

## A DYNAMIC METHOD OF MEASURING THE MASS TRANSFER COEFFICIENT FOR PHYSICAL ABSORPTION IN COLUMNS

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Received July 10th, 1975

The dynamic response of a wetted-wall and of a packed gas absorber to sudden inlet gas composition change was investigated both experimentally and theoretically for the case of physical, isothermal absorption. Oxygen dissolved in air-saturated water was desorbed into pure nitrogen stream in: (i) a 2.68 cm I.D. wetted-wall glass column either 1.44 or 2.65 m long, (ii) 14.3 cm I.D. plexiglass pipe packed to a height of 0.51 m with 1.5 cm polypropylene Raschig rings. Various gas and liquid flow rates were used. The outlet gas and liquid phase oxygen concentrations were continuously monitored using rapidly responding oxygen electrodes. Two different methods of calculation which consider the probe response speed in the evaluation of  $k_1a$  and of the forward gas velocity  $u_g$  by the dynamic measuring technique are presented: the moment method and a modified Heineken method. The latter method enables the determination of  $k_1a$  from a single point of the probe response curve almost immediately after the experiment. A model of piston flow in the two phases was used. Reliability of  $k_1a$  values determined by the dynamic methods was verified by comparing them with values of  $k_1a$  determined under steady-state conditions of column operation. The modified method gave more accurate  $k_1a$  values than the moment method.

A method which would allow for a reliable and rapid determination of the mass transfer coefficient while applicable under universal conditions would represent an important contribution to the inspection, control, and simulation of industrial apparatuses. We have attempted to find such a procedure which would make it possible to measure the mass transfer coefficient and, eventually, other parameters of a mathematical model of the process concerned in a simple and realistic manner so as to meet the requirements of shop operation.

Gray and Prados<sup>1</sup> have applied frequency analysis to evaluate a model of piston flow in the two phases. The mass transfer coefficient, the holdup in the liquid phase, and the holdup in the gaseous phase were the parameters. These parameters were evaluated from response data for the gaseous phase and, hence, the CO<sub>2</sub>—H<sub>2</sub>O system was used, *i.e.*, a highly soluble gas. The experimental results obtained with well soluble gases may be affected by thermal effects and by longitudinal mixing rather more than would gases of lower solubility. In addition to the model quoted, these authors also deal with the model of a cascade of mixers and the model of piston flow with axial mixing. However, the model of axial dispersion flow does not even consider mass transfer.

More recent work by Sakata and Prados<sup>2</sup> considers a more complex model taking account not only of the parameters mentioned but also of the coefficients of longitudinal effective diffusivity for both phases. However, the model equations cannot be solved analytically for the case of physical absorption, and thus they require lengthy evaluation procedures to be employed. Bradley and Andre<sup>3</sup> resorted to a numerical solution of the piston flow model for both phases without axial mixing to describe the dynamic behavior of CO<sub>2</sub> absorption in monoethanolamine solutions. Mellish<sup>4</sup>, in his brief survey, states that axial mixing is of little importance within the range of velocities usually considered; this has also been confirmed experimentally by Gray and Prados<sup>1</sup> for low input signal frequencies.

The requirements imposed on the method make it clear that it is of advantage to make use of dynamic experiments applying a concentration shock at one of the input concentrations. Such experiments can easily be carried out using any type of apparatus. The paper by Bandyopadhyay and coworkers<sup>5</sup> presenting a dynamic method of determining the aeration capacity of fermentors is an example. The choice of system, *i.e.*, the system tracer species—liquid and gas phase, remains a question. From the standpoint of an earlier developed experimental method<sup>6</sup> and with regard to the requirement for simplicity of evaluation, it is oxygen that appears to be an advantageous tracer species. Inasmuch as oxygen solubility is low, the contribution by mass transfer in gas phase can usually be neglected in comparison to the capacity of the gas phase. The measuring devices used may be placed in any gas or liquid phase, as long as it does not attack the sensor chemically. The dynamic behavior of the oxygen probe proper has been described in detail in literature<sup>6-8</sup>.

## THEORETICAL

Consider the same model as Gray and Prados<sup>1</sup>. The following conservation equations of solute component for the gas and liquid phases under the assumptions that holdups and flow rates are constant can be derived

$$h_g \frac{\partial c_g}{\partial t} - \dot{V}_g \frac{\partial c_g}{\partial z} = -N, \quad (1)$$

$$h_l \frac{\partial c_l}{\partial t} - \dot{V}_l \frac{\partial c_l}{\partial z} = N. \quad (2)$$

Consider that in time  $t < 0$  the shared component concentration in the gas being introduced into the column is  $c_g^0$  and that the liquid being introduced into the column is saturated with this gas. Hence, there is no interfacial phase transport in times  $t < 0$ , and at  $t = 0$  the shared component concentration in the gas entering the column is suddenly changed to the value  $c_g^+$ . The set (1) and (2) will thus be solved for the conditions

$$c_g(z < Z, 0) = c_g^0, \quad (3)$$

$$c_g(Z, t \geq 0) = c_g^+, \quad (4)$$

$$c_l(z, 0) = c_l^0, \quad (5)$$

$$c_1(0, t > 0) = c_1^0. \quad (6)$$

We assume that the absorption-due change of the component concentration in gas is negligible. This holds well for the absorption of slightly soluble gases such as oxygen or nitrogen, especially at higher values of the ratio  $\dot{V}_g/\dot{V}_1$  or in pure gas absorption. Then the equation (1) is transformed to

$$\frac{\partial c_g}{\partial t} - u_g \frac{\partial c_g}{\partial z} = 0, \quad (7)$$

which, together with (3) and (4), yields the solution

$$c_g(z, t) = c_g \left( Z, t - \frac{Z - z}{u_g} \right), \quad (8)$$

where

$$u_g = \dot{V}_g/h_g. \quad (9)$$

The resistance to mass transfer being concentrated in the liquid phase in case of low solubility gases, the mass transfer rate  $N$  may be expressed as

$$N = k_1 a (m c_g - c_1), \quad (10)$$

where  $m$  is the equilibrium factor. Substituting (10) and (8) into (2) we obtain an equation leading, with conditions (5) and (6), to the solution

$$c_1 = c_1^+ (1 - \exp \{-k_1 a A t\}) \quad \text{for } t \in \langle 0, t_{\max} \rangle, \quad (11)$$

and

$$c_1^k = c_1^+ (1 - \exp \{-k_1 a Z/\dot{V}_1\}) \quad \text{for } t \gg t_{\max}, \quad (12)$$

where

$$u_1 = \dot{V}_1/h_1, \quad (13)$$

$$A = u_1 u_g / (\dot{V}_1 [u_1 + u_g]), \quad (14)$$

$$t_{\max} = Z(u_g + u_1)/(u_g u_1), \quad (15)$$

In case that the column exit concentration is monitored by the oxygen probe according to Hospodka and Čáslavský<sup>9</sup>, the bias of the probe reading due to slow oxygen diffusion across the probe membrane must be taken into account. Using the model of one-dimensional molecular diffusion of oxygen across the probe mem-

brane, Heineken<sup>7</sup> and Linek<sup>8</sup> have derived the actual probe response to a concentration change defined by the equation (11) in the form

$$\Gamma_1 = 1 - \frac{\pi \sqrt{B}}{\sin(\pi \sqrt{B})} \exp\{-Bkt\} - 2 \sum_{n=1}^{\infty} (-1)^n \frac{\exp\{-n^2 kt\}}{n^2/B - 1} \quad (16)$$

where

$$B = k_1 a A/k. \quad (17)$$

The pairs of values  $\Gamma_1, t$  can be evaluated from the response recordings. Zero time may either be determined as that time in which the step change of input gas concentration was effected or, alternatively, the algorithm proposed by Heineken<sup>7</sup> may be used wherein the zero time  $t_0$  is considered as a parameter of the equation (16) in which the substitution  $t' = t + t_0$  is employed. A nomograph proposed by Linek<sup>6,8</sup> may be used to evaluate the former case. This procedure makes it possible to determine the  $B$  values from the probe response curves  $\Gamma_1$  almost immediately after the experiment. In addition to above methods, the values of the parameter  $B$  may be calculated by the method of moments. For instance, for the zero moment  $\mu_1^0$  of the response  $(1 - \Gamma_1)$  we derive the relation

$$\begin{aligned} \mu_1^0 = \int_0^{t_{\max}} (1 - \Gamma_1) dt &= \frac{\pi^2}{6k} + \frac{1}{Bk} - \frac{\exp\{-Bkt_{\max}\}}{k \sqrt{B} \sin(\pi \sqrt{B})} - \\ &- \frac{2B}{k} \sum_{n=1}^{\infty} (-1)^n \frac{\exp\{-n^2 kt_{\max}\}}{n^2(n^2 - B)}. \end{aligned} \quad (18)$$

If known relationships between flow rates, holdups, mean residence times of the phases, and the column height are used, the quantity  $A$  can be expressed as a function of those quantities on which we are informed by the experiment. Let us show how the mean residence time  $\tau_g$  of the gas phase can directly be determined from the gas phase response. Both Heineken<sup>7</sup> and Linek<sup>6,8</sup> give the following equation for a normalized probe response to a step change of concentration effected at the time  $t = 0$

$$\Gamma^1 = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\{-n^2 kt\}. \quad (19)$$

Hence, the probe response to the column exit concentration change of the diffusing component in the gas phase, given by the equations (3), (4), and (8) is

$$\begin{aligned} \Gamma_g &= 0 && \text{for } t \leq \tau_g \\ \Gamma_g &= 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\{-n^2 k(t - \tau_g)\} && \text{for } t \geq \tau_g. \end{aligned} \quad (20)$$

The mean residence time  $\tau_g$  or, respectively, the mean traveling velocity  $u_g$  of gas in column can be determined either from the zero moment  $\mu_g^0$  of the response  $(1 - \Gamma_g)$  for which it holds that

$$\mu_g^0 = \int_0^\infty (1 - \Gamma_g) dt = \tau_g + \pi^2/6k = Z/u_{gm} + \pi^2/6k \quad (21)$$

or from an arbitrary pair of values  $\Gamma_g$ ,  $t$  from the recording for which  $\Gamma_g > 0$ . For instance, the relationship

$$t_{0.5} = \tau_g = \ln(0.25)/k = Z/u_{gt} + \ln(0.25)/k \quad (22)$$

can be derived from (20) for the time  $t_{0.5}$  read off from the response curve for  $\Gamma_g = 0.5$ .

## EXPERIMENTAL

*Experimental equipment and procedure.* The measurements were made using a column with a wetted wall and a packed absorption column. The apparatus is schematically represented in the Fig. 1. It consisted of the column 15, the tempering and liquid saturating part 13, the liquid supply tank 18, the purification, tempering, and saturating lines for gas 4 through 8, and the regulatory and measuring devices 1, 3, 8, and 14.

The wetted-wall column was constituted by a vertical glass tube of 0.0268 m I.D. and 1.44 or 2.65 m length, with a liquid film flowing down along its interior surface. A ring of fine sand,

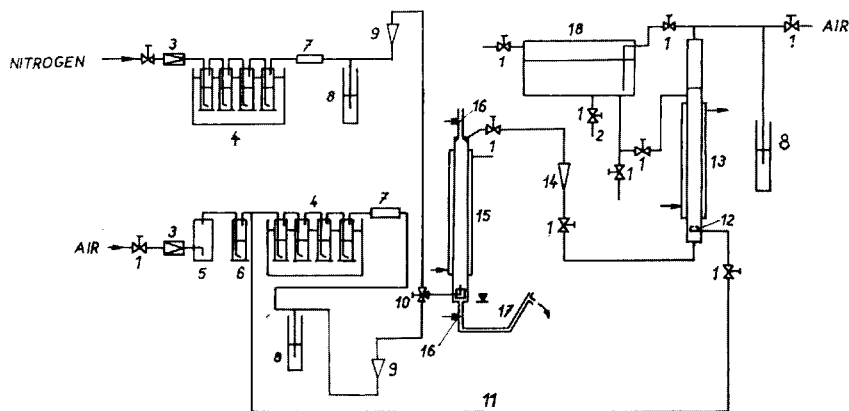


FIG. 1  
Scheme of Apparatus

cm wide, was glued to the tube just under the inlet for liquid. This has cut down the length of the inlet region of smooth film. The column was equipped with a controlled-temperature jacket.

The packed column consisted of a poly(methyl methacrylate) cylinder of 143 mm I.D. and 0.516 m height. The column was filled with polypropylene Raschig rings of diam. 15 mm to the level of 0.51 m. The column was described in detail elsewhere<sup>10</sup>.

The gas circuits included the reduction station 3, the water vapor saturation 4, calming vessel 5, filters 6, 7 intended to catch water droplets, and the pressure controller 8. Air nitrogen were used. The gases were led from the flow meters 9 to the three-way cock 10 located just before the column inlet. The oxygen probe was located at the column exit in the gas phase. The gas was allowed to escape into the atmosphere. The method used to effect the entry and the discharge of both the phases in the wetted-wall column is illustrated in the Fig. 2. The liquid phase (distilled water) was pumped to the tank 18 with discharge 2 and, before entering the column, was saturated with air (inlet tube 11, in the tempered saturating device 13 with gas distributor 12. Herefrom it was led to a distributor (Fig. 2) at the column head *via* the rotameter 14. It was discharged from the column under the gas inlet through the oxygen probe casing 16, escaping to sewage through the syphon seal 17. A dissolved oxygen analyzer was used to measure oxygen concentration. Its principle is based on the polarographic method of two noble metal electrodes maintained at a constant polarizing voltage. The probe reading is proportional to the equilibrium partial pressure of oxygen in the medium studied under steady-state conditions. A detailed description of the probe and its preparation for measurement has been given elsewhere<sup>9</sup>. High speed transistorized recorders TZ 21-S were used to record the responses.

The step changes of concentration were effected by suddenly changing the type of gas (air-nitrogen) passing through the column by means of turning the three-way cock 10. The experiment Proper was conducted so that the air-saturated liquid and the air were introduced into the column. The readings of the probes ( $s^0$ ) corresponding to the oxygen concentrations in the two phases were recorded. Subsequently, nitrogen was substituted for air by means of the cock 10 and, at the same time, the recorder paper motion was switched on. The response was recorded both in the gas and in the liquid leaving the column. On attaining a steady state, the probe reading ( $s^k$ ) was recorded. Then the water flow was stopped, the discharge of nitrogen from the column was closed, and hence, nitrogen started passing around the probe in the liquid phase. The steady-state value of the recording of  $s^+$  thus obtained corresponded to a zero oxygen concentration. Typical response curves of probes placed in gas and in liquid are shown in the Fig. 3. It is clear from the figure how the normalized responses  $\Gamma_1$  and  $\Gamma_g$  were read off.

The inlet and outlet section can have a considerable effect on the transient behaviour of the system. These were treated here by assuming that flows in tubes could be represented by transport delays, and that the bulk holdup elements (the liquid pool in the base of the absorber and the volume of the gas line) could represent the transfer lags.

The holdup of liquid in the column  $h_l$  was determined by weighing the liquid discharged from the column on suddenly stopping the inflow of liquid into the column.

Measurements to determine the membrane constant from the response to the sudden gas concentration change were conducted in a glass tube equipped with a cock and holding a probe. A detailed description of how the membrane constant is determined can be found in<sup>6</sup>.

The measurements were taken at a temperature of 25 and of 20°C in wetted-wall column and packed column, respectively, under atmospheric pressure; the membranes on the probe were from polypropylene  $8 \cdot 10^{-6}$  or  $15 \cdot 10^{-6}$  m thick. Runs were made at five liquid flow rate levels ( $V_L \cdot 10^6 = 2.0, 3.5, 5.0, 6.6, 8.2$  m<sup>3</sup>/s) and the three gas flow rate levels ( $V_g \cdot 10^4 = 1.08, 1.67, 2.17$  m<sup>3</sup>/s for  $Z = 1.44$  m and  $V_y \cdot 10^4 = 1.67, 2.84, 4.13$  m<sup>3</sup>/s for  $Z = 2.65$  m) with the

wetted-wall column and at five liquid ( $V_L \cdot 10^6 = 16.7, 25.0, 33.3, 41.7, 50.0 \text{ m}^3/\text{s}$ ) and five gas flow ( $V_g \cdot 10^4 = 0.14, 1.0, 1.67, 2.83, 28.4 \text{ m}^3/\text{s}$ ) rates with the packed column. Ten replications were made of each treatment.

## RESULTS AND DISCUSSION

The constants of the membranes used were determined first using a described method<sup>6</sup>. The constant of the membrane used to analyze the liquid and the gas phases in the wetted-wall column was  $k = 0.482$  and  $0.548 \text{ s}^{-1}$ , respectively, and  $k = 0.22$  and  $0.715 \text{ s}^{-1}$ , respectively, in the packed column.

The values of the forward velocity of gas,  $u_g$ , and of liquid,  $u_l$ , were calculated by the relations (9) and (13) from the data on liquid holdup, volumetric discharge rates of the two phases, and tube cross section. The zero moments  $\mu_g^0$  of the responses measured in the gas phase at column exit were obtained by numerical quadrature,

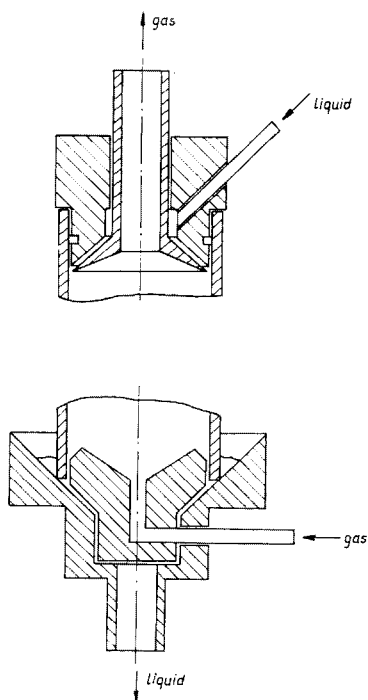


FIG. 2

Sketch of the Top and Bottom Parts of Wetted-Wall Column

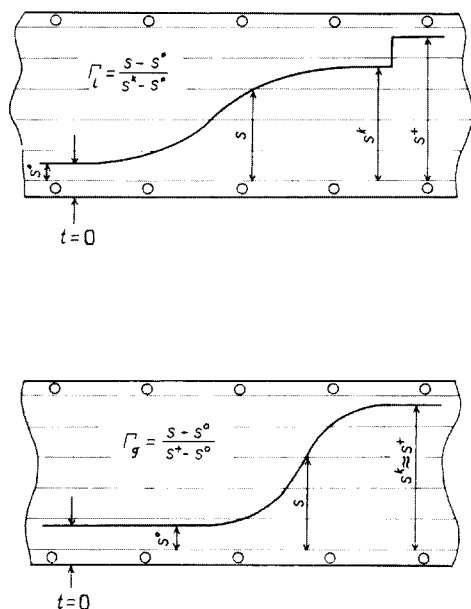


FIG. 3

Typical Example of Oxygen Probe Response Curves in Outlet Gas and Liquid Phase to Sudden Inlet Gas Composition Change

and were used in turn to calculate the forward gas velocities  $u_{gm}$  using the relation (21). In the Fig. 4, the values thus obtained are compared with the forward gas velocities  $u_g$  determined from the volumetric discharge rates of gas and from the liquid holdups. In the figure are also presented the forward velocities  $u_{gt}$  calculated from the time  $t_{0.5}$  using the relation (22). The points in the figure represent mean values of ten replications of experiment. Dispersion coefficients of both  $u_{gm}$  and  $u_{gt}$  values were in the interval from 7 to 14 and from 5 to 10% for wetted-wall and packed column, respectively. The figure indicates that these two sets of values ( $u_{gt}$  and  $u_{gm}$ ) are not in good agreement only at extremely low gas flow rates in packed column ( $u_g < 0.03 \text{ m s}^{-1}$ ). At values  $u_g$  higher than  $0.1 \text{ m s}^{-1}$  the differences between these values are small and do not exceed 10%. Fig. 4 shows that the values of  $u_{gt}$  and  $u_g$  are in good agreement suggesting that the piston flow model for the gas passing through the apparatus is plausible. Only the values  $u_1$  and  $u_g$  determined from the flow rates and holdups of the liquid are used in subsequent calculations.

The values of the inlet and exit concentrations of oxygen in the liquid phase, measured under steady-state conditions of column operation, were used to calculate the values  $(k_1a)_{st}$  from the relation (12). Oxygen probe readings were sampled from the response recordings of liquid at the column exit over a period from the moment of the sudden gas concentration change at column inlet ( $t = 0$ ) to the time  $t = t_{max}$  at equal time intervals of 0.635 s. From the values thus obtained, the mass transfer coefficient values  $(k_1a)_{dyn}$  were calculated from the zero moments  $\mu_1^0$  of the responses measured in the liquid phase column exit using the equation (18). Using readings from the diagram showing the dependence  $(1 - \Gamma_1)$  vs  $kt$  and given in<sup>6,8</sup> we determined the values of  $(k_1a)_{.7}$  from a single point of the probe response curve ( $\Gamma_1 \sim 0.7$ ,  $t$ ) employing a method described in detail in<sup>6</sup>. Zero time in the record can be taken as the time in which the step change of input gas concentration was

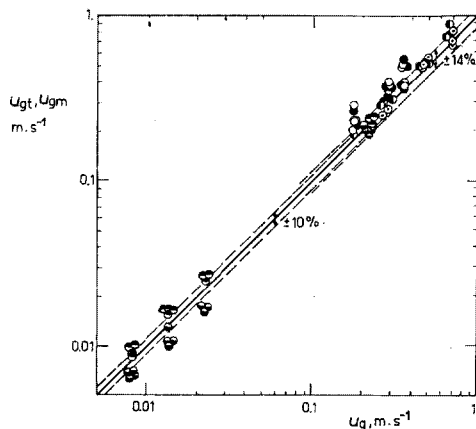


FIG. 4

Comparison of the Forward Velocity of Gas  $u_g$  Calculated from (9) with the Values  $u_{gm}$  and  $u_{gt}$  Calculated from (21) and (22)

Wetted-wall column: ○  $Z = 1.44 \text{ m}$ ,  $u_{gt}$ ; ●  $Z = 1.44 \text{ m}$ ,  $u_{gm}$ ; ⊙  $Z = 2.65$ ,  $u_{gt}$ ; ⊗  $Z = 2.65$ ,  $u_{gm}$ ; packed column: ⊕  $Z = 0.51 \text{ m}$ ,  $u_{gt}$ ; ⊖  $Z = 0.51 \text{ m}$ ,  $u_{gm}$ .



effected. The accuracy of the determination of zero time can be judged by comparing the values of  $k_1 a$  determined from various pairs of  $\Gamma_1$  and  $t$  read from the same record. If the determination was correct, then the values of  $k_1 a$  are constant and independent of the chosen pair  $\Gamma_1$  and  $t$ . For example, the values of  $k_1 a$  read from the diagram (Fig. 2 in ref.<sup>6</sup>) for different pair of  $\Gamma_1$  and  $t$  are 5.97, 6.15, 6.19, 6.09  $\cdot 10^{-5}$   $\text{m}^2 \text{s}^{-1}$  for  $\Gamma_1 \sim 0.4, 0.5, 0.6$  and  $0.7$ , respectively. The data were obtained in packed absorption column at  $\dot{V}_1 = 2.5 \cdot 10^{-5} \text{m}^3 \text{s}^{-1}$  and  $\dot{V}_g = 10^{-4} \text{m}^3 \text{s}^{-1}$ . A similar results were obtained under all experimental conditions used. The data show that the values of  $k_1 a$  do not depend on the  $\Gamma_1$  and  $t$  chosen. The error of  $k_1 a$  caused by the error of experimentally determined values of  $k$  and  $t$  can be evaluated and the method is described in<sup>6</sup>.

Fig. 5 presents a comparison of the values  $(k_1 a)_{\text{dyn}}$  with the values  $(k_1 a)_{\text{st}}$  obtained at steady-state conditions. The subsequent figure, Fig. 6, gives an analogical comparison of the values  $(k_1 a)_{.7}$  obtained from diagram readings with the values  $(k_1 a)_{\text{st}}$ . The points in the figures represent mean values of ten replications of each treatment. Dispersion coefficients were approximately 5% for  $(k_1 a)_{\text{st}}$  values, 12% and 10% for both  $(k_1 a)_{\text{dyn}}$  and  $(k_1 a)_{.7}$  values in wetted-wall and packed absorption column, respectively. The figures indicate that the values of  $(k_1 a)_{.7}$  determined by modified Heineken method agree with the values  $(k_1 a)_{\text{st}}$  better than the values of  $(k_1 a)_{\text{dyn}}$  determined by the moment method.

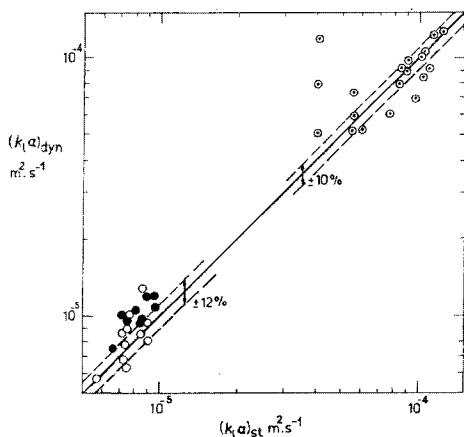


FIG. 5

Comparison of  $(k_1 a)_{\text{dyn}}$  Values Calculated from Zero Moment of Response Curve (18) with  $(k_1 a)_{\text{st}}$  Values Measured Under Steady State Conditions of Column Operation

Wetted-wall column,  $\circ$   $Z = 1.44$  m,  $\bullet$   $Z = 2.65$  m;  $\odot$  packed column.

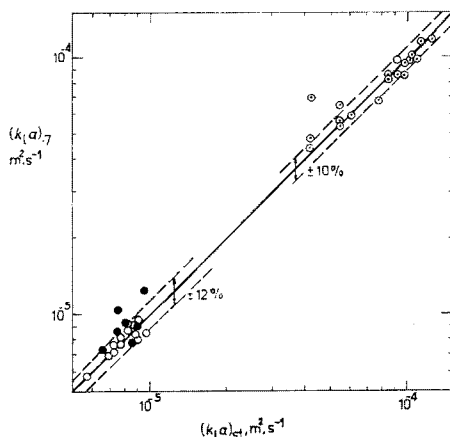


FIG. 6

Comparison of  $(k_1 a)_{.7}$  Values Determined by Modified Heineken Method for  $\Gamma_1 = 0.7$  with  $(k_1 a)_{\text{st}}$  Values

Wetted-wall column,  $\circ$   $Z = 1.44$  m,  $\bullet$   $Z = 2.65$  m;  $\odot$  packed column.

## CONCLUSION

The dynamic method, widely used for measuring the mass transfer coefficient  $k_1 a$  in fermentation tanks, was successfully applied to determine the mass transfer model parameter in absorption columns. The procedure was tested on laboratory apparatus. The method consists in monitoring the absorber response to a sudden change of oxygen concentration in the inlet gas using rapidly responding oxygen probes applicable in various liquid and gaseous media. The method allows to evaluate  $k_1 a$  very rapidly and without computer processing.

## LIST OF SYMBOLS

$A$	quantity defined by (14)
$a$	mass transfer area per unit length of column
$B$	quantity defined by (17)
$c$	concentration
$h$	holdup per unit length of column
$k$	membrane constant
$k_1$	mass transfer coefficient
$m$	equilibrium coefficient
$N$	mass transfer rate per unit length of column
$s$	reading in record
$t$	time
$t_{\max} = \tau_g + \tau_1$	
$u$	interstitial velocity
$\dot{V}$	volumetric flow rate
$Z$	height of packing
$z$	longitudinal distance from top of packing
$\mu^0$	zero moment of response curve
$\Gamma$	normalized response of oxygen probe
$\tau$	mean residence time

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