hinshelwood type. Figure 4 shows that for $r = kC_A/(1+K_A C_A)$, (S.E.) ranges between that corresponding to first and zero order homogeneous irreversible kinetics as the parameter $(K_A C_{A_0})$ varies from zero to infinity. Equation (13) corresponds to a case with adsorption of one of the reaction products and is plotted on Fig. 5. For this case (S.E.) approaches that of first order kinetics as $(K_S C_{A_0})$ tends to zero, and when this parameter becomes very large, Eq. (13) tends to the following limiting function:

$$\lim_{(K_S C_{A_0}) \to \infty} \text{(S.E.)} = \left\{ x_e^2 \Big/ 2(1 - 0.5x_e) \left[\ln \frac{1}{1 - x_e} - x_e \right] \right\} - 1 \quad (16)$$

As shown by Fig. 5 even for this limiting case (S.E.) remains rather small up to conversions of 5% to 7%, no matter how large $(K_S C_{A_0})$ becomes. This is a striking result because in this case, the large variation of reaction rate even for very low conversions would suggest that the differential method is only applicable if the exit conversion is nearly zero, and the permissible range of 5% to 7% was not to be expected. Hence, the magnitude of the relative variation of reaction rate is not a criterion to decide whether or not the differential method can be applied.

Equation (14) gives the expression of (S.E.) for the simplest case of simultaneous adsorption of a reactant and a reaction product. As this is a combination of the two cases considered previously, it can be shown that (S.E.) ranges between that for zero order rate equation and the limiting function given by Eq. (16) as the parameters $(K_A C_{A_0})$ and $(K_S C_{A_0})$ vary from zero to infinity.

It may be concluded that the differential method can be used to establish the rate equation even for rather large conversions, without introducing serious error. This fact modifies substantially the general criterion about differential reactors.

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