

Oxygen Transfer Coefficients by Dynamic Model Moment Analysis

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Summary

A new method to estimate the oxygen transfer coefficient (K_{La}) from the experimental dynamic response data is presented. Employing a linear model which allows for gas phase, diffusion film, and oxygen electrode dynamics, the first moment of the response curve is simply related to the sum of the model parameters. Two separate experiments are used to characterize the measurement dynamics and to measure the unknown K_{La} parameter. The simple calculation procedure involves only measuring the area above the response curves.

INTRODUCTION

Matters concerning oxygen uptake rates and oxygen transfer capacities are of utmost importance to the fermentation industries and for efficient biological waste-water treatment. Physical and chemical methods for measuring the oxygen transfer capacity have been employed to characterize bioreactor equipment and aeration devices. Each method has disadvantages, but perhaps the simplest and best is the dynamic K_{La} method as applied to gas-liquid systems under nongrowth conditions. The technique involves lowering the dissolved oxygen concentration—usually by nitrogen stripping. The aeration is then started, and the rising dissolved oxygen concentration is followed with an oxygen electrode. In its original form the method did not take the response time of the electrode into account, which caused large errors. In recent years a number of workers have presented models for describing the electrode response and for correcting the measurements.¹⁻³ Since the detailed physical process of time-dependent diffusion through a liquid film and polymer membrane is complex, many of the mathematical

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formulations have been necessarily tedious and difficult to apply. Recently another possible source of error, the gas dynamics, has been identified.⁴ This applies especially to intensely agitated tank reactors, which exhibit a well-mixed gas phase. After the nitrogen stripping process, which begins the experiment, the gas phase is pure nitrogen. During aeration the nitrogen dilutes the gaseous oxygen and is displaced at a rate dependent on the mean gas residence time. It was shown by simulation that large errors can be expected if the gas and electrode dynamics are not taken into account.⁴

THEORY

In the present paper the differential equation model, which includes gas, electrode, and film dynamics, is solved through Laplace-transform techniques to obtain the response curve moments in terms of the unknown parameter $K_L a$.

Oxygen Balances

The well-mixed flowing gas phase is described by:

$$\frac{dc_G}{dt} = \frac{c_0 - c_G}{V_G/G} - K_L a (c^*_L - c_L) \frac{V_L}{V_G} \quad (1)$$

The well-mixed batch liquid-phase oxygen balance is

$$\frac{dc_L}{dt} = K_L a (c^*_L - c_L) \quad (2)$$

where the equilibrium oxygen solubility relation is

$$c^*_L = (RT/H)c_G \quad (3)$$

In dimensionless form the equations are, for the gas phase:

$$\frac{d\bar{c}_G}{d\bar{t}} = (1 - \bar{c}_G) - K_L a \tau_G \frac{V_L}{V_G} \frac{RT}{H} (\bar{c}_G - \bar{c}_L) \quad (4)$$

and for the liquid phase

$$d\bar{c}_L/d\bar{t} = K_L a \tau_G (\bar{c}_G - \bar{c}_L) \quad (5)$$

where the dimensionless variables are

$$\bar{c}_G = \frac{c_G}{c_0}, \quad \bar{c}_L = \frac{c_L}{c_0(RT/H)}, \quad \bar{t} = \frac{t}{\tau_G}$$

Initial conditions corresponding to the experimental method are at $\bar{t} = 0$; $\bar{c}_L = \bar{c}_G = 0$.

Oxygen Electrode Dynamic Model

A semiempirical second-order response lag is proposed. It consists of a first-order diffusion film lag

$$\frac{d\bar{c}_F}{d\bar{t}} = \frac{\bar{c}_L - \bar{c}_F}{\tau_F/\tau_G} \quad (6)$$

in series with a first-order membrane response relation:

$$\frac{d\bar{c}_E}{d\bar{t}} = \frac{\bar{c}_F - \bar{c}_E}{\tau_E/\tau_G} \quad (7)$$

where \bar{c}_F is the dimensionless diffusion film concentration: $c_F/[c_0(RT/H)]$, and \bar{c}_E is the dimensionless electrode output: $c_E/[c_0(RT/H)]$. The time constant for the film and electrode lags are τ_F and τ_E ; initially at $\bar{t} = 0$, $\bar{c}_E = \bar{c}_F = \bar{c}_L = 0$.

Model Solution

Taking the Laplace transforms of the linear ordinary differential equations (4)–(7), one obtains

$$s\bar{c}_G(s) = \frac{1}{s} - \bar{c}_G(s) - K_L a \tau_G \frac{V_L}{V_G} \frac{RT}{H} [\bar{c}_G(s) - \bar{c}_L(s)] \quad (4a)$$

$$s\bar{c}_L(s) = K_L a \tau_G [\bar{c}_G(s) - \bar{c}_L(s)] \quad (5a)$$

$$s\bar{c}_F(s) = \frac{\bar{c}_L(s) - \bar{c}_F(s)}{\tau_F/\tau_G} \quad (6a)$$

$$s\bar{c}_E(s) = \frac{\bar{c}_F(s) - \bar{c}_E(s)}{\tau_E/\tau_G} \quad (7a)$$

where the transform of variable $\bar{c}_i(\bar{t})$ is denoted by $\bar{c}_i(s)$. Combining and solving for $\bar{c}_E(s)$ gives

$$\bar{c}_E(s) = \frac{1}{s} + \frac{a_9}{s + a_{11}} + \frac{a_{10}}{s + a_{12}} + \frac{a_{13}s + a_{14}}{s^2 + a_5s + a_6} \quad (8)$$

Since $a_5/a_6 > 1$, the inversion yields the electrode response time as:

$$\bar{c}_E(\bar{t}) = 1 + a_9 e^{-a_{11}\bar{t}} + a_{10} e^{-a_{12}\bar{t}} + a_{15} e^{-a_{16}\bar{t}} \times \sinh a_{17}\bar{t} + a_{18} e^{-a_{16}\bar{t}} \cosh a_{17}\bar{t} \quad (9)$$

where the a 's are defined in the Appendix.

Equation (9) can be used with nonlinear parameter estimation techniques to obtain the unknown parameters $K_L a$, τ_F , and τ_E from the experimental $\bar{c}_E(\bar{t})$ data. It is, however, considerably more

convenient to estimate the parameters from the moments of the response curves. This method of parameter estimation for linear differential equation systems has been recently reviewed.⁵ It involves taking the derivatives $[d^n F(s)/ds^n]$ to obtain the n th moment of the impulse response. The resulting set of n algebraic equations can be solved for the n unknown parameters. Because of the practical difficulty of obtaining accurate higher moments, the method is most successfully used when not more than two parameters are to be obtained from a single response curve.

Proceeding, the first moment α_1 is obtained by differentiating eq. (8):

$$\alpha_1 = \frac{1}{K_L a} + \frac{RT}{H} \frac{V_L}{V_G} (\tau_G) + \tau_E + \tau_F \quad (10)$$

where the first moment of the impulse response curve α_1 can be shown to be determined from the \bar{c}_E vs. t step response curve as:

$$\alpha_1 = \int_0^{\infty} (1 - \bar{c}_E) dt \quad (11)$$

Thus eqs. (10) and (11) can be used to obtain $K_L a$ when τ_E and τ_F are known. In order to avoid the inaccuracies of higher moments, it is preferable to perform separate experiments to measure the electrode characteristics. Thus τ_E is assumed to be independent of the properties and turbulence in the liquid and is easily obtained from the step response curve where c_L is changed stepwise.

This experiment must be performed at conditions where the influence of the diffusion film is small, for example, in highly turbulent oxygen saturated water. Under these conditions the step response of the electrode can be approximately described by eq. (7), which allows τ_E to be obtained from a \bar{c}_E vs. t response curve at the point where $\bar{c}_E = 0.63$. The experiment to measure τ_F is performed under the same conditions as the $K_L a$ experiment. Thus, aeration rate, stirring rate, liquid-phase composition, and electrode location should be identical to the experiment in which $K_L a$ is to be measured. Practically, the step changes required to measure τ_E and τ_F can best be achieved by rapidly moving the electrode from a nitrogen stream into oxygen saturated liquid.

The response curve to measure τ_F is analyzed by considering the transfer function which is obtained from eqs. (6) and (7) and is given by

$$\bar{c}_E(s) = \frac{1}{[\tau_E(s) + 1][\tau_F(s) + 1]} \quad (12)$$

On differentiating and setting s equal to zero, the first moment is

$$\alpha_{1E} = \tau_E + \tau_F \quad (13)$$

where α_{1E} is the area above the step response curve and mathematically is expressed as:

$$\alpha_{1E} = \int_0^{\infty} (1 - \bar{c}_E) dt \quad (14)$$

Thus α_{1E} is obtained from the step response curve which is performed at the same conditions as the K_La experiments. The electrode constant τ_E is obtained from step response experiments in highly turbulent oxygen saturated water and is calculated using eq. (13).

EXPERIMENTAL RESULTS AND DISCUSSION

Equipment

All measurements were made with air-water and air-water-carboxymethylcellulose (CMC) systems using a 50 liter propeller stirred bioreactor with draft tube. Details of the design and operating characteristics of the reactor are reported elsewhere.⁶ Gas hold-up in this closed system does not depend on stirrer speed. The oxygen electrode used in this work to measure dissolved oxygen was the Instrumentation Laboratories (IL) Model 530. It was positioned in the outer draft tube annulus. A second electrode (Beckman) having a nonsterilizable rapidly responding (0.6 sec) membrane was used in the oxygen gas tracer experiments. The reactor was thermostatted at 30°C. The experimental results reported in what follows are sufficient to demonstrate the proposed method. They were selected from many experiments⁷ and are typical in respect to their agreement with the theory.

Gas-Phase Dynamics

The gas-phase oxygen balance (eq. (4)) assumes that the outlet gas and the gas which is in contact with the liquid have equal concentrations. This would normally be expected to hold true for reactors with considerable backmixing of the dispersed gas phase. High bubble coalescence rates are not required because segregation or inhomogeneities will not influence the first-order transfer process.

The well-mixed gas-phase assumption will be valid if the mean reactor gas concentration is equal to the outlet concentration. A simple way of checking this assumption for any particular situation is to compare gas tracer step or pulse responses to the theoretical

expectation. The tracer gas should have low solubility so that absorption in the liquid is negligible. In the present case, oxygen was used as a tracer gas, and its concentration was monitored in the gas phase. Consideration of the transfer term coefficient for 1,250 rpm using measured parametric values gives a value of 0.21 for $(K_L a \tau_G)(V_L/V_G)(RT/H)$; it is therefore reasonable to neglect the transfer term in eq. (4). The theoretical response to a step input is then

$$\bar{c}_G = 1 - e^{-t/\tau_G}$$

In Figure 1 the experimental and theoretical tracer response curves are plotted which confirm that the gas phase is close to a well-mixed condition at low and high stirrer speeds. Similar results were obtained for all stirrer speeds used.

Electrode Time Constant

The electrode time constant was obtained in water at stirring rates above 1,000 rpm, corresponding to 2 m/sec liquid velocity parallel to the electrode membrane face, by measuring the step response. The input c_L step was created by placing the electrode into the fermentor after equilibration in a nitrogen atmosphere. Figure 2 shows response curves in water from this experiment at various stirring speeds.

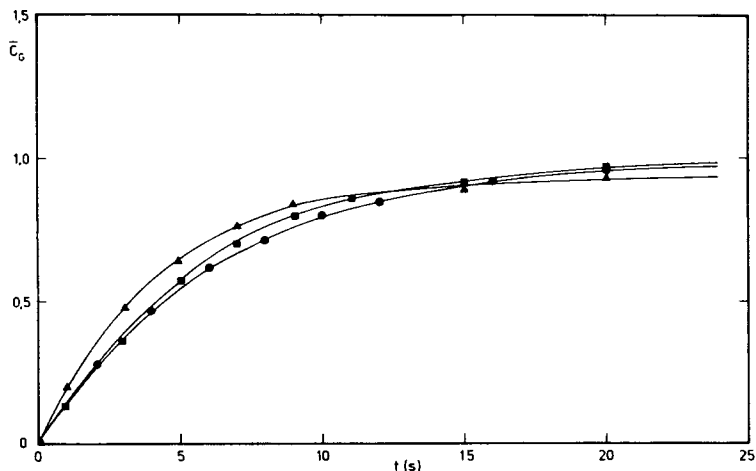


Fig. 1. Gas tracer step response experiments and comparison with theory. Experimental conditions: $G = 3020$ liter/hr; $V_L = 45$ liter; $V_G = 5.25$ liter. (\blacktriangle) 500 rpm; (\blacksquare) 1,250 rpm; (\bullet) theory.

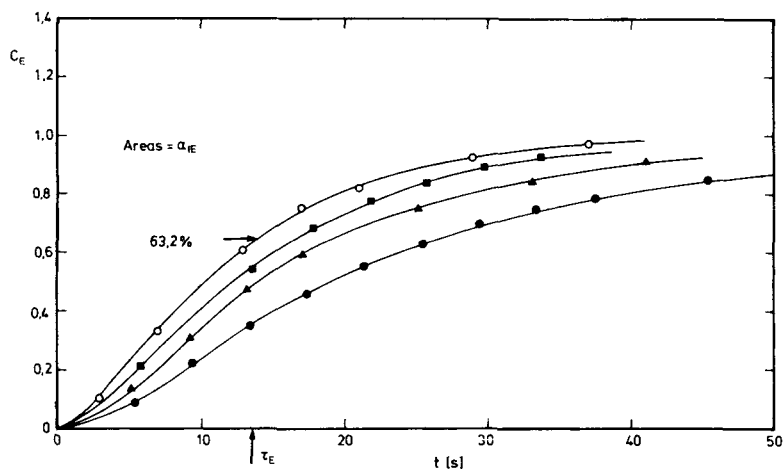


Fig. 2. Electrode response in water to a step change in c_L as a function of stirrer speed. τ_E is obtained from the 63.2% point at high rpm. α_{1E} is obtained from the areas above the curves or at the 63.2% point (approx.). (●) $\alpha_{1E} = 25.4$, rpm = 250; (▲) $\alpha_{1E} = 13.4$, rpm = 500; (■) $\alpha_{1E} = 15.6$, rpm = 750; (○) $\alpha_{1E} = 14.2$, rpm = 1,000.

The electrode response at 1,250 rpm, shown in Figure 3, is the same as the electrode response at 1,000 rpm. From this it was concluded that the liquid film diffusion influence was eliminated ($\tau_F = 0$) above 1,000 rpm for this water system and reactor configuration. Figure 3 shows that the "S" character does not completely disappear, but that the simple first-order electrode response model of eq. (7) can be used to describe the electrode dynamics to a good approximation. From this curve, τ_E is obtained at $\bar{c}_E = 0.632$ and is equal to 14.2 sec. A pure dead time of 3 sec was subtracted from the data.

Liquid Film Time Constant

At turbulence levels within the range of normal fermentor conditions, the electrode response is described well by a second-order lag relation consisting of two terms, the first-order film and electrode relations of eqs. (6) and (7). This has been verified over a range of stirrer speeds from 250 to 1,500 rpm for both water and CMC solutions. Figure 4 shows the results of two such experiments in which step response curves are used to calculate τ_F at 250 rpm for water and CMC systems. Here the area above each curve is α_{1E} .

The theoretical curves in Figure 4 are obtained from numerical solution to eqs. (6) and (7) using τ_E as obtained from experiments

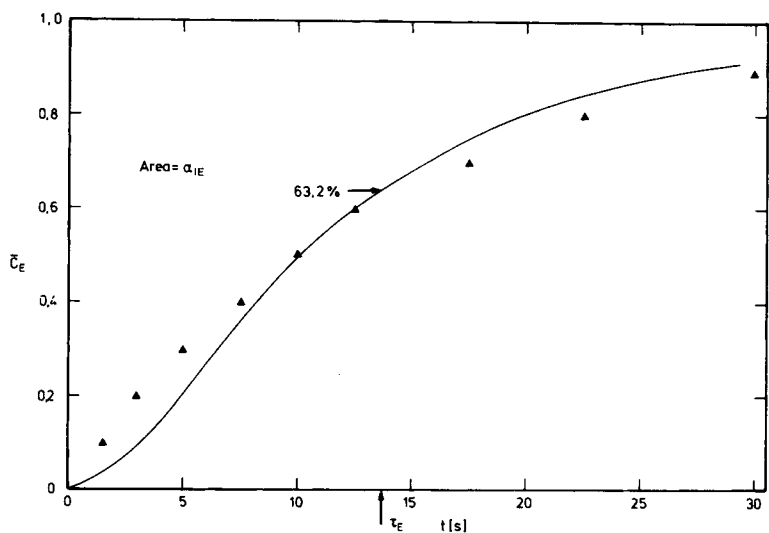


Fig. 3. Electrode step responses with film diffusion fitted to a first-order ($\tau_F = 0$) model. (—) Experiment; (\blacktriangle) theory. Parameters: $\tau_E = 14.2$; $\tau_F = 0$; $\alpha_{1E} = 14.2$; rpm = 1250.

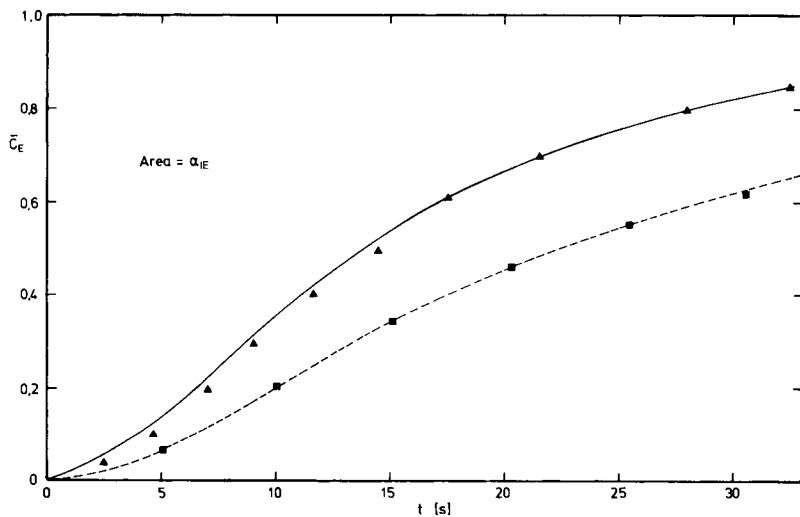


Fig. 4. Electrode step responses with film diffusion fitted to a second-order model. (---) 2% CMC, expt.; (—) H₂O, expt.; (\blacksquare , \blacktriangle) theory. Parameters for water: $\tau_E = 14.2$; $\tau_F = 4.4$; $\alpha_{1E} = 18.6$; rpm = 250. Parameters for 2% CMC: $\tau_E = 12.0$; $\tau_F = 19.6$; $\alpha_{1E} = 31.6$; rpm = 750.

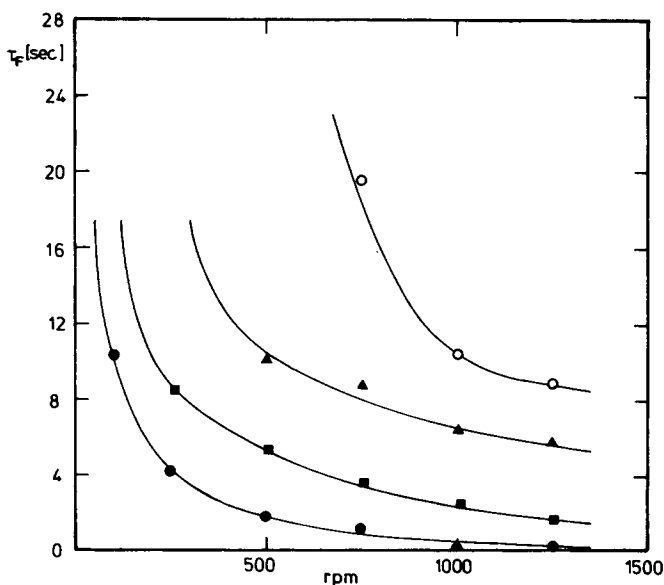


Fig. 5. Diffusion film time constant (τ_F) dependence on stirrer speed and CMC concentration. (●) H₂O, $\eta = 1.0$ cP; (■) 0.5% CMC, $\eta = 15.0$ cP; (▲) 1.0% CMC, $\eta = 54.0$ cP; (○) 2.0% CMC, $\eta = 645.0$ cP.

and τ_F from eq. (13). This figure, which is typical of the results obtained, shows that the second-order lag model fits the data well.

Values of τ_F must be obtained for each $K_L a$ experimental condition to characterize the diffusion film effects. Figure 5 gives results from representative experiments which show how τ_F varies with stirrer speed using water and CMC solutions. The large differences in τ_F between the water and CMC systems are caused by the large viscosity differences as given in the figure.

Oxygen Transfer Coefficient

The response curve as obtained by deoxygenating with nitrogen and beginning the aeration at $t = 0$ is analyzed using eq. (10). With known values of τ_E and τ_F , $K_L a$'s can be calculated from α_1 , which is the area above the c_E vs. t response curve. Figures 6 and 7 show examples of response curves for water systems which are compared with the theoretical curves, as obtained by numerical solution of eqs. (4)–(7) or from the analytical solution of eq. (9) using for parameters those found by the method described here.

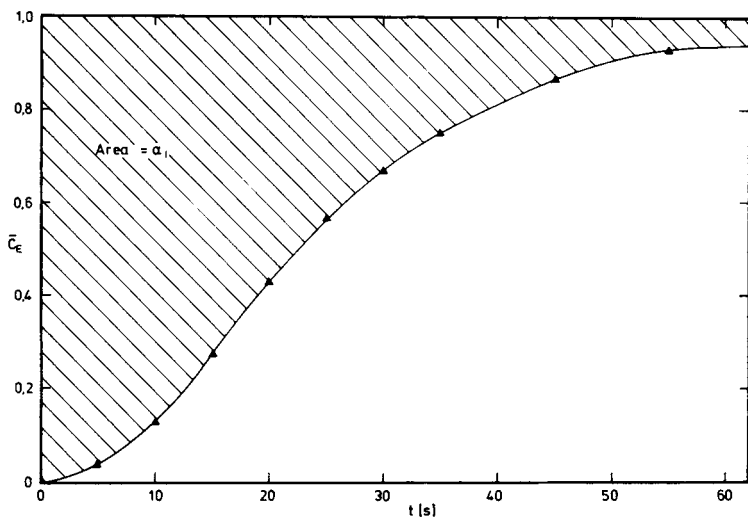


Fig. 6. Dynamic K_{La} response curve at high stirrer speed compared with theory. Parameters: $K_{La} = 0.21$; $\alpha_{1E} = 14.2$; $\alpha_1 = 26.52$; $\tau_E = 14.2$; $\tau_F = 0$; $\tau_G = 5.96$; rpm = 1250; $RT/H = 0.03$; $V_L/V_G = 8.8$. (—) Experiment; (\blacktriangle) theory.

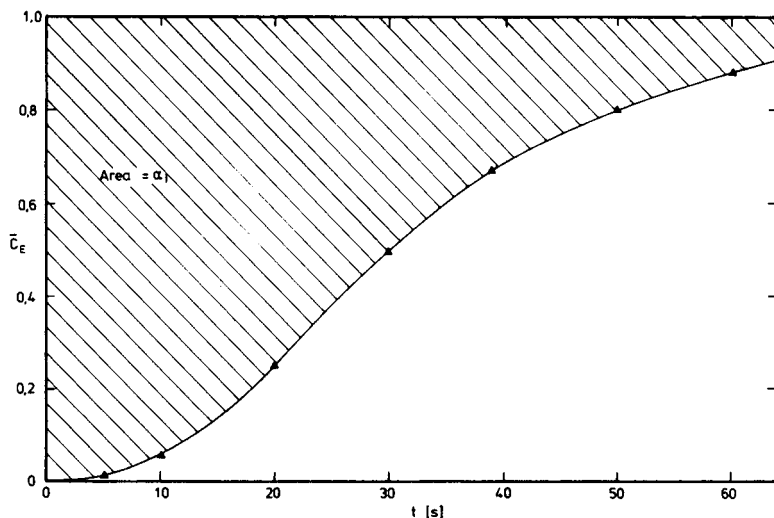


Fig. 7. Dynamic K_{La} experiment at low stirrer speed compared with theory. Parameters: $K_{La} = 0.039$; $\alpha_{1E} = 16.1$; $\alpha_1 = 49.4$; $\tau_E = 14.2$; $\tau_F = 1.9$; $\tau_G = 5.96$; rpm = 500; $RT/H = 0.03$; $V_L/V_G = 8.8$. (—) Experiment; (\blacktriangle) theory.

TABLE I

Experimental K_La Values* and Electrode and Diffusion Film Time Constants

System	V_L/V_G	τ_G (sec)	rpm	τ_E (sec)	τ_F (sec)	K_La (sec ⁻¹)
Water	8.8	5.96	500	14.2	1.9	0.0393
	8.8	5.96	750	14.2	1.4	0.0846
	8.8	5.96	1000	14.2	0.0	0.1479
	8.8	5.96	1250	14.2	0.0	0.2095
2% CMC	8.8	11.92	500	14.2	38	0.0101
	8.8	11.92	700	14.2	19.6	0.0131
	8.8	11.92	1000	14.2	10.4	0.0188
	8.8	11.92	1250	14.2	9.0	0.0219

* Experiments conducted under a range of stirrer speeds for air-water systems with 0 and 2% CMC additive.

Table I summarizes the K_La values obtained by experiment for a range of stirrer speeds for air-water systems with 0 and 2% CMC additive. Also shown in Table I are the results of separate experiments to measure the electrode and diffusion film time constants.

CONCLUSION

The response of the electrode without diffusion film effects can be fit approximately by a first-order model (Fig. 3) and the empirical fit of the second-order (film and electrode) model is excellent (Fig. 4). It appears therefore that this model with empirically determined time constants will adequately describe the response of the measurement device to a change in c_L . The relative importance of the two constants is seen from eq. (13) and Table I. For very viscous systems, τ_F can be much larger than τ_E , whereas for water τ_F is less than 15% of τ_E . These results prove that for viscous systems the film diffusion influence cannot be neglected.

The K_La experiment, whose dynamics depends upon both the gas and the liquid phase, is well described by the theory. The relative influence of the gas phase is quantitatively given by eq. (10), which expresses the contribution of the individual time constants to the area above the response curve. The larger the gas residence time τ_G , the more important will be the gas dynamics. For the water system studied here, the gas dynamics contributes to the total dynamics about one-half as much as the electrode. For the CMC system with its large gas residence time, the effects of the gas and

the electrode are about equal. The importance of considering the complete process dynamics when performing dynamic K_La measurements is emphasized by the fact that for the lowest K_La reported here, the sum of the gas, electrode, and film contributions to α_1 , was 40%, while for the highest K_La , it was over 80%.

The method reported here accounts for the dynamic gas and liquid film effects which have been shown to be important, but which have not been included in any previous K_La method. Particularly important for the practicing engineer or microbiologist is the ease with which the experiments are performed and the simplicity of the calculational procedure.

APPENDIX*

$$\begin{aligned}
 a_1 &= K_La, & a_2 &= (RT/H)(V_L/V_G)\tau_G \\
 a_3 &= \tau_G, & a_4 &= \tau_E^{-1} \\
 a_5 &= 1 + a_1(a_2 + a_3), & a_6 &= a_1a_3 \\
 a_7 &= \tau_F^{-1}, & a_8 &= a_1a_3^3 a_4 a_7 \\
 a_9 &= a_8/[a_{11}(a_{11} - a_{12})(a_{11}^2 - a_5a_{11} + a_6)] \\
 a_{10} &= -a_8/[a_{12}(a_{11} - a_{12})(a_{12}^2 - a_5a_{12} + a_6)] \\
 a_{11} &= a_3a_4, & a_{12} &= a_3a_7, & a_{13} &= -(1 + a_9 + a_{10}) \\
 a_{14} &= -(a_6 + a_{11} + a_{12}) - a_9(a_5 + a_{12}) \\
 & & & & & - a_{10}(a_5 + a_{11}) - a_{13}(a_{11} + a_{12}) \\
 a_{15} &= \frac{a_{14} - a_{13}E/T}{T(E^2 - 1)^{1/2}a_6} \\
 a_{16} &= E/T, & a_{17} &= (E^2 - 1)^{1/2}/T \\
 a_{18} &= a_{13}/a_6T^2, & 2TE &= a_6/a_6, & T^2 &= a_6^{-1}
 \end{aligned}$$

Nomenclature

a_i	constants, functions of the process parameters as defined in the appendix
c	oxygen concentration, mol/liter
G	gas phase flow rate, liter/sec
H	Henry's coefficient, liter atm/mol
K_La	oxygen mass transfer coefficient, sec ⁻¹
R	gas constant, liter atm/mol °K
s	Laplace parameter
t	time, sec
T	absolute temperature, °K

* T and E are defined here only by the above relations and are used only in the appendix.

V	volume, liter
α_i	moments of impulse response curves and area above curves
η	viscosity, cP
τ	time constants and residence time, sec

Subscripts and Superscripts

E	refers to electrode
F	refers to diffusion film
G	refers to gas phase
L	refers to liquid phase
0	refers to inlet
—	overbar refers to dimensionless variables
*	refers to apparent values

This cooperative work was accomplished in the Institute of Microbiology (Professor A. Fiechter) and the Chemical Engineering Laboratory (Professor J. R. Bourne).

References

1. V. Linek, M. Sobotka, and A. Prokop, *Biotechnol. Bioeng.*, **15**, 429 (1973).
2. C. W. Robinson and C. R. Wilke, *Biotechnol. Bioeng.*, **15**, 755 (1973).
3. F. G. Heineken, *Biotechnol. Bioeng.*, **12**, 145 (1970).
4. I. J. Dunn and A. Einsele, *J. Appl. Chem. Biotechnol.*, **25**, 707 (1975).
5. N. D. P. Dang, *J. Ferment. Technol.*, **54**, 396 (1976).
6. D. Karrer and A. Einsele, 5th International Fermentation Symposium, Berlin, 1976.
7. D. Karrer, Ph.D. thesis, to be published.

Accepted for Publication December 28, 1976