

Appendix

KINETIC ANALYSIS OF CATALYST DEACTIVATION  
BY IRREVERSIBLE SURFACE POISONING\*

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ABSTRACT

A theoretical model of catalyst deactivation by a first order heterogeneous reaction is presented for a kinetically controlled configuration. The deactivation rate is shown to be a function of the first Damkohler similarity parameter and the ratio of initial adsorption site density to poison concentration in the feed stream. The model provides explicit functions for interpretation of experimental observations in terms of kinetic parameters of catalyst deactivation and reactant conversion.

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## INTRODUCTION

The loss in catalyst activity and/or selectivity caused by surface adsorbed feed-stream impurities and reaction intermediates is an important aspect of chemical reactor design. It requires detailed information on the kinetics of catalyst performance with and without surface poisoning, parameters that are difficult to evaluate experimentally in the presence of diffusional mass transport to the surface and into the pores of the catalyst.

In the classical analysis of Wheeler<sup>1,2</sup> the poisoning of a porous catalyst pellet was considered in terms of two theoretical models: one, called "pore-mouth poisoning," in which the impurity adspecies deposition progresses from the entrance to the interior of the catalyst pore; the other, referred to as "homogeneous poisoning," in which a uniform distribution of impurity adspecies throughout the internal surface of the catalyst pore prevails. Various aspects of the diffusional transport of catalyst poison and its penetration into porous media of different geometric configurations have been considered.<sup>2-6</sup> Such analyses utilize the concept of the "effectiveness factor." The effectiveness factor is dependent on the boundary layer flow, the catalyst geometry, and the Thiele modulus, a nondimensional material parameter incorporating the ratio of reaction time to pore diffusion time.

To carry out experimental measurements of the intrinsic rate of catalyst deactivation it is convenient to select operating conditions which are not subject to diffusional limitations. Internal diffusion is negligible at low values of the Thiele modulus,<sup>1,3</sup> external diffusion to the catalyst surface is negligible at high Reynolds numbers. Criteria

for the neglect of diffusion in the bulk flow are presented in the Appendix.

In the following analysis we examine the change in the activity of a powdered, nonporous catalyst caused by progressive occupation of active surface sites with irreversibly bound adspecies in the absence of diffusional limitations. This model defines the experimental approach needed for the evaluation of the intrinsic rate constant of catalyst poisoning.

## II THEORETICAL DEVELOPMENT

Our model considers the passage of a gas mixture containing reactants and contaminants through a catalyst bed made up of nonporous catalyst particles so that all surface sites are in contact with the gas stream. The catalyst bed lies between two cross sections of a tube that holds the flowing gas. The average gas flow is nearly uniform at velocity  $V$  (or space velocity  $U = V/L$ , where  $L$  is the bed depth) so that variables, such as the local concentration  $n$  of contaminant species, are uniform over each cross section and functions only of the distance  $x$  into the bed and the time  $t$ . The rate of catalyst deactivation by the contaminant in the feed stream is taken to be of first order in  $n$  and the number density  $s$  of active sites. The differential equation for convective transport of the contaminant species through the catalyst reads:

$$-\left(\frac{\partial n}{\partial t} + V\frac{\partial n}{\partial x}\right) = kn s \quad (1)$$

where  $k$  is the rate constant for catalyst deactivation. The conditions under which diffusion can be neglected are examined in Appendix B.

The poisoning process is considered to involve a gaseous contaminant species that is irreversibly adsorbed so that the site density is reduced at the rate:

$$\frac{\partial s}{\partial t} = -kns \quad (2)$$

Although the differential system is nonlinear, a general solution can be obtained by changing to the characteristic independent variables

$$\sigma = x/V \text{ and } \tau = t - (x/V).$$

Equations (1) and (2) become:

$$\frac{\partial s}{\partial x} = \frac{\partial s}{\partial \sigma} = -kns \quad (3)$$

The parameter  $\sigma$  is constant at each site, and  $\tau$  is constant on each infinitesimal volume of gas as it moves through the bed. The first equality shows that there is a single function whose partial derivatives are  $n$  and  $s$ . By taking the function to be  $(1/k) \ln \varphi$  one obtains:

$$n = \frac{1}{k} \frac{\partial \ln \varphi}{\partial \tau} = \frac{1}{k\varphi} \frac{\partial \varphi}{\partial \tau} \quad (4)$$

$$s = \frac{1}{k} \frac{\partial \ln \varphi}{\partial \sigma} = \frac{1}{k\varphi} \frac{\partial \varphi}{\partial \sigma}$$

The second equality in Equation (3) becomes

$$\frac{\partial^2 \varphi}{\partial \sigma \partial \tau} = 0$$

which has the general solution

$$\varphi = P(\sigma) + Q(\tau)$$

where  $P$  and  $Q$  are arbitrary functions of their arguments. By equation (4)

$$n = \frac{1}{k} \frac{Q'}{P + Q} ; \quad s = \frac{1}{k} \frac{P'}{P + Q} \quad (5)$$

where the prime denotes the derivative.

Functions  $P$  and  $Q$  are determined by the auxiliary conditions:

$$s = s_0 \text{ at } \tau = 0$$

$$n = n_1 \text{ at } x = 0 \text{ or } \sigma = 0$$

where  $s_0$  and  $n_1$  are constants. By integration one obtains:

$$P(\sigma) = [P(o) + Q(o)] e^{ks_0\sigma} - Q(o)$$

$$Q(\tau) = [P(o) + Q(o)] e^{kn_1\tau} - P(o)$$

so that by equation (5)

$$n = n_1 \theta / (\theta + \xi - 1) \quad (6a)$$

$$s = s_0 \xi / (\theta + \xi - 1) \quad (6b)$$

where

$$\theta = e^{kn_1\tau} = e^{kn_1 \left( t - \frac{x}{V} \right)}$$

and

$$\xi = e^{ks_0\sigma} = e^{ks_0 x/V}.$$

Since the catalyst sites progressively occupied by the poison are no longer participating in the conversion of reactant in the feed gas, the poisoning of the catalyst will be reflected in the change in catalytic conversion of reactant. For a first-order rate  $R$  of conversion of reactant present at concentration  $r$  one obtains :

$$R = - \left( \frac{\partial r}{\partial t} + V \frac{\partial r}{\partial x} \right) = k_c r s \quad (7)$$

where  $k_c$  is the first order rate constant. By introduction of the expression for the site density  $s$ , Equation (6b), and integration one finds

$$\frac{r}{r_i} = [\theta/(\theta + \xi - 1)]^{k_c/k}$$

where  $r_i$  is the reactant concentration at the catalyst bed inlet. It follows from Equation (6a) that

$$r/r_i = (n/n_i)^{k_c/k} \quad (8)$$

so that results of the following analysis and computations of the variations in poison concentration have immediate applicability to variations in reactant concentration through the catalyst bed.

The local rate of product formation is given by:

$$P_\tau = A \int_0^L \gamma R dx$$

where A represents the cross-sectional area of the catalyst bed, R the rate of reactant conversion (Equation 7), and  $\gamma$  the stoichiometric coefficient. By change of variables one obtains

$$P_\tau = (\kappa r_i A \gamma / s_o) \int_1^{\xi_L} \theta^K (\theta + \xi - 1)^{-(\kappa + 1)} d\xi$$

with  $\kappa$  defined by  $\kappa = k_c/k$  and subscript L denoting values at  $x = L$ . The integration can be carried through to give

$$P_\tau = (r_i A \gamma / s_o) \{1 - [\theta_L / (\theta_L + \xi_L - 1)]^{\kappa + 1}\}$$

Since  $\theta_L = 1$  when  $\tau = 0$ , the ratio  $\rho = P_\tau / P_o$  takes the form:

$$\rho = \{1 - [\theta_L / (\theta_L + \xi_L - 1)]^{\kappa + 1}\} / (1 - \xi_L^{-\kappa}) \quad (9)$$

which on differentiation yields:

$$\frac{d\rho}{d\theta_L} = -K (\xi_L - 1) \theta_L^{K-1} (\theta_L + \xi_L - 1)^{-K-1} / (1 - \xi_L^{-K}) \quad (10)$$

$$\frac{d^2\rho}{d\theta_L^2} = K(\xi_L - 1) \theta_L^{K-2} [2\theta_L - (K-1)(\xi_L - 1)] (\theta_L + \xi_L - 1)^{-K-2} / (1 - \xi_L^{-K}).$$

It is apparent that  $\rho$  decreases with  $\theta$  as poisoning of the catalyst bed progresses. The second derivative indicates that the rate of decrease of  $\rho$  is greatest at the start, when  $\tau = 0$  and  $\theta_L = 1$ , if  $(K-1)(\xi_L - 1) \leq 2$ . Otherwise the maximum decrease in the rate occurs at a later time.



## DISCUSSION

The analysis suggests the experimental data that are required to deduct kinetic parameters for catalyst deactivation by surface poisoning in the absence of diffusional limitations. Specifically, the rate constant for the deposition of impurity adspecies may be evaluated from the progressive penetration of the contaminant through the catalyst bed as manifested by its buildup in concentration in the exit gas. At the same time, the progressive decrease in the rate of product formation as monitored in the exit gas stream allows calculation of the rate constant for chemical conversion of reactant. In the present analysis the poisoned sites have been taken to be identical to those needed for catalytic activity.

For reduction of experimental data on the exit stream it is convenient to write Equation 6a in the following form:

$$\ln[(n_1/n_L) - 1] = \ln(\xi_L - 1) - kn_1[t - (L/V)] \quad (11)$$

where the subscript L denotes values at  $x = L$ . Thus, from experimental measurements of the concentration of gaseous poison at the inlet and outlet of the catalyst bed, the poisoning rate constant  $k$  can be evaluated by graphical means from a plot of the quantity  $\ln[(n_1/n_L) - 1]$  versus the time parameter  $[t - (L/V)]$  (Figure 1). The latter parameter represents the difference between the total exposure time and the reciprocal space velocity. The slope of the resulting line yields the rate constant  $k$  for a given level of gaseous poison in the feed stream. The density of adsorption sites for the poison  $s_0$  can be obtained from the intercept, which by the definition of  $\xi$  is given by

$$\ln(\xi_L - 1) = \ln[\exp(ks_o/U) - 1] .$$

To identify the governing parameters one may rewrite Equation (11) as

$$\ln[(n_1/n_L) - 1] = \ln(\exp D_1 - 1) - (D_1/\beta)(Ut - 1) , \quad (12)$$

$$D_1 = ks_o/U , \quad \beta = s_o/n_1$$

Thus the solution for the inlet-to-exit concentration ratio of catalyst poison is a function of the dimensionless time  $Ut$  and parameters  $D_1$  and  $\beta$ . Parameter  $\beta$  is the ratio of site density to gas-phase poison concentration, whereas  $D_1$  is the first similarity parameter of Dankohler, the ratio of reaction time to contact time. Typical parameter values of practical interest are given in Table 1 and the solution lines are presented in a semilogarithmic dimensionless plot in Figure 1.

A striking feature of the time history of the poison concentration in the exit stream is the point of inflexion exhibited by the curves in a linear plot in Figure 2. This point is identified as the time of "breakthrough." One may show by differentiating Equation (12) that breakthrough occurs when the concentration of poison in the exit stream is just half that in the feed. This exposure time is denoted by  $t_{1/2}$  and computed for typical parameters in Table 1. From Equation (12) with  $n_L = n_1/2$ ,

$$Ut_{1/2} = 1 + (\beta/D_1) \ln(\exp D_1 - 1) . \quad (13)$$

Since the expression on the right can be shown to be an increasing function of  $D_1$  and  $\beta$ , breakthrough at a given space velocity is delayed

if either  $\beta$  or  $D_1$  is increased. This type of response may be achieved by increasing the reaction rate constant for poisoning or the site density, or by decreasing the concentration of poison species in the feed stream. A reduction in space velocity  $U$  delays the breakthrough both by its explicit effect in Equation (13) and by its implicit effect on  $D_1$ .

For the cases examined in Figure 2, the values of  $Ut_{1/2}$  are orders of magnitude greater than 1. For these conditions the breakthrough time becomes proportional to  $\beta$  and therefore inversely proportional to  $n_1$ , as found to be the case (Table 1).

The curves of Figure 1 or 2 with all parameters the same except for different values of  $k$  are seen to cross. Such crossovers are typical for the system under study. Thus, for example, an increase in  $D_1$  will delay breakthrough, but it will increase the amount of early catalyst poisoning.

The poison concentration as a function of position in the catalyst bed at fixed times can also be evaluated by means of Equation (6a). A dimensionless semilogarithmic plot of the local poison concentration relative to that in feed stream as a function of catalyst bed depth is shown in Figure 3. From the linear plot (Figure 4) one notes that at early times the gradient of the poison concentration through the catalyst bed is large near the entrance and decreases steadily as the exit is approached. At later times the gradient goes through a maximum at some intermediate location in the catalyst bed. One may show, using the formulas for  $n_x^-$  and  $n_{xx}$  given in the Appendix, that the two types of variation are separated by the curve for  $t = t^*$  where  $t^*$  is given by

$$t^* = (1/kn_1) \ln[2\beta/(\beta + 2)]$$

For  $t < t^*$  the gradient decreases through the bed. For  $t > t^*$  the gradient increases to a maximum some distance into the bed and then decreases. If  $t$  is sufficiently greater than  $t^*$ , the maximum poison concentration gradient lies outside the bed.

The rather complex formula for the change in product-formation rate (Equation 9) can be simplified when  $U \gg ks_0$ . Under these conditions  $\xi_L \doteq 1 + ks_0/U$  and Equation (9) reduces to

$$\rho = \theta_L^{-1} = \exp[-kn_1 t(1 - 1/Ut)] .$$

Thus for  $Ut \gg 1$ ,  $\ln \rho$  is a linear function of  $t$  with slope  $-kn_1$  and intercept zero. This function offers a convenient approach to the empirical evaluation of the poisoning rate constant  $k$ .

#### REFERENCES

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Appendix

THE NEGLECT OF DIFFUSION

If diffusive transport is included, the mass balance for poison concentration  $n$  reads:

$$\frac{\partial n}{\partial t} + v \frac{\partial n}{\partial x} - D \frac{\partial^2 n}{\partial x^2} = -kns$$

rather than Equation (1). The neglect of diffusion is justified if the ratio  $Q$  of the diffusive term to the convective one is small:

$$Q = D \frac{\partial^2 n}{\partial x^2} / v \frac{\partial n}{\partial x}$$

By Equation (6a)

$$\frac{\partial n}{\partial x} = n_1 \frac{kn_1}{v} \theta \frac{1 - (\beta + 1)\xi}{(\theta + \xi - 1)^2}$$

$$\frac{\partial^2 n}{\partial x^2} = n_1 \left( \frac{kn_1}{v} \right)^2 \theta \frac{1 + \theta + (\beta^2 - 2\beta - 2)\xi + (\beta + 1)^2 \xi(\xi - \theta)}{(\theta + \xi - 1)^3}$$

so that

$$Q = (D kn_1 / v^2) [Q_1 - Q_2 - Q_3]$$

$$Q_1 = \beta + 1$$

$$Q_2 = \frac{\beta}{(\beta + 1) \xi - 1}$$

$$Q_3 = 2(\beta + 1) / \left[ 1 + \frac{(\beta + 1)\xi - 1}{(\beta + 1)\theta - \beta} \right]$$

Bounds on the factor of  $Q$  in the brackets are needed. Since  $\beta > 0$ ,  $\xi \geq 1$ , and  $\theta \geq 1$ , one finds that

$$0 < Q_2 < 1$$

$$0 < Q_3 < 2(\beta + 1)$$

so that

$$-(\beta + 2) < Q_1 - Q_2 - Q_3 < \beta + 1$$

Hence  $Q$  is small and diffusion is properly neglected if

$$|Q| < Q^*$$

where  $Q^*$  is defined as

$$Q^* = (D k n_1 / V^2) (\beta + 2)$$


It is noteworthy that  $Q^*$  may be written as the product:

$$Q^* = (m/Re)^2 (\beta + 2)$$

$$m = L(k n_1 / D)^{1/2}$$

$$Re = LV/D$$

where  $m$  is a Thiele modulus that measures the relative importance of reaction and diffusion,  $Re$  is the Reynolds number that compares diffusive to convective flow, and  $(\beta + 2)$  is a nondimensional measure of the capacity of the catalyst for retention of poison adsorbate. In accordance



with these dimensionless parameters, diffusional limitations vanish at low Thiele modulus, high Reynolds number, and a large density ratio of surface sites to poison molecules.



Table 1

LIST OF PARAMETERS AND DERIVED QUANTITIES FOR  
CATALYST POISONING

U (min <sup>-1</sup> )	k (min <sup>-1</sup> ppm <sup>-1</sup> )	n <sub>1</sub> (ppm)	D <sub>1</sub> <sup>*</sup>	β × 10 <sup>-5</sup>	t <sub>1/2</sub> × 10 <sup>-2</sup> (min)
10 <sup>3</sup>	10 <sup>-2</sup>	1	10	10	10
		2		5	5
		5		2	2
		10		1	1
	5 × 10 <sup>-3</sup>	1	5	10	10
		2		5	5
		5		2	2
		10		1	1
2 × 10 <sup>3</sup>	10 <sup>-2</sup>	1	5	10	5
		2		5	2.5
		5		2	1
		10		1	0.5

\* D<sub>1</sub> = k s<sub>0</sub>/U, β = s<sub>0</sub>/n<sub>1</sub> with s<sub>0</sub> = 10<sup>6</sup> ppm = 10<sup>19</sup> sites/cm<sup>3</sup>.

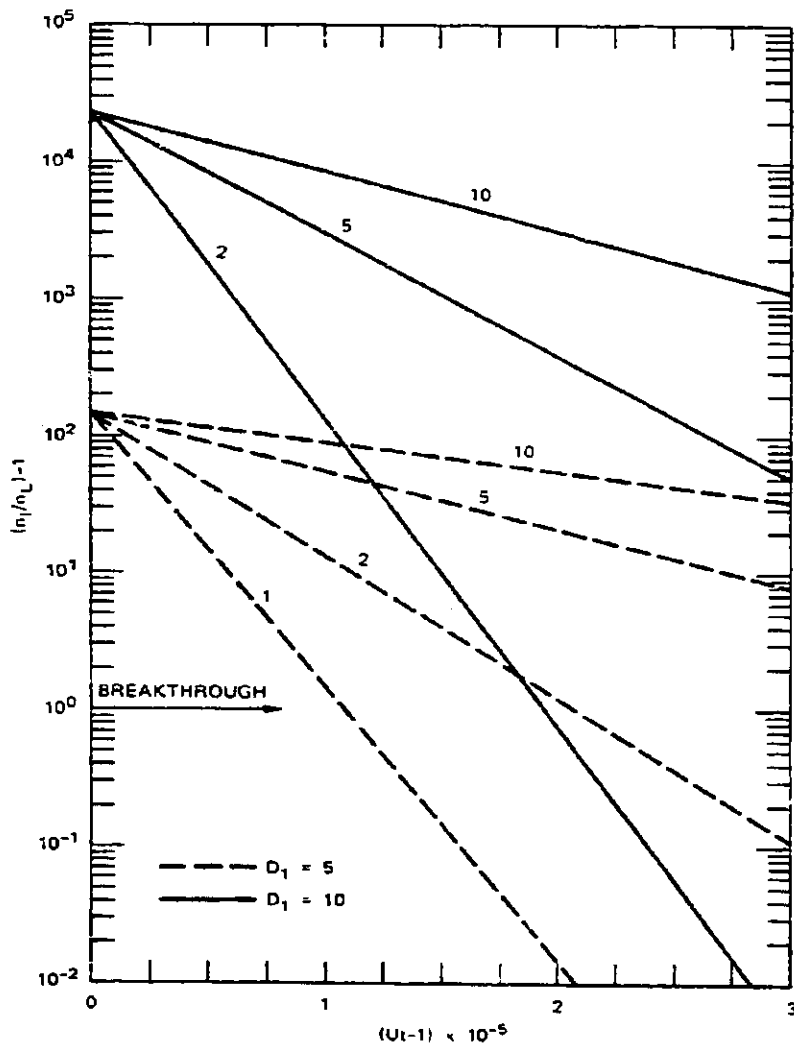
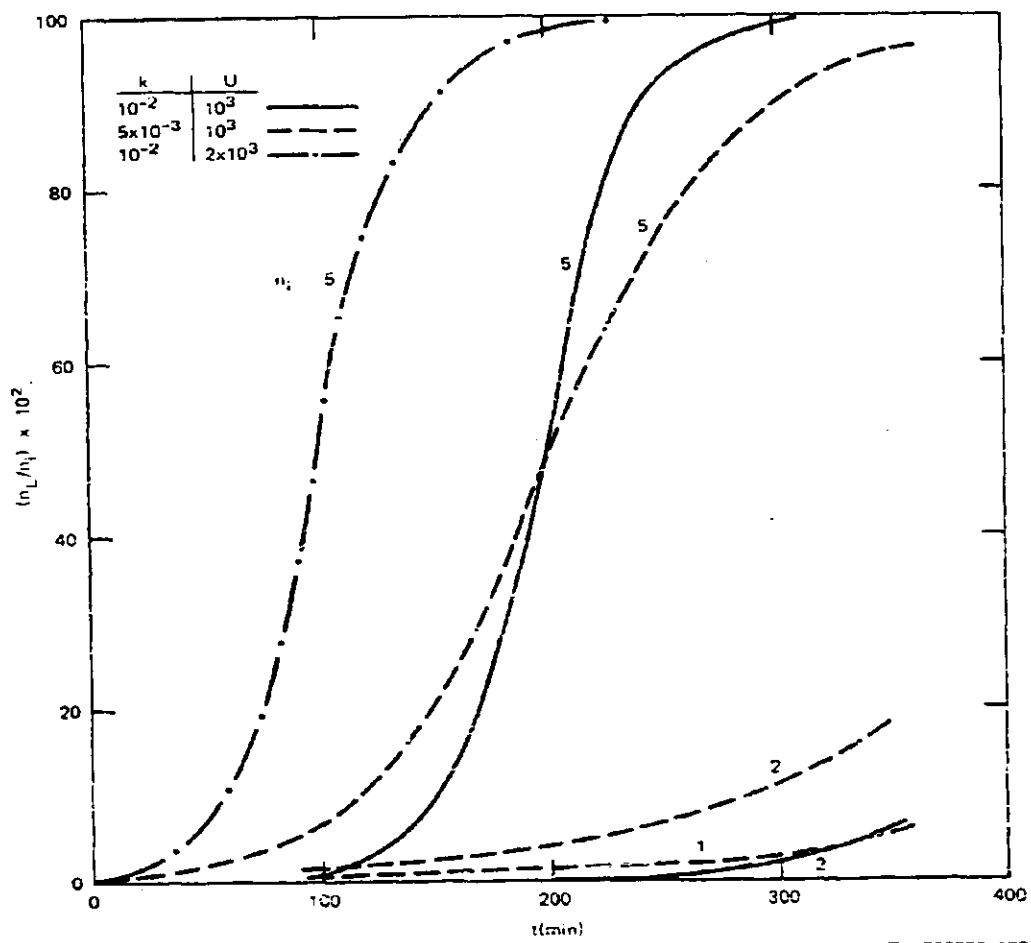
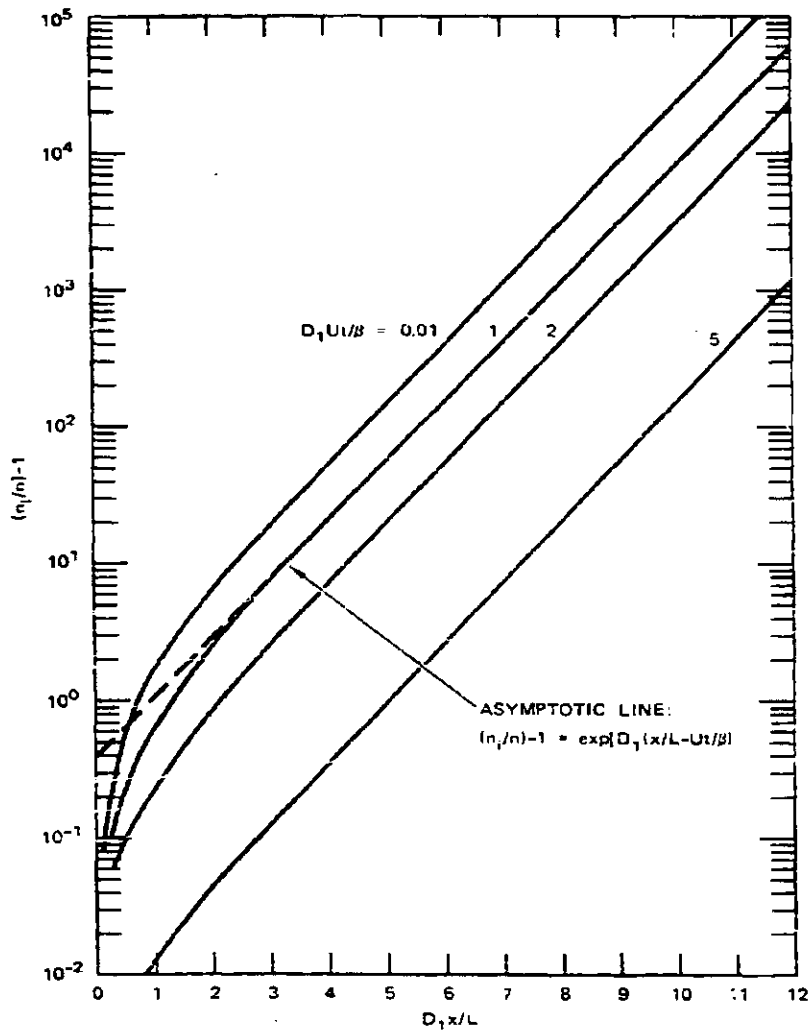


FIGURE 1 DIMENSIONLESS ANALYSIS OF POISON UPTAKE BY CATALYST SURFACE  
 (The numbers on the curves are values of  $\beta \times 10^{-5}$ )



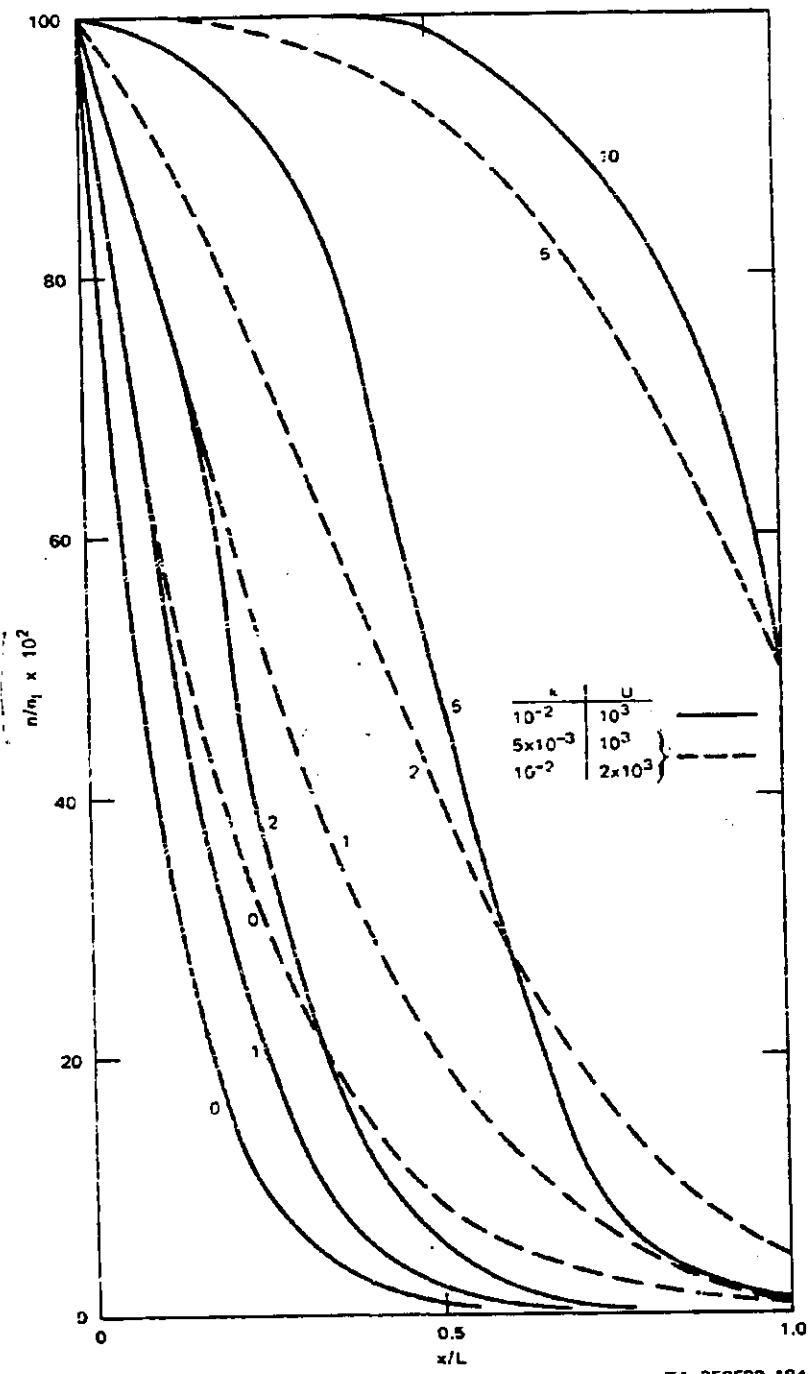
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FIGURE 2 TIME VARIATION OF POISON IN EXIT GAS AT VARIOUS INLET CONCENTRATIONS, SPACE VELOCITIES AND POISONING RATES



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FIGURE 3 DIMENSIONLESS ANALYSIS OF POISON DISTRIBUTION IN CATALYST BED (NUMBERS ON CURVES REFER TO VALUES OF  $(D_1/b) [Ut - (x/L)]$ ; CURVES ARE ASYMPTOTIC TO  $(n_1/n) - 1 = \exp\{D_1 [(x/L) - (Ut/b)]\}$ )



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FIGURE 4 POISSON DISTRIBUTION IN CATALYST BED  
 (The numbers on the curves are values of  $kn_0[t - (x/LU)]$ .)