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Frequency Response Analysis of a Closed Diffusion Cell with Two Resonators

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Abstract. This paper deals with frequency response (FR) analysis of a closed diffusion cell system with two resonators, that is both the LHS and RHS volumes are modulated. The analysis is made for a homogeneous particle described by a single effective diffusivity as well as a biporous pellet described by macropore and micropore diffusions. It is shown that if the perturbation of the volume of the reservoir #2 is lagged behind that of the reservoir #1 by $3\pi/2$, the pressure response in reservoir #1 is significantly enhanced with larger amplitude as well as phase angle. When the perturbations of the two reservoirs are out of phase, the heat effect is reduced and can become insignificant when the two perturbations are completely out of phase ($\psi = \pi$). Under such a condition, the pressure difference between the two reservoirs could be doubled. In the case of biporous pellets, it is shown that the FR behaviours obtained for micropore diffusion control and macropore diffusion control are well distinguished. In the former case, the FR system reduces to a traditional batch adsorber one while in the latter case, the FR behaviour is the same as for a two resonator system with homogeneous particles. This difference can be used for the discrimination of micropore and macropore diffusion processes.

Keywords: frequency response, diffusion cell, kinetics, diffusion, heat effects

Introduction

Knowledge of adsorption dynamics is important in understanding the transport of adsorbates inside a porous medium as well as in the design of large scale adsorbers. This dynamics is a very complex problem as it is affected by the structure of the solid as well as the type of adsorbate used. Since it is an important problem, chemical engineers have utilised a number of techniques to study and measure this adsorption kinetics. One of the most recently introduced methods is the frequency response method. Basically in this method, an initially equilibrated batch adsorber is disturbed by changing the adsorber volume in a periodic manner, usually in the form of a sinusoidal perturbation. The amplitude of the volume perturbation is very small compared to the adsorber volume, and as a result of this, the system can be linearized and the response in pressure will be also periodic with the same frequency as the forcing volume perturbation. It is this pressure response that researchers make use of to extract valuable information about the system dynamics (Jost, 1964; Freet, 1975; Mankin, 1977; Yasuda and Saeki, 1978; Yasuda, 1982; Yasuda and Sugasawa, 1984; Van-Den-Begin and Rees, 1989; Shen and Rees, 1991; Sun and Bourdin, 1993; Sun et al., 1994; Jordi and Do, 1992, 1994).

In our recent paper, we presented a FR method with a closed diffusion cell instead of a batch adsorber (Sun and Do, 1995). The system is composed of a particle bounded by two reservoirs, and once the system is at equilibrium the volume of one reservoir is periodically perturbed and the pressures of the two reservoirs are monitored. We have observed that the information we can gather experimentally is richer than that obtained by using the traditional FR method on a batch adsorber; hence providing a better understanding of the system dynamics.

Along the same line, in this paper we utilise the same closed diffusion cell system, but now we allow the modulation of the two chambers' volume (dual resonators). The perturbations of these two volumes can be in phase or out of phase with each other. We will utilize the out of phase perturbation of the two volumes to achieve the conditions whereby the pressure responses of the two reservoirs can be enhanced. We note here that if the two volume perturbations are exactly in phase with each other and have the same frequency, this operation is identical to the traditional FR method acting on a batch adsorber containing one slab particle. What is interesting in this study is the out of phase property of the two volume perturbations.

Effective diffusion mechanism and heat effects are considered in this work. These are sufficient in this theoretical work to bring out all the features exhibited by the system having dual resonators. The study will cover both a homogeneous particle and a bidispersed porous particle.

Theory

Consider a number of identical porous particles of homogeneous or bi-porous structure bounded by two closed reservoirs (Fig. 1). Initially the volumes of the two reservoirs are maintained at their mean values V_{e1} and V_{e2}, respectively. A dose of pure component adsorbing gas is introduced into the system and sufficient time is allowed to ensure equilibrium is established between the gas phase of the two reservoirs and the particle. The gas phase concentration at equilibrium is C_e and the adsorbed phase concentration at equilibrium is $C_{\mu e}$.

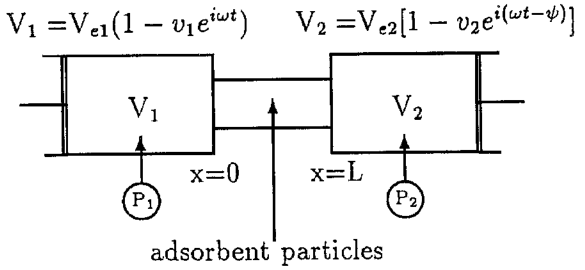


Figure 1. Schematic of a closed diffusion cell with two resonators.

Once the equilibrium is established, the volumes of the reservoirs 1 and 2 are perturbed sinusoidally around their equilibrium values V_{e1} and V_{e2}. These two perturbations are at the same frequency and the volume of the reservoir 2 is perturbed with a phase delay ψ. The volume perturbations can be written in complex notation, such as:

$$V_1 = V_{e1}(1 - v_1 e^{i\omega t}) \tag{1}$$

$$V_2 = V_{e2}\left[1 - v_2 e^{i(\omega t-\psi)}\right] \tag{2}$$

The perturbations in volume (v_1 and v_2) are assumed to be very small to ensure the system linearity. As a consequence, all the system responses (such as the concentrations of the two reservoirs, the adsorbed phase concentration and the particle temperature) are in harmonic with the same frequency as that of the volume perturbations. The volume perturbations are exactly in phase when $\psi = 0$ and exactly out of phase when $\psi = \pi$.

Note that if the relative amplitude of the volume perturbation for the reservoir 2, v_2, is set to be zero, this problem reduces to the diffusion cell FR with a single resonator studied in our previous paper (Sun and Do, 1995). On the other hand, if the two volumes are perturbed exactly in phase ($\psi = 0$) and with the same amplitude ($v_1 = v_2$), the present system reduces to the traditional batch adsorber FR system with diffusion length being half of the particle length. The objective of this paper is to determine optimal conditions for the perturbations of the two reservoirs such that the pressure responses in the two reservoirs could be enhanced.

The model development will be based on the following assumptions:

1. Mass transfer inside the particle is described by the simple Fickian diffusion.
2. There is no any surface barrier on the particle surfaces, that is the equilibrium is instantaneously attained on the surfaces.
3. The temperatures in the two reservoirs are assumed to be constant.
4. The system is linear as a result of very small perturbations.

FR Solution for a Homogeneous Particle

The mass balance in the particle is given by a single diffusion equation:

$$\frac{\partial \Delta C_\mu}{\partial t} = D_\mu \frac{\partial^2 \Delta C_\mu}{\partial x^2} \tag{3}$$

where C_μ is the adsorbed concentration in the particle and D_μ is the effective diffusivity.

The adsorbed concentrations at the boundaries are in equilibrium with the corresponding gas phase concentrations C_1 and C_2 and given by the following linearized adsorption isotherm:

$$\Delta C_\mu|_{x=0} = K_C \Delta C_2 - K_T \Delta T \tag{4}$$

$$\Delta C_\mu|_{x=L} = K_C \Delta C_1 - K_T \Delta T \tag{5}$$

where the equilibrium parameters K_C and K_T represent the slopes of the adsorption equilibrium, respectively, evaluated at the equilibrium values (C_e, T_e); ΔC_μ, ΔC and ΔT are the differential quantities with respect to the equilibrium values.

Assuming that the temperature is uniform inside the particle, the heat balance in the particle is:

$$C_S \frac{d\Delta T}{dt} = -ha_p \Delta T + (-\Delta H) \frac{d\overline{\Delta C_\mu}}{dt} \tag{6}$$

where C_S is the volumetric heat capacity of the particle, h is the heat transfer coefficient between the particle and its surroundings, a_p is the external heat exchange surface area per unit particle volume, and ΔH is the heat of adsorption. $\overline{\Delta C_\mu}$ represents the volumetric average concentration in the particle:

The mass balances for the two reservoirs are:

$$\frac{d(C_1 V_1)}{dt} = -\frac{V_s}{L} D_\mu \left.\frac{\partial \Delta C_\mu}{\partial x}\right|_{x=L} \tag{7}$$

$$\frac{d(C_2 V_2)}{dt} = \frac{V_s}{L} D_\mu \left.\frac{\partial \Delta C_\mu}{\partial x}\right|_{x=0} \tag{8}$$

where V_s is the volume of the porous particle and L is the length of the particle. Linearising the products of the pressures and volumes in the above equations, we get:

$$\frac{d\Delta C_1}{\partial t} + \beta_1 \frac{D_\mu}{K_C L} \left.\frac{\partial \Delta C_\mu}{\partial x}\right|_{x=L} = v_1 C_e i\omega e^{i\omega t} \tag{9}$$

$$\frac{d\Delta C_2}{dt} - \beta_2 \frac{D_\mu}{K_C L} \left.\frac{\partial \Delta C_\mu}{\partial x}\right|_{x=0} = v_2 C_e i\omega e^{i(\omega t - \psi)} \tag{10}$$

in which we have used Eqs. (1) and (2). Here β_1 and β_2 are nondimensional capacity parameters, defined as:

$$\beta_1 = \frac{V_s K_C}{V_{e1}}; \qquad \beta_2 = \frac{V_s K_C}{V_{e2}} \tag{11}$$

The parameter β_1 is simply the ratio of the amount adsorbed in the particle at equilibrium to the equilibrium amount in the RHS reservoir. Similarly, the parameter β_1 is the ratio of the amount adsorbed in the particle at equilibrium to the equilibrium amount in the LHS reservoir. When $V_{e2} = 0$ (that is $\beta_2 \to \infty$), the diffusion cell system is reduced to the traditional batch adsorber system with particle having slab geometry.

The solution procedure of the above system is the same as that used in our previous paper dealing with a single resonator (Sun and Do, 1995). Therefore, only the final solutions are given here.

The periodic steady state solutions for the concentrations in the two reservoirs are:

$$\Delta C_1 = \frac{v_1[\beta_2 + i\omega t_d(\delta_c - i\delta_s) + F_T] + \beta_1 v_2 e^{-i\psi}(b + G_T)}{\beta_1 + \beta_2 + \beta_1\beta_2(\delta_c - i\delta_s) + i\omega t_d(\delta_c - i\delta_s) + Q_T} \times C_e e^{i\omega t} \tag{12}$$

$$\Delta C_2 = \frac{v_2[\beta_1 + i\omega t_d(\delta_c - i\delta_s) + E_T] + \beta_2 v_1 e^{i\psi}(b + G_T)}{\beta_1 + \beta_2 + \beta_1\beta_2(\delta_c - i\delta_s) + i\omega t_d(\delta_c - i\delta_s) + Q_T} \times C_e e^{i(\omega t - \psi)} \tag{13}$$

where t_d is the time constant for diffusion defined as L^2/D_μ and

$$b = \frac{1}{\cosh[(1+i)\lambda]} \quad (\lambda = \sqrt{\omega t_d/2})$$

$$\delta_c - i\delta_s = \frac{\sinh 2\lambda + \sin 2\lambda}{2\lambda(\cosh 2\lambda + \cos 2\lambda)} - i\frac{\sinh 2\lambda - \sin 2\lambda}{2\lambda(\cosh 2\lambda + \cos 2\lambda)}$$

$$E_T = H_T[\beta_1(\delta_c - i\delta_s) + 2(1-b)];$$

$$F_T = H_T[\beta_2(\delta_c - i\delta_s) + 2(1-b)]$$

$$G_T = H_T(\delta_c - i\delta_s);$$

$$Q_T = H_T[(\beta_1 + \beta_2)(\delta_c - i\delta_s) + 2(1-b)]$$

$$H_T = \gamma \frac{i\omega t_h}{1 + i\omega t_h}$$

The functions δ_c and δ_s represent the FR characteristics for a pure diffusion process in the adsorbent particles.

The solution for the particle temperature is:

$$\Delta T = \frac{K_C H_T(1-b)}{K_T[i\omega t_d(\delta_c - i\delta_s) + 2H_T(1-b)]} \times (\Delta C_1 + \Delta C_2) \tag{14}$$

The adsorbed phase concentration is given by:

$$\begin{aligned}\Delta C_\mu = {} & (K_C\Delta C_1 - K_T\Delta T)\frac{\sinh\left[(1+i)\lambda\frac{x}{L}\right]}{\sinh[(1+i)\lambda]} \\ & + (K_C\Delta C_2 - K_T\Delta T) \\ & \times \left\{\cosh\left[(1+i)\lambda\frac{x}{L}\right] - \frac{\sinh\left[(1+i)\lambda\frac{x}{L}\right]\cosh\left[(1+i)\lambda\right]}{\sinh[(1+i)\lambda]}\right\}\end{aligned} \tag{15}$$

The volumetric average concentration is:

$$\Delta\bar{C}_\mu = \frac{\cosh[(1+i)\lambda] - 1}{(1+i)\lambda \sinh[(1+i)\lambda]}(K_C\Delta C_1 - K_T\Delta T + K_C\Delta C_2 - K_T\Delta T) \tag{16}$$

In the above equations, t_h is the time constant for the heat exchange and γ is a non-dimensional thermal parameter describing the nonisothermality of the system:

$$t_h = \frac{C_S}{ha_p}; \qquad \gamma = \frac{(-\Delta H)K_T}{C_S} \tag{17}$$

The larger are these thermal parameters, t_h and γ, the more important will be the heat effect. If one of these two parameters is equal to zero, the system will be isothermal.

We can see that the solutions for ΔC_1 and ΔC_2 (Eqs. 12 and 13) can be interchanged by swapping the indexes 1 and 2 and by changing ψ to $-\psi$ as one would expect physically. By setting v_2 to zero, that is for a single resonator FR system, the solutions given by Equations 12 and 13 reduce to those given in our previous paper (Sun and Do, 1995). On the other hand, if the volume of the reservoir 2 is infinitely small (that is $\beta_2 = \infty$), the resulting solution reduces to that for a batch adsorber FR system (Sun and Bourdin, 1993):

$$\Delta C_1 = \frac{1 + H_T(\delta_c - i\delta_s)}{1 + (\beta_1 + H_T)(\delta_c - i\delta_s)} v_1 C_e e^{i\omega t} \tag{18}$$

The difference in concentration between the two reservoirs, which can be directly measured experimentally using a differential pressure transducer, is obtained from Eqs. (12) and (13):

$$\begin{aligned}C_1 - C_2 &= \frac{(\beta_2 v_1 - \beta_1 v_2 e^{-i\psi})(1-b) + (v_1 - v_2 e^{-i\psi})[i\omega t_d(\delta_c - i\delta_s) + 2H_T(1-b)]}{\beta_1 + \beta_2 + \beta_1\beta_2(\delta_c - i\delta_s) + i\omega t_d(\delta_c - i\delta_s) + Q_T} \\ &\quad \times C_e e^{i\omega t}\end{aligned} \tag{19}$$

If the two reservoirs have identical volumes and relative amplitudes of modulation, that is $v_1 = v_2 = v$ and $\beta_1 = \beta_2 = \beta$, Eq. (19) is reduced to:

$$\begin{aligned}C_1 - C_2 &= (1 - e^{-i\psi}) \\ &\quad \times \frac{\beta(1-b) + [i\omega t_d(\delta_c - i\delta_s) + 2H_T(1-b)]}{\beta_1 + \beta_2 + \beta_1\beta_2(\delta_c - i\delta_s) + i\omega t_d(\delta_c - i\delta_s) + Q_T} \\ &\quad \times vC_e e^{i\omega t} \\ &= (1 - e^{-i\psi})(C_1 - C_2)|_{\text{single resonator}}\end{aligned} \tag{20}$$

where $(C_1 - C_2)|_{\text{single resonator}}$ is the differential concentration obtained with a single resonator case where one of the two volumes are kept constant. When the perturbations of the two reservoirs are in phase ($\psi = 0$), the differential concentration is equal to zero due to the symmetry. On the other hand, when the volume perturbations are out of phase ($\psi = \pi$), the differential concentration with two resonators behaves exactly as for the system having a single resonator except that its amplitude is twice larger.

The in-phase and out-of-phase components for the RHS and LHS concentration responses are based on their own volume perturbations and defined as the real and imaginary parts of the RHS terms of the following equations:

$$\frac{v_1 C_e}{|\Delta C_1|}e^{-i\varphi_1} - 1 = \beta_1 \frac{1 + \beta_2(\delta_c - i\delta_s) + G_T - \frac{v_2}{v_1}e^{-i\psi}(b + G_T)}{\beta_2 + i\omega t_d(\delta_c - i\delta_s) + F_T + \beta_1\frac{v_2}{v_1}e^{-i\psi}(b + G_T)} \tag{21}$$

$$\frac{v_2 C_e}{|\Delta C_2|}e^{-i(\psi + \varphi_2)} - 1 = \beta_2 \frac{1 + \beta_1(\delta_c - i\delta_s) + G_T - \frac{v_1}{v_2}e^{i\psi}(b + G_T)}{\beta_1 + i\omega t_d(\delta_c - i\delta_s) + E_T + \beta_2\frac{v_1}{v_2}e^{i\psi}(b + G_T)} \tag{22}$$

where $|\Delta C_1|$ and $|\Delta C_2|$, φ_1 and φ_2, are the amplitudes and the phase angles of ΔC_1 and ΔC_2, respectively.

In the limit of low frequencies, the perturbation is much slower than the mass transfer dynamics; hence the system is always under quasi-equilibrium conditions, that is the concentrations in the two reservoirs are in phase with the volume perturbations:

$$\lim_{\omega\to 0}\Delta C_1=\lim_{\omega\to 0}\Delta C_2=\frac{C_e\left(\frac{v_1}{\beta_1}+\frac{v_2}{\beta_2}e^{-i\psi}\right)}{1+\frac{1}{\beta_1}+\frac{1}{\beta_2}} \tag{23}$$

The corresponding amplitudes and phase angles at zero frequency are explicitly written as:

$$\lim_{\omega\to 0}|\Delta C_1|=\lim_{\omega\to 0}|\Delta C_2| = C_e\frac{\sqrt{\left(\frac{v_1}{\beta_1}\right)^2+\left(\frac{v_2}{\beta_2}\right)^2+2\frac{v_1v_2}{\beta_1\beta_2}\cos\psi}}{1+\frac{1}{\beta_1}+\frac{1}{\beta_2}} \tag{24}$$

$$\lim_{\omega\to 0}\tan\varphi_1=\lim_{\omega\to 0}\tan\varphi_2=-\frac{\frac{v_2}{\beta_2}\sin\psi}{\frac{v_1}{\beta_1}+\frac{v_2}{\beta_2}\cos\psi} \tag{25}$$

It can be seen that when $\psi=0$, that is the perturbations of the two reservoirs are in phase, the amplitudes of ΔC_1 and ΔC_2 at low frequencies attains the maximum but the phase angles approach zero. On the other hand, the phase angles can attain the maximum when the perturbations are out of phase ($\psi=\pi$), but in this case the amplitudes of the concentrations get the minimum value.

At very high frequencies, the perturbation is too fast for the mass transfer to occur into the particle. Therefore, the concentrations in the reservoirs respond directly in phase with the volume perturbations as if there is no particle in the system:

$$\lim_{\omega\to\infty}|\Delta C_1|=v_1C_e;\quad \lim_{\omega\to\infty}\varphi_1=0 \tag{26}$$

$$\lim_{\omega\to\infty}|\Delta C_2|=v_2C_e;\quad \lim_{\omega\to\infty}\varphi_2=-\psi \tag{27}$$

At very low frequencies, the amplitude of the differential concentration (C_1-C_2) tends to zero and the corresponding phase angle has the following limiting value:

$$\lim_{\omega\to 0}(\tan\varphi_{12})=-\tan\frac{\psi}{2}+\left[1-\frac{v_1(2+\beta_2)}{v_2(2+\beta_1)}\right]\frac{1}{\sin\psi} \tag{28}$$

In particular, for a completely symmetrical system ($\beta_1=\beta_2$ and $v_1=v_2$), we have:

$$\lim_{\omega\to 0}\varphi_{12}=\pi-\frac{\psi}{2} \tag{29}$$

The asymptotic values at very high frequencies are given by:

$$\lim_{\omega\to\infty}(|C_1-C_2|)=C_e\sqrt{v_1^2+v_2^2-2v_1v_2\cos\psi} \tag{30}$$

$$\lim_{\omega\to\infty}\tan\varphi_{12}=\frac{\sin\psi}{\frac{v_1}{v_2}-\cos\psi} \tag{31}$$

FR Solution for a Bi-Porous Pellet

For simplicity, we assume here that the temperature is uniform in the pellet, that is the heat conductivity of the pellet is assumed to be very large.

Mass balance in the crystals:

$$\frac{\partial\Delta C_\mu}{\partial t}=\frac{D_\mu}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\Delta C_\mu}{\partial r}\right) \tag{32}$$

$$\left.\frac{\partial\Delta C_\mu}{\partial r}\right|_{r=0}=0 \tag{33}$$

$$\Delta C_\mu|_{r=R}=K_c\Delta C_p-K_T\Delta T \tag{34}$$

where C_p is the gas phase concentration in the macropores and R is the radius of the crystals.

Mass balance in the macropores:

$$\frac{\partial\Delta C_p}{\partial t}+\frac{1-\epsilon}{\epsilon}\frac{\partial\overline{\Delta C}_\mu}{\partial t}=D_p\frac{\partial^2\Delta C_p}{\partial x^2} \tag{35}$$

$$\Delta C_p|_{x=0}=\Delta C_2 \tag{36}$$

$$\Delta C_p|_{x=L}=\Delta C_1 \tag{37}$$

where D_p is an effective coefficient accounting for the Knudsen diffusion and/or the viscous flow in the macropores.

The heat balance in the pellet:

$$C_S\frac{d\Delta T}{dt}-(1-\epsilon)|\Delta H|\frac{d\overline{\overline{\Delta C}}_\mu}{dt}=-ha_p\Delta T \tag{38}$$

where $\overline{\overline{\Delta C}}_\mu$ represents the total amount adsorbed in the pellet.

The mass balances for the gas phase in two reservoirs are:

$$\frac{d\Delta C_1}{dt}+\frac{V_s}{V_{e1}L}D_p\frac{\partial \Delta C_p}{\partial x}\bigg|_{x=L}=v_1C_ei\omega e^{i\omega t} \tag{39}$$

$$\frac{d\Delta C_2}{dt}-\frac{V_s}{V_{e2}L}D_p\frac{\partial \Delta C_p}{\partial x}\bigg|_{x=0}=v_2C_ei\omega e^{i(\omega t-\psi)} \tag{40}$$

The solution of frequency response is given by:

$$\Delta C_1 = \frac{v_1[\alpha_2 f_1+i\omega t_{dp}f_1d_1-H_T(2-2W+\alpha_2f_1d_1)]+\alpha_1f_1v_2e^{-i\psi}(W-H_Td_1)}{(\alpha_1+\alpha_2)f_1+i\omega t_{dp}f_1d_1+\alpha_1\alpha_2f_1^2d_1-H_T[2-2W+(\alpha_1+\alpha_2)f_1d_1]}\times C_ee^{i\omega t} \tag{41}$$

$$\Delta C_2 = \frac{v_1\alpha_2f_1(W-H_Td_1)+v_2e^{-i\psi}[\alpha_1f_1+i\omega t_{dp}f_1d_1-H_T(2-2W+\alpha_1f_1d_1)]}{(\alpha_1+\alpha_1)f_1+i\omega t_{dp}f_1d_1+\alpha_1\alpha_2f_1^2d_1-H_T[2-2W+(\alpha_1+\alpha_2)f_1d_1]}\times C_ee^{i\omega t} \tag{42}$$

where $t_{dp}=L^2/D_p$ and the equilibrium constants are defined as:

$$\alpha_1=\frac{\epsilon V_s}{V_{e1}};\quad \alpha_2=\frac{\epsilon V_s}{V_{e2}};\quad K=\frac{1-\epsilon}{\epsilon}K_C;$$
$$\gamma=\frac{(1-\epsilon)|\Delta H|}{C_S}K_T \tag{43}$$

The other variables are given by:

$$\delta_c-i\delta_s=\frac{3(\sinh 2\lambda-\sin 2\lambda)}{2\lambda(\cosh 2\lambda-\cos 2\lambda)}-\frac{3}{2\lambda}\left[\frac{\sinh 2\lambda+\sin 2\lambda}{\cosh 2\lambda-\cos 2\lambda}-\frac{1}{\lambda}\right]\quad\left(\lambda=\sqrt{\frac{\omega R^2}{2D_\mu}}\right)$$

$$H_T=\frac{i\omega t_h(\delta_c-i\delta_s)\gamma K_C f_2}{f_1K_T+i\omega t_h[f_1K_T+\gamma(\delta_c-i\delta_s)(f_1K_T+f_2K_C)]}$$

$$f_1=1+K(\delta_c-i\delta_s);\quad f_2=-K\frac{K_T}{K_C}(\delta_c-i\delta_s)$$

$$\lambda_1=\sqrt{\frac{\omega t_{dp}f_1}{2}};\quad W=\frac{1}{\cosh[(1+i)\lambda_1]}$$

$$d_1=\frac{\sinh 2\lambda_1+\sin 2\lambda_1-i(\sinh 2\lambda_1-\sin 2\lambda_1)}{2\lambda_1(\cosh 2\lambda_1+\cos 2\lambda_1)}$$

Results and Discussion

FR Analysis for a Homogeneous Particle

As explained earlier, the two resonator FR system can reduce to a batch adsorber FR system when the volume of one reservoir becomes very small. This transition is shown in Fig. 2 wherein the normalised amplitude and the phase angle of ΔC_1 are plotted for a lagged in phase perturbation ($\psi=\frac{3}{4}\pi$). It can be seen that the smaller the volume of the reservoir 2 (that is the larger β_2), the larger the amplitude of ΔC_1 at low frequencies but the smaller the magnitude of the phase angle. As the volume V_{e2} decreases to zero, the concentration response approaches that given by the batch adsorber FR system ($\beta_2=\infty$). On the other hand, if one keeps constant the mean volumes of the reservoirs (V_{e1} and V_{e2}) but decreases gradually the relative amplitude of the perturbation of the reservoir 2, v_2, the behaviour of the system approaches that of the single resonator FR system, as shown in Fig. 3.

One of the major concerns in the FR techniques is how to get accurate experimental FR data. The accuracy of FR data is essentially determined by the magnitudes of both the amplitude and the phase angle of the pressure response. The larger the amplitude and the phase angle, the more accurate the experimental FR data. In a traditional batch adsorber FR, however, the phase angle of the pressure response is generally very small. This is shown in Fig. 4 wherein the amplitude and phase angle of the concentration ΔC_1 are plotted for $\beta_1=2$ under isothermal conditions. Also are plotted the concentration response in the modulating

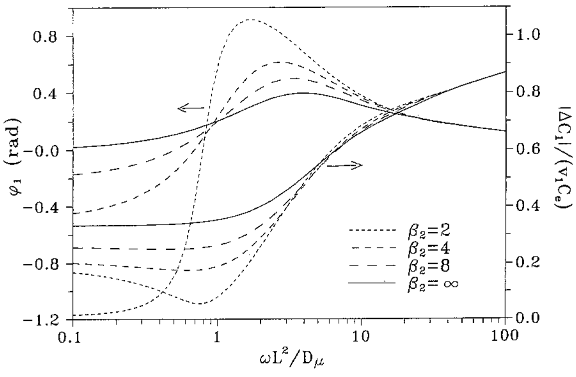


Figure 2. Effect of the volume of the reservoir 2 on the amplitude and phase angle of C_1 with $\psi=\frac{3}{4}\pi$, $\beta_1=2$ and $v_1=v_2=0.02$. $\beta_2=\infty$ corresponds to the batch adsorber FR system. The isothermal condition is assumed here as for Figs. 2–6.

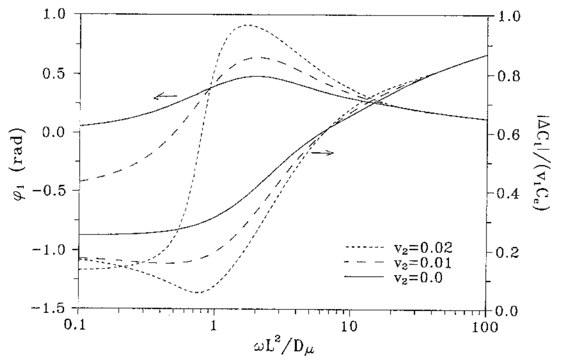


Figure 3. Effect of the relative amplitude of volume perturbation of the reservoir 2 on the amplitude and phase angle of C_1 with $\psi = \frac{3}{4}\pi$, $\beta_1 = \beta_2 = 2$ and $v_1 = 0.02$. $v_2 = 0$ corresponds to the single resonator diffusion cell FR system.

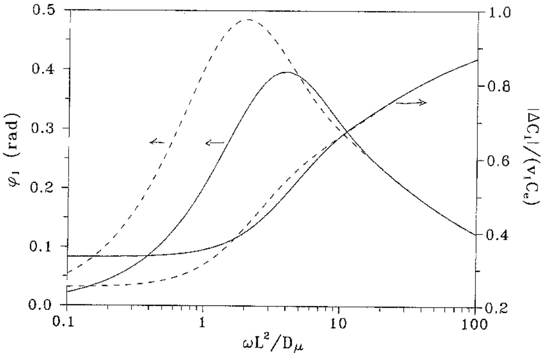


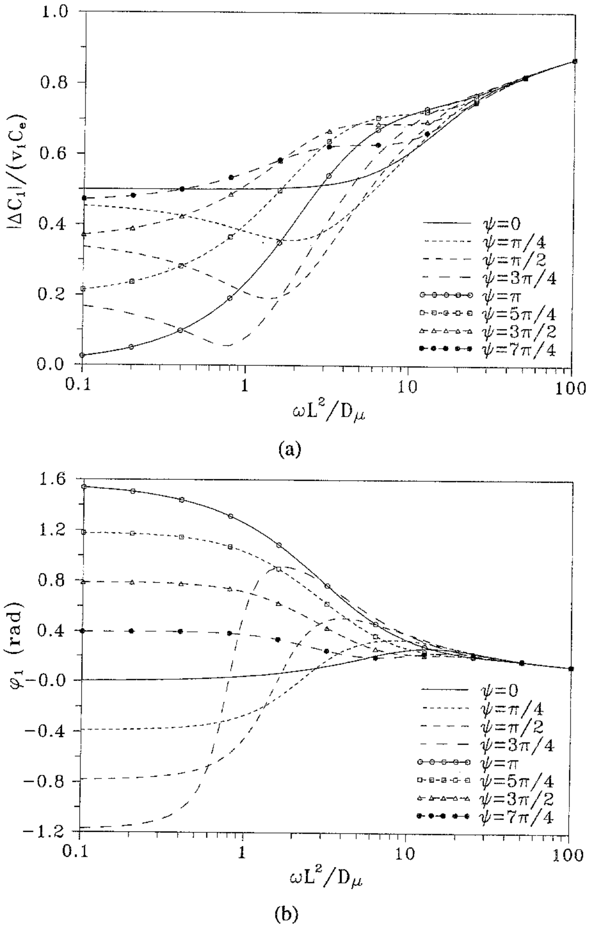
Figure 4. Amplitudes and phase angles of the concentration in the modulating volume for a batch adsorber FR (solid lines) and a diffusion cell FR with one single resonator (dashed lines). Simulations are made under isothermal conditions using $\beta_1 = 2$) and $\beta_2 = 2$ for the diffusion cell FR.

reservoir for a single resonator diffusion cell FR system obtained with $\beta_1 = \beta_2 = 2$. We can see that the phase angle of the concentration response for the batch adsorber FR is very small and its maximum value occurring at the resonant frequency does not exceed $\frac{\pi}{8}$. In the case of single resonator diffusion cell FR, the magnitude of the phase angle is slightly larger but still less than $\frac{\pi}{6}$. As a result, it would be difficult to determine accurately experimental FR data.

We will now investigate whether the concentration responses can be further enhanced by using two resonators, where the phase delay between the two volume perturbations, ψ, will be the key parameter in dictating the FR response. Here we will study only the concentration response in one reservoir and the differential response between the two reservoirs. The analysis of the other reservoir response is not necessary as a result of the symmetry between the two reservoirs. Moreover, to better understand the contributions of mass and heat transfers separately, only the isothermal case is first studied. The effect of heat transfer is then analyzed to show how heat transfer would alter the FR of the mass transfer.

Effect of ψ on the Concentration Response C_l

In Fig. 5, we plot the normalised amplitudes and phase angles of ΔC_1 obtained with different values of the phase delay between the two volume perturbations for two identical reservoirs ($\beta_1 = \beta_2 = 2$, $v_1 = v_2 = 0.02$). The values of ψ vary from 0 to 0.75π giving in phase perturbations (lagged if $\psi > 0$), and from π to 1.75π giving out of phase perturbations (lagged if $\psi > \pi$).



(a)

(b)

Figure 5. Amplitudes (a) and phase angles (b) of C_1 for different values of ψ for two identical reservoirs ($\beta_1 = \beta_2 = 2$ and $v_1 = v_2 = 0.02$).

1. *In Phase Perturbation ($\psi = 0$).* The system is symmetrical and can be divided into two identical FR systems which are equivalent to a batch adsorber FR with diffusion path being half of the particle length and with half of the particle volume. The amplitude of the concentration response at low frequencies is relatively large as a result of a smaller particle volume. Moreover, it is noted that the variations of the FR are shifted towards higher frequencies due to a shorter diffusion path.
2. *Out of Phase Perturbation ($\psi = \pi$).* In this case, we can readily obtain from Eqs. 12, 13, 14 and 16:

$$\Delta C_1 + \Delta C_2 = \Delta T = \Delta \bar{C}_\mu = 0$$
$$(\text{with} \quad \beta_1 = \beta_2;\ v_1 = v_2) \tag{44}$$

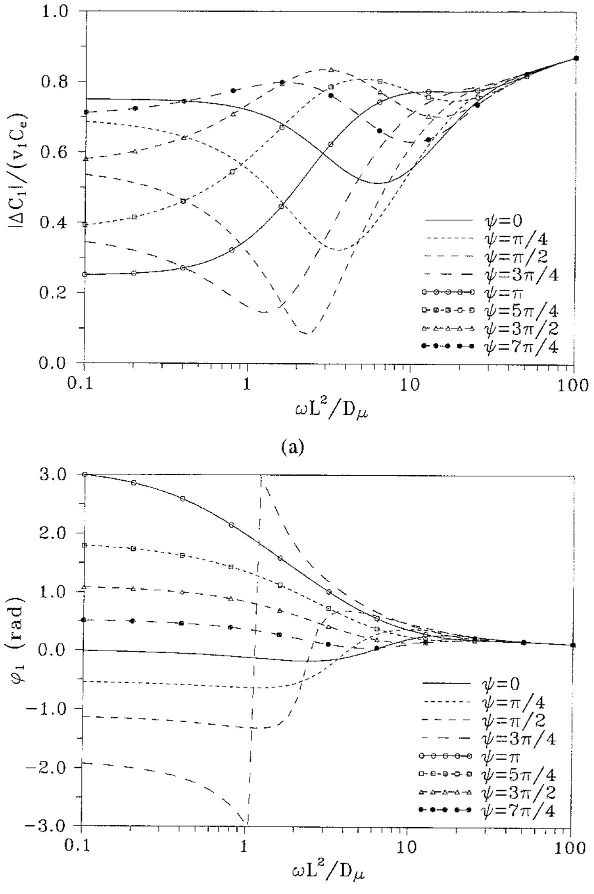
   This means that with the out of phase perturbation, the variations of the gas concentrations in the two reservoirs have opposite behaviour; the amount of adsorbate coming out of the particle into one reservoir is exactly the same as that diffusing into the particle from the other reservoir. The total amount adsorbed in the particle remains constant (Eq. 44) and therefore no temperature change occurs in the particle. At very low frequencies, the amount of mass adsorbed or desorbed by the particle can exactly compensate the concentration changes in the reservoirs caused by the volume variations. Therefore, the amplitude of the concentration response is equal to zero (Fig. 5a). As the frequency increases, the diffusional resistances in the particle become larger and the mass exchanged between the particle and the reservoirs is smaller, leading to the increase of the amplitude up to 1 at very high frequencies (Fig. 5a). On the other hand, the phase angle decreases continuously with the frequency from $\frac{\pi}{2}$ at zero frequency to 0 at very high frequencies (Fig. 5b).
3. *Lagged in Phase Perturbations ($0 < \psi < \pi$).* We have shown in the last two paragraphs that the in phase perturbation leads to the largest amplitude at low frequencies while the out of phase perturbation yields the smallest one. As a consequence, as the phase delay between the two reservoir perturbations, ψ, is increased from zero to π, the system exhibits a behaviour more toward the out of phase behaviour with smaller amplitudes at low frequencies. As the frequency increases, the amplitude decreases first with the frequency and attains a local minimum before increasing with the frequency. This behaviour can be qualitatively explained as follows. As the frequency increases, the diffusional resistances in the particle become larger. This increase of the diffusional resistances alters mostly the mass transfer due to the volume change of the remote reservoir, V_2, as the adsorbate must pass through the particle to get to the reservoir V_1. As a result, the mass transfer from the remote reservoir is delayed, leading to the decrease in the amplitude. As the frequency increases further, the mass transfer inside the particle becomes too slow for both sides, leading to the amplitude increase.

   The behaviour of the phase angle can be observed from Fig. 5b. The response of ΔC_1 is lagged at low frequencies (that is $\varphi_1 < 0$) and becomes in advance with respect to the volume perturbation at high frequencies. At low frequencies, the larger the phase delay of the volume perturbation of the reservoir 2, the larger the magnitudes of the phase angle φ_1.
4. *Lagged out of Phase Perturbations ($\pi < \psi < 2\pi$).* When ψ increases from π to 2π, the perturbations become more and more in phase and therefore the amplitude increases continuously with the frequency. In the intermediate range of frequency, the concentration amplitudes are larger than those given by the in-phase perturbations. The phase angle, φ_1, remains always positive, meaning that the response of ΔC_1 is always in advance with respect to the volume perturbation. Furthermore, it can be seen that the phase angle of ΔC_1 increases with the phase delay of the reservoir 2.

As can be seen from Fig. 5, the phase delay between two volume perturbations, ψ, has generally opposite effects on the amplitude $|\Delta C_1|$ and the phase angle φ_1 both at low and high frequencies. For example, the out of phase perturbation ($\psi = \pi$) gives the largest phase angle and the smallest amplitude at low frequencies. However, the enhancement of both the amplitude and the phase angle can be achieved at intermediate frequencies, in particular with out of phase perturbations ($\psi > \pi$). This feature is interesting since it is in this range where the mass transfer mostly affects the FR characteristics. From the comparison of Fig. 5 and Fig. 4 which shows the concentration response obtained for a traditional batch adsorber FR system, we can easily see that the two resonator FR system can give considerably enhanced concentration response when volume perturbations are made such that the phase delay between the volume perturbations, ψ, is around

$\frac{3}{2}\pi$. In this case, both the amplitude and the phase angle are significantly larger. Another point which can be noted from this comparison is that with perturbations of the two volumes, the frequency range wherein the FR varies as a result of transfer resistances is widened, particularly towards to lower frequencies.

In the case of two identical reservoirs, the out of phase perturbations with ψ near π give largest phase angles, as can be seen from Fig. 5b. However, the corresponding amplitudes are very small at relatively low frequencies and tend to zero at very slow frequencies as a result of the symmetry between the two reservoirs. This undesirable feature can be avoided by using two reservoirs having different volumes and/or different relative amplitudes of volume modulation. In Fig. 6 are plotted the amplitudes and the phase angles of C_1 calculated with two equal volumes ($\beta_1 = \beta_2 = 2$) but different relative amplitudes of modulation ($v_1 = 0.02$ and $v_2 = 0.04$). The behaviour is qualitatively similar to the previous results with two identical reservoirs but the magnitudes of the amplitude and the phase angle are significantly larger than those obtained with two identical reservoirs. For example, the out of phase perturbation ($\psi = \pi$) gives very large phase angles (π at zero frequency) and the pressure amplitude has a minimum normalised value of 0.25 which is quite acceptable. If larger amplitudes of the concentration response are preferred, we can use a lagged out of phase perturbation. As an example, the case of $\psi = \frac{5}{4}\pi$ leads to a minimum value of 0.4 for the normalised amplitude and the corresponding phase angle is still quite large ($> \pi/2$ at low frequencies). Note that with the difference in the magnitude of volume perturbation of the two reservoirs, the case $\psi = 0$ is no longer equivalent to a batch adsorber FR system as a result of system asymmetry.



(a)

(b)

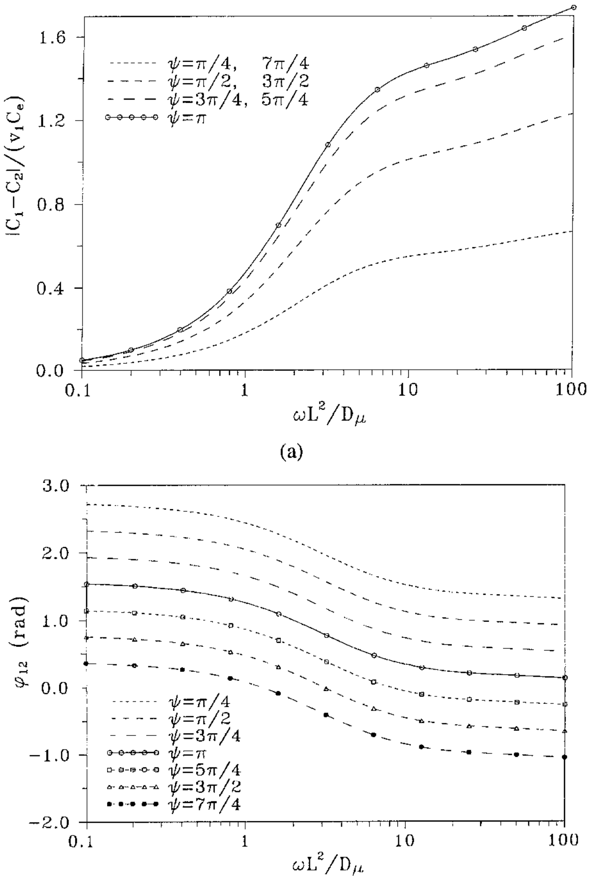
Figure 6. Amplitudes (a) and phase angles (b) of C_1 for different values of ψ for two different reservoirs ($\beta_1 = \beta_2 = 2$ and $v_1 = 0.02$, $v_2 = 0.04$).

Effect of ψ on the Differential Response $C_1 - C_2$

Another variable which can be practically monitored is the pressure difference between the two reservoirs. This differential pressure can be easily measured experimentally using a differential transducer. The response of the pressure difference for the present two resonator system is very similar to that of the single resonator FR system when the two reservoirs are identical (Eq. 22). In particular, when the two volume perturbations are exactly out of phase ($\psi = \pi$), the responses in the two cases are the same except that the magnitude of the amplitude is twice larger for a two resonator system. The response of the differential concentration with different phase delays for the volume perturbations is plotted in Fig. 7 for the case of two identical reservoirs. When the volume perturbations are in phase ($\psi = 0$), the amplitude of the differential pressure is equal to zero. Note also that, as a result of the symmetry between the two reservoirs, the amplitude is the same for in phase and out of phase perturbations with complementary angles, that is $\frac{1}{4}\pi$ and $\frac{7}{4}\pi$; $\frac{1}{2}\pi$ and $\frac{3}{2}\pi$ and $\frac{3}{4}\pi$ and $\frac{5}{4}\pi$. We can see that the in phase perturbations with $\psi = \sim\pi$ give mostly desirable results for the differential response $C_1 - C_2$.

Effect of Heat Transfer

Periodic adsorption and desorption cause inevitably the particle temperature to vary; the temperature change



(a)

(b)

Figure 7. Amplitudes (a) and phase angles (b) of the differential response $C_1 - C_2$ with different values of ψ in the case of two identical reservoirs ($\beta_1 = \beta_2 = 2$ and $v_1 = v_2 = 0.02$).

affects in turn the amount adsorbed or desorbed in the particle and thus the concentration responses in the reservoirs. The larger is the amount of adsorbate adsorbed or desorbed by the particle, the larger will be the temperature variations. In Fig. 8 is plotted the amplitude of the particle temperature for different values of the phase delay between the volume perturbations, ψ. When the volume perturbations are in phase ($\psi = 0$), the change in the total amount adsorbed by the particle is the largest, leading to the largest temperature variation. As the phase delay ψ increases, that is the volume perturbations are more and more out of phase, the amount adsorbed in the particle decreases and the temperature variation also decreases. When the volume perturbations are exactly out of phase ($\psi = \pi$), there is no change in the total adsorbed amount in the particle and therefore the temperature remains to be constant. In this case, the system is isothermal.

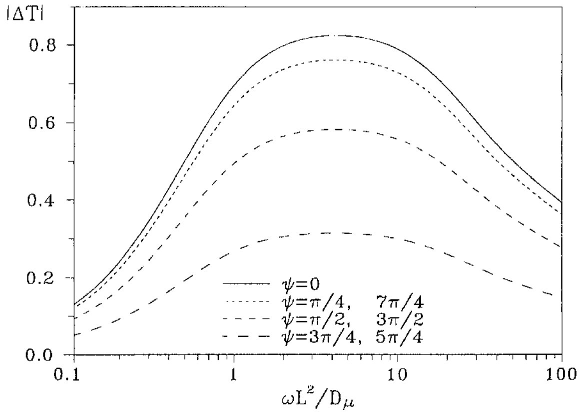
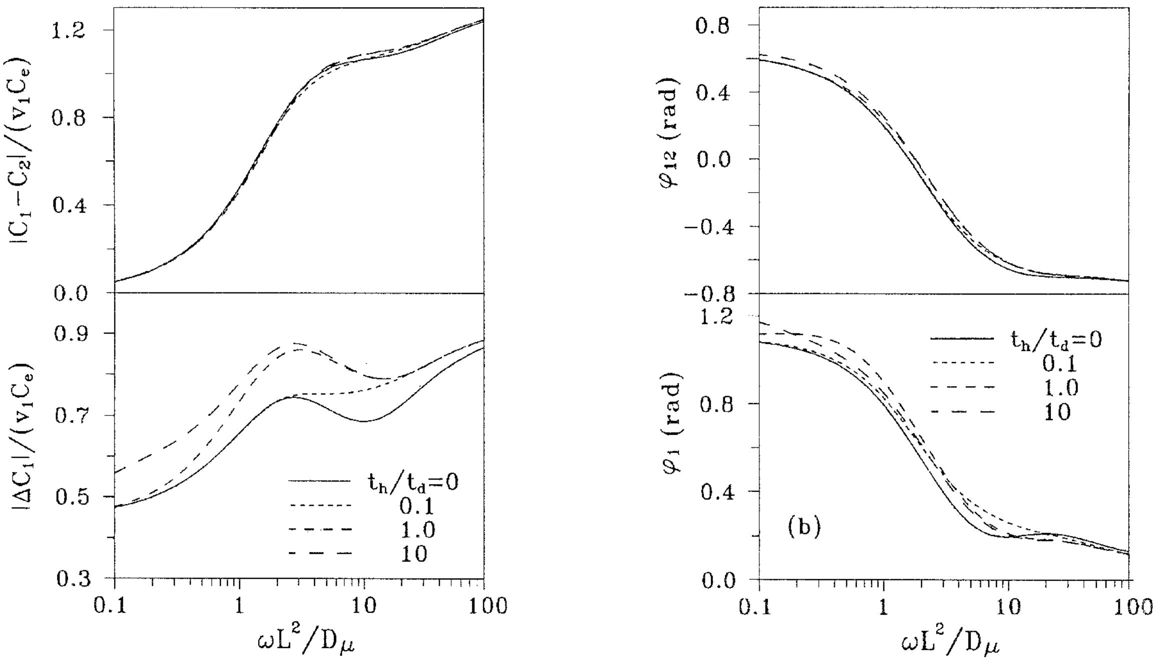


Figure 8. Amplitude of the particle temperature, ΔT, for different values of ψ in the case of two identical reservoirs ($\beta_1 = \beta_2 = 2$ and $v_1 = v_2 = 0.02$). The values of the thermal parameters used were $\gamma = 1$ and $t_h = 1$.

To show the heat effect on the concentration responses, we plot the response of ΔC_1 and $C_1 - C_2$ in Fig. 9 for a phase delay of $\psi = \frac{3}{2}\pi$ under the non-isothermal condition. The curves were obtained using two different reservoirs $\beta_1 = 1$, $\beta_2 = 2$, $v_1 = v_2 = 0.02$ and $\gamma = 1$. Since a temperature variation always tends to decrease the mass exchange between the particle and reservoirs, the magnitudes of ΔC_1's amplitude become larger when the heat transfer is slower (that is t_h is larger). We can observe that the heat effect is significant on the absolute concentration response ΔC_1 but this effect is much smaller on the differential response $C_1 - C_2$. For two identical reservoirs, $C_1 - C_2$ is even not altered by the heat effect. This confirms our previous result obtained for a single resonator diffusion cell FR system (Sun and Do, 1995). The physical reason of this is that heat transfer affects in an equitable way the concentrations in the two reservoirs and therefore, the sensitivity of the concentration difference on the heat effect is extremely small.

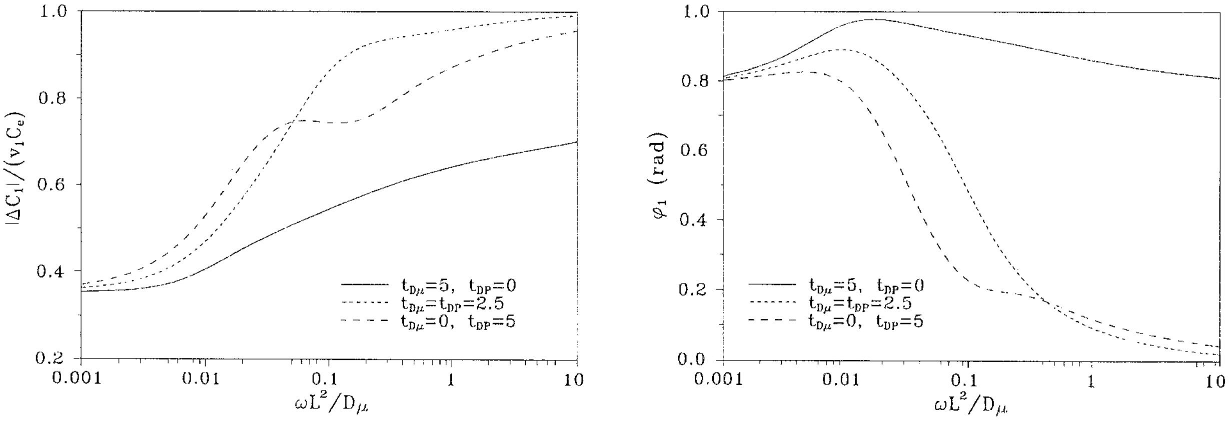
FR Analysis for a Biporous Pellet

Two different diffusion processes are involved in the pellet model: micropore diffusion and macropore diffusion. If the rate of micropore diffusion is very fast ($D_\mu \to \infty$), the pellet behaves like a homogeneous particle with a single effective diffusion coefficient $D_e = D_p/(1 + K)$. The FR behaviour of such a system is similar to that of a homogeneous



(a) (b)

Figure 9. Amplitudes (A) and phase angles (B) of C_1 and $C_1 - C_2$ under nonisothermal conditions. Parameters used: $\psi = \frac{3}{2}\pi$, $\beta_1 = 2$, $\beta_2 = 2$, $v_1 = v_2 = 0.02$ and $\gamma = 1$. The values of t_h/t_d are given in the figures and $t_h = 0$ corresponds to the isothermal case.



(a) (b)

Figure 10. Amplitudes (a) and phase angles (b) of C_1 for a biporous pellet with $\psi = \frac{3}{2}\pi$. solid lines: $t_{D\mu} = 5$, $t_{DP} = 0$ (micropore diffusion control); short dashed lines: $t_{D\mu} = t_{DP} = 2.5$ and long dashed lines: $t_{D\mu} = 0$, $t_{DP} = 5$ (macropore diffusion control).

particle discussed previously. In the opposite case, if the macropore diffusion resistance is negligible, i.e., $D_p \to \infty$, the gas molecules will pass instantaneously from one reservoir to the other and the variations of the RHS and LHS concentrations will be identical ($\Delta C_1 = \Delta C_2$). The system is reduced to a batch adsorber one with a twice bigger chamber volume and with a single volume modulation which has the following amplitude and phase angle:

$$v' = \frac{1}{2}\sqrt{v_1^2 + 2v_1v_2 \cos\psi + v_2^2} \tag{45}$$

$$\tan\psi' = -\frac{v_2 \sin\psi}{v_1 + v_2 \cos\psi} \tag{46}$$

The transition between the two limiting cases is shown in Fig. 10 in the case of a lagged out of phase perturbation ($\psi = \frac{3}{2}\pi$). The FR curves were obtained using the following equilibrium parameters: $K_C = 7140$, $K_T = 0.39$, $K = 1.67 \times 10^4$, $\gamma = 0.5$, $t_h = 10$ s (nonisothermal sorption) and $\alpha_1 = \alpha_2 = 1.2 \times 10^{-4}$ (the same volume for the two reservoirs). $t_{D\mu}$ and t_{DP} are respectively time constants for micropore and macropore diffusion and are defined as:

$$t_{D\mu} = \frac{R^2}{15D_\mu}; \quad t_{DP} = (1+K)\frac{L^2}{3D_p} \tag{47}$$

In the case of micropore diffusion control ($t_{DP} = 0$), the system behaves like a traditional batch FR system: the concentration amplitude increases continuously with the frequency and approaches a limiting value of $\frac{\sqrt{2}}{2}$ at high frequencies (see Eq. 45); the phase angle, starting from $\frac{\pi}{4}$ at zero frequency (see Eq. 25), increases first with the frequency and then decreases after a maximum down to $\frac{\pi}{4}$ which corresponds to the phase angle of the volume modulation (Eq. 46). In the case of macropore diffusion control ($t_{D\mu} = 0$), the system reduces to a homogeneous particle and has a behaviour similar to that shown in Fig. 5. It is noted that the FR curves shown in Fig. 10 are well different, suggesting that the present method is very sensitive to the competition between micropore and macropore diffusion, much more than the batch adsorber FR system.

Conclusions

In this paper, the frequency response of a diffusion cell system with two resonators has been analysed, both for homogeneous particles and biporous pellets. The theoretical models developed include the Fickian diffusion mechanisms for mass transfer in the adsorbent particles as well as the heat dissipation process between the particles and the surroundings. The objective of introducing a second resonator is to enhance the response of gas pressures in the reservoirs and thus to have more accurate FR measurements. This enhancement is necessary as in traditional batch adsorber FR systems the amplitude and the phase angle of the pressure response are often very small, making accurate determination of FR characteristics often difficult.

It has been shown that if the volume perturbation of one reservoir, say reservoir 2, is out of phase with respect to the perturbation of reservoir 1 with the phase delay being about $\psi \sim 1.5\pi$, the pressure response in the reservoir 1 can be enhanced with significantly larger phase angles and amplitudes. The enhancement can even be more significant when the two reservoirs have different volumes or volume variations. When the differential pressure between the two reservoirs is taken as the monitored variable, the greatest enhancement can be achieved by using in phase perturbations with ψ near π. Moreover, this pressure difference proved to be much less sensitive to the heat effect than the absolute response ΔC_1 or ΔC_2 is. It has also been demonstrated that the heat effect can be reduced with the use of out of phase perturbations as a result of small net changes in the amount adsorbed in the particles. The heat effect is completely cancelled when the volume perturbations are exactly out of phase ($\psi = \pi$).

For biporous pellets, it has been shown that the system behaves as a two resonator diffusion cell FR with a homogeneous particle when macropore diffusion controls alone the overall kinetics. On the other hand, when micropore diffusion is the only rate-limiting mechanism, the system reduces to a batch adsorber FR one with a single resonator. The resulting FR curves are well distinct, proving that the two resonator system has a high sensitivity to the competition between micropore and macropore diffusion mechanisms. This high sensitivity is of great practical interest for the discrimination of micropore and macropore diffusion coefficients.

Nomenclature

a_p: external heat transfer surface area per unit particle volume, m^{-1}
C: gas phase concentrations in the reservoirs, kmol/m^3
C_S: volumetric heat capacity of the porous particle, J/m^3/K
C_μ: adsorbed phase concentration, kmol/m^3
D_p: diffusion coefficient in macropores, m^2/s
D_μ: effective diffusion coefficient in the porous particle, m^2/s
h: heat transfer coefficient between the adsorbent particle and the surroundings, W/m^2 K
ΔH: heat of adsorption, J/kmol
K_C: equilibrium constant
K_T: derivative of the adsorption isobar, kmol/m^{3}K
L: length of adsorbent particles, m
R: gas constant, J/kmol K
t: time, s
t_d: time constant for micropore diffusion ($= L^2/D_\mu$), s
t_{dp}: time constant for macropore diffusion ($= L^2/D_p$), s

$t_{D\mu}$: time constant for micropore diffusion defined in Eq. 47, s
t_{DP}: time constant for macropore diffusion defined in Eq. 47, s
t_h: time constants for heat exchange ($t_h = C_S/ha_p$), s
T: temperature, K
v: relative amplitudes of the volume perturbations
V: volumes of the reservoirs, m^3
V_e: mean volumes of the reservoirs, m^3
V_s: volume of the porous particle, m^3
x: spatial coordinates in the particle, m
$|\,|$: amplitudes

Greek Letters

β: ratio of the amounts in the particle and reservoirs at equilibrium
γ: non-dimensional thermal parameter ($= K_T|\Delta H|/C_S$)
ϵ: pellet porosity
φ: phase angle of the gas phase concentrations
φ_{12}: phase angle of the differential concentration $C_1 - C_2$
ψ: phase delay of the volume perturbation of the reservoir 2 with respect to that of the reservoir 1
ω: angular frequency of the volume perturbation, s^{-1}

Subscripts

1: reservoir 1
2: reservoir 2
12: difference between the two reservoirs
e: equilibrium state

Superscripts

$-$: volume average values

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