atoms is relatively hindered due to steric reasons. One would expect that O_2 develops a rounded pit in the early stage which leads to a circular pit. When tungsten carbide is present on the surface, 0 atoms are expected to be present near the surface because tungsten carbide is effective in dissociating O_2. It might involve an oxygen spillover process similar to the hydrogen spillover phenomenon (Levy and Boudart, 1974). With 0 atoms the steric factor should not be important and indeed hexagonal pits are formed by 0 atoms from the gas phase (Wong et al., 1983). A spillover mechanism was earlier proposed for chromia catalyzed carbon oxidation (McKee, 1970; Baker, 1981). A further for the tungsten being in the form of tungsten carbide is that any metallic tungsten would have been oxidized, at least on the surface layers, under our conditions, and tungsten oxide behaves very differently in its catalytic activity. Our results on WO_3 catalyzed carbon oxidation will be reported shortly.

The orientation of the hexagonal etch pits has been determined by in situ electron diffraction using TEM. All sides of the pits are in the $\langle 1,0\bar{1}0 \rangle$ direction i.e., they are zigzag surfaces, which is the orientation shown in Figure 4, as well as the orientation of the hexagonal pits etched by 0 atoms (Wong et al., 1983). Deep pits created by catalyst particles are mostly circular, but in a few cases hexagonal, e.g., by Fe_2O_3 (Thomas, 1965; McKee, 1970). The mechanism proposed here may also be operative in deep pits formation.

LITERATURE CITED

Baker, R. T. K., "In Situ Electron Microscopy Studies of Catalyst Particle Behavior," *Catal. Rev.*, **19**(2), 161 (1979).

Baker, R. T. K., and J. J. Chludzinski, "Catalytic Gasification of Graphite by Chromium and Copper in O_2, H_2O and H_2," *Carbon*, **19**, 75 (1981).

Dawson, I. M., and E. A. C. Follett, "The Oxidation of Graphite," *Proc. Roy. Soc.*, London, **A274**, 386 (1963).

Essenhigh, R. H., "Fundamentals of Coal Combustion," *Chemistry of Coal Utilization*, M. A. Elliott, ed., Wiley, New York, Chap. 19 (1981).

Feates, F. S., "Radiolytic Oxidation of Single Crystals of Graphite by O_2, CO_2 and CH_4-CO_2 Mixtures," *Trans. Faraday Soc.*, **64**, 3093 (1968).

Hennig, G. R., "Electron Microscopy of Reactivity Changes Near Lattice Defects in Graphite," *Chem. and Phys. of Carbon*, P. L. Walker, Jr., ed., Arnold, Leeds, England, **2**, 1 (1966).

Johnson, J. L., "Fundamentals of Coal Gasification," *Chemistry of Coal Utilization*, M. A. Elliott, ed., Wiley, New York, Chapter 23 (1981).

Levy, R. B., and M. Boudart, "The Kinetics and Mechanism of Spillover," *J. Catal.*, **32**, 304 (1974).

McKee, D. W., "Metal Oxides as Catalysts for the Oxidation of Graphite," *Carbon*, **8**, 623 (1970).

Montet, G. L., and G. E. Myers, "Electron Microscopy Investigation of the Reaction of Water Vapor with Graphite," *Carbon*, **6**, 627 (1968).

Thomas, J. M., "Microscopic Studies of Graphite Oxidation," *Chem. and Phys. of Carbon*, P. L. Walker, Jr., ed., Arnold, Leeds, England, **1**, Chapt. 3 (1965).

Thomas, J. M., "Reactivity of Carbon: Some Current Problems and Trends," *Carbon*, **8**, 413 (1970).

Toth, L. E., *Transition Metal Carbides and Nitrides*, Academic Press, New York (1971).

Tu, C. M., H. Davis, and H. C. Hottel, "Combustion Rate of Carbon: Combustion of Spheres in Flow Gas Streams," *Ind. Eng. Chem.*, **26**, 749 (1934).

Walker, Jr., P. L., F. Rusinko, Jr., and L. G. Austin, "Gas Reactions of Carbon," *Adv. in Catalysis*, **11**, 133 (1959).

Yang, R. T., and M. Steinberg, "Kinetics of C-CO_2 Reaction at High Temperatures," *Ind. Eng. Chem. Fundam.*, **16**, 235 (1977).

Wong, C., R. T. Yang, and B. L. Halpern, "The Mode of Attack of Oxygen Atoms on the Basal Plane of Graphite," *J. Chem. Phys.* (March, 1983).

Yang, R. T., and C. Wong, "The Role of Surface Diffusion in the Langmuir-Hinshelwood Mechanism," *Chem. Eng. Commun.*, **11**, 317 (1981a).

Yang, R. T., and C. Wong, "Mechanism of Single-Layer Graphite Oxidation," *Science*, **214**, 437 (1981b).

Yang, R. T., and C. Wong, "Kinetics and Mechanism of Oxidation of Basal Plane on Graphite," *J. Chem. Phys.*, **75**, 4471 (1981c).

Manuscript received December 3, 1981; revision received March 2, and accepted March 17, 1982

Approximate Global Rates: Reactions Affected by Diffusion and Chemical Deactivation

HONG H. LEE

Department of Chemical Engineering
University of Florida
Gainesville, FL 32611

INTRODUCTION

Global rates have been obtained for reactions affected by both diffusion and chemical deactivation (Lee and Butt, 1982a). These global rates were used to simplify the design of heterogeneous reactions. These results, however, were restricted to the limiting cases of uniform and shell-progressive deactivation. In this paper, we remove this restriction and obtain global rates for a general case of deactivation.

When a pellet of uniform catalytic activity is deactivated, the outer surface loses the activity more rapidly than the inner part due to its direct exposure to poisoning species, resulting in a nonuniform pellet with its activity increasing monotonically toward pellet center. For such a pellet, the flux at the outer surface can be accurately approximated (Lee, 1981a) by:

$$-D_e \frac{dc}{dx}\bigg|_{\text{surface}} \equiv D_e\bar{P} \simeq \left[2\bar{f}D_e \int_{C_c}^{C_b} r_c(C)dC\right]^{1/2} \qquad (1)$$

provided that a certain condition is met. Here the function representing the activity distribution resulting from deactivation is denoted by f and the overbar denotes evaluation at the pellet surface. The bulk-fluid and pellet center concentrations are denoted by C_b and C_c, respectively. For the diffusion-limited reactions being considered, the pellet center concentration can be set at zero.

Assumptions made in writing Eq. 1 are that the external mass transfer resistance is negligible and that the pellet is isothermal. The effective diffusivity D_e is assumed constant. The restriction placed on Eq. 1 is that the following condition be met (Lee, 1981a):

$$\left|\frac{\bar{f}' D_e^{1/2}}{\bar{f}(2\bar{f})^{1/2}}\right| \left[\frac{\int_0^{C_b}\int_0^{C} r_c(\alpha)\,d\alpha\,dC}{\left(\int_0^{C_b} r_c(C)\,dC\right)^{3/2}}\right] \ll 1 \tag{2}$$

where $f' = df/dx$. The left hand side of this relationship is essentially the fractional error involved in using Eq. 1. This condition is usually met unless $\bar{f} \ll \bar{f}'$ since the second term in the left hand side is much smaller than unity. This can readily be seen if we write the condition for an nth order reaction for which $r_c = kC^n$:

$$\left|\frac{\bar{f}'}{\bar{f}^{3/2}}\right| \left(\frac{1}{\phi}\right) \left[\frac{(n+1)^{1/2}}{\sqrt{2}(n+2)}\right] \ll 1 \tag{2a}$$

where ϕ is the usual Thiele modulus for an nth order reaction. For the diffusion-limited reactions being considered, the condition is readily met unless the surface activity $\bar{f}$ is quite small. Another factor that favors the condition is the slope $\bar{f}'$ which is not steep for the deactivation being considered, i.e., intermediate between uniform and shell-progressive deactivation. Further development to follow will be subject to this restriction of Eq. 2.

Let us represent the intrinsic rate of reaction unaffected by deactivation by:

$$r_c = kg(c) \tag{3}$$

One-dimensional steady state mass balance for a pellet undergoing deactivation is:

$$D_e \frac{d^2C}{dx^2} = k(1-\gamma)g(c) \tag{4}$$

where the fraction of catalyst deactivated γ is a function of both time and the pellet coordinate x. A comparison between this equation and the mass balance used for the result of Eq. 1 shows that

$$f = 1 - \gamma \tag{5}$$

The internal effectiveness factor η_i is defined as

$$\eta_i = \frac{\text{observed rate}}{\text{intrinsic rate for fresh catalyst at surface conditions}} \tag{6}$$

It follows from this definition and Eq. 1 that

$$\eta_i = \frac{D_e\bar{p}}{L\bar{r}_c} = \frac{\left[2(1-\bar{\gamma})D_e \int_0^{C_b} r_c(C)\,dC\right]^{1/2}}{L\bar{r}_c} \tag{7}$$

APPROXIMATE GLOBAL RATES FOR INDEPENDENT POISONING

The global rate of main reaction can be obtained from the definition of the internal effectiveness factor with the aid of Eqs. 1, 3 and 7:

$$\mathcal{R} = \frac{1}{L}\left[2k_s(1-\bar{\gamma})D_e \int_0^{C_b} g(C)\,dC\right]^{1/2} \tag{8}$$

where the intrinsic rate constant at the pellet surface temperature k_s is still a local quantity. The rate of deactivation, when it is caused by chemisorption of poisoning species, is given (Lee and Butt, 1982b) by:

$$Q\frac{d\gamma}{dt} = \frac{k_pN(1-\gamma)}{[1+G(C)]^n} \tag{9}$$

where G is a function of the concentration of the species of interest, representing the product inhibition. Here, N is the concentration of poisoning species and Q is the poisoning capacity of pellet in moles poisoning species per unit pellet volume. Since the quantity of interest is $\bar{\gamma}$, this equation is rewritten at the surface:

$$Q\frac{d\bar{\gamma}}{dt} = \frac{\bar{k}_pN_b(1-\bar{\gamma})}{[1+G(C_b)]^n} \tag{10}$$

Let us define reactor point effectiveness as

$$\mathscr{E} = \frac{\text{observed rate}}{\text{intrinsic rate for fresh catalyst at bulk-fluid conditions}} \tag{11}$$

From the definition, we have:

$$\mathscr{E} = \frac{\mathcal{R}}{r_c(C_b,k_b)} = \frac{k_s}{k_b}\eta_i \tag{12}$$

The rate constant ratio appearing in the above equation can be very well approximated (Lee 1981b) by:

$$\left(\frac{k_s}{k_b}\right)^{1/2} = 1 + 1.2\epsilon\left[\frac{L(-\Delta H)\mathcal{R}}{2hT_b}\right] \tag{12a}$$

where h is external heat transfer coefficient and ϵ is the Arrhenius number. The global rate in terms solely of bulk-fluid quantities is obtained when Eq. 12a is used in Eq. 8:

$$\mathcal{R} = \frac{J^{1/2}/L}{1 - \dfrac{1.2\epsilon(-\Delta H)}{2hT_b}J^{1/2}} \tag{13}$$

$$J = 2k_b(1-\bar{\gamma})D_e \int_0^{C_b} g(C)\,dC \tag{14}$$

This global rate can be used as such in the right hand side of reactor conservation equations, resulting in a transformation of the heterogeneous reactor problem with deactivation into a homogeneous one. Note that $\bar{\gamma}$ is given by Eq. 10.

The global rate of poisoning reaction is obtained in a similar manner. The pellet conservation equation for the poisoning species (Lee and Butt, 1982b) is:

$$D_p\frac{d^2N}{dx^2} = r_p = \frac{k_pN(1-\gamma)}{[1+G(C)]^n} \tag{15}$$

Since the inhibition term $G(C)$ is usually much smaller than unity, an arithmetic average may be used to approximate the denominator:

$$H(C_b) = \frac{[L+G(C_b)]^n + [1+G(C=0)]^n}{2} \tag{16}$$

Then, the procedures identical to those used in arriving at Eq. 1 lead to:

$$(\eta_i)_p = \frac{1}{L}\left[\frac{D_pH(C_b)}{\bar{k}_p(1-\bar{\gamma})}\right]^{1/2} \tag{17}$$

where $(\eta_i)_p$ is the internal effectiveness factor for the poisoning reaction. With the assumption that the heat liberated by the poisoning reaction is negligible compared to that by the main reaction, the ratio of rate constants of poisoning reaction can be written as

$$\left[\frac{\bar{k}_p}{(k_p)_b}\right]^{1/2} = 1 + 1.2\epsilon_p\left[\frac{L(-\Delta H)\mathcal{R}}{2hT_b}\right] \tag{18}$$

which follows from the condition:

$$h(T_s - T_b) = L\mathcal{R}(-\Delta H)$$

and the approximation (Lee, 1981b)

$$\left[\frac{\bar{k}_p}{(k_p)_b}\right]^{1/2} = 1 + 1.2\epsilon_p(T_s/T_b - 1)/2$$

Here ϵ_p is the Arrhenius number for the poisoning reaction and T_s is surface temperature. Following the procedures similar to those used in arriving at Eq. 13, the global rate of poisoning reaction $\mathcal{R}_p$ can be obtained with the aid of the rate expression for the poisoning reaction (Eq. 15):

TABLE 1. GLOBAL RATES: DIFFUSION-LIMITATION AND DEACTIVATION

$$r_c = kg(C)$$

Independent Deactivation

$$\mathscr{R} = \frac{\sqrt{J}/L}{1 - \frac{1.2\epsilon(-\Delta H)}{2hT_b}\sqrt{J}} \quad ; J = 2k_b(1-\overline{\gamma})D_e \int_0^{C_b} g(C)dc$$

$$\mathscr{R}_p = \frac{[(k_p)_b y D_p H(C_b)]^{1/2}}{L[1 + G(C_b)]^n}\left\{1 + \frac{1.2\epsilon_p L(-\Delta H)}{2hT_b}\mathscr{R}\right\}$$

$$y_i = y_{i-1} - \Delta t\left[\frac{(k_p)_s N_b y}{Q[1 + G(C_b)]^n}\right]_{i-1}; y \equiv 1 - \overline{\gamma}$$

$$(T_s)_{i-1} \text{ for } (k_p)_s|_{i-1}\text{: } h(T_s - T_b)|_{i-1} = L\mathscr{R}(-\Delta H)|_{i-1}$$

i: grid point in time

$$H(C_b) = \{[1 + G(C_b)]^n + [1 + G(C_b = 0)]^n\}/2$$

Dependent Deactivation:

$$\mathscr{R} = \frac{\sqrt{J}/L}{1 - \frac{1.2\epsilon(-\Delta H)}{2hT_b}\sqrt{J}} ; J = 2k_b(1-\overline{\gamma})D_e \int_0^{C_b} g(C)dc$$

$$\text{Parallel: } y_i = y_{i-1} - \Delta t\left\{\frac{\overline{k}_p(C_A)_b y}{Q\left[1 + \sum_{i \neq A}(K_iC_i)^{m_i}\right]^n_{\text{bulk}}}\right\}_{i-1} \quad ; y = 1 - \overline{\gamma}$$

$$\text{Series: } y_i = y_{i-1} - \Delta t\left\{\frac{\overline{k}_p(C_B)_b y}{Q\left[1 + \sum_{i \neq B}(K_iC_i)^{m_i}\right]^n_{\text{bulk}}}\right\}_{i-1}$$

$$(T_s)_{i-1} \text{ for } \overline{k}_p|_{i-1}\text{: } h(T_s - T_b)|_{i-1} = L\mathscr{R}(-\Delta H)|_{i-1}$$

i: grid point in time

$$\mathscr{R}_p = \left[\frac{(k_p)_b(1-\overline{\gamma})D_pH(C_b)}{L[1 + G(C_b)]^n}\right]^{1/2}\left\{1 + \frac{1.2\epsilon_pL(-\Delta H)\mathscr{R}}{2hT_b}\right\} \tag{19}$$

Here again, the global rate is expressed in terms solely of bulk-fluid quantities.

The global rates developed can now be used as such in the right hand side of the following reactor conservation equations:

$$\mathscr{L}_C\{C_b;T_b,N_b\} = -\mathscr{R}$$

$$\mathscr{L}_T\{T_b;C_b,N_b\} = \mathscr{R}(-\Delta H)$$

$$\mathscr{L}_p\{N_b;C_b,T_b\} = -\mathscr{R}_p$$

Now that the global rates are given in terms solely of bulk-fluid quantities, thereby eliminating the need to solve the diffusion-deactivation problem for the pellet along with a finite external heat transfer resistance. Here, $\mathscr{L}_C$, $\mathscr{L}_T$ and $\mathscr{L}_p$ are linear operators operating on C_b, T_b and N_b respectively for the conservation equations. The equations necessary for this transformation are summarized in Table 1.

APPROXIMATE GLOBAL RATES FOR DEPENDENT DEACTIVATION

The dependent deactivation can be treated according to the models given below:

$$\text{Parallel: } A + S \xrightarrow{k} B + S$$

$$A + S \xrightarrow{k_p} A \cdot S$$

$$\text{Series: } A + S \xrightarrow{k} B + S$$

$$B + S \xrightarrow{k_p} B \cdot S$$

where S denotes active sites. The rate constant of deactivation reactions k_p should be much smaller than that of main reaction k. Otherwise, the catalyst cannot be useful in the form of pellets since it will be deactivated too fast. This is precisely the reason why a fluidized-bed is used when k_p is of the same order of magnitude of k, as in catalytic cracking of gas oil. For k_p much smaller than k, the rate of reaction for the species of interest (A) can be approximated in both cases by:

$$r_c = kg(C)$$

where C is the concentration of species A. In both cases, then, the global rate of main reaction is given by Eq. 13. The kinetics of deactivation can be written from the models:

$$\text{Parallel: } r_p = \frac{\overline{k}_pC_A(1-\gamma)}{\left[1 + \sum_{i \neq A}(K_iC_i)^{m_i}\right]^n} \tag{20}$$

$$\text{Series: } r_p = \frac{\overline{k}_pC_B(1-\gamma)}{\left[1 + \sum_{i \neq B}(K_iC_i)^{m_i}\right]^n} \tag{21}$$

where m_i assumes a value of ½ or 1 depending on the mode of adsorption: ½ for dissociative adsorption and 1 for molecular adsorption. The constant n can assume a value ranging from 1 to 3 depending on the mechanism and controlling step of main reaction. The surface activity $(1 - \overline{\gamma})$ necessary for $\mathscr{R}$ follows directly from Eqs. 20 and 21:

$$\text{Parallel: } \frac{d}{dt}(Q\overline{\gamma}) = \frac{\overline{k}_p(C_A)_b(1-\overline{\gamma})}{\left[1 + \sum_{i \neq A} (K_iC_i)^{m_i}\right]^n_{\text{bulk}}} \tag{22}$$

$$\text{Series: } \frac{d}{dt}(Q\overline{\gamma}) = \frac{\overline{k}_p(C_B)_b(1-\overline{\gamma})}{\left[1 + \sum_{i \neq B} (K_iC_i)^{m_i}\right]^n_{\text{bulk}}} \tag{23}$$

Reaction stoichiometry allows an expression of $(C_B)_b$ in terms of $(C_A)_b$ for use in the equations developed. The equations necessary for the transformation of the heterogeneous reactor problem to a homogeneous one are also summarized in Table 1.

CONCLUDING REMARKS

Global rates have been developed for the reactions limited by diffusion and affected by deactivation intermediate between uniform and shell-progressive. These global rates allow the treatment of a heterogeneous reactor design problem with deactivation as a homogeneous one. The global rates obtained, however, are not applicable to the entire space of the intermediate deactivation regime but rather limited to a subspace in which the pellet center concentration approaches zero (diffusion-limited reactions) and the pellet surface activity does not approach zero such that the condition of Eq. 2 (or Eq. 2a for an nth-order reaction) is satisfied. For diffusion-limited reactions being considered, the condition of Eq. 2 is usually met as Eq. 2a indicates unless the surface activity is quite small. In such cases, more terms can be added to the flux expression of Eq. 1 (Lee, 1981a).

NOTATION

C = concentration of key species
C_b = bulk concentration
C_c = pellet center concentration
C_A = concentration of species A
C_B = concentration of species B
D_e = effective diffusivity of key reactant
D_p = effective diffusivity of poisoning species
f = activity distribution function
f' = df/dx
g = concentration dependence of the rate of main reaction
$G(c)$ = product inhibition term in kinetics of poisoning reaction
h = film heat transfer coefficient
$H(C_b)$ = function defined by Eq. 16
$(-\Delta H)$ = heat of reaction
J = function defined by Eq. 14
k = rate constant of main reaction
k_b = k evaluated at T_b
k_p = rate constant of poisoning reaction
k_s = k evaluated at T_s
L = characteristic dimension of pellet
n = order of reaction; constant in Eq. 15
N = concentration of poisoning species
P = dC/dx
Q = poisoning capacity of pellet in moles poisoning species per pellet volume
r_c = intrinsic kinetics of main reaction (= $kg(C)$)
r_p = intrinsic kinetics of poisoning reaction
$\mathcal{R}$ = global rate of main reaction based on pellet volume
$\mathcal{R}_p$ = global rate of poisoning reaction based on pellet volume
T = temperature
x = pellet coordinate
y = $1 - \overline{\gamma}$

Greek Letters

γ = fraction of catalyst deactivated
ϵ = Arrhenius number, E/RT_b
ϵ_p = E_p/RT_b
$\mathcal{E}$ = reactor point effectiveness defined by Eq. 11
η_i = internal effectiveness factor defined by Eq. 6
$(\eta_i)_p$ = internal effectiveness for poisoning reaction given by Eq. 17
ϕ = Thiele modulus, $L(kC_b^{n-1}/D_e)^{1/2}$

Subscripts

b = bulk fluid
c = pellet center
s = pellet surface

LITERATURE CITED

Lee, H. H., "Generalized Effectiveness Factor for Pellets with Nonuniform Activity Distribution: Asymptotic Region of Strong Diffusion Effect," *Chem. Eng. Sci.*, 36, 1921 (1981a).

Lee, H. H., "An Approximate Approach to Design and Analysis of Heterogeneous Catalytic Reactors," *AIChE J.*, 27, 558 (1981b).

Lee, H. H., and J. B. Butt, "Heterogeneous Catalytic Reactors Undergoing Chemical Deactivation: II Design and Analysis: The Approach of Reactor Point Effectiveness," *AIChE J.* 28, 410 (1982).

Lee, H. H., and J. B. Butt, "Heterogeneous Catalytic Reactors Undergoing Chemical Deactivation: I. Deactivation Kinetics and Pellet Effectiveness," *AIChE J.* 28, 405 (1982).

Manuscript received September 22, 1981; revision received February 11, and accepted March 4, 1982.

Fine Structure of the CSTR Parameter Space

V. K. KWONG
and T. T. TSOTSIS

Dept. of Chemical Engineering
University of Southern California
Los Angeles, CA 90007

In a recent communication by the same title, Williams and Calo (1981) have examined the "fine structure" of the CSTR parameter space. The authors have suggested the existence of five additional regions of stability behavior resulting by subdivision of the regions already presented by Uppal, Ray and Poore (1974) in their classical paper on "The Dynamic Behavior of a CSTR." Williams and Calo (1981) discovered the additional regions of stability behavior by considering the demarcations created in the parameter space by the coincidence of the Damkohler numbers corresponding to the roots of the trace, s_1,s_2 and of the determinant of the stability matrix

---

0001-1541-83-6545-0343-$2.00.