Single-Pellet Cell for the Measurement of Intraparticle Diffusion and Convection

Z. P. Lu, J. M. Loureiro, A. E. Rodrigues
Laboratory of Separation and Reaction Engineering, School of Engineering, University of Porto,
4099 Porto Codex, Portugal

Dynamic analysis of single-pellet cell for the measurement of diffusion and convection in porous catalysts is revisited. A complete mathematical model for the "diffusion-convection" cell is solved, and the relation between zero- and first-order moments of the cell response and operating parameters is derived. The validity region of the "simplified" boundary condition at the bottom of the pellet is quantified. The effect of the operating parameters on the cell time response to a tracer impulse is analyzed to check the practical range of operation of the system. It also is compared with the chromatographic technique.

Introduction

Single-pellet diffusion cell has been widely used in the measurement of effective diffusivities in porous catalysts (Suzuki and Smith, 1972; Dogu and Smith, 1975, 1976; Furusawa et al., 1976; Al-Rqobah et al., 1988) using nonadsorbable and/or adsorbable tracers. Extension to gas-solid reaction (Dogu et al., 1986) has also been made. Baiker et al. (1982) and Cresswell and Orr (1982) compared the diffusion-cell technique with chromatographic techniques, such as the single-pellet string reactor for the measurement of effective diffusivities. The diffusion-cell technique has some problems related to particle orientation, anisotropy and difficulty of a pellet being representative of commercial catalysts, as already pointed out by Gibilaro and Waldram (1981); however, it is a simple and fast technique and thus it is a valuable tool for screening adsorbents and catalysts.

The dynamic analysis of the diffusion cell has been carried out in most cases by using moment analysis: parameters are obtained from moments of cell response curves. Dudukovic (1982), however, was able to solve analytically for the outlet concentrations of the top and bottom chambers when the input signal is a step function on tracer concentration, and Do and Smith (1984) provided the general transient solution for pulse input.

There are some problems related to the practical range of operation of diffusion cells and boundary conditions associated with the chambers at the top and bottom of the pellet. This was recognized by Burghardt and Smith (1979) and Do and Smith (1984) who discussed the importance of the accumulation terms in the mass balance of the chambers as well as mass transfer at both faces of the pellet. This question was also addressed by Frost (1981) in the framework of a flow-through diffusion cell.

The technique has been recently extended to include the measurement of effective diffusivities and intraparticle convective flow in a porous pellet using a "diffusion-convection" cell. The technique extends previous work by imposing a pressure drop ΔP across the pellet in contrast with diffusion cell measurements in which $\Delta P = 0$.

The importance of intraparticle forced convection in the enhancement of catalyst effectiveness factor in the intermediate region of Thiele modulus was recognized first by Nir and Pismen (1977). It was also discussed when measuring effective diffusivity by the chromatographic technique (single-pellet string reactor) leading to a simple result (Rodrigues et al., 1982).

$$\tilde{D}_e = \frac{D_e}{f(\lambda')} \tag{1}$$

with

$$f(\lambda') = \frac{3}{\lambda'}\left(\frac{1}{\tanh \lambda'} - \frac{1}{\lambda'}\right) \tag{2}$$

where $\tilde{D}_e$ is the "apparent" effective diffusivity that lumps diffusion and convection, D_e is the "true" effective diffusivity

---

Correspondence concerning this article should be addressed to A. E. Rodrigues.

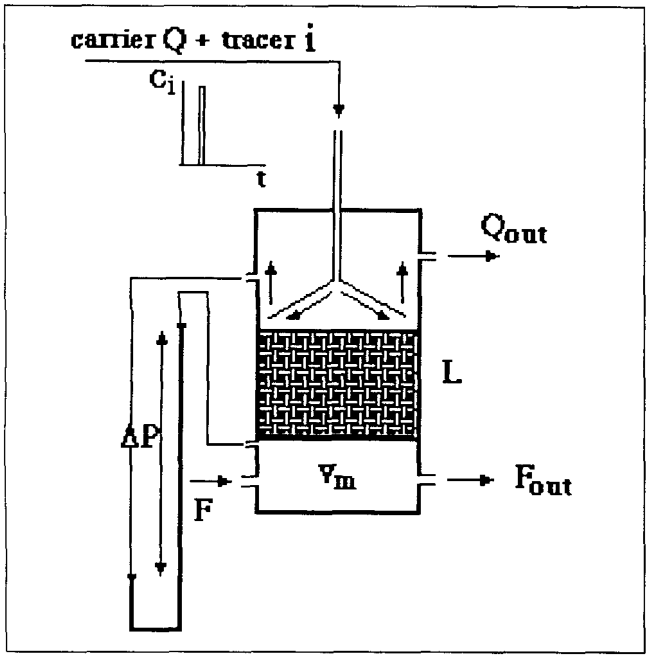

Figure 1. Diffusion-convection cell system.

and $\lambda' = (v_o \ell / D_e)$ is the intraparticle Peclet number that is the ratio between convective and diffusive flows (v_o is the intraparticle convection velocity and ℓ the half thickness of the catalyst).

"Diffusion-Convection" cell to our knowledge was used first by Cresswell (1985) and more recently by Dogu et al. (1989). The analysis provided by Dogu et al. (1989) for the diffusion-convection cell follows previous work by the authors for the diffusion cell; however, problems already recognized for the diffusion cell regarding boundary conditions and operating ranges have not been quantified (Rodrigues, 1991). Fott and Petrini (1982) used a related arrangement to measure permeability of porous catalysts. A review on methods for experimental measurement of effective diffusivity was given by Haynes (1988).

It is the purpose of this work: to solve the complete model of the diffusion-convection cell; to quantify the validity of simplified boundary conditions used by Dogu et al. (1989); to provide physical insight on the practical range of operation of such a cell; and to relate the analysis of the diffusion-convection cell with known results from chromatographic measurements of diffusion and convection in large-pore catalysts.

Mathematical Model of the Diffusion-Convection Cell

The diffusion-convection cell is shown in Figure 1, following the arrangement of Cresswell (1985) and Dogu et al. (1989). The mathematical model of the system includes:

- *Unsteady-state mass balance of nonadsorbable tracer in a volume element of the pellet*:

$$\frac{\partial^2 C_i}{\partial x^2} - \lambda \frac{\partial C_i}{\partial x} = \tau_d \frac{\partial C_i}{\partial t} \tag{3}$$

with the associated initial condition:

$$t=0,\ 0<x\leq 1,\ C_i=0 \tag{3a}$$

and the boundary conditions:

$$x=0,\ C_i = M\delta(t) \tag{3b}$$

$$x=1,\ \left(-\frac{dC_i}{dx}+\lambda C_i\right)\Bigg|_{x=1} = Bi\left(C_i\Bigg|_{x=1} - C_i^{\text{out}}\right) \tag{3c}$$

- *Mass balance to the bottom chamber:*

$$\left(-\frac{dC_i}{dx}+\lambda C_i\right)\Bigg|_{x=1} = (\lambda + R)\ C_i^{\text{out}} + \frac{\beta \tau_d}{\epsilon_p}\frac{dC_i^{\text{out}}}{dt} \tag{4}$$

with the associated initial condition:

$$t=0,\ C_i^{\text{out}}=0 \tag{4a}$$

In the above equations, $x = (z/L)$ is the dimensionless axial coordinate in the pellet, t is the time variable, and M is the amount injected (n moles) divided by the flow rate Q in the top chamber: $M = (n/Q)$.

Model parameters are:

i) $\lambda = \dfrac{v_o L}{D_e}$

is the intraparticle Peclet number relating intraparticle convective flow and diffusive flow or the ratio between time constants for convection and diffusion: $\lambda = (\tau_c/\tau_d)$, where $v_o = (B_o/\mu L)\ \Delta P$ is the intraparticle convective velocity, and B_o is the pellet permeability.

ii) $Bi = \dfrac{k_f L}{D_e}$

is the mass Biot number related to mass transfer between the bottom face of the pellet and the fluid stream in the bottom chamber.

iii) $R = \dfrac{FL}{AD_e}$

is the ratio between the flow rate in the bottom chamber and diffusive flow from the pellet: $R = (F/Q_d)$.

iv) $\beta = \dfrac{V_m}{AL}$

is the ratio between bottom chamber volume and pellet volume.

v) $\tau_d = \dfrac{\epsilon_p L^2}{D_e}$

is the time constant for diffusion inside pellet, where ϵ_p is the pellet porosity.

It should be pointed out that Bi and R are really not independent parameters, since the film mass transfer coefficient k_f depends on the flow rate F through the bottom chamber.

In various articles including the recent one by Dogu et al. (1989), several simplifications were made:

i) $C_i\Big|_{x=1} = C_i^{\text{out}}$

This assumption corresponds to the case in which mass transfer resistance between bottom pellet surface and fluid stream in the bottom chamber is negligible.

ii) The accumulation term in the mass balance for the bottom chamber, Eq. 4, is neglected; the simplification is that the volume of the bottom chamber is small and thus that term becomes smaller than the others in the mass balance.

iii) λ is neglected when compared with R in the mass balance for the bottom chamber.

With these simplifications, the boundary condition of Dogu et al. (1989) is:

$$\left(-\frac{dC_i}{dx}+\lambda C_i\right)\Bigg|_{x=1}=RC_i\Bigg|_{x=1} \tag{4b}$$

which is Eq. 10 in the article by Dogu et al. (1989) using our notation. Note that parameter λ introduced first by Nir and Pismen (1977) is simply related to parameter D in Dogu's article: $\lambda = 2D$.

Model Eqs. 3-4 can be solved by using the Laplace transform technique leading to the transfer function relating the outlet concentration of the bottom chamber and the input:

$$G_{\text{out}}(s)=\frac{\overline{C}_i^{\text{out}}(s)}{\overline{C}_i(x=0,s)}=$$

$$\frac{Bi\ (r_1-r_2)\ e^{\lambda}}{\left(\lambda+R+\frac{\beta\tau_d}{\epsilon_p}s\right)[r_1e^{r_2}-r_2e^{r_1}+Bi(e^{r_1}-e^{r_2})]+Bi(r_1e^{r_2}-r_2e^{r_1})} \tag{5}$$

where

$$r_1,\ r_2=\frac{\lambda}{2}\pm\sqrt{(\lambda/2)^2+s\tau_d} \tag{5a}$$

and for the pellet:

$$G(s)=\frac{\overline{C}_i(x=1,s)}{\overline{C}_i(x=0,s)}=\frac{1}{Bi}\left(\lambda+R+\frac{\beta\tau_d}{\epsilon_p}s+Bi\right)G_{\text{out}}(s) \tag{6}$$

The moments of the curve (concentration/M) vs. time at $x = 1$ and at the outlet of the bottom chamber are, respectively:

$$m_n=(-1)^n\frac{d^nG(s)}{ds^n}\Bigg|_{s=0}\ ;\quad m_n'=(-1)^n\frac{d^nG_{\text{out}}(s)}{ds^n}\Bigg|_{s=0} \tag{7}$$

and are summarized in Table 1.

Results adapted from Dogu et al. (1989) using the simplified boundary condition at $x = 1$ are referred to $[C_i(t)/M]$:

$$m_o'=m_o=\frac{e^{\lambda}}{R\frac{e^{\lambda}-1}{\lambda}+1} \tag{8a}$$

$$\mu_1'=\mu_1=\tau_d\frac{R\frac{\lambda(1+e^{\lambda})-2(e^{\lambda}-1)}{\lambda^3}+\frac{e^{\lambda}-\lambda-1}{\lambda^2}}{R\frac{e^{\lambda}-1}{\lambda}+1} \tag{8b}$$

It should be noted that the use of the "simplified" boundary condition implies that $m_o' = m_o$ and $\mu_1' = \mu_1$: the concentration response of the bottom cell is equal to the concentration response at the outlet of the bottom chamber.

Now, if the analysis is carried out by lumping convection and diffusion in an "apparent" effective diffusivity $\tilde{D}_e$, we get from Eqs. 7a-7d (Table 1), by allowing $\lambda\rightarrow 0$, the following results:

Table 1. Moments of the Response at the Pellet Bottom $(\overline{C}_i|_{x=1})/M$, m_n and at the Outlet of the Bottom Chamber $(\overline{C}_i^{\text{out}}/M)$, m_n'

Moments	Calculated from $G(s)$	Calculated from $G_{\text{out}}(s)$	Eq.
$m_o'=G_{\text{out}}(0)$		$\frac{Bi\ e^{\lambda}}{R\ Bi\frac{e^{\lambda}-1}{\lambda}+R+\lambda+Bi\ e^{\lambda}}$	7a
$m_o=G(0)$	$\frac{1}{Bi}(\lambda+R+Bi)m_o'$		7b
$\mu_1'=\frac{m_1'}{m_o'}$ $=-\frac{G_{\text{out}}'(0)}{G_{\text{out}}(0)}$		$\tau_d\frac{m_o'}{Bi\ e^{\lambda}}f(Bi,R,\lambda,\beta)$	7c
$\mu_1=\frac{m_1}{m_o}$ $=-\frac{G'(0)}{G(0)}$	$\mu_1'-\frac{\tau_d\beta}{\epsilon_p(\lambda+R+Bi)}$		7d
	$f(Bi,R,\lambda,\beta)=\frac{\beta}{\epsilon_p}\left(1+Bi\frac{e^{\lambda-1}}{\lambda}\right)+Bi\frac{\lambda e^{\lambda}-e^{\lambda}-1}{\lambda^2}$ $+R\ Bi\frac{\lambda(1+e^{\lambda})-2(e^{\lambda}-1)}{\lambda^3}+(R+\lambda)\frac{e^{\lambda}-\lambda-1}{\lambda^2}$		7e

$$m'_{oo}=\frac{\tilde{Bi}}{\tilde{Bi}(1+\tilde{R})+\tilde{R}} \tag{9a}$$

$$m_{oo}=\frac{\tilde{R}+\tilde{Bi}}{\tilde{Bi}(1+\tilde{R})+\tilde{R}} \tag{9b}$$

$$\mu'_{1o}=\frac{\tilde{\tau}_d}{6}\,\frac{\tilde{Bi}\left(\frac{6\beta}{\epsilon_p}+\tilde{R}+3\right)+3\tilde{R}+\frac{6\beta}{\epsilon_p}}{\tilde{Bi}(1+\tilde{R})+\tilde{R}} \tag{9c}$$

$$\mu_{1o}=\mu'_{1o}-\frac{\tilde{\tau}_d\beta}{\epsilon_p(\tilde{R}+\tilde{Bi})} \tag{9d}$$

where $\tilde{R}$, $\tilde{Bi}$, and $\tilde{\tau}_d$ are based on $\tilde{D}_e$ and the second subscript o refers to $\lambda = 0$.

Simplified results from Dogu et al. (1989) are then:

$$m_{oo}=\frac{1}{1+\tilde{R}} \tag{10a}$$

$$\mu_{1o}=\frac{\tilde{\tau}_d}{6}\,\frac{\tilde{R}+3}{1+\tilde{R}} \tag{10b}$$

Region of Validity for the Simplified Boundary Condition at $x = 1$

From the above results, it appears that the complete and simplified solutions are similar if the parameter R is high. For low R, the simplified solution leads to nonsense results. Our goal is to quantify the region of validity of the approximation made for the boundary condition at the bottom pellet surface. The strategy follows two points:

1. It is expected by physical understanding of the problem that:

$$\frac{d\mu'_1}{d\lambda}<0 \tag{11}$$

which is not satisfied by Eq. 8b (simplified solution) at low R. Thus, to verify Eq. 11, we get from Eq. 8b:

$$R^2f_1(\lambda)+Rf_2(\lambda)+f_3(\lambda)>0 \tag{11a}$$

where

$$f_1(\lambda)=\lambda e^{2\lambda}-4e^{2\lambda}+2\lambda^2e^{\lambda}+8e^{\lambda}-\lambda-4\geq 0$$

$$f_2(\lambda)=\lambda(e^{2\lambda}-2\lambda^2e^{\lambda}+4\lambda e^{\lambda}-8e^{\lambda}+2\lambda+7)\geq 0$$

$$f_3(\lambda)=\lambda^2(-\lambda e^{\lambda}+2e^{\lambda}-\lambda-2)\leq 0$$

for $\lambda > 0$, we get from Eq. 11a:

$$R>\frac{-f_2(\lambda)+\sqrt{f_2^2(\lambda)-4f_1(\lambda)f_3(\lambda)}}{2f_1(\lambda)} \tag{11b}$$

which is the condition to be fulfilled for the approximation to be acceptable. Figures 2a and 2b show the first moment μ'_1 as a function of λ at various R for the "complete" and "simplified" boundary conditions, respectively. From the complete solution at high λ and low R, $\mu'_1 \approx (\tau_d/\lambda)(1+\beta/\epsilon_p)$ and at high λ and high R, $\mu'_1 \approx (\tau_d/\lambda)$, as shown in Figure 2a. At high λ, the slope of μ'_1 vs. λ in log-log paper is (-1). However, from the simplified model at high λ, $\mu'_1 \approx (\tau_d/\lambda)\,[(R+1)/R]$ and so at low R, μ'_1 would go to infinity. If λ is small (Rodrigues et al., 1991b) and for low R, we have $\mu'_1 \approx \tau_d(1/2+\beta/\epsilon_p)$; at high R, $\mu'_1 \approx (\tau_d/6)[(3+Bi)/(1+Bi)] \approx \tau_d/6$.

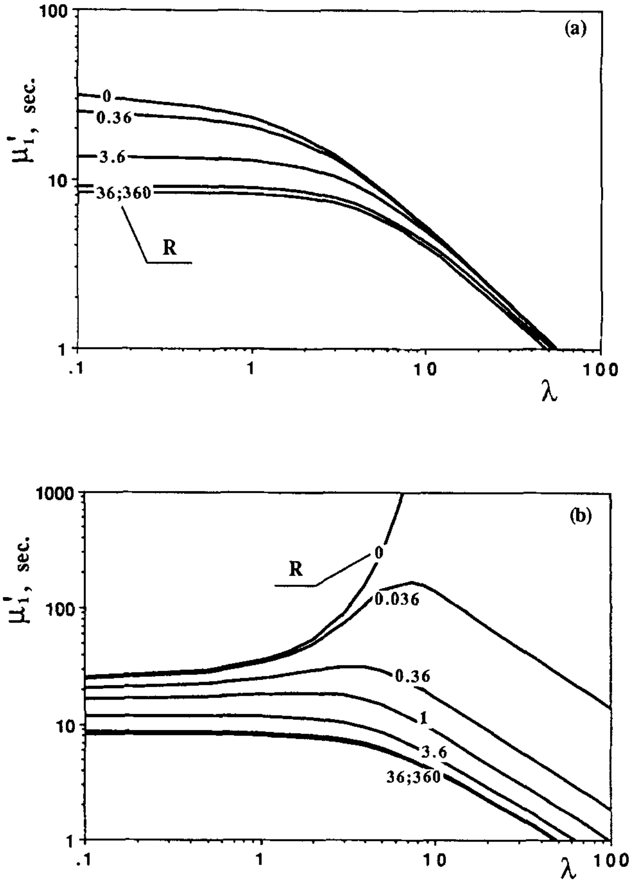

Figure 2. First moment of C_l (out) vs. time curves as a function of λ for various R ($\beta = 0.1$, $\tau_d \approx 49.1$ s).

(a) Complete boundary condition.

(b) Simplified boundary condition.

2. The simplified boundary condition will be acceptable if:

$$\text{error}=\left|1-\frac{(m_{oo}/m_o)\text{simplified}}{(m'_{oo}/m'_o)\text{complete}}\right|\times 100\leq e\text{ percent} \tag{12}$$

This equation provides the second condition to be fulfilled in such a way that the approximation is good enough:

$$R\geq f_4(e\text{ percent},\,\beta,\,\lambda) \tag{12a}$$

Zero-order moments of the concentration curves $[C_l^{\text{out}}(t)/M]$ at the outlet of the bottom chamber as a function of λ for various R are shown in Figures 3a and 3b for the "complete" and "simplified" boundary condition cases. Figures 4a and 4b show zero moments of $[C_l^{\text{out}}(t)/M]$ as a function of R for various λ for the "complete" and "simplified" solution, respectively. At low R, the zero moment of the complete

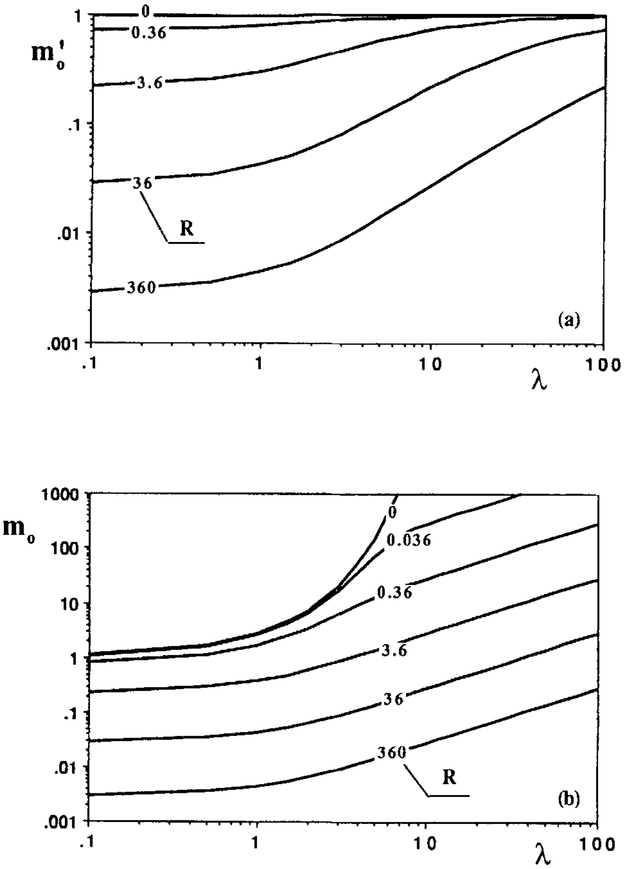

Figure 3. Zero moment of $[C_i\text{ (out)}]/M$ vs. time curves as a function of λ for various R ($\beta = 0.1$, $\tau_d \approx 49.1$ s).

(a) Complete boundary condition.
(b) Simplified boundary condition.

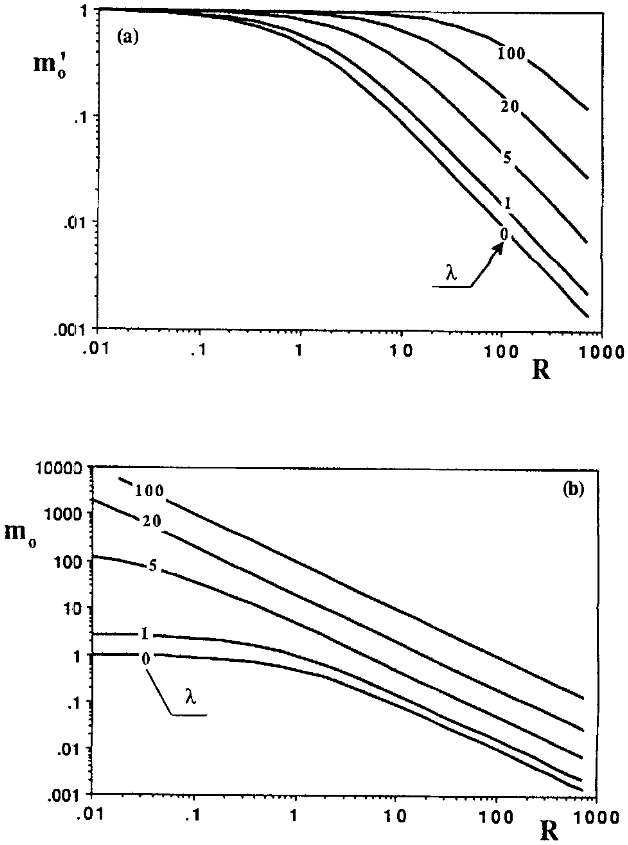

Figure 4. Zero moment of $[C_i\text{ (out)}]/M$ vs. time curves as a function of R for various λ ($\beta = 0.1$, $\tau_d \approx 49.1$ s).

(a) Complete boundary condition.
(b) Simplified boundary condition.

solution is $m_o' \approx Bi\,e^{\lambda}/(\lambda + Bi\,e^{\lambda}) \approx 1$ as shown in Figure 4a. At high R and small λ, $m_o' \approx Bi/[R(1+Bi)]$, while at high R and high λ, $m_o' \approx \lambda/(R+\lambda)$. In any case, m_o' vs. R in the region of high R has a slope (-1) in log-log coordinates.

Again, it appears that there exists a validity region of the simplified solution, since for low R the "simplified" solution leads to values of m_o larger than unity.

Calculations were carried out using the base data from Dogu's article (1989): $\epsilon_p = 0.68$, $L = 1.3$ cm, $A = 1.54$ cm^2, and $D_e = 0.0234$ cm^2/s, so that $\tau_d \approx 49.1$ s.

Figure 5a shows the validity region (shaded area for $e\% = 1$) for the simplified boundary condition at $x = 1$ for a diffusion-convection cell with $\beta = 0.1$. The effect of the acceptable error imposed is also displayed in this figure. Obviously, if the allowed error increases, the region of validity increases too.

In the above calculation, we estimated the film mass transfer coefficient between the pellet bottom surface and fluid stream in the bottom chamber by using $Sh = 0.664\,Re^{1/2}\,Sc^{1/3}$ where $Sh = (k_f d)/D$, $Re = [\rho(F+v_o A)d^2]/(\mu\beta LA)$, $Sc = \mu/(\rho D)$, and d is the diameter of the pellet.

For the case treated here, $R = 360$ approximately corresponds to $F = 10$cm^3/s and $R = 36$ to $F = 1$ cm^3/s. Many authors reported diffusion-cell work in the range of $F = 0.5$ to 5 cm^3/s: around $R = 18$ to 180. The quantification of the validity region enables us to check in each case under study whether we can use or not the simplified boundary condition. For example, using data from Cresswell (1985), that is, pellet permeability $B_o = 6.3\times10^{-9}$ cm^2 and $D_e = 0.19$ cm^2/s at atmospheric pressure (100 kPa), the intraparticle Peclet numbers $\lambda = 1$ and 10 correspond to $\Delta P = 0.5$ kPa and 5 kPa, respectively; however, at high pressure (1,000 kPa) for the same pressure drops, $\lambda = 10$ and 100, respectively. In such cases, to set an error on the zero moment less than 5% (between experimental results and model simulations using the "sim-

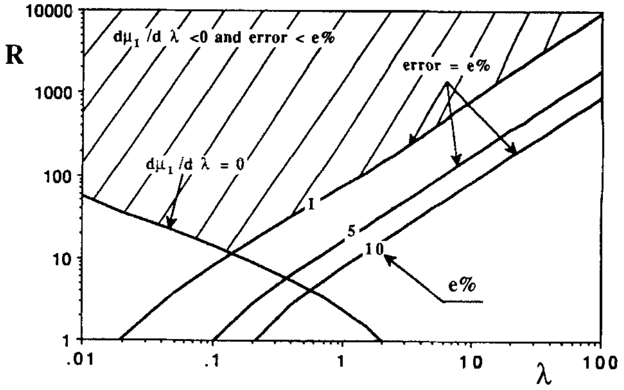

Figure 5. Validity region of the simplified boundary condition for a diffusion-convection cell ($\beta = 0.1$).

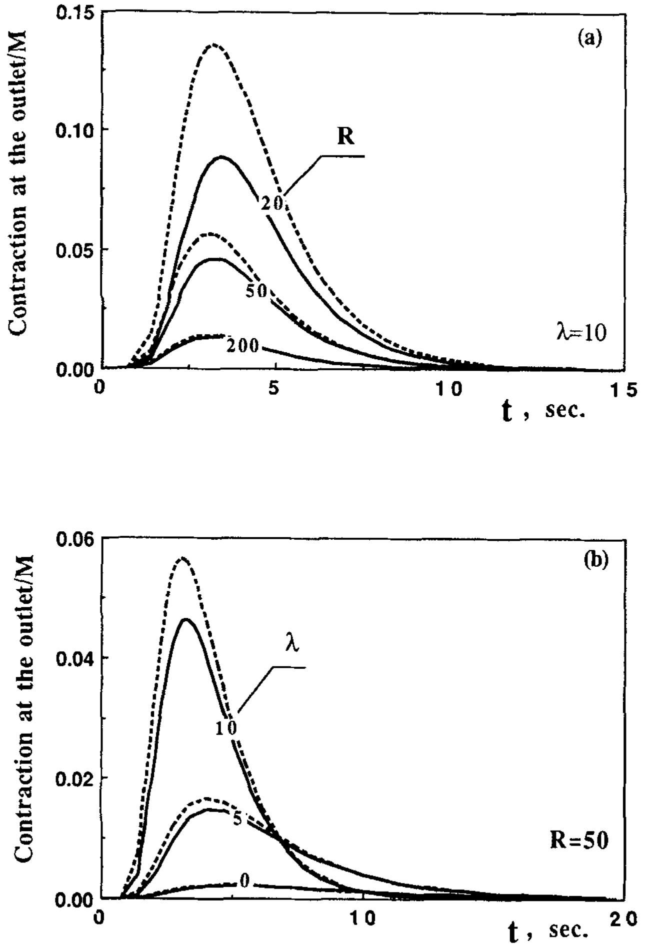

Figure 6. Diffusion-convection cell responses to a tracer impulse using (——— complete boundary condition, - - - - - simplified boundary condition).

(a) Effect of R(R = 20, 50, 200) on $[C_i\ (out)]/M$ vs. time curves at λ = 10, Bi = 100, β = 0.1 and τ_d = 50s.

(b) Effect of λ (λ = 0, 5, 10) on $[C_i\ (out)]/M$ vs. time curves at R = 50, Bi = 100, β = 0.1 and τ_d = 50 s.

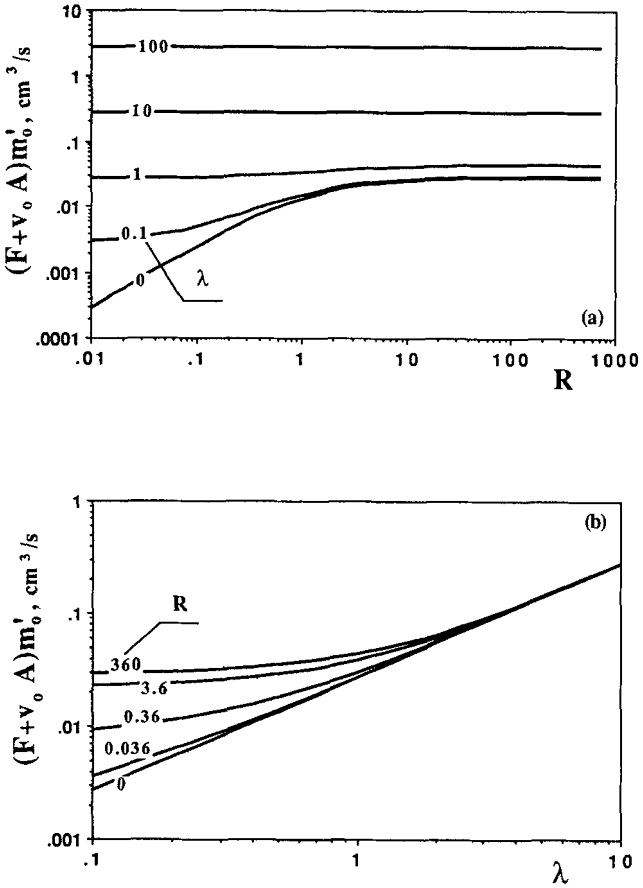

Figure 7. Amount of tracer recovered $m_o'F_{out}$ at outlet of the bottom chamber for a diffusion-convection cell using complete boundary condition.

(a) $(F+v_oA)m_o'$ as a function of R for various λ.
(b) $(F+v_oA)m_o'$ as a function of λ for various R.

plified" boundary condition), R should be larger than 150 ($F \approx 34$ cm^3/s) and 2,000 ($F \approx 450$ cm^3/s) for $\lambda = 10$ and 100, respectively. When the intraparticle Peclet number λ is very small, the diffusion model (Rodrigues et al., 1991a) should be used. However, if one measures both diffusivity and convective flow from the zero and first moments or check the diffusivity by the first-moments (Dogu et al., 1989) using the "simplified" boundary condition, the physical restriction from the first moment in Figure 5 should be taken into account.

Diffusion-Convection Cell Response to a Tracer Impulse of Concentration

From the transfer function $G_{out}(s)$, Eq. 5, we can get the concentration at the outlet of the bottom chamber divided by M, that is, C_i^{out}/M as a function of time. This was done by using the fast Fourier transform technique.

For the simplified boundary condition concentration at $x = 1$, we show in Figure 6a the effect of R on (C_i^{out}/M) vs. time curves at $\lambda = 10$ and $\tau_d = 50$ s.

The effect of $R(R=20, 50, 200)$ at $\lambda = 10$ and the effect of $\lambda(\lambda=0, 5, 10)$ at $R = 50$ on the (C_i^{out}/M) vs. time curves with $\tau_d = 50$ s, $\beta = 0.1$ and $Bi = 100$ are shown in Figures 6a and 6b, respectively. The dashed lines correspond to the "simplified" boundary condition cases under similar operating conditions. It is clear that for $R = 20$ (small flow rate F in the bottom chamber) and high λ (large convective flow through the pellet), the outlet response is very sensitive to the boundary condition used, since the film mass transfer resistance, the accumulation in the bottom chamber, and the contribution of convective flux to the total flow rate out of the bottom chamber are neglected in the "simplified" boundary condition. It is also clear that the difference in the zero moments (areas below the curves), when using the "complete" and "simplified" boundary conditions, increases when λ increases and R decreases. When R is very high, the outlet concentration is small and then there is a limit imposed by the sensitivity of the detector.

The amount of tracer recovered at the outlet of the bottom chamber is $Mm_o'F_{out}$ (with $F_{out} = F + Av_o$), and thus the fraction of tracer recovered is $[(m_o'F_{out})/Q] < 1$. Figures 7a and 7b show $m_o'F_{out}$ as a function of R (at various λ) and λ (at various R).

It is clear that $Q > v_o A$, so that $Q > (\lambda/R)F$, and the fraction recovered is always less than unity. At high λ, the fraction of tracer recovered at the outlet of the bottom chamber is $v_o A/Q = Q_c/Q$, that is, the ratio between convective flow through the pellet and the flow rate in the top chamber. At small λ and high R, the fraction recovered is $(AD_e/L)[Bi/(1+Bi)]/Q$, which is approximately $AD_e/(LQ) = Q_d/Q$, that is, the ratio between "diffusive" flow through the pellet and the flow rate in the top chamber. At small λ and small R, the fraction recovered is again $v_o A/Q = Q_c/Q$.

Measurements: Chromatographic Technique vs. Diffusion-Convection Cell

The measurement of effective diffusivities by using the chromatographic technique is a well-known topic in chemical engineering. Data analysis is based mainly on the moment method (Rodrigues et al., 1991a). Some basic points should be reminded: the shape of a chromatographic peak is mainly determined by the nature of the equilibrium adsorption isotherm. In any case, the zero-order moment (area under the curve) is the amount of tracer injected divided by the flow rate. The first moment μ_1 (retention time, stoichiometric time, or mean residence time) depends on the slope of the adsorption equilibrium isotherm, if it is linear; for a nonadsorbable tracer, the retention time $t_r = \epsilon_t \tau = [\epsilon + (1-\epsilon)\epsilon_p]\tau$ is the total porosity times the space time $\tau\,[\tau = (V/Q)]$. The first moment is the center of gravity of the peak. The second moment μ_2 and the variance σ^2 ($\sigma^2 = \mu_2 - \mu_1^2$) measure in some way the broadening of the peak and contain the effect of all dispersive effects: axial dispersion, film mass transfer, intraparticle diffusion, and intraparticle convection.

The classic analysis of chromatographic data is based on a model that considers intraparticle diffusion as the only mechanism for mass transfer inside the particle. In large-pore supports, this description can be dangerous depending on the flow rate at which experiments are carried out; in fact, it lumps in an "apparent" effective diffusivity $\tilde{D}_e$, the effect of diffusion and convection. However, if chromatographic data are analyzed by a model considering separately "true" effective diffusivity D_e and intraparticle convection (measured by the parameter λ), one can show (Rodrigues et al., 1982; Rodrigues and Ferreira, 1988) that model equivalence leads to:

$$\tilde{D}_e = \frac{D_e}{f(\lambda')} \tag{13}$$

where

$$f(\lambda') = \frac{3}{\lambda'}\left[\frac{1}{\tanh\lambda'} - \frac{1}{\lambda'}\right] \tag{14}$$

with

$$\lambda' = \frac{v_o \ell}{D_e} \text{ (ℓ is half-thickness of the slab catalyst).}$$

This analysis was used to explain the experiments carried out at different flow rates, which lead to $\tilde{D}_e$ depending on the flow rate (Ahn, 1980).

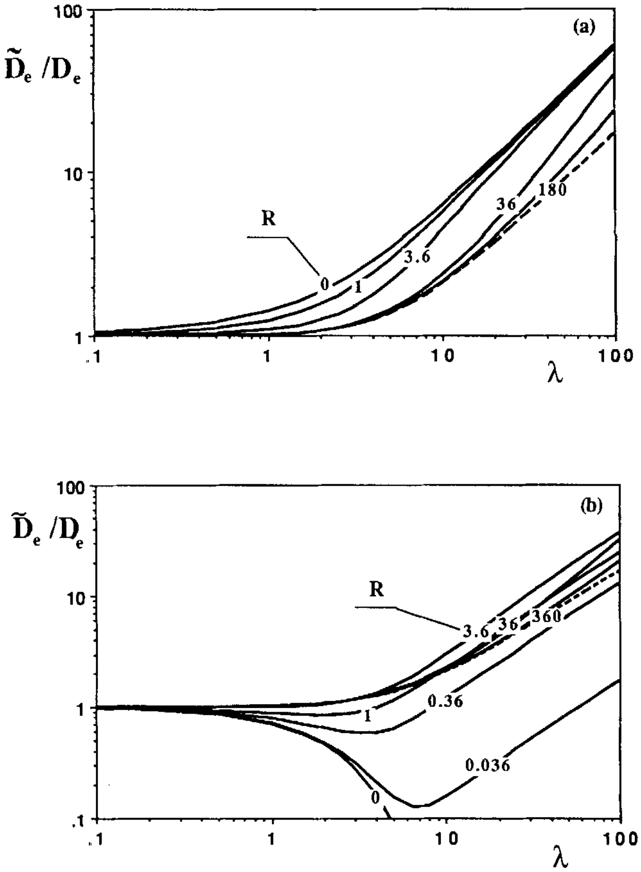

Figure 8. Ratio between "apparent" diffusivity and diffusivity obtained from the diffusion-convection cell as a function of λ for various R ($R \approx 36F$ for the case treated here, dotted line corresponding to $F \to \infty$).

(a) Using the complete boundary condition.
(b) Using the simplified boundary condition.

Now, it is obvious that the diffusion-convection cell is a different arrangement and the role played by the flow through a fixed-bed chromatographic column is not immediately translated for the flow rate in the bottom chamber.

It is clear, however, from the complete solution or the simplified solution that when $F \to \infty$, that is, $R \to \infty$, by equating the first moment μ_1' and μ_{1o}' (when $\lambda = 0$), that is, Eqs. 7c and 9c or Eqs. 8b and 10b, we get:

$$\tau_d \frac{\dfrac{\lambda(1+e^{\lambda}) - 2(e^{\lambda}-1)}{\lambda^3}}{\dfrac{e^{\lambda}-1}{\lambda}} = \frac{\tilde{\tau}_d}{6} \tag{15}$$

which is:

$$\frac{\tilde{\tau}_d}{\tau_d} = f\left(\frac{\lambda}{2}\right) \text{ or } \frac{\tilde{D}_e}{D_e} = \frac{1}{f\left(\dfrac{\lambda}{2}\right)} \tag{16}$$

where

$$f\left(\frac{\lambda}{2}\right)=\frac{3}{\left(\frac{\lambda}{2}\right)}\left[\frac{1}{\tanh\left(\frac{\lambda}{2}\right)}-\frac{1}{\left(\frac{\lambda}{2}\right)}\right]$$

as shown for the chromatographic technique by Rodrigues et al. (1982).

If a similar development is carried out for the "diffusion-convection" cell at other values of F, we get the general solution by using "complete" boundary condition at $x = 1$ shown in Figure 8a in terms of $(\tilde{D}_e/D_e) = f(\lambda,R)$. For $F \rightarrow \infty$, we get Eq. 16 which is represented by the dotted line. At a given λ, if F decreases the ratio $(\tilde{D}_e/D_e)$ increases. For the base case studied, $F \approx (R/36)$, so that in this plot the influence of F is represented (flow rate in the bottom chamber).

If we draw a similar plot using the solution with "simplified" boundary condition by equating Eqs. 8b and 10b, we get $(\tilde{D}_e/D_e)$ vs. $f(\lambda,R)$ as shown in Figure 8b. It is obvious that this figure carries again the message that the "simplified" boundary condition fails in a certain region of R, leading to nonsense results: $(\tilde{D}_e/D_e) < 1$.

Conclusions

The analysis of the transient behavior of a "diffusion-convection" cell by using a "complete" boundary condition at the bottom of the pellet was carried out and the relations between the zero and first moments and the operating parameters were derived. These relationships are used to obtain the diffusivity and convective flow in such cells.

The validity region for the use of the "simplified" boundary condition was discussed and quantified.

Tracer impulse responses of the "diffusion-convection" cell in the time domain were obtained by using the fast Fourier transform technique. The effect of parameters R and λ on the cell response for complete and simplified models were compared. For a given porous pellet/trace gas system, the practical range of operation of a "diffusion-convection" cell is related directly with cell geometry, flow rates in the top and bottom chambers and imposed ΔP across the pellet. Ultimately, the sensitivity of the available detectors will determine the practical limits of the cell operation.

The diffusion-convection model of a single pellet cell is compared with an "apparent" diffusion model ($\lambda = 0$) based on the equivalence of first-order moments; when $F \rightarrow \infty$, $\tilde{D}_e/D_e = 1/f(\lambda/2)$ (enhancement of diffusivity by convection), a result already known from chromatographic measurements.

Acknowledgment

We thank JNICT and Fundação Oriente for their financial support.

Notation

A = cross area of pellet, cm^2
B_o = permeability, cm^2
Bi = Biot number $(=k_fL/D_e)$, dimensionless
C_i = tracer concentration, mol/m^3
d = diameter of pellet, cm
D = molecular diffusivity, cm^2/s
D_e = intraparticle effective diffusivity inside pellet, cm^2/s
$\tilde{D}_e$ = "apparent" intraparticle diffusivity, cm^2/s
F = flow rate in the bottom chamber of diffusion-convection cell, cm^3/s
$G(s)$ = transfer function
k_f = film mass transfer coefficient, cm/s
ℓ = half thickness of the pellet, cm
L = pellet length, cm
M = area of injected tracer peak $(=n/Q)$, mol·s/m^3
m_n = moment of order n
m_o = zero moment, dimensionless
m_{oo} = zero moment, for $\lambda = 0$, dimensionless
n = amount of injected tracer, mol
ΔP = pressure drop across the pellet, g/cm·s^2
Q = flow rate into the top chamber of diffusion-convection cell, cm^3/s
Q_c = convection flow rate through the pellet $(=v_oA)$, cm^3/s
Q_d = diffusion flow rate through the pellet $(=AD_e/L)$, cm^3/s
R = ratio $(=FL/AD_e = F/Q_d)$ between flow rate in bottom chamber and diffusion flow rate through pellet, dimensionless
t = time, s
v_o = intraparticle convective velocity $(=(B_o/\mu L)\Delta P)$, cm/s
V_m = volume of bottom chamber, cm^3
x = reduced axial coordinate in the pellet, dimensionless
z = axial coordinate in the pellet, cm

Greek letters

β = ratio between the volume of bottom chamber and pellet, dimensionless
λ = intraparticle Peclet number $(=v_oL/D_e = \tau_d/\tau_c)$ in diffusion-convection cell, dimensionless
λ' = intraparticle Peclet number $(=v_o\ell/D_e = \lambda/2)$ in chromatography, dimensionless
ϵ_p = pellet porosity
ρ = density of fluid, g/cm^3
τ_d = time constant for intraparticle diffusion $(=\epsilon_pL^2/D_e)$, s
τ_c = time constant for intraparticle convection $(=\epsilon_pL/v_o)$, s
μ = fluid viscosity, g/cm·s
μ_1 = first moment, s
μ_{1o} = first moment for $\lambda = 0$, s

Superscript

$'$ = outlet of the bottom chamber

Literature Cited

Ahn, B., Étude des Charactéristiques Diffusionelles de Transfert de Matière dans un Réacteur Catalytique à Lit Fix d'Oxydation Menagée," Thesis, Univ. Tech. Compiègne (1980).

Al-Rqobah, H., E. Kam, and R. Hughes, "Dynamic Determination of Diffusion in Porous Particles," *Chem. Eng. Res. Dev.*, **66**, 275 (1988).

Baiker, A., M. New, and W. Richarz, "Determination of Intraparticle Diffusion Coefficients in Catalyst Pellet: a Comparative Study of Measuring Methods," *Chem. Eng. Sci.*, **37**(4), 643 (1982).

Burghardt, A., and J. Smith, "Dynamic Response of a Single Catalyst Pellet," *Chem. Eng. Sci.*, **34**, 267 (1979).

Cresswell, D., "Intraparticle Convection: Its Measurement and Effect on Catalyst Activity and Selectivity," *Appl. Cat.*, **15**, 103 (1985).

Cresswell, D., and N. Orr, "Measurement of Binary Diffusion Coefficients Within Porous Catalysts," *Residence Time Distribution Theory in Chemical Engineering*, A. Petho and R. Noble, eds., Verlag (1982).

Do, D. D., and J. M. Smith, "Transient Response of Diffusion Cell Containing a Porous Solid," *Chem. Eng. Sci.*, **39**(12), 1689 (1984).

Dogu, G., and J. Smith, "A Dynamic Method for Catalyst Diffusivities," *AIChE J.*, **21**(1), 58 (1975).

Dogu, G., and J. Smith, "Rate Parameters for Dynamic Experiments With Single Catalyst Pellet," *Chem. Eng. Sci.*, **31**, 123 (1976).

Dogu, T., A. Keskin, G. Dogu, and J. Smith, "Single-Pellet Moment Method for Analysis of Gas-Solid Reaction," *AIChE J.*, **32**(5), 743 (1986).

Dogu, G., A. Pekediz, and T. Dogu, "Dynamic Analysis of Viscous Flow and Diffusion in Porous Solids," *AIChE J.*, **35**(18), 1370 (1989).

Dudukovic, M., "An Analytical Solution for the Transient Response in a Diffusion Cell of the Wicke-Kallenbach Type," *Chem. Eng. Sci.*, **37**(2) 153 (1982).

Fott, P., and G. Petrini, "Determination of Transport Parameters of Porous Catalysts from Permeation Measurements," *Appl. Cat.*, **2**, 367 (1982).

Frost, A. C., "Measurement of Effective Diffusivity from Effluent Concentration of a Flow Through Diffusion Cell," *AIChE J.*, **27**(5), 813 (1981).

Furusawa, T., M. Suzuki, and J. M. Smith, "Rate Parameters in Heterogeneous Catalysis by Pulse Technique," *Cat. Rev. Sci. Eng.*, **13**, 43 (1976).

Gibilaro, L., and S. Waldram, "Measurement of Effective Binary Gas Diffusion Coefficients in Porous Catalysts," *J. Cat.*, **67**, 392 (1981).

Haynes, H. W., "The Experimental Estimation of Catalyst Effective Diffusivity," *Cat. Rev. Sci. Eng.*, **30**(4), 563 (1988).

Nir, A., and L. Pismen, "Simultaneous Intraparticle Forced Convection, Diffusion and Reaction in a Porous Catalyst I," *Chem. Eng. Sci.*, **32**, 35 (1977).

Rodrigues, A. E., Letter to the Editor, *AIChE J.*, **37**, 1117 (1991).

Rodrigues, A. E., B. Ahn, and A. Zoulalian, "Intraparticle-Forced Convection Effect in Catalyst Diffusivity Measurements and Reactor Design," *AIChE J.*, **28**(4), 541 (1982).

Rodrigues, A. E., and R. Ferreira, "Convection, Diffusion and Reaction in Large-Pore Catalysts," *AIChE Symp. Ser.*, **266**(84), 80 (1988).

Rodrigues, A. E., Z. P. Lu, and J. M. Loureiro, "Residence Time Distribution of Inert and Linearly Adsorbed Species in Fixed-Bed Containing 'Large-Pore' Supports: Applications in Separation Engineering," *Chem. Eng. Sci.*, **46**, 2765 (1991a).

Rodrigues, A. E., Z. P. Lu, J. M. Loureiro, and M. D. LeVan, "Pressurization of Adsorption Beds," NSF-CNRS Workshop on Adsorption Processes for Gas Separation, Gif-sur-Yvette, France (1991b).

Suzuki, M., and J. M. Smith, "Dynamic of Diffusion and Adsorption in a Single Catalyst Pellet," *AIChE J.*, **18**(2), 326 (1972).

Wang, C. T., and J. M. Smith, "Tortuosity Factors for Diffusion in Catalysts," *AIChE J.*, **29**(1), 132 (1983).

Manuscript received Jan. 2, 1991, and revision received Nov. 4, 1991.