ANALYSIS OF OBSERVABILITY OF MODEL PARAMETERS FOR PHYSICAL ABSORPTION OF POORLY SOLUBLE GASES IN PACKED BEDS

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Received June 15th, 1981

Expressions have been derived for four possible transfer functions of a model of physical absorption of a poorly soluble gas in a packed bed column. The model has been based on axially dispersed flow of gas, plug flow of liquid through stagnant and dynamic regions and interfacial transport of the absorbed component. The obtained transfer functions have been transformed into the frequency domain and their amplitude ratios and phase lags have been evaluated using the complex arithmetic feature of the EC-1033 computer. Two of the derived transfer functions have been found directly applicable for processing of experimental data. Of the remaining two one is useable with the limitations to absorption on a shallow layer of packing, the other is entirely worthless for the case of poorly soluble gases.

Mathematical modelling of absorption in packed bed columns has been studied in the literature fairly frequently. Existing models fall into two categories: The differential models, such as the plug flow model, the axially dispersed model[1], the model with stagnant and dynamic regions[2] (the cross flow model), *etc.*, stated as a set of differential equations, and the stage or cell models dividing the packed section into the cascade of hypothetical stages. A single stage may be either perfectly mixed or with stagnant and dynamic regions with mutual exchange of mass[3,4], the back flow[5], recycle between the stages[6], *etc.* A review and brief characteristics of existing models have been given in ref.[7].

The parameters of models have been evaluated from experimental data by different methods. These methods may be classified depending on the character of the experiment, as static or dynamic. In the former case, the parameters are evaluated from steady state concentration profiles of the absorbed component along the column length. In the latter case, the evaluation is based on the transient course of concentration in the exit stream from the apparatus in response to a suitable input signal.

As an advantage of the static methods appears measurement of steady state concentrations and the fact that the model equations are substantially simplified by the absence of the accumulation term. The measurement of longitudinal concentration profiles, however, causes mechanical disruption of the system. These difficulties are avioded by dynamic methods. Measurement of transient concentrations, however, calls for the use of either probes with an instantaneous response or, at least with known dynamic characteristics to be used for calculations of the transient concentrations from the measured response of the probe. The dynamic methods utilize

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various types of input signals and the processing carried out either directly in the time or in the Laplace or the frequency domain.

The choice of the absorption system is closely associated with the choice of the measuring system while the availability of suitable probes becomes often the controlling factor. Among the most frequently used detection systems are the conductivity probes, scintillation detectors and spectrophotometers for liquid and katharometers and scintillation detectors for the gas phase. By a suitable choice of the tracer one can study the dynamics of the flows of phases separately, or accompanied by interfacial mass transfer.

The dynamics of the gas phase together with the interfacial mass transfer has been studied by Hatton and Woodborn[8] using the water–air–CO_2 system and by Burghardt and Bartelmus[9] on the water–air–NH_3 system by the static method. Simultaneous evaluation of the parameters of axially dispersed model in both phases with interfacial mass transfer has been tested by Linek and coworkers[10] for the water–air–N_2 system and a step change of oxygen concentration in the gas phase. Oxygen electrodes were used to measure the concentration in both the gas and liquid phase at the outlet. The model parameters were evaluated from the transient characteristics by nonlinear regression.

The oxygen electrode enables the measurement of oxygen concentration in both the gas and liquid phase. The reading of the oxygen electrode is proportional to the partial pressure of oxygen and the measurements in the liquid phase are thus sufficiently sensitive in spite of the prevailing low concentrations. The oxygen electrode, however, is not a probe with instantaneous response.

TABLE I

A total number of parameters of the resulting model of the absorption for different flow models in both phases

Model[a]		Number of equations	Number of parameters
Liquid phase	Gas phase		
PF	PF	2	3
AD	PF	2	4
PF	AD	2	4
AD	AD	2	5
PF	CF	3	6
AD	CF	3	7
AD	ACF	3	8
CF	PF	3	6
CF	AD	3	7
ACF	AD	3	8
CF	CF	4	10
CF	ACF	4	11
ACF	ACF	4	12

[a] PF plug flow model, AD axially dispersed model, CF cross flow model (stagnant and dynamic zones), ACF axially dispersed cross flow model.

Its dynamics must therefore be known in the study of relatively fast phenomena in order to make appropriate corrections of the measured data.

The results obtained in the study of the dynamics of absorption of oxygen in water may be generalized to absorption of low solubility gases. The aim of this work has been to determine the observability of parameters of the below described mathematical model of physical absorption by the frequency response method and to assess the utility of individual transfer functions.

THEORETICAL

Application of ever more complicated mathematical models to two-phase flow with interfacial mass transfer brings along the problem of increasing number of parameters of the resulting model. Table I shows the number of parameters involved in dependence on the model describing the behaviour of the gas and the liquid phase. In order to reduce the number of parameters to a degree allowing its evaluation from experimental data and using information from earlier measurements[11], as a reasonable compromise appears a combination of the model with stagnant and

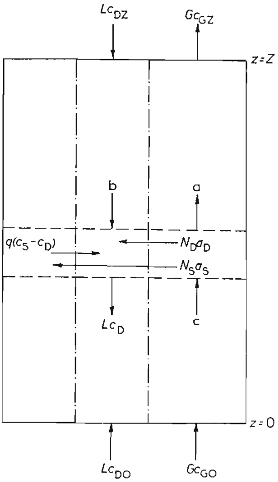

FIG. 1

A diagram of the absorption model with dynamic and static liquid regions and axial dispersion in the gas phase *a* $Gc_G + G(\partial c_G/\partial z)\,dz - h_GE(\partial c_G/\partial z) - h_GE(\partial^2 c_G/\partial z^2)\,dz$, *b* $Lc_D + L(\partial c_D/\partial z)\,dz$, *c* $Gc_G - h_GE(\partial c_G/\partial z)$

dynamic regions (the cross flow model) for the liquid phase and the axially dispersed flow for the gas phase. Such a combination should provide a sufficiently faithful description of mass transfer while preserving the physical meaning of all parameters involved.

The chosen model contains a total of seven parameters, *i.e.* the axial dispersion coefficient, gas hold-up, the dynamic and static hold-up of liquid, the volume mass transfer coefficients between gas and the stagnant liquid, between gas and the dynamic liquid and the coefficient of mass exchange between the stagnant and the dynamic liquid hold-up. The scheme of the model is shown in Fig. 1.

The balance equations for the underlying model of absorption, provided that the flow rates of phases remain constant, take the following form

$$L\frac{\partial x_D}{\partial z} + k_{LD}a_D\left(\frac{x_G}{m} - x_D\right) + q(x_S - x_D) = h_D\frac{\partial x_D}{\partial t}\,, \tag{1}$$

$$k_{LS}a_S\left(\frac{x_G}{m} - x_S\right) - q(x_S - x_D) = h_S\frac{\partial x_S}{\partial t}\,, \tag{2}$$

$$Eh_G\frac{\partial^2 x_G}{\partial z^2} - G\frac{\partial x_G}{\partial z} - k_{LD}a_D\left(\frac{x_G}{m} - x_D\right) - k_{LS}a_S\left(\frac{x_G}{m} - x_S\right) = h_G\frac{\partial x_G}{\partial t}\,. \tag{3}$$

From the standpoint of mathematical processing it is convenient to work with concentrations that are deviations from their steady state values. After effecting the appropriate transformation the resulting set of equations is formally identical with the set (*1*)–(*3*), and, consequently, the concentrations x_D, x_S, x_G shall be taken to be the deviations from the steady state values. The initial conditions then take the form

$$t = 0\,, \quad x_D = x_S = x_G = 0\,. \tag{4}$$

The Laplace transform of the set (*1*)–(*3*), with the initial conditions (*4*) yields one algebraic and two ordinary differential equations, one first, the other second order. The Laplace transforms of the concentrations x_D, x_S, x_G shall be designated X_D, X_S, X_G. The algebraic equation can be easily used to eliminate the concentration X_S while the set reduces to two equations in two unknowns X_D, X_G.

$$\frac{dX_D}{dz} - A_1X_D + A_2X_G = 0\,, \tag{5}$$

$$A_5\frac{d^2X_G}{dz^2} - \frac{dX_G}{dz} + A_3X_D - A_4X_G = 0\,. \tag{6}$$

After solving the set, the solution for X_S can, of course, be easily obtained too from the mentioned algebraic equation. This, however, shall not be done, owing to the small practical importance of x_S, which is not a directly measurable quantity.

The set (5), (6) may be reduced to a single differential equation to be solved

$$\frac{d^3X_D}{dz^3} - \left(A_1 + \frac{1}{A_5}\right)\frac{d^2X_D}{dz^2} + \frac{A_1 - A_4}{A_5}\frac{dX_D}{dz} + \frac{A_1A_4 - A_2A_3}{A_5}X_D = 0\,. \quad (7)$$

The parameters A_i in Eqs (5)–(7) are given by the following expressions

$$A_1 = \frac{1}{L}\left(h_Ds + k_{LD}a_D + \frac{h_Ssq + k_{LS}a_Sq}{h_Ss + q + k_{LS}a_S}\right), \quad (8)$$

$$A_2 = \frac{1}{L}\left(\frac{k_{LD}a_D}{m} + \frac{k_{LS}a_S}{m}\frac{q}{h_Ss + q + k_{LS}a_S}\right), \quad (9)$$

$$A_3 = \frac{1}{G}\left(k_{LD}a_D + k_{LS}a_S\frac{q}{h_Ss + q + k_{LS}a_S}\right), \quad (10)$$

$$A_4 = \frac{1}{G}\left(\frac{k_{LD}a_D}{m} + \frac{k_{LS}a_S}{m}\frac{h_Ss + q}{h_Ss + q + k_{LS}a_S} + h_Gs\right), \quad (11)$$

$$A_5 = h_GE/G\,. \quad (12)$$

Solution to Eq. (7) may be obtained in the form

$$X_D = k_1\exp(\lambda_1z) + k_2\exp(\lambda_2z) + k_3\exp(\lambda_3z)\,, \quad (13)$$

where $\lambda_1, \lambda_2, \lambda_3$ are roots of the following characteristic equation

$$\lambda^3 - \left(A_1 + \frac{1}{A_5}\right)\lambda^2 + \frac{A_1 - A_4}{A_5}\lambda + \frac{A_1A_4 - A_2A_3}{A_5} = 0 \quad (14)$$

and k_1, k_2, k_3 are constants to be determined from the boundary conditions. A solution for the concentration X_G is obtained by substituting into Eq. (5) in the form

$$X_G = a_1k_1\exp(\lambda_1z) + a_2k_2\exp(\lambda_2z) + a_3k_3\exp(\lambda_3z)\,, \quad (15)$$

where

$$a_1 = (A_1 - \lambda_1)/A_2\,, \quad (16)$$

$$a_2 = (A_1 - \lambda_2)/A_2\,, \tag{17}$$

$$a_3 = (A_1 - \lambda_3)/A_2\,. \tag{18}$$

From here it is apparent that altogether we have only three so far undetermined constants. For their determination we shall do with the three boundary conditions of the original set and no additional conditions need be sought as done by some authors[12]. The constants k_1, k_2, k_3 take, for the boundary conditions

$$X_G = X_{GO} + (h_G E/G)(\mathrm{d}X_G/\mathrm{d}z)\,, \quad z = 0^+\,, \tag{19}$$

$$\mathrm{d}X_G/\mathrm{d}z = 0\,, \quad z = Z\,, \tag{20}$$

$$X_D = X_{DZ}\,, \quad z = Z\,, \tag{21}$$

the following form

$$\begin{aligned} k_1 = B\{&a_2 a_3[b_3\lambda_2 \exp(\lambda_2 Z) - b_2\lambda_3 \exp(\lambda_3 Z)]\,X_{DZ} + \\ &+ \exp[(\lambda_2 + \lambda_3)\,Z]\,(a_3\lambda_3 - a_2\lambda_2)\,X_{GO}\}\,, \end{aligned} \tag{22}$$

$$\begin{aligned} k_2 = B\{&a_1 a_3[b_1\lambda_3 \exp(\lambda_3 Z) - b_3\lambda_1 \exp(\lambda_1 Z)]\,X_{DZ} + \\ &+ \exp[(\lambda_1 + \lambda_3)\,Z]\,(a_1\lambda_1 - a_3\lambda_3)\,X_{GO}\}\,, \end{aligned} \tag{23}$$

$$\begin{aligned} k_3 = B\{&a_1 a_2[b_2\lambda_1 \exp(\lambda_1 Z) - b_1\lambda_2 \exp(\lambda_2 Z)]\,X_{DZ} + \\ &+ \exp[(\lambda_1 + \lambda_2)\,Z]\,(a_2\lambda_2 - a_1\lambda_1)\,X_{GO}\}\,, \end{aligned} \tag{24}$$

where

$$b_1 = 1 - h_G E\,\lambda_1/G\,, \tag{25}$$

$$b_2 = 1 - h_G E\,\lambda_2/G\,, \tag{26}$$

$$b_3 = 1 - h_G E\,\lambda_3/G\,, \tag{27}$$

$$\begin{aligned} B = \{&a_1 a_2 \exp(\lambda_3 Z)\,[b_2\lambda_1 \exp(\lambda_1 Z) - b_1\lambda_2 \exp(\lambda_2 Z)] + \\ &+ a_1 a_3 \exp(\lambda_2 Z)\,[b_1\lambda_3 \exp(\lambda_3 Z) - b_3\lambda_1 \exp(\lambda_1 Z)] + \\ &+ a_2 a_3 \exp(\lambda_1 Z)\,[b_3\lambda_2 \exp(\lambda_2 Z) - b_2\lambda_3 \exp(\lambda_3 Z)]\}^{-1}\,. \end{aligned} \tag{28}$$

Substituting into Eqs (*13*) and (*15*) and by inverse transform one may obtain profiles of both concentrations along the column length. We are concerned though by the interrelationships between the inlet and the outlet concentrations. Substituting $z = Z$ one obtains from Eqs (*13*) and (*15*) two expressions containing the quantities $X_{GO}, X_{DO}, X_{GZ}, X_{DZ}$, which are the Laplace images of concentrations in the gas phase, (subscript G), in the dynamic part of the liquid hold-up (subscript D), at the column bottom (subscript O), *i.e.* at the gas inlet, and at the column top (subscript Z), *i.e.* at the liquid inlet end. These four concentrations may be combined to give four transfer functions by putting always one of the independently adjustable concentrations (either X_{GO}, or X_{DZ}) equal to zero. This means that the corresponding inlet stream is not being perturbed.

The four mentioned transfer functions are as follows

$$X_{GZ}/X_{GO} = B \exp\left[(\lambda_1 + \lambda_2 + \lambda_3) Z\right] \left[a_1\lambda_1(a_2 - a_3) + \right.$$
$$\left. + a_2\lambda_2(a_3 - a_1) + a_3\lambda_3(a_1 - a_2)\right], \qquad (29)$$

for

$$X_{DZ} = 0, \qquad (30)$$

$$X_{DO}/X_{DZ} = B\left[a_1\lambda_1 \exp(\lambda_1 Z)(a_2b_2 - a_3b_3) + a_2\lambda_2 \exp(\lambda_2 Z)(a_3b_3 - \right.$$
$$\left. - a_1b_1) + a_3\lambda_3 \exp(\lambda_3 Z)(a_1b_1 - a_2b_2)\right], \qquad (31)$$

for

$$X_{GO} = 0, \qquad (32)$$

$$X_{DO}/X_{GO} = B[(a_3\lambda_3 - a_2\lambda_2) \exp[(\lambda_2 + \lambda_3) Z] +$$
$$+ (a_1\lambda_1 - a_3\lambda_3) \exp[(\lambda_1 + \lambda_3) Z] +$$
$$+ (a_2\lambda_2 - a_1\lambda_1) \exp[(\lambda_1 + \lambda_2) Z]], \qquad (33)$$

for

$$X_{DZ} = 0, \qquad (34)$$

$$X_{GZ}/X_{DZ} = B\, a_1a_2a_3[b_3(\lambda_2 - \lambda_1) \exp[(\lambda_1 + \lambda_2) Z] +$$
$$+ b_2(\lambda_1 - \lambda_3) \exp[(\lambda_1 + \lambda_3) Z] +$$
$$+ b_1(\lambda_3 - \lambda_2) \exp[(\lambda_2 + \lambda_3) Z]], \qquad (35)$$

for

$$X_{GO} = 0. \qquad (36)$$

The response of the column to a periodic signal of the frequency ω may be obtained easily from the derived transfer functions by substituting $s = i\omega$ where i is the imaginary unit. The transfer functions then represent complex numbers with the magnitude equalling the amplitude ratio, P, of the outlet and inlet stream and the negatively taken ratio of the imaginary and the real part determines the tangent of the phase lag, ϕ, confined into the interval between 0 and $\pi/2$.

Also the coefficients of the characteristic equation, determining the roots $\lambda_1 - \lambda_3$, are generally complex numbers. The routine of solution is such that Eq. *(14)* is first multiplied by a polynomial with complex conjugate coefficients. The resulting sixth order equation with real coefficients is then solved by standard methods. From the six roots found one then chooses those that are roots of the original equation with complex coefficients.

The above derived expressions for the transfer functions, or the frequency responses, contain transcendental functions and, consequently, analytical separation of the imaginary and the real part is impossible.

The separation may be accomplished only numerically for a given set of parameters. In the derivation it was also assumed that the equilibrium constant, m, is independent of the concentration, which is sufficiently accurately fulfilled for poorly soluble gases or when the perturbation of the inlet stream is small. The derived expressions also do not account for eventual thermal effects of the dissolution. The assumption of zero heat of dissolution is also well satisfied for poorly soluble gases.

RESULTS AND DISCUSSION

The applicability of the above derived transfer functions in the form of frequency responses for the purpose of evaluating the model parameters has been tested on a computer. All four transfer functions, in the form of the coordinates of the Bode plots (P, ϕ) were evaluated for the case of absorption of oxygen in water at 20°C in a 2 m deep packed bed with the voidage of 0·4, in the range of angular velocities between zero and 1 rad/s. The principal set of data used was as follows: $h_D = 0{\cdot}05$, $h_S = 0{\cdot}05$, $h_G = 0{\cdot}3$, $k_{LD}a_D = 0{\cdot}05\ \mathrm{s}^{-1}$, $k_{LS}a_S = 0{\cdot}05\ \mathrm{s}^{-1}$, $q = 0{\cdot}04\ \mathrm{s}^{-1}$, $G = 0{\cdot}2\ \mathrm{m\,s}^{-1}$, $L = 0{\cdot}004\ \mathrm{m\,s}^{-1}$, $m = 30$, $E = 0{\cdot}02\ \mathrm{m}^2\,\mathrm{s}^{-1}$. The flow rates of both phases fall roughly into the middle of the operating range of the packed bed columns. To these flow rates correspond also the values of gas and liquid hold-up, h_L and h_G, obtained from earlier measured experimental data[11]. The liquid hold-up was divided into the stagnant and the dynamic part in the ratio 1 : 1. The volume liquid side mass transfer coefficient, which in this case represents the overall transfer coefficient, was estimated from the correlation of Onda and coworkers[13].

$$Sh = 0{\cdot}0097 Re^{0{\cdot}67} Sc^{0{\cdot}5} Ga^{0{\cdot}33}\,, \qquad (37)$$

and was taken equal for the dynamic and the stagnant liquid. The coefficient of exchange of liquid between the dynamic and the static hold-up was taken from the results of the work[11] while the axial dispersion coefficient was taken from experimental data in ref.[14].

The effect of individual parameters was investigated in such a way that the coordinates of the Bode plot were computed for 3 to 5 values of the examined parameter while the remaining parameters were either kept constant, or, in case that the examined parameter was one of the hold-ups, were adjusted so as to keep the sum of the hold-ups equal to the bed voidage. The ivnestigated ranges of the influence of individual parameters are summarized in Table II.

The calculations have been performed on an EC-1033 computer utilizing its complex arithmetic and double precision feature. To solve the characteristic equation

TABLE II

A review of the investigated parameters ranges

Parameter	E $m^2 s^{-1}$	h_G	h_D	h_S	$k_{LD}a_D$ s^{-1}	$k_{LS}a_S$ s^{-1}	q s^{-1}
E	0·001	0·3	0·05	0·05	0·05	0·05	0·04
	0·005	0·3	0·05	0·05	0·05	0·05	0·04
	0·01	0·3	0·05	0·05	0·05	0·05	0·04
	0·02	0·3	0·05	0·05	0·05	0·05	0·04
	0·05	0·3	0·05	0·05	0·05	0·05	0·04
	0·1	0·3	0·05	0·05	0·05	0·05	0·04
	0·5	0·3	0·05	0·05	0·05	0·05	0·04
h_G	0·02	0·3	0·05	0·05	0·05	0·05	0·04
	0·02	0·25	0·075	0·075	0·05	0·05	0·04
	0 02	0·2	0·1	0·1	0·05	0·05	0·04
$h_D/(h_D + h_S)$	0·02	0·3	0·025	0·075	0·05	0·05	0·04
	0·02	0·3	0·05	0·05	0·05	0·05	0·04
	0·02	0·3	0·075	0·025	0·05	0·05	0·04
	0·02	0·3	0·1	0·0	0·05	0·05	0·04
$k_{LD}a_D$, $k_{LS}a_S$	0·02	0·3	0·05	0·05	0·005	0·005	0·04
	0·02	0·3	0·05	0·05	0·01	0·01	0·04
	0·02	0·3	0·05	0·05	0·05	0·05	0·04
	0·02	0·3	0·05	0·05	0·1	0·1	0·04
q	0·02	0·3	0·05	0·05	0·05	0·05	0·005
	0·02	0·3	0·05	0·05	0·05	0·05	0·01
	0·02	0·3	0·05	0·05	0·05	0·05	0·04
	0·02	0·3	0·05	0·05	0·05	0·05	0·1

(*14*) a subroutine POLRT[15], handling solution of algebraic equations, have been used.

The transfer function X_{GZ}/X_{GO} represents the ratio of the Laplace transforms of concentrations of the absorbed component in the exit and the inlet stream of the gas phase. The calculations of the corresponding frequency characteristic indicate that although the transfer function contains all seven parameters, the amplitude ratio and the phase lag in the investigated parameter range depend practically on the gas hold-up and the axial dispersion coefficient, *i.e.* on the gas phase related parameters only. For a given frequency the amplitude ratio decreases with increasing axial dispersion coefficient, see Fig. 2, as well as with the gas hold-up.

The phase lag (the phase lag equals the phase shift in magnitude but has an opposite sign) is independent of the axial dispersion coefficient for E below 0·02 $m^2 s^{-1}$, see Fig. 3. Above this value the phase lag decreases with increasing value of the axial dispersion coefficient, but a high degree of axial dispersion is not typical for packed beds. Further the phase lag grows with increasing hold-up of gas. The dependences of the phase lag on frequency are for low values of the axial dispersion coefficient practically linear and resemble the plug low case for which this dependence is exactly linear. With increasing axial dispersion the increase of the phase lag grows weaker compared to the linear course.

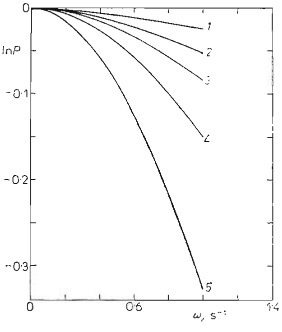

FIG. 2

Frequency characteristic of the amplitude ratio for the transfer function X_{GZ}/X_{GO} and five values of axial dispersion coefficient. *1* $E = 0{\cdot}001\ m^2\ s^{-1}$, *2* $E = 0{\cdot}005\ m^2\ s^{-1}$, *3* $E = 0{\cdot}01\ m^2\ s^{-1}$, *4* $E = 0{\cdot}02\ m^2\ s^{-1}$, *5* $E = 0{\cdot}05\ m^2\ s^{-1}$

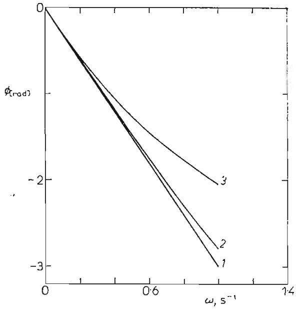

Fig. 3

Frequency characteristic of the phase angle for the transfer function X_{GZ}/X_{GO} and three values of axial dispersion coefficient. *1* $E = 0{\cdot}02\ m^2\ s^{-1}$, *2* $E = 0{\cdot}1\ m^2\ s^{-1}$, *3* $E = 0{\cdot}5\ m^2\ s^{-1}$

From the obtained data it is apparent that both the gas hold-up and the axial dispersion coefficient markedly affect the transfer characteristic of the system as given in Eq. (*29*) and it may be therefore expected that these characteristics can be obtained from experimental frequency response. The transfer function (*29*) cannot be, however, used for evaluation of the remaining parameters.

The transfer function X_{DO}/X_{DZ} represents the ratio of the Laplace transforms of concentrations of the absorbed component in the exit and the inlet liquid stream. From the computed dependences it is apparent that both the amplitude ratio and the phase lag display a marked dependence on all parameters of the model. For the chosen absorption system, however, the amplitude ratio remains in all cases less that 10^{-5} and as such it is unmeasurable by available analytical means. As a consequence, the transfer function (*31*) is worthless from the experimental standpoint.

The transfer function X_{DO}/X_{GO} is the ratio of the Laplace images of concentration of the absorbed component in the outlet liquid and the inlet gas stream. Numerical results show that the amplitude ratio is always less than $0{\cdot}0\overline{3}$ (value given by the equilibrium constant $m = 30$) and it might therefore appear that the measurements in the liquid phase would be insufficiently sensitive. For the case of absorption of oxygen in water and with the aid of the oxygen electrode as a concentration sensing device, the signals of the electrode in both the gas and the liquid phase will range between zero and unity and as such will be well measurable. It is so because the signal of the oxygen electrode is not proportional to the concentration but rather to the equivalent partial pressure of oxygen on the respective phase. It thus suffices to scale the experimental data from the liquid phase measurements by the equilibrium constant m.

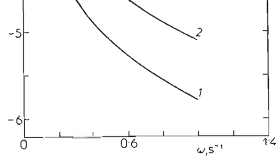

FIG. 4

Frequency characteristic of the amplitude ratio for the transfer function X_{DO}/X_{GO} and four values of volume mass transfer coefficient $k_{LD}a_D$ or $k_{LS}a_S$: *1* $k_{LD}a_D = 0{\cdot}005\ s^{-1}$, *2* $k_{LD}a_D = 0{\cdot}01\ s^{-1}$, *3* $k_{LD}a_D = 0{\cdot}05\ s^{-1}$, *4* $k_{LD}a_D = 0{\cdot}1\ s^{-1}$

The dependence of the amplitude ratio of the frequency response corresponding to the transfer function (*33*) on frequency for different values of individual model parameters are qualitatively very similar. Fig. 4 shows for instance the dependence of the mass transfer coefficient $k_{LD}a_D$ and $k_{LS}a_S$. From these results it follows that for a given frequency the amplitude ratio decreases with increasing fraction of the dynamic liquid hold-up at constant overall hold-up, and with the axial dispersion coefficient for $E \geqq 0{\cdot}02\ m^2\ s^{-1}$. On the contrary, the amplitude ratio increases with the gas hold-up and with the coefficients q, $k_{LD}a_D$ and $k_{LS}a_S$. The influence of the coefficient q, however, is very weak, see Fig. 5.

Also the dependences of the phase lag on frequency are qualitatively fairly similar for all selected values of model parameters; from the linear course they deviated toward lower value of the phase lag. Individual, parameters, however, exercise opposite influence on the phase lag than that on the amplitude ratio. The phase lag grows with increasing axial dispersion coefficient, increasing fraction of the dynamic liquid hold-up at constant overall hold-up and decreases with increasing gas hold-up

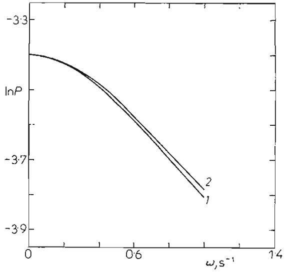

FIG. 5

Frequency characteristic of the amplitude ratio for the transfer function X_{DO}/X_{GO} and two values of the mass exchange coefficient between the static and the dynamic hold-up. *1* $q = 0{\cdot}005\ s^{-1}$, *2* $q = 0{\cdot}1\ s^{-1}$

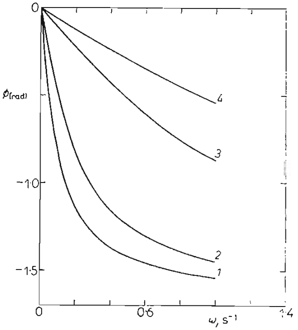

FIG. 6

Frequency characteristic of the phase angle for the transfer function X_{DO}/X_{GO} and four values of the volume mass transfer coefficient $k_{LD}a_D$ or $k_{LS}a_S$. *1* $k_{LD}a_D = 0{\cdot}005\ s^{-1}$, *2* $k_{LD}a_D = 0{\cdot}01\ s^{-1}$, *3* $k_{LD}a_D = 0{\cdot}05\ s^{-1}$, *4* $k_{LD}a_D = = 0{\cdot}1\ s^{-1}$

and the volume mass transfer coefficients while the effect of the coefficient q is again very small.

The computed dependences indicate that the phase lag corresponding to this transfer function is generally small and in the investigated frequenccy range never exceeded $\pi/2$, see Fig. 6. Since the phase lag in the upper part of the investigated frequence range equals in the time domain about 1 s, it is probable that the measurement shall carry a considerable experimental error. Accordingly, the major portion of the information provided by this transfer function should come from the amplitude ratio.

It may be therefore summarized that the transfer function (*33*) depends significantly on all model parameters except the coefficient of exchange q, where the corresponding dependence is weak. The transfer function (*33*) is therefore applicable for evaluation of all parameters excepting q.

The transfer function X_{GZ}/X_{DZ} is the ratio of the Laplace transforms of concentrations of the absorbed component in the gas exit and the inlet liquid stream. The computed values of the amplitude ratio are smaller, or at zero frequency equal to the fraction L/G, which amounted for the basic set of data to 0·02. For the used water--air–O_2 system and the oxygen electrodes the signal of the electrode in the gas phase would be still about 30 times smaller and the measurement would be insufficiently sensitive. Thus the transfer function (*35*) cannot be used for analysis of our system either.

CONCLUSION

Four transfer functions have been derived for a mathematical model of a packed bed absorption column incorporating axial dispersion in the gas phase, the existence of the stagnant regions and the dynamic regions with the plug flow in the liquid phase plus interfacial mass transfer.

The calculations of the frequency responses, performed for the absorption of oxygen in water in a bed 2 m long with the void fraction equalling 0·4, showed that the transfer function X_{GZ}/X_{GO} may be used for the determination of the gas phase parameters, *i.e.* the dispersion coefficient and the gas hold-up. The influence of only these parameters may be explained by the following reasoning. For a poorly soluble gas the loss of species due to absorption excercises only negligibly on the concentration profile in the gas phase. Hence the absorbed gas functions with respect to the gas phase essentially as a tracer not subject to interfacial transfer.

The transfer function X_{DO}/X_{GO} is affected by all seven parameters of the model and may be therefore utilized for the determination of the parameters characterizing the liquid flow, namely the stagnant and the dynamic liquid hold-up, and the volume mass transfer coefficient into both parts of the liquid hold-up. The evaluation of the coefficient of mass exchange between the dynamic and the static hold-up, q, from this transfer function shall be apparently accompanied by difficulties owing to the small sensitivity of X_{DO}/X_{GO} to q.

The transfer function X_{DO}/X_{DZ} proved to be unusable for parameter evaluation due to the fact that the found amplitudes were much too low even for a sensitive probe as the oxygen electrode. This conclusion though is valid apparently only for the region of parameters investigated in this paper, namely for the relatively large length of the packed section. This length of the packed section brings about essentially total desorption of the gas from the liquid fed on the top, spare for undetectable traces. It may be expected though that for a substantially shorter column this transfer function would supply measurable responses subject to the effect of all parameters of the model including that of q. From the experimental point of view, however, this approach, especially for low solubility gases does not appear very practical and to a similar purpose may serve a response to a perturbation of the liquid stream without interfacial transfer[11].

Also the transfer function X_{GZ}/X_{DZ} has been found as inapplicable for the evaluation of parameters of the mathematical model. In contrast to the preceding transfer function, which in a different parameter domain would provide basis for data processing, this transfer function is inapplicable for poorly soluble gases in the whole parameter domain. This is so because in case of poorly soluble gases the liquid stream cannot be perturbed sufficiently strongly in order to induce a measurable response in the gas phase.

The above findings pertain to the case of linear equilibrium relationship and zero heat of absorption. Both these assumptions are usually well met in case of poorly soluble gases.

LIST OF SYMBOLS

$A_1 - A_5$	constants defined by Eqs *(8)*–*(12)*
a	specific interfacial surface
$a_1 - a_3$	constants defined by Eqs *(16)*–*(18)*
B	constant defined by Eq. *(28)*
$b_1 - b_3$	constants defined by Eqs *(25)*–*(27)*
E	axial dispersion coefficient
G	superficial gas velocity
h	hold-up
i	imaginary unit
k_L	mass transfer coefficient
$k_1 - k_3$	constants defined in Eqs *(22)*–*(24)*
L	superficial liquid velocity
m	equilibrium constant
N	rate of absorption
P	amplitude ratio
q	coefficient of mass exchange between dynamic and stagnant liquid

s	Laplace parameter
t	time
X	Laplace transform of concentration x
x	concentration defined as a deviation from steady state value
Z	bed depth
z	axial coordinate
$\lambda_1 - \lambda_3$	roots of characteristic equation *(14)*
ϕ	phase angle
ω	angular velocity

Subscripts

D	dynamic liquid
G	gas phase
S	stagnant liquid
Z	column top
O	column bottom

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Translated by the author V. S.