Determination of the mechanism of the reaction between CO2 and alkanolamines.

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I declare that this is an independent work according to the exam regulations of the Norwegian University of Science and Technology (NTNU)

Date and signature: ..............................................
Dedicated to

My Parents for their endless prayers
My uncle and aunt for their moral support
&
My institute NFC institute of Engineering &
Technological training, Multan
ABSTRACT

Emission control of greenhouse gases especially CO₂ has become an environmental challenge. CO₂ capture by absorption in amine is so far the only CCS technique that has been industrially acknowledged. Chemical absorption of CO₂ in amine solution is a complex process and needs investigation for better understanding.

An experimental study has been conducted to understand the kinetics of CO₂ absorption in non-aqueous DEA solution at 293K in a stirred cell reactor with a smooth and flat gas liquid interface. Experiments were repeated to ensure the reproducibility of data and the results were compared with literature to ensure the validity of this work. Physio-chemical properties of all chemicals like density, diffusivity and viscosity were taken from literature whereas solubility data was generated by experimentation. Solubility data was also validated by comparison with literature.

Experimental data for reaction kinetics was treated with both zwitterion and termolecular mechanism. Based on the findings from this work, the order of reaction is 1.78 with respect to amine. Furthermore, Parity plot between calculated and experimental CO₂ fluxes have been generated to elaborate the argument and it could be concluded that for non-aqueous system both studied mechanisms shows less than 10% deviation and hence can give satisfactory results. It is recommended to continue this work at different temperatures for better understanding.
ACKNOWLEDGEMENT

“All praise goes to Almighty Allah, Who is the creator of this universe”

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Muhammad Awais
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<thead>
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<tbody>
<tr>
<td>C</td>
<td>Concentration ((mol/L))</td>
</tr>
<tr>
<td>D</td>
<td>Diffusivity ((m^2/s))</td>
</tr>
<tr>
<td>(Ha)</td>
<td>Hatta number</td>
</tr>
<tr>
<td>N</td>
<td>Flux ((mol/m^2s))</td>
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<tr>
<td>(M)</td>
<td>Molar concentration ((mol/L))</td>
</tr>
<tr>
<td>V</td>
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<tr>
<td>P</td>
<td>Total pressure ((Pa))</td>
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<tr>
<td>(E_{A\infty})</td>
<td>Infinite enhancement factor</td>
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<tr>
<td>(\mu)</td>
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<td>E</td>
<td>Activation energy</td>
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<tr>
<td>(E_A)</td>
<td>Enhancement factor</td>
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<td>Enhancement factor for penetration theory</td>
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<tr>
<td>(k_B)</td>
<td>Rate constant of base</td>
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<tr>
<td>(K_G)</td>
<td>Mass transfer coefficient</td>
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<td>(K_l)</td>
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<td>(k_{obs})</td>
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<tr>
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<td>Flux of CO(_2)</td>
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<tr>
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<tr>
<td>(Re)</td>
<td>Reynold number</td>
</tr>
<tr>
<td>t</td>
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</tr>
<tr>
<td>m</td>
<td>mass of solvent</td>
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### Greek Letters

<table>
<thead>
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<th>Symbol</th>
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<tbody>
<tr>
<td>(\alpha)</td>
<td>Loading ((mol.mol^{-1}))</td>
</tr>
<tr>
<td>(\mu)</td>
<td>Viscosity ((Pa \times s))</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Density</td>
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Subscripts

$Ab$ Absorbed
$Am$ Amine
$B$ Bulk
$calc$ Calculated
$exp$ Experimental
$g$ Gas phase
$i$ Interface ; Species $i$
$k$ Species $k$
$l$ Liquid phase
$obs$ Observed
$\pm$ Mean

Superscripts

$Am$ Amine
$E$ Excess
$In$ Inlet
$out$ Outlet
$T$ Termolecular mechanism; Total
$Z$ Zwitterion mechanism
$o$ Initial condition

Abbreviations

B Base
CO$_2$ Carbon Dioxide
DEA Diethanolamine
L Liter
M Molarity
H$_2$O Water
H$_2$SO$_4$ Sulfuric acid
N$_2$ Nitrogen
N$_2$O Nitrous oxide
1 INTRODUCTION

1.1 BACKGROUND

Climate change is one of the major challenges of 21st century. Greenhouse gases (GHS) i.e. carbon dioxide (CO$_2$), methane (CH$_4$), and nitrous oxide (N$_2$O), per fluorocarbons PFCs, hydro fluorocarbons (HFCs) and sulphur hexafluoride (SF$_6$) in addition to ozone-depleting substances (ODS, chlorofluorocarbons (CFCs), hydro chlorofluorocarbons (HCFCs) are considered to be responsible for global warming and climate change. Out of these greenhouse gases Carbon dioxide contributes about 76.7%, methane about 14.3%, nitrous oxide about 7.8% and rest by F-gases to the greenhouse effect [1]. Over the last three decades GHG emissions have increased by an average of 1.6% per year with carbon dioxide (CO$_2$) emissions from the use of fossil fuels growing at a rate of 1.9% per year [1]. Mostly CO$_2$ emission is produced from the fossil fuel use (74%) while 22.6% from the feedstock emission and the rest from the cement industry and natural gas flaring. Fossil fuel comprises 80% of total world energy demand [2]. With increase in CO$_2$ emissions, the CO$_2$ concentration in atmospheric has reached 379 ppm in 2005. This is about 100 ppm higher compared to the pre-industrial level [1]. Increase in greenhouse gas contributes to raise global mean temperature and global average sea level and to lessen the Northern hemisphere snow cover [3]. These trends underline the demand to develop technologies to reduce CO$_2$ emission associated with the use of fossil fuels. Carbon dioxide Capture and Storage (CCS) offers this opportunity to reduce CO$_2$ emission.
1.2 Carbon Capture and Storage (CCS)

CCS is defined as a system of technologies that integrates CO$_2$ capture, transportation and geological storage. Each stage of CCS is in principle technically available and has been used commercially for many years [4]. To capture CO$_2$, different technologies are being used by the industry from gas streams, where it could be an undesirable contaminant or is needed to be separated as a product gas. There are three primary methods for CO$_2$ capture; pre-combustion capture, post-combustion capture and oxy-fuel processes. Post-combustion capture involves scrubbing of CO$_2$ from flue gas of a combustion process. Oxy fuel combustion refers to combustion of fuel in pure oxygen, thereby produce a CO$_2$-rich gas. In a pre-combustion process, gasification is followed by CO$_2$ separation prior to the use of produced hydrogen as a fuel gas. CO$_2$ transport is done for over 30 years in North America; over 30 metric tons of CO$_2$ from natural and anthropogenic sources are transported per year through 6200 km of CO$_2$ pipelines in the USA and Canada, mainly for enhanced oil recovery [5]. CO$_2$ is transported at high pressure through a network of pipeline. Ships, trucks and trains have also been used for CO$_2$ transportation in early CCS demonstration projects and in regions with inadequate storage.

CO$_2$ storage involves injection of supercritical CO$_2$ into a geologic formation. On geological timescales this CO$_2$ will partly be fixed in minerals by carbonation reactions. There are three common options for geological CO$_2$ storage; saline aquifers, oil and gas reservoirs, and deep unminable coal seams [4]. It is expected that saline aquifer formations provide the largest storage capacities for CO$_2$, followed by oil and gas reservoirs. A number of projects involving the injection of CO$_2$ into oil reservoirs have been conducted in the USA and Canada. Most of these projects use CO$_2$ for enhanced oil recovery.
1.3 CO₂ CAPTURE TECHNOLOGIES

There are four basic methods for CO₂ capture methods are from fossil fuels as shown in figure 1.1.

![CO₂ Capture Techniques Diagram]

*Figure 1.1 CO₂ Capture techniques [3]*

1.3.1 Pre-combustion capture

In pre-combustion carbon dioxide capture, CO₂ is separated from the fossil fuel (coal or natural gas) before combustion. In this process, fossil fuel is converted into synthesis gas, a mixture of CO and H₂. This synthesis gas is then sent to a water gas shift reactor where it reacts with steam to produce a mixture of CO₂ and H₂. CO₂ is then separated from the (high pressure) gas mixture and H₂ is send to the turbine to be combusted.
Separation of CO$_2$ from H$_2$ is less energy and cost effective than post combustion capture due to the higher concentration and partial pressure of CO$_2$. Development is ongoing in this technology to reduce the amount of steam for water gas shift reaction. Combining CO$_2$ sorption with water-gas shift activity is an alternative promising technology under development.

1.3.2 Post-combustion capture

Carbon dioxide post-combustion capture is one of the most mature capture technologies due to its reputation and implementation within many other industrial applications [7].

Separation of CO$_2$ from gas mixtures is a commercially applied technology which is in use at hundreds of locations around the world. There are many small facilities in operation today which use amine based solvents to capture significant flows of CO$_2$ from flue gas. The general chemical absorption process of CO$_2$ from flue gas is shown schematically in Figure 1.3.

In the absorber, the gas is contacted with a liquid phase amine, and the component to be absorbed normally called the solute, in which the CO$_2$ is transferred to the liquid phase. The liquid containing CO$_2$, the “rich” liquid, is sent to a desorber stage where the absorption equilibrium is reversed, normally by increasing the temperature or reducing the pressure, and the solute, CO$_2$ is released together with water vapor. The gas mixture is cooled and water is condensed out and returned to the desorber top as recycle. The CO$_2$ is then compressed where more water condensate and sent out for storage. Heat from the CO$_2$-lean solvent is then
transferred to the CO$_2$ rich solvent in a heat exchanger referred as a lean-rich heat exchanger.

![Figure 1.3 Basic flow diagram for CO$_2$ absorption from flue gas with chemical solvent [8]](image)

Post-combustion capture is a mature technology, though considerable R&D efforts are undertaken, as there is a need for new solvents which require less energy for regeneration, less corrosive, lower solvent loss rates via degradation and evaporation. Alternative means of capturing CO$_2$, such as Solid adsorption, membrane separations and chemical looping processes are also being studied which may be able to improve the overall efficiency of the process in near future.

### 1.3.3 Oxy fuel-combustion capture

In traditional power plants, fuel combustion is carried out using air, and the nitrogen (N$_2$) in the air ends up in the flue gas. However in oxy-fuel combustion process nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that mainly contains CO$_2$ and H$_2$O that can easily be separated by cooling. The water is condensed and after phase separation a gas stream rich with CO$_2$ is obtained. In this, Oxygen separation unit is the most expensive part which is
usually done by low temperature (cryogenic) air separation. Systematic flow diagram for oxy fuel combustion is shown in figure 1.4. Oxy-fuel processes have a further disadvantage that they are difficult to implement as a retrofit option for existing installations.

![Figure 1.4 Systematic flow diagram for oxy fuel combustion [6]](image)

### 1.4 Commercial Solvents for CO₂ Post Combustion Capture Process

The development of aqueous amine solutions as acid gas absorption liquid started with the work of R.R. Bottoms for which a patent was also granted in 1930 [9]. Triethanolamine (TEA) was the first alkanolamine to be used commercially in early gas-treating plants. Monoethanolamine (MEA), Diethanolamine (DEA), and Methyl-diethanolamine (MDEA) were also proved to be of principal commercial interest for gas purification [9]. Triethanolamine (TEA) was found to be less attractive mainly due to its low absorption capacity, lower reactivity and relatively poor stability. Diisopropanolamine (DIPA) [10] was used in the Adip process, in the Sulfinol process, as well as in the SCOT process for Claus plant tail gas purification but gradually replaced by Methyl-diethanolamine (MDEA). Although MDEA was described by Kohl and coworkers at Fluor Daniel as a selective absorbent for H₂S in the presence of CO₂ as early as 1950, its use
in industrial processes has only become important in recent years. [9] A different type of alkanolamine, 2-(2-aminoethoxy) ethanol, commercially known as Diglycolamine (DGA), was first proposed by Blob and Riesenfeld (1955). This compound couples the stability and reactivity of mono ethanolamine with the low vapor pressure of di-ethyleneglycol therefore, can be used in more concentrated solutions than mono ethanolamine first proposed by Blob and Riesenfeld (1955) [9].

Commercially available solvents are continuously being improved for better CO₂ absorption performance. The most important characteristics for a solvent are CO₂ loading (cyclic capacity), absorption rate, chemical binding energy, and absorption and desorption temperatures [11].

A low binding energy comes together with a low reactivity for CO₂ and similarly high absorption rate is usually accompanied by high binding energy. The absorption rate determines the dimensions of the absorber and the capital costs of absorber make up about 40% of the total costs of the amine-based CO₂ capture plant [12].

The cyclic loading of the solvent is the difference of CO₂ loading between lean and rich in terms of mole of CO₂ per kilogram of solvent. A high cyclic loading will result in lower solvent circulation flow rate in the amine plant, which will lower the dimensions of the solvent heat exchanger, reboiler, amine pumps, absorber, and piping. It will also decrease the electricity consumption of pumps and the energy required for solvent heating. In addition, a smaller absorber will lower the flue gas blower energy requirements and dimensions.

The absorption temperature determines the costs and the energy requirements of the flue gas coolers. By bringing the absorption temperature closer to desorption will decrease the costs of the solvent heat exchanger. For CO₂ capture in a power-plant setting, the desorption temperature determines the temperature of the steam that has to be extracted from the steam turbine. Bolland and Undrum (2003), showed that there is a strong dependency between the energy output of the steam cycle and the steam temperature [13]. For specific solvents, lowering desorption
temperature will mean a higher lean CO₂ loading and thus a smaller cyclic loading.

Higher solvent concentrations is not always possible, due to the corrosive nature of amine based solvents. The stability of the amine based solvent and the specific solvent costs are also important characteristics when it comes to the operational cost, influencing solvent make-up and replacement costs. Furthermore, evaporative losses, associated health risks and the impact on the environment are also becoming increasingly important. Formation of degradation products also play an essential role in the corrosion [14]. The corrosion mainly affects the stripper, reboiler and lean-rich heat exchangers. Reducing the degradation rate will result in lowering the Operational and the Capital of the critical parts in the CO₂ capture plant. Despite several studies on each aqueous amine based solvents in past, the above mentioned aspects are still not entirely met by the current commercial solvents for CO₂ absorption.

1.5 Motivation and Scope of This Work

The interest in the study of reaction between CO₂ and alkanolamine has been growing for past two decades. Several amine based solvents (Individual and mixed amine systems) for their enhancement for CO₂ capture have been proposed. Usually gas treating processes are operated with aqueous amine solutions but non aqueous solvents and their mixture with water are also used due to their lower energy requirements in regeneration. A detailed knowledge of the reaction kinetics between CO₂ and these solvents is needed in order to deepen fundamental understanding of the reaction, to describe the effect of chemical reaction on mass transfer rates and to represent the reaction rate as function of process variables (e.g. temperature, pressure and reactant concentration) [15]. Such information is useful for reactor designing and performance prediction.

Primary and secondary alkanolamine react with CO₂ to form carbamate. MEA and DEA are extensively studied amines and kinetic behavior of large number of
such amines in aqueous and non-aqueous amines is well established. For MEA general agreement exist for rate constants and reaction order because various techniques have been used e.g. the rapid mixing method, wetted wall, stopped flow technique, tracer diffusion method and continuously stirred cell [16]. For DEA there is no general agreement on reaction order and reaction rate constants and some researchers suggest first or second order kinetics while other report as fractional order between one and two with respect to amine concentration in both aqueous and non-aqueous solvents [15].

The zwitterion mechanism is extensively used to describe chemical reaction kinetics. A single step termolecular (direct) mechanism is also presented. Sada [17] investigated the reaction between CO$_2$ and MEA at 303 in both aqueous and non-aqueous solvents and found a gradual change in reaction order from 1 to 1.90. Sada [17] also studied DEA in water, ethanol, methanol and 2-propanol solution and found reaction order changing from 1.42 to 2. Alvaraz-Fuster [18] reported reaction order 2 for MEA in both ethanol and ethylene glycol; however these authors were not able to find reaction order other than whole number due to used interpretation method. Versteeg and van Swaaij [19] also studied reaction kinetics between CO$_2$ and DEA in ethanol and butanol solutions and they found reaction order between 1 and 2 in ethanol while for butanol it was found to be second order. Crooks and Donnellan [20] also reported second order reaction between DEA and CO$_2$ in anhydrous ethanol. Comparison made on these results in aqueous and non-aqueous solutions, Versteeg [21] concluded that occurrence of reaction order in amine varied between 1 and 2 which can only be explained satisfactory by zwitterion mechanism. Da Silva and Svenden [22] studied the mechanism for carbamate formation from CO$_2$ and alkanolamine in aqueous solutions by Ab Initio Study and suggested a single step, third order reaction is the most likely which is in good agreement with experimental data. The validity of termolecular molecular is said to be questionable by Versteeg [21] because it not able to explain the occurrence of broken order kinetics as was observed by
Sada [23], Versteeg and Van Swaaij [19] and Crooks and Donnellan [20] for non-aqueous systems [21]. Moreover, the experimental data presented by Little [24] for blends of secondary amines cannot be understood by termolecular mechanism whereas it can be profoundly explained by zwitterion mechanism [24].

Based on the literature review above, the objective of this work is to characterize the kinetics and mechanism of CO$_2$ absorption into non aqueous solvent. Experiments were performed for DEA-Ethanol solution using continuously stirred cell for different concentration in range of 0.2-3.2 mole/m$^3$ at 20°C temperature. This work equally aims at applying the zwitterion and termolecular mechanism in the interpretation of experimental data.
2 THEORETICAL BACKGROUND

2.1 REACTION MECHANISM FOR PRIMARY AND SECONDARY AMINES

The overall forward reaction between CO$_2$ and primary or secondary amines is being represented as:

$$CO_2 + R_1R_2NH \rightleftharpoons R_1R_2NCOOH$$ \hspace{1cm} (2.1)

$$R_1R_2NCOOH + R_1R_2NH \rightleftharpoons R_1R_2NCOO^- + R_1R_2NH^+$$ \hspace{1cm} (2.2)

The first step being bimolecular, second order and rate determining, while second step is supposed to take place instantaneously. However this scheme is substantial simplification for the reaction mechanism that actually occurs [21].

1.1.1 Zwitterion Mechanism

Zwitterion mechanism was originally proposed by Caplow (1968) and reintroduced by Danckwerts (1979). It consists of a two-step mechanism, i.e. the reaction between CO$_2$ and the amine proceeds through the formation of an intermediate called zwitterion (reaction 2.3) and the deprotonation of the zwitterion by a base B (reaction 2.4).

$$CO_2 + R_1R_2NH \xrightleftharpoons{K_i}{K_{-i}} R_1R_2NH^+COO^-$$ \hspace{1cm} (2.3)

$$R_1R_2NH^+COO^- + B \xrightleftharpoons{K_p}{K_{-p}} R_1R_2NCOO^- + BH^+$$ \hspace{1cm} (2.4)

R$_1$ and R$_2$ represents substituted group attached to the amine group; B represents a base molecule which may be a hydroxyl ion, water or an amine-functionality. In this work only DEA will be considered and solvent will be pure ethanol.

By applying the pseudo-steady-state condition for the zwitterion concentration, the overall forward reaction rate can be expressed as:
\[-r_{\text{CO}_2-R,R,NH}^z = \frac{k_2[\text{CO}_2][R_1R_2NH]}{1 + \sum k_b[B]} \quad 2.5\]

\[\sum K_b[B] \text{ Represents deprotonation of the zwitterion by any base such as CO}_3^2, \]

HCO\textsubscript{3}\textsuperscript{-}, H\textsubscript{2}O, OH\textsuperscript{-} or R\textsubscript{1}R\textsubscript{2}NH, as well as by combination of bases.

If the zwitterion formation is the rate determining step i.e. \(1 \geq K_{-1} / \sum K_b[B]\), then equation 2.5 can be simplified to:

\[-r_{\text{CO}_2-R,R,NH}^z = k_2[\text{CO}_2][R_1R_2NH] \quad 2.6\]

Equation 2.6 shows a first order rate dependency with respect to both amine and CO\textsubscript{2} concentration.

If the deprotonation of the zwitterion is the rate determining step i.e. \(K_{-1} / \sum K_b[B] \geq 1\) then equation 2.5 becomes:

\[-r_{\text{CO}_2-R,R,NH}^z = \frac{k_2 \sum k_b[B]}{k_{-1}}[\text{CO}_2][R_1R_2NH] \quad 2.7\]

For this work amine is the only reacting base \(B\), this suggest a broken order dependency from one to two with respect to amine concentration. For this case the forward reaction can be expressed as:

\[-r_{\text{CO}_2-R,R,NH}^z = \frac{[\text{CO}_2][R_1R_2NH]}{1 + \frac{1}{k_2 + k_{R,R,NH}[R_1R_2NH]}} \quad 2.8\]

2.1.2 Single-step termolecular mechanism (Direct mechanism)

Termolecular mechanism was originally proposed by Crooks and Donnellan (1989) [20] who suggested that the bonding of amine to CO\textsubscript{2} and
proton transfer take place simultaneously and the initial product is loosely bound encounter complex. Most of these complexes break up to give reagent molecules again but a few react with a second amine molecule to give an ionic product.

Da Silva and Svandsen [22] have reviewed this mechanism by using ab-initio calculations and a solvation model and suggested that most probable mechanism was similar to one proposed by Crooks and Donnellan [20]. Any zwitterion like intermediate would be likely to have a very short lifetime. They concluded that in any case, the single step mechanism was the most suited to describe the nature of reaction taking place between amine and CO$_2$. An important observation from that work was that termolecular mechanism could explain broken order kinetics too, it had previously been argued that termolecular mechanism could not account for this observation by Versteeg et al. [21].

\[ \text{In reaction 2.9, if amine and water are dominating bases the forward reaction rate for termolecular mechanism can be written as:} \]

\[ -r^T_{CO_2-R,R_NH} = \left\{ k^T_{R,R_NH} [R_1R_2NH] + k^T_{H_2O} [H_2O] \right\} [CO_2][R_1R_2NH] \]

\[ \text{2.10} \]

For zwitterion mechanism, equation 2.6 and equation 2.8 will be the same if the deprotonation of zwitterion is rate determining step.

For this work where the only base is amine, the forward rate equation 2.10 can be written as:

\[ -r^T_{CO_2-R,R_NH} = \left\{ k^T_{R,R_NH} [R_1R_2NH] \right\} [CO_2][R_1R_2NH] \]

\[ \text{2.11} \]
2.1.3 Reaction mechanism for tertiary alkanolamines

Donaldson and Nguyen suggested the mechanism in which tertiary alkanolamines cannot react directly with CO$_2$. These amines have a base-catalytic effect in the hydration of CO$_2$. This was also confirmed by Versteeg and Van Swaaij by the absorption of CO$_2$ into a water free solution of MDEA and ethanol [19]. They concluded that CO$_2$ was only physically absorbed and also agreed with the proposed reaction mechanism [25].

$$R_1R_2R_3N + H_2O + CO_2 \xrightarrow{K} R_1R_2R_3NH^+ + HCO_3^- \quad 2.12$$

At higher pH values (pH =13), a direct reaction between CO$_2$ and tertiary amine has been reported by Jørgensen and Faurholt [26]. However, the rate of this reaction can be neglected at lower pH values (pH < 11) [19]. Versteeg and Swaaij [27] showed that the rate of absorption of CO$_2$ into an MDEA-ethanol solution could be described as physical absorption which was almost identical to absorption of N$_2$O in the same solution.

The overall rate of reaction for all CO$_2$ reaction in aqueous amine solutions can be represented as follows:

$$r_{overall} = \left\{ k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k\left[R_1R_2R_3N\right] \right\}[CO_2] \quad 2.13$$

$k_{ov}$ is given by:

$$r_{ov} = \left\{ k_{H_2O}[H_2O] + k_{OH^-}[OH^-] + k\left[R_1R_2R_3N\right] \right\} \quad 2.14$$

And $k_{app}$ is:

$$k_{app} = k\left[R_1R_2R_3N\right] \quad 2.15$$
2.1.4 Determination of kinetic rate constant

For the absorption of CO$_2$ into aqueous amine solution, the overall reaction rate can be expressed as follows:

$$r_{ov} = r_{CO_2-R_2NH} + r_{CO_2-OH^-}$$  \hspace{1cm} \text{(2.16)}

The apparent kinetic rate constant ($k_{app}$) can be defined as:

$$k_{app} = k_{ov} - k_{OH^-}^*$$ \hspace{1cm} \text{(2.17)}

In this case where no water is present it can be modified to:

$$k_{app} = k_{ov}$$ \hspace{1cm} \text{(2.18)}

A graphical method can be used, i.e. by plotting $(k_{app}/[R_1R_2NH])$ against the $[R_1R_2NH]$ value for termolecular mechanism according to equation 2.11, value of slope is $k_{R1R2NH}^T$ itself. If equation 2.5 for zwitterion mechanism holds, then the plot between $[R_1R_2NH]/k_{app}$ and $1/[R_1R_2NH]$ should yield a straight line with slope $\frac{k_2k_b}{k_1}$ and intercept $k_2$. This method was used by Versteeg and van Swaaij [25], Crooks and Donnellan [20].

2.2 Mass transfer with a chemical reaction

In chemical absorption, the reaction rate is an important feature of the mass transfer. The absorption flux is enhanced by the chemical reaction and can be expressed as:

$$N_A = \frac{k_l}{E_A k_l - \frac{RT}{Hk}} (C_A^* - C_{A,b})$$ \hspace{1cm} \text{(2.19)}

Where $E_A$ is the enhancement factor, i.e. the ratio of the liquid side mass transfer coefficient in the presence of chemical reaction to the physical
coefficient under the conditions of equal mass transfer driving force. Two simplifications can be incorporated with equation 2.19 as:

1. If the experiments are performed under conditions of very low loading (zero loading assumption), the concentration of solute (CO\(_2\)) in the bulk (\(C_{A,b}\)) liquid is zero and equation 2.19 reduces to:

\[
N_A = \frac{C_A^*}{1 + \frac{RT}{E_A k_f + H k_g}}
\]

2. If the experiments are performed with pure CO\(_2\), then the gas-side mass transfer resistance can be omitted and equation becomes:

\[
N_A = E_A k_l C_A^*
\]

Thus in reactive absorption information on enhancement factor \(E_A\) is necessary. However a large number of enhancement factor equations exist based on a variety of mass transfer models, from the well-known two film model (Lewis and Whitman) [28] to the penetration and surface renewal model (Higbie) [29] If irreversible or reversible reactions are assumed then expression for \(E_A\) will also vary.

The complexity of choosing a model can be simplified by using the pseudo-first order irreversible approach. As mentioned previously, the reaction order with respect to the amine concentration varies from 1 to 2 and the concentration of amine is normally in relatively large excess compared to the concentration of CO\(_2\) in liquid phase.

### 2.2.1 Two film model

Two film model initially proposed by Whitman and Lewis and Whitman in 1924 [28] aims at developing a description of the mass transfer process when a gas phase is in contact with a liquid phase. In this model the assumption was
made that a stagnant film of thickness (δ) exists at the gas/liquid interface while the bulk liquid is well-mixed. Mass transport was assumed to take place by steady state molecular diffusion through the film while mass transfer by convection within this layer was assumed to be insignificant. Beyond the thin layers, mixing is sufficient to eliminate concentration gradients (as can be seen in Figure 2.1).

![Figure 2.1 Two film model for mass transfer between liquid and gas phases [30]](image)

The mass transfer from gas phase to liquid phase without any reaction is determined at steady state from the mass balance of the solute (\(\text{CO}_2=\text{A}\)) as:

\[
D_A \frac{\partial^2 C_A}{\partial x^2} = 0 \quad \text{For } 0 \leq x \leq \delta
\]

2. 22

With boundary conditions:

\[
x = 0, C_A = C_{A,i}
\]

\[
x = \delta, C_A = C_{A,b}
\]

2. 23

The solution will give the flux of solute through the gas-liquid interface as:

\[
N_A = k_i (C_{A,i} - C_{A,b})
\]

2. 24

Where the mass transfer coefficient \(k_i\) is equal to \(D_A/\delta\).
For a pseudo-first order irreversible reaction, Hatta (1932) presented the analytical solution for the mass transfer for the film model. Starting from the mass balance for the solute:

\[
D_A \frac{\partial^2 C_A}{\partial x^2} = k_i C_A \quad \text{for } 0 \leq x \leq \delta
\]  

Inserting two boundary conditions given below, resulted in an enhancement factor as:

\[
x = 0, C_A = C_{A,i} \\
x = \delta, D_A \left( \frac{\partial C_A}{\partial x} \right)_\delta = k_i C_A V_b
\]  

\[
E_{A,film} = \frac{Ha}{\tanh(Ha)}
\]  

A further simplification can be made if Ha >> 1, then \(E_{A,film} \approx Ha\) where \(Ha = \sqrt{\frac{k_{ov} D_A}{k_l}}\)

### 2.2.2 Penetration theory

The penetration theory was proposed by Higbie in 1935 [29]. It is assumed that the gas-liquid interface is made up of a variety of small liquid elements, which are continuously brought to the surface from the bulk of the liquid by the motion of the liquid phase itself. Each liquid element is considered to be stagnant, and the concentration of the dissolved gas in the element is considered equal to the bulk liquid concentration when the element reaches the surface. The residence time at the phase interface is the same for all elements. Mass transfer takes place by unsteady molecular diffusion in the various elements of the liquid surface.
The mass transfer from gas phase to liquid phase is determined as an unsteady state condition from the mass balance of the solute as:

$$D_A \frac{\partial^2 C_A}{\partial x^2} = \frac{\partial C_A}{\partial t} \quad \text{(2.28)}$$

With initial and boundary conditions:

$$C_A(x, 0) = 0$$
$$C_A(0, t) = C_{A,i} \quad \text{(2.29)}$$
$$C_A(\infty, t) = C_{A,b}$$

The solution will lead to an average rate of mass transfer over the time interval $0$ to $t^*$ as:

$$N_A = k_l (C_{A,i} - C_{A,b}) \quad \text{(2.30)}$$

Where the mass transfer coefficient $k_l$ is equal to $k_l = \frac{2D_A}{\pi t^*}$

For a pseudo-first order irreversible reaction, the enhancement factor can be expressed as (reported in van Swaiij & Versteeg (1993) and from Danckwerts (1970)).

$$E_{A,\text{pen}} = Ha \left[ 1 + \frac{\pi}{8Ha^2} \text{erf} \left( \frac{4Ha^2}{\pi} \right) + \frac{1}{2Ha} \exp \left( \frac{4Ha^2}{\pi} \right) \right] \quad \text{(2.31)}$$

As for the film model, if $Ha >> 1$, then the simplification for the enhancement factor derived from the penetration model is $E_{A,\text{pen}} \approx Ha$.

### 2.2.3 Surface renewal model

Danckwerts in 1951 [31] proposed the surface renewal model which is an extension of the penetration theory where it was assumed that the liquid elements stay the same time at the phase interface. In the surface renewal model
the liquid elements do not stay the same time at the phase interface. The distribution of surface element contact times is described by a distribution function $\Psi(t) = se^{-st}$, where

$$\Psi(t) = \begin{cases} \frac{1}{t^*} & \text{for } t < t^* \\ 0 & \text{for } t > t^* \end{cases}$$

The rate of absorption at the surface is then the average of the rates of absorption in each element and can be expressed as:

$$N_A = \int_0^\infty N_{A,inst}(t)\psi(t)dt = \frac{D_A}{\pi} (C_{A,i} - C_{A,b}) \int_0^{\infty} se^{-st}dt = k_i (C_{A,i} - C_{A,b})$$

The mass transfer coefficient resulting from this model is then $k_i = \sqrt{D_A s}$

In both the penetration and surface renewal models, the unknown thickness of the film has vanished and been replaced by an unknown contact time $t^*$ or an unknown retention time distribution parameter. For a pseudo-first order irreversible reaction, the mass balance for the solute for the diffusion, reaction and accumulation can be written as:

$$D_A \frac{\partial^2 C_A}{\partial x^2} - k_i C_A = \frac{\partial C_A}{\partial t}$$

With boundary conditions:

$$C_A(x,0) = 0$$
$$C_A(0,t) = C_{A,i}$$
$$C_A(\infty, t) = 0$$

Implementing the Laplace transform and inserting the boundary conditions, Equation 2.34 can be rewritten as:

$$D_A \frac{\partial^2 C_A}{\partial x^2} - k_i \left( \frac{k_i + s}{D_A} \right) \overline{C_A} = 0$$
By using inverse transformation, the solution of Equation 2.36 can be written as the distribution of concentration $C_A(x,t)$ as:

$$\frac{C_A}{C_{A,i}} = \frac{1}{2} \exp \left( -x \sqrt{\frac{k_i}{D_A}} \right) \text{erfc} \left( \frac{x}{2D_A t} - \sqrt{k_i t} \right) + \frac{1}{2} \exp \left( x \sqrt{\frac{k_i}{D_A}} \right) \text{erfc} \left( \frac{x}{2D_A t} + \sqrt{k_i t} \right)$$

Equation 2.37 can be simplified for large value of $k_i t$ to:

$$\frac{C_A}{C_{A,i}} = \exp \left( -x \sqrt{\frac{k_i}{D_A}} \right)$$

The rate of absorption in an element having a surface age $t$ can be calculated as:

$$N_A(t) = \sqrt{k_i D_A C_{A,i}} \left[ \text{erfc}(\sqrt{k_i t} + \frac{e^{-k_i t}}{\sqrt{\pi k_i t}}) \right]$$

The average absorption rate at the surface can be determined using Danckwert’s age function as:

$$N_A(t) = \sqrt{D_A (k_i + s) C_{A,i}} = \sqrt{D_A \left( k_i \left( 1 + \frac{k_i^2}{D_A} \right) \right)} = \sqrt{k_i} C_{A,i} \sqrt{1 + \frac{k_i D_A}{k_i^2}}$$

Then the enhancement factor for this model can be expressed as:

$$E_{A,\text{surf}} = \sqrt{1 + \frac{k_i D_A}{k_i^2}} = \sqrt{1 + Ha^2}$$

For $Ha \gg 1$, the enhancement factor $E_{A,\text{surf}} \approx Ha$.

The conclusion can be made that the enhancement factors derived from the three different models for mass transfer for the pseudo-first order irreversible reaction
are very similar. The largest deviation among the model is found to be 7.6% for
$Ha = 1$ (van Swaaij & Versteeg, 1992).

The regime of the reaction can be determined from the absolute value of $Ha$ and
the ratio between $Ha$ and $E_{A\infty}$ (the infinite enhancement factor), i.e.:

1. Slow reaction regime ($Ha < 0.3$), no enhancement caused by the
chemical reaction. The absorption flux depends on the physical mass
transfer coefficient and since the mass transfer coefficient is strongly
liquid flow rate dependent, the absorption flux will also be liquid flow
rate dependent.

2. Fast reaction/ pseudo-first order regime ($3 < Ha \ll E_{A\infty}$), gives weak to
strong enhancement of the mass transfer rate due to the reaction. In this
regime the absorption flux is independent of the physical mass transfer
coefficient and, hence independent of liquid flow rate.

3. Instantaneous reaction regime ($3 < E_{A\infty} \ll Ha$), the reaction is said to
be instantaneous with respect to the mass transfer and the absorption flux
is limited by diffusion of the reactants.

A transition regime for ($0.3 < Ha < 3$) also exists. Expressions for the infinite
enhancement factor for the different mass transfer models can be found in van

Astarita et al. (1983) uses a term called the ratio of the diffusion time ($t_D$) over
the reaction time ($t_R$), denoted $\theta = t_D / t_R$, to classify the reaction regimes based
on the film model. The diffusion time ($t_D$) is the time needed for molecular
diffusion to make the concentration uniform, and the reaction time ($t_R$) is a
required time for the chemical reaction to proceed to such an extent that the
concentration of the limiting reactant is changed significantly. Three different
regimes can be represented as:
1. Slow reaction if ($\theta \ll 1$), the reaction is too slow to have any significant influence on the diffusion phenomena and no enhancement will take place.

2. Fast reaction if ($\theta \gg 1$), the reaction is fast enough to result in a significant change in limiting reactant concentration and rate enhancement results.

3. Instantaneous reaction if ($\theta \to \infty$), the reaction is infinitely fast and chemical equilibrium is established instantaneously.
3 MATERIALS AND METHODS

3.1 MATERIALS

Chemicals used for this work with their physical properties and purity are listed in the table below:

Table 1 Specifications of chemicals used in this work

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS No.</th>
<th>Manufacturer</th>
<th>Molecular Formula (g/g mole)</th>
<th>Mol. weight</th>
<th>Purity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Di-ethanolamine</td>
<td>111-42-2</td>
<td>Sigma Aldrich</td>
<td>HN(CH₂CH₂OH)₂</td>
<td>105.14</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Tetra-butyl ammonium hydroxide solution</td>
<td>2052-49-5</td>
<td>Sigma Aldrich</td>
<td>(CH₃CH₂CH₂CH₂)₄N(OH)</td>
<td>259.47</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Ethanol</td>
<td></td>
<td>Assink Chemie</td>
<td>C₂H₆O</td>
<td>46.068</td>
<td>&gt;99.8%</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>10024-97-2</td>
<td>Air Liquide BV</td>
<td>N₂O</td>
<td>44</td>
<td>&gt;99%</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>124-38-9</td>
<td>Air Liquide BV</td>
<td>CO₂</td>
<td>44</td>
<td>&gt;99.9%</td>
</tr>
<tr>
<td>Molecular sieves, 3 Å</td>
<td>308080-99-1</td>
<td>Sigma Aldrich</td>
<td>KₙNa₁₂₋ₙ[((AlO₂)₁₂(SiO₂)₁₂].ₓH₂O</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Solutions of different molarities were prepared using di-ethanolamine (DEA) and ethanol listed above. DEA was used as provided by sigma Aldrich. 99.8% denatured ethanol was provided by Assink Chemie BV with small fraction of water as main impurity. To achieve highest purity, calculated amount of molecular sieves 8-12 mesh were added in ethanol to further remove water contents. Enough time was given for molecular sieves to absorb water contents.
to their capacity before using ethanol for experimentation. All other chemicals were used as received.

### 3.1.1 Experimental Section

All experiments were carried out in closed stirred cell contractor with smooth gas-liquid interface and was operated batch wise with respect to liquid and gas phases. A schematic drawing of the set-up is presented in Fig. 3.1 below.

![Stirred cell experimental setup](image)

*Figure 3.1 Stirred cell experimental setup [32]*

Absorption experiments were carried out at 20°C. The reactor consists of jacketed glass (ID = 15.02cm) with upper and lower parts which seal on ground flanges giving total interfacial area of 177.1861cm². There were two set of stirrer in the reactor which were equipped with molten in magnets and was driven externally. For this work only one stirrer was used because the reactor was half full and also the stirrer position doesn’t have any effect on
mass transfer for ethanol [33]. The stirrer speed is always set at constant value of 157 rpm for each experiment which was the maximum speed that could be setup for that apparatus because of the maximum output of the power supply attached with the stirrer and stirring beyond this limit may disturb smooth interface for gas-liquid contact. Total volume of the reactor was 4335 cm$^3$ out of which 2050 cm$^3$ was filled with the solution for each experiment. This specific volume of the solution was selected in order to dip stirrer support completely and to give a flat horizontal gas–liquid interface which was possible only in the middle of the reactor as shown in figure 3.2. Hence total volume available for gas phase inside the reactor was 2285 cm$^3$.

![Stirred cell reactor](image)

*Figure 3.2 Stirred cell reactor*

The reactor was connected to a gas supply vessel (gas bomb) filled with carbon dioxide or nitrous oxide from gas cylinders. Total volume of gas bomb was 583.2652 cm$^3$ including lines connecting with the reactor. Both reactor and gas bomb were equipped with digital pressure transducers and thermocouples. The pressure transducers connected to the stirred cell reactor and gas bomb are HEISE DXD pressure transducers (range 0–30 psi or 0–2 bar absolute, error $\pm 0.02\%$). The measured signals were recorded with a computer using labVIEW.
A text file is then generated by labVIEW giving total pressure in reactor (mbar), pressure in gas bomb (mbar) with their temperatures as well as the temperature of the gas above the liquid in the reactor with respect to time of gas absorption into the solution.

For first experiment a certain amount of CO$_2$ in gas bomb is collected from the main supply source and let the pressure be stable for a while inside the gas bomb. First set of absorption study at any concentration in unloaded solution is named as $\alpha_1$. Figure 3.3 below shows a typical absorption measurement curve:

![Typical absorption curve](image)

*Figure 3.3 Typical absorption curve*

At first the reactor is at vapor pressure of the solution. When CO$_2$ is injected, it goes to the maximum pressure and then start decreasing with the absorption of CO$_2$ into the amine solution. After some time when almost all CO$_2$ is absorbed, it reaches to steady state pressure in the reactor. For each concentration, after achieving steady end pressure, more CO$_2$ gas at higher CO$_2$ pressure in gas bomb than $\alpha_1$ was added to reactor and reaction conditions were verified (Equation 3.5). Results obtained from second loading were named as $\alpha_2$ and this procedure
continued till $\alpha_0$ in the same solution with higher CO$_2$ pressure in the reactor each time. It should be noted that at the end of every experimental stage the pressure in the reactor is either equal (for first two, three sets for higher concentrations) or greater than initial vapor pressure due to presence of un-absorbed CO$_2$ in the solution which is resulted due to decrease in free amine with increase in loading.

A typical curve at the end of one set of experiments at one concentration is shown in figure 3.4.

![Figure 3.4](image)

Figure 3.4 typical curves at the end of one set of experiments for 0.8M DEA in ethanol

Total amount of CO$_2$ absorbed into the amine solution, for each value of $\alpha$, was calculated theoretically using a real gas law where the gas compressibility factor was calculated based on 2$^{nd}$ viral coefficient. No sample was drawn in between but after completing experiments till $\alpha_0$, the end solution was analyzed for total CO$_2$ by non-aqueous titration according to method described by Jonnes et al.[34], Verbrugge [35] to verify the amount of CO$_2$ absorbed with theoretically calculated.
3.1.2 Determination of Carbon Dioxide

The equipment for the determination of carbon dioxide is presented in Fig. 3.3 below.

![Figure 3.5 Metrohm 716 DMS titrino setup for CO2 analysis](image)

It consists of a round bottom flask with 2M boiling sulphuric acid with sufficient nitrogen supply. Small amount of sample is injected into the acid using syringe through a septum. Carbon dioxide that is physically and chemical bonded to the solution, sulphuric acid and ethanol evaporated are directed to titration flask through a condenser. Water at 2°C is passed continuously through the condenser to condense ethanol and sulphuric acid vapors back into the round bottom flask. Carbon dioxide is transferred to the titration vessel with a nitrogen flow of 50 ml/min. The titration flask having 3 volume % MEA in dimethyl form amide
(DMF) and thymolptalein, as an indicator, is stirred sufficiently and specific nitrogen flow ensured that all carbon dioxide is reacted with primary amine MEA. The solution is kept on constant pH by maintaining constant blue color in the flask.

Standardization of titrant is performed for 0.1M sodium carbonate standard solution used as sample. Initial pH was noted before the sample was injected into boiling acid, after some time, the solution in titration flask became more acidic. The blue color disappeared and pH started to decrease till all carbon dioxide is absorbed. An automatic Metrohm 716 DMS Titrino was used to carry out the titration. Using correct setting and feeding initial pH, the solution was titrated against 0.1M Tetra-butyl ammonium hydroxide (TBAH) provided by sigma Aldrich. The addition of titrant continued till the pH of the initial conditions is reached. This was also verified by color transition to blue. Two consecutive titration results giving less than 2.5% error were taken as final amount of TBAH solution used against injected amount of solution.

Amount of carbon dioxide present in the solution can be calculated by:

\[
\text{Amount of CO}_2 (\text{mole/kg}) = \frac{\text{Amount of TBAH used} \times \text{Concentration of TBAH}}{\text{Amount of sample added}}
\] 3.1

3.1.3 Physico-chemical parameters

3.1.3.1 Physical solubility and liquid side mass transfer coefficient:

In order to verify the conditions of pseudo first order absorption experiments, \( m_{CO_2} \cdot \sqrt{D_{CO_2}} \) and mass transfer coefficient \( k_l \) are the most important physicochemical parameters (equation 3.5, 3.6). As \( CO_2 \) reacts with alkanolamines, so it is not possible to determine physical solubility \( (m_{CO_2}) \) or diffusivity \( (D_{CO_2}) \) of carbon dioxide in alkanolamine solutions directly. These parameters were measured using \( CO_2-N_2O \) analogy [36] [37] as \( N_2O \) is almost identical in configuration, molecular volume and electronic structure. It was concluded that the ratio of \( CO_2 \) solubility to \( N_2O \) solubility remained constant for
the various solutions and that the “N$_2$O analogy” could be applied to estimate the solubility of CO$_2$ in alkanolamine solutions according to the given equation [36]:

$$ m_{i,CO_2} = \frac{m_{CO_2}^E}{m_{N_2O}^E} m_{i,N_2O} \quad 3.2 $$

And:

$$ k_{i,CO_2} = \frac{k_{i,CO_2}^E}{k_{i,N_2O}^E} k_{i,N_2O} \quad 3.3 $$

Where superscript E refers measurements in pure ethanol.

3.1.3.2 Diffusivity and viscosity:

Diffusivity of CO$_2$ and N$_2$O in pure ethanol solvent, solution viscosity and density have been reported by Alvarez-fuster [18], Sada [17] [23], Versteeg [19] and Little [33] at different concentration and temperature conditions. Snigder [38] presented following temperature based relation for CO$_2$ and N$_2$O diffusivity in ethanol [38].

For CO$_2$ in ethanol:

$$ D_{CO_2} (m^2 / s) = 336.5 \times 10^{-9} \exp \left( -\frac{1314.7}{T / K} \right) \quad 3.4 $$

For N$_2$O in ethanol:

$$ D_{N_2O} (m^2 / s) = 345.0 \times 10^{-9} \exp \left( -\frac{1310.4}{T / K} \right) \quad 3.5 $$

3.2 METHODS

In each set of experiments freshly prepared solution was fed into the reactor and was degassed using vacuum pump to strip off all inert gas
contaminants present in the solution. After degassing, the pressure in the reactor was almost the same with the vapor pressure of the solution in the reactor at that temperature. A vapor liquid equilibrium was allowed to establish before starting the experiments. The pressure recorded in the reactor before starting the experiment is the vapor pressure of the solution \( P_{vap} \) and was used to calculate actual pressure of \( \text{CO}_2 \) in the reactor by subtracting from total pressure in the reactor:

\[
P_{\text{CO}_2} = P_{\text{tot}} - P_{\text{vap}}
\]

After equilibrium has achieved, pure \( \text{CO}_2 \) (for kinetics experiments) was introduced into the reactor. The initial pressure \( P_{\text{CO}_2} \mid t=0 \) and average loading for each experiment could be adjusted by means of amount of \( \text{CO}_2 \) added to the reactor. The decrease in pressure with time due to absorption of pure \( \text{CO}_2 \) into solutions was studied and called \( \alpha_1 \). Reaction kinetics were studied in first order reaction regime where following condition was satisfied as stated in equation 3.7. The decrease in \( P_{\text{CO}_2} \) during these experiments caused \( E_\infty \) to increase steadily, therefore condition in 3.7 were always satisfied in time-pressure curve.

\[
2 < H \alpha \ll E_{\text{CO}_2,\infty}
\]

Where:

\[
H \alpha = \frac{\sqrt{k_{ov} \cdot D_{\text{CO}_2}}}{k_1}
\]

And:

\[
E_{\text{CO}_2,\infty} = \sqrt{\frac{D_{\text{CO}_2}}{D_{\text{DEA}}}} + \sqrt{\frac{D_{\text{DEA}}}{D_{\text{CO}_2}}} \cdot \frac{[\text{DEA}],RT}{\nu_{\text{CO}_2} m_{\text{CO}_2} P_{\text{CO}_2}}
\]
Transient absorption rates were thus given by:

\[
V_g \frac{dC_g^b}{dt} = -k_i a (mC_g^b - C_i^b) \tag{3.10}
\]

Where:

\[
m = \frac{C_i^i}{C_g^i} \tag{3.11}
\]

The superscripts \(b\) and \(i\) refers to the bulk and interface and \(m\) can be regarded as a distribution coefficient. The conservation of mass gives:

\[
V_g C_g^o + V_i C_i^o = V_g C_g^b + V_i C_i^b \tag{3.12}
\]

\[
C_g^c = \frac{V_g C_g^o + V_i C_i^o}{mV_i + V_g} \tag{3.13}
\]

Where the superscripts \(0\) and \(\infty\) refers to the initial and infinite time. Solving Equations (3.10), (3.12) and (3.13) with respect to \(C_g^b\) and \(t\) using the following initial condition:

\[
C_g^b = C_g^o \text{ at } t = 0 \tag{3.14}
\]

Which gives:

\[
\ln \left[ \frac{C_g^b - C_g^c}{C_g^o - C_g^c} \right] = \frac{(mV_i + V_g)(k_i a)t}{V_g V_i} \tag{3.15}
\]

For our case of partial pressure it could be modified as:

\[
\ln \left[ \frac{P(t) - P^\infty}{P^o - P^\infty} \right] = \frac{(mV_i + V_g)}{V_g V_i} k_LAt \tag{3.16}
\]
From this relation between pressure decrease and time the liquid phase mass transfer coefficient $k_L$ can be calculated by plotting the left side of Equation (3.16) versus the time $t$ and finding the slope (see figure 3.6).

The absorption experiments for determining $k_L$ value were allowed to reach equilibrium in order to obtain dimensionless solubility:

$$m = \frac{(P^o - P^\infty)V_g}{(P^\infty - P_{vap})V_l} \quad 3.17$$

For our closed reactor with gas volume $V_g$, from a mass balance (equation 3.12), the pressure-time relation (equation 3.16) can be rearranged as:

$$\ln P_{CO_2}|t = - \frac{m_{CO_2}A}{V_g} \sqrt{k_{ov} D_{CO_2}} \cdot t + \ln P_{CO_2}|t=0 \quad 3.18$$

The overall reaction rate constant $k_{ov}$ was determined from the slope in $\ln P_{CO_2}$ and time graph in the region where conditions in equation 3.7 was met. A typical pressure-time curve is shown in figure 3.6.

![Figure 3.6 Typical plot between time and ln(P_C02) showing data used for k_0v calculation](image)
It can be seen in figure 3.6 that $\ln(P_{CO_2})$ and time plot is not straight which goes down until reached to steady state so we have to take the straight line region where slope is almost constant.

If condition (3.7) is fulfilled then the reaction is regarded as pseudo first order. The CO$_2$ absorption rate into the solution is described by:

$$J_{CO_2} \cdot A = \sqrt{k_{ov} D_{CO_2} \cdot m_{CO_2} P_{CO_2} \frac{A}{RT}} \quad \text{(mole.m}^{-2}.\text{s}^{-1})$$

3. 19

The apparent reaction rate $k_{app}$ for carbamate formation for this system was calculated from overall rate constant $k_{ov}$ as:

$$K_{app} = K_{ov} - K_{OH}^[OH^-]$$

3. 20

For our case, without presence of OH$^-$ it would be as:

$$K_{app} = K_{ov}$$

3. 21

On the basis of zwitterion and termolecular (direct) mechanism respectively, $k_{app}$ can then be expressed as:

$$k_{app} = \frac{[DEA]}{1 + \frac{1}{k_2 + k_{DEA}[DEA]}}$$

3. 22

And:

$$k_{app} = \{k_{DEA}^[DEA]\} [DEA]$$

3. 23
4 RESULTS AND DISCUSSION

4.1 PHYSICAL SOLUBILITY AND MASS TRANSFER COEFFICIENT

In table 4.1 the values of the term \( m \sqrt{D} \) and mass transfer coefficient \( (k_L) \) for \( \text{CO}_2 \) in ethanol and \( \text{N}_2\text{O} \) in both ethanol and DEA in ethanol solutions are presented.

*Table 4.1 \( m \sqrt{D} \) for \( \text{N}_2\text{O} \) and \( \text{CO}_2 \) in DEA-ethanol solutions at 293K*

<table>
<thead>
<tr>
<th>[DEA] mole/m³</th>
<th>Gas</th>
<th>( m \sqrt{D} \times 10^{-4} ) m.s(^{1/2} )</th>
<th>( K_L \times 10^5 ) m/sec</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( \text{CO}_2 )</td>
<td>1.37</td>
<td>-</td>
<td>Versteeg and Swaaij 1988</td>
</tr>
<tr>
<td>0</td>
<td>( \text{CO}_2 )</td>
<td>1.64</td>
<td>-</td>
<td>Alvarez-Fuster et al. 1981</td>
</tr>
<tr>
<td>0</td>
<td>( \text{CO}_2 )</td>
<td>1.73</td>
<td>-</td>
<td>Little et al. 1991</td>
</tr>
<tr>
<td>0</td>
<td>( \text{CO}_2 )</td>
<td>1.77</td>
<td>-</td>
<td>William Kunerth</td>
</tr>
<tr>
<td>0</td>
<td>( \text{CO}_2 )</td>
<td>1.75</td>
<td>6.85</td>
<td>This work</td>
</tr>
<tr>
<td>0</td>
<td>( \text{N}_2\text{O} )</td>
<td>1.44</td>
<td>-</td>
<td>Versteeg and Swaaij 1988</td>
</tr>
<tr>
<td>0</td>
<td>( \text{N}_2\text{O} )</td>
<td>1.88</td>
<td>-</td>
<td>William Kunerth 1921</td>
</tr>
<tr>
<td>0</td>
<td>( \text{N}_2\text{O} )</td>
<td>1.82</td>
<td>7.79</td>
<td>This work</td>
</tr>
<tr>
<td>201</td>
<td>( \text{N}_2\text{O} )</td>
<td>1.72</td>
<td>7.36</td>
<td>This work</td>
</tr>
<tr>
<td>401</td>
<td>( \text{N}_2\text{O} )</td>
<td>1.51</td>
<td>6.85</td>
<td>This work</td>
</tr>
<tr>
<td>805</td>
<td>( \text{N}_2\text{O} )</td>
<td>1.14</td>
<td>5.60</td>
<td>This work</td>
</tr>
<tr>
<td>1602</td>
<td>( \text{N}_2\text{O} )</td>
<td>1.00</td>
<td>4.31</td>
<td>This work</td>
</tr>
<tr>
<td>3201</td>
<td>( \text{N}_2\text{O} )</td>
<td>0.7</td>
<td>2.20</td>
<td>This work</td>
</tr>
</tbody>
</table>

Solubility of \( \text{CO}_2 \) in solvent does not seem to be dependent on amine concentration \([39]\) \([40]\) however diffusivity of \( \text{CO}_2 \) is much dependent on amine concentration which can be concluded from table 4.1 and appendix. The solubility
of CO₂ and N₂O in the solvents for zero loading are well in line with values previously reported [19] [18] [33] [41]. The only difference is with Versteeg [25] whose value is much lower than this work but also with other references as well. The mass transfer coefficients are specific to the gaseous component, the solvent, and the type/geometry of the reactor applied, thus cannot be compared directly to values from other sources [41].

4.2 APPARENT RATE OF REACTION

In Fig 4.1 the apparent kinetic rate constant based on equation 3.18 and 3.20 from this work is shown as function of DEA concentration. The apparent rate constant \( k_{app} \) from Versteeg 1988 [25] and Crooks and Donnellan 1988 [20] (stopped flow) are also shown for comparison. The absorption results are well in line with the literature date presented in figure below.

![Figure 4.1 k<sub>app</sub> with concentration of DEA in ethanol at 293K](image-url)

*Figure 4.1* \( k_{app} \) with concentration of DEA in ethanol at 293K
From figure 4.1, it could be concluded that the results obtained from this work are in agreement with Crooks [20] and Versteeg [25] at lower concentrations. As the concentration increases more than 1000 mole/m$^3$ the literature data and current start deviating. The data of crooks [20] at higher concentration shower higher $k_{app}$ values while Versteeg [25] show otherwise with comparison to this work. The reason of this difference is due to the values used for physical properties as can be seen in table 4.1.

By assuming $k_{app} = k' [DEA]^n$ and fitting the points with power correlation, the obtained order of the reaction is presented in table 4.2. The agreement on reaction order from this work is found with Alvarez-Fuster [18] and Sada [17] with values 2.0 and 1.74 respectively and Versteeg [25] suggested that it varies between 1.5 and 2 for high and lower amine concatenation respectively.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Order of reaction (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alvarez-Fuster [18]</td>
<td>2.0</td>
</tr>
<tr>
<td>E. Sada [17]</td>
<td>1.74</td>
</tr>
<tr>
<td>Versteeg [25]</td>
<td>1.54</td>
</tr>
<tr>
<td>Crook [20]</td>
<td>1.93</td>
</tr>
<tr>
<td>This work</td>
<td>1.78</td>
</tr>
</tbody>
</table>

There is some discrepancy in the results for absorption at $[DEA] = 0.2M$ in this work where the condition of pseudo-first order (equation 3.7) is not fulfilled as obtained $Ha$ number was 1.88 due to low concentration of amine. This discrepancy for lower amine concentration (less than 0.4M) can be overcome by carrying out experimentation at lower stirrer speed.

Another problem which is observed at higher amine concentration is interfacial turbulence during absorption at higher CO$_2$ partial pressures. In this work
experiments carried out at higher $P_{CO_2}$ values were not used for calculating reaction rate constants and order of the reaction, however this does not mean that the influence was completely excluded.

4.3 Initial/Forward Reaction Rate Constants

The initial reaction rate constant can be determined in the first run of the experiment, i.e. when the loading of the solution was nearly zero. The proposed method by Danckwerts (1979) was used to estimate the initial/forward kinetic rate constants for both mechanisms i.e. the reaction rate constant is function of amine concentration having second and third order reaction rate constants $k_2, k_{DEA}^z$. The reaction rate constants can be calculated by plotting $\frac{[DEA]}{k_{app}}$ against $\frac{1}{[DEA]}$ (equation 2.8) which should yield a straight line with slope $\frac{1}{k_{DEA}^z}$ and intercept $\frac{1}{k_2}$. Such plot is shown in figure 4.2 below.

![Figure 4.2 The Zwitterion mechanism plot for DEA-ethanol at 293K](image)

Figure 4.2 The Zwitterion mechanism plot for DEA-ethanol at 293K
When the intercept of equation is set to zero then the Termolecular kinetic rate constant can be determined, as seen in figure 4.3.

According to equation 2.11 if termolecular (direct) mechanism holds then the plot of $k_{app}/[DEA]$ against $[DEA]$ should also yield a straight line passing through the origin i.e intercept=0; slope of the line gives the value of $k_2$ as shown if figure 4.3.

![Graph](image)

*Figure 4.3 Termolecular mechanism plot for DEA-ethanol at 293K*

The derived rate constants according to zwitterion and termolecular mechanism are shown in table 4.3 below for DEA ethanol solutions and for sake of comparison, the reaction rate constants from earlier works for the same system are also listed in the same table.

From the comparison made in table 4.3, it can be seen that for zwitterion mechanism both $k_2$ and $k_{DEA}$ seems to agree with the previous work of Versteeg (1988), however the deviation reaches to 26% for $k_{DEA}$ and less than 5% for $k_2$.  

40
Agreement for $k_{DEA}$ is also found with Alvarez’s work however they did not reported the $k_2$ value.

The $k_2$ value is much larger than $k_{DEA}$ which means that the zwitterion has faster kinetic rate than $k_{DEA}$. The process of zwitterion in the system was expected to be very short thus the life time is very short [42]. When $\frac{1}{k_2}$ was set to zero, the existing of the zwitterion is most likely extremely short and cannot be observed. The kinetic rate constant ($k_{DEA}$) for termolecular is found to agree with zwitterion within 15% which is smaller than that of the suggested value of Versteeg 1988 [25].

Table 4. 3 Fitted rate parameters for reaction between carbon dioxide and di-ethanolamine in ethanol at 293K

<table>
<thead>
<tr>
<th>Amine Conc. Mole/m³</th>
<th>T (K)</th>
<th>$k_2$ m³/mol.s</th>
<th>$k_{DEA}\times10^{-4}$ m⁶/mol².s</th>
<th>Reference</th>
<th>Mechanism Adopted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3 – 2.2</td>
<td>293</td>
<td>-</td>
<td>1.3</td>
<td>Alveraz 1981 [18]</td>
<td>Zwitterion</td>
</tr>
<tr>
<td>0.5 – 1.5</td>
<td>303</td>
<td>0.29</td>
<td>2.0</td>
<td>E. Sada 1985 [17]</td>
<td>Zwitterion</td>
</tr>
<tr>
<td>0.49 – 2.937</td>
<td>293</td>
<td>0.215</td>
<td>1.5</td>
<td>Versteeg 1988 [19]</td>
<td>Zwitterion</td>
</tr>
<tr>
<td>0.2 – 3.2</td>
<td>293</td>
<td>0.209</td>
<td>1.11</td>
<td>This work</td>
<td>Zwitterion</td>
</tr>
<tr>
<td>0.2 – 3.2</td>
<td>293</td>
<td>-</td>
<td>0.959</td>
<td>This work</td>
<td>Termolecular</td>
</tr>
</tbody>
</table>

The kinetic rate constants of both mechanism were used to recalculate the experimental CO₂ flux observed from the experiments as seen in figure 4.4.

It is seen that the suggested kinetic rate constants gave a similar deviation (within 10%) of the predicted CO₂ flux similar. The reported $k_2$ value could also be associated with the experimental error, hence both mechanisms are practically similar.
4.4 MASS TRANSFER IN THE DEA/CO$_2$/ETHANOL SYSTEM

For calculation of absorption experiments it was assumed that the reaction between DEA and CO$_2$ can be described by an irreversible pseudo first order reaction whereas at higher loading the actual reaction is not irreversible (equation 2.1 and 2.2). So the influence of its reversibility is neglected. The backward reaction can be determined from the experimental data at higher loading. The apparent kinetic rate constant for loaded system as function of loading at different concentration can be seen in figure 4.5. It can been seen from above figure that CO$_2$ loading has inverse effect on the apparent kinetic rate constant for all concentrations except for 3.2M DEA. For 3.2M the apparent kinetic rate constant first increases with CO$_2$ loading and then start decreasing after loading of 0.05 mole CO$_2$/mole amine. The reason for this behavior could be that for same $P_{CO_2}$ the solution has more free amine present to absorb CO$_2$ at higher concentrations than that of lower concentration for the same $P_{CO_2}$. Same amount
of CO₂ absorbed in higher concentration will reflect less loading than that of lower concentrations which results into higher kinetic rate.

Figure 4.5 $k_{app}$ with loading in different DEA concentrations in ethanol at 293K

4.5 Sensitivity Analysis

The data for physical properties is scarcely available in literature. Most of the physical properties (solubility, diffusivity, viscosity and density) varied ±10% in the literature. The parameter sensitivity test for only 0.8M DEA-ethanol at 293K is applied and physical properties (solubility and diffusivity) are varied ±10% and the deviation between calculated apparent rates as well as order of the reaction and their original values caused by the variation were shown in table 4.4.
Table 4. Parameter sensitivity for 0.8M DEA apparent kinetic rate constant at 273K

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( k_{app} )</th>
<th>Order of reaction ( (n) )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+10%</td>
<td>-10%</td>
</tr>
<tr>
<td>( m_{CO_2} )</td>
<td>-17.4%</td>
<td>+23.5%</td>
</tr>
<tr>
<td>( D_{CO_2} )</td>
<td>-9.2%</td>
<td>+11.3%</td>
</tr>
</tbody>
</table>

At lower DEA-ethanol lack of data for these physical properties exist so large variation in final results can be expected at lower concentrations. From the physical properties test, it can be seen that the kinetic rate constant are sensitive to solubility and \( CO_2 \) diffusivity in amine solutions and hence these are the key physical properties in the kinetic experiments. Sample of raw data of \( CO_2 \) absorbed by unloaded DEA-ethanol solution from the experiments in stirrer cell can be seen in the appendix.
The kinetics of carbon dioxide absorption into non aqueous amine solution (DEA-ethanol) were performed in a stirrer contactor at different amine concentrations at 293K. Two reaction mechanisms, i.e. the termolecular and zwitterion mechanisms were implemented to interpret the experimental data.

The physical solubility for N₂O and CO₂ in pure ethanol and for N₂O at different concentrations was also studied at this temperature which is found to be with line with literature data. The apparent rate of reaction increases with concentration while has inverse relation with CO₂ loading at all concentrations. The reaction order with respect to amine concentration was found to be 1.78 which vary with concentration.

The reaction rate constant for DEA was calculated based on zwitterion and termolecular mechanism and the values obtained were found to be in agreement with the literature. Parity plots for calculated and experimental flux was also plotted for comparison. Practically both mechanism are similar.
6 Future Recommendations

- To verify the results presented in this work, experimental work should also be done at different temperatures.
- The degassing of the solution in the reactor should be done at a very lower temperature to avoid loss of volatile solvent at experimental temperatures.
- CO$_2$ or N$_2$O gases should be cooled to the liquid temperature before injection into the reactor. The gas is observed at higher temperature even after giving some time to settle down. For this purposes water bath is suggested for gas bomb.
- The cooling system installed for the apparatus is not much efficient in controlling the temperature. The temperature of the liquid inside the reactor is dependent to the ambient temperature which varies with the temperature in the lab during the experiments.
- Physical properties (density, viscosity and diffusivity of CO$_2$) should be estimated by experimentation rather than to have the data from literature because there is not much data available at very low amine concentration and data interpolation in between two points cannot be relayed due to large variations.
7 REFERENCES


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- Risk assessment
- Safety data sheets
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Physical solubility and liquid side mass transfer \( K_L \) for \( N_2O \) in 0.2M DEA-Ethanol at 20°C

### Calculation of "m"

| \( P_{end} \) | 189.2 mbar | Total Reactor Volume | 4335 ml | Diameter of Reactor | 15.02 cm |
| \( P_{vap} \) | 66.6 mbar | Volume of Liquid | 2050 ml |
| \( P_{initial} \) | 520 mbar | Volume of Gas | 2285 ml |

\[
m = \frac{(P_{initial} - P_{end}) * V_g}{(P_{end} - P_{vap}) * V_{liq}}
\]

* Always remember to subtract \( P_{vap} \) from all pressure values

\[
m = 3.007512
\]

### Calculation of "\( K_L \)"

Slope from graph = -0.0024
Area of Reactor = 177.1866

\[
K_L = \frac{0.007508329 \text{ cm/sec}}{(m*V_l) + V_g*A}
\]

\[
K_L = 7.50833E-05 \text{ m/sec}
\]
Physical solubility and liquid side mass transfer $K_L$ for N$_2$O in 0.4M DEA-Ethanol at 20C

**Calculation of "m"**

\[
m = \frac{(P_{\text{initial}} - P_{\text{end}}) \cdot V_g}{(P_{\text{end}} - P_{\text{vap}}) \cdot V_{\text{liq}}}\]

* Always remember to subtract $P_{\text{vap}}$ from all pressure values

\[
m = 2.97807
\]

**Calculation of "K_L"**

Slope from graph = -0.0022
Area of Reactor = 177.1866

\[
K_L = \frac{-\text{slope} \cdot V_g \cdot V_l}{((m \cdot V_l) + V_g) \cdot A}
\]

\[
K_L = 6.93214E-05 \text{ m/sec}
\]
Physical solubility and liquid side mass transfer $K_L$ for $N_2O$ in 0.8M DEA-Ethanol at 20°C

**Calculation of "m"**

<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{end}}$</td>
<td>201.1 mbar</td>
<td>Total Reactor Volume</td>
<td>4335 ml</td>
<td>Diameter of Reactor</td>
</tr>
<tr>
<td>$P_{\text{vap}}$</td>
<td>79.7 mbar</td>
<td>Volume of Liquid</td>
<td>2050 ml</td>
<td></td>
</tr>
<tr>
<td>$P_{\text{initial}}$</td>
<td>499 mbar</td>
<td>Volume of Gas</td>
<td>2285 ml</td>
<td></td>
</tr>
</tbody>
</table>

\[
m = \frac{(P_{\text{initial}} - P_{\text{end}}) \cdot V_g}{(P_{\text{end}} - P_{\text{vap}}) \cdot V_{\text{liq}}} \]

* Always remember to subtract $P_{\text{vap}}$ from all pressure values

\[
m = 2.90043
\]

**Calculation of "$K_L$"**

Slope from graph = -0.0018  
Area of Reactor = 177.1866

\[
K_L = \frac{-\text{slope} \cdot V_g \cdot V_l}{(m \cdot V_l) + V_g} \cdot \frac{V_l}{A}
\]

\[
K_L = 5.78142E-05 \text{ m/sec}
\]
Physical solubility and liquid side mass transfer $K_L$ for N$_2$O in 1.6M DEA-Ethanol at 20°C

**Calculation of "m"**

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{end}$</td>
<td>195 mbar</td>
<td>Total Reactor Volume</td>
<td>4335 ml</td>
<td>Diameter of Reactor</td>
<td>15.02 cm</td>
</tr>
<tr>
<td>$P_{vap}$</td>
<td>70.5 mbar</td>
<td>Volume of Liquid</td>
<td>2050 ml</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$P_{initial}$</td>
<td>497 mbar</td>
<td>Volume of Gas</td>
<td>2285 ml</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$$m = \frac{(P_{initial} - P_{end}) \cdot V_g}{(P_{end} - P_{vap}) \cdot V_{liq}}$$  
* Always remember to subtract $P_{vap}$ from all pressure values

$$m = 2.70377$$

**Calculation of "$K_L$"**

Slope from graph = -0.0013

Area of Reactor = 177.1866

$$K_L = \frac{-\text{slope} \cdot V_g \cdot V_l}{((m \cdot V_l) + V_g) \cdot A}$$

$$K_L = 4.39053E-05 \text{ m/sec}$$
Physical solubility and liquid side mass transfer $K_L$ for N$_2$O in 3.2M DEA-Ethanol at 20C

**Calculation of "m"**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{\text{end}}$</td>
<td>213.2 mbar</td>
<td>Total Reactor Volume</td>
</tr>
<tr>
<td>$P_{\text{vap}}$</td>
<td>65.1 mbar</td>
<td>Diameter of Reactor</td>
</tr>
<tr>
<td>$P_{\text{initial}}$</td>
<td>523 mbar</td>
<td>Volume of Liquid</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Volume of Gas</td>
</tr>
</tbody>
</table>

$$m = \frac{(P_{\text{initial}} - P_{\text{end}}) \times V_g}{(P_{\text{end}} - P_{\text{vap}}) \times V_{\text{liq}}}$$

* Always remember to subtract $P_{\text{vap}}$ from all pressure values

$$m = 2.331625$$

**Calculation of "$K_L$"**

Slope from graph = -0.00062
Area of Reactor = 177.1866

$$K_L = 0.00232006 \text{ cm/sec}$$

$$K_L = \frac{(-\text{slope} \times V_g \times V_l)}{((m \times V_l) + V_g) \times A}$$

$$K_L = 2.32006E-05 \text{ m/sec}$$
### Kinetics of 0.2M DEA in Ethanol at 20°C

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Vapor Pressure (mbar)</th>
<th>Initial Pressure (mbar)</th>
<th>Equilibrium Pressure (mbar)</th>
<th>Slope</th>
<th>$k_{app}$ (sec$^{-1}$)</th>
<th>Ha</th>
<th>$P_{CO2}$ (mbar)</th>
<th>$E_{\infty}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>67.1</td>
<td>104.2</td>
<td>67.8</td>
<td>-0.00269</td>
<td>4.3</td>
<td>1.93</td>
<td>37.1</td>
<td>131.83</td>
</tr>
<tr>
<td>2</td>
<td>68.1</td>
<td>128.4</td>
<td>71.2</td>
<td>-0.002547</td>
<td>3.9</td>
<td>1.83</td>
<td>60.3</td>
<td>81.11</td>
</tr>
<tr>
<td>3</td>
<td>71.2</td>
<td>168.8</td>
<td>77.4</td>
<td>-0.002442</td>
<td>3.6</td>
<td>1.75</td>
<td>97.6</td>
<td>50.11</td>
</tr>
<tr>
<td>4</td>
<td>77.4</td>
<td>253.0</td>
<td>89.5</td>
<td>-0.002366</td>
<td>3.3</td>
<td>1.70</td>
<td>175.6</td>
<td>27.85</td>
</tr>
<tr>
<td>5</td>
<td>89.5</td>
<td>304.9</td>
<td>108.1</td>
<td>-0.002264</td>
<td>3.1</td>
<td>1.62</td>
<td>215.4</td>
<td>22.71</td>
</tr>
<tr>
<td>6</td>
<td>108.1</td>
<td>356.6</td>
<td>133.6</td>
<td>-0.002174</td>
<td>2.8</td>
<td>1.56</td>
<td>248.5</td>
<td>19.68</td>
</tr>
<tr>
<td>7</td>
<td>133.6</td>
<td>418.9</td>
<td>166.4</td>
<td>-0.002105</td>
<td>2.6</td>
<td>1.51</td>
<td>285.3</td>
<td>17.14</td>
</tr>
</tbody>
</table>

- Liquid Volume: 2050.0 cm$^3$
- Gas Volume Reactor: 2285.0 cm$^3$
- Surface Area: 177.2 cm$^2$
- Physical Solubility of CO$_2$: 2.98
- Diffusivity of CO$_2$: $3.14 \times 10^{-9}$ m$^2$/sec
**Kinetics of 0.4M DEA in Ethanol at 20C**

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Vapor Pressure (mbar)</th>
<th>Initial Pressure (mbar)</th>
<th>Equilibrium Pressure (mbar)</th>
<th>Slope</th>
<th>( k_{app} ) (sec(^{-1}))</th>
<th>Ha</th>
<th>( P_{CO2} ) (mbar)</th>
<th>( E_\infty )</th>
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Liquid Volume: 2050.0 cm\(^3\)
Gas Volume Reactor: 2285.0 cm\(^3\)
Surface Area: 177.2 cm\(^2\)
Physical Solubility of CO\(_2\): 2.955
Diffusivity of CO\(_2\): 2.49E-9 m\(^2\)/sec
## Kinetics of 0.8M DEA in Ethanol at 20°C

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Vapor Pressure (mbar)</th>
<th>Initial Pressure (mbar)</th>
<th>Equilibrium Pressure (mbar)</th>
<th>Slope</th>
<th>$k_{app}$ (sec$^{-1}$)</th>
<th>Ha</th>
<th>$P_{CO2}$ (mbar)</th>
<th>$E_\infty$</th>
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- Liquid Volume: 2050.0 cm$^3$
- Gas Volume Reactor: 2285.0 cm$^3$
- Surface Area: 177.2 cm$^2$
- Physical Solubility of CO$_2$: 2.878
- Diffusivity of CO$_2$: 1.49E-9 m$^2$/sec
### Kinetics of 1.6M DEA in Ethanol at 20°C

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<th>Ha</th>
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## Kinetics of 3.2M DEA in Ethanol at 20°C

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Liquid Volume: 2050.0 cm$^3$
Gas Volume Reactor: 2285.0 cm$^3$
Surface Area: 177.2 cm$^2$
Physical Solubility of CO$_2$: 2.313
Diffusivity of CO$_2$: 0.858E-9 m$^2$/sec
**CO₂ Loading calculation with 2ⁿᵈ varial coefficient for 0.2M DEA-Ethanol solution**

2ⁿᵈ virale coefficient for gas (ref DIPPR):

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<th>C</th>
<th>D</th>
<th>E</th>
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<th>Datafile B</th>
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## CO₂ Loading calculation with 2\textsuperscript{nd} variational coefficient for 0.4M DEA-Ethanol solution

### 2\textsuperscript{nd} virial coefficient gassen (ref DIPPR):

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<tr>
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<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tr>
<td>CO₂</td>
<td>5.44E-02</td>
<td>-3.64E+01</td>
<td>1.50E+06</td>
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### Belading Datafile A Meting Datafile B

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<td>1</td>
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<td>1</td>
<td>0</td>
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</table>

| P       | mbar    | 264.9 | 109.9 | 398.2 | 139.6 | 598.3 | 181.5 | 801.7  | 224.1 | 906.3 | 249.5 | 1007.7 | 274.8 | 1200.5 | 314.8 | 1403.9 | 357.6 | 1598.8 | 411.9 |
| B       | -        | 0.000121 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 | -0.00012 |
| Z       | -        | 0.9987208 | 0.998457 | 0.998059 | 0.99932 | 0.997122 | 0.999126 | 0.996088 | 0.999008 | 0.99554 | 0.99764 | 0.995001 | 0.998654 | 0.994157 | 0.998479 | 0.991233 | 0.990255 | 0.992232 | 0.997982 |
| n       | mol     | 0.0061796 | 0.002581 | 0.000932 | 0.003264 | 0.013957 | 0.000429 | 0.018781 | 0.005242 | 0.02131 | 0.005864 | 0.023761 | 0.006438 | 0.028163 | 0.007346 | 0.032859 | 0.008372 | 0.037537 | 0.009655 |

| CO₂ naar reactor | mol | 0.003599 | 0.006056 | 0.0009728 | 0.013539 | 0.015446 | 0.017322 | 0.020816 | 0.024487 | 0.027882 |
| cum            | mol  | 0.003599 | 0.009655 | 0.019383 | 0.032922 | 0.048368 | 0.065691 | 0.086507 | 0.110994 | 0.138876 |

| Reactor | 0   | 1   | 0   | 1   | 0   | 1   | 0   | 1   | 0   | 1   | 0   | 1   | 0   | 1   | 0   | 1   | 0   | 1   | 1   |
| P       | mbar    | 69.3  | 69.6 | 69.6 | 70.8 | 70.8 | 72.7 | 72.7 | 75.9 | 75.9 | 80.1 | 80.1 | 87   | 87   | 94.6 | 94.6 | 104.9 | 104.9 | 118.9 |
| B       | -        | -0.000128 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 | -0.00013 |
| Z       | -        | 0.9996346 | 0.999633 | 0.999633 | 0.999627 | 0.999627 | 0.999616 | 0.999599 | 0.999599 | 0.999577 | 0.999577 | 0.999541 | 0.999541 | 0.999501 | 0.999447 | 0.999447 | 0.999373 |
| n       | mol     | 0.0065017 | 0.006532 | 0.006532 | 0.006643 | 0.006643 | 0.006623 | 0.006623 | 0.007123 | 0.007123 | 0.007519 | 0.007519 | 0.008164 | 0.008164 | 0.008876 | 0.008876 | 0.009843 | 0.009843 | 0.011158 |

| CO₂ in gasfase (cum) | mol | 3.02E-05 | 0.000141 | 0.000321 | 0.000621 | 0.001017 | 0.001663 | 0.002374 | 0.003341 | 0.004656 |
| CO₂ in vloeistof (cum) | mol | 0.003569 | 0.009515 | 0.019062 | 0.032301 | 0.047351 | 0.064028 | 0.084133 | 0.107653 | 0.13422 |

| CO₂ belading mol CO₂/mol amine | 0.008932 | 0.023786 | 0.047655 | 0.080752 | 0.118378 | 0.160071 | 0.210332 | 0.269133 | 0.335551 |
| mol CO₂/kg solution | 0.002165 | 0.005772 | 0.011565 | 0.019596 | 0.028727 | 0.038845 | 0.051042 | 0.065311 | 0.081429 |
| P_CO₂ mbar | 0.3 | 1.5 | 3.4 | 6.6 | 10.8 | 17.7 | 25.3 | 35.6 | 49.6 |
### CO₂ Loading calculation with 2\(^{nd}\) varial coefficient for 0.8M DEA-Ethanol solution

#### 2\(^{nd}\) virial coefficient gassen (ref DIPPR):

<table>
<thead>
<tr>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>5.44E-02</td>
<td>-3.64E+01</td>
<td>-1.50E+06</td>
<td>8.59E+16</td>
</tr>
<tr>
<td>N₂O</td>
<td>4.34E-02</td>
<td>-3.41E+01</td>
<td>-1.61E+06</td>
<td>-3.20E+16</td>
</tr>
</tbody>
</table>

#### Belading Data

<table>
<thead>
<tr>
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<th>Datafile B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Belading</td>
<td>Meting</td>
</tr>
</tbody>
</table>

#### Gasbommetje

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<td>29.04</td>
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<td>0.998069</td>
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<td>0.009834</td>
<td>0.013628</td>
<td>0.017247</td>
<td>0.021358</td>
<td>0.024662</td>
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#### Reactor Data

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<td>0.006523</td>
<td>0.006635</td>
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<tr>
<td>CO₂ in gas phase (cum) mol</td>
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<td>3.14E-05</td>
<td>8.76E-05</td>
<td>0.00163</td>
<td>0.000275</td>
<td>0.00038</td>
<td>0.000062</td>
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<tr>
<td>CO₂ in liquid phase (cum) mol</td>
<td>0.003299</td>
<td>0.003934</td>
<td>0.019172</td>
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<td>0.04986</td>
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<td>0.095522</td>
<td>0.123754</td>
<td>0.155406</td>
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#### CO₂ belading

- **mol CO₂/mol amine** | 0.004123 | 0.011743 | 0.023965 | 0.040966 | 0.062325 | 0.08889 | 0.119441 | 0.154692 | 0.194257 |
- **[CO₂]t mol CO₂/kg solution** | 0.001973 | 0.005619 | 0.011468 | 0.019575 | 0.029825 | 0.042537 | 0.057156 | 0.074025 | 0.092959 |
- **P_{CO₂} mbar** | 0 | 0.3 | 0.9 | 1.7 | 2.9 | 4 | 6.4 | 9.1 | 11.8 |
## CO₂ Loading calculation with 2nd varial coefficient for 1.6M DEA-Ethanol solution

<table>
<thead>
<tr>
<th>2nd virial coefficient gassen (ref DIPPR):</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
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<tbody>
<tr>
<td>CO₂</td>
<td>5.44E-02</td>
<td>-3.64E+01</td>
<td>-1.50E+06</td>
<td>8.59E+16</td>
<td>-1.40E+19</td>
</tr>
<tr>
<td>N₂O</td>
<td>4.34E-02</td>
<td>-3.41E+01</td>
<td>-1.61E+06</td>
<td>3.20E+16</td>
<td>-3.56E+18</td>
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<table>
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<th>Datafile B</th>
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<td>2/9</td>
</tr>
<tr>
<td>CO₂-belading</td>
<td>3/9</td>
<td>4/9</td>
</tr>
<tr>
<td>CO₂-belading</td>
<td>5/9</td>
<td>6/9</td>
</tr>
<tr>
<td>CO₂-belading</td>
<td>7/9</td>
<td>8/9</td>
</tr>
<tr>
<td>CO₂-belading</td>
<td>9/9</td>
<td>1/10</td>
</tr>
</tbody>
</table>

| CO₂ naar reactor                          | mol       | 0.003393 | 0.006187 |
| CO₂ naar reactor                          | cum       | 0.003393 | 0.009586 |

| Reactor                                   | mbar     | 0.2      | 0.4      | 0.6      | 0.7      | 1       |

| CO₂ in gas phase (cum)                    | mol      | 1.93E-05 | 3.81E-05 | 5.42E-05 | 6.58E-05 | 9.21E-05 |
| CO₂ in liquid phase (cum)                 | mol      | 0.003374 | 0.009422 | 0.019474 | 0.032957 | 0.049555 |
| CO₂ belading                              | mol CO₂/mol amine | 0.002108 | 0.005964 | 0.012171 | 0.020598 | 0.031222 |
| [CO₂]t                                    | mol CO₂/kg solution | 0.001961 | 0.005546 | 0.011318 | 0.019154 | 0.029033 |
| P_{CO₂}                                   | mbar     | 0.2      | 0.4      | 0.6      | 0.7      | 1       |

### CO₂ Loading calculation with 2nd varial coefficient for 1.6M DEA-Ethanol solution

1. **Loading calculation with 2nd varial coefficient for 1.6M DEA-Ethanol solution**

   - **CO₂** Loading calculation
     - **CO₂-belading**
       - Datafile A
       - Datafile B
     - **Gasbommetje**
       - N/L/S/LS
       - LS

   - **CO₂ naar reactor**
     - mol
     - cum

   - **Reactor**
     - mbar
     - °C

   - **CO₂ in gas phase (cum)**
     - mol
     - 1.93E-05
     - 3.81E-05
     - 5.42E-05
     - 6.58E-05
     - 9.21E-05

   - **CO₂ in liquid phase (cum)**
     - mol
     - 0.003374
     - 0.009422
     - 0.019474
     - 0.032957
     - 0.049555

   - **CO₂ belading**
     - mol CO₂/mol amine
     - 0.002108
     - 0.005964
     - 0.012171
     - 0.020598
     - 0.031222

   - **[CO₂]t**
     - mol CO₂/kg solution
     - 0.001961
     - 0.005546
     - 0.011318
     - 0.019154
     - 0.029033

   - **P_{CO₂}**
     - mbar
     - 0.2
     - 0.4
     - 0.6
     - 0.7
     - 1

2. **2nd virial coefficient gassen (ref DIPPR):**

   - **CO₂**
     - 5.44E-02
     - -3.64E+01
     - -1.50E+06
     - 8.59E+16
     - -1.40E+19

   - **N₂O**
     - 4.34E-02
     - -3.41E+01
     - -1.61E+06
     - -3.20E+16
     - -3.56E+18

3. **Belading Meting**

   - Datafile A
   - Datafile B

4. **CO₂-belading**

   - 1/9
   - 2/9
   - 3/9
   - 4/9
   - 5/9
   - 6/9
   - 7/9
   - 8/9
   - 9/9

5. **Gasbommetje**

   - N/L/S/LS
   - LS

6. **P_{CO₂} mbar**

   - 0.2
   - 0.4
   - 0.6
   - 0.7
   - 1
## CO₂ Loading calculation with 2nd variational coefficient for 3.2M DEA-Ethanol solution

### 2de variële coefficient gassen (ref DIPPR):

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
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<tbody>
<tr>
<td>CO₂</td>
<td>5.4E-02</td>
<td>-3.6E+01</td>
<td>1.5E+06</td>
<td>8.59E+16</td>
<td>1.40E+19</td>
</tr>
<tr>
<td>N₂O</td>
<td>4.34E-02</td>
<td>-3.41E+01</td>
<td>1.61E+06</td>
<td>3.20E+16</td>
<td>4.56E+18</td>
</tr>
</tbody>
</table>

### Reactor in gas phase (cum)

<table>
<thead>
<tr>
<th></th>
<th>P mbar</th>
<th>T °C</th>
<th>B</th>
<th>Z</th>
<th>n mol</th>
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</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>63.9</td>
<td>20.17</td>
<td>-0.00012</td>
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<tr>
<td>N₂O</td>
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<td>20.2</td>
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</table>

### Reactor in liquid phase (cum)

<table>
<thead>
<tr>
<th></th>
<th>P mbar</th>
<th>T °C</th>
<th>B</th>
<th>Z</th>
<th>n mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3.48E-07</td>
<td>2.87E-05</td>
<td>0.999971</td>
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<tr>
<td>N₂O</td>
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<td>0.031391</td>
<td>0.050901</td>
<td>0.072622</td>
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</table>

### CO₂ belading

<table>
<thead>
<tr>
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<th>P ☺ mbar</th>
<th>B</th>
<th>Z</th>
<th>n mol</th>
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<tbody>
<tr>
<td>CO₂</td>
<td>0.00012</td>
<td>0.006061</td>
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### CO₂ belading

<table>
<thead>
<tr>
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<th>P mbar</th>
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<th>n mol</th>
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<tr>
<td>CO₂</td>
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</table>
Flux calculation from Experimental values

<table>
<thead>
<tr>
<th>[DEA] (mole/m³)</th>
<th>k_{app} (sec⁻¹)</th>
<th>D_{CO₂} (m²/sec)</th>
<th>m_{CO₂}</th>
<th>P_{CO₂} (mbar)</th>
<th>P_{CO₂} (bar)</th>
<th>√K_{app}D_{CO₂} (m/s^½)</th>
<th>Flux {J}_{CO₂} mole/m².s</th>
</tr>
</thead>
<tbody>
<tr>
<td>201</td>
<td>4.3</td>
<td>3.14E-09</td>
<td>2.98</td>
<td>37.1</td>
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<tr>
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<tr>
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Flux calculation from zwitterion mechanism

\[ k_{DEA}^z = 1.11 \times 10^{-4} \text{ m}^6/\text{mole}^2 \cdot \text{s} \]

\[ k_2 = 0.209166 \text{ m}^2/\text{mole} \cdot \text{s} \]

<table>
<thead>
<tr>
<th>[DEA] (mole/m\textsuperscript{3})</th>
<th>k\textsubscript{app} (sec\textsuperscript{-1})</th>
<th>D\textsubscript{CO2} (m\textsuperscript{2}/sec)</th>
<th>m\textsubscript{CO2}</th>
<th>P\textsubscript{CO2} (mbar)</th>
<th>P\textsubscript{CO2} (bar)</th>
<th>(\sqrt{k_{app} \cdot D_{CO2}}) (m/s\textsuperscript{1/2})</th>
<th>Flux J\textsubscript{CO2} (mole/m\textsuperscript{2}.s)</th>
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</table>
**Flux calculation from termolecular mechanism**

\[ k^T_{\text{DEA}} = 9.59 \times 10^{-5} \text{ m}^6/\text{mole}^2.\text{s} \]

<table>
<thead>
<tr>
<th>[DEA] (mole/m³)</th>
<th>( k_{\text{app}} ) (sec⁻¹)</th>
<th>( D_{\text{CO}_2} ) (m/sec)</th>
<th>( m_{\text{CO}_2} )</th>
<th>( P_{\text{CO}_2} ) (mbar)</th>
<th>( P_{\text{CO}_2} ) (bar)</th>
<th>( \sqrt{K_{\text{app}} \cdot D_{\text{CO}_2}} ) (m/s⁻¹/²)</th>
<th>Flux ( J_{\text{CO}_2} ) mole/m².s</th>
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<tbody>
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<td>37.1</td>
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Order of the reaction calculation and literature comparison

<table>
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<tr>
<th>This work</th>
<th>Crook</th>
<th>Versteeg 1988</th>
</tr>
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<tbody>
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<td>$k_{ov} / k_{app}$ sec⁻¹</td>
<td>[DEA] mole/m³</td>
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<td>529.1</td>
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</tr>
<tr>
<td>950</td>
<td>89</td>
<td>1343.42</td>
</tr>
<tr>
<td>1000</td>
<td>96</td>
<td>2262.58</td>
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<tr>
<td>1050</td>
<td>106</td>
<td>2388.55</td>
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<tr>
<td>1190</td>
<td>143</td>
<td>2613.48</td>
</tr>
<tr>
<td>1250</td>
<td>145</td>
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<td>1500</td>
<td>206</td>
<td></td>
</tr>
<tr>
<td>1580</td>
<td>245</td>
<td></td>
</tr>
</tbody>
</table>
Order of reaction, n = 1.7833

This work

Order of reaction, n = 1.9306

Crook 1988
Versteeg 1988

Order of reaction, $n = 1.5218$

$y = 0.0023x^{1.5218}$
## Hazardous activity identification process

### Unit: Kjemisk prosessteknologi  
**Date:** 23-01-2013

**Line manager:** Naveen Ramachandran / Greet Versteeg (Procede Group BV, The Netherlands)

**Participants in the identification process (including their function):** Muhammad Awais (Operator), Naveen Ramachandran (Co supervisor)

### Short description of the main activity/main process:

<table>
<thead>
<tr>
<th>ID no.</th>
<th>Activity/process</th>
<th>Responsible person</th>
<th>Laws, regulations etc.</th>
<th>Existing documentation</th>
<th>Existing safety measures</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleaning of equipment</td>
<td>Operator</td>
<td></td>
<td>Wearing Proper PPE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Preparation of sample</td>
<td>Operator</td>
<td></td>
<td>Wearing Proper PPE</td>
<td></td>
<td>To be prepared in specified chamber where air flow is available</td>
</tr>
<tr>
<td>3</td>
<td>Sample loading in equipment</td>
<td>Operator</td>
<td></td>
<td>Wearing Proper PPE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Sample taking from equipment</td>
<td>Operator</td>
<td></td>
<td>Wearing Proper PPE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Draining of chemical from equipment</td>
<td>Operator</td>
<td></td>
<td>Wearing Proper PPE</td>
<td></td>
<td>waste container to be disposed properly or recycled</td>
</tr>
<tr>
<td>6</td>
<td>Cleaning of equipment after experiment</td>
<td>Operator</td>
<td></td>
<td>Wearing Proper PPE</td>
<td></td>
<td>Vent valve should be open during cleaning and drying period</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## Risk assessment

**Unit:** Kjemisk prosessteknologi  
**Date:** 23-01-2013

**Line manager:** Naveen Ramachandran / Greet Versteeg (Procede Group BV, The Netherlands)

**Participants in the identification process (including their function):** Muhammad Awais (Operator), Naveen Ramachandran (Co Supervisor)

### Signatures:

<table>
<thead>
<tr>
<th>ID no.</th>
<th>Activity from the identification process form</th>
<th>Potential undesirable incident/strain</th>
<th>Likelihood:</th>
<th>Consequence:</th>
<th>Risk value</th>
<th>Comments/status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cleaning of equipment</td>
<td>breakage of glass ware, Chemical fumes</td>
<td>3</td>
<td>A</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>Preparation of sample</td>
<td>spillage of amines, Alcohol</td>
<td>4</td>
<td>B</td>
<td>B</td>
<td>B</td>
</tr>
<tr>
<td>3</td>
<td>Sample loading in equipment</td>
<td>spillage of chemical</td>
<td>4</td>
<td>B</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>4</td>
<td>Sample taking from equipment</td>
<td>spillage of chemical</td>
<td>4</td>
<td>B</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>5</td>
<td>Draining of chemical from equipment</td>
<td>spillage of chemical</td>
<td>4</td>
<td>B</td>
<td>A</td>
<td>A</td>
</tr>
<tr>
<td>6</td>
<td>Cleaning of equipment after experiment</td>
<td>breakage of glass ware</td>
<td>3</td>
<td>A</td>
<td>B</td>
<td>A</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1. IDENTIFICATION OF THE SUBSTANCE/MIXTURE AND OF THE COMPANY/UNDERTAKING

1.1 Product identifiers

Product name: Diethanolamine

Product Number: D8885
Brand: Sigma-Aldrich
Index-No.: 603-071-00-1
CAS-No.: 111-42-2

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses: Laboratory chemicals, manufacture of substances

1.3 Details of the supplier of the safety data sheet

Company: Sigma-Aldrich Chemie BV
Stationplein 4
3331 LL ZWIJNDRECHT
NETHERLANDS

Telephone: +31 78-620-5411
Fax: +31 78-620-5421
E-mail address: eurtechserv@sal.com

1.4 Emergency telephone number

Emergency Phone #: 112

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

Classification according to Regulation (EC) No 1272/2008 [EU-GHS/CLP]
Acute toxicity, Oral (Category 4)
Specific target organ toxicity - repeated exposure (Category 2)
Skin irritation (Category 2)
Serious eye damage (Category 1)

Classification according to EU Directives 67/548/EEC or 1999/45/EC
Harmful if swallowed. Harmful. Danger of serious damage to health by prolonged exposure if swallowed. Irritating to skin. Risk of serious damage to eyes.

2.2 Label elements

Labelling according Regulation (EC) No 1272/2008 [CLP]

Pictogram

Signal word: Danger

Hazard statement(s)
H302: Harmful if swallowed.
H315: Causes skin irritation.
H318: Causes serious eye damage.
H373: May cause damage to organs through prolonged or repeated exposure.

Precautionary statement(s)
P280: Wear protective gloves/eye protection/face protection.
P305+P351+P338: IF IN EYES: Rinse cautiously with water for several minutes. Remove
contact lenses, if present and easy to do. Continue rinsing.

Supplemental Hazard
Statements

Hazard symbol(s)

R-phrase(s)
R22 Harmful if swallowed
R38 Irritating to skin
R41 Risk of serious damage to eyes
R48/22 Harmful: danger of serious damage to health by prolonged exposure if swallowed.

S-phrase(s)
S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.
S36/37/39 Wear suitable protective clothing, gloves and eyewash protection.
S45 If swallowed, seek medical advice immediately and show this container or label.

2.3 Other hazards - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances
Synonyms: 2-hydroxyethyl)amine
2.2-iminodiethanol

Formula: C₄H₁₁NO₂
Molecular Weight: 105.14 g/mol

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethanolamine</td>
<td></td>
</tr>
<tr>
<td>CAS-No.</td>
<td>111-42-2</td>
</tr>
<tr>
<td>EC-No.</td>
<td>203-888-0</td>
</tr>
<tr>
<td>Index-No.</td>
<td>603-071-00-1</td>
</tr>
</tbody>
</table>

4. FIRST AID MEASURES

4.1 Description of first aid measures

General advice
Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled
If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact
Wash off with soap and plenty of water. Consult a physician.

In case of eye contact
Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed
Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

4.3 Indication of any immediate medical attention and special treatment needed
No data available
5. **FIREFIGHTING MEASURES**

5.1 Extinguishing media

   Suitable extinguishing media
   Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture

   Carbon oxides, nitrogen oxides (NOx)
   Nature of decomposition products not known.

5.3 Advice for firefighters

   Wear self contained breathing apparatus for fire fighting if necessary.

5.4 Further information

   no data available

6. **ACCIDENTAL RELEASE MEASURES**

6.1 Personal precautions, protective equipment and emergency procedures

   Use personal protective equipment. Avoid breathing vapors, mist or gas. Ensure adequate ventilation.
   Evacuate personnel to safe areas.

6.2 Environmental precautions

   Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the
   environment must be avoided.

6.3 Methods and materials for containment and cleaning up

   Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed
   containers for disposal.

6.4 Reference to other sections

   For disposal see section 13

7. **HANDLING AND STORAGE**

7.1 Precautions for safe handling

   Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.

7.2 Conditions for safe storage, including any incompatibilities

   Store in cool place. Keep container tightly closed in a dry and well-ventilated place. Containers which are
   opened must be carefully resealed and kept upright to prevent leakage.
   Air sensitive.

7.3 Specific end uses

   no data available

8. **EXPOSURE CONTROLS/PERSONAL PROTECTION**

8.1 Control parameters

   Components with workplace control parameters

8.2 Exposure controls

   Appropriate engineering controls
   Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and
   at the end of workday.

   Personal protective equipment

   Eye/face protection
   Tightly fitting safety goggles. Faceshield (8-inch minimum). Use equipment for eye protection
   tested and approved under appropriate government standards such as NIOSH (US) or EN
   166(EU).
Skin protection
Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove’s outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

The selected protective gloves have to satisfy the specifications of EU Directive 89/686/EEC and the standard EN 374 derived from it.

Immersion protection
Material: Nature latex/Chloroprene
Minimum layer thickness: 0.6 mm
Break through time: > 480 min
Material tested: Lepren® (Aldrich Z677556, Size M)

Splash protection
Material: Nitrile rubber
Minimum layer thickness: 0.11 mm
Break through time: > 30 min
Material tested: Dermatrix® (Aldrich Z677272, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)5659 873000, e-mail sales@kcl.de, test method: EN374
If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection
Complete suit protecting against chemicals. The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection
Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

a) Appearance Form viscous liquid
b) Odour no data available
c) Odour Threshold no data available
d) pH 11.0 - 12 at 105 g/l at 25 °C
e) Melting point/freezing point Melting point/range: 26 °C
f) Initial boiling point and boiling range 217 °C at 200 hPa
g) Flash point 138 °C - closed cup
h) Evaporation rate no data available
i) Flammability (solid, gas) no data available
j) Upper/lower flammability or explosive limits Upper explosion limit: 10.6 % (V)
   Lower explosion limit: 1.6 % (V)
k) Vapour pressure no data available
l) Vapour density 3.63 - (Ar = 1.0)
m) Relative density 1.097 g/mL at 25 °C
n) Water solubility 105 g/l at 20 °C - completely soluble
o) Partition coefficient: n-octanol/water log Pow: -2.18
p) Autoignition temperature no data available
q) Decomposition temperature no data available
r) Viscosity no data available
s) Explosive properties no data available
t) Oxidizing properties no data available

5.2 Other safety information
no data available

10. STABILITY AND REACTIVITY
10.1 Reactivity
no data available
10.2 Chemical stability
no data available
10.3 Possibility of hazardous reactions
no data available
10.4 Conditions to avoid
no data available
10.5 Incompatible materials
Oxidizing agents, Copper, Zinc, Iron
10.6 Hazardous decomposition products
Other decomposition products - no data available

11. TOXICOLOGICAL INFORMATION
11.1 Information on toxicological effects
Acute toxicity
LD50 Oral - rat - 710 mg/kg
LD50 Dermal - rabbit - 12,000 mg/kg
LD50 Intraperitoneal - rat - 120 mg/kg
LD50 Intravenous - rat - 778 mg/kg
Skin corrosion/irritation
Skin - rabbit - Mild skin irritation - 24 h - Draize Test
Serious eye damage/eye irritation
Eyes - rabbit - Severe eye irritation - 24 h
Respiratory or skin sensitization
no data available
Germ cell mutagenicity
no data available
Carcinogenicity
IARC: 3 - Group 3: Not classifiable as to its carcinogenicity to humans (Diethanolamine)
Reproductive toxicity
no data available
Specific target organ toxicity - single exposure
no data available

Specific target organ toxicity - repeated exposure
no data available

Aspiration hazard
no data available

Potential health effects
- Inhalation: May be harmful if inhaled. May cause respiratory tract irritation.
- Ingestion: Harmful if swallowed.
- Skin: May be harmful if absorbed through skin. May cause skin irritation.
- Eyes: Causes eye burns.

Signs and Symptoms of Exposure
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Additional Information
RTECS: KL2975000

12. ECOLOGICAL INFORMATION

12.1 Toxicity
- Toxicity to fish: mortality NOEC - Cyprinodon variegatus (sheephead minnow) - 540 mg/l - 96 h
  - LC50 - Pomphantes promelas (fathead minnow) - 1,460 mg/l - 96 h
- Toxicity to daphnia and other aquatic invertebrates: mortality NOEC - Daphnia magna (Water flea) - <4,2 mg/l - 11 d
  - EC50 - Daphnia magna (Water flea) - 55 mg/l - 48 h

12.2 Persistence and degradability
- Biodegradability: Result: > 90 % - Readily biodegradable

12.3 Bioaccumulative potential
no data available

12.4 Mobility in soil
no data available

12.5 Results of PBT and vPvB assessment
no data available

12.6 Other adverse effects
- Harmful to aquatic life.
  no data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods
- Product: Offer surplus and non-recyclable solutions to a licensed disposal company.
- Contaminated packaging: Dispose of as unused product.

14. TRANSPORT INFORMATION

14.1 UN number
- ADR/RID: -
- IMDG: -
- IATA: -

Sigma-Aldrich - D9885
### 14.2 UN proper shipping name

<table>
<thead>
<tr>
<th>ADR/RID</th>
<th>IMDG</th>
<th>IATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Not dangerous goods</td>
<td>Not dangerous goods</td>
<td>Not dangerous goods</td>
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</tbody>
</table>

### 14.3 Transport hazard class(es)

<table>
<thead>
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<th>IMDG</th>
<th>IATA</th>
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</thead>
<tbody>
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</table>

### 14.4 Packaging group

<table>
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<th>IMDG</th>
<th>IATA</th>
</tr>
</thead>
<tbody>
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</tbody>
</table>

### 14.5 Environmental hazards

<table>
<thead>
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<th>ADR/RID</th>
<th>IMDG Marine pollutant</th>
<th>IATA</th>
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</thead>
<tbody>
<tr>
<td>no</td>
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<td>-</td>
</tr>
</tbody>
</table>

### 14.6 Special precautions for user

No data available

---

### 15. REGULATORY INFORMATION

This safety datasheet complies with the requirements of Regulation (EC) No. 1907/2006.

#### 15.1 Safety, health and environmental regulations/legislation specific for the substance or mixture

No data available

#### 15.2 Chemical Safety Assessment

No data available

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### 16. OTHER INFORMATION

Further information

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