

Modeling the Formation of Degradation Compounds during Thermal Degradation of MEA

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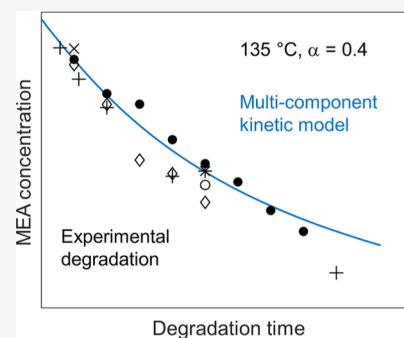
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ABSTRACT: A kinetic model has been developed to predict thermal degradation of aqueous solutions of monoethanolamine (MEA) in carbon capture. The model focusses on both the degradation rate of the amine and the formation rates of selected degradation products as a function of time, temperature, and loading. Experimental literature data on thermal degradation of MEA were used to develop, fit, and evaluate the model. The model was found to have an average relative deviation of 17.5%, most of which was caused by uncertainty in experimental data. The degradation model was also compared to a cyclic degradation campaign. The concentration of 1-(2-hydroxyethyl)-2-imidazolidinone (HEIA), one of the more stable thermal degradation products, is well-predicted with the thermal degradation model. However, the results also indicate that oxidative and thermal degradation mechanisms interact and that this interaction influences the concentration of several thermal degradation products.



INTRODUCTION

A reduction in carbon emissions is essential in reaching climate goals. One of the most promising processes for reducing these emissions in the short term is amine-based postcombustion carbon capture, as it is a process that can be retrofitted to current industrial installations. The flue gas, which contains the CO₂, is brought into contact with an aqueous amine solvent in an absorber, where it is selectively removed. The loaded solvent is then heated and introduced into the stripper. The higher temperatures in the stripper cause the CO₂ to desorb, regenerating the solvent.¹

Current research mainly focuses on improving the effectiveness and sustainability of the process, making it more attractive for implementation. One of the main challenges is extending the lifetime of the solvent by limiting losses through vaporization, entrainment, or solvent degradation and deactivation. Solvent degradation is problematic as it is responsible for a significant fraction of the amine losses but also because of the production of degradation products. These products have been shown to influence the performance of the capture plant by increasing foaming and viscosity or leading to higher corrosion rates in the plant.²

One of the degradation mechanisms is carbamate polymerization, often referred to as thermal degradation with CO₂. This form of degradation occurs at elevated temperatures in the capture process, for example, in the stripper and reboiler. A reduction in temperature at these locations can significantly reduce the degradation rate but can, at the same time, lead to higher specific energy requirements for regeneration.³ A good understanding of the degradation rates and mechanisms and the impact of degradation products on the process is thus

essential for efficient operation and the protection and maintenance of equipment.^{3,4}

In this work, the thermal degradation of monoethanolamine (MEA) is studied in more detail. Aqueous solutions of MEA are commonly used in carbon capture processes, and substantial data are available on degradation under typical process conditions. Several degradation models have been proposed to predict thermal degradation rates of MEA.^{5,6} The role of these models is to predict not only solvent losses in the process but also the formation of degradation products. This information is valuable for obtaining a better understanding of the effects of different solvent management strategies and the influence of degradation inhibitors.

However, the degradation models in the literature are often not in agreement, as a result of different model reactions and rate equations or the use of different data sets, which are often limited to experimental measurements by the authors themselves. Therefore, this work collects experimental data on the thermal degradation of MEA, which is then used to develop, fit, and evaluate a new degradation model. The developed model aims to predict quantitatively the solvent losses and degradation product formation as a function of time and other process conditions, such as temperature and loading.

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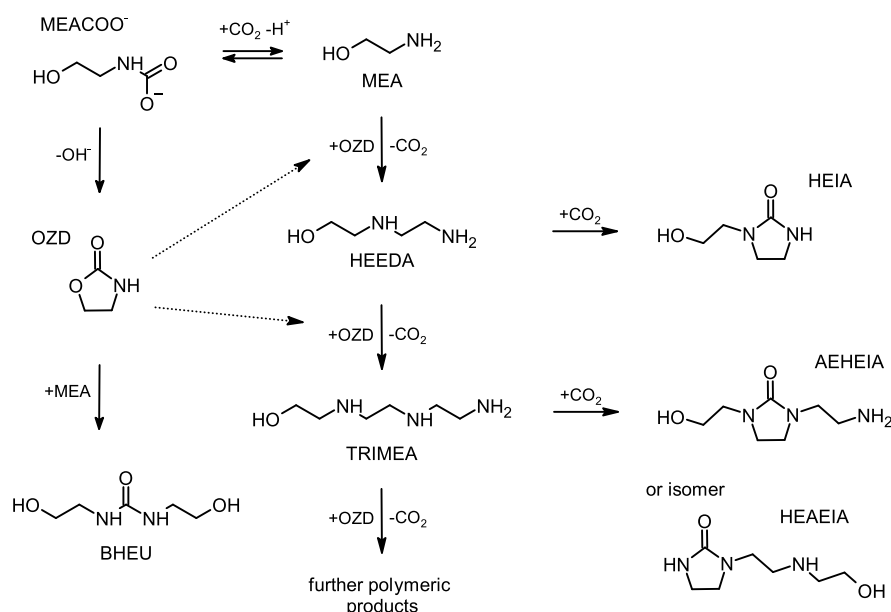


Figure 1. Overview of degradation reactions for carbamate polymerization of MEA as suggested by Davis⁵ and Lepaumier et al.⁸

Table 1. Amines and Thermal Degradation Compounds Considered in the Degradation Model

compound name	abbreviation	molecular formula	M_w (g/mol)	CAS registry
monoethanolamine	MEA	C ₂ H ₇ NO	61.08	141-43-5
2-oxazolidinone	OZD	C ₃ H ₅ NO ₂	78.08	497-25-6
<i>N</i> -(2-hydroxyethyl)-ethylenediamine	HEEDA	C ₄ H ₁₂ N ₂ O	104.15	111-41-1
1-(2-hydroxyethyl)-2-imidazolidinone	HEIA	C ₅ H ₁₀ N ₂ O ₂	130.15	3699-54-5
<i>N</i> -(2-hydroxyethyl)-diethylenetriamine	TRIMEA	C ₆ H ₁₇ N ₃ O	147.14	1965-29-3
<i>N</i> -(2-aminoethyl)- <i>N'</i> -(2-hydroxyethyl)imidazolidinone	AEHEIA	C ₇ H ₁₅ N ₃ O ₂	173.22	1402137-23-8
<i>N</i> -[2-[(2-hydroxyethyl)amino]ethyl]imidazolidin-2-one	HEAEIA	C ₇ H ₁₅ N ₃ O ₂	173.22	1154942-78-5
1,3-bis(2-hydroxyethyl)urea	BHEU	C ₅ H ₁₂ N ₂ O ₃	148.16	15438-70-7

Degradation Mechanism. An overview of the suggested degradation reactions is given in Figure 1 and the relevant compounds are listed in Table 1. The carbamate formed when CO₂ reacts with MEA is susceptible to degradation, and at increased temperatures, it undergoes ring closure and is dehydrated to form 2-oxazolidinone (OZD). OZD is sensitive to nucleophilic attacks and reacts with MEA, leading to the formation of dimers and oligomers, imidazolidinones, and other cyclic compounds. The cyclization of the carbamate leading to the formation of OZD is the rate-limiting reaction. This rate was found to be dependent on both temperature and CO₂ loading. Higher CO₂ loadings have been shown to increase degradation rates, possibly either by forming more of the carbamate or by increasing the availability of proton donors, which can catalyze the dehydration.³

The degradation mechanism of MEA has been discussed in the literature.^{5,7–11} Polderman et al.⁷ suggested a polymerization mechanism in which OZD reacted with MEA to form 1-(2-hydroxyethyl)-2-imidazolidone (HEIA). Subsequently, HEIDA was suggested to react with water to form *N*-(2-hydroxyethyl)-ethylenediamine (HEEDA) while expelling a molecule of CO₂. This was thought to be an equilibrium reaction that is influenced by temperature and the concentration of CO₂.

Davis⁵ later showed that the formation of HEEDA from HEIA is very limited under stripper conditions, whereas HEEDA readily reacts with CO₂ to form imidazolidone. HEIA is a relatively stable compound due to its five-ring structure,

and experimental degradation results show that the compound accumulates in the solution over time. After an initial increase, the concentration of HEEDA remains more or less constant for the rest of the experiments, confirming its role as an intermediate. This mechanism was also suggested by Lepaumier et al.⁸

Additionally, Davis⁵ found that HEEDA could react with OZD to form a trimer, *N*-(2-hydroxyethyl)-diethylenetriamine (TRIMEA), and further polymeric compounds. TRIMEA can react with CO₂ and form a cyclic urea through internal condensation. Depending on which amine group reacts with CO₂, two different isomers can be formed: *N*-(2-aminoethyl)-*N'*-(2-hydroxyethyl)imidazolidinone (AEHEIA) or *N*-[2-[(2-hydroxyethyl)amino]ethyl]imidazolidin-2-one (HEAEIA).^{5,10,12} Because the isomers are similar in structure and no commercial standard was available, no consensus has been reached as to which isomer is the most likely product.¹⁰

Another common degradation product is the urea of MEA, also known as 1,3-bis(2-hydroxyethyl)urea (BHEU). The formation of this product was reported by Yazvikova et al.¹³ A mixture of MEA and OZD was heated to 200 °C in the absence of water and the urea was observed as the only degradation product. The reaction mechanisms for BHEU and HEEDA are similar, and the exact route depends on where the cleavage of the OZD ring occurs. Lepaumier et al.¹² also proposed another mechanism for the formation of BHEU. In this case, MEA directly reacts with the carbamic acid of MEA to form the urea. However, under aqueous conditions, the ion

Table 2. Overview of Thermal Degradation Data from the Literature

source	temperature (°C)	loading	days	no. experimental measurements									
				MEA	CO ₂	OZD	HEEDA	HEIA	TRIMEA	HEAEBIA	AEHEIA	BHEU	
17	105–135	0.1–0.4	7–35	9	12	9	9						
10	135	0.1–0.5	7–35	25	20	5 ^a	5	5				5	
5	100–150	0.1–0.5	2–112	24			24	24	24	24			
6	120–140	0.44	7–21	6		6 ^a	6	6					
14	135	0.4	7–56	8			8				8		
15	125–145	0.4	0.6–7	3		1	1	1		1		1	1
18	160	0.19–0.37	14–56	6		6 ^a	6	6					
16	135	0.1–0.4	7–35	7	9	7	7	7					7
total	100–160	0.1–0.5	0.6–112	88	41	34	66	49	24	33	6	8	

^aThe concentration of OZD was measured using GC–MS and possibly also contains BHEU (see analytical methods).

pair of the protonated MEA and the MEA carbamate is more stable than the carbamic acid, so this reaction is unlikely to occur in an aqueous MEA solvent.¹²

Kinetic Degradation Models in the Literature. Kinetic models to describe thermal degradation of MEA have been developed by Davis⁵ and Léonard et al.⁶ Léonard et al.⁶ used HEIA as a surrogate for all the intermediates and degradation products but only analyzed the concentration of MEA. The degradation rate was determined by multiplying the reaction rate coefficient with the initial concentration of CO₂. The concentration of MEA has not been included in the rate equation because it is not considered to be limiting. The temperature dependence of the reaction rate coefficient was modeled using the Arrhenius equation.

The kinetic model by Davis⁵ is more extensive, including most of the degradation products, except for OZD and BHEU. No reliable experimental data were available on the concentration of OZD at the time, and Davis⁵ suggested that even if analytical methods would be improved, some of the OZD is likely to convert back to MEA carbamate during the cooling and handling of the samples. It was assumed that the concentration of OZD was in equilibrium with carbamate, which itself is directly related to the CO₂ concentration. At loadings below 0.5, it was assumed that the vast majority of CO₂ in the solution would be present in the form of carbamate, and as such, the concentration of CO₂ was used as a surrogate for OZD.

Analyses of degradation samples by Davis⁵ showed that the trimer was not an end product and could react with OZD and CO₂ to form other polymeric compounds and imidazolidones. The concentrations were significantly lower than those of other modeled compounds. Due to the sparse data on these compounds, they were not modeled directly but grouped together as further polymeric products. The reactions from the oligomers (HEEDA and TRIMEA) to the imidazolidones (HEIA and HEAEBIA) were modeled as rate-limited equilibrium reactions.⁵

Davis⁵ used the Arrhenius equation to describe the temperature dependency of the reactions and the pre-exponential factor and activation energy were fitted for each reaction. The pre-exponential factor and activation energy for the reaction from HEAEBIA to TRIMEA could not be determined due to insufficient experimental data of HEAEBIA and is estimated instead. The activation energy for the initial degradation reaction, describing the consumption of MEA, is comparable to the activation energy fitted by Léonard et al.⁶

METHODOLOGY

Model Development and Assumptions. The model in this work is an adapted version of the model by Davis⁵ and the following degradation reactions are taken into account



$$R_1 = k_1[\text{MEA}][\text{CO}_2] \quad (1)$$



$$R_2 = k_2[\text{HEEDA}][\text{CO}_2] \quad (2)$$



$$R_3 = k_3[\text{HEEDA}][\text{CO}_2] \quad (3)$$



$$R_4 = k_4[\text{TRIMEA}][\text{CO}_2] \quad (4)$$



$$R_5 = k_5[\text{MEA}][\text{CO}_2] \quad (5)$$

The equilibrium reactions from HEEDA and TRIMEA to the imidazolidones HEIA and AEHEIA are assumed to be irreversible. This assumption is based on degradation experiments, which showed that the reaction rate for the production of HEIA from HEEDA was significantly larger than the reverse reaction.⁵ Furthermore, concentration profiles of degradation products from experimental studies used in this work (see Table 2) also suggest that rate limitations are predominant, since an increase in concentration of HEIA has no immediate effect on the concentration of HEEDA. The model was tested by including these reverse and equilibrium reactions, but no improvements were observed.

Davis⁵ used the concentration of CO₂ as a surrogate for the carbamate and OZD concentrations. However, at higher loadings ($\alpha \approx 0.5$), nearly all of the MEA is saturated and a fraction of CO₂ will be present as carbonates and bicarbonates. The MEA carbamate concentration is thus lower than expected in these cases, and as a result, the degradation rate is expected to be overpredicted. In an attempt to include this behavior in the model, speciation models in AspenPlus and CO2SIM (in-house software) were used to predict the carbamate concentrations in the solutions. These were then used in the degradation model as a surrogate for the OZD concentration. The resulting degradation model, however, clearly under-predicted degradation in the experiments with a loading of 0.5.

The use of the total CO₂ concentration as a surrogate was also tested and gave a much better result. Intuitively, this is difficult to understand as one would expect the carbamate concentration to be directly proportional to the formation rate of OZD and thus the overall degradation rate. An explanation could be that the dehydration of the carbamate is the rate-limiting step. The availability of protons (e.g., in the shape of MEAH⁺) could then be rate-determining. Finally, it was decided to continue to use the total concentration of CO₂ as a surrogate for the OZD concentration.

The cyclic urea that is formed when TRIMEA reacts with CO₂ has been identified in the literature as AEHEIA¹⁰ or HEAEIA.^{5,14} Huang et al.¹⁵ reported to have identified and quantified both isomers in the degradation samples, but methods for identification are not elaborated and commercial standards of either of the isomers were not used. Because of the uncertainty, the model considers only one of the isomers, AEHEIA. Compounds that are identified as HEAEIA are assumed to be AEHEIA instead. Since the concentration of the isomers is low compared to the other degradation product, there should not be a significant error in the model in case both isomers are formed in reality.

The collection of experimental data used in this work includes liquid chromatography and mass spectroscopy (LC–MS) measurements of BHEU,^{15,16} which makes it possible to include the urea in the model. Where the formation of OZD is a result of an intramolecular reaction of the MEA–carbamate, BHEU is expected to be formed through an intermolecular reaction of MEA and carbamate.¹¹ The concentration of CO₂ is used as a surrogate for the carbamate concentration in this reaction as well. It is assumed that the urea is a stable end product and reverse reactions are not considered. Since all but one of the measured concentrations of BHEU were from experiments at 135 °C, temperature dependence is not considered for this reaction, and the activation energy is set at zero.

System of Equations. In the model, the change in concentration of a compound over time is described using eq 6. The change is equal to the sum of production and consumption in all the reactions (n_r). The degree of change in each reaction is the product of the stoichiometric coefficient ($v_{i,r}$), the reaction rate coefficient (k_r) in m³·mol⁻¹·s⁻¹, and the reactant concentrations (c_j) in mol/m³. Here, n_j is the number of reactants.

$$\frac{dc_i}{dt} = \sum_{r=1}^{r=n_r} \left(v_{i,r} k_r \prod_{j=1}^{j=n_j} c_j \right) \quad (6)$$

The reaction rate coefficient is defined using an adjusted form of the Arrhenius equation, see eq 7. Here, k_{ref} is the reaction rate coefficient at the reference temperature (T_{ref}) in m³·mol⁻¹·s⁻¹. This temperature was chosen to be 400 K as it was close to the average temperature of the degradation experiments. E_A is the activation energy in J/mol, and R is the ideal gas constant in J·K⁻¹·mol⁻¹.

$$k_r = k_{\text{ref}} \cdot \exp \left(\frac{-E_A}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right) \quad (7)$$

This form of the Arrhenius equation yields the same results as the conventional form but changes the interaction between the pre-exponential factor and the activation energy. For example, a change in activation energy will have no influence

on the reaction rate coefficient for a reaction at reference temperature. This allows the parameters to be changed more independently and simplifies the optimization.

Objective Function. To find the reaction rate parameters for the degradation model, an objective function is defined. This objective function describes the quality of the fit as a function of the parameter estimates. An optimization algorithm can then be used to search for the optimal reaction rate parameters. The objective function should be designed such that the contribution of each deviation from experimental data is representable to the expected accuracy of this data. Measurements with higher analytical uncertainty are more likely to result in a larger deviation between the modeled and experimental values and should be weighted accordingly.

This work uses data of various reactants and products from different sources, obtained using a range of analytical methods, including LC–MS, gas chromatography MS (GC–MS), and titration. Detailed information on the used analytical equipment and its accuracy, use of duplicates, dilution factors, and other extensive error analyses is in most cases not provided. Therefore, it is not easy to evaluate the accuracy and precisions of the different analytical techniques and it is assumed that the deviations are the same for all measurements.

A root-mean-square error objective function was initially used to fit the kinetic parameters, but the mean average error of the model was found to be nearly ten times larger than the analytical error observed in in-house LCMS calibration measurements. This indicates that other factors could play a significant role and influence the results of the degradation experiments. Furthermore, the concentration and absolute deviations of the degradation products and intermediates were found to be proportional. Both are thus a consequence of an increased degradation rate. The deviations of MEA and CO₂ were found to be less correlated with the rate of degradation. However, since the concentration of these compounds is higher, more dilution is required prior to analysis. As more dilution will lead to higher uncertainty, it is expected that the uncertainty is also proportional to the concentration for these compounds.

Since the error's exact nature is unknown, there is no clear reason to penalize more significant outliers using a root-mean-square function. Instead, a mean absolute error function was used, as given in eq 8. To account for the proportionality of the error, a weighing factor (w_i) is used, which is equal to the inverse experimental concentration (c_i). In case the concentration of the products is low, however, the weighing factor can become unrealistically high and distort the results. If the experimental concentration is below the expected analytical error (ϵ_A), the inverse of this expected error is used as the weighing factor instead. From in-house LC–MS measurements, the analytical error is found to be in the range of 25–50 mol/m³ depending on the compound, so the expected analytical error is set at a value of 50 mol/m³.

$$f(x) = \sum_{i=1}^{i=n} w_i \cdot |c_i - \hat{c}_i| \quad (8)$$

$$w_i = \min \left(\frac{1}{c_i}, \frac{1}{\epsilon_A} \right) \quad (9)$$

Optimization. Optimization of the objective function can be challenging, especially when the number of parameters (reaction rate coefficients and activation energies) is increased.

The complexity of the model may cause local optimization algorithms, such as Newton's method, to have problems finding a global minimum. For this reason, the optimization in this work is done using the particle swarm optimization (PSO) algorithm as implemented in MATLAB (R2019a). The PSO algorithm uses a swarm of particles which are distributed throughout the search space and evaluates the objective function at their location. The particles will then move through the search space based on the location of their own historical minimum and the location of the global minimum. Over time, the particles converge at a solution.

Global optimization algorithms such as PSO are generally better suited for multivariable optimization because they can overcome local minima. The default PSO algorithm settings were used as they provided satisfactory results. The number of particles was increased to 50 particles per model parameter as the optimization was not computationally demanding and this increased the accuracy of the optimization.

In the first step, the model was optimized using a constant activation energy of 100 kJ/mol for all the reactions. This provided a good estimation of the reaction rate coefficients at reference temperature, so the parameter ranges for the optimization of the complete system could be determined. Next, all the parameters were optimized. The optimization was run several times and the parameter boundaries as well as the initial guesses were adjusted to check if the same solution was obtained.

Repeatability and Lack-of-Fit F -Test. The sum of residual errors describes the deviation between the model and the experimental data. This deviation is the result of two factors: the variance of the measurements and the limitations of the model. These variances can be quantified and compared to test if the model is adequate or if there is a lack of fit.

The data set used in this work contains 24 sets of experiments that share the same model parameters (initial concentration, loading, temperature, and duration). These can give an insight in the repeatability of the degradation experiments and can be used to calculate the sum of pure experimental errors (SEP) using eq 10. For every set of replicates (i), the experimental measurements in the set (j) are compared to the average concentration of the set (\bar{c}_i). Note that the same weighting factor ($w_{i,j}$) as for the objective function (see eq 9) is used in this equation.

$$SEP = \sum_{i=1}^{i=n_s} \sum_{j=1}^{j=n_r} w_{i,j} |c_{i,j} - \bar{c}_i| \quad (10)$$

The sum of errors due to lack of fit (SELOF) makes up the rest of the residual error and is equal to the difference of sum of residual errors and the SEP. An F -statistic (F^*) is then determined by taking the ratio between the mean error due to lack of fit and the mean pure error (see eq 11). Here, n is the number of experimental measurements, p is the number of fitted parameters (coefficients and activation energies), and m is the total number of distinct replicate values.

$$F^* = \frac{\frac{SELOF}{m-p}}{\frac{SEP}{n-m}} \rightarrow F_{0.95,(m-p),(n-m)} \quad (11)$$

The statistical significance of the F -statistic is then compared to an F -distribution at 95% confidence, with the corresponding degrees of freedom. In case the F -statistic is smaller than the fence value of the F -distribution, there is no significant lack of

fit. If the F -statistic is larger, on the other hand, the contribution of the error due to lack of fit is statistically significant and the model is inadequate. Or in other words, the error between the model and experimental data cannot primarily be explained by the deviations in experimental results.

Experimental Data from the Literature. An overview of the available experimental data on carbamate polymerization is given in Table 2. Although some of the experiments are conducted below or around the conventional stripper temperature of 120 °C, most experiments are run at higher temperatures, as illustrated in Figure 2. The conditions cause

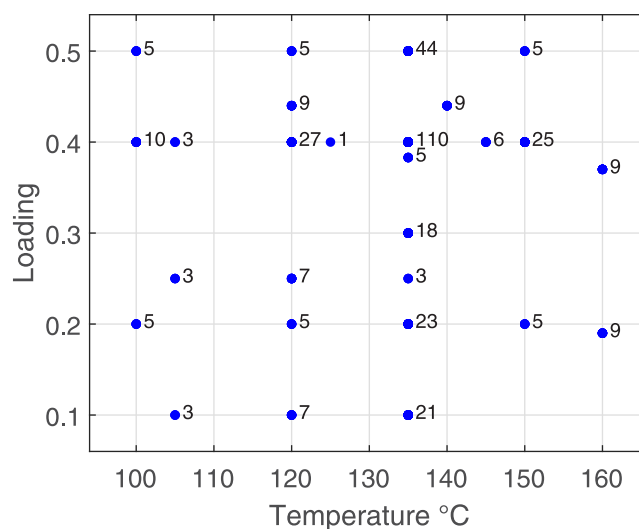


Figure 2. Overview of the number of data points under a given condition. The data points represent measurements of all components in all publications.

the degradation rate to increase and reduce the time required to observe significant degradation and product formation. This is done under the assumption that only the reaction rates change with temperature, but the reaction mechanism remains the same. Similarly, some of the experiments are run at high loadings to increase the degradation rate. These loadings are higher than commonly found in the stripper and reboiler and thus not representable.

The majority of the experimental data consist of measurements of MEA, HEEDA, and HEIA as these are the most prominent compounds. Less data are available on CO₂, OZD, and AEHEIA as these compounds are less commonly analyzed. The data on TRIMEA have only been reported by Davis⁵ most likely because the concentration of this compound is relatively low. Finally, limited data are available for BHEU and except from the single measurement by Huang et al.,¹⁵ all experiments where BHEU was measured were conducted at 135 °C. This, in combination with the relatively short degradation time of the experiments by Huang et al.,¹⁵ makes it difficult to evaluate the temperature dependency of the BHEU formation rate.

Experimental Procedures and Analytical Methods. The experimental data in Table 2 are from similarly performed degradation studies. In general, a solution of MEA and water was prepared, which was then loaded with CO₂. The loaded solvent was then placed inside a stainless-steel cylinder, which was hereafter closed. The cylinders were placed inside an oven at the specified temperature, without being stirred or agitated.

After a specified time, the cylinders were removed from the oven and cooled down, after which the solvent was analyzed.

In the experiments by Zoannou et al.,¹⁸ a larger vessel with more solvent was used. The solvent and pure CO₂ were introduced into the vessel and a total organic carbon analyzer was used to monitor the loading. When the specified loading was reached, the gas valve was closed and any CO₂ that was not absorbed was vented. The vessel was then sealed and placed in a convection oven for the duration of the experiment. The preparations and experimental conditions are thus similar to the cylinder experiments. However, the measurements at 160 °C showed unrealistically high degradation, to the point where nearly all MEA was consumed, so this data has been excluded from the dataset.

Several analytical methods have been used to determine the concentrations of MEA, CO₂, and degradation products in the literature studies. Titration methods are used to determine the concentration of CO₂ and sometimes also that of the amine.^{10,14,17} However, a downside of amine titration is that some of the intermediates and products, for example, HEEDA, can interact similar to the main amine and give a displaced representation of the actual concentration of MEA. Therefore, although titration is a relatively quick and inexpensive analytical method, the results are less accurate, and titration measurements have not been used for model fitting.

As alternatives to titration, LC–MS and ion chromatography are used to analyze the concentration of MEA and also some of the degradation products.^{6,10,15,16} These analytical methods give a better representation of the actual concentration of MEA, since the compounds in the solution are separated before quantification.

GC–MS is also used to identify and quantify degradation products.^{6,10,18} In-house analytical experience has shown that OZD and BHEU are hard to separate and identify individually using GC–MS. Although not explicitly reported, there are some indications that other works face similar challenges, as significantly higher concentrations of OZD are reported by studies that analyze using GC–MS^{6,10,18} compared to the results obtained in studies where LC–MS is used.^{15–17} This could indicate that the OZD which is analyzed with GC–MS is in reality the sum of OZD and BHEU. Additionally, the formation of BHEU was not reported in any of the GC–MS studies.

RESULTS

Optimized Model Parameters. The optimized parameters are given in Table 3. Although the rate coefficients are significantly lower for reactions 1 and 5, the reaction rate is in the same order of magnitude for all the reactions. The reason for this is that both reactions 1 and 5 have MEA as a reagent, which is present in much higher concentrations compared to the other compounds.

Table 3. Optimized Parameters for the Carbamate Polymerization Model

reaction	k_{ref} [m ³ ·mol ⁻¹ ·s ⁻¹]	E_A [kJ/mol]
1 (MEA to HEEDA)	1.599×10^{-11}	151.1
2 (HEEDA to TRIMEA)	3.054×10^{-10}	142.6
3 (HEEDA to HEIA)	1.117×10^{-10}	121.5
4 (TRIMEA to AEHEIA)	2.839×10^{-10}	136.2
5 (MEA to BHEU)	1.281×10^{-12}	

Lack-of-Fit *F*-Test. An overview of the variations for the data set and the fitted results is given in Table 4. In total, there

Table 4. Overview of the Variations and the Lack-of-Fit Evaluation

variation source	total variation	mean variation	degrees of freedom	<i>F</i> -statistic	<i>F</i> -fence
SE	50.0	0.175	286	0.96	1.63
SEP	5.65	0.182	31		
SELOF	44.4	0.174	255		

are 24 sets of replicates with mostly 2, 3, or 4 replicates each. The total number of distinct replicate values and thus the degrees of freedom for the SEP is 31. The mean deviation in the replicates is 18.2%, which is roughly similar to the mean deviation of the model. The results from the *F*-test also show that the lack of fit is not significant as the *F*-statistic is lower than the 95% *F*-distribution fence.

The variation in experimental results is also illustrated in Figure 3a. All the experimental observations in this figure describe degradation of a 30 wt % solution of MEA, with a loading of 0.4 and at a temperature of 135 °C. Although the experiments are identical on paper, there is still a significant deviation in the measured amine concentrations, which explains the substantial pure experimental error. Similar observations are made for the degradation products (e.g., Figure 4a).

Model Deviations and Trends. An overview of the relative deviations for each component is given in Figure 5. The mean relative deviation is 17.5%. The components have deviations that roughly average out around zero. The majority of the deviations are located around the average and only a few points show significant relative deviation, primarily for HEEDA, HEIA, or AEHEIA. Further inspection shows that these high relative deviations are caused by low absolute concentrations. Although the object function was designed to address this issue by limiting the weight of these points using a minimal analytical error, it is not entirely successful. It is possible that the analytical errors were more significant than expected for some of the measurements or that other errors were at play. Nevertheless, the contribution of the few high relative deviations is limited.

Figure 6 shows the model's relative deviations in MEA concentration for each of the experimental works. The model appears to overpredict the concentration of MEA for some of the experiments (e.g., Davis⁵ and Eide-Haugmo¹⁰). This means that the degradation in these experiments is relatively high with respect to the rest of the experiments. The experimental results by Léonard et al.,⁶ on the other hand, show less degradation than predicted. The figure thus illustrates that there are potentially some systematic errors at play. This agrees with the observations in Figures 3 and 4. Since the experimental methods for each of the studies are nearly identical, the reason for the discrepancies is unknown.

The absolute and relative deviations for HEIA as a function of several parameters are given in Figures 7 and 8, respectively. Figure 7 shows that the absolute deviations increase as the extent of degradation increases through higher temperatures, loadings, or longer durations. However, the last points (at 112 days) give low deviations as these experiments were performed at low loadings and/or temperatures leading into only a small amount of degradation. By applying weights according to eqs 8

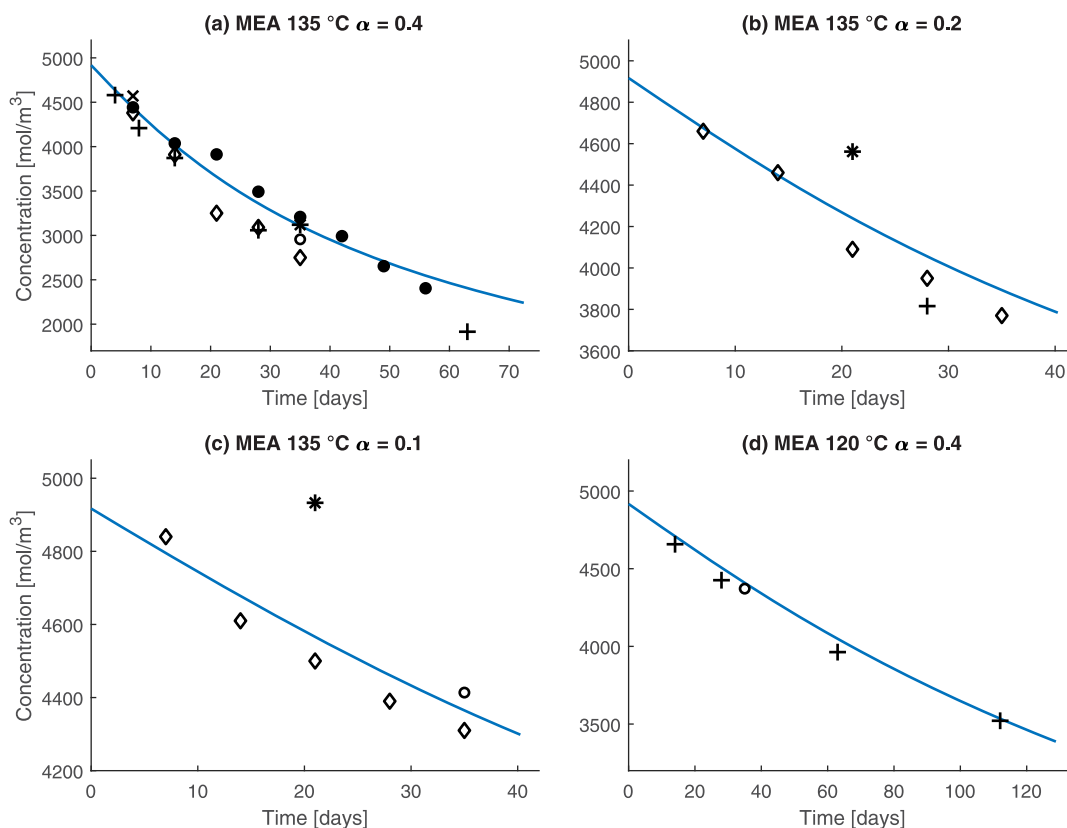


Figure 3. Modeled concentrations of MEA as a function of time for various loadings and temperatures compared to experimental measurements from the literature [(*) Høisæter et al.,¹⁶ (+) Davis,⁵ (\diamond) Eide-Haugmo,¹⁰ (\circ) Grimstvedt et al.,¹⁷ (\times) Huang et al.,¹⁵ and (\bullet) Zhou et al.¹⁴

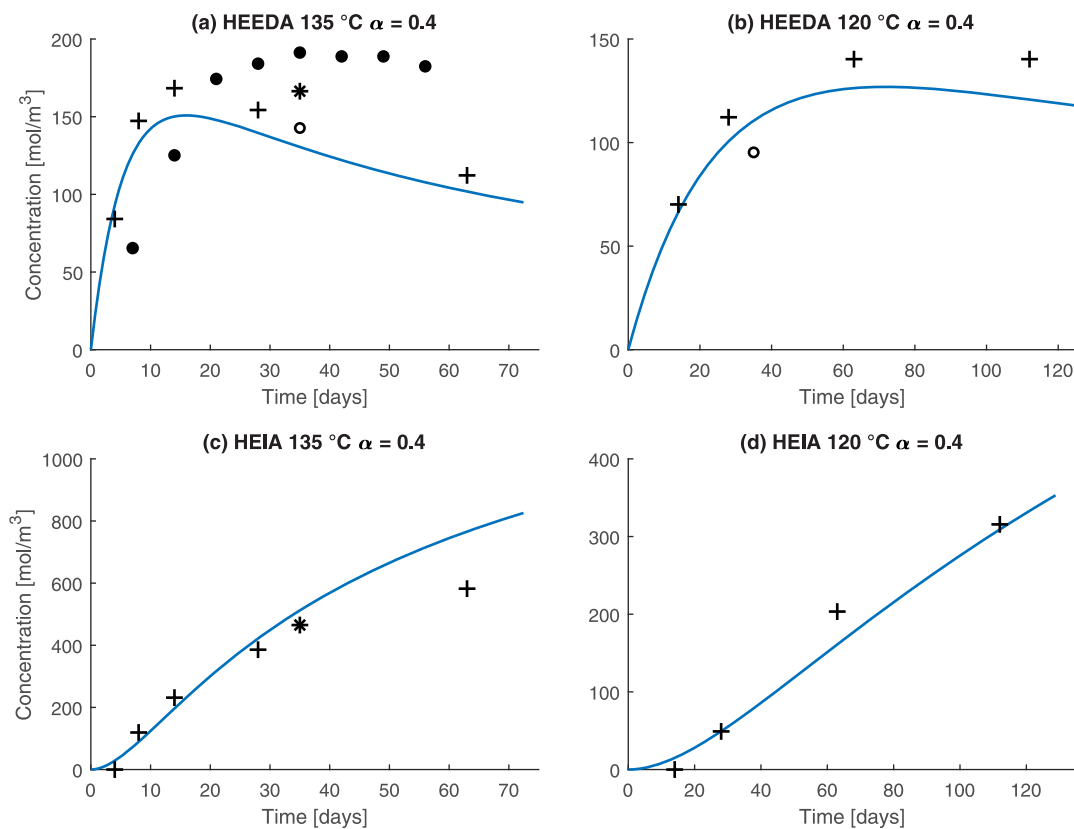


Figure 4. Modeled concentrations of the degradation products HEEDA and HEIA as a function of various loadings and temperatures compared to experimental measurements from the literature [(*) Høisæter et al.,¹⁶ (+) Davis,⁵ (\circ) Grimstvedt et al.,¹⁷ and (\bullet) Zhou et al.¹⁴

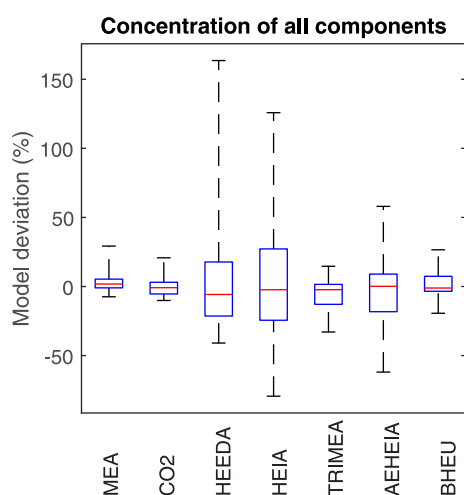


Figure 5. Box plot of the weighted deviations of the model in comparison with the experimental results for each of the components.

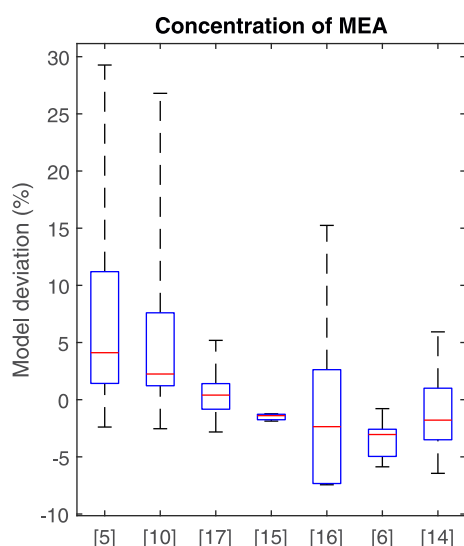


Figure 6. Box plot of the weighted deviations of the model for MEA in comparison with the experimental results for each of the experimental works (Davis,⁵ Eide-Haugmo,¹⁰ Grimstvedt et al.,¹⁷ Huang et al.,¹⁵ Høisæter et al.,¹⁶ Léonard et al.,⁶ and Zhou et al.¹⁴).

and 9, the contributions of the measurements are more balanced (see Figure 8). A similar behavior was observed for HEEDA and the other degradation products.

The absolute and relative model deviations for MEA are given in Figures 9 and 10. The relative deviation is smaller for MEA compared to the other degradation compounds. Figure 10 shows that the predictions of the model are accurate for higher concentrations of MEA, in which case the degradation is limited. In the case of high temperature or/and a high loading leading to more degradation, the model tends to overpredict the concentration of MEA, which means there is more degradation in the experiments than predicted.

One potential reason for the overprediction at high temperatures could be related to the formation rate of BHEU. Since there was not enough experimental data at different temperatures (experimental data for this compound were mainly available at 135 °C), the reaction rate was assumed to be temperature-independent. Experiments at higher temperatures could therefore produce more BHEU

and consume more MEA, which could explain why the model shows less degradation at high temperatures.

At a loading of 0.5, the overprediction of MEA corresponds with an underprediction of several degradation products, for example, HEIA (see Figures 7 and 8). The results thus suggest that there is more degradation than the model is able to represent at high loadings.

However, it is important to note that the deviations for MEA are in the same order of magnitude as the pure experimental error (18.2%). Experiments with significant degradation were found to deviate considerably from each other. Although there appears to be a trend that higher degradation leads to larger deviations in the model, it is important to consider that this could be the result of experimental uncertainty.

Comparison with Literature Models. The models of Davis⁵ and Léonard et al.⁶ have been implemented and were used to compare and evaluate the model developed in this work. The models were run starting with a fresh 30 wt % MEA solution loaded with CO₂ and under the specified conditions. The models were then assessed on their initial degradation rate and the total consumption rate of MEA at the beginning of the run. The model of Davis,⁵ which also contained reaction rate equations for the formation of degradation products, was also used to evaluate the production rate of HEIA. The model by Léonard et al.⁶ does not go in further detail on the formation of degradation products. First, the models were evaluated for a range of temperatures in the case of a rich solvent at a loading of 0.4. The results of the comparison are given in Figures 11 and 12.

The figures show the high-temperature dependency of the reaction rates, which is a result of significant activation energies in the Arrhenius equation. This dependency has been reported in the literature before.^{19,20} At lower temperatures, the model developed in this work predicts relatively high degradation rates. However, due to limited degradation under these conditions, the absolute differences remain limited. As the temperature and degradation rate increase, the model by Davis⁵ predicts similar MEA losses as the current model. The model by Léonard et al.,⁶ on the other hand, deviates more significantly from the current model and predicts lower degradation rates throughout the entire temperature range. At a temperature of 120 °C, the degradation rate is predicted to be 14.5 mol/m³/day. At this temperature, the model by Davis⁵ predicts a degradation rate of 15.6 mol/m³/day (+7.7%) and the model by Léonard et al.⁶ predicts a rate of 9.57 mol/m³/day (−34.0%).

With regard to HEIA, the model by Davis⁵ predicts significantly higher concentrations. At higher temperatures, the relative deviation appears to decrease, but at 135 °C, this deviation is still +40%. This is in agreement with the observation that the experimental concentrations of HEIA reported by Davis⁵ were slightly higher than measured by other researchers. The deviations between the models for the other degradation products were roughly in the same order of magnitude.

The models were then also evaluated at a constant temperature of 120 °C, which is the typical temperature of the reboiler in the stripper of the capture plant. The results of this comparison are given in Figures 13 and 14. The degradation rate and formation rate of HEIA show a more linear dependency on loading. As a result, the found model deviations are relatively constant as a function of temperature. At 120 °C, the model by Davis⁵ predicts a slightly higher

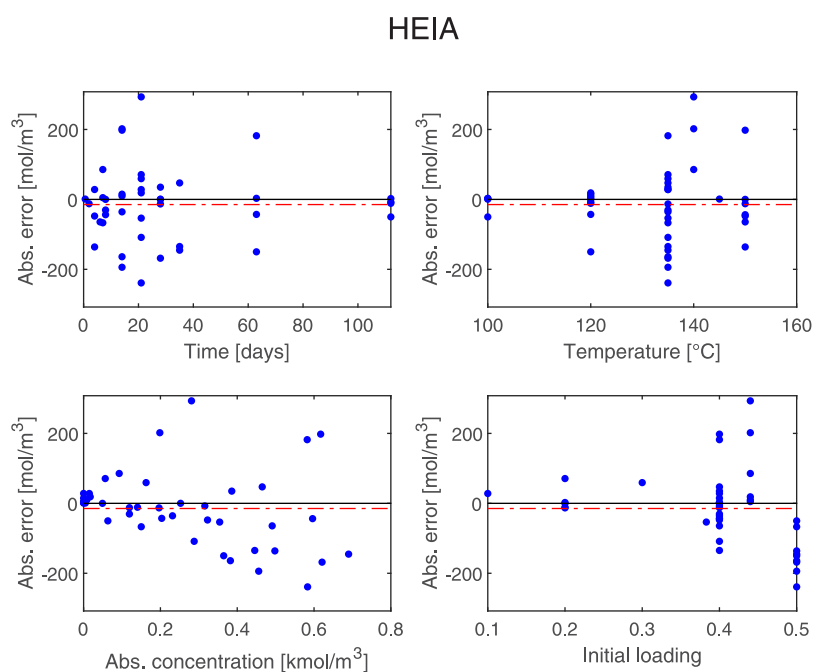


Figure 7. Absolute deviations for HEIA as a function of time, temperature, concentration, and initial loading. The red line indicates the average deviation.

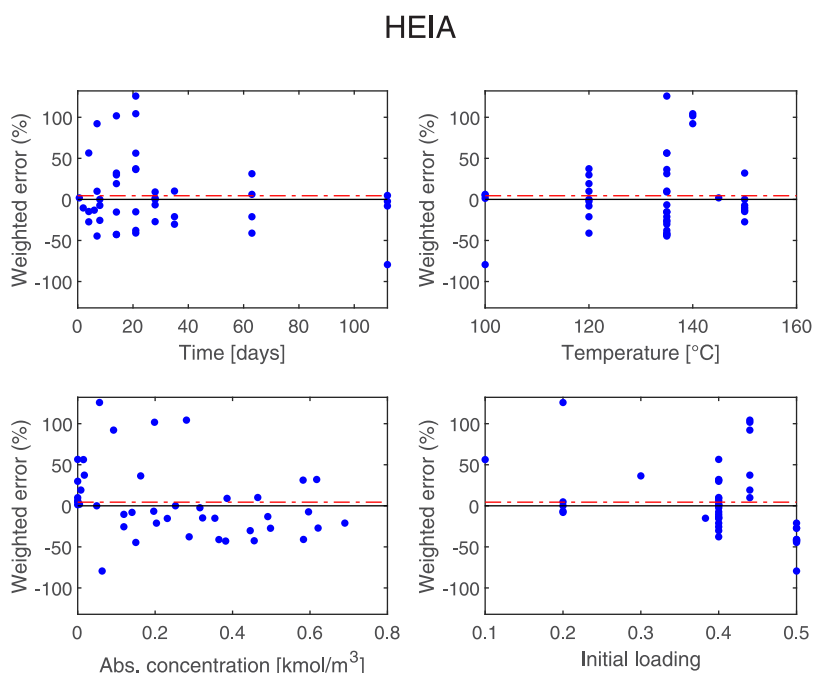


Figure 8. Relative deviations for HEIA as a function of time, temperature, concentration, and initial loading.

consumption of MEA, whereas the model by Léonard et al.⁶ predicts a significantly lower degradation rate. More HEIA is predicted to be formed by the model of Davis.⁵

Lack-of-Fit *F*-test for Literature Models. The models by Davis⁵ and Léonard et al.⁶ have been evaluated using all the data shown in Table 2, and the results are given in Table 5. The mean variation for the model by Davis⁵ was found to be 18.5%, which is slightly higher than the model from this work, but the *F*-statistic is still within the *F*-fence. This indicates that there is no significant lack of fit for the model.

Since the model by Léonard et al.⁶ does not quantify the formation of degradation products, it is evaluated only using data of MEA measurements. The same has been done for the other models to be able to compare the results. The mean relative deviation of the model by Davis⁵ is the lowest, followed by the model from this work and the model by Léonard et al.⁶

The lower mean relative deviations indicate that the uncertainty for the degradation products is high compared to the uncertainty in the MEA measurements. In addition, the mean pure experimental error (MSEP) of the MEA replicates

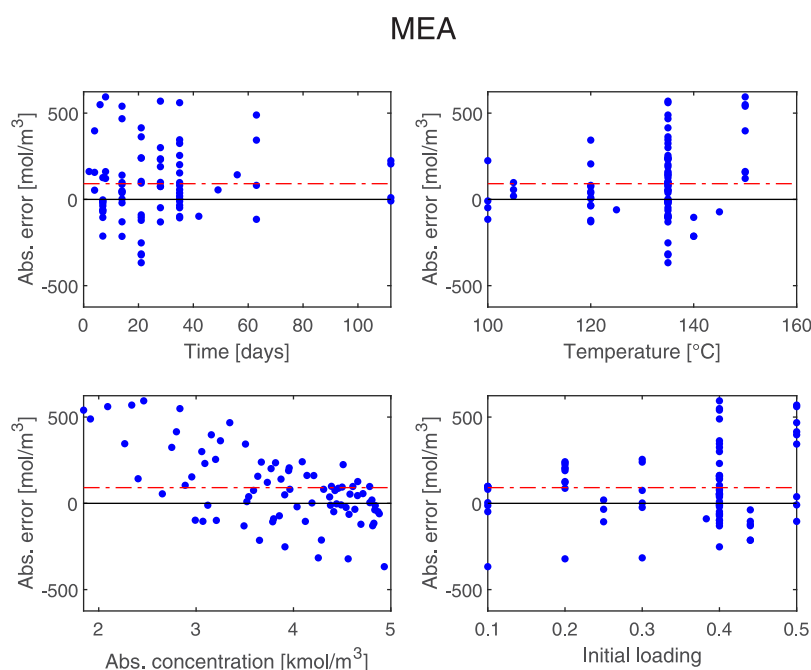


Figure 9. Absolute deviations for MEA as a function of time, temperature, concentration, and initial loading.

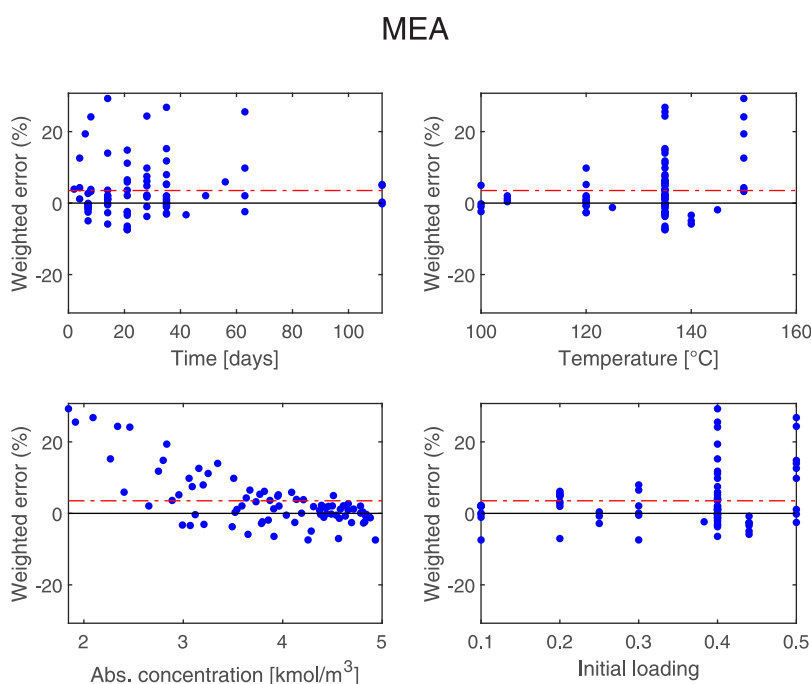


Figure 10. Relative deviations for MEA as a function of time, temperature, concentration, and initial loading.

is 7.1%, which is also significantly lower than the MSEP of the complete replicate data set. Therefore, also in this case, it appears that the experimental error limits the accuracy of the model. None of the models appear to have a lack of fit.

Experimental Uncertainty. The model deviations and the pure experimental error are more significant than the expected analytical error, which was also used in the objective function (see eqs 8 and 9). Only for less abundant components, such as the intermediate HEEDA, can the experimental uncertainty be explained by analytical deviations. The source of the uncertainty is thus expected to be experimental rather than analytical.

Despite the similarities of the experimental methods across the investigated works, there are some differences that could result in experimental uncertainty. In some experiments,^{8,10} glass containers were used to prevent metallic ions from leaching into the solvent. Nevertheless, this was not found to have significant effect on degradation.^{8,10} Also, in the error analysis of this work, no trends were observed with regard to the use of glass cylinders.

Furthermore, the temperature in the degradation ovens could potentially deviate and fluctuate during the experiments. In general, however, temperature control in degradation ovens is good and the deviations in the degradation model as a result

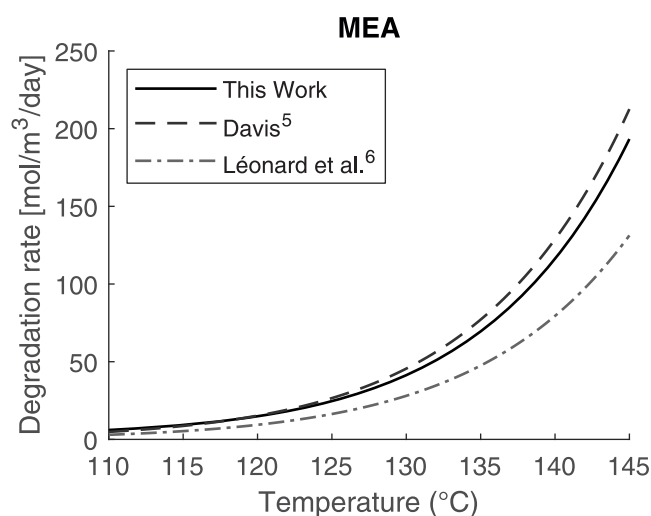


Figure 11. Comparison of the initial degradation rates of the models at a loading of 0.4.

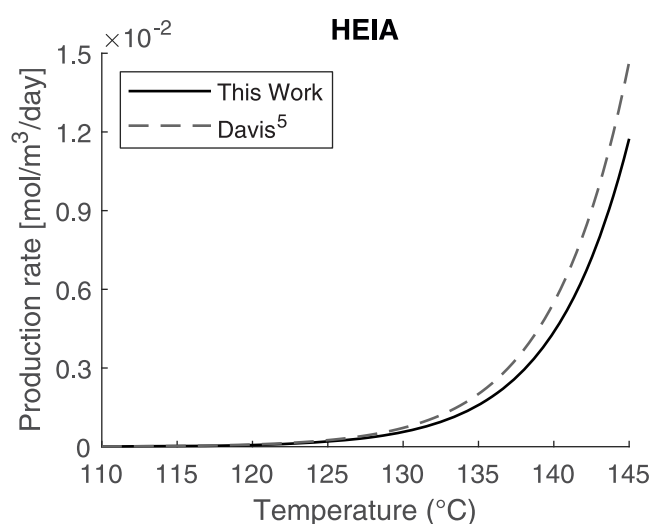


Figure 12. Comparison of the initial production rates of HEIA of the models at a loading of 0.4.

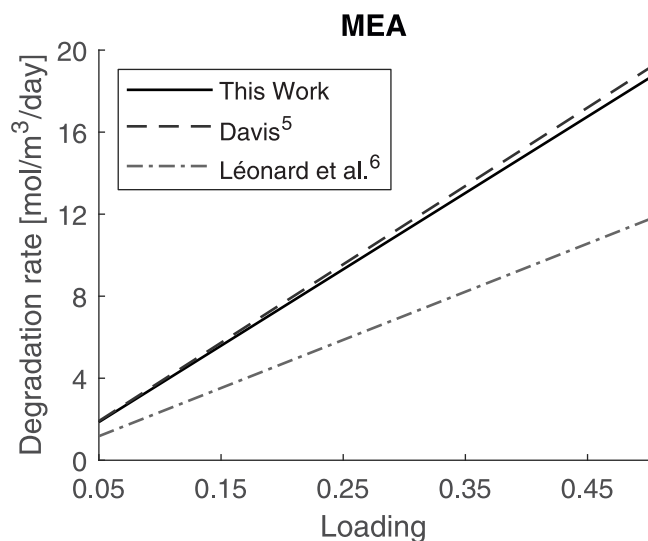


Figure 13. Comparison of the initial degradation rates of the models at 120 °C.

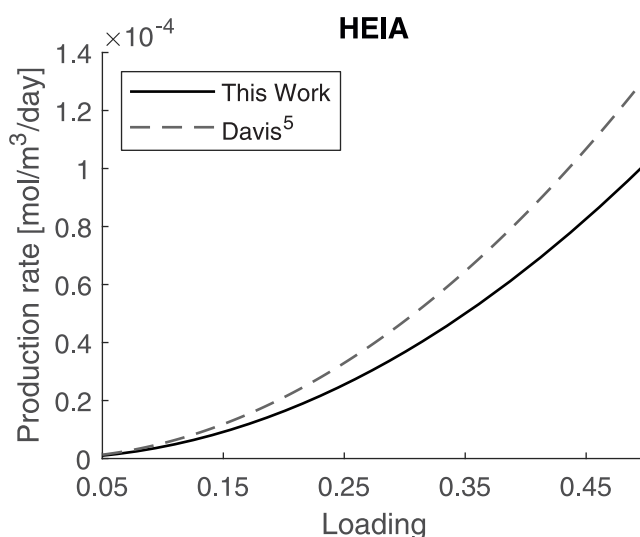


Figure 14. Comparison of the initial production rates of HEIA of the models at 120 °C.

Table 5. Variances and Lack-of-Fit *F*-Test of the Compared Models (This Work, Model by Davis,⁵ and Model by Léonard et al.⁶) for the Entire Data Set and for the Measurements of MEA Only

model	mean rel. error (%)	number of experiments	number of replicates	<i>F</i> -statistic	<i>F</i> -fence
this work	17.5	295	55	0.96	1.64
Davis ⁵	18.5	295	55	1.01	1.64
Léonard et al. ⁶ (MEA only)	8.1	82	25	1.17	2.16
this work (MEA only)	6.1	82	25	0.81	2.16
Davis ⁵ (MEA only)	5.0	82	25	0.62	2.16

of the expected temperature fluctuations were negligible compared to the model's error with respect to the experimental data.

Another parameter that is important in the experiments is the loading of the solution. In-house experience has shown that it can be challenging to accurately load a solvent gravimetrically and deviations up to 0.03 mol CO₂/mol MEA are not uncommon. Eide-Haugmo¹⁰ measured the CO₂ concentrations of the initial solutions in her work, which were found to deviate between 0.005 and 0.025 mol CO₂/mol MEA from the targeted loading. Other experimental works^{5,6,14,15,17} only report the targeted loading, while analytical results of the initial loaded solutions are often not given. Also, there could be a loss of CO₂ while transferring the solution during preparation of the degradation cylinders. Although not quantified, we expect this loss to be insignificant.

To assess the impact of a deviation in loading, the degradation model is used to simulate degradation experiments at 130 °C and around a loading of 0.3, which is approximating the average of the experimental data set. The initial loading is varied and the loss of MEA and production of HEIA and HEEDA are compared to the reference values at a loading of 0.3.

The sensitivity of the model with respect to the initial loading is shown in Figure 15. The figure shows that a deviation in the initial loading of 0.03 mol CO₂/mol MEA can have a significant effect on the solvent consumption and the

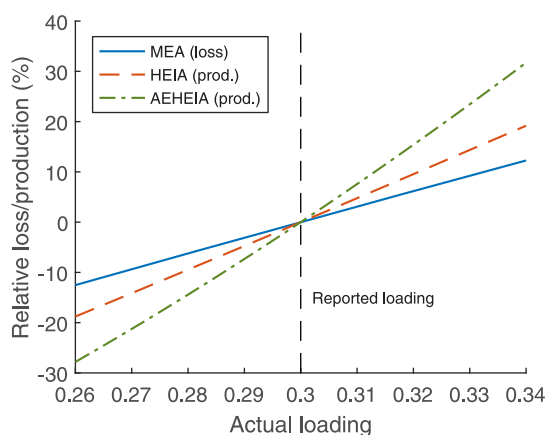


Figure 15. Effect of inaccurate initial loadings on the loss of MEA and production of HEIA and AEHEIA in modeled degradation experiments at 130 °C for 5 weeks.

production of degradation products, both of which are under- or overpredicted by 10–20%. This deviation is comparable with the pure experimental error and the mean relative deviation of the model, given in Table 4. Furthermore, the variations in the initial loading have a higher impact on the production of HEIA and AEHEIA than on the consumption of MEA, which is in line with the higher experimental uncertainty of degradation products observed in Figure 5.

The deviations in the solvent loading are thus expected to be the main cause of the observed experimental uncertainty. This can be reduced by analyzing and reporting the initial CO₂ loading instead of only providing the target loading. To get a loading closer to the target value, one could aim slightly higher during the gravimetric loading, measure the CO₂ concentration, and compensate for the difference by adding some unloaded solvent. Given the strong influence of the loading, it remains important to weigh the cylinders before and after degradation and to be critical toward leakages.

Model Performance for Circulative Degradation Rig and Pilot Operation. Vevelstad et al. investigated solvent degradation of a 40 wt % aqueous MEA solvent in the solvent degradation rig (SDR).²¹ The setup simulates an absorption/desorption system and uses a synthetic flue gas with 3 vol % CO₂, 12 vol % O₂, and 10 ppmv NO_x. During the 8 week campaign, the concentration of NO_x and reboiler temperature were varied. NO_x was increased to 100 ppmv from week 4 up to and including week 7. The stripper temperature was generally kept at 120 °C but was increased to 140 °C during weeks 5 and 6 to evaluate the degree of degradation at higher temperatures.

The conditions in different process parts and solvent volumes in them are given in Table 6. In the desorber sump, the CO₂ has been stripped from the solvent and the temperatures are equal to the reboiler temperature. The overflow of the reboiler sump was collected in a buffer vessel before passing through the heat exchanger. The temperature in this vessel is observed to be roughly 10 °C lower than the reboiler temperature due to heat losses to the environment.

The rich inlet temperature was observed to be 75 °C with a reboiler temperature of 120 °C and around 95 °C in the case of a reboiler temperature of 140 °C. For the plate heat exchanger, both the rich and lean flows were considered, and the holdup volume on each side was reported to be around 0.61 L. The temperature of the lean inlet was assumed to be 10

Table 6. Overview of the Estimated Degradation Volumes and Conditions in the SDR Equipment

	desorber sump	lean buffer vessel	rich inlet	heat exchanger
temperature (°C)	120/140	110/130	75–95	40–105
volume (L)	0.27 (5.4%)	0.29 (5.8%) ^a	0.02 (0.4%)	1.22 (24.4%)
loading	0.24–0.26	0.24–0.26	0.46–0.49	±0.25 and 0.48

^aThe level in the lean buffer vessel was not reported but it was assumed to be 50% of the total volume.

°C higher than the rich outlet temperature. The temperature corresponding with the average degradation rate in the heat exchanger was assumed to be 5 °C lower than the maximum temperature on each side, and this was used in the model.

Since the degradation experiment in the SDR was aimed at studying both oxidative and thermal degradation, as well as degradation by NO_x, the observed consumption of MEA is larger than that predicted using the degradation model, which only considers the thermal contribution. It is thus not possible to evaluate the thermal degradation model using these results. However, three of the thermal degradation products were also analyzed in the SDR experiment: HEEDA, HEIA, and BHEU. The model considers the formation rate of BHEU to be independent of the temperature because all but one of the measurements for this compound were at 135 °C. With most temperatures in the SDR setup well below this temperature, the thermal degradation model predicts a three times higher concentration of BHEU at the end of the experimental campaign. This also illustrates that the formation of BHEU is temperature-dependent and experimental data at different temperatures are needed.

Figure 16 shows that the concentration of HEEDA is overpredicted using the model. The measured concentrations

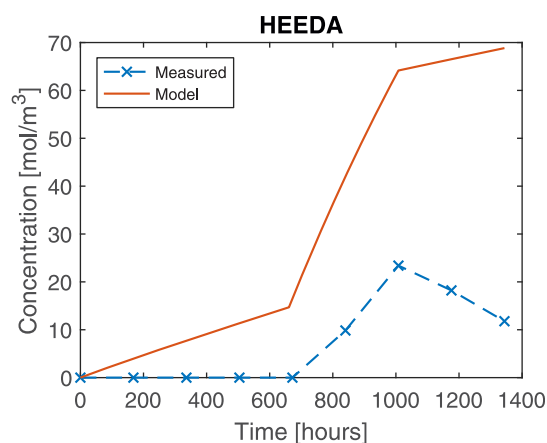


Figure 16. Modeled and experimental concentration profile of HEEDA during the SDR campaign.²¹

in the first 4 weeks were negligible. Only when the stripper temperature was increased to 140 °C for the next 2 weeks, the formation of HEEDA was observed. The rate at which the concentration increases is lower compared to the model prediction. This can be caused by either a lower production rate or additional consumption of the intermediate. This difference is expected to be caused by oxidative degradation,

due to the presence of oxygen in the flue gas of the degradation rig.

Vevelstad et al.²² investigated thermal degradation of MEA with an already oxidatively degraded solvent, from which they concluded that the same degradation products were formed and solvent loss was comparable to thermal degradation with a fresh solvent. Therefore, instead of oxidative degradation influencing thermal degradation, it is more likely that HEEDA partakes in oxidative degradation. This also explains the absence of HEEDA in the first weeks of the campaign and also the decrease in concentration during the final 2 weeks when the stripper temperature is reduced again.

Lepaumier et al.²³ showed that HEEDA is susceptible to oxidative degradation, so it is a possibility that it reacts with the dissolved oxygen in the absorber. Generally, however, the concentration of HEEDA is relatively low and the oxidative degradation reactions are probably not selective due to their radical nature, so the loss of HEEDA through oxidative degradation is expected to be limited.

A more probable alternative is the reaction between HEEDA and oxidative degradation products. Lepaumier et al.²³ suggested that HEEDA reacts with glycolic acid, which is followed by an intramolecular dehydration to form piperazinones, such as 4-(2-hydroxyethyl)piperazin-2-one (4HEPO). Gouedard¹¹ proposes an alternative mechanism, in which HEEDA reacts with glyoxal to form a vicinal diol that can be dehydrated to form the piperazinones. 4HEPO was also found to be a significant degradation product in the circulative degradation rig.²¹ The results thus suggest that HEEDA is consumed for the production of piperazinones when exposed to oxidative degradation products.

Furthermore, Huang et al.¹⁵ investigated the impact of flue gas contaminants on thermal degradation of MEA. It was found that the addition of 5000 ppm of nitrite significantly increased the production of HEEDA. Huang et al. proposed a slightly adjusted pathway for the degradation of MEA in which the nitrite reacts with a hydroxyl group on the MEA, after which this intermediate can react with another MEA and form HEEDA through an intermolecular substitution to cleave nitrite. Therefore, the NO_x in the flue gas of the SDR, which forms nitrite upon dissolution, could have increased the formation of HEEDA. This effect is not directly visible in the SDR results since a higher concentration of HEEDA would be expected in that case. The effect is possibly reduced by the relatively low concentration of NO_x in the flue gas and may be overshadowed by the consumption of HEEDA through reactions with oxidative degradation products. It would be interesting to see and compare the concentration profiles of the degradation products without the addition of NO_x .

The concentration of HEIA, on the other hand, seems to be well-predicted, as illustrated in Figure 17. Initially, at a normal stripper temperature, the formation of HEIA is limited and the degradation model is in line with the experimental results. When the stripper temperature is increased, both show an increase in HEIA production, with a slightly higher concentration for the model at the end of week 6. For the remainder of the experiment, the increase in HEIA concentration appears to be similar for both, with a difference of around 2 mol/m^3 . The formation of HEIA is considered to be a function of the concentration of HEEDA and CO_2 in the degradation model, and in the literature, it has been confirmed that HEEDA is a predecessor of HEIA. Since the concentration of CO_2 is controlled in the SDR, an overestimation of HEEDA

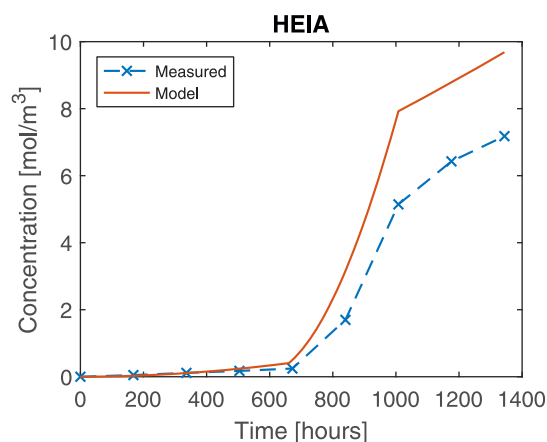


Figure 17. Modeled and experimental concentration profile of HEIA during the SDR campaign.²¹

is thus expected to also result in an overestimation of HEIA. However, this is not the case.

The model results also show that most of the thermal degradation takes place in the reboiler sump and the rich side of the heat exchanger, the latter mostly due to relatively high volumes in the heat exchanger. According to the degradation model, the thermal degradation rate in a typical reboiler ($a = 0.2$, $120 \text{ }^\circ\text{C}$) is nearly twice as large as the rate in a typical rich stripper inlet ($a = 0.5$, $100 \text{ }^\circ\text{C}$). This combined with a relatively large retention time in the reboiler causes it to be one of the main contributing locations of thermal degradation. When the stripper temperature is increased, this effect will become even more pronounced. A higher stripper temperature will have an effect on the temperature in the other parts of the plant, but due to the strong temperature dependency of the degradation reaction, the increase in degradation will be more substantial in the reboiler. In the case of the SDR, around 60% of the thermal degradation is expected to take place in the reboiler sump at a stripper temperature of $140 \text{ }^\circ\text{C}$.

Degradation of a 30 wt % MEA solvent was also investigated in a postcombustion capture pilot plant by Moser et al. in an 18-month test at Niederaussem.²⁴ For the first 335 days, the capture plant was operated without applying solvent management strategies or active reclaiming. The accumulated data for this period on degradation product concentrations can be used to evaluate the degradation model.

Solvent degradation of MEA in the Niederaussem plant was found to be lower compared to other capture plants and this is also reflected on the measured concentrations of HEEDA and HEIA. Like the comparison with SDR data, HEEDA is overpredicted substantially using the model, possibly due to the same reasons discussed previously.

The measured and modeled concentrations of HEIA over the course of the pilot run are shown in Figure 18. For the first 50 days, the concentration of HEIA seems to be well-predicted by the degradation model. Afterward, however, the growth in HEIA concentration stagnates in the capture plant, whereas the model predicts an increase. HEIA is considered to be a stable degradation compound and is expected to accumulate in the solution. The results at Niederaussem, however, suggest that either the formation of HEIA is slowed down or HEIA is consumed in consecutive reactions through, for example, polymerization or precipitation. It is hard to find a clear reason

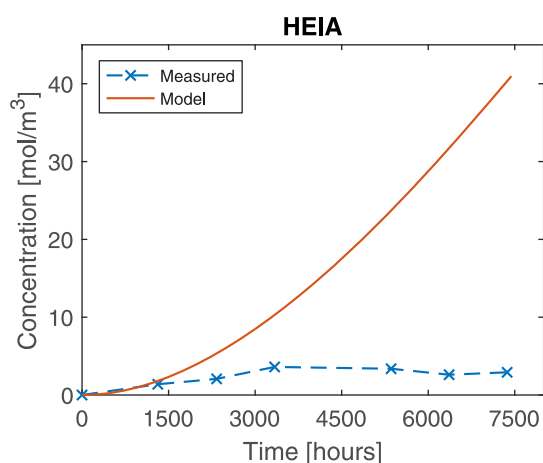


Figure 18. Modeled and experimental concentration profile of HEIA during the Niederaussem campaign.²⁴

for this behavior since it is not observed in the laboratory-scale studies.

It is important to consider that the duration of the laboratory-scale experiments, on which the degradation model is based, is limited and in most cases below 100 days. There could thus be a change in the degradation mechanisms or rates after extended exposure, and it would be interesting to investigate if a similar behavior is observed in laboratory-scale experiments over an extended period.

CONCLUSIONS

In this work, a model describing carbamate polymerization of aqueous MEA solutions was developed and fitted using a collection of experimental data from the literature. The model has an average relative deviation of 17.5%, most of which is a result of high experimental uncertainty and limited reproducibility. In comparison with the developed model, the degradation model by Davis⁵ slightly overpredicts degradation, whereas the model by Léonard et al.⁶ underpredicts degradation for the majority of conditions.

The current model overpredicted the concentration of MEA for experiments with high loadings. The reason for this behavior is unclear. However, analysis of experimental variances in replicates showed that the observed deviations are still in the same magnitude of the expected experimental variance. Since degradation under these conditions is often not encountered in postcombustion capture plants, more research could help to clarify the observed behavior, but model improvements will probably be limited.

The degradation model was able to predict the formation of HEIA in the SDR campaign accurately and the degradation product is shown to be a promising indicator of thermal degradation. The concentration of HEIA is usually low in comparison with other degradation products, so it is not a good indicator for the quality of the solvent but rather may help to quantify the degree of thermal degradation. Concentrations of HEIA in the Niederaussem capture plant were found to differ substantially from the model predictions. The low degradation rates during the campaign and the concentration profile of HEIA are unexpected and the data should be investigated in more detail as it is possible that other factors influenced the degradation mechanism or reaction rates.

The observed concentrations of HEEDA in the campaigns were not in agreement with the predictions from the degradation model. The conditions in the pilot plant campaigns are not as controlled as the laboratory-scale experiments and the presence of oxygen can influence the degradation mechanisms. The carbamate polymerization reactions are likely to interact with oxidative degradation reactions, which would explain the unexpected concentration profiles of HEEDA. Future research should therefore focus on clarifying this interaction between oxidative and thermal degradation as details on these mechanisms could be valuable for further development of the degradation model.

Finally, the use of more consistent experimental methodologies and more elaborate reporting of experimental conditions, assumptions and calculations, and analytical methods are required to improve the quality of the experimental results. This should lead to better reproducibility and more accurate model development.

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Notes

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NOMENCLATURE

- α CO₂ loading factor (mol/mol)
- c molar concentration (mol/m³)
- \hat{c} modeled molar concentration (mol/m³)
- \bar{c} average molar concentration (mol/m³)

ϵ_A expected analytical error (mol/m³)
 E_A activation energy (J/mol)
 k_r reaction rate coefficient (m³·mol⁻¹·s⁻¹)
 k_{ref} reaction rate coefficient at T_{ref} (m³·mol⁻¹·s⁻¹)
 R ideal gas constant (8.314 J·mol⁻¹·K⁻¹)
 T temperature (K)
 T_{ref} reference temperature (400 K)
 ν stoichiometric coefficient
 w weighing factor

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