

## Mass Transfer in a Closed Stirred Gas/Liquid Contactor

### Part 1: The Mass Transfer Rate $k_L S$

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#### Abstract

Liquid phase mass transfer rates  $k_L S$  for the absorption of oxygen in tap water and in aqueous ionic solutions have been determined in two closed stirred tank contactors for a power input between 3 and 70 W/kg and (impeller diameter)/(tank diameter) ratios  $D_i/T$  of 0.3, 0.35 and 0.4. The contactors had diameters of 0.19 and 0.6 m. The dispersed phase fraction was 1% by volume in all experiments. The values of  $k_L S$  were determined using two different techniques:

- (1) a transient physical absorption method; and
- (2) the sulphite method.

The corresponding results were in good agreement with each other.

For a gas fraction of 1% by volume the results could be well correlated by the following equations:

$$k_L S = 0.05 \left( \frac{n D_i^2}{T^{1.5}} \right)^{1.95} \quad \text{for tap water}$$

and

$$k_L S = 0.11 \left( \frac{n D_i^2}{T^{1.5}} \right)^{2.1} \quad \text{for a solution of } 0.6 \text{ kmol NaCl/m}^3.$$

#### INTRODUCTION

In a stirred tank contactor gas and liquid may be brought into intimate contact with each other. In a continuous flow reactor gas and liquid are fed separately into the reactor. For the discharge of gas there are two different possibilities.

(1) The gas escapes from a free liquid level, as in an open stirred tank contactor. In this case the contactor acts as a gas/liquid mixer and as a gas/liquid separator.

(2) The gas and the liquid leave the reactor through the same line. There is no free liquid level in the reactor; we will call this type of arrangement a "closed tank reactor". The separation takes place in a second apparatus.

The main advantage of a closed tank contactor is that the gas hold-up is, to a certain limit, an independent variable. The possibility of independent variation of the hold-up in the reactor may be of technological as well as of scientific interest. This study was restricted to experiments in a closed tank contactor without a continuous throughput of gas and liquid. The aim was to determine a scale-up rule for the mass transfer rate  $k_L S$  in this type of contactor.

The mass transfer rate  $k_L S$  is a function of

- (1) the stirrer speed  $n$ ,
- (2) the impeller diameter  $D_i$ ,
- (3) the tank diameter  $T$ ,
- (4) the gas fraction  $\epsilon$  and
- (5) the physical properties of the gas and liquid phases.

The mass transfer rate was determined as a function of variables (1), (2) and (3). The physical properties were not varied, but the mass transfer rate was determined in two different solutions:

- (a) tap water, in which the bubbles coalesce very quickly, and
- (b) an ionic solution of 0.6 kmol NaCl/m<sup>3</sup> or 0.8 kmol Na<sub>2</sub>SO<sub>4</sub> or Na<sub>2</sub>SO<sub>3</sub>/m<sup>3</sup>, in which the coalescence rate is very low.

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## EXPERIMENTAL

*The reactor*

Figure 1 shows a schematic drawing of the experimental set-up. Two cylindrical tanks of 0.6 and 0.19 m

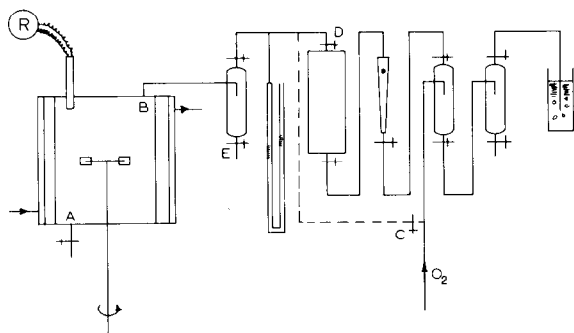


Fig. 1. Experimental set-up.

diameter and with a height equal to the diameter were used. The tanks were equipped with four baffles, the width of the baffles being one-tenth of the vessel diameter, and were closed with a cover. The cover of the large tank had the shape of a cone with a very small top so that the air in the vessel could be removed more easily through a valve in the centre.

Turbine impellers with six flat blades were used as stirrers. Voncken<sup>1</sup> proposed a turbine design with the relative dimensions of the impeller diameter : blade width : blade height being in the ratio 20 : 5 : 4. The stirrers were placed in the centre of the vessel. In both tanks three sizes were used with (impeller diameter)/(tank diameter) ratios of 0.3, 0.35 and 0.4. The impellers were driven by an electric motor and the stirrer speed was measured by means of a stroboscope.

The smaller vessel was made of Perspex, whereas the larger vessel and all the stirrers were made of stainless steel. Water and oxygen could be supplied to or sucked from the vessel through valves in the bottom and in the vessel cover. Oxygen was supplied to the reactor from a gas cylinder via a safety trap, a flowmeter, a pressure surge vessel and a second safety gas trap. An extra safety gas trap together with a small bubble column and a manometer were connected to the oxygen supply line to control the pressure.

*Procedure*

Using the experimental set-up described above, the

mass transfer rate  $k_L S$  was determined using two different experimental techniques:

- (1) a transient physical absorption method, and
- (2) the sulphite method.

In the first method oxygen was absorbed in water from which the oxygen had been completely removed by stripping with either pure nitrogen, pure helium or pure argon. The vessel was completely filled with this oxygen-free water. A known amount of water was tapped off through valve A and the same volume of pure oxygen was metered into the reactor through inlet B. Then stirring was commenced and the oxygen started to be absorbed and the nitrogen, helium or argon started to be desorbed.

While the valves C, D and E were closed, extra oxygen could be drawn into the reactor through inlet B to maintain constant pressure during the absorption process. (The solubility of  $O_2$  is greater than that of the other gases.) The rate of the absorption process was determined by measuring the rate at which the oxygen concentration in the liquid changed. The oxygen concentration in the liquid was measured with a MEAM cell and recorded on a KIPP-BD-5 using a chart speed of 1.2 cm/s.

Mancy<sup>2</sup> and Barendrecht<sup>3</sup> have given an extensive description of the MEAM cell. The important property of this cell is that the measured current  $i(t)$  is proportional to the oxygen activity.

The interpretation of the results of this transient physical absorption method will be explained in the next section. The method is similar to that used by Gal-Or *et al.*<sup>4</sup> and Robinson and Wilke<sup>5</sup>.

In the second technique oxygen was absorbed in a  $0.8 \text{ kmol Na}_2\text{SO}_3/\text{m}^3$  solution. This technique has been used and discussed by several authors<sup>6,7</sup>. In their experiments the absorption rate was determined by measuring the sulphite concentration as a function of time. In our experiments the volumetric gas flow rate  $\phi_v$  into the closed reactor was measured with a Flowrator R and the oxygen concentration in the liquid was measured with the MEAM cell.

The solution was prepared by dissolving the sulphite in water from which nitrogen had been completely removed by stripping with pure oxygen.

## THE TRANSIENT METHOD

The response of the MEAM cell depends on the rate of change of the oxygen concentration in the liquid and the dynamic behaviour of the cell.

The rate of change of the oxygen concentration and the change of the concentration of the desorbing component (e.g. nitrogen) are given by the following pair of simultaneous differential equations:

$$\frac{dc_O}{dt} = \frac{k_L S}{1-\epsilon} (c_{O,i} - c_O) \approx k_L S (c_{O,i} - c_O) \quad (1)$$

$$\frac{dc_N}{dt} = \frac{-k_{L,N} S}{1-\epsilon} (c_{N,i} - c_N) \approx -k_{L,N} S (c_{N,i} - c_N) \quad (2)$$

This approximation is valid since  $1 - \epsilon = 0.99$ . The ratio  $k_L/k_{L,N}$  is determined by the diffusivities of oxygen and nitrogen in water and by the hydrodynamics at the interface of the bubbles:

(1) the bubbles in tap water have in general a mobile interface and hence

$$\frac{k_L}{k_{L,N}} = \left( \frac{D_O}{D_N} \right)^{1/2} \quad (3a)$$

(2) the bubbles in ionic solutions have in general a rigid interface and hence

$$\frac{k_L}{k_{L,N}} = \left( \frac{D_O}{D_N} \right)^{2/3} \quad (3b)$$

The numerical values of the diffusion coefficients, which have been measured by Wise and Houghton<sup>6</sup>, are given in Table 1.

The two simultaneous differential equations (1) and (2) may be solved by use of the following conditions.

(a) There is equilibrium at the gas/liquid interface:

$$c_{O,i} = y/m_O \quad c_{N,i} = z/m_N \quad (4)$$

(b) During the experiment oxygen is sucked into the reactor to keep a constant total pressure. Since the

gas pressure and the gas volume are constant, the sum of the oxygen and nitrogen concentrations in the gas is a constant. Thus

$$y + z = E \quad (5)$$

(c) The total amount of nitrogen in the tank is constant, and thus

$$c_N(1 - \epsilon) + c_{N,i} m_N \epsilon = E(1 - \epsilon)/m_N \quad (6)$$

(d) The initial conditions are

$$\begin{aligned} \text{for } t = 0: \\ c_N = E/m_N \quad z = 0 \\ c_O = 0 \quad y = E \end{aligned} \quad (7)$$

Using these conditions the solution for  $c_O$  becomes

$$c_O/c_{O,eq} = 1 - \exp(-k_L St) - A \{ \exp(-Bk_{L,N} St) - \exp(-k_L St) \} \quad (8)$$

and the result for  $c_N$  is

$$c_N/c_{N,eq} = 1 + D \exp(-Bk_{L,N} St) \quad (9)$$

where

$$c_{O,eq} = E/m_O B \quad c_{N,eq} = CE/m_N \quad (10)$$

$$A = \frac{k_L}{D(k_{L,N} B - k_L)} \quad A = 1 \text{ if } k_L = k_{L,N}$$

$$B = \frac{m_N + (1 - \epsilon)/\epsilon}{m_N} \approx \frac{m_N \epsilon + 1}{m_N \epsilon} \quad (11)$$

$$C = \frac{1 - \epsilon}{\epsilon \{ m_N + (1 - \epsilon)/\epsilon \}} \approx \frac{1}{m_N \epsilon + 1}$$

$$D = \frac{m_N}{(1 - \epsilon)/\epsilon} \approx m_N \epsilon$$

TABLE 1  
Physical properties

Concentration (kmol/m <sup>3</sup> )	$\rho_c$ (Ns/m <sup>2</sup> $\times 10^3$ )	$\eta_c$ (kg/m <sup>3</sup> $\times 10^{-3}$ )	$D_O$ (m <sup>2</sup> /s $\times 10^9$ )	$D_N$ (m <sup>2</sup> /s $\times 10^9$ )	$D_{Ar}$ (m <sup>2</sup> /s $\times 10^9$ )	$D_{He}$ (m <sup>2</sup> /s $\times 10^9$ )	$m_O$	$m_N$	$m_{Ar}$	$m_{He}$
0	1	1	2.3	2.6	2.3	6.8	30.5	66	30.2	108
0.6 (NaCl)	1.05	1.04	2.19	2.48	2.19	6.5	38	84	38.5	114
0.8 (Na <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>3</sub> )	1.45	1.088	1.58	1.79	1.58	4.7	65	173	55.5	135

The numerical values of  $m_O$ ,  $m_N$ ,  $m_{He}$  and  $m_{Ar}$  are given in Table 1. With these values,  $c_O$  and  $c_N$  can be calculated as a function of the dimensionless parameter  $k_L St$ . In Fig. 2 the calculated values of

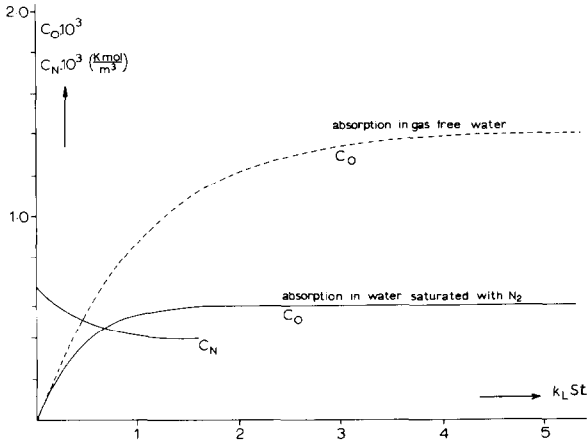


Fig. 2. The oxygen and nitrogen concentration as a function of the parameter  $k_L St$  for absorption of oxygen in nitrogen saturated water and in gas-free water (dotted line).

$c_O$  and  $c_N$  are plotted as a function of  $k_L St$  and are compared with the line (dotted) representing the transient oxygen dissolution in gas-free water. This line is calculated from eqn. (1) with the boundary conditions  $c_O = 0$  at  $t = 0$  and  $c_O = E/m_O$  at  $t = \infty$ . An important observation is that the slopes of both curves for  $k_L St = 0$  are the same. The rate at which the equilibrium concentration is reached in these experiments, when the liquid is saturated with another gas, is apparently larger than the true absorption rate. This apparent rate is  $Bk_L S$ , whereas the true rate is  $k_L S$ . The existence of the apparent rate is due to the fact that the change in the driving force ( $c_{O,i} - c_O$ ) is mainly determined by the rate of change of the interface concentration  $c_{O,i}$ . This rate is determined by the desorption rate of the desorbing component.

The accuracy of the transient physical absorption method can be checked by determining the absorption rate from three different "apparent" rates. Therefore Ar, He and  $N_2$  were used as the desorbing components. The "apparent" rates have been plotted in Fig. 3 as a function of the dimensionless parameter  $k_L St$ . It can be seen that the maximum difference in absorption rates is about a factor two (namely, for the combinations  $O_2/Ar$  and  $O_2/He$ ).

The response of the MEAM cell to the oxygen concentration change in the liquid (eqn. (8)) will be

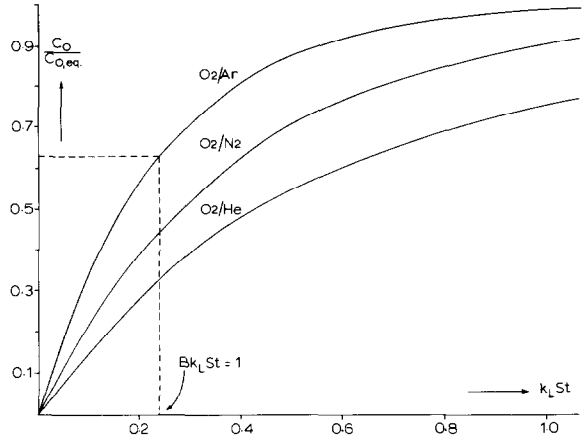


Fig. 3. The relative oxygen concentration as a function of  $k_L St$  for the absorption of oxygen in Ar-,  $N_2$ - or He-saturated water.

discussed with reference to the construction of the cell, which is shown in Fig. 4. The cell consists of a

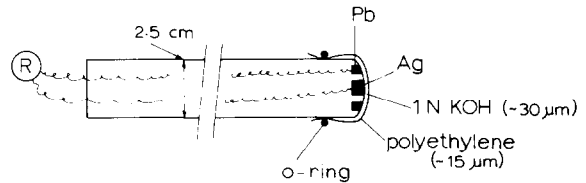


Fig. 4. A sketch of the membrane.

silver cathode and a lead anode. The cathode and anode are covered with a membrane consisting of two parts: (1) a thin layer of paper soaked in a 1N KOH solution and (2) a polyethylene membrane 10–15  $\mu m$  thick. It can be shown that the resistance to the transfer of oxygen from the liquid to the cathode is concentrated in the polyethylene layer. The concentration distribution of oxygen in the polyethylene is calculated from Fick's second law:

$$D_{O,p} \frac{\delta^2 c_{O,p}}{\delta x^2} = \frac{\delta c_{O,p}}{\delta t} \tag{12}$$

with the following boundary conditions:

$$\begin{aligned} t = 0, & \quad c_{O,p} = 0 \quad \text{for } 0 \leq x \leq a \\ t > 0, & \quad c_{O,p} = 0 \quad \text{for } x = a \\ t > 0, & \quad x = 0 \quad c_{O,p} = m_{O,p} c_O(t) \end{aligned}$$

and  $c_O(t)$  is given by eqn. (8).

The rate of oxygen transfer through the membrane which is measured by the MEAM cell is

$$\phi_O'' = -D_{O,p} \left( \frac{dc_{O,p}}{dx} \right)_{x=a} \quad (13)$$

and at equilibrium

$$\phi_{O,eq}'' = -D_{O,p} c_{O,p}(x=0)/a \quad (14)$$

A schematic concentration distribution at equilibrium is given in Fig. 5, in which the proportionality  $m_{O,p}$  has been chosen arbitrarily.

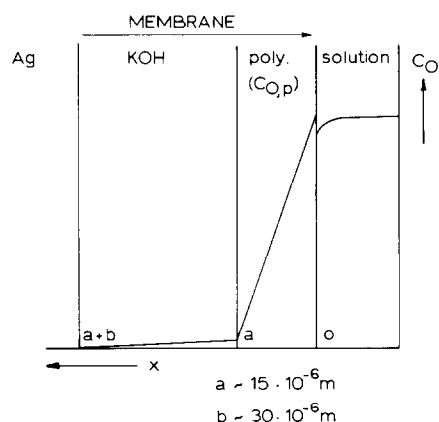


Fig. 5. A schematic oxygen concentration distribution in the membrane.

The measured electric current through the cell is proportional to the flux  $\phi_O''$ , and the relative change of the flux is

$$\frac{i(t)}{i_{eq}} = \frac{\phi_O''}{\phi_{O,eq}''} = a \frac{(dc_{O,p}/dx)_{x=a}}{c_{O,p}(x=0)} \quad (15)$$

The derivative in the quotient in eqn. (15) is derived from the solution of eqn. (12) and its associated boundary conditions. This problem can be solved by Laplace transformation with respect to  $t$ . The result is a complicated series expansion for  $c_{O,p}$ . It can be proved that this series solution may be differentiated term by term with respect to  $x$ . Substituting  $x = a$  we get the desired formula for the quotient in the right-hand side of eqn. (15):

$$\frac{i(t)}{i_{eq}} = 1 - (1-A)(k_L S \tau)^{1/2} \frac{\exp(-k_L S t)}{\sin(k_L S \tau)^{1/2}} -$$

$$- A(Bk_{L,N} S \tau)^{1/2} \frac{\exp(-Bk_{L,N} S t)}{\sin(Bk_{L,N} S \tau)^{1/2}} + 2 \sum_{n=1}^{\infty} (-1)^n \left\{ 1 - (1-A) \frac{(n\pi)^2}{(n\pi)^2 - k_L S \tau} - A \frac{(n\pi)^2}{(n\pi)^2 - Bk_{L,N} S \tau} \right\} \exp\left\{ - (n\pi)^2 \frac{t}{\tau} \right\} \quad (16)$$

For all experiments the diffusion time  $\tau$ , which is equal to  $a^2/D_{O,p}$ , has been determined for every freshly prepared cell by measuring the response to a step in the oxygen concentration. Then relation (16) holds if  $k_L S = \infty$  is substituted:

$$\frac{i(t)}{i_{eq}} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left\{ - (n\pi)^2 \frac{t}{\tau} \right\} \quad (17)$$

By substitution of this value for the diffusion time  $\tau$  and by substitution of the proper equation (3a) or (3b) for  $k_{L,N}$ , an expression is obtained for  $i(t)/i_{eq}$  as a function of  $t$ , with  $k_L S$  as an unknown parameter and  $A$ ,  $B$ ,  $D_O$  and  $D_N$  as known parameters.

For every gas combination and each different solution a graphical representation was made of eqn. (16) as a function of time for various values of  $k_L S$ . The measured values of  $i(t)/i_{eq}$  were plotted on the same scale and compared with the calculated graphs. The measured values of  $k_L S$  could be determined by comparing the two graphs.

## THE SULPHITE METHOD

The sulphite method uses the oxidation of sodium sulphite to sodium sulphate. Without the use of a catalyst this reaction is slow. However, the oxygen concentration  $c_O$  in the bulk is close to zero. Thus the mass transfer process can be described by the following equation:

$$\phi_O = k_L S V c_{O,i}(t) \quad (18)$$

The interface concentration  $c_{O,i}$  is a function of time since the feed often contains a small amount of nitrogen. Since nitrogen accumulates in the gas and liquid phases, the oxygen concentration  $y$  in the gas phase decreases with time and consequently, so does the interface concentration  $c_{O,i}$ . As the sum  $y + z$  of the oxygen and nitrogen concentrations in the gas phase is constant (eqn. (5)), the rate of change of the

oxygen concentration can be derived from the rate of change of the nitrogen concentration:

$$\frac{dy}{dt} = -\frac{dz}{dt} \tag{19}$$

The relation between  $y$  and  $c_{O,i}$  is

$$y = c_{O,i} m_O \tag{20}$$

A mass balance for the nitrogen in the reactor gives an expression for  $dz/dt$ :

$$\phi_N = \epsilon V \frac{dz}{dt} + (1 - \epsilon)V \frac{dc_N}{dt} \tag{21}$$

It can be shown that  $c_N$  is approximately equal to  $c_{N,i}$ , which means that the mass transfer rate of nitrogen from the gas phase to the liquid phase is not a limiting factor. Thus

$$c_N = z/m_N \tag{22}$$

The ratio between  $\phi_O$  and  $\phi_N$  is

$$\frac{\phi_O}{\phi_N} = \frac{q}{1 - q} \tag{23}$$

By substituting eqns. (18) and (21) into eqn. (23) and eliminating  $c_N$ ,  $z$  and  $y$  using eqns. (22), (19) and (20), an ordinary differential equation in  $c_{O,i}$  is obtained. The solution of this equation is

$$c_{O,i}(t) = c_{O,i}(t=0) \exp(-k_L S t/F) \tag{24}$$

where  $F$  is substituted for the term

$$\frac{q}{1 - q} \frac{m_O}{m_N} \left\{ \epsilon(m_N - 1) + 1 \right\}$$

which is roughly  $q/(1 - q)$  if  $\epsilon = 0.01$ . Thus the absorption rate becomes

$$\phi_O = k_L S V c_{O,i}(t=0) \exp(-k_L S t/F) \tag{25}$$

The mass flow  $\phi_O$  through the liquid/gas interface can be easily calculated from the volumetric flow rate  $\phi_v$  into the reactor:

$$\phi_O = \frac{\phi_v \rho_O q}{32} - \epsilon V \frac{dy}{dt} \tag{26}$$

It can easily be shown that the second term on the right-hand side of this equation is much smaller than the first term.

If  $\ln \phi_O$  is plotted as a function of time, then  $k_L S$  can be calculated from the intercept at  $t = 0$  and from the slope if  $q$  has been determined.

DISCUSSION OF RESULTS

About 150 results were obtained using the transient absorption technique. The accuracy of this technique was checked by

- (1) the use of three different desorbing gases, and
- (2) the use of the sulphite method.

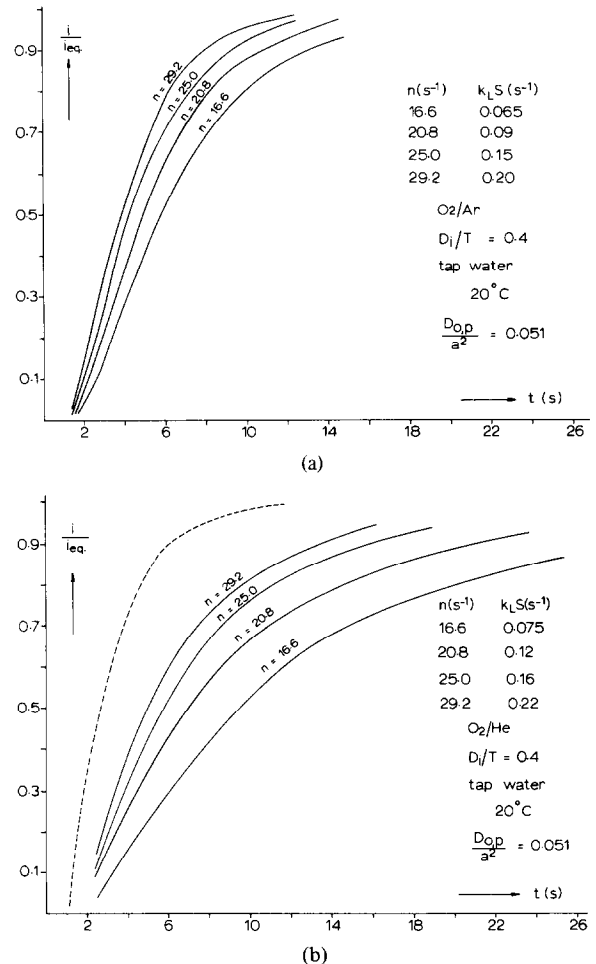


Fig. 6. An illustration of the measured graphs of the relative electric current as a function of time for the absorption of oxygen in Ar-saturated water (a) and in He-saturated water (b).

In a previous section it has been explained that the “apparent” mass transfer rate  $Bk_L S$  depends on the physical properties of the desorbing gas. He, N<sub>2</sub> and Ar were used as gases to be desorbed. Then the value of  $B$  could be varied about a factor two. As an illustration for this difference in the “apparent” rates the measured graphs for the absorption of O<sub>2</sub> in Ar-saturated water and in He-saturated water are shown in Fig. 6(a) and (b), respectively. It can be seen that for the same conditions but for a different desorbing gas (Ar and He), the graphs are very different but the measured values of  $k_L S$  are almost the same. From Table 2 we notice that  $k_L S$  values obtained using O<sub>2</sub>/Ar are always about 10–20% smaller than those obtained using O<sub>2</sub>/He. This might be due to the fact that the time needed to get complete dispersion of the gas phase is not completely negligible. However, the difference between  $k_L S$  values obtained by using O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/He is much less. Therefore these  $k_L S$  values are considered to be the most correct values. In most experiments a correction was made automatically for the time needed for complete dispersion of the gas phase. This was a consequence of the fact that the shapes of the measured and computed curves were compared with each other. In general this correction in the smaller vessel was less than 1 s, but in the larger vessel it was between 1 and 4 s.

The sulphite method was primarily used to check the transient method. It was assumed that the physical properties (density, viscosity and solubility of oxygen) for the Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>SO<sub>3</sub> solutions were the same. The values of  $k_L S$  for the 0.8 kmol Na<sub>2</sub>SO<sub>4</sub>/m<sup>3</sup> solutions obtained by the transient technique are compared in Table 2 with those obtained using the sulphite technique. The average difference of 8.5% indicates good agreement between the methods.

The product  $k_L S$  was determined by means of the transient physical absorption technique, with a gas hold-up of 1% by volume, as a function of the stirrer speed  $n$  and the impeller diameter  $D_i$ :

- (a) in the smaller vessel in tap water and in ionic solutions, and
- (b) in the larger vessel in tap water and in a solution of 0.6 kmol NaCl/m<sup>3</sup> only.

The following proportionalities were derived from the results by means of regression analyses:

$$\begin{aligned}
 k_L S &\sim n^{1.95} && \text{for tap water at constant } D_i \text{ and } T \\
 k_L S &\sim n^{2.1} && \text{for ionic solutions at constant } D_i \\
 &&& \text{and } T \\
 k_L S &\sim D_i^{3.9} && \text{for tap water at constant } n \text{ and } T \\
 k_L S &\sim D_i^{4.2} && \text{for ionic solutions at constant } n \\
 &&& \text{and } T
 \end{aligned}$$

TABLE 2  
 $k_L S$  values in the smaller vessel

$D_i/T$	$n$ (s <sup>-1</sup> )	$k_L S$ in tap water					$k_L S$ in 0.8 kmol Na <sub>2</sub> SO <sub>4</sub> /m <sup>3</sup>	$k_L S$ in 0.8 kmol Na <sub>2</sub> SO <sub>3</sub> /m <sup>3</sup>	
		O <sub>2</sub> /Ar	O <sub>2</sub> /He	O <sub>2</sub> /N <sub>2</sub>					
0.3	16.6	0.02	0.02	0.02	0.025	0.023	0.025	0.03	0.035
	20.8	0.03	0.03	0.04	0.04	0.04	0.04	0.055	
	24.9	0.045	0.045	0.055	0.055	0.058	0.055	0.075	
	29.2	0.055	0.06	0.07	0.07	0.075	0.07	0.11	
	33.3	0.07	0.07	0.085	0.1	0.095	0.09	0.15	
0.35	16.6	0.038	0.045	0.05	0.045	0.04	0.045	0.065	0.065
	20.8	0.06	0.06	0.07	0.065	0.07	0.065	0.11	
	25.0	0.085	0.09	0.1	0.095	0.1	0.095	0.15	
	29.2	0.11	0.12	0.14	0.14	0.13	0.14	0.23	
	33.3	0.15	0.15	0.18	0.18	0.18	0.18	0.35	
0.4	11.6							0.06	0.065
	16.6	0.06	0.065	0.075	0.075	0.068	0.07	0.12	
	20.8	0.08	0.09	0.11	0.12	0.1	0.1	0.18	
	24.9	0.14	0.15	0.15	0.16	0.15	0.15	0.26	
	29.9	0.2	0.2	0.2	0.22	0.21	0.22	0.35	

Apparently

$$k_L S \sim (nD_i^2)^{1.95} \quad \text{for tap water}$$

$$k_L S \sim (nD_i^2)^{2.1} \quad \text{for ionic solutions}$$

The results in both vessels could be well correlated by the following equations:

$$k_L S = 0.05 \left( \frac{nD_i^2}{T^{1.5}} \right)^{1.95} \quad \text{for tap water} \quad (27)$$

$$k_L S = 0.11 \left( \frac{nD_i^2}{T^{1.5}} \right)^{2.1} \quad \text{for ionic solutions} \quad (28)$$

The experimental values of  $k_L S$  have been plotted as a function of  $nD_i^2/T^{1.5}$  for tap water and ionic solutions respectively in Fig. 7(a) and (b). The pro-

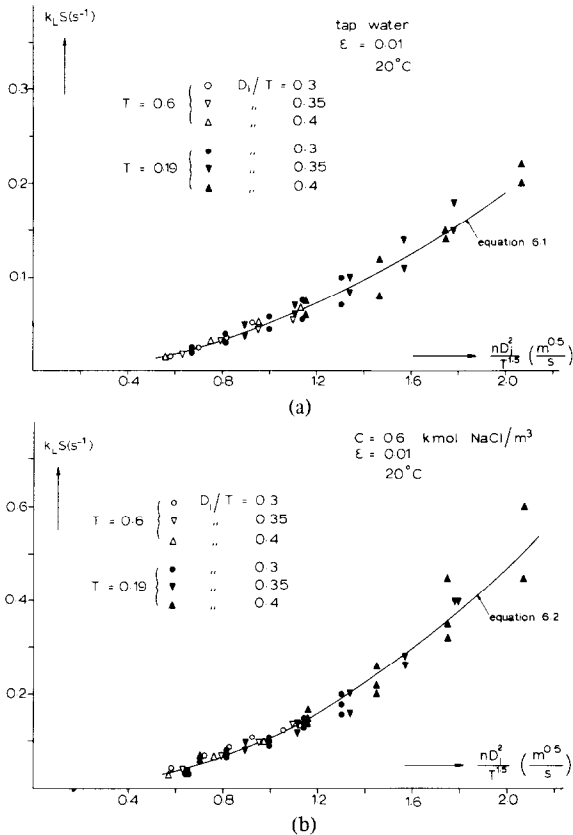


Fig. 7. The determined values of  $k_L S$  as a function of the group  $nD_i^2/T^{1.5}$ ; (a) in tap water and (b) in a solution of 0.6 kmol NaCl/m<sup>3</sup>.

portionality of  $k_L S$  with the stirrer speed  $n^{2.1}$  (in ionic solutions) has been demonstrated by other authors for liquid/liquid dispersions, e.g. van

Heuven<sup>9</sup> and Madden and Damerall<sup>10</sup>. However, van Heuven concluded from measurements in different vessels with constant  $D_i/T$  that  $k_L S$  was proportional to  $(nD_i)^{2.1}$ , whereas from our results it follows that  $k_L S$  is proportional to  $(nD_i^{0.5})^{2.1}$  if  $D_i/T$  is constant. Some authors, e.g. Calderbank<sup>11</sup>, have suggested that  $k_L$  and  $S$  are both determined by the specific power consumption of the stirrer ( $n^3 D_i^5/T^3$ ). However, our eqns. (27) and (28) may also be written as

$$k_L S = 0.05 \left( \frac{n^3 D_i^5}{T^3} \right)^{0.65} \left( \frac{D_i}{T} \right)^{0.65} \frac{1}{T^{0.33}}$$

for tap water

$$k_L S = 0.11 \left( \frac{n^3 D_i^5}{T^3} \right)^{0.7} \left( \frac{D_i}{T} \right)^{0.7} \frac{1}{T^{0.35}}$$

for ionic solutions

Thus from our results it follows that the mass transfer rate does not depend only on the specific power consumption, but also on the size of the impeller and apparently also on the size of the tank. The above results indicate that on scale-up the specific power per unit volume necessary to obtain a given value of  $k_L S$  increases with the tank diameter. The relations are limited to gas fractions of 1% by volume.

CONCLUSIONS

- (1) The transient physical absorption technique is apparently a reliable technique to determine the mass transfer rate  $k_L S$  in the smaller vessel. However, this technique has limited applications. It is only suitable for low gas fractions and high stirrer speeds.
- (2) The results could be well correlated by the empirical equations

$$k_L S = 0.05 \left( \frac{nD_i^2}{T^{1.5}} \right)^{1.95} \quad \text{for tap water}$$

$$k_L S = 0.11 \left( \frac{nD_i^2}{T^{1.5}} \right)^{2.1} \quad \text{for a solution of 0.6 kmol NaCl/m}^3$$

for  $\epsilon = 0.01$ . The constants in these equations have the dimensions of roughly s/m. These constants depend on the physical properties of the systems and on the gas fraction  $\epsilon$ .

- (3) The product  $k_L S$  in a closed tank reactor is not a unique function of the power dissipation per unit mass  $n^3 D_i^5/T^3$  (for low gas fractions).



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## NOMENCLATURE

$a$	thickness of polyethylene layer, m
$A$	constant defined in eqn. (11)
$b$	thickness of KOH layer, m
$B$	substitution constant defined in eqn. (11)
$c_N$	nitrogen concentration in the liquid, kmol/m <sup>3</sup>
$c_{N,eq}$	nitrogen concentration in the liquid at equilibrium, kmol/m <sup>3</sup>
$c_{N,i}$	nitrogen concentration in the liquid at gas/liquid interface, kmol/m <sup>3</sup>
$c_O$	oxygen concentration in the liquid, kmol/m <sup>3</sup>
$c_{O,eq}$	oxygen concentration in the liquid at equilibrium, kmol/m <sup>3</sup>
$c_{O,i}$	oxygen concentration in the liquid at gas/liquid interface, kmol/m <sup>3</sup>
$c_{O,p}$	oxygen concentration in polyethylene, kmol/m <sup>3</sup>
$C$	substitution constant defined in eqn. (11)
$D$	substitution constant defined in eqn. (11)
$D_i$	impeller diameter, m
$D_N$	diffusion coefficient of nitrogen in the liquid, m <sup>2</sup> /s
$D_O$	diffusion coefficient of oxygen in the liquid, m <sup>2</sup> /s
$D_{O,p}$	diffusion coefficient of oxygen in the polyethylene, m <sup>2</sup> /s
$E$	sum of oxygen and nitrogen concentrations in the gas phase, kmol/m <sup>3</sup>
$F$	substitution constant defined in eqn. (24)
$i(t)$	electric current as a function of time, A
$i_{eq}$	electric current at equilibrium, A
$k_L$	mass transfer coefficient for oxygen in the liquid, m/s
$k_{L,N}$	mass transfer coefficient for nitrogen in the liquid, m/s
$m_{Ar}$	concentration distribution for argon (air/water)
$m_{He}$	concentration distribution for helium (air/water)

$m_N$	concentration distribution for nitrogen (air/water)
$m_O$	concentration distribution for oxygen (air/water)
$m_{O,p}$	concentration distribution for oxygen (poly/water)
$n$	integer in eqn. (16)
$n$	stirrer speed, 1/s
$q$	volumetric oxygen fraction in the feed
$S$	interfacial area per unit reactor volume, 1/m
$T$	tank diameter, m
$V$	volume of the tank, m <sup>3</sup>
$x$	length parameter, m
$y$	concentration of oxygen in the gas phase, kmol/m <sup>3</sup>
$z$	concentration of nitrogen in the gas phase, kmol/m <sup>3</sup>

## Greek symbols

$\epsilon$	the gas fraction in the tank
$\eta_c$	dynamic viscosity of the continuous phase, Ns/m <sup>2</sup>
$\rho_c$	density of the continuous phase, kg/m <sup>3</sup>
$\rho_O$	density of oxygen in the gas phase, kg/m <sup>3</sup>
$\tau$	diffusion time in polyethylene layer, s
$\phi_N$	nitrogen feed, kmol/s
$\phi_O$	oxygen feed, kmol/s
$\phi''_O$	oxygen mass flux, kmol/m <sup>2</sup> s
$\phi''_{O,eq}$	oxygen mass flux at equilibrium, kmol/m <sup>2</sup> s
$\phi_v$	volumetric feed, m <sup>3</sup> /s

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