ABSORPTION OF PURE AND OF DILUTED GASES ACCOMPANIED BY CHEMICAL REACTION IN A MECHANICALLY AGITATED GAS–LIQUID CONTACTOR

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Theoretical and experimental studies were made of the rate of diluted gas absorption accompanied by chemical reaction in a mechanically agitated, aerated reactor. Several methods of experimental data processing have been proposed, aiming to the objective of determining the interfacial area of dispersion a, the mass transfer coefficient k_L^0, and the volumetric mass transfer coefficient $k_L^0 a$. The use of Danckwerts' type equation for evaluating a and k_L^0 is discussed for a reaction which is second order with respect to the dissolved gas. The effects of oxygen concentration changes in bubbles and of interfacial area changes due to different absorption rates have been taken into account. Data reliability was tested by comparison with results obtained for pure gas absorption. The model consisted of absorption of oxygen–nitrogen mixtures of various concentration into a sulfite solution with or without cobalt catalyst. It has been found that the classical chemical method yields the same values as does the Danckwert's type equation method used for a second order chemical reaction (DTM). In absorption of diluted gases, experimental data can be correlated satisfactorily on the basis of a perfectly mixed gas phase in the reactor even for a relatively high level of conversion. The volumetric mass transfer coefficient values $k_L^0 a$ obtained by the DTM agree with those calculated from absorption rate in absence of catalyst as long as the value $k_L^0 a < 0.1\ \mathrm{s}^{-1}$. At higher $k_L^0 a$ values the values obtained by DTM are markedly higher than those obtained in absence of catalyst. The difference between these values increases with increasing $k_L^0 a$ values. The results of measurements of the effect of oxygen partial pressure on the absorption rate without catalyst suggest that, even in this case, the absorption rate is accelerated chemically.

Numerous papers have been devoted to gas–liquid contacting in mechanically agitated vessels. The most systematic research in this field has been done in the Netherlands[1-3]. The problems attracting considerable discussion are those concerning the measurement of interfacial area and of the mass transfer coefficient. Two measuring techniques have been used: a photographic technique and a chemical method. The latter method has found more frequent application since it is faster and allows to take direct measurements of the integral characteristics. However, these advantages seem to be offset by the challenging problems on whose solution the application of this method is contingent if the hazards of erroneous interpretation of results are to be avoided. To apply it correctly, it is necessary to know the kinetics of the

model reaction. In case a diluted gas is used for absorption, it is also essential to know the residence time distribution of the gas phase, needed for the calculation of a and k_L^0.

Absorption of oxygen into a sodium sulfite solution in the presence of cobalt catalyst represents the model used most frequently for these purpose. The reaction kinetics has been studied thoroughly by many authors[2,4-7]. After it had been found that the reaction kinetics data depend on the purity of solutions used and thus cannot be taken over from literature, a method was proposed[8] permitting to draw a complete picture on the effect of pH, temperature, and catalyst concentration upon the kinetic reaction constant for the kind of sulfite used just on the basis of a single value of the reaction rate constant obtained by measurement under defined conditions. The order of reaction with respect to oxygen has been the subject of several studies[2,5,7,9,10]. The reaction order value equals 2 and 1 at low and high oxygen partial pressures, respectively. The transition of the order value occurs within such a narrow range of p_{O_2} values that it may be considered to occur suddenly (*cf.* figures in literature[5,9,10]). Investigation by Linek and Mayr-hoferová[5,10] have shown that the order value transition takes place at a certain oxygen concentration at the interface. This value appears to depend on the purity of sulfite used. Nevertheless, available information always allows to select experimental conditions such as to maintain a definite and constant reaction order value in all experiments. However, the results of some earlier work[1,11,12] on the mass transfer characteristics of gas–liquid contactors have suffered from using an incorrect reaction order value.

Most authors have used air for absorption. As the oxygen concentration in bubbles is subject to alternation during bubble residence in reactor, the driving force of absorption depends on the mixing conditions for the gas phase. Reith[2] has done quite an amount of work to investigate this. He concluded that neither the bubble size distribution nor the mixing conditions cause any appreciable error, as long as the conversion of the gas phase is not too high (smaller than 20%). In practice, however, this type of contactor is used very often at very low gas flow rates with high conversion of the gas phase. It would be desirable to find by experiment the maximum conversion values at which the notion of ideal flow (piston flow and perfectly agitated gas phase) are viable in estimating the driving-force of absorption.

The difficulties involved in making a correct selection of the absorption driving force value are avoided if pure gases are used for the absorption. Then the gas concentration is not changed by passage through the reactor and the residence time distribution of indivudal bubbles in the system is unimportant. However, the absorption of pure gases proceeds much more rapidly than that of diluted gases, and significant reduction of the interfacial area may take place as a consequence of bubble shrinkage by absorption. Linek and Mayrhoferová[13] have ascertained that the fractional decrease in the gas hold-up and interfacial area in a mechanically agitated gas–liquid contactor depends only on the relative amount of gas absorbed. In contrast, Mehta and Sharma[14] have stated that the decreased area and hold-up may rather be due to the fact that the effect of absorption rate on area and holdup was measured at agitating velocities lower than a critical velocity (beyond which only impeller speed is important), *i.e.*, in a region where the gas flow rate is likely to be important and hence the absorption rate may have an effect on effective interfacial area. This objection by Mehta and Sharma seem to be irrelevant since the greatest decrease of area has been observed at 550 r.p.m., *i.e.*, exactly in the supercritical region. It has also been observed by Reith[2] that area values measured with pure oxygen are smaller than those measured with air. His experiments were being conducted in the supercritical region of stirrer speed. His explanation is that pure oxygen bubbles shrink during their stay in the reactor. Hence we assume that the decrease in area and hold-up should not be ascribed to a subcritical stirrer speed, as Mehta and Sharma[14] did, but that it represents a phenomenon of a different character,

occurring at both the subcritical and the supercritical agitating velocities; it should always be considered when comparing results obtained under identical operational conditions but with different relative amounts of gas absorbed.

Absorption of oxygen in aqueous sulfite solution without cobalt catalyst is accompanied by a moderately fast reaction. Numerous authors, for instance Reith[2] and others[3,15-18], assume that in this case the mass transfer coefficient equals the mass transfer coefficient for absorption without chemical reaction (physical absorption) and that the bulk concentration of oxygen is nearly zero. However, Sharma and Danckwerts[19] express the opinion that it is not always easy to satisfy both the conditions which would garantee no reaction in the film and zero bulk oxygen concentration, and this is why many a measurement have suffered from errors due to oxygen reaction in the film. Thus it would not be free from hazards to consider oxygen absorption in sulfite solution without catalyst as a case of simple physical absorption.

A hypothesis has been put forward[20] suggesting that the increase in $k_L^0 a$ values measured by physical absorption, might be accounted for by chemisorption-induced interfacial turbulence. However, it has not been proved[21-25] that any interfacial turbulence occurs in mechanically agitated bubble reactor.

We consider it desirable to make a systematic study of absorption of pure and of diluted oxygen in aqueous sodium sulfite solution in a mechanically agitated gas–liquid contactor, both with and without cobalt catalyst, covering a broader range of operational conditions. The results of experiments thus obtained will allow to test the validity of statements made by us about the effect of bubble shrinkage caused by an absorption, the residence time distribution of the gas phase for the calculation of a and $k_L^0 a$ at various degrees of gas phase conversion, the order of reaction, and the possible enhancement of absorption by reaction accompanying absorption in absence of catalyst.

THEORETICAL

In this work, the film model of absorption with n-th order irreversible chemical reaction is used for determining effective interfacial area and liquid-side mass transfer coefficient. Using the film model, Reith[2] derived relations for the absorption rate N of gas component accompanied with an n-th order reaction with one of the liquid components

$$NA = \Phi k_L^0 A (c^+ - c_L) \tag{1}$$

for the boundary conditions

$$c = c^+ \quad \text{at} \quad x = 0$$

and

$$AD \frac{dc}{dx} = k_n c_L^n (V_L - \delta A) \quad \text{at} \quad x = \delta = D/k_L^0. \tag{2}$$

The chemical enhancement factor, Φ, and dimensionless bulk concentration, $\alpha_\delta = c_L/c^+$, have been calculated[2] for various values of reaction order n, Hatta number Ha and parameter B on a digital computer. The parameter B represents the ratio of the bulk volume of the liquid V_L to the film volume δA. It was shown[2], that the following Danckwerts' type equation is a reasonable approximation of the exact

solution of the relevant differential equations

$$NA \approx (c^+ - c_L) A \left[\frac{2}{n+1} k_n(c^+)^{n-1} D + (k_L^0)^2 \right]^{1/2} . \tag{3}$$

Classical Chemical Method

If the rate of an accompanying chemical reaction is high enough to ensure that

$$Ha = \frac{\left[\dfrac{2}{n+1} k_n(c^+)^{n-1} D \right]^{1/2}}{k_L^0} \gg 1 , \tag{4}$$

and the bulk liquid concentration of solute c_L is zero then holds[2] the following very good approximation

$$NA = c^+ A \left[\frac{2}{n+1} k_n(c^+)^{n-1} D \right]^{1/2} . \tag{5}$$

The condition for c_L to be zero is

$$k_L^0 A c^+ \ll V_L k_n(c^+)^n . \tag{6}$$

Hence, if the kinetic constant of reaction, solubility, and diffusion coefficient are known the over-all rate of absorption NA, determined experimentally, allows to calculate the total interfacial area A using the relation (5). The condition (4) usually may be considered to hold as long as $Ha > 3$.

The Danckwerts' Type Equations Method for Second Order Reaction

The method is based on measuring the over-all absorption rate NA with different values of k_2 in a region where the effects of hydrodynamics and chemical reaction on mass transfer coefficient are comparable. A method of determining interfacial area in this region using exact numerical integration of the relevant film model differential equations was used by Hirner and Blenke[26]. We present a method for determination both of a and k_L^0 using the Danckwerts' type equation (3) for second order reaction. The "Danckwerts' plot" method is described[19] for $c_L = 0$, first order reaction, and a constant value of c^+, *i.e.*, for absorption of pure gases. In the case that diluted gases are used, the component concentration in the gas mixture is changed during passage through the reactor. Therefore it is of advantage to use[22] a modification of the equation (3),

$$Y = E + FX ,$$

where

$$Y = \left(NA/c^+\right)^2 , \quad X = k_2 c^+ . \tag{7}, (8)$$

From an experimentally determined plot of Y against X one can calculated intercept E and slope F following from approximative relation (3) as

$$E = \left(A' k_L^{0'}\right)^2 , \quad F = 2(A')^2 D/3 . \tag{9}, (10)$$

The plot of X against Y obtained in our experiments gave always straight line. For illustration, the plots determined under some of experimental conditions are shown in Fig. 1. The area and mass transfer coefficient determined by this procedure based on approximative relation (3) will be called "mass transfer area A'" and "mass transfer coefficient $k_L^{0'}$". Inasmuch as we used the approximative relation (3), it is necessary that the values A' and $k_L^{0'}$ be multiplied by the appropriate correction factors

$$\eta_a = A/A' , \quad \eta_k = k_L^0/k_L^{0'} , \tag{11}, (12)$$

where η_a and η_k are factors used to correct area A' and mass transfer coefficient $k_L^{0'}$ values based on Eq. (3) to values which would be obtained from non-approximative formulas for the rate of absorption. The evaluation of these factors is the following.
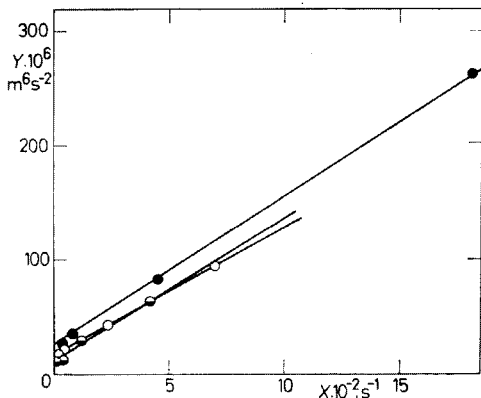

FIG. 1

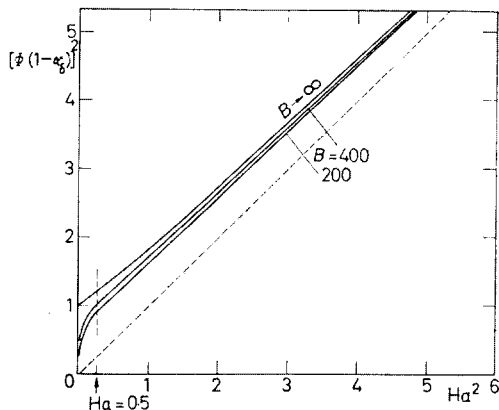Plot of Y against X

◐ No 711—; ○ No 712—; ● No 713—.

FIG. 2

$[\Phi(1 - \alpha_\delta)]^2$ as a Function of Ha^2 Obtained by Numerical Integration of the Film Model Differential Equations

Taken from Reith[2] — Table (I — 1) for $n = 2$.

Comparing the approximative relation (3) with (1) and substituting the expressions for Ha and α_δ, we obtain

$$k_L^0 A\, c^+(1 - \alpha_\delta) = A'\, c^+[(k_L^0\, \text{Ha})^2 + (k_L^{0\prime})^2]^{1/2} , \qquad (13)$$

where A and k_L^0 represent the correct values of interfacial area and of mass transfer coefficient. Substituting from (11) and (12), Eq. (15) can be converted to the form

$$[\Phi(1 - \alpha_\delta)]^2 = (\eta_a \eta_k)^{-2} + (\text{Ha}/\eta_a)^2 . \qquad (14)$$

The values of η_a and η_k depend on B and on the interval of Hatta number used in the experiments, from which the values A' and $k_L^{0\prime}$ were calculated. The dependence of $[\Phi(1 - \alpha_\delta)]^2$ on Ha^2 for $n = 2$ and various B values obtained by numerical solution of the film model (given by Reith[2]) are shown in Fig. 2. The dependences are practically straight lines as long as $\text{Ha} \geqq 0.5$ and $B \geqq 100$. In this region, therefore, the correction factors may be calculated to sufficient accuracy from the lowest and upper bounds of the interval of Hatta numbers actually used $(\text{Ha}_1, \text{Ha}_2)$

$$\eta_a \approx \left[\frac{\text{Ha}_1^2 - \text{Ha}_2^2}{[\Phi(1 - \alpha_\delta)]_2^2 - [\Phi(1 - \alpha_\delta)]_1^2} \right]^{1/2} , \qquad (17)$$

$$\eta_k \approx \left[\frac{[\Phi(1 - \alpha_\delta)]_2^2 - [\Phi(1 - \alpha_\delta)]_1^2}{[\Phi(1 - \alpha_\delta)]_1^2\, \text{Ha}_2^2 - [\Phi(1 - \alpha_\delta)]_2^2\, \text{Ha}_1^2} \right]^{1/2} . \qquad (16)$$

For illustration, Table I lists correction factors calculated for $n = 2$ for several intervals of Ha number and B values. Both the enhancement factor Φ and the concentration α_δ were taken from Table $(I-1)$ by Reigh[2]. Characteristic values of B in our expetiments were $200 - 2000$ and the Hatta numbers ranged $0.5 - 7$ approximately. Thus, the values of the factors η_a and η_k varied within an interval from 1.04 and

TABLE I
Correction Factor Values as Calculated from Eqs (11) and (12) for 2nd Order Reaction
 $(\Phi, \alpha_\delta$ — taken from Table $(I-1)$ by Reith[2]).

Interval of Ha number	$B \to \infty$		$B = 400$		$B = 200$	
	η_a	η_k	η_a	η_k	η_a	η_k
0.03 — 0.5	1.56	0.614	0.510	7.0	0.512	11.12
0.3 — 3.0	1.04	0.968	1.03	1.13	1.02	1.20
0.5 — 10.	1.01	1.02	1.00	1.12	1.00	1.16
3.0 — 30.	1.00	1.87	1.00	1.93	1.00	1.88

0·958, resp., for the lowest stirrer speed and for absorption of 30% O_2 to 1·01 and 1·20, resp., for the highest stirrer speed and pure oxygen absorption.

DETERMINATION OF VOLUMETRIC MASS TRANSFER COEFFICIENT

Firstly, it can be calculated from the results of Danckwerts' type equation method (DTM) as follows from (9), (11), and (12)

$$k_L^0 a = E^{1/2} \eta_a \eta_k / V_L . \tag{15}$$

Secondly, it can be calculated from the rate of absorption if the following necessary conditions are fulfilled

$$\text{Ha} \ll 1 , \tag{18}$$

and (6). Then the relation (1) can be simplified[2] to

$$NA = c^+ V_L k_L^0 a . \tag{19}$$

DRIVING FORCE FOR THE ABSORPTION

On the condition that the gas phase in reactor is perfectly mixed the c^+ value represents the equilibrium concentration of oxygen with gas leaving the reactor

$$c^+ = c_2^+ \tag{20}$$

and, on the condition of piston flow of bubbles through the dispersion, the mean logarithmic value of the equilibrium concentration of oxygen between the reactor inlet and reactor outlet, which reduces to

$$c^+ = (c_1^+ + c_2^+)/2 \tag{21}$$

as long as the difference in the values of c_1^+ and c_2^+ is small. Presuming validity of Henry's law, the over-all mass balance and the oxygen balance around the reactor may be used to derive the following relation for

$$c_2^+ = \frac{1}{\text{He } RT} \frac{P_b y_1 \dot{V}_1 - NA \, RT}{\dot{V}_1 - NA \, RT/(P_b - p_{H_2O})} , \tag{22}$$

and for

$$(c_1^+ + c_2^+)/2 = \frac{1}{2 \text{ He } RT} P_b y_1 + \frac{P_b y_1 \dot{V}_1 - NA \, RT}{\dot{V}_1 - NA \, RT/(P_b - p_{H_2O})} \tag{23}$$

needed to calculate the variables X and Y.

KINETIC DATA ON SULFITE OXIDATION

The reaction rate constant may be calculated from the rate N_s of oxygen absorption into the sulfite solution across the interface in a mechanically agitated non-aerated reactor by the relation (see reference[5] for details)

$$N_s = (c_s^+)^{3/2} \left[\tfrac{2}{3}k_2'D\right]^{1/2} . \tag{24}$$

A relation shown below has been derived[8] permitting to calculate the reaction rate constant k_2', determined by experiment for given temperature T', pH and catalyst concentration c'_{CoSO_4}, for other values of temperature, pH and catalyst concentration

$$k_2 = k_2' \frac{c_{CoSO_4}}{c'_{CoSO_4}} \left[\frac{pH - 7{\cdot}9 + 0{\cdot}04t}{pH' - 7{\cdot}9 + 0{\cdot}04t}\right]^2 \exp\left\{-\frac{E^+}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)\right\} . \tag{27}$$

EFFECT OF ASBORPTION RATE ON INTERFACIAL AREA

The interfacial area drop caused by bubble shrinkage due to gas absorption is adequately described for our instalation by the relation[13]

$$A/A^0 = 0{\cdot}2(1 - \dot{V}_2/\dot{V}_1)/(1 - (\dot{V}_2/\dot{V}_1)^{0{\cdot}2}) . \tag{26}$$

According to (26), the experimentally determined over-all absorption rates NA were corrected for absorption-due area reduction: $NA^0 = NA \cdot A^0/A$.

EXPERIMENTAL

Experiments were carried out in a 29 cm dia. perspex agitated contactor, which was provided with a 10 cm dia., 6-bladed turbine agitator. The volume of liquid phase in the reactor was always $0{\cdot}0182$ m^3. This contactor was the same as that used by Linek and Mayrhoferová[13]. A non-aerated reactor, which was the same to that used by Linek and Mayrhoferová[5], was used for the kinetic measurement.

Aqueous sodium sulfite solutions containing $0{\cdot}8$M-Na$_2$SO$_3$ were oxidized with pure oxygen and with mixtures of oxygen with nitrogen of concentrations 30 vol.% O$_2$ and 60% O$_2$ approximately. Prior to entering the contactor, the gas phase was saturated with water. The inlet oxygen concentration in the gas phase was measured with Orsat analyser. Temperature was kept constant in all experiments and was equal to 20°C. Absorption rate was calculated from decrease of sulfite concentration during an experiment, determined by an iodometric back titration. Initial solution pH varied around $8{\cdot}5$. Several measurements were taken with each contactor. batch. The solution was discarded after the sulfite concentration decreased below $0{\cdot}45$M.

Absorption rate measurement in aerated contactor were carried out at various gas flow rates, stirrer r.p.m., and catalyst concentrations. The experimental conditions used are listed in Table II. The method used to denote individual experiments is also clear from the table. For instance, the run bearing the number 4235 is an experiment performed under the following conditions: $f = 650$ r.p.m., $\dot{V}_1 = 25$ l min^{-1}, $\alpha = 100\%$, $c_{CoSO_4} = 2 \cdot 10^{-4}$M.

The reaction rate constants were calculated from the absorption rate $N_s = 4.98 \cdot 10^{-7}$ kmol . . m^{-2} s^{-1} of pure oxygen in non-aerated reactor at pH' 8·53, P_b 750 Torr, T' 293 K, and $c'_{CoSO_4} =$ $= 5 \cdot 10^{-5}$M.

RESULTS AND DISCUSSION

Order of Reaction with Respect to Oxygen

Consider the oxidation of sodium sulfite solution with pure oxygen in a mechanically agitated contactor. For a typical case the following data are representative: $k_L^0 =$ $= 5 \cdot 10^{-4}$ m s^{-1}, $c^+ = 6.4 \cdot 10^{-4}$M. For $c_{CoSO_4} = 2 \cdot 10^{-4}$M, pH 8·5, and $t = 20°C$ we obtain Ha ≈ 3.5 from (4) for $n = 2$. Thus, the condition given by expression (4) is satisfied and the rate of absorption is given by Eq. (5). From this follows that the order n can be determined from the slope of absorption rate dependence on the c^+ value, plotted in logarithmic coordinates. These relations are plotted against c_2^+ in Fig. 3 for some of the arrangements, both for the absorption rate NA not corrected and the absorption rate NA^0 corrected by Eq. (26) for area reduction due to absorption. In the region of low absorption rates where the correction is small, the slopes of the dependence for NA and NA^0 clearly differ to an insignificant degree and are equal to 1·5 considering the error of measurement. Hence the order of reaction equals 2. This is in good agreement with other published data[2,5,9]. In the region of higher absorption rates where the correction is significant, the slope of the dependence for NA differ from the value of 1·5 to a great extend. However, the slope again equal 1·5 after the correction for area reduction due to bubble shrinkage has

TABLE II

Survey of Experimental Conditions and Their Notation
— Denotes variation, *i.e.*, number 41−1 denotes experiments 4111, 4121 and 4131.

Number of experiment				f	$\dot{V}_1$	α	c_{CoSO_4}
f	$\dot{V}_1$	α	c_{CoSO_4}	min^{-1}	1 min^{-1}	—	kmol m^{-3}
1	1	1	1	350	16·8	28·4	$5 \cdot 10^{-6}$
2	2	2	2	450	25	60·3	10^{-5}
3		3	3	550		100	$5 \cdot 10^{-5}$
4			4	650			$7.5 \cdot 10^{-5}$
5			5	385			$2 \cdot 10^{-4}$
6			0	510			0
7				630			
8				690			
9				725			

been made. This supports the view that it is necessary to introduce the correction whenever results obtained at different absorption rates are being compared.

The reaction order value was also measured in non-aerated reactor. The experimental results indicated a slope of $1 \cdot 5$ giving an order of reaction $n = 2$.

We conclude that the order of reaction is $n = 2$ with respect to oxygen in the experiment performed.

Classical Chemical Method

In experiments where $c_{CoSO_4} = 2 \cdot 10^{-4} M$ the condition given by expression (4) holds and thus the interfacial area can be calculated from (5). Its values were calculated from both the uncorrected absorption rates NA and the rates NA^0, corrected for area reduction using (26). A graphical comparison of the areas A_{30}^0 (calculated for absorption of diluted oxygen, i.e., 30% O_2) and A_{100}^0 (for absorption of pure oxygen) is shown in Fig. 4. The area values were calculated under the presumption of perfectly mixed gas phase, i.e., $c^+ = c_2^+$. The values agrees with each other ($\pm 10\%$) as long as the stirrer r.p.m. are below 690 min^{-1}. The same result was obtained by comparing A_{60}^0 with A_{100}^0. The adequacy of correction (26) for area

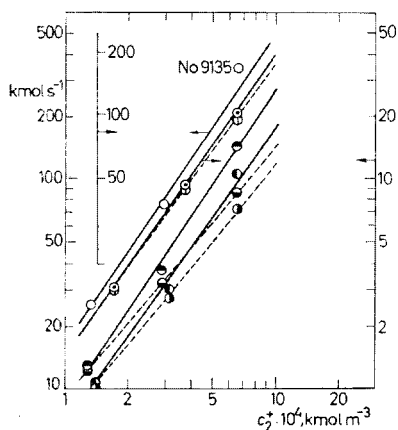
FIG. 3

Oxygen Absorption Rate in the Aerated Reactor as a Function of an Equilibrium Oxygen Concentration c_2^+

Values of NA^0: ○ experiments $91-5$; ⊙ $51-5$, slope of the line $1 \cdot 45$; ◔ $81-5$, slope $1 \cdot 49$; ◑ $71-5$, slope $1 \cdot 45$. Values of NA: ○ experiments $51-5$; ◓ $81-5$; ◐ $71 \cdot 5$.
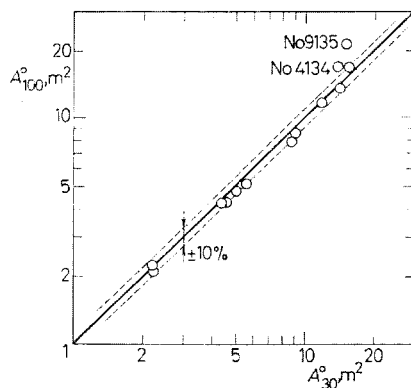
FIG. 4

A Comparison of Areas Calculated by CCM for Absorption of Pure Oxygen A_{100}^0 and for Absorption of Diluted Oxygen A_{30}^0

reduction in comparing area values determined from pure and diluted oxygen absorption is illustrated in Fig. 5 showing a graphical comparison of the A_{30} and A_{100} areas which has been calculated from absorption rates NA without correction for area reduction. The two areas are not in agreement except for stirrer speeds below $490 \ \text{min}^{-1}$, *i.e.*, except at low absorption rates at which the correction is insignificant.

We conclude that the values of area as determined from absorption of diluted and of pure oxygen are in agreement even when the absorption rates largely differ, provided that the area reduction due to absorption is taken into acount.

Driving Force for Absorption

In determining the interfacial area by CCM and DTM methods, the driving force for the absorption was calculated (a) as if the gas phase were perfectly mixed (PM) from (22) and (b) as if the gas phase flowed with piston flow (PF) through the contactor from (23). In the case of pure oxygen absorption the degree of mixing in the gas phase is not relevant and thus the area values are not rendered incorrect by any eventual error in driving force estimation. It has been found by comparing area determined from absorption of pure oxygen on the one hand and of diluted gases on the other hand that, for PM model, the area difference is higher than 10% only for conditions $41-4$ and $91-5$ (Fig. 4), whereas, for PF model, it is higher than 10% for same but also for conditions $71-5$ and $81-5$.
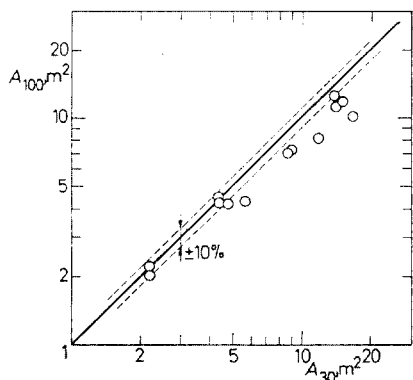

FIG. 5

A Comparison of the Areas Calculated by CCM for Absorption of Pure Oxygen A_{100} and for Absorption of Diluted Oxygen A_{30}
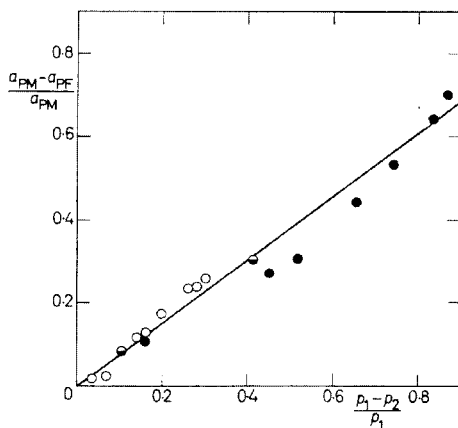
FIG. 6

Relative Difference between Interfacial Areas Based on the PM and PF Models as a Function of Relative Decrease of Partial Pressure of Solute Gas in the Reactor

$\circ$ Our data; $\ominus$ ref.[13]; $\bullet$ ref.[14].

Mehta and Sharma[14] studied the residence time distribution of the gas for the calculation of a and $k_L^0 a$. They compared the values of a based on the piston flow model with those based on the model of perfectly mixed gas phase in the reactor. They found that when a is based on PF, the values of a decreases as the reaction rate increases. This is in agreement with our results (Table III) as can be seen in Fig. 6 giving a graphical comparison of the values of a based on PF and PM as a function of the relative decrease of partial pressure of solute gas in the reactor. Mehta and Sharma[14] have found that their experimental data can be satisfactorily correlated on the basis of PM in the gas phase even for relatively high levels of conversion η of the solute gas. The conversion η represents the graction of the solute gas i absorbed from the gas stream: $\eta = N_i A / \dot{n}_{i1}$. In their experiments, the maximum value of conversion values was about 0·89. This value is higher than the conversion values of 0·77 and 0·53 obtained in our experiments 91—5 and 41—4, respectively, in which a discrepancy was found between A_{100}^0 on the one hand and A_{30}^0 or A_{60}^0 on the other hand. We believe that this discrepancy is due to the random errors of the absorption rates, experimentally determined under the conditions 9135 and 4134. This view is supported by the following facts: (a) the difference between A_{100}^0 and A_{30}^0 (Table III) was insignificant in many other experiments in which conversion values exceeding that of the 4134 experiment were achieved (e.g., 0·69 and 0·59 in 8135 and 7135, resp.). (b) The absorption rates NA^0 for 9135 and 4134 do not fit the NA^0 vs $(c_2^+)^{1.5}$ relationship which was verified experimentally for all the other conditions (Fig. 3, point N^0 9135 denoted by an arrow). If we consider such NA^0 values for the conditions 9135 and 4134 which would satisfy the above relation, we obtain area values A_{100}^0 which do not appreciably differs from the values A_{30}^0 and A_{60}^0 (Table III).

TABLE III

Residence Time Distribution of Gas

No	Inlet partial pressure atm	Outlet partial pressure atm	$a^0 . 10^{-2}$, m^{-1} CCM based on	
			Piston flow model	perfectly mixed
1 214	0·28	0·27	1·19	1·21
1 234	1·	1·	1·24	1·24
5 115	0·28	0·28	1·18	1·21
5 135	1·	1·	1·17	1·17
6 115	0·28	0·24	2·75	3·11
6 135	1·	1·	2·95	2·95
4 213	0·28	0·235	6·84	7·80
4 233	1·	1·	7·50	7·50
8 115	0·28	0·196	6·76	9·10
8 135	1·	1·	9·30	9·30
4 114	0·28	0·225	6·38	7·70
4 134	1·	1·	9·35	9·35 — 8·50[a]
9 115	0·28	0·20	6·35	8·35
9 125	0·58	0·43	7·35	9·62
9 135	1·	1·	12·0	12·0 — 9·15[a]

[a] Calculated from NA^0 determined from the relation $NA^0 \sim (c_+^2)^{1.5}$ (Fig. 3).

We conclude that experimental data can be correlated satisfactorily using the model of a perfectly mixed gas phase in the reactor even for relatively very high levels of conversion. The notion of piston flow leads to incorrect values of driving force for absorption.

Danckwerts' Type Equation Method

Area was calculated assuming validity of the PM model, and the correction by (26) for area reduction was taken into account. The results of area measurements by DTM and CCM are graphically compared in Fig. 7 for various oxygen concentration in the gas phase. The values determined by CCM do not differ from those obtained by DTM within the experimental error. The variances of estimate of the regression constants E and F yielded[22] the mean relative variance of calculated area values as $S_A = 6\%$. Our results of area measurement are compared with Reith's data in Fig. 8. Since we have ascertained that the value of area was independent of both the flow rate and the oxygen concentration, the values plotted in the Fig. 8 are the mean values of a^0 determined at given stirrer speed. It can be seen that our results are in good agreement with Reith's. Reith carried out his experiments in the sulfite system.

Volumetric Mass Transfer Coefficient

The values of k_L^0 and of $k_L^0 a$ as calculated by DTM are listed in Table IV. The mean relative scatter of the calculated k_L^0 values is 20% and that of the $k_L^0 a$ values is 26%.

The second method of calculating $k_L^0 a$, i.e., from the relation (19), has been employed[2,3,12] for the case of absorption into a sulfite solution without catalyst addition (WCM). Difficulties arising from the determination of the rate constant k_2 are encountered in making decision as to whether the necessary conditions (6) and (18) have been met for this case of absorption. In this case the rate constant value is determined exclusively by the concentration of trace impurities present in the chemicals and water used. Their concentration differs even among production batches. The validity of the condition (6) has been verified experimentally by measuring the concentration of dissolved oxygen in the liquid phase using an oxygen probe. The oxygen probe reading did not exceed a value of 8% of the equilibrium oxygen concentration in the charge. Details on the method of taking oxygen probe measurements have been given elsewhere[23]. It was assumed that the condition given by expression (18) holds.

The $k_L^0 a$ values calculated by WCM are listed in Table IV. All corrections by Eq. (26) made for area reduction were insignificant, as the maximum error was 3%. The relative oxygen concentration drop in the gas phase during passage through the reactor also was so small in these experiments that the degree of mixing in gas phase was not important. The driving force was calculated as if the PM model true.

It follows from the results listed in Table IV that the $k_L^0 a$ values obtained by DTM are dependent of the concentration of the gas phase used. The k_L^0 value significantly increases with increasing gas concentration. This is at variance with the model notions used. It does not seem, however, to be caused by an incorrect estimate of the driving force for the absorption, since the gas phase concentration dependence of k_L^0 has been observed also at low agitation velocities $(f \leqq 450 \text{ min}^{-1})$, $i.e.$, in experiments where the change in oxygen concentration during passage through the reactor was always so small $(<5\%)$ that the error introduced by driving force was unimportant. Considering the error variance, the values of k_L^0 determined by absorption of pure oxygen are in agreement with the results of Caldebank[24] $(k_L^0 = = 4 \cdot 5 \cdot 10^{-4} \text{ m s}^{-1})$. Nevertheless it seems that DTM does not yield correct k_L^0 values in absorption of diluted gases.

Another discrepancy is made apparent by the Fig. 9 showing a graphical comparison of $k_L^0 a^0$ values determined by DTM and by WCM. Considering the scatter of experimental data, the two values agree with each other as long as the value $k_L^0 a^0 < 0 \cdot 1 \text{ s}^{-1}$. At higher $k_L^0 a^0$ values, the values obtained by DTM are markedly higher (even by 80%) than those obtained by WCM. The difference cannot be explained by an incorrect driving force estimate, because higher values were also obtained for absorption of pure oxygen. Nor can this difference be atributed to an eventual inadequacy of the correction for area reduction, because the values of $k_L^0 a$ calculated by DTM are substantially higher than the respective values calculated
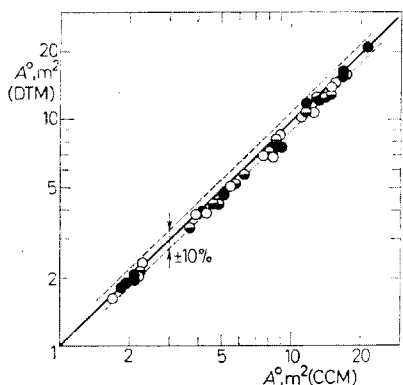

FIG. 7

A Comparison of the Results of Area Measurements by DTM and CCM

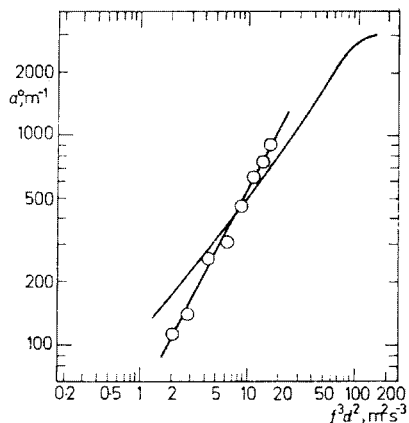   ◗ 30% O_2; ○ 60% O_2; ● pure oxygen.

FIG. 8

A Comparison of our Results of Area Measurement with Reith's Data

    ○ Our data; — ref.[2].

TABLE IV

Values of Mass Transfer Coefficient and Volumetric Mass Transfer Coefficient as Determined by DTM and WCM

Number of experiment	DTM				WCM
	$k_L^0 \cdot 10^4$ m s^{-1}	$k_L^{0'}a' \cdot 10^2$ s^{-1}	$k_L^{0'}a'^0 \cdot 10^2$ s^{-1}	$k_L^0 a^0 \cdot 10^2$ s^{-1}	$k_L^0 a^0 \cdot 10^2$ s^{-1}
111—	3·01	2·62	2·61	2·63	2·42
112—	3·96	3·30	3·33	3·42	2·69
113—	2·74	3·16	3·06	3·09	3·22
121—	2·22	2·41	2·41	2·43	2·57
122—	2·59	2·89	2·89	2·97	2·92
123—	3·56	3·53	3·54	3·57	3·11
211—	2·44	5·59	5·65	5·70	6·12
212—	2·89	6·24	5·54	5·69	6·20
213—	4·06	8·72	8·94	9·02	7·10
221—	3·23	5·41	5·15	5·20	5·82
222—	3·27	6·81	6·87	7·05	6·04
223—	3·64	8·00	8·06	8·15	7·98
311—	3·59	10·6	11·3	11·4	9·50
312—	3·36	12·8	13·0	13·3	10·8
313—	4·50	17·9	18·9	19·1	12·2
321—	2·19	9·78	9·82	12·0	9·45
322—	2·87	13·0	13·2	15·6	10·5
323—	4·47	15·5	17·6	17·8	12·8
411—	3·96	22·1	22·6	26·4	13·4
412	4·20	23·5	24·7	27·7	16·0
413—	3·26	27·1	28·3	32·8	20·5
421—	2·97	14·6	19·9	23·9	13·6
422—	2·28	17·9	17·8	20·8	16·3
423—	5·04	31·0	33·8	37·8	20·2
511—	2·85	3·37	3·37	3·40	3·32
512—	2·93	3·84	3·79	3·90	3·80
513—	3·74	4·36	4·20	4·24	4·38
611—	3·53	9·85	9·90	10·0	7·50
612—	4·20	11·4	11·6	12·0	8·40
613—	5·05	13·3	13·4	13·5	10·0
711—	3·51	20·0	20·2	24·0	12·7
712—	3·92	21·3	22·0	24·6	14·6
713—	4·60	27·8	30·2	34·0	18·5

by WCM for both the corrected values NA^0 and the values NA without correction (Table IV).

Another discrepancy still, found for absorption without catalyst addition, issues from the measurement of the exponent m of the relation

$$NA^0 = k_L^0 a^0 \, V_L (c^+)^m . \qquad (27)$$

The theoretical value of exponent m should equal 1 according to the relation (19). The actual exponent values (Table V) increase with increasing velocity of agitation from 1·1 to 1·3. For illustration, the relation (25) for some conditions is plotted in Fig. 10. The exponent values $m > 1$ cannot be ascribed either to an incorrect driving force estimate or an inadequate correction by (26) for area reduction, because the absorption rates were small in these experiments. The values of oxygen concentration drop in gas phase during passage through the reactor varied about 3% and the values of correction by (26) varied about 5%.

The origin of values of the exponent m higher than 1 may be as follows. Even in absence of catalyst, the rate of the accompanying reaction of oxygen with the sulfite ions in high enough not only to maintain a zero oxygen concentration in the interior
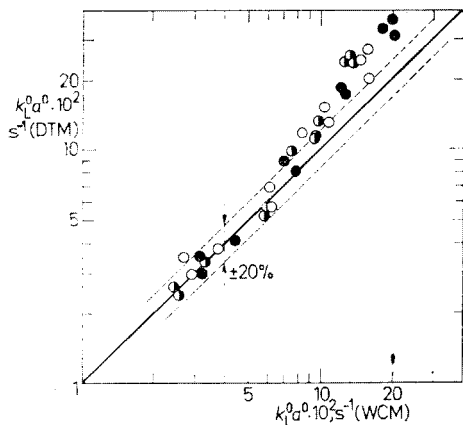

FIG. 9

A Comparison of the Results of Volumetric Mass Transfer Coefficient Measurement by DTM and WCM
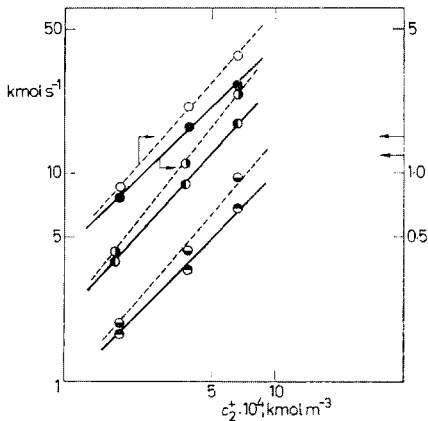
◑ 30% O_2; ○ 60% O_2; ● pure oxygen.

FIG. 10

NA^0 resp. $NA^0/(Ha^2 + 1)^{1/2}$ as a Function of c_2^+

Values of NA^0: ◕ experiments 22−0, slope of the line 1·18; ◑ 42−0, slope 1·3; ○ 12−0, slope 1·16. Values of $NA^0/(Ha^2 + 1)^{1/2}$: ◓ experiments 22−0, slope 1·04; ◖ 42−0, slope 1·11; ● 12−0, slope 1·0.

of liquid phase but also to allow the reaction with oxygen to proceed to a small extent inside the liquid film at the interface; *i.e.*, the condition (18) does not hold and the absorption is accelerated chemically. Rather than the relation (19), the relation (3) then has to be applied which may be rewritten using (4) to the form

$$NA = c^+ A \, k_L^0 [\text{Ha}^2 + 1]^{1/2} . \tag{28}$$

It has been described[18] that the value of $k_L^0 a$ for absorption of pure oxygen into sulfite solution without catalyst in mechanically agitated, aerated reactor is higher by a factor roughly 1·4 than that for absorption of pure oxygen into a sulfate solution having the same concentration as the sulfite solution. A hypothesis has been proposed in the paper quoted[18] suggesting that the higher value of $k_L^0 a$ in the sulfite solution is to the accounted for by the higher pH of solution. However, the results of our recent experiments make us to conclude that this increase is due to an acceleration of absorption by chemical relation; thus this acceleration is significant even in the absence of catalyst. Apparently, the matter may concern a catalytic effect of trace impurities present in the chemicals and water used. If this hypothesis is correct, the value of exponent m' of the relation

$$\frac{NA^0}{[\text{Ha}^2 + 1]^{1/2}} = k_L^0 \, A^0 (c^+)^{m'} \tag{29}$$

should equal 1. The value of the factor $\text{Ha}_{100}^2 = 0.96$ for absorption of pure oxygen into sulfite solution without catalyst is based on the experimentally determined acceleration value of 1·4. The values of the factor Ha_α^2 for oxygen concentrations other than 100% were calculated from the relation $\text{Ha}_\alpha^2 = \text{Ha}_{100}^2 (c_\alpha^+ / c_{100}^+)$ following

TABLE V
Experimental Values of Exponent m and m' of the Relations (27) and (29), respectively

Number of experiment	m	m'
11 — 0	1·22	1·06
12 — 0	1·16	1·00
21 — 0	1·11	0·97
22 — 0	1·18	1·04
31 — 0	1·19	1·04
32 — 0	1·23	1·06
41 — 0	1·30	1·10
42 — 0	1·30	1·11

from (4) for $n = 2$. The calculated values of exponent m' are listed in Table V. For illustration, the relations (29) for some conditions are plotted in Fig. 10. It can be said that, with regard to experimental error, the value of exponents m' are in agreement with the theoretical value of unity. This supports the hypothesis on the acceleration of oxygen absorption into sulfite solutions by a reaction even in absence of catalyst. On the other hand, however, this interpretation of results increases still further the differences between respective $k_L^0 a$ values determined by DTM and by WCM. Thus we are forced to conclude that so far we have not been able to find a working hypothesis such as to explain the phenomenon while avoiding all contradictions with the any experimental fact mentioned in the paper. We have to limit ourselves to stating that DTM gives higher values of $k_L^0 a$, higher than those usually given in the literature for mechanically agitated reactors.

An explanation of the enormously high values obtained by DTM, based on Danckwerts' z-factor[16], does not seem to be relevant, since it cannot be presumed that a well agitated, aerated reactor would allow for the existence at the gas–liquid interface of points with stagnant liquid which would reduce the area effective for gas absorption. Nor can the oxygen concentration dependence of k_L^0 or $k_L^0 a$ be ascribed to an erroneous estimate of the mean driving force for absorption sine the absorption rates were so small in these experiments that the gas concentration was altered by about 3% during passage through the reactor.

LIST OF SYMBOLS

a	interfacial area per unite volume of liquid phase
A	total interfacial area
A'	interfacial area determined by DTM using approximative relation (11)
B	$= V_L/(\delta A)$ parameter
c	concentration
d	stirrer diameter
D	molecular diffusion coefficient
E, F	regression constants defined by (9) and (10)
E^+	energy of activation
f	stirrer speed
Ha	Hatta number defined by (3)
k_n	n-th order reaction rate constant
k_L^0	physical absorption mass transfer coefficient
$k_L^{0\prime}$	mass transfer coefficient determined by DTM using approximative relation (11)
m	exponent in (27)
m'	exponent in (29)
n	reaction order
N	absorption rate
p	partial pressure
P_b	barometrical pressure
R	gas constant
t, T	temperature and absolute temperature

$\dot{V}$ volumetric gas flow rate
X, Y quantities defined by (8) and (7)
α reading of Orsat analyzer
α_δ $= c_L/c^+$
δ $= D/k_L^0$ effective film thickness
η conversion of gas phase
η_a correction factor defined by (11)
η_k correction factor defined by (12)
Φ chemical enhancement factor

Indexes

1, 2   inlet, outlet
o   value corrected for area reduction due to absorption by (19)
$+$ equilibrium value of concentration

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