

# On the Numerical Modeling of Gas Absorption into Reactive Liquids in a Laminar Jet Absorber

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The laminar jet absorber is one of the most widely used laboratory units for the study of mass transfer during gas absorption. (Rinker et al., 2000). The laminar jet absorber is used to measure the absorption rate (dependent variable) of gas into liquid as a function of various operating conditions (independent variables) such as temperature, pressure, liquid concentration, and contact time. By repeating the experiment over a range of values of operating variables, the functional dependency of the dependent variable on the independent variables can be determined. This is called the differential experiment from which fundamental data such as diffusivity, mass transfer coefficients, reaction-rate constants, and enhancement factors are determined. Usually, the study of the kinetics of reaction involves both the solution of a system of partial differential equations that represent the system and experimental work. Although these procedures have been used extensively to study the mechanism of gas absorption into liquids (Scriven and Pigford, 1959; Sada et al., 1976; Rinker et al., 2000), no effective nor detailed numerical scheme to solve these diffusive partial differential equations have been reported.

For example, Scriven and Pigford (1959) used Cartesian coordinates to describe the absorption process in terms of a two-dimensional steady-state model in which the velocity distribution near the surface of the jet caused by the viscous drag in the nozzle and the gravitational acceleration are taken into consideration. The solution of the model to predict the absorption rate was obtained through a perturbation type technique. A close agreement between the predicted and measured absorption rate of CO<sub>2</sub> into water at 298 K was reported. Based on their results, the authors suggested that it was unlikely that the predictions of the absorption rate based on uniform rod-like flow will be more than 2 to 3% in error. However, these results were based on the absorption of a gas into a non-reactive liquid at a specific temperature.

Also, under certain conditions, absorption measurements obtained with a liquid-jet can be simulated using an unsteady-state diffusion model referred to as the penetration model. Many researchers have utilized this model to predict the reaction rate constant between gas and chemical solvents in a laminar jet absorber. Sada et al. (1976) has solved the nonlinear partial-differential equations of the penetration model for CO<sub>2</sub> absorption into a monoethanolamine-jet. As a first step, the equations of the model were transformed into a dimensionless form. Then the solution was approximated by the time centered, implicit

A comprehensive numerically solved absorption-rate/kinetics model that takes into account the coupling between chemical equilibrium, mass transfer, and the chemical kinetics of all the possible chemical reactions involved was developed for the absorption of a gas into a reactive liquid. Also, absorption rate measurements to determine the kinetics of the process were obtained in a laminar jet absorber and used to validate this new model. The results show that the model used in conjunction with our numerical method is capable of predicting the gas absorption rates, enhancement factors, and the kinetics of the reaction. Also the model predicted kinetic data for the absorption of CO<sub>2</sub> into monoethanolamine (MEA) solutions that were found to be in accordance with published kinetic data. These results show that the developed numerically solved absorption-rate/kinetics model is both accurate and efficient.

Un modèle numérique de vitesse d'absorption/cinétique complet tenant compte du couplage entre l'équilibre chimique, le transfert de matière et la cinétique chimique de toutes les réactions chimiques possibles concernées, a été mis au point pour l'absorption d'un gaz dans un liquide réactif. En outre, on a mesuré la vitesse d'absorption pour déterminer la cinétique du procédé dans un absorbeur à jet laminaire, permettant ainsi la validation de ce nouveau modèle. Les résultats montrent que le modèle utilisé conjointement à notre méthode numérique est capable de prédire la vitesse d'absorption du gaz, les facteurs d'amélioration et la cinétique de la réaction. Le modèle prédit également les données cinétiques pour l'absorption du CO<sub>2</sub> dans des solutions de monoéthanolamine (MEA), qui s'avèrent en accord avec les données cinétiques publiées. Ces résultats montrent que le modèle numérique de vitesse d'absorption/cinétique mis au point est précis et efficace.

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finite-difference method. However, these implicit equations were simplified by linearizing the reaction terms prior to the resulting set of simultaneous linear equations being solved by the method of tri-diagonal equations. A comparison of experimental data with predicted curves in terms of enhancement factors was used to extract the reaction rate constant. The main two deficiencies of this approximation/linearization method are that (1) linearizing the reaction term is not accurate as it introduces some errors in the results because the reaction term for CO<sub>2</sub> reaction with MEA is not linear; and (2) solving the partial differential equations implicitly provides a less accurate solution, is difficult to program, and takes more CPU time than the explicit solution implemented in this work (Aboudheir et al., 1999).

In recent kinetic studies of gas absorption into reactive solutions, a system of partial differential and nonlinear algebraic equations has been developed to describe the diffusion-reaction process in a laminar jet absorber (Rinker et al., 2000). The penetration model was used to set up the differential equations while the method-of-lines was used to transfer the partial differential equations into a system of ordinary differential equations. After approximating the spatial derivatives with finite difference expressions, the resulting large system of ordinary differential-algebraic equations was solved by a software package. This numerical procedure is longer and more complicated than the explicit procedure recommended in this work (Aboudheir et al., 1999).

Regarding the laminar jet absorber, it can be seen from the above literature that using the penetration model, which is an unsteady state model, to simulate the absorption process is more suitable than the steady-state model. In addition, the non-linear partial differential equations in the literature cited above have been subject to simplification and/or linearization processes before they were solved numerically. This procedure introduces some inaccuracies and errors into the solutions. In this work, detailed information about developing the absorption rate model and solving this model numerically for a laminar jet absorber is provided. The developed numerical scheme is therefore suitable for solving the partial differential equations without any simplification. It is easy to program and manage, and provides accurate results.

## Reaction Mechanism

The problem considered is the prediction of the rate of chemical absorption of gas into a reactive liquid. The system selected to test the numerical model is CO<sub>2</sub> absorption into aqueous monoethanolamine (MEA) because the kinetics of this system is well defined at low MEA concentrations within the temperature range from 293 to 313K (Versteeg et al., 1996). The zwitterion mechanism, introduced in the field of gas absorption by Danckwerts (1979), is accepted as the mechanism for the reactions between CO<sub>2</sub> and primary amines such as aqueous MEA (Little et al., 1992). This mechanism involves the reaction of MEA (RNH<sub>2</sub>) with CO<sub>2</sub> to form a zwitterion intermediate (RNH<sub>2</sub><sup>+</sup>COO<sup>-</sup>) which is subsequently deprotonated by a base (B) to produce a carbamate (RNHCOO<sup>-</sup>), where R refers to CH<sub>2</sub>CH<sub>2</sub>OH. Any base (such as RNH<sub>2</sub>, OH<sup>-</sup>, H<sub>2</sub>O, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>) present in the solution may contribute to the deprotonation of the zwitterion. The contribution of each base to the overall reaction rate depends on its concentration as well as its strength.

Reactions 1 to 10 may occur when CO<sub>2</sub> absorbs into and reacts with aqueous MEA. All the species represented are in aqueous solution.

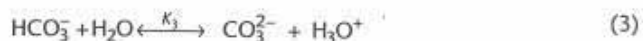
Ionization of water:



Dissociation of dissolved CO<sub>2</sub> through carbonic acid:



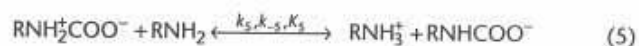
Dissociation of bicarbonate:



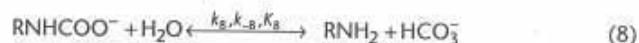
Zwitterion formation from MEA and CO<sub>2</sub> reaction:



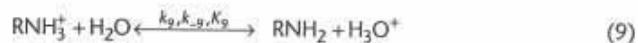
Carbamate formation by deprotonation of the zwitterion:



Carbamate reversion to bicarbonate (hydrolysis reaction):



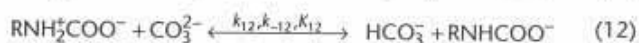
Dissociation of protonated MEA:



Bicarbonate formation:



Since CO<sub>2</sub> loaded aqueous MEA solutions were used in the experimental work, the concentrations of bicarbonates and carbonates in the aqueous solutions may be significant. As such, the contributions of these species to the deprotonation of the zwitterion were investigated. As a result, additional reactions 11 and 12 became essential in describing the mechanism:



Based on this, the general rate of reaction of CO<sub>2</sub> with MEA via the zwitterion mechanism could be described as in Equation (13) (Versteeg et al., 1996):

$$r_{4,zwit} = \frac{[CO_2][RNH_2] - \frac{k_{-1}}{k} [RNHCOO^-] \frac{\sum k_b [BH^+]}{\sum k_b [B]}}{\frac{1}{k} + \frac{k_{-1}}{k \sum k_b [B]}} \quad (13)$$

When CO<sub>2</sub> reacts with aqueous MEA, the formation of zwitterion has been shown to be the rate-determining step (Versteeg et al, 1996) whereas zwitterion deprotonation is considered to be relatively fast in comparison to the reversion rate to CO<sub>2</sub> and MEA. This means:

$$\frac{k_{-1}}{k \sum k_b [B]} \ll \frac{1}{k} \quad (14)$$

In this case, the above general rate expression, Equation (13), reduces to Equation (15), where the reaction rate is first-order in both the MEA and the CO<sub>2</sub> concentrations (Versteeg et al. 1996):

$$r_{4,zwit} = k_L (CO_2) (RNH_2) = k_{app} (CO_2) \quad (15)$$

Equation (15) is a situation that can occur if a large excess of RNH<sub>2</sub> is used in the experiment and is constant throughout the liquid phase.

### Model Equations

In general, the absorption of a gas into liquid with constant diffusivity and density is governed by Equation (16) (Astarita, 1967). This implies that molecular transport is equal to the sum total of convection ( $u \cdot \nabla C$ ), accumulation ( $\partial C / \partial t$ ), and reaction rate ( $r$ ), noting that if the diffusant is being created by the reaction,  $r$  will be negative in this equation.

$$D \nabla^2 C = u \cdot \nabla C + \frac{\partial C}{\partial t} + r \quad (16)$$

The assumption of constant diffusivity and density is valid in the case of a laminar jet absorber because the change of concentration does not represent a substantial variation in the mole-fraction of the diffusant due to the short contact time.

Equation (16) can be simplified considerably when considering the hydrodynamic conditions of the laminar jet and by assuming the following: (a) Penetration theory is applicable for the transport of gas into liquid, in which absorption takes place by unsteady molecular diffusion in the liquid; (b) the penetration depth of the absorbed molecules is much smaller than the jet diameter, because of the short contact time between gas and liquid-jet (Scriven and Pigford, 1959). As a result, the curvature effects of the cylindrical liquid-jet can be neglected, and the gas absorbing liquid can be regarded as an infinitely deep liquid with a flat surface; (c) the diffusion in the axial direction (i.e. the direction of flow) is negligible; (d) the liquid is quiescent (Danckwerts, 1970) so that no convection movements affect the transport of the dissolved gas. Under all these conditions, Equation (16) simplifies to the diffusion equation in Equation (17), which governs the variation in time and space of the concentration of the reactants and the products in the liquid phase (one equation for each component or material balance).

This equation is the one most frequently used to represent the absorption of gas into liquid jets.

$$D \frac{\partial^2 C}{\partial x^2} = \frac{\partial C}{\partial t} + r \quad (17)$$

The chemical species in reactions 1 to 12 have been renamed for convenience in the numerical treatment as follows: C<sub>1</sub> = [CO<sub>2</sub>], C<sub>2</sub> = [RNH<sub>2</sub>], C<sub>3</sub> = [RNH<sub>3</sub><sup>+</sup>], C<sub>4</sub> = [HCO<sub>3</sub><sup>-</sup>], C<sub>5</sub> = [OH<sup>-</sup>], C<sub>6</sub> = [CO<sub>3</sub><sup>-</sup>], C<sub>7</sub> = [H<sub>3</sub>O<sup>+</sup>], C<sub>8</sub> = [RNHCOO<sup>-</sup>], and C<sub>9</sub> = [H<sub>2</sub>O].

Equations (18) to (22) (based on Equation 17) represent the diffusion of the gas accompanied with reaction into the liquid near the interface:

CO<sub>2</sub> reaction balance:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} + r_2 + r_{4,zwit} + r_{10} \quad (18)$$

The total CO<sub>2</sub> balance:

$$\frac{\partial C_1}{\partial t} + \frac{\partial C_4}{\partial t} + \frac{\partial C_6}{\partial t} + \frac{\partial C_8}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} + D_4 \frac{\partial^2 C_4}{\partial x^2} + D_6 \frac{\partial^2 C_6}{\partial x^2} + D_8 \frac{\partial^2 C_8}{\partial x^2} \quad (19)$$

Total MEA balance:

$$\frac{\partial C_2}{\partial t} + \frac{\partial C_3}{\partial t} + \frac{\partial C_8}{\partial t} = D_2 \frac{\partial^2 C_2}{\partial x^2} + D_3 \frac{\partial^2 C_3}{\partial x^2} + D_8 \frac{\partial^2 C_8}{\partial x^2} \quad (20)$$

Charge balance:

$$\frac{\partial C_3}{\partial t} + \frac{\partial C_7}{\partial t} - \frac{\partial C_4}{\partial t} - \frac{\partial C_5}{\partial t} - 2 \frac{\partial C_6}{\partial t} - \frac{\partial C_8}{\partial t} = 0 \quad (21)$$

Carbamate balance:

$$\frac{\partial C_8}{\partial t} = D_8 \frac{\partial^2 C_8}{\partial x^2} + r_8 - r_{4,zwit} \quad (22)$$

Equilibrium instantaneous reactions:

In order to eliminate the likelihood of using very large reaction rates for the instantaneous reactions (reactions 1, 3, and 9) from the model equations, their equilibrium constant expressions were used to complete the model equations for concentration profile calculations. These equilibrium constant expressions are given below in Equations (23) to (25).

$$K_1 = C_5 C_7 \quad (23)$$

$$K_3 = \frac{C_6 C_7}{C_4} \quad (24)$$

$$K_9 = \frac{C_2 C_7}{C_3} \quad (25)$$

The above eight equations (Equations 18 to 25) were solved for the concentration profiles of the eight chemical species, C<sub>1</sub>, C<sub>2</sub>,

...,  $C_g$ , subject to the initial and boundary conditions given in Equations (26) to (29).

Initial conditions:

for all chemical species,  $j = 1, 2, \dots, 8$ .

$$C_j(x, 0) = C_j^0 \quad \text{at } t = 0 \text{ and } 0 \leq x \leq \infty \quad (26)$$

Boundary conditions:

for all chemical species,  $j = 1, 2, \dots, 8$ .

$$C_j(\infty, t) = C_j^0 \quad \text{at } x = \infty \text{ and } 0 \leq t \leq \tau \quad (27)$$

for all volatile chemical species,  $j = 1$ .

$$C_j(0, t) = C_j^* = \frac{P_j}{H_{e_j}} \quad \text{at } x = 0 \text{ and } 0 \leq t \leq \tau \quad (28)$$

for all non-volatile chemical species,  $j = 2, 3, \dots, 8$ .

$$\frac{dC_j}{dx}(0, t) = 0 \quad \text{at } x = 0 \text{ and } 0 \leq t \leq \tau \quad (29)$$

It should be noted that in the numerical procedure involving non-volatile chemical species, Equation (29) is only used in combination with the diffusion/reaction partial differential Equations (18) to (22) in order to calculate the concentration of 5 of the chemical species. Then, Equation (23), (24) and (25) (the equilibrium and nonlinear algebraic equations) are subsequently used to calculate the three remaining species.

Using the obtained concentration profile data of the absorbed gas,  $C_1$ , the local absorption rate per unit area was calculated using Equation 30.

$$N = -D_1 \left( \frac{\partial C_1}{\partial x} \right)_{x=0} \quad (30)$$

The term  $\left( \frac{\partial C_1}{\partial x} \right)_{x=0}$  is the concentration gradient at the surface and it is a function of time. The average absorption rate per unit area of solute gas by the liquid jet of length  $h$  is obtained by integrating Equation (30) over the contact time as shown in Equation (31) (Astarita, 1967; Danckwerts, 1970).

$$N_{ave} = -\frac{D_1}{\tau} \int_0^\tau \left( \frac{\partial C_1}{\partial x} \right)_{x=0} dt \quad (31)$$

When the dissolved gas reacts with the liquid, it is often convenient to present the effect of a chemical reaction in terms of the enhancement factor,  $E$ , defined as the ratio of the absorption rate of a gas into a reacting liquid to that if there was no reaction, as given in Equation (32).

$$E = \frac{N_{ave}}{k_L^0 (C^* - C^0)} \quad (32)$$

$N_{ave}$  was obtained from Equation (31) whereas  $k_L^0$  was evaluated from  $k_L^0 = 4/d\tau\sqrt{DL/h}$ , an expression that is valid in the case of laminar jet absorber (Danckwerts, 1970; Astarita et al., 1983).

Numerical calculation of the kinetics of the reaction is usually achieved by interpreting experimental-absorption data with the aid of a numerically solved absorption-rate model such as the one presented above. For each absorption rate experiment, the predicted enhancement factor ( $E_{pred}$ ) is fitted to the experimentally observed enhancement factor ( $E_{exp}$ ), with the apparent reaction-rate constant ( $k_{app}$ ) as an adjustable parameter. In this work, the root finding algorithm of Muller's method (entitled ZREAL) as documented in the IMSL MATH/Library (Visual Numerics Inc., 1994) was used to find the zero of the real function:

$$f(k_{app}) = E_{exp} - E_{pred} \quad (33)$$

Then the experimental apparent reaction-rate constants ( $k_{app}$ ) obtained at one temperature but at different operating conditions (concentration, loading, and contact time) were fitted to the reaction rate expression in Equation (34) in order to obtain the reaction-order with respect to MEA as well as the intrinsic reaction-rate constant at that temperature:

$$k_{app} = k(\text{MEA})^n \quad (34)$$

## Numerical Implementation

The partial differential equation for unsteady molecular diffusion, Equation (17), can be solved explicitly or implicitly by a number of finite-difference methods, such as the simple explicit method, the simple implicit method, the Barakat-Clark method (Barakat and Clark, 1966), and the DuFort-Frankel method (DuFort and Frankel, 1953). After examining the relative accuracy of these methods in solving a convective-diffusive equation when the time step ( $\nabla t$ ) and the grid interval ( $\nabla x$ ) are reduced gradually (Aboudheir et al., 1999), Barakat-Clark method was selected because it is unconditionally stable, provides an accurate solution, and takes less CPU time than the Implicit method.

Accordingly, Equations (18) to (22), were discretized according to the Barakat-Clark scheme by replacing the second derivative of  $C$  with two intermediate-concentration values  $UC$  and  $VC$  according to Equations (35) and (36) respectively.

$$\frac{\partial^2 UC}{\partial x^2} = \frac{UC_{i+1}^n - UC_i^n - UC_i^{n+1} + UC_{i-1}^{n+1}}{\Delta x^2} \quad (35)$$

$$\frac{\partial^2 VC}{\partial x^2} = \frac{VC_{i+1}^{n+1} - VC_i^{n+1} - VC_i^n + VC_{i-1}^n}{\Delta x^2} \quad (36)$$

Similarly, the time derivative of  $C$  was replaced with the forward discretization in two intermediate-concentration values as given in Equations (37) and (38).

$$\frac{\partial UC}{\partial t} = \frac{UC_i^{n+1} - UC_i^n}{\Delta t} \quad (37)$$

$$\frac{\partial VC}{\partial t} = \frac{VC_i^{n+1} - VC_i^n}{\Delta t} \quad (38)$$

This discretization technique was applied, similar terms were collected, and the equations for the explicit calculation of  $UC_i^{n+1}$  and  $VC_i^{n+1}$  were rearranged for each chemical species. Subsequently, the concentration at any time level  $(n + 1)$  was obtained as the arithmetic average of  $UC_i$  and  $VC_i$ . That is  $C_i^{n+1} = (UC_i^{n+1} + VC_i^{n+1}) / 2$ .

After obtaining the variation, of the concentration of the dissolved gas in the liquid in time and space by the above procedure, the slope at the interface  $(\partial C_1 / \partial x)_{x=0}$  in Equation (31) was calculated by the forward finite-difference approximation (Equation 39) at each time level.

$$\frac{\partial C_1}{\partial x} = \frac{-(C_1)_{i+2}^n + 4(C_1)_{i+1}^n - 3(C_1)_i^n}{2\Delta x} \quad (39)$$

Then at  $x = 0$ , which means  $i = 1$ , for each time level  $n$ , Equation (39) gives the value of the slope as given in Equation (40).

$$\text{Slope} = \left. \frac{\partial C_1}{\partial x} \right|_{x=0} = \frac{-(C_1)_3^n + 4(C_1)_2^n - 3(C_1)_1^n}{2\Delta x} \quad (40)$$

The integration in Equation (31) was evaluated by using the trapezoidal integration method over the contact time  $\tau$ , from which the absorption rate per unit area was predicted according to Equation (31). This predicted chemical absorption rate ( $N_{ave}$ ) was the one used to calculate the predicted enhancement factor ( $E$  given in Equation 32) obtained as the ratio of the chemical absorption rate to the value of the rate by purely physical absorption  $[k_1^0(C_1^* - C_1^0)]$ , all evaluated under similar hydrodynamic conditions.

In the case of kinetics calculations, the predicted enhancement factor is calculated as above but with the apparent reaction-rate constant as an adjustable parameter. Subsequently, the reaction term between  $\text{CO}_2$  and MEA in the model was changed to  $r_{4,zwit} = k_{app}(C_1)^n$ . In this case  $k_{app}$  is the output of the program from which the reaction order and reaction rate constants were calculated (Equation 34).

A computer program was developed to simulate absorption rates and enhancement factors from known kinetics and operating conditions as well as to predict the kinetics of the reaction by interpreting absorption-experimental data. For simulating the behaviour of the absorption process (in terms of concentration profiles, absorption rate, and/or enhancement factors from known kinetics), the numerical model required all the operating conditions and physico-chemical properties of the system. On the other hand, for obtaining kinetic parameters (such as orders of reactions and/or reaction-rate constants),  $k_{app}$  was used as an adjustable parameter in the absorption rate model to obtain the best fit for the experimental absorption data. Usually the apparent reaction-rate constants are found by using this technique at different operating conditions but at a given temperature. In order to get the individual reaction rate constants and reaction order, the reaction mechanism expression was fitted to the experimental apparent reaction-rate data using optimization or data fitting techniques. The detailed procedure, flowcharts, and the Fortran-90 computer code for this absorption-rate/Kinetics model are documented elsewhere (Aboudheir, 2002).

## Model Parameters

The calculation of the concentration profiles using the numerical model presented in this work requires knowledge of the physico-chemical properties of the fluids involved in the absorption process. These include density, viscosity, solubility, diffusivity, reaction rate constants, equilibrium constants, and bulk concentrations of all chemical species present in the system.

The density and viscosity of aqueous MEA solution were calculated according to the correlations developed by Weiland et al. (1998). The  $\text{N}_2\text{O}$  analogy was used to determine the solubility and diffusivity of  $\text{CO}_2$  in amine solutions. The solubility of  $\text{N}_2\text{O}$  in amine solutions was calculated from a semi-empirical model of the excess Henry's constant proposed by Wang et al. (1992). The enhanced parameters for this semi-empirical model by Tsai et al. (2000) were adapted in this work. The diffusivity of  $\text{N}_2\text{O}$  in MEA was calculated from the simple correlation developed by Ko et al. (2001). On the other hand, the diffusivity of MEA in the aqueous MEA solutions was calculated from the correlation developed by Snijder et al. (1993).

The forward rate coefficients of  $\text{CO}_2$  reaction with water and hydroxide ( $k_2$  and  $k_{10}$ ) were calculated from the correlations reported by Pinsent et al. (1956). When using the model for simulation, the reaction-rate constant for the carbamate formation  $k$  (equivalent to the sum of reactions 4, 5, and 9) was calculated by the correlation developed by Versteeg et al. (1996). This reaction rate constant is applicable because it was developed from kinetic experimental data presented in the literature up to 1992 (believed to be the most accurate reaction rate constant available in the literature). The equilibrium constants for the chemical reactions (as used in the mass transfer model and the vapour-liquid equilibrium model) are available in the literature. The equilibrium constants  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_{10}$  ( $K_{10} = K_2/K_1$ ) were obtained from the correlations reported by Edwards et al. (1978). The equilibrium constants  $K_8$  and  $K_9$  were calculated from the simple correlations developed by Kent and Eisenberg (1976). The equilibrium constant of the carbamate formation reaction  $K$  (sum of reactions 4, 5, and 9) was calculated by the correlation developed by Barth et al. (1986). Each physical and chemical property was programmed in a Fortran-90 subroutine within a computer module, where it could be called up and utilized as required.

A vapour-liquid equilibrium (VLE) model to estimate the  $\text{CO}_2$  partial pressure and the liquid bulk concentrations of all of the chemical species was developed based on the reactions discussed above. The input data of the model included the initial concentration of the MEA solution, the initial  $\text{CO}_2$  loading of the MEA solution, the equilibrium constants of the reactions, and the solubility of  $\text{CO}_2$  into MEA solution. It was assumed that all of the chemical reactions were at equilibrium whereas the concentration of water was assumed to remain constant because its concentration was much larger than the concentration of all other chemical species and also because of the short contact time in the laminar jet absorber. The concentrations for the remaining eight chemical species shown in the above chemical reactions were calculated by solving the mass balance equations and the Henry's law correlation, all of which are represented by nonlinear algebraic equations. Again, details of this VLE model including the computer program written in Fortran-90 are documented elsewhere (Aboudheir, 2002).

## Experimental Work

A laminar jet apparatus was designed, tested and used to generate the experimental data required to validate the absorption-rate/kinetics model. The apparatus combined various features of

the designs of Danckwerts (1970) Astarita et al. (1983), and Al-Ghawas et al. (1989). The main materials used in measuring the rate of gas absorption in laminar jet absorber were CO<sub>2</sub> with a purity of 99.9%, N<sub>2</sub>O with a purity of 99.5%, and MEA with a purity of 99.0%. The experimental kinetics data were obtained by absorption of CO<sub>2</sub> into aqueous MEA solutions. The free MEA concentrations were in the range from 0.193 to 3.158 mol/L with an average CO<sub>2</sub> loading of 1.81 mol/L. All the kinetics experiments were conducted at atmospheric pressure at temperatures in the range from 293 to 313K. Details of this experimental work are documented elsewhere (Aboudheir et al., 2003; Aboudheir 2002).

## Results and Discussion

Before obtaining the kinetics of CO<sub>2</sub> reaction with aqueous MEA solution, the numerical scheme chosen for solving the partial differential equations was validated by predicting the behaviour of two physical absorption systems, CO<sub>2</sub>-Water and N<sub>2</sub>O-MEA systems. In the absence of reaction, Equation 17 reduces to the form:  $D_1 \partial^2 C_1 / \partial x^2 = \partial C_1 / \partial t$ . The initial and boundary conditions required to solve this equation for the case of CO<sub>2</sub> absorption into water or N<sub>2</sub>O absorption into amines are:  $C_1(x, 0) = C_1^0$  for  $t = 0$  and  $0 \leq x \leq \infty$ ;  $C_1(0, t) = C_1^*$  for  $x = 0$  and  $t \leq 0$ ; and  $C_1(\infty, t) = C_1^0$  for  $x = \infty$  and  $t \leq 0$ . The numerical solution of this equation produces the concentration distribution of the gas in the liquid-jet, from which the absorption rate was calculated numerically by Equation (31). Figure 1 shows the concentration profiles for N<sub>2</sub>O absorption into an MEA-jet at 298 K at various contact times. As seen in Figure 1, the penetration depth of the diffused N<sub>2</sub>O into MEA solution did not exceed 0.0015 cm for the contact time of about 0.005 s, which is a typical contact-time for the liquid jet absorber apparatus. This penetration depth amounted to only 3% of the MEA-jet diameter measured in the experimental work (the jet-diameter is approximately 0.05 cm). A similar behaviour was obtained for CO<sub>2</sub> absorption in water amplifying the fact that both cases are situations that arise due to physical absorption.

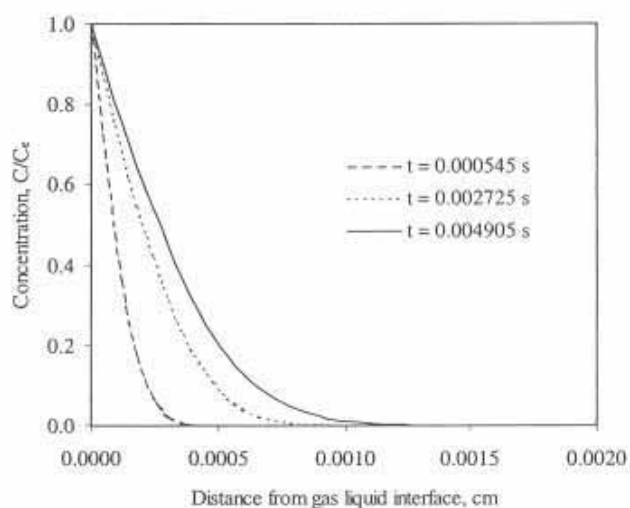


Figure 1. Concentration profiles of N<sub>2</sub>O absorption into 1 mol/L MEA-jet at 298K and at various contact times.

The measured absorption rates within the temperature range from 288 to 333 K and the predicted absorption rates calculated from the numerical model were compared in the parity plot shown in Figure 2. This shows an excellent agreement between the measured and predicted absorption rates for CO<sub>2</sub> absorption into water-jets. The average absolute deviation of the measured rates from the predicted rates is 3.5%. Similar excellent results were obtained for the N<sub>2</sub>O absorption into MEA-jet at 298K with an average absolute deviation of 4.6%. These results confirm that the formulated model to predict the absorption rate in laminar jet absorber as well as the numerical scheme implemented to solve it are effective and accurate.

The chemical absorption rate model developed in this work was also utilized to calculate concentration profiles. Figure 3 shows the concentration profiles of all chemical species in a liquid-jet at the end of the contact time when CO<sub>2</sub> was absorbed into a loaded MEA solution at 313K. This figure confirms two points: (1) the penetration depth of the diffused CO<sub>2</sub> gas into the liquid did not exceed 0.0008 cm for the contact time of about 0.01 s. This penetration depth amounted to less than 1.5% of the liquid-jet diameter. As a result, the liquid-jet can be regarded as infinitely deep liquid and the curvature effects of the cylindrical liquid-jet can be neglected; (2) the concentration profile of MEA clearly shows a significant depletion of free MEA towards the gas-liquid interface. This indicates that the assumption of pseudo first-order reaction to drive the simplified kinetics models is not accurate because the concentration of the reactive species, [MEA], is not in a large excess and is not constant throughout the liquid phase. This highlights the importance of applying a numerical model to obtain reaction kinetics from absorption experimental data.

The reaction between CO<sub>2</sub> and MEA solutions was investigated further in the laminar jet absorber within the temperature range of 293-313K by applying the absorption-rate/kinetics model developed in this work. It is well known that the accuracy of the deduced kinetic data decreases with increasing depletion of free

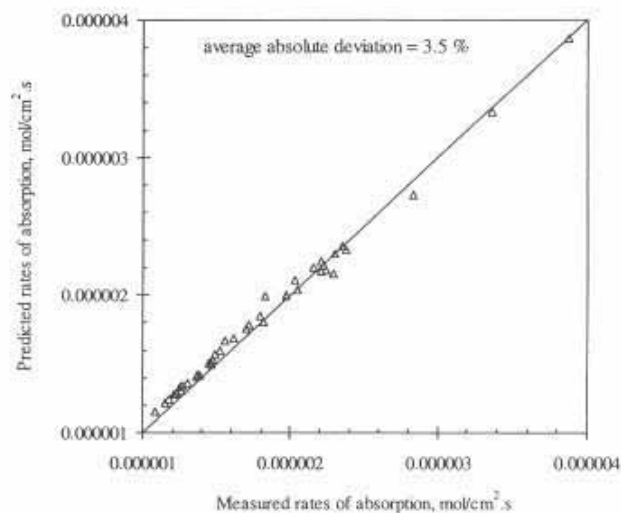


Figure 2. Comparison of measured and predicted CO<sub>2</sub> absorption rates into water within the temperature range from 288 to 333K in the laminar jet absorber.

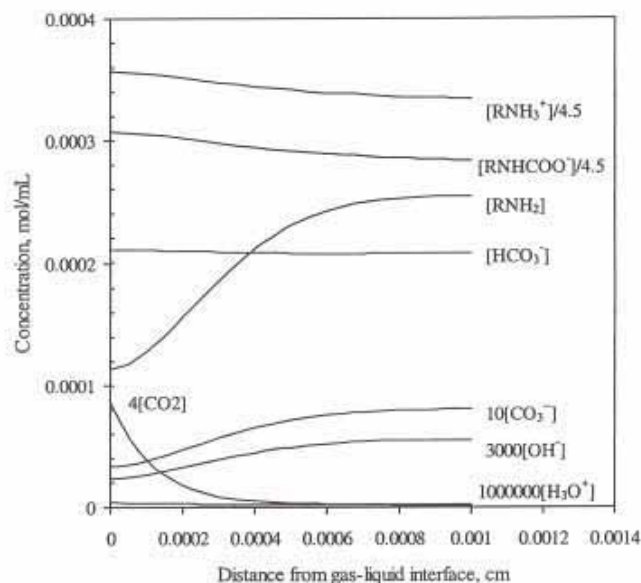


Figure 3. Concentration profiles of all species in liquid film near the interface at the end of contact time. Total [MEA] = 3.04 mol/L, loading = 0.493 mol/mol, free [MEA] = 0.254 mol/L,  $P_{CO_2}$  = 87.87 kPa, contact time = 0.0097 s, and  $T = 313$  K.

amine towards the gas-liquid interface (see Figure 3), because the absorption flux is increasingly determined by diffusion (Littel et al, 1992). Therefore, in order to minimize the effect of the diffusion limitation, loaded MEA solutions were used to generate experimental kinetics data. This resulted in the difference between bulk and interfacial concentrations of free amine being kept as low as possible during the experiment. For each absorption rate data obtained experimentally, the calculated enhancement factor (calculated numerically by Equation 32) was fitted to the experimentally observed enhancement factor with the apparent reaction-rate constant,  $k_{app}$  as an adjustable parameter. The experimental results of these apparent reaction-rate constants are presented in Figure 4. A definite temperature dependence of the overall reaction rate can be observed for the three temperatures studied (293, 303, and 313K). The data presented in Figure 4 were regressed in order to obtain the orders of reaction and the reaction rate constant at each temperature. The results are given in Table 1. The obtained order of reaction is approximately one. Since the order of one with respect to  $CO_2$  was assumed in the derivation of the kinetic equation (Equation 15, ), this result shows that the order for MEA is indeed one and that a second order overall is valid within this temperature range and MEA concentrations. This is in agreement with the reported data in the literature (Versteeg et al., 1996).

An Arrhenius plot was obtained using the second-order rate constants presented in Table 1. The results are shown in Figure 5. Also included in this figure are three published predictions representing three kinetic-models. The first model,  $k = 9.77 \times 10^{10} \exp(-4955/T)$ , was developed by Hikita et al. (1977) and it is the most frequently referenced model in the literature. The second model,  $k = 4.4 \times 10^{11} \exp(-5400/T)$ , was developed by

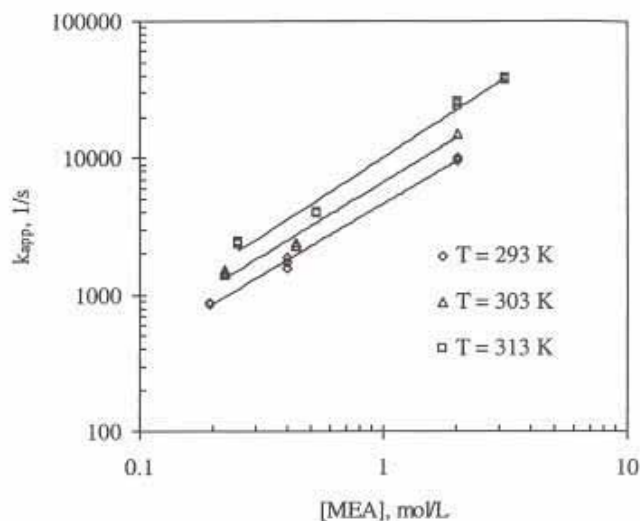


Figure 4. Experimental results of the apparent reaction-rate constants for  $CO_2$  reaction with aqueous MEA solutions.

Table 1. Apparent reaction order and second-order rate constant for  $CO_2$  absorption into MEA solutions, when assuming  $r = k_{app} [CO_2]$  and  $k_{app} = k [MEA]^2$

T (K)	[MEA] (mol/L)	Ave $[CO_2]_{tot}$ (mol/L)	z (reaction order)	k (L/mol.s)
293	0.193 - 2.016	~ 1.81	1.04	4615
303	0.223 - 2.021	~ 1.81	1.08	6674
313	0.254 - 3.158	~ 1.83	1.16	10119

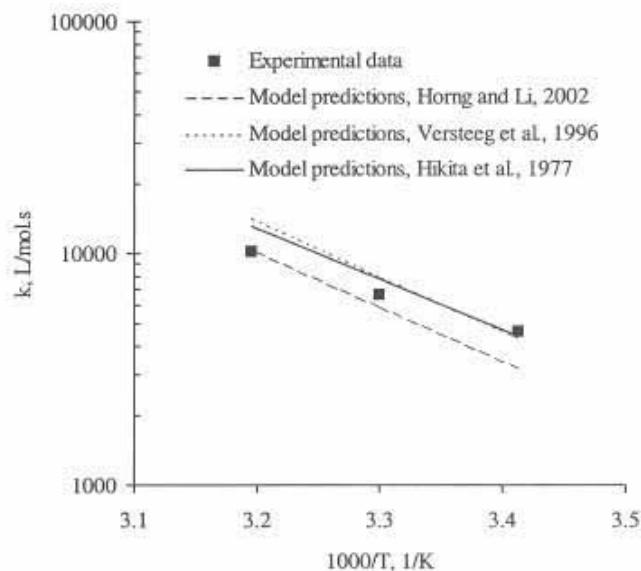


Figure 5. Arrhenius plot for the reaction between  $CO_2$  and aqueous MEA solutions.

Versteeg et al. (1996) based on the kinetic data presented in the literature up to year 1992. The third model,  $k = 3.014 \times 10^{11} \exp(-5376.2/T)$ , was developed by Horng and Li (2002). This model is the most recently published model in the literature. Figure 5 shows that the reaction rate constants obtained in this work are in agreement with the kinetic data reported in the literature. Thus, the overall results confirm that the absorption rate/enhancement factor data obtained in the laminar jet apparatus are accurate. As well, the absorption-rate/kinetics model developed in this work and the numerical techniques implemented to solve its equations are accurate and efficient. However, a close examination of Figure 5 shows that the activation energies obtained from the three published models are more or less the same but different from the experimental data obtained in the present work. A change in activation energy implies a change in the rate controlling mechanism. This can be attributed to the fact that although the concentrations of free MEA used in the four studies were similar, the actual MEA concentrations used in the present work were much higher so as to compensate for using pre CO<sub>2</sub> loaded MEA solutions in our studies. The higher actual MEA concentrations together with presence of pre-loaded CO<sub>2</sub> is responsible for the change in the controlling mechanism, and hence the difference in activation energies.

## Conclusion

A rigorous absorption-rate/kinetics model for the absorption of CO<sub>2</sub> with chemical reaction has been developed. This model takes into account the coupling between chemical equilibrium, mass transfer, and chemical kinetics of all possible chemical reactions. The mathematical model is capable of predicting gas absorption rates and enhancement factors from the system hydrodynamics and the physico-chemical properties as well as predicting the kinetics of reaction from experimental absorption data. A numerical method to solve the system of unsteady-state partial-differential equations has also been developed. Unlike the previous literature, all the model equations (partial differential equations and nonlinear algebraic equations) were solved simultaneously without introducing any simplifications or linearization. In addition, the Barakat-Clark scheme (Barakat and Clark, 1966) for solving the model equations has been introduced and applied successfully for the first time in the chemical reaction-engineering field. This explicit finite difference scheme was found to be very suitable because it is unconditionally stable and gives accurate predictions for the concentration profiles and the absorption rates of gas into liquid. Finally, the absorption-rate/kinetics model has proven to extract accurate kinetics from experimental absorption data as well as give accurate predictions for the behaviour of three absorption systems; namely, CO<sub>2</sub>-Water, N<sub>2</sub>O-MEA, and CO<sub>2</sub>-MEA.

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## Nomenclature

$C_j$	concentration of component $j$ in the liquid, (mol/L)
$D_j$ or $D$	diffusivity of component $j$ , (cm <sup>2</sup> /s)
$E$	enhancement factor
$h$	jet length, (cm)
$He$	Henry's law constant, (kPa-L/mol)
$[j]$	concentration of component $j$ , (mol/L)
$k$	second order reaction-rate constant, (L/mol-s)
$k_{app}$	apparent pseudo-first-order reaction-rate constant, (1/s)
$k_b$	second order reaction-rate constant for base B, (L/mol-s)
$k_f$ or $k_j$	first or second order reaction-rate constant, 1/s or (L/mol-s)
$K_j$ or $K_i$	equilibrium constant of component $j$ or reaction number $i$
$k_L^0$	physical mass transfer coefficient, (cm/s)
$L$	liquid flow rate, (mL/s)
$N$	mass transfer flux of $j$ , (mol/s.cm <sup>2</sup> ) interfacial area
$P_j$	partial pressure of $j$ , (kPa)
$r_j$ or $r$	reaction rate of component $j$ , (mol/L-s)
$t$	time, (s)
$T$	temperature, (K)
$u$	velocity, (cm/s)
$UC$	intermediate concentration value in the numerical treatment, (mol/L)
$VC$	intermediate concentration value in the numerical treatment, (mol/L)
$x$	spatial variables measured from the interface into the liquid bulk, (cm)

## Greek Symbols

$\Delta t$	time increment, s $O(\Delta x^2)$
$\Delta x$	space increment, cm
$O(\Delta x^2)$	the remainder in Taylor series expansion and of the order $(\Delta x^2)$
$\tau$	contact time, (s)
$\pi$	constant = 3.1416

## Subscripts

0	initial condition
<i>app</i>	apparent
<i>ave</i>	average condition
<i>exp</i>	experimental
<i>i</i>	interface or designated number or lattice parameter in one-dimensional grid
<i>j</i>	generalized component $j$ or designated number
<i>pred</i>	predicted
<i>zwit</i>	zwitterion reaction mechanism

## Superscript

*	property at the gas-liquid interface, interfacial condition
0	bulk condition
<i>n</i>	denote the time level $t$
<i>z</i>	order of reaction

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