

Chapter 2

Chapter 2

***Interfacial areas and gas hold-ups
in a mechanically agitated gas-liquid reactor
at elevated pressures from 0.1 to 1.7 MPa.***

Chapter 2

ABSTRACT

Interfacial areas and gas hold-ups have been determined at pressures up to 1.7 MPa in a glass vessel of 88 mm diameter and of standard geometry. Superficial gas velocities between 0.25 and 2.00 cm/s have been used and the agitation rate varied between 4 and 30 rps.

The interfacial areas have been determined with the chemical method using the model reaction between CO₂ and aqueous diethanolamine (DEA) and hold-ups by observation of height differences.

Realistic values of the interfacial areas could be determined provided the conversion levels of CO₂ in the gas phase were kept below 80%. In contrast to the scarce information in literature the gas hold-up as well as the interfacial area are found to be independent of the reactor pressure.

Chapter 2

1. INTRODUCTION

In the previous Chapter we reviewed all literature data on mass transfer phenomena in gas-liquid reactors at elevated pressures. We concluded that the liquid phase mass transfer coefficient k_L is independent of pressure but not so the gas phase mass transfer coefficient k_G which appeared to be inversely proportional with pressure to the power n , where n is determined by the mass transfer mechanism. Furthermore we concluded that there is no common agreement about the influence of pressure on the interfacial area and the gas hold-up both in two and three phase bubble columns and mechanically agitated reactors. We therefore decided to investigate the influence of the operating pressure on the interfacial area and the gas hold-up in these reactor types in order to improve upon our understanding of the mass transfer phenomena at elevated pressures. The results will be used for a better modelling of these reactors, see Westerterp et al(1988), and also may lead to a better design and understanding of high pressure gas-liquid reactors.

In this paper we restrict ourselves to the mechanically agitated gas-liquid reactor and present our results on the interfacial areas and the gas hold-ups in a small agitated gas-liquid reactor operating at pressures up to 1.7 MPa, see also Oyevaar et al(1988). The interfacial areas are determined by the chemical method using the model reaction between CO_2 and aqueous diethanolamine(DEA). The gas hold-ups have been measured by taking the height differences between the gassed and the non-gassed dispersion level.

The mechanically agitated reactor is a very popular device for contacting gases with liquids and slurries. It has a number of advantages such as the ease with which the liquid phase residence time and the degree of turbulence can be varied. The mechanically agitated reactor can be operated semi-batchwise for the liquid phase or for pure gas as a dead-end reactor. The main disadvantage is that both the liquid and the gas phase are almost completely backmixed. A considerable amount of information on two and three phase mechanically agitated reactors is available and comprehensive reviews are given by Van Landeghem(1980), Charpentier(1982) and Joshi et al(1982). These reviews are restricted to research at atmospheric pressure and do not take into account a possible influence of the pressure on the mass transfer parameters in a mechanically agitated reactor.

In Chapter 1 we concluded that in gas-liquid systems the initial bubble size at a single orifice decreases with increasing pressure. Several authors, see Kling(1962) and LaNauze and Harris(1974), attributed the reduction in size of the bubbles to the increased contribution of the momentum or the kinetic energy to the bubble formation process, as caused by higher pressures. Sagert and Quinn(1976) observed for some gases an increase in the coalescence time of the gas bubbles when they increased the pressure in their gas-liquid systems. Both phenomena, initially smaller bubbles and larger coalescence times, cause smaller bubbles with lower rising velocities. This gives rise to larger interfacial areas and gas hold-ups in gas-liquid reactors.

Sridhar and Potter(1980a, 1980b) observed an increase in the interfacial areas of as much as 75% in a mechanically agitated reactor ($D = 0.13$ m) for a pressure increase from 0.1 to 1.0 MPa. They

Chapter 2

worked with O₂-cyclohexane as gas-liquid system and determined local interfacial areas in the reactor with a light transmission probe. These local values were integrated to arrive at an average value for the interfacial area. They attributed the increase of the interfacial area to the increase with pressure of the kinetic energy content of the inlet gas flow. They correlated their results by multiplying the equation of Calderbank(1958) with a factor $(E_T/P_G)(\rho_G/\rho_{air})^{0.16}$ to

$$a = 1.44 \left[\frac{(\frac{P_G}{V})^{0.4} \rho_L^{0.2}}{\sigma_L^{0.6}} \right] \left(\frac{v_G}{v_S} \right)^{0.5} \left(\frac{E_T}{P_G} \right) \left(\frac{\rho_G}{\rho_{air}} \right)^{0.16} \quad (1)$$

The part (E_T/P_G) represents the ratio of the total (kinetic and mechanical) energy supplied to the reactor and the power input by agitation only. A second correction factor for the gas density had to be applied, so it was not possible to account for the influence of pressure solely by the increase in kinetic energy content of the gas inlet flow. Furthermore it is very questionable, as is also put forward by Miller(1981), whether all the 'extra' kinetic energy of the inlet gas flow is used to create 'extra' interfacial area.

Contrarily to these results Vafopoulos et al(1976) observed no influence of pressure on $k_L a$, a and ϵ_G in a mechanically agitated reactor ($D = 0.44$ m). They worked with an air-water system and within the same pressure range from 0.1 to 1.0 MPa. They determined the values of $k_L a$ by physical absorption of O₂ and measured gas hold-ups by taking the height difference between the gassed and non-gassed dispersion levels. These gas hold-ups were used together with average bubble diameters evaluated from photographs taken through the transparent wall of their reactor to calculate interfacial areas. All three parameters are not influenced by pressure and Vafopoulos et al(1976) state that this is caused by the fact that the liquid properties remain constant within this pressure range.

So there is no general agreement between the two different groups of researchers with respect to the influence of the operating pressure on the mass transfer parameters in a mechanically agitated reactor. A systematic investigation of this important effect seems to be justified.

2. CHEMICAL METHOD

2.1. Theory.

The chemical method will be used to determine the interfacial areas. The method is based on the theory of chemically enhanced absorption of a gas phase component A into a liquid in which an irreversible reaction occurs with a liquid phase component B. By a careful choice of the physico-chemical conditions it is possible to determine either a , $k_L a$ or $k_G a$, see Sharma and

Chapter 2

Danckwerts(1970) and Westerstorp et al(1984).

The general equation for the chemically enhanced mole flux J_A of a component A from the gas phase into the liquid, as derived by Danckwerts(1970) using the penetration theory, is

$$J_A = \frac{k_L \sqrt{1 + Ha^2} \left(m c_{A,G} - \frac{c_{A,L}}{1 + Ha^2} \right)}{1 + \frac{m k_L \sqrt{1 + Ha^2}}{k_G}} \quad (2)$$

The Hatta number, Ha, equals

$$Ha = \frac{\sqrt{\frac{2}{n+1} k_{a,p} c_{A,L}^p (m c_{A,G})^{n-1} D_A}}{k_L} \quad (3)$$

if the chemical reaction rate in the liquid is given by $R_c = k_{a,p} (c_{B,L})^p (c_{A,L})^n$. If the reaction is fast enough to consume all absorbed A in the film or if the bulk volume is much greater than the film volume, the bulk concentration of component A in the liquid $c_{A,L}$ equals zero. Together with the fact that in most gas-liquid reactors and systems with moderate reaction rates and low gas solubilities no gas phase mass transfer limitation occurs, Eq. (2) becomes

$$J_A = k_L m c_{A,G} E_A = k_L m c_{A,G} \sqrt{1 + Ha^2} \quad (4)$$

provided

$$Al Ha^2 \gg 1 \text{ and} \quad (5)$$

$$k_G \gg m k_L \sqrt{1 + Ha^2} \text{ with} \quad (6)$$

$$Al = \frac{(1 - \varepsilon_G) k_L}{a D_A} \text{ and} \quad (6a)$$

$$E_A = \sqrt{1 + Ha^2} \quad (6b)$$

Chapter 2

In Eq. (6b) E_A is the enhancement factor which accounts for the effect of the liquid phase reaction on the rate of absorption. With no depletion of the component B in the liquid film and a reaction first order with respect to the absorbing component A the Hatta number becomes

$$Ha = \frac{\sqrt{k_{1,p} c_{RL}^p D_A}}{k_L} \quad (7)$$

provided

$$Ha \ll E_{A\infty} \quad (8)$$

where according to the penetration theory

$$E_{A\infty} = \sqrt{\frac{D_A}{D_B}} + \sqrt{\frac{D_B}{D_A}} \frac{c_{RL}}{m c_{AG} v_B} \quad (9)$$

$E_{A\infty}$ is the enhancement factor for infinitely fast reactions. According to Eq. (6b) the value of E_A becomes within 10% equal to unity for $Ha < 0.5$ and equal to Ha for $Ha > 2$:

$$Ha < 0.5 : E_A = 1 \text{ and } J_A = k_L m c_{AG} \quad (10)$$

$$Ha > 2 : E_A = Ha \text{ and } J_A = m c_{AG} \sqrt{k_{1,p} c_{RL}^p D_A} \quad (11)$$

Application of this theory to chemical reactors makes it possible to determine volumetric liquid phase mass transfer coefficients and interfacial areas from absorption rate measurements, because $\phi_A = J_A a V_R$. This requires a knowledge of the physico-chemical parameters and of the driving force to check the criteria and to make the correct evaluations.

2.2. Gas-liquid model systems.

The reaction between oxygen and aqueous sodium sulphite solutions catalyzed by cobaltous ions Co^{2+} has been used extensively as a model system. However, there is still disagreement about the reaction kinetics and especially about the reaction order in oxygen. This is probably caused by the sensitivity of the reaction towards small impurities in the water, the catalyst or the sulphite salt, see

Chapter 2

Linek and Vacek(1981). The main advantage of this reaction is the possibility to change the reaction rate constant over a wide range by changing the Co^{2+} catalyst concentration. However, it is restricted to aqueous solutions; moreover, the non-coalescing behaviour of this ionic system also limits its use, see Bartos and Satterfield(1986).

The reaction between CO_2 and aqueous alkanolamine solutions was first introduced by Danckwerts and Sharma(1966). Later Sridharan and Sharma(1976) showed that the reaction between CO_2 and alkanolamines in organic and viscous solutions can also be used for the same purpose. The reaction rate can be varied by choosing the amine type. In recent years alkanolamines have been used to determine mass transfer parameters in various reactor types, see a.o. Mehta and Sharma(1971), Midoux et al(1984), Versteeg(1988c) and Bartos and Satterfield(1986). Advantages of the reaction between CO_2 and alkanolamines are:

1. the ability to meet the different regimes of the chemical method by choosing different amines and different concentrations.
2. the possibility to work with both aqueous, organic and viscous solutions as well.
3. the certainty that the reaction order in CO_2 is equal to one.

The main disadvantage is the rather high solubility of CO_2 compared to other gases; this generally results in high CO_2 conversions making the evaluation of the mass transfer parameters sensitive towards the gas phase mixing model chosen.

3. EXPERIMENTAL

3.1. Chemical system.

Blauwhoff et al(1984) reviewed the data available on the kinetics of primary (MEA), secondary (DEA, DIPA) and tertiary (TEA, MDEA) alkanolamine solutions in water and provided additional data for DEA, DIPA, TEA and MDEA at 298 K. From their results it can be concluded that aqueous solutions of diethanolamine (DEA) at 298 K fulfill the criteria to measure interfacial areas with the chemical method in a mechanically agitated gas-liquid reactor.

Commercial grade aqueous DEA solutions of 80 vol% with a purity of $\geq 98\%$, supplied by BASF, are used in the absorption experiments. The reaction rates of this alkanolamine are determined and compared with the results of Blauwhoff et al(1984) and Versteeg and van Swaaij(1988a). An excellent agreement in reaction rates at 298 K is found for DEA concentrations between 0.5-2.0 mol/l. The kinetic experiments are carried out in stirred vessels with a smooth gas-liquid interface. The experimental set-up is identical to that of Blauwhoff et al(1984); in our case the pressure decrease is followed by a pressure transducer connected to a microcomputer, which, using Eq. (11), directly calculates the absorption rate constant $m (k_{1,p} (c_{B,L})^p D_A)^{0.5}$. From this constant the pseudo first order overall reaction rate constant $k_{ov} = k_{1,p} (c_{B,L})^p$ can be calculated,

provided m and D_A are known.

The overall reaction rate constant is determined separately for the first twenty fresh or regenerated batches of DEA solutions as used in our absorption experiments: no significant influence of impurities or degeneration products is found. For the following batches k_{ov} is no more determined. The overall reaction rate constant is also not influenced by the CO_2 -load in the liquid. This indicates that the deprotonation of the "zwitterion" is not influenced by the hydroxyl ion and that the absorption rate of CO_2 is not influenced by the bicarbonate formation reaction, see Blauwhoff et al(1984).

Interfacial areas in the reactor can be evaluated with Eq. (11) without knowledge of the exact values of the parameters m , $k_{1,p} \cdot c_{B,L} \cdot p$ and D_A provided we are sure that the condition $E_A = Ha$ is fulfilled. In that case the value of the absorption rate constant $m (k_{1,p} (c_{B,L})^p D_A)^{0.5}$ as directly evaluated from a kinetic experiment can be used in the absorption experiments and in Eq. (11). This avoids the cumulative errors arising from calculation, estimation and measurement of the separate parameters.

About 70 kinetic experiments have been executed at 298 K to determine an empirical correlation for the absorption rate constant $m (k_{1,p} (c_{B,L})^p D_A)^{0.5}$ as a function of the free DEA concentration from 0.2 to 2.0 mol/kg. The correlation is given in Table 1 together with experimentally determined correlations for the solubility m , the viscosity μ_L and the density ρ_L as a function of the total DEA concentration. If the value of k_L in the mechanically agitated reactor is known we can now choose the conditions where $2 < Ha \ll E_{A,ov}$.

Table 1. Data for the DEA-water system at 298 K.

$$m \sqrt{k_{1,p} c_{DEAL}^p D_{CO_2}} = 9.39 \cdot 10^{-4} [DEA]_{tot}^{0.38} - 2.61 \cdot 10^{-4} \quad m/s \quad (12)$$

$$m = .791 - .044 [DEA]^* \quad (13)$$

$$\rho_L = 995.8 + 15.55 [DEA] - 1.141 [DEA]^2 \quad kg/m^3 \quad (14)$$

$$\mu_L = 10^{-3} \exp(-.1135 + .257 [DEA] + 4.694 \cdot 10^{-2} [DEA]^2) \quad Ns/m^2 \quad (15)$$

[DEA] in mol/kg and [DEA]* in mol/l

Chapter 2

We did not take into account a possible reversibility of the reactions concerned. Alkanolamines actually react reversibly with CO_2 . Versteeg et al(1988a, 1988b) showed that for great deviations from irreversibility the application of the equations above in kinetic and absorption experiments can cause considerable errors. With their numerical model we checked this for different CO_2 partial pressures, DEA concentrations and conversions and we concluded that no serious deviations from irreversibility occur in our kinetic and absorption experiments.

3.2. Experimental installation.

An experimental installation has been constructed to perform absorption experiments at elevated pressures. Provisions have been made for a quick exchange of the reactor. Either a mechanically agitated reactor ($H/D = 1$) or a column reactor ($H/D = 6.2$) can be installed. In this paragraph we will only consider the mechanically agitated reactor. The flow sheet of the installation is given in Fig. 1. Except for the reactor all parts are made of 316 stainless steel.

3.2.1. The reactor.

The mechanically agitated reactor, see Fig. 2, is a modified high pressure autoclave made of glass and manufactured by SFS(Zürich). It has a diameter of $D = 88$ mm and a total height equal to 190 mm. The reactor can be operated at pressures up to 2.0 MPa and is thermostated at 298 K. The reactor operates continuously with respect to both the gas and the liquid phase and is equipped with a standard six-bladed disc turbine impeller with a diameter of $D_i/D = 0.4$, installed at a height of $h/D = 0.33$ above the flat bottom plate. Four baffles of width $W/D = 0.1$ are mounted in the reactor. The dispersion level is maintained at a height of $H/D = 1$ by using an overflow vessel. A gas mixture of CO_2 and N_2 is introduced into the reactor via a sparger located centrally below the impeller. The sparger is either a sintered plate of $d_s = 1.0$ cm and an average pore diameter of $30 \mu\text{m}$ or a simple tube of $d_s = 3.0$ mm. The agitation rate is regulated with a variable gear motor and is monitored continuously with a tachometer. A three-way valve is installed in the gas inlet line just before the reactor for gas hold-up measurements.

3.2.2. The gas system.

Carbon dioxide (Hoek Loos, purity ≥ 99.5 vol%) and nitrogen (Hoek Loos, purity ≥ 99.90) are taken from gas bottles. After pressure regulation by two Tescom series 2200 pressure regulators the gases are supplied to the reactor over four Brooks series 5850 TR and series 5851 TR mass flow controllers, which keep both the gas flow rate and the gas composition constant. The flow rates applied for N_2 range from 0 to $2.5 \cdot 10^{-3} \text{ nm}^3/\text{s}$ and for CO_2 from 0 to $8.3 \cdot 10^{-5} \text{ nm}^3/\text{s}$. The gases are mixed in a helical heat exchanger and the inlet temperature of the gas is controlled with an electric heating coil, which is connected to a Eurotherm temperature regulator. The pressure in the installation is controlled by a Tescom series 2300 backpressure regulator in the outlet gas flow.

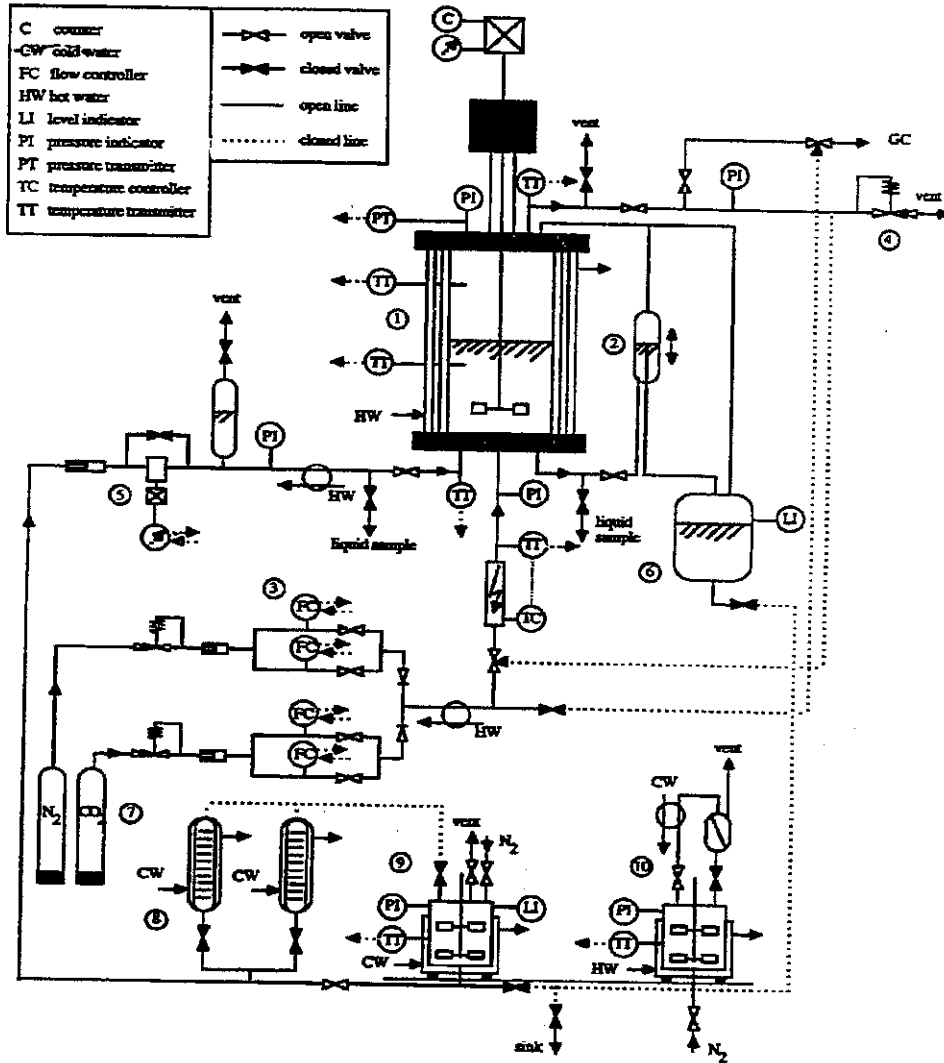


Figure 1: The experimental installation; reactor (1), overflow vessel (2), mass flow controllers (3), backpressure regulator (4), liquid pump (5), liquid buffer vessel (6), gas bottles (7), liquid burners (8) and liquid storage (9) and regeneration (10) vessels.

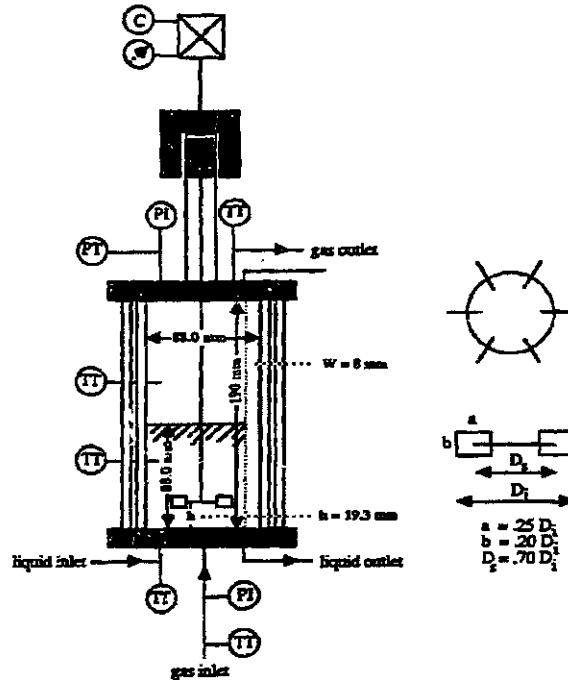


Figure 2: The experimental mechanically agitated reactor with a standard turbine disc impeller.

The in- and outlet gas flows are sampled continuously by switching a three-way valve. The CO_2 concentrations are determined on-line by means of a Varian series 3300 gas chromatograph equipped with a thermal conductivity detector and an automatic sampling valve. The gas chromatograph is connected to a Hewlett Packard 3392A integrator, which initiates the sample taking and evaluates the results. Helium is used as carrier gas and a $1/8$ " diameter 1.5 m long Porapak-P column for the analysis.

3.2.3. The liquid system.

Fresh or regenerated DEA solutions are fed from a storage vessel with a volume of $V_L = 60$ l into the reactor by means of a LEWA-membrane pump type EKM-1. The DEA solutions in the storage vessel are kept at a constant temperature between 280 and 290 K by means of cooling water, which flows through the jacket of the vessel. The pump has a maximum capacity of $1 \cdot 10^{-5} \text{ m}^3/\text{s}$ and the

Chapter 2

liquid flow is adjusted either manually or automatically by changing the stroke length of the pump. Two burettes are available for calibration of the liquid flow rate.

The liquid feed is kept at a constant temperature of 298 K by means of two helical heat exchangers between the liquid pump and the reactor. The liquid flows through the reactor and via an overflow vessel into a liquid buffer vessel with a volume of $V_L = 28$ l. When the buffer vessel is filled up completely, the experiments have to be stopped and the buffer is emptied into the regeneration vessel.

The regeneration vessel with a volume of $V_L = 60$ l is kept at temperatures between 350 and 370 K by means of hot water from a thermostat. Under agitation by two turbine impellers the CO_2 contained in the DEA solution in the regeneration vessel is stripped continuously from the solution with nitrogen. Regenerated solutions are recycled to the storage vessel and used for new absorption experiments.

Liquid samples are taken to determine the DEA concentration and the CO_2 -liquid load for each fresh or regenerated batch of DEA solution. The DEA concentration is determined with a standard acid-base titration and the amount of absorbed CO_2 by means of the method described by Verbrugge(1979) and used by Blauwhoff et al(1984).

3.2.4. Automation.

The experiments in the installation are partly automated by means of a HP 9816 microcomputer and a HP 3497A data acquisition and control unit. The mass flow controllers and the liquid pump can be adjusted automatically by the computer.

The reactor pressure and temperatures, the in- and outlet temperatures and the set points of the mass flow controllers and of the liquid pump are continuously monitored by the computer. Other process parameters such as the agitation rate, the DEA concentration, the CO_2 -liquid load as well as the results from the gas analyses have to be fed manually into the computer. The computer calculates the flow rates, the superficial gas velocity as well as the CO_2 concentrations in the gas streams and continuously displays the process conditions. After an experiment all data are stored in datafiles to be processed by data manipulation programs later on.

3.3. Experimental procedure.

Before an absorption experiment is carried out, the desired reactor pressure, the superficial gas velocity, the desired CO_2 fraction in the gas feed and the estimated DEA and CO_2 concentrations in the liquid feed are supplied to the computer. The computer then calculates the set points for the mass flow controllers and the liquid pump. The liquid flow is adjusted on the basis of a maximum allowable DEA conversion of 20%, if all CO_2 is absorbed from the gas phase.

The DEA concentrations in the solutions, which are used to determine the interfacial areas, vary between 0.8 and 1.1 mol/kg. For a realistic value of the liquid phase mass transfer coefficient k_L for

Chapter 2

aqueous solutions in an agitated reactor equal to $2 \cdot 10^{-4}$ m/s, see Westerterp et al(1984) and Mehta and Sharma(1971), this results in Hatta numbers in the range of 4, see Eq. (7). The CO_2 -fraction in the gas feed ranges from 1 to 2%. For values of $D_{\text{DEA}}/D_{\text{CO}_2} = 0.5$ and of $m = 0.7 - 0.8$ at a temperature of 298 K this results in values of $E_{A,m} > 30$ at all pressures.

At atmospheric conditions the mass transfer coefficient in the gas phase k_G is a factor 1000 larger than the mass transfer coefficient in the liquid phase k_L . Even after taking into account the inverse proportionality between k_G and the square root of pressure, as found by Versteeg et al(1987), this results in a gas phase resistance which never accounts for more than 2% of the total resistance to mass transfer at 2.0 MPa. The gas phase mass transfer resistance therefore can be neglected. Thus all the criteria for the application of Eq. (11) are met with and the interfacial area can be determined from absorption rate measurements under the experimental conditions mentioned.

For each absorption experiment the CO_2 concentrations in the in- and outlet gas flow and the DEA concentration and the CO_2 -liquid load in each fresh or regenerated batch of DEA solution used are determined. From

$$\dot{Q}_{\text{CO}_2} = \dot{Q}_v (c_{\text{CO}_2, G, \text{in}} - c_{\text{CO}_2, G, \text{out}}) \quad (16)$$

the absorption rate is calculated.

4. RESULTS

4.1. Visual and photographic observations.

In order to get a first qualitative impression of the performance of the reactor at elevated pressures several photographs were taken of a nitrogen in water dispersion at different pressures. In these experiments the gas was introduced into the reactor through the sintered plate. Some photographs are presented in Figs 3, 4 and 5. Fig. 3 shows pictures at three different agitation rates at a constant pressure 0.1 MPa and at a constant superficial gas velocity $v_G = 0.5$ cm/s. The gas fraction in the dispersion increases with increasing agitation rate. The critical agitation rate for a fully developed dispersion, see Westerterp et al(1963), seems to be somewhere between 11.7 and 15.0 rps. Figs 4 and 5 show photographs of the dispersion in the reactor at the same agitation rates and superficial gas velocity, but for two different pressures of $P = 0.6$ and 1.1 MPa. Both series show an increase of the gas fraction with increasing agitation rate.

At constant agitation rate we visually observe an increase of the gas fraction in the dispersion with increasing pressure. This is in contrast with the findings of Vafopoulos et al(1976), who found no influence of pressure in a transparent mechanically agitated reactor with $D = 0.44$ m, $D_i/D = 0.33$.

Chapter 2

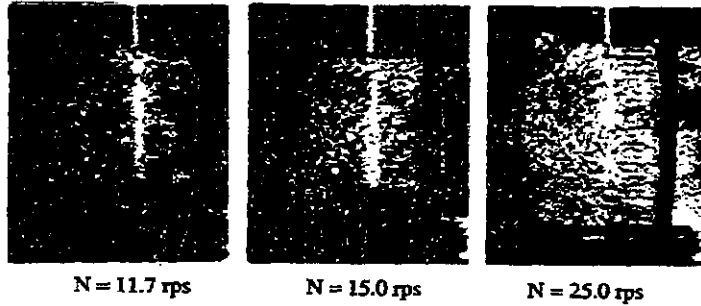


Figure 3: Photographic observations at $P = 0.1 \text{ MPa}$ and $v_G = 0.50 \text{ cm/s}$.

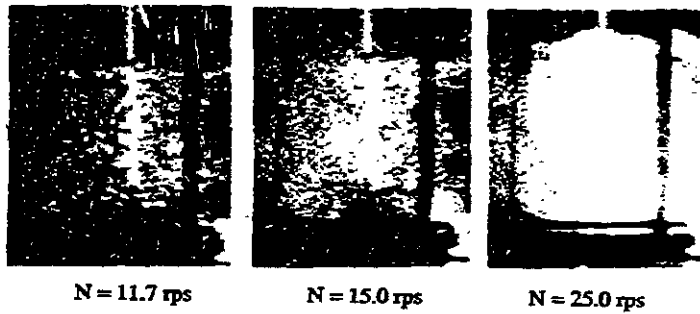


Figure 4: Photographic observations at $P = 0.6 \text{ MPa}$ and $v_G = 0.50 \text{ cm/s}$.

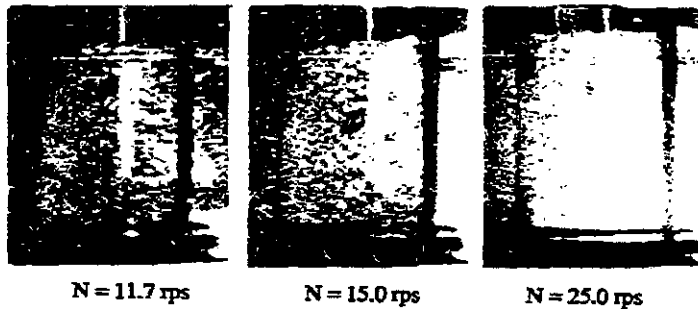


Figure 5: Photographic observations at $P = 1.1 \text{ MPa}$ and $v_G = 0.50 \text{ cm/s}$.

Chapter 2

$H/D = 1$ and $v_G = 0.22 - 1.75$ cm/s. For pressures between 0.1 and 1.0 MPa they determined photographically the bubble diameters and calculated the interfacial areas in an air-water dispersion. They observed no influence of pressure on both parameters. We recall, see Charpentier(1982) and Joshi et al(1982), that the photographic technique is subject to serious uncertainties and only gives local values of bubble diameters and interfacial areas at the wall.

4.2. Evaluation of the absorption experiments.

4.2.1. Driving force for mass transfer.

To determine the interfacial area from an absorption experiment the liquid phase is assumed to be ideally mixed. In Eq. (12) from Table 1 the concentration $[DEA]_{free}$ refers to the free DEA concentration. The total DEA concentration is corrected for the CO_2 -liquid load in the feed and for the amount of CO_2 absorbed from the gas phase, as part of the DEA in the feed and in the reaction mixture itself is already converted. The resulting free DEA concentration is used for the calculation of the absorption rate constant from Eq. (12). The interfacial areas in the reactor can now be evaluated by combining Eqs (11) and (16) to

$$a = \frac{\phi_v (c_{CO_2,G,in} - c_{CO_2,G,out})}{m V_R \sqrt{k_{Lp} c_{DEA}^p D_{CO_2} \Delta c_{CO_2,G}}} \quad (17)$$

in which $\Delta c_{CO_2,G}$ is the average driving force for mass transfer. If the residence time distribution (RTD) of the gas phase is equivalent to that of a continuous stirred tank reactor (CSTR), then $\Delta c_{CO_2,G}$ is equal to the CO_2 concentration in the gas outlet

$$\Delta c_{CO_2,G} = c_{CO_2,G,out} \quad (18)$$

For a gas phase in plug flow (PFR) $\Delta c_{CO_2,G}$ is equal to the logarithmic mean difference between the in and outlet gas phase concentration

$$\Delta c_{CO_2,G} = \frac{(c_{CO_2,G,in} - c_{CO_2,G,out})}{\ln(c_{CO_2,G,in} / c_{CO_2,G,out})} \quad (19)$$

The relatively high solubility of CO_2 , compared to an oxygen system, can result in considerable CO_2 conversions in the gas phase. From Eqs (17), (18) and (19) it can be seen that for a high gas phase conversion:

Chapter 2

1. large differences between the calculated mass transfer parameters are obtained for the two extremes of the mixing in the gas phase.
2. large errors in the calculated mass transfer parameters will be found even for a small deviation from an assumed mixing behaviour of the gas phase.

Only very limited data on the RTD of the gas phase are available despite the extensive research on mechanically agitated gas-liquid reactors throughout many years. The studies of Hanhart et al(1963) and Gal-Or and Resnick(1966) indicate that above the critical agitation rate N_0 the RTD of the gas phase is equivalent to that of a cascade in between one and two completely mixed tank reactors in series. At otherwise identical experimental conditions both Mehta and Sharma(1971) and Hassan and Robinson(1980) determined interfacial areas at different levels of conversion of the absorbing gas phase component. This allowed them to study the influence of the gas phase conversion on the evaluation of the interfacial areas. Mehta and Sharma(1971) proved qualitatively that in their experiments with various CO_2 -amine systems the gas phase was completely mixed at agitation rates above the critical agitation rate N_0 . Hassan and Robinson(1980) reported for coalescing systems and conversions below 80% that for all practical calculations the gas phase can be considered to be completely mixed.

4.2.2. Absorption experiments.

In a series of absorption experiments at different CO_2 conversion levels (40 - 99%) we examined the sensitivity of our interfacial area determinations towards the CO_2 conversion in the gas phase for the two extremes in the mixing behaviour. Experiments were carried out with the sintered gas inlet at four superficial gas velocities of $v_G = 0.25, 0.50, 0.75$ and 1.00 cm/s and at three agitation rates of $N = 8.3, 16.7$ and 25.0 rps respectively. These experiments were carried out at seven pressures of $P = 0.11, 0.2, 0.3, 0.5, 0.7, 0.9$ and 1.1 MPa respectively.

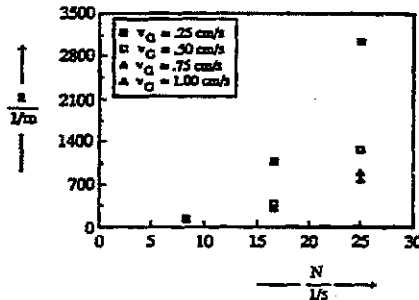


Figure 6: Interfacial area vs. the agitation rate at $P = 3$ MPa and complete mixing of the gas phase.

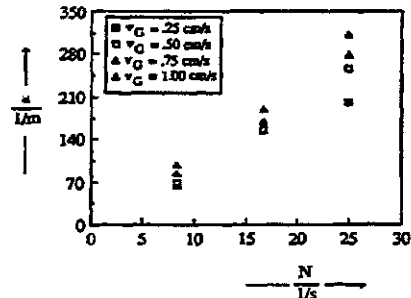


Figure 7: Interfacial area vs. the agitation rate at $P = 3$ MPa and plug flow of the gas phase.

Chapter 2

Table 2. Experimental data for absorption experiments at P = .3 MPa.
Data: [DEA] = 0.79 mol/kg.

$v_G \cdot 10^2$	N	$y_{CO_2, in}$	ζ_{CO_2}	a (CSTR)	a (PFR)
m/s	rps		%	l/m	l/m
.25	8.3	.0210	74	139	65
.25	16.7	.0210	96	1097	153
.25	25.0	.0210	99	3027	200
.50	8.3	.0195	51	101	69
.50	16.7	.0195	79	383	155
.50	25.0	.0195	93	1263	257
.75	8.3	.0198	44	115	85
.75	16.7	.0198	68	317	169
.75	25.0	.0198	86	890	287
1.00	8.3	.0198	39	127	98
1.00	16.7	.0198	62	321	190
1.00	25.0	.0198	80	782	313

Interfacial areas measured at P = 0.3 MPa are plotted versus the agitation rate in Figs 6 and 7 for the driving force as given by Eqs (18) and (19) respectively. The experimental data are given in Table 2; these are characteristic for the results at other pressures. Evaluation of the experiments with the assumption of a completely mixed gas phase at the two lowest gas velocities and the highest agitation rates results in extremely large values for the interfacial areas. This is caused by the extremely high CO₂ conversions in the gas phase of > 90 %. Assuming plug flow behaviour for the gas phase results in an increase in the interfacial area with increasing gas velocities and a linear increase in the interfacial area with increasing agitation rate. The divergence of the interfacial area at $v_G = 0.25$ cm/s and N = 25.0 rps, displayed in Fig. 7, suggest a partial depletion of the gas bubbles.

Westermarck et al(1963) showed that for $N < N_0$ the interfacial area is hardly affected by the agitation rate and only depends on the superficial gas velocity whereas for $N > N_0$ it depends linearly on the agitation rate and is not affected by the superficial gas velocity. This was confirmed by Mehta and Sharma(1971) and van Dierendonck(1970) and for $N < N_0$ by Sridhar and Potter(1980a). Only Sridhar and Potter(1980a) found for $N > N_0$ an influence of the superficial gas velocity on the interfacial area and the gas hold-up. However, they observed an increase in the interfacial areas with increasing superficial gas velocities and not a decrease as is shown in Fig. 6.

Evaluation of our absorption experiments at one gas velocity with Eq. (19) for the driving force for mass transfer results in a linear increase of the interfacial areas over the whole range of agitation rates. The assumption of a completely mixed gas phase leads to a better approximation of the interfacial areas in a mechanically agitated reactor which has to exhibit a critical agitation rate as found in literature and observed visually. We therefore concluded that the gas phase must be

Chapter 2

considered completely mixed for a correct evaluation of the absorption experiments.

An additional problem are the extremely high conversions at low gas velocities and high agitation rates. As stated before, these high gas phase conversions can cause large errors in the calculation of the interfacial areas even for small deviations from the assumed mixing behaviour. This is illustrated in Fig. 6 in which the calculated interfacial areas above the critical agitation rate N_0 and at the lowest gas velocity $v_G = 0.25$ cm/s are extremely large and not realistic. This is probably caused by small deviations from the assumed complete mixing of the gas phase. It is also shown in Fig. 6 that the interfacial areas evaluated from experiments with CO_2 conversions below 80% and above the critical agitation rate N_0 are practically equal. This is in agreement with the results of Westerterp et al(1963) and others. We therefore concluded that the CO_2 conversions have to be kept below 80% in order to make a correct evaluation of the interfacial areas.

The first conclusion regarding the mixing in the gas phase agrees with Mehta and Sharma(1971), while both the conclusions about the mixing and the maximum conversion level are in accordance with the conclusions of Hassan and Robinson(1980).

4.3. Interfacial areas.

The conditions of a maximum gas phase conversion of 80% lead experimentally to the use of minimum superficial gas velocities of $v_G = 0.50, 0.75$ and 1.00 cm/s at agitation rates of $N = 11.7, 16.7$ and 25.0 rps respectively. In the following only experiments done at superficial gas velocities above the minimum allowable are presented and the interfacial areas are calculated on the basis of a completely mixed gas phase.

Table 3. Averaged interfacial areas at different conversion levels.

Data: $[\text{DEA}] = 0.8 - 0.9$ mol/kg and $y_{\text{CO}_2, \text{in}} = 0.0204$.

v_G cm/s	N rps	ζ_{CO_2} %	a (CSTR) m^2
0.50	8.3	56	124
0.75	8.3	46	124
0.75	16.7	68	305
1.00	8.3	41	132
1.00	16.7	61	306
1.00	25.0	79	762

Chapter 2

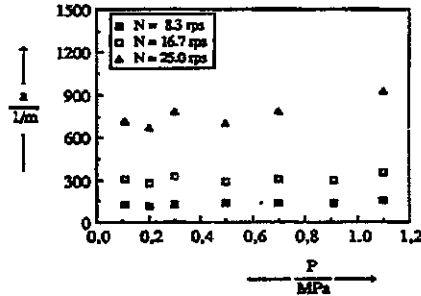


Figure 8: Interfacial area vs. the reactor pressure at $v_G = 1.00$ cm/s and complete mixing of the gas phase.

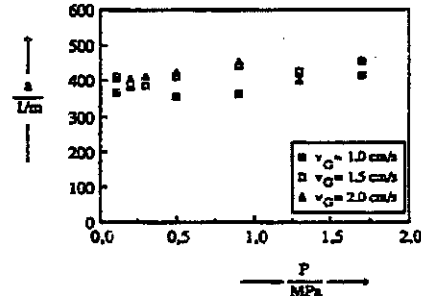


Figure 9: Interfacial area vs. the reactor pressure at $N = 16.7$ rps and complete mixing of the gas phase.

Table 4. Interfacial areas at different pressures and $N = 16.7$ rps.
Data: [DEA] = 0.8 - 1.1 mol/kg.

P MPa	$a (v_G = 1.00 \text{ cm/s})$ m^{-1}	$a (v_G = 1.50 \text{ cm/s})$ m^{-1}	$a (v_G = 2.00 \text{ cm/s})$ m^{-1}
0.11	365	411	405
0.20	384	388	404
0.30	385	386	411
0.50	355	413	425
0.90	362	444	456
1.30	419	428	401
1.70	418	455	459

The interfacial areas determined at $v_G = 1.00$ cm/s are plotted versus the reactor pressure in Fig. 8: there is no influence of pressure at all!! Fig. 8 is representative for all our experiments. Also at other gas velocities and agitation rates no influence of pressure could be detected as long as the CO_2 conversion conditions were fulfilled!! The interfacial areas and CO_2 conversions, which are determined for these experiments at different pressures, are averaged and are given in Table 3.

At the agitation rate of $N = 16.7$ rps - higher than the critical agitation rate N_0 which is around 12.5 rps - an additional serie of experiments was carried out with the single o.ifice as gas inlet. Interfacial areas were determined for three superficial gas velocities of $v_G = 1.00, 1.50$ and 2.00 cm/s and at seven pressures up to 1.7 MPa respectively. The results are given in Table 4 and plotted

Chapter 2

in Fig. 9; again there is no significant influence of the operating pressure to be found!! The accuracy of the separate experiments has been determined to be equal to 5%. A distinction between the interfacial areas for the three superficial gas velocities cannot be made because of the accuracy and the small influence of v_G on the interfacial areas at $N = 16.7$ rps, which is above N_0 .

So no influence of pressure on the interfacial areas can be observed in all experiments reported here in the pressure range of 0.1 to 1.7 MPa. This is in contrast to the findings of Sridhar and Porter(1980a, 1980b), who used a light transmission probe to determine the interfacial areas and reported an increase in the interfacial areas of as much as 75% for an increase from atmospheric pressure up to 1.1 MPa.

4.4. Gas hold-ups.

The absorption experiments are laborious and time consuming. Additional gas hold-up measurements were carried out to get a quick impression of the influence of the operating pressure on the gas hold-up at several agitation rates and in three gas-liquid systems. The gas hold-ups were determined by measuring the height difference between the gassed and the non-gassed dispersion level. The gassed dispersion height H was always equal to the diameter of the reactor D . The surface of the dispersion is severely disturbed at agitation rates below $N = 10$ rps by irregular outbursts of large bubbles and at agitation rates above $N = 25$ rps by the high shear forces. This leads to inaccuracies in the measurements of around 10%, while the more accurate values are obtained at intermediate agitation rates. Dispersions of nitrogen in an aqueous DEA solution with similar composition as used in the absorption experiments, in a fresh unconverted DEA solution and in water have been investigated. Two superficial gas velocities of $v_G = 1.00$ and 2.00 cm/s are used over a wide range of agitation rates from $N = 4.2$ to 29.2 rps. The fresh DEA solution showed foaming at higher agitation rates.

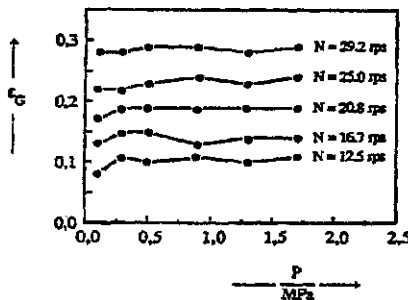


Figure 10: Gas hold-up in water vs. the reactor pressure at $v_G = 2.00$ cm/s.

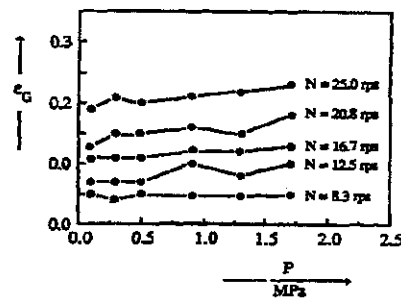


Figure 11: Gas hold-up in a DEA solution partially loaded with CO_2 vs. the reactor pressure at $v_G = 2.00$ cm/s.

Chapter 2

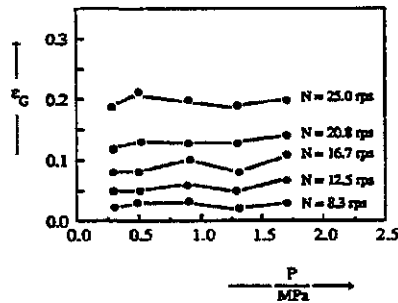


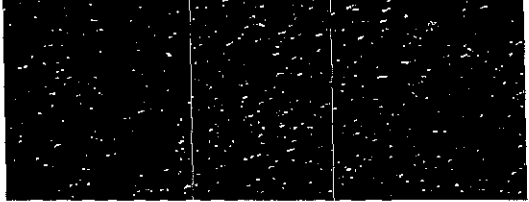
Figure 12: Gas hold-up in an unconverted DEA solution vs. the reactor pressure at $v_G = 2.00$ cm/s.

Table 5. Gas holdups at different agitation rates in water and in a DEA solution partially loaded with CO_2 . Data: $[\text{DEA}] = .9$ mol/kg and $[\text{CO}_2] = .09$ mol/kg.

N rpm	ϵ_G (water)	ϵ_G (DEA)	ϵ_G (water)	ϵ_G (DEA)
	($v_G = 1.00$ cm/s)	($v_G = 1.00$ cm/s)	($v_G = 2.00$ cm/s)	($v_G = 2.00$ cm/s)
4.2	0.032	0.022	0.042	0.032
8.3	0.044	0.034	0.046	0.047
12.5	0.070	0.055	0.102	0.082
16.7	0.102	0.078	0.140	0.117
20.8	0.135	0.117	0.187	0.153
25.0	0.183	0.150	0.230	0.210
29.2	0.228	0.192	0.285	

For $v_G = 2.00$ cm/s the results are plotted in Figs 10, 11, and 12: again no significant influence of pressure on the gas hold-up can be observed!!! The results at $v_G = 1.00$ cm/s are also independent of pressure. These results are opposite to the photographic observations in Figs 3, 4 and 5; they accentuate the care which should be taken in interpreting visual or photographic observations. They are also opposite to the results of Sridhar and Potter(1980b), who determined gas hold-ups in their reactor with the manometric method and found a clear influence of pressure, see further comments in the discussion.

The gas hold-ups, which are determined in the two non-foaming systems at the different pressures, are averaged and the results are given in Table 5. They are compared in Figs 13 and 14 for both superficial gas velocities respectively; the gas hold-ups in the DEA solution are lower than



Chapter 2

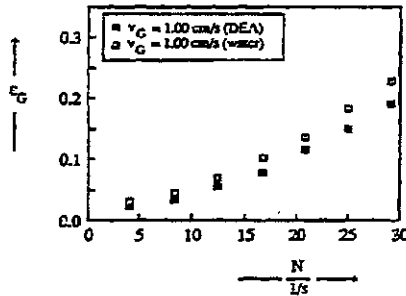


Figure 13: Average gas hold-up in water and in a DEA solution partially loaded with CO₂ vs. the agitation rate at v_G = 1.00 cm/s.

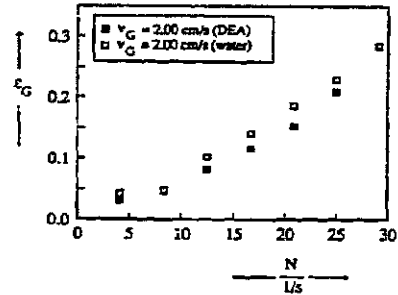


Figure 14: Average gas hold-up in water and in a DEA solution partially loaded with CO₂ vs. the agitation rate at v_G = 2.00 cm/s.

the gas hold-ups in water. The gas hold-ups for both systems show a strong dependence on the agitation rate above $N = 12.5$ rps and a weak dependence below $N = 12.5$ rps. It is also shown that the gas hold-ups above the critical agitation rate are dependent on the superficial gas velocity.

5. DISCUSSION

The seemingly contradictory results from our photographic observations and from our interfacial area and gas hold-up determinations once again demonstrate the pitfalls of local methods such as photographic or visual observations through the wall of a vessel. The local values at the wall are not necessarily representative for the averaged overall values of the bubble diameters and the interfacial areas in an agitated vessel.

Sridhar and Potter(1978, 1980a) used a light transmission probe and determined inside the reactor at about 40 locations the interfacial areas, which were averaged to obtain an overall value for the entire reactor. The size of their probe, which consisted of stainless steel tubes of 5 mm diameter, is larger than their average bubble diameter of 3 - 4 mm: in our view this may cause serious disturbances to the hydrodynamics in the vessel and specially at the sampling point. Although Sridhar and Potter(1980a) also present some values of the interfacial area close to the impeller, probably the interfacial area in the impeller region itself, where the smallest bubbles can be found, could not be determined by them because of the geometric limitations of their probe. We suspect that the results of Sridhar and Potter(1978, 1980a) depend on the experimental technique and are not representative for the true interfacial area in an agitated gas-liquid dispersion.

Sridhar and Potter(1980b) also determined, using the manometric method, an increase in the gas hold-up with an increase in the reactor pressure. They corrected their measurements for the dynamic pressure difference caused by the radial and tangential flow of the liquid. It is our experience that this

Chapter 2

dynamic pressure difference is very sensitive to the local position of the sampling points and leads to considerable errors especially in small mechanically agitated reactors. With a simple calculation it can be evaluated that a difference in liquid velocity at two sampling points of 1 m/s already leads to a static head difference of around 5 cm.

It is obvious that the pressure independence found in the gas hold-up measurements supports the results of the absorption experiments, which are quite complex and in which several assumptions were made to evaluate the interfacial areas. The gas hold-up results show the same dependence on the agitation rate as the interfacial areas evaluated on the basis of a completely mixed gas phase.

The use of Eq. (18) is restricted to a micromixed gas phase. In the mechanically agitated reactor the dispersed gas bubbles are subjected to finite coalescence and breakup rates and moreover, the bubble diameters are not uniform. If the absorption rate is first order in the component being absorbed from the gas phase, which is the case for our CO₂ system, Eq. (18) can also be applied to a completely segregated gas phase with a uniform bubble diameter, see Hanhart et al(1963). Compared to a bubble column, the bubble diameter distribution in the mechanically agitated reactor is rather small, but still not uniform. This means that for higher CO₂ conversions we should also take into account the bubble size distribution as explained by Midoux et al(1980) and Schumpe and Deckwer(1980). This will be discussed in Chapter 5.

6. CONCLUSIONS AND FINAL REMARKS

Based on the scarce literature results about the RTD of the gas phase together with the characteristic behaviour of the reactor and our own experiments, we may conclude qualitatively that at agitation rates above the critical agitation rate N_0 the gas phase is completely mixed. Furthermore we may conclude that for $N > N_0$ the CO₂ conversion in the gas phase has to be kept below 80% to determine realistic values for the interfacial areas.

In a small mechanically agitated reactor we find no influence of operating pressures up to 1.7 MPa on the interfacial areas in an aqueous DEA solution. In this system and in water we also find - within this pressure range and over a wide range of agitation rates - no influence on the gas hold-up. Before general and final conclusions regarding the influence of the operating pressure on the mass transfer parameters in mechanically agitated gas-liquid reactors can be drawn further research in larger vessels and at higher pressures is required. To this end we have developed an experimental installation for pressures up to 10 MPa and we will report the results as obtained in this installation in Chapter 4.

This study indicates that correlations for the mass transfer parameters as derived on the basis of experiments at atmospheric pressures, also can be used in high pressure mechanically agitated gas-liquid reactors.

Chapter 2

Acknowledgements - The investigations were supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Scientific Research (NWO). We also acknowledge H. Borkink for his assistance in the experimental work and G. Schorhaar for his technical support.

NOTATION

a	specific interfacial area, m^2/m^3 dispersion
Al	Hinterland coefficient, Eq. (6a)
c	concentration, mol/m^3
Δc	driving force for mass transfer, mol/m^3
d	diameter, m
d_i	gas inlet diameter, m
D	vessel diameter, m
D_i	impeller diameter, m
D_A	diffusivity of component A in the liquid phase, m^2/s
D_B	diffusivity of component B in the liquid phase, m^2/s
E_A	enhancement factor, Eq. (5b)
$E_{A,\infty}$	enhancement factor for an infinitely fast reaction, Eq. (5)
E_T	total energy input into the dispersion, W
h	impeller height, m
H	dispersion height, m
Ha	Hatta number, Eq. (3)
J	mole flux, $mol/m^2 \cdot s$
k	mass transfer coefficient, m/s
k_{ov}	overall reaction rate constant, 1/s
$k_{n,p}$	reaction rate constant for a reaction of the order (n,p) , $m^{3(p+n-1)}/mol^{(p+n-1)} \cdot s$
m	distribution coefficient, $c_L = m c_G$
N	agitation rate, 1/s
N_G	critical agitation rate, 1/s
P	pressure, Pa
P_G	gassed power input, W
R_C	chemical reaction rate, $mol/m^3 \cdot s$
v	superficial velocity based on the empty cross-sectional area of the vessel, m/s
v_S	minimal rising velocity of the gas bubbles, m/s
V	volume, m^3
W	baffle width, m
y	molar fraction in the gas phase

Greek symbols

ϵ	hold-up
ϕ	flow rate, m^3/s or mole/s
μ	dynamic viscosity, $N \cdot s/m^2$
ν_B	stoichiometric coefficient of component B ($\nu_A = 1$)
ρ	density, kg/m^3
σ	surface tension, N/m
ζ	conversion

Chapter 2

Subscripts/Superscripts

A	component originally in the gas phase
air	air
B	component originally in the liquid phase
free	free amine
G	gas
in	inlet
L	liquid
n	reaction rate order for component A in the liquid phase
out	outlet
p	reaction rate order for component B in the liquid phase
R	reactor
v	volumetric

REFERENCES

- Bartos, T. M. and Satterfield, C. N., 1986, Effects of finely divided solids on mass transfer between a gas and an organic liquid, *AIChE J.* 32, 773-781.
- Blauwhoff, P. M. M., Versteeg, G. F. and van Swaaij, W. P. M., 1984, A study on the reaction between CO₂ and alkanolamines in aqueous solutions, *Chem. Eng. Sci.* 39, 207-225.
- Calderbank, P. H., 1958, Physical rate processes in industrial fermentation. Part 1: The interfacial area in gas-liquid contacting with mechanical agitation, *Trans. Instn Chem. Engrs* 36, 443-463.
- Charpentier, J. C., What's new in absorption with chemical reaction, *Trans. Instn Chem. Engrs* 60, 131-156.
- Danczkewits, P. V. and Sharma, M. M., 1966, The absorption of carbon dioxide into solutions of alkalis and amines, *Chem. Eng.* 10, CE244-CE288.
- Danczkewits, P. V., 1970, *Gas-Liquid Reactions*, McGraw-Hill Book Company, London.
- Dierendonck, L.L. van, 1970, Vergrotingsregels voor gasbelwassers, Ph. D. Thesis, University of Twente, The Netherlands.
- Gal-Or, B. and Resnick, W., 1966, Gas residence time in agitated gas-liquid contactor, *Ind. Eng. Chem. Des. Dev.* 5, 15-19.
- Hanhart, J., Kramers, H. and Westerterp, K. R., 1963, The residence time distribution of the gas in an agitated gas-liquid reactor, *Chem. Eng. Sci.* 18, 503-509.
- Hassan, I. T. M. and Robinson, C. W., 1980, Mass-transfer-effective bubble coalescence frequency and specific interfacial area in a mechanically agitated gas-liquid contactor, *Chem. Eng. Sci.* 35, 1277-1289.
- Joshi, J. B., Pandit, A. B. and Sharma, M. M., 1982, Mechanically agitated gas-liquid reactors, *Chem. Eng. Sci.* 37, 813-844.
- Kling, G., 1962, Über die Dynamik der Blasenbildung beim Begasen von Flüssigkeiten unter Druck, *Int. J. Heat Mass Transfer* 5, 211-223.

Chapter 2

- LaNauze, R. D. and Harris, I. J., 1974, Gas bubble formation at elevated pressures, *Trans. Instn Chem. Engrs* **52**, 337-348.
- Linek, V. and Vacek, V., 1981, Chemical engineering use of catalyzed sulphite oxidation kinetics for the determination of mass transfer characteristics of gas-liquid contactors, *Chem. Eng. Sci.* **36**, 1747-1768.
- Mehta, V. D. and Sharma, M. M., 1971, Mass transfer in mechanically agitated contactors, *Chem. Eng. Sci.* **26**, 461-479.
- Midoux, N., Laurent, A. and Charpentier, J. C., 1980, Limits of the chemical method for the determination of physical mass transfer parameters in mechanically agitated gas-liquid reactors, *AIChE J.* **26**, 157-162.
- Midoux, N., Morsi, B. I., Purwasasmita, M., Laurent, A. and Charpentier, J. C., 1984, Interfacial area and liquid side mass transfer coefficient in trickle bed reactors operating with organic liquids, *Chem. Eng. Sci.* **39**, 781-794.
- Miller, D. N., 1981, Comment on "Gas hold-up and bubble diameter in pressurized gas-liquid stirred vessels", *Ind. Eng. Chem. Fund.* **20**, 105-107.
- Oyevaar, M. H., Zijl, A. D. and Westerterp, K. R., 1988, Interfacial areas and gas hold-ups at elevated pressures in a mechanically agitated gas-liquid reactor, *Chem. Eng. Techn.* **11**, 1-10.
- Sagert, N. H. and Quinn, M. J., 1976, The coalescence of H₂S and CO₂ bubbles in water, *Can. J. Chem. Eng.* **54**, 392-398.
- Schumpe, A. and Deckwer, W.-D., 1980, Analysis of chemical methods for determination of interfacial areas in gas-liquid dispersions with non-uniform bubble sizes, *Chem. Eng. Sci.* **35**, 2221-2233.
- Sharma, M. M. and Danckwerts, P. V., 1970, Chemical methods of measuring interfacial area and mass transfer coefficients in two-fluid systems, *Brit. Chem. Eng.* **15**, 522-528.
- Sridhar, T. and Potter, O. E., 1978, Interfacial area measurements in gas-liquid agitated vessels. Comparison of techniques, *Chem. Eng. Sci.* **33**, 1347-1353.
- Sridhar, T. and Potter, O. E., 1980a, Interfacial areas in gas-liquid stirred vessels, *Chem. Eng. Sci.* **35**, 683-695.
- Sridhar, T. and Potter, O. E., 1980b, Gas hold-up and bubble diameters in pressurized gas-liquid stirred vessels, *Ind. Eng. Chem. Fund.* **19**, 21-26.
- Sridharan, K. and Sharma, M. M., 1976, New systems and methods for the measurement of effective interfacial area and mass transfer coefficients in gas-liquid contactors, *Chem. Eng. Sci.* **31**, 767-774.
- Vafopoulos, L., Sztatecsny, K. and Moser, F., 1975, Der Einfluss des Partial- und Gesamtdruckes auf den Stoffaustausch, *Chem.-Ing.-Techn.*, MS 266.
- Van Landeghem, H., 1980, Multiphase reactors: mass transfer and modelling, *Chem. Eng. Sci.* **35**, 1912-1949.
- Verbrugge, P., 1979, Ph. D. Thesis, University of Delft, The Netherlands.

Chapter 2

- Versteeg, G. F., Blauwhoff, P. M. M. and Van Swaaij, W. P. M., 1987, The effect of diffusivity on gas-liquid mass transfer in stirred vessels. Experiments at atmospheric and elevated pressures, *Chem. Eng. Sci.* **42**, 1103-1119.
- Versteeg, G. F. and van Swaaij, W. P. M., 1988a, On the kinetics between CO₂ and alkanolamines both in aqueous and non-aqueous solutions. Part 1: Primary and secondary amines, *Chem. Eng. Sci.* **43**, 573-585.
- Versteeg, G.F., Kuipers J. A. M., van Beckum, F. P. H. and van Swaaij, W. P. M., 1988b, Mass transfer with complex reversible chemical reaction. Single reversible chemical reaction, submitted for publication in *Chem. Eng. Sci.*
- Versteeg, G. F. and van Swaaij, W. P. M., 1988c, Absorption of CO₂ and H₂S in aqueous alkanolamine solutions using a fixed-bed reactor with cocurrent downflow operation in the pulse flow regime, submitted for publication to *Chem. Eng. Proc.*
- Westerterp, K. R., van Dierendonck, L. L. and de Kraa, J., 1963, Interfacial areas in agitated gas-liquid contactors, *Chem. Eng. Sci.* **18**, 157-176.
- Westerterp, K. R., van Swaaij, W. P. M. and Beenackers, A. A. C. M., 1984, *Chemical Reactor Design and Operation*, John Wiley & Sons, New York.
- Westerterp, K. R., van Gelder, K. B., Janssen, H. J. and Oyevaar, M. H., 1988, Development of catalytic hydrogenation reactors for the fine chemicals industry, *Chem. Eng. Sci.* **43**, 2229-2236.