

DEGRADATION OF DIETHANOLAMINE SOLUTIONS

by

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ABSTRACT

Raw natural gas contains acid gases such as H_2S and CO_2 which must be removed before the gas can be sold. The removal of these gases is called "sweetening" and the use of Diethanolamine (DEA) as a solvent has become widely accepted by industry. The process is simply based on the absorption and desorption of the acid gases in aqueous DEA. Side reactions can occur when DEA reacts with the CO_2 to produce degradation compounds. This degradation causes a loss in valuable DEA and an increase in plant operating costs.

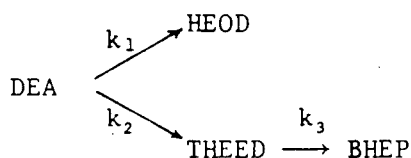
The reaction between DEA and CO_2 was studied experimentally, using a 600 ml stirred autoclave, to determine the effect of temperature, DEA concentration, and reaction pressure. Degraded DEA samples were analysed using gas chromatography. A fast, simple, and reliable technique was developed to analyse degraded DEA samples, which was ideally suited to plant use. Over 12 degradation compounds were detected in the degraded DEA solutions using gas chromatography and mass spectroscopy.

Degradation mechanisms are proposed for the production of the various compounds. It was found that the degradation of DEA was very sensitive to temperature, DEA concentration, and CO_2 solubility of less than 0.2 g CO_2 /g DEA. To study the effect of CO_2 solubility, which is a function of reaction pressure, simple solubility experiments were performed to cover the range of 100–200°C, 413.7–4137 kPa (60–600 psi) partial pressure of CO_2 and DEA concentration of 10, 20, and 30 wt % DEA.

It was found that the reaction between DEA and CO_2 was extremely complex consisting of a mixture of equilibria, parallel, series, and ionic reactions. However, the overall degradation of DEA could be simply described by a pseudo first order reaction.

The main degradation products were HEOD, THEED, and BHEP.* It was concluded that CO_2 acted as a catalyst being neither consumed nor produced during the degradation of DEA to THEED and BHEP. HEOD was produced from DEA and CO_2 , but was found to be unstable and could be converted back to DEA or react to form THEED and BHEP.

The following simple kinetic model was developed to predict the degradation of DEA and the production of the major degradation compounds:-



The model covered the ranges of DEA concentration 0-100 wt % DEA, 90-175°C, and CO_2 solubilities greater than 0.2 g CO_2 /g DEA.

Attempts were made to purify degraded DEA solutions. It has been claimed that activated carbon filters are useful in removing degradation compounds. However, tests with activated carbon proved it to be incapable of removing any of the major degradation compounds.

* See Nomenclature

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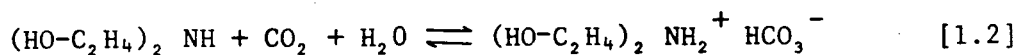
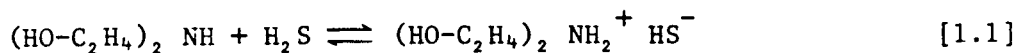
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CHAPTER 1

INTRODUCTION

Raw natural gas leaving the geological formation frequently contains undesirable compounds such as hydrogen sulphide, carbon dioxide, and water. The acid gases and the water must be removed before the natural gas can be sold in order to minimize pipe line corrosion, pumping costs, health hazards, and pollution when the gas is finally burnt or converted. Purification, or 'sweetening', of large volumes of 'sour' natural gas requires a process which is efficient and inexpensive. Further, in order for a purification process to be efficient, it must be regenerative, simple, and relatively trouble free. The use of aqueous diethanolamine (DEA) has emerged as the best approach to the sweetening of sour natural gas.

The process is based on the reaction of a weak base (DEA) with a weak acid (H_2S or CO_2) to give a water soluble salt. The reactions may be summarized as follows:-



These reactions are reversible and the equilibria may be shifted by regulating the temperature.

The basic industrial process (see Fig. 1.1) consists essentially of contacting the sour natural gas with a counter current stream of an aqueous DEA solution (usually about 15-30 wt % DEA) at 30-50°C and at

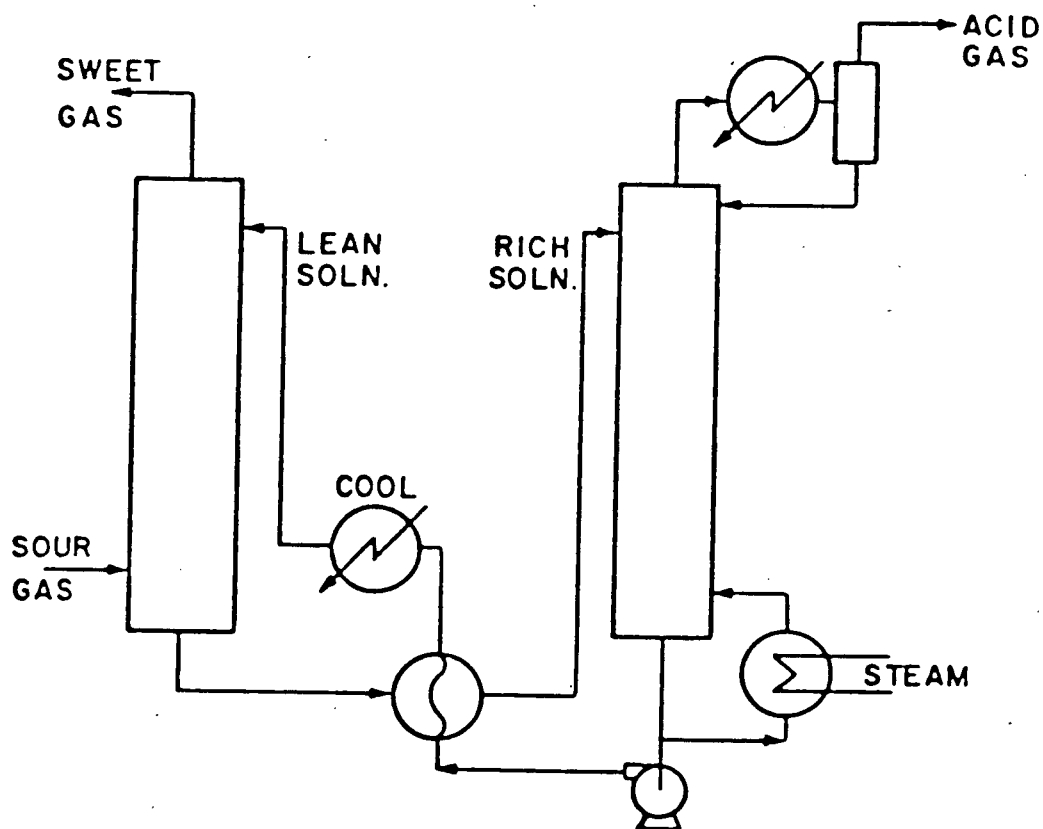


Figure 1.1 Flow sheet of the basic amine process

pressures ranging from atmospheric to well over 6895 kPa (1000 psi). The acid gases are absorbed by the DEA and the 'rich' DEA is then pumped to an amine stripper. In the stripper the pressure is reduced and the temperature raised to 100-120°C, which is sufficient to remove all but trace quantities of the acid gases. The 'lean' DEA is then recycled back to the absorber.

DEA's popularity is based on several factors:- low energy requirements compared with most other solvents, high affinity for acid gases, and resistance to degradation. Degradation is defined as the irreversible transformation of DEA into undesirable compounds. Plant experience has shown, however, that degradation does occur and with, at times, surprising speed. Incidents have been reported in which gas plants have lost their entire DEA inventory within a matter of days.

Degradation is undesirable for three main reasons. First, it represents a loss of valuable DEA; second, the degradation products accumulate leading to equipment fouling; third, it is suspected that some degradation products are highly corrosive. Plant operators have tried to solve the problem by changing operating conditions and/or installing activated carbon filters.¹ The filters are believed to absorb the degradation compounds. In some cases these measures are successful, but in others they are inadequate for reasons which are not clearly understood. Furthermore, satisfactory procedures for one gas plant are often ineffective for others. There can therefore be no doubt that the Canadian gas processing industry incurs multimillion dollar costs every year due to DEA losses and increased maintenance resulting from DEA degradation. Consequently, there is a strong incentive to learn how to prevent (or at least minimize) DEA degradation.

1.1 Objectives of the present study

Although DEA samples from industrial sweetening units are routinely analysed to monitor the purity of the solution and to detect degradation compounds, very little has been published in the open literature on DEA degradation. Furthermore the available studies are purely qualitative and no attempt has been made to explain quantitatively the degradation behavior.

Thus the main objectives of this study are:-

- a) To develop a simple analytical technique for analysing degraded DEA solutions. Preferably, the technique should be suited for plant use.
- b) To isolate and identify the primary degradation compounds.
- c) To determine the degradation rates as a function of temperature, pressure, and initial DEA concentration.
- d) To elucidate a reaction mechanism for the production of the various degradation compounds.
- e) To develop a kinetic model which can predict the degradation of DEA and the production of degradation compounds under typical industrial conditions.
- f) To propose ways of reducing DEA degradation in industrial sweetening units.
- g) To investigate ways of purifying degraded DEA solutions and to study the effectiveness of activated carbon.

Since DEA degradation results primarily from reaction with CO_2 , the present study emphasizes degradation due to CO_2 rather than H_2S and other compounds such as O_2 , CS_2 and COS .

CHAPTER 2

LITERATURE REVIEW

The DEA sweetening process has been widely accepted for removing CO_2 and H_2S from natural gas.²⁻⁷ There have been several studies mainly directed at improving plant performance⁸⁻¹¹ and removing degradation products.^{1,12,8} In addition there are several handbooks available which review natural gas processing and present general analytical methods for routine analysis of gas treating solutions.¹³⁻¹⁷

However, there are surprisingly few references dealing specifically with DEA degradation and the analysis of the degradation products. In fact most of the experimental studies have been limited to the absorption of CO_2 into DEA which takes place in a matter of seconds whereas degradation takes place over a period of months.¹⁸⁻²⁹

2.1 Absorption of CO_2 in aqueous DEA solutions

The mechanism of CO_2 absorption, unlike that of H_2S , is not simple and involves the establishment of several equilibrium reactions. Although the literature on CO_2 absorption is extensive, the absorption is still not fully understood.

When a CO_2 molecule dissolves in water, due to its acidic chemical characteristics it first hydrates to form carbonic acid, H_2CO_3 (see Eq. 2.1. in Table 2.1). The H_2CO_3 molecule, in turn, slightly dissociates to form hydrogen (H^+) and bicarbonate (HCO_3^-) ions. The bicarbonate ion

Table 2.1 Equations governing CO₂ absorption in aqueous DEA solution (R denotes C₂H₄OH)

<i>Acid-base reaction</i>	
$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$	[2.1]
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{HCO}_3^- + \text{H}^+$	[2.2]
$\text{HCO}_3^- \rightleftharpoons \text{CO}_3^{--} + \text{H}^+$	[2.3]
$\text{R}_2\text{NH} + \text{H}_2\text{O} \rightleftharpoons \text{R}_2\text{NH}_2^+ + \text{OH}^-$	[2.4]
$\text{R}_2\text{NH} + \text{H}^+ \rightleftharpoons \text{R}_2\text{NH}_2^+$	[2.5]
$\text{CO}_2 + \text{OH}^- \rightleftharpoons \text{HCO}_3^-$	[2.6]
$\text{R}_2\text{NH}_2^+ + \text{HCO}_3^- \rightleftharpoons [\text{R}_2\text{NH}_2^+][\text{HCO}_3^-]$	[2.7]
$2\text{R}_2\text{NH}_2^+ + \text{CO}_3^{--} \rightleftharpoons [\text{R}_2\text{NH}_2^+]_2[\text{CO}_3^{--}]$	[2.8]
$[\text{R}_2\text{NH}_2^+]_2[\text{CO}_3^{--}] + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 2[\text{R}_2\text{NH}_2^+][\text{HCO}_3^-]$	[2.9]
<i>Carbamate formation</i>	
$\text{R}_2\text{NH} + \text{CO}_2 \rightleftharpoons \text{R}_2\text{NH}^+\text{COO}^-$	[2.10]
$\text{R}_2\text{NH}^+\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{R}_2\text{NCOO}^- + \text{H}_3\text{O}^+$	[2.11]
$\text{R}_2\text{NH}^+\text{COO}^- + \text{OH}^- \rightleftharpoons \text{R}_2\text{NCOO}^- + \text{H}_2\text{O}$	[2.12]
$\text{R}_2\text{NH}^+\text{COO}^- + \text{R}_2\text{NH} \rightleftharpoons \text{R}_2\text{NCOO}^- + \text{R}_2\text{NH}_2^+$	[2.13]
$\text{R}_2\text{NCOO}^- + \text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{R}_2\text{NH}_2^+ + \text{HCO}_3^-$	[2.14]

and the DEA molecule may then react thereby forming the DEA bicarbonate (see Eq. 2.7). The solubility of CO_2 in water is thus enhanced by the presence of DEA. This is due to DEA being alkaline and forming hydroxyl ions (OH^-) with water. The OH^- can then also react directly with CO_2 to form HCO_3^- (see Eq. 2.6). The overall rate of CO_2 absorption by these acid-base reactions is quite slow, especially when compared to the absorption of H_2S . The difference between these rates of absorption has led to the development of amine processes that are able to selectively absorb H_2S .^{30,31,32}

A second set of CO_2 absorption reactions also occurs involving the labile hydrogen atom present in the DEA molecule. In this case the CO_2 molecule reacts directly according to Eq. 2.10 with the DEA molecule to form a zwitterion complex, i.e., a dipole molecule which is extremely unstable.²³ The zwitterion is then rapidly deprotonated by water, OH^- or another amine molecule (see Eqns. 2.11 to 2.13), to form the DEA carbamate, R_2NCOO^- . The rate of CO_2 absorption via the carbamate reactions is much faster than the CO_2 acid-base reaction, but still somewhat slower than the H_2S absorption reaction.

Astarita et al.²¹ proposed that the enhancement of CO_2 solubility in water by DEA is due to a rather complex "mass transfer with chemical reaction" mechanism. In the region near the gas-liquid interface, CO_2 was postulated to dissolve in the water and undergo the fast carbamate reactions. The reactions were believed to be fast enough to cause a steep CO_2 concentration profile near the gas-liquid interface and thereby increasing the mass transfer rate. The carbamate ion diffuses into the bulk of the liquid where it reverts to bicarbonate and liberates free amine (see Eq. 2.14). The amine is then able to diffuse back to

the interface region where it can react with additional CO_2 . This results in an increased solubility of CO_2 by converting CO_2 to HCO_3^- . The qualitative behaviour is shown in Fig. 2.1.

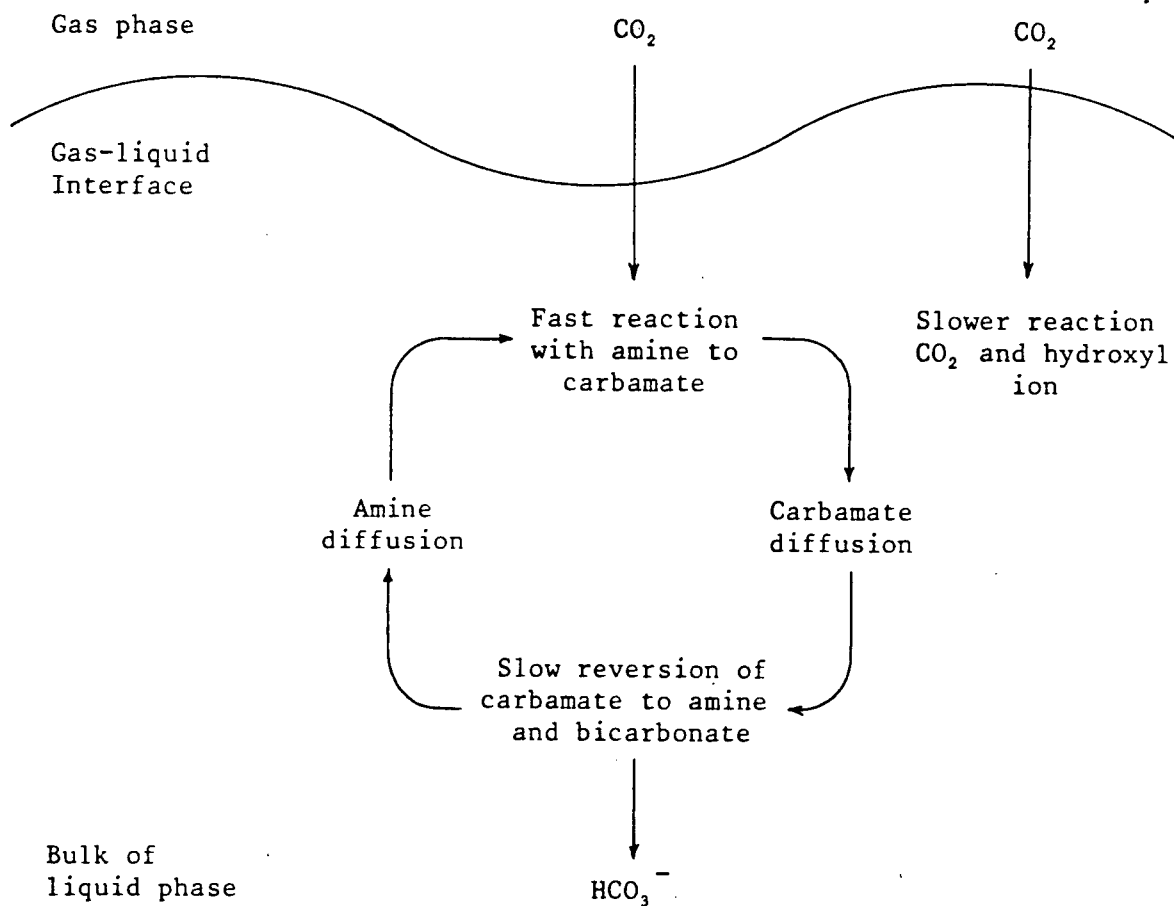
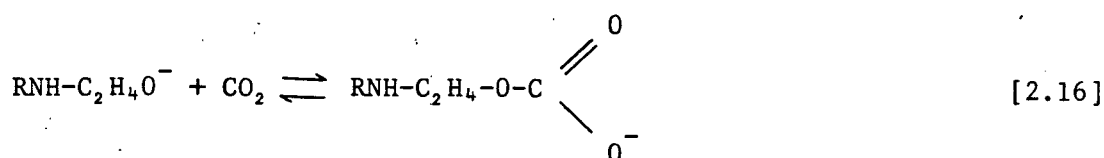
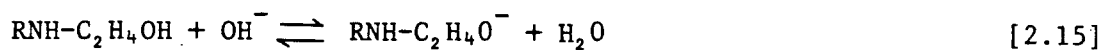


Fig. 2.1 Shuttle mechanism for CO_2 absorption into aqueous amine solutions

Jorgensen³³ has proposed an additional reaction between CO_2 and DEA. In this case the CO_2 reacts with an alcohol group in the DEA molecule to form an alkyl carbonate.



However, this reaction occurs only in strongly alkaline solutions ($\text{pH} > 13$) and at low temperatures.²⁶ It is therefore unlikely to be of importance in natural gas treating units. Several authors have also proposed the existence of the $\text{R}_2\text{NCOO}^- \text{R}_2\text{NH}_2^+$ complex.^{24,25,29} However, in aqueous solutions this complex can be considered to be almost completely dissociated.

Thus the gas treating solution can be considered to be a complex mixture of ionized species in equilibria consisting mainly of H^+ , OH^- , HCO_3^- , R_2NCOO^- , R_2NH_2^+ , as well as the molecules CO_2 and R_2NH .

2.2 DEA degradation

Besides the establishment of the ionic equilibria within the gas treating solution, there are certain side reactions by which DEA and DEA carbamate ($\text{R}_2\text{NCOO}^- \text{H}^+$)* undergo further change. DEA, in general, is not easily recovered from these compounds and these side reactions are termed the "degradation reactions."

DEA degradation is a complex phenomenon. Smith and Younger,^{5,11,12} as well as Nonhebel¹⁶ have reported that degradation apparently depends on temperature, pressure, gas composition, amine concentration, pH, and the presence of metal ions. However, the quantitative relationships between these variables and degradation have not been reported. It is, therefore, impossible to predict DEA degradation rates or, alternatively, to estimate improvements from changes in operating variables. The situation is further complicated by the fact that the degradation products are large organic molecules which are difficult to detect and identify.

* DEA carbamate is written in the ionic form, $\text{R}_2\text{NCOO}^- \text{H}^+$, since in aqueous solutions it can only exist as ions. Carbamic acid, R_2NCOOH , is extremely unstable and reverts to DEA and CO_2 ; R_2NCOOH has never been isolated.

HEOD or 3-(2-hydroxyethyl)-2-oxazolidone was regarded as an intermediate and somewhat unstable compound. The authors also noted the presence of other degradation products but did not characterize them owing to the lack of suitable analytical techniques.

Equations 2.17 and 2.18 indicate that CO_2 acts like a catalyst, i.e., it is neither consumed nor formed. If the reaction scheme is correct, then DEA degradation is governed by a first order kinetic equation provided CO_2 is present in excess. Since DEA and CO_2 are primarily present as ions in aqueous solutions, it is unlikely that the above reactions are realistic.

Using more sophisticated analytical techniques, Hakka et al.³⁵ were also able to detect N,N,N'-tris(2-hydroxyethyl)ethylenediamine, or THEED in degraded DEA solutions. However, they did not propose a reaction mechanism for its formation. According to Hakka et al., THEED occurred frequently in gas treating solutions and was one of the major degradation compounds.

These authors and others^{2,3,36} found that both BHEP and THEED have acid gas removal properties virtually identical to those of DEA. However, under gas treating conditions, only one of the nitrogen atoms in the BHEP or THEED molecule is likely to combine with the acid gas. Hence, on a weight basis, the capacity of the treating solution falls with increasing DEA degradation.

Smith and Younger¹² and others⁴¹ have discussed DEA degradation and mentioned several other degradation compounds. One of these compounds was found to have the same retention time as triethanolamine, or TEA, in the gas chromatographic analysis.

In many cases the DEA treating solution contains small amounts

of monoethanolamine, or MEA. This compound can also degrade^{38,39,40} forming oxazolidone (OZD), 1-(2-hydroxyethyl)imidazolidone (HEI), N,N'-bis(hydroxyethyl) urea (BHEU), and N-(hydroxyethyl)ethylenediamine (HEED).

In a recent study by Blanc et al.³⁶ the authors reacted DEA with CO₂ and in another experiment with HEOD. Both experiments were conducted in a sealed autoclave at temperatures of 90-130°C. They proposed various reaction mechanisms for the production of HEOD, THEED, and BHEP and other degradation compounds. However, they provided no quantitative data in support of these mechanisms.

Choy^{41,42} performed a series of controlled experiments and found that DEA degradation appears to be first order between 165-185°C and at CO₂ pressures ranging from 1207-4137 kPa (175-600 psi). Degradation rates were, however, affected by initial DEA concentration, which cannot be explained in terms of a simple first order mechanism. Furthermore, several degradation compounds were detected, and although their chemical structure was not determined, their concentration changes with time suggested a series of simultaneous and consecutive degradation reactions. Recent work by Kennard and Meisen⁴³⁻⁴⁵ have confirmed that DEA degradation is not a simple first order reaction.

There is another type of degradation compound which are called heat stable salts. These salts occur when a stronger acid than H₂S or CO₂ reacts with the amine forming an unregenerable salt, i.e., DEA is not easily recovered by the action of increasing the temperature since the bond is too stable. These stronger acids were described in the early work by Henry and Grennert.^{46,47} Blanc et al.³⁶ later identified them as formic, acetic, propionic, and oxalic acids. The production of

these acids has been attributed to the presence of oxygen although the mechanism for production is not clearly understood. Since the present study is concerned with the reaction between DEA and CO_2 , heat stable salts will not be considered further.

Degradation compounds of high molecular weight have been proposed^{7,34} but not identified. These compounds may be linear polycarbamides containing polyalkylene amine structures.

Other studies have been mainly concerned with the effect of degradation products on corrosion.^{10,15,34,35,18} DEA itself is not considered corrosive, but degraded DEA solutions can attack mild steel. It has been suggested,³⁶ however, that since the pH of 30 wt % to DEA is in the range of 11.5-10 at temperatures of 20-100°C then the corrosion of mild steel becomes impossible. Further, it has been shown that the major degradation compounds BHEP and THEED are relatively noncorrosive.^{2,3,34,35,36} The corrosion may, therefore, be caused by other trace impurities such as cyanides, chlorides, or the organic acids.

2.3 Analysis of DEA and its degradation products

A quantitative study on DEA degradation is dependent on a reliable analytical procedure for measuring the degradation compounds. The analysis of DEA and its degradation compounds has proven to be rather difficult because the degradation products tend to:

- a) have fairly low vapour pressures;
- b) decompose at elevated temperatures;
- c) be highly polar; and
- d) occur in low concentrations.

There is another problem which arises from the fact that degraded solutions are a complex mixture of ionized species in equilibrium. The

process of analysis may have the effect of shifting the equilibrium and it therefore becomes impossible to isolate and measure each component in the form in which it exists in the degraded solution. For example, it is impossible to isolate the carbamate R_2NCOOH since it readily decomposes to CO_2 and DEA.

Henry and Grennert^{46,44} were amongst the first researchers interested in the detection and measurement of DEA salts in refinery samples. They investigated four types of acidic materials: a) organic acids, b) chlorides, c) cyanides and thiocyanates, and d) sulphites, sulphates, and thiosulphates. They used mainly potentiometric titration for the DEA analysis. They also discussed conventional wet chemical methods such as titration and kjeldahl total nitrogen determination, as well as other methods for the determination of total sulphur, sulphide, mercaptide, sulphate, thiocyanate, cyanide, chloride, carbonate, alkalinity, and sodium. This study was however limited because it failed to detect organic degradation compounds. The "Gas Conditioning Fact Book," published by Dow Chemical Company¹⁵ provides a description of conventional wet chemical methods for testing DEA samples. However, these methods are again unsuitable for identifying DEA degradation compounds.

A comprehensive study on the analysis of DEA gas treating solutions was produced by Gough.³⁷ Here an attempt was made to describe analytical schemes that would lead to a useful interpretation of quality. Two schemes were described: a) a comprehensive scheme for component analysis, used when detailed information on composition is required; b) a simple scheme for quality evaluation, useful on a routine basis and providing information required for routine plant operation. Unfortunately this study was also not suitable for observing and identifying

the individual degradation compounds.

Brydia and Persinger⁴⁸ described a chromatographic technique for analysing ethanolamines. Because direct chromatographic procedures were not entirely successful (excessive peak tailing due to strong hydrogen bonding), derivatization prior to chromatographic separation was investigated. Trifluoroacetyl anhydride was used to convert non volatile amines into volatile amine trifluoroacetyl derivatives. The authors experienced problems with reproducibility, precision, and the presence of water. Piekos et al.⁴⁹ eliminated these shortcomings by converting the alkanolamines to trimethylsilyl derivatives. N,O-bis(trimethylsilyl) acetamide was used which reacts with both the amino and hydroxyl groups of the alkanolamines. The process is called silylation and produces fairly stable compounds which are more easily separated and identified by gas chromatography. The addition of a trimethylsilyl group also decreases the polarity of the alkanolamine and reduces hydrogen bonding. Silylated compounds are more volatile and more stable due to the reduction of reactive sites. Successful separation of MEA, DEA, and TEA derivatives was conducted and the presence of up to 5% of water could be tolerated, provided there was a large excess of silylating agent.

A recent paper by Saha et al.⁵⁰ investigated problems arising from converting the amines to stable derivatives prior to analysis by gas chromatography. For example, derivative preparation is time consuming, the derivative reactions may be incomplete and the derivatives may not be stable for long periods. Consequently the use of organic polymer beads as the column packing for G.C. analysis of alkanolamines was investigated. The authors found that Tenax G.C.,⁵¹ which is a porous polymer based on 2,6-diphenyl-paraphenylene oxide, was able to separate

alkanolamines with excellent results. The authors were able to separate an aqueous mixture of MEA, DEA, and TEA in less than eight minutes using a 1/8" O.D, 4' long stainless steel column. No sample preparation was required and the column was unaffected by the presence of water.

Probably the only study dealing specifically with the analysis of DEA and its degradation products was that performed by Choy and Meisen.⁵² Their technique consisted of first drying the degraded DEA sample by air stripping, dissolving it in dimethyl formamide and silylating it with N,O-bis(trimethylsilyl)acetamide. The silylated compounds were then separated using a 1/8" O.D, 6' long stainless steel column packed with 8% OV17 on 80/100 mesh chromosorb followed by flame ionization detection. Although the method was reliable and accurate, it was time consuming and unsuitable for plant use. In particular, the silylation stage required considerable care particularly with regard to the removal of water.

Other methods for the analysis of amines and amine related compounds have been reported. These studies include paper chromatography,^{53,54} salting out chromatography,⁵⁵ and thin layer chromatography.⁵⁶ All these methods suffered from excessive tailing and lack of reproducibility. Also none of these methods have been applied to DEA degradation compounds.

CHAPTER 3

DEVELOPMENT OF THE ANALYTICAL TECHNIQUE

Before a study of DEA degradation could be undertaken a reliable, quantitative method of analysis of DEA and its degradation products had to be developed. The method should be rapid, highly sensitive, and require minimal sample size and preparation. Furthermore it is desirable for the method to be applicable for industrial as well as laboratory use.

Many methods have been investigated for the analysis of DEA and its degradation products such as wet chemistry, infra red and ultra violet spectroscopy, paper and thin layer chromatography. However, they all tend to have drawbacks such as being generally inaccurate, non-specific, unreliable, and expensive. In addition, these methods tend to be slow and inconvenient. Choy⁴¹ stated that gas chromatography was probably the most promising analytical technique. As mentioned before, one of the problems of analysing DEA and its products is their low vapour pressure. This requires the use of high injection and column temperatures. However poor thermal stability of DEA leads to problems with the reproducibility of measurements. Also, the polar hydroxyl and amino groups have a strong affinity for most column packings. This results in long elution times, large peak broadening, and peak asymmetry. The presence of water in the sample also creates problems since only a few column packings can tolerate aqueous samples.

3.1 Gas chromatographic technique

Choy's method⁵² using derivative gas chromatography although reliable, was felt to be too time consuming and unsuitable for plant use. This was due to the complicated sample preparation since the silylation reactions were extremely sensitive to water. Furthermore, there is the problem of incomplete silylation of all compounds. Silylation of the hydrogen bound to the nitrogen atom of alkanolamines is known to be difficult.⁵⁴

An attempt was therefore made to find a simpler and more direct technique for analysing DEA and its degradation compounds. A thorough review of the literature yielded an article by Saha et al.⁵⁰ who used Tenax G.C. to separate alkanolamines. Tenax G.C. is a porous polymer based on 2,6-diphenyl-paraphenylene oxide which has a weakly interacting surface and can be used at temperatures up to 450°C. According to the manufacturers, columns may be operated for several weeks at temperatures up to 400°C without significant baseline drift and decomposition of the packing. Since the organic polymer beads are solids, mass transfer is rapid and fast elution and sharp peaks are obtainable.

Using a temperature programmable gas chromatograph (Hewlett Packard Model 5830A), a 1/8" O.D, 6' long stainless steel column packed with Tenax G.C. (purchased from Alltech Associates, Illinois) was tested and found to be successful. Two other packings, which could tolerate aqueous samples, were also tested; these being 4% Carbowax 20m on 60/80 mesh Carbopack B⁵⁸ (purchased from Supelco Inc., Penna.) and 28% Pennwalt 223 + 4% KOH on 80/100 mesh Gas-chrom R⁵⁹ (purchased from Applied Science Lab. Inc., Penna.). Both columns were found to be unsuitable due to either low sensitivity on excessive peak tailing.

3.1.1 Evaluation of the Tenax G.C. column. Initial tests were performed with solutions made by mixing distilled water with reagent grade MEA, DEA, and TEA. Using a flame ionization detector, nitrogen as the carrier gas and temperature programming, excellent separation was obtained. From the literature review it was apparent that the main degradation compounds are HEOD, THEED, and BHEP. Unfortunately only BHEP could be obtained commercially. Therefore standards for HEOD and THEED were prepared in the laboratory and their synthesis is described in chapter 4. All three compounds were easily separated with the Tenax column. A paper by Alltech Associates Inc.⁶⁰ indicated that stainless steel causes ethanolamine to undergo catalytic degradation. However, no evidence of degradation within the column was observed for any of the compounds tested. Although the inlet port and column were operated at high temperatures (up to 300°C), there was no observable thermal decomposition of the tested compounds. This was confirmed by the sharp, symmetric, and highly reproducible peaks.

3.1.2 Operating conditions. After several initial trials, optimum conditions were found for the separation of DEA and its degradation products. Table 3.1 summarizes the facilities and operating conditions used for the separation.

Temperature programming was used in order to achieve a good separation of all degradation compounds, since these compounds varied considerably in molecular weight and polarity. The maximum temperature of 300°C was adopted to ensure that all compounds were volatilized. However, even at this temperature it is possible that some of the very heavy degradation compounds, such as the polylinear carbamides did not elute. Usually a 1 μ L sample in conjunction with an attenuation value of 13-14, was found

Table 3.1 Analytical equipment and operating conditions for G.C. analysis

Gas Chromatograph

Manufacturer	Hewlett Packard
Model	5830A
Detector	H ₂ flame ionization

Chromatographic Column

Material	Stainless steel
Dimensions	1/8" O.D, 6' long
Packing	Tenax G.C., 60/80 mesh

Operating Conditions

Carrier gas	N ₂ at 25 ml/min
Injection port temp.	300°C
Detector port temp.	300°C
Column temp.	Isothermal at 150°C for 0.5 min., then temperature raised at 8°C/ min to 300°C

Syringe

Manufacturer	Hamilton Co.
Model	701, 10μL, with fixed needle and Chaney adapter
Injected sample size	1μL

to be suitable for the detection and separation of all compounds. However, in some cases the sample size was increased to 2 μ L or more to detect trace quantities of degradation compounds.

3.2 Analytical procedure and performance

Typically 1.0 μ L samples of the degraded DEA solution were injected directly into the column with a precision syringe fitted with a Chaney adapter. The adapter was used to ensure that a constant volume of sample was injected into the column. To improve the accuracy, a needle guide was used at the injection port. This guide not only protects the fragile syringe needle, but serves as a spacer for needle penetration and lengthens the septum life by using a single hole for repeated injections. Needle guides were found to be indispensable for high precision work.

The analysis was usually performed for a period of 30 minutes in order to ensure the elution of heavy compounds. After each run the column had to be cooled from 300°C to 150°C which took about 5 minutes. Therefore, a complete analysis required a total of about 35 minutes.

DEA and known degradation products could be detected accurately down to concentrations of about 0.5 wt %. The reproducibility was excellent (typically within $\pm 5.0\%$ with a new column) and peak tailing and baseline drift did not represent special difficulties. Figures 3.1 and 3.2 show examples of the separation achieved with the Tenax G.C. column.

3.2.1 Column performance. The column itself required no special care and was conditioned simply by passing nitrogen through it at its maximum operating temperature (300°C) for 8-10 hours. The column has a fairly long life; for example, one column was in continual use for nearly a year. However, when a column fails, it fails rapidly and

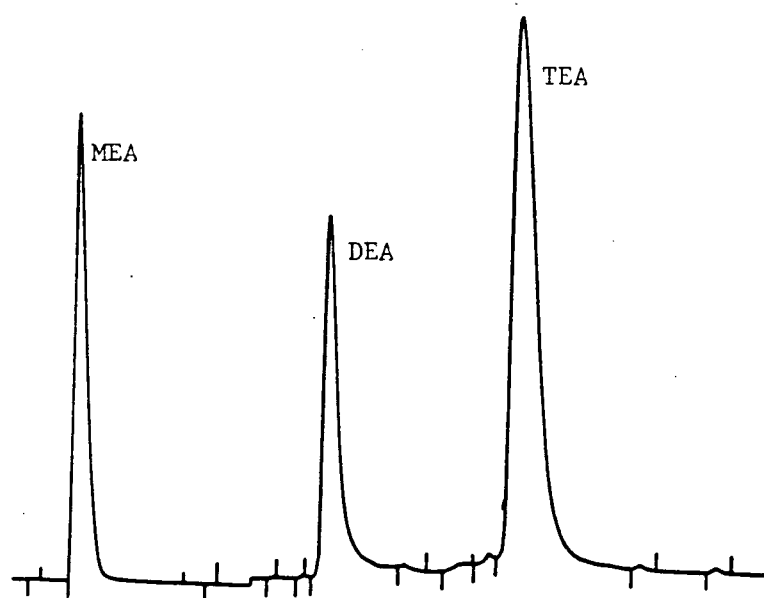


Figure 3.1 Typical chromatogram for MEA, DEA, and TEA

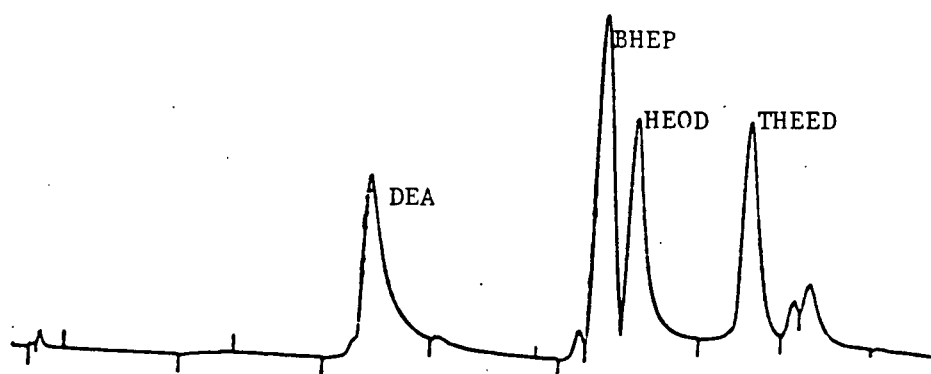


Figure 3.2 Typical chromatogram of a degraded DEA solution

becomes incapable of separating the heavy compounds. It is likely that the column becomes clogged with the polylinear carbamide compounds, which probably never leave the column. Thus the more degraded the sample the shorter the column life.

In some cases a 9' column was used instead of the standard 6' column. This improved the separation of degraded compounds, especially the separation of BHEP and HEOD. Also it allowed a direct comparison to be made between the results of this study and those of Blanc et al.³⁶ who used a 9' Tenax G.C. column. However, the longer column increased the elution times, and most analyses were therefore performed using the 6' column.

3.3 G.C. calibration

Calibration plots of concentration versus peak area were produced simply by injecting known concentrations of the various degradation compounds into the chromatograph and noting the peak area which was automatically calculated by the chromatograph's computer. At least five injections were made for each concentration and the peak area averaged. Figures 3.3 to 3.6 show the calibration for DEA, HEOD, BHEP, and THEED. This form of calibration did not use an internal standard and is termed 'direct calibration'.

3.4 Maintenance of chromatographic equipment

Generally very little maintenance is required. Basically the chromatograph and syringes must be kept clean. In some cases deposits tend to build up in the injection port and have to be removed. Furthermore, deposits accumulate on the detector jets and can result in excessive spiking (or noise) on the chromatogram. The cleaning of the flame ionization detector is difficult and the removal of the probes is not recommended unless absolutely necessary. An easier method is to inject 10-30 μ L

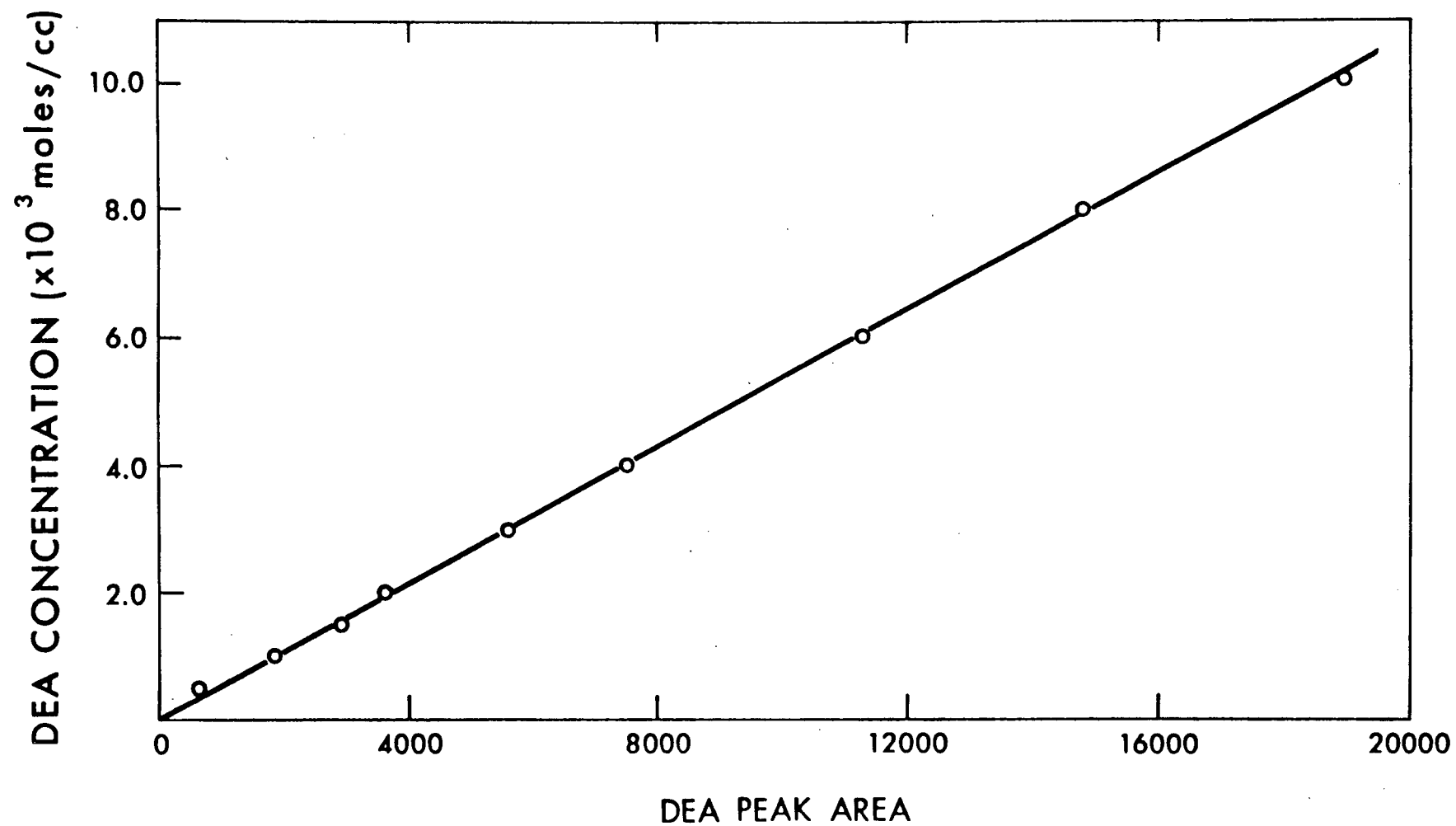


Figure 3.3 Calibration plot for DEA

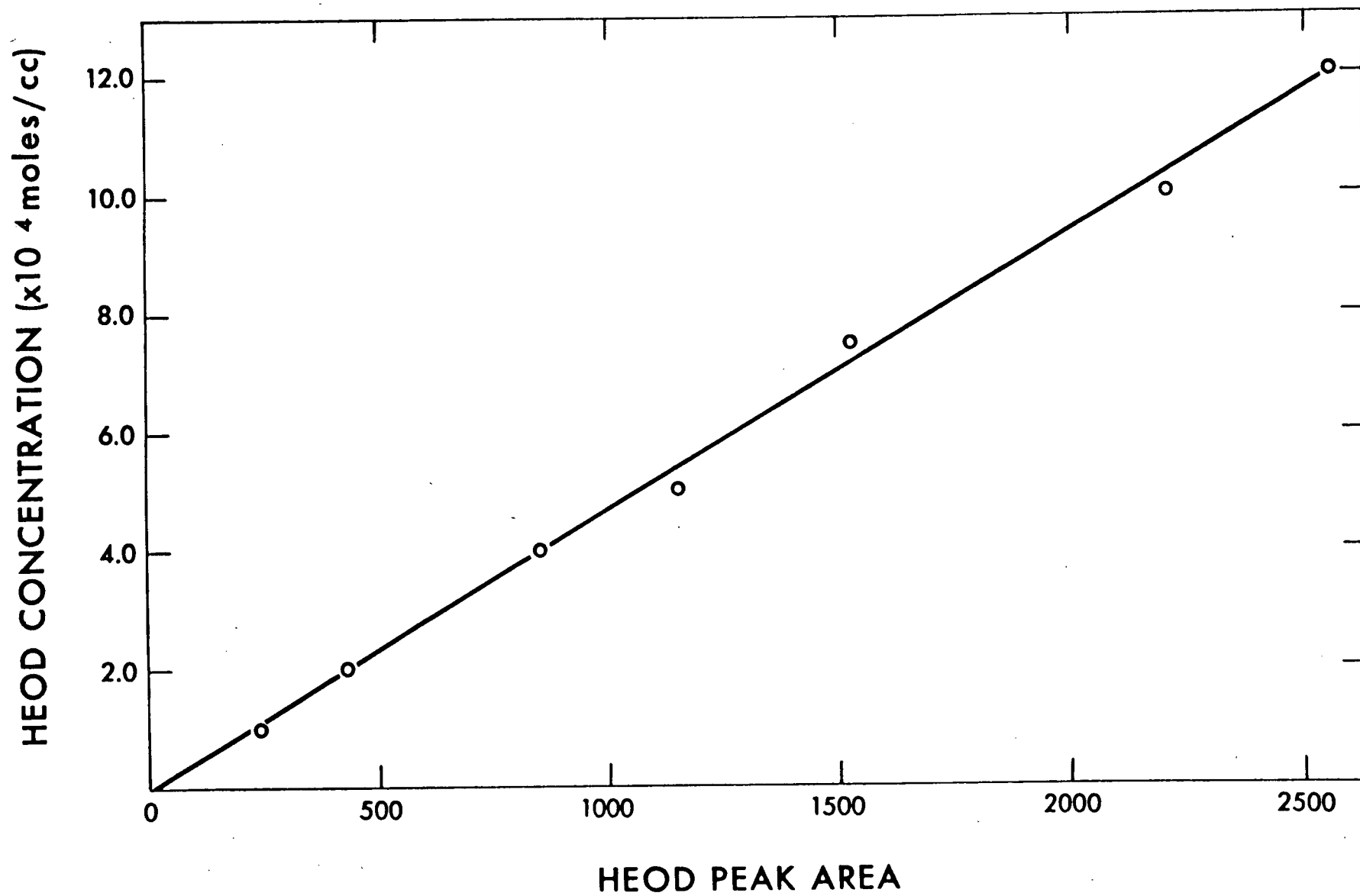


Figure 3.4 Calibration plot for HEOD

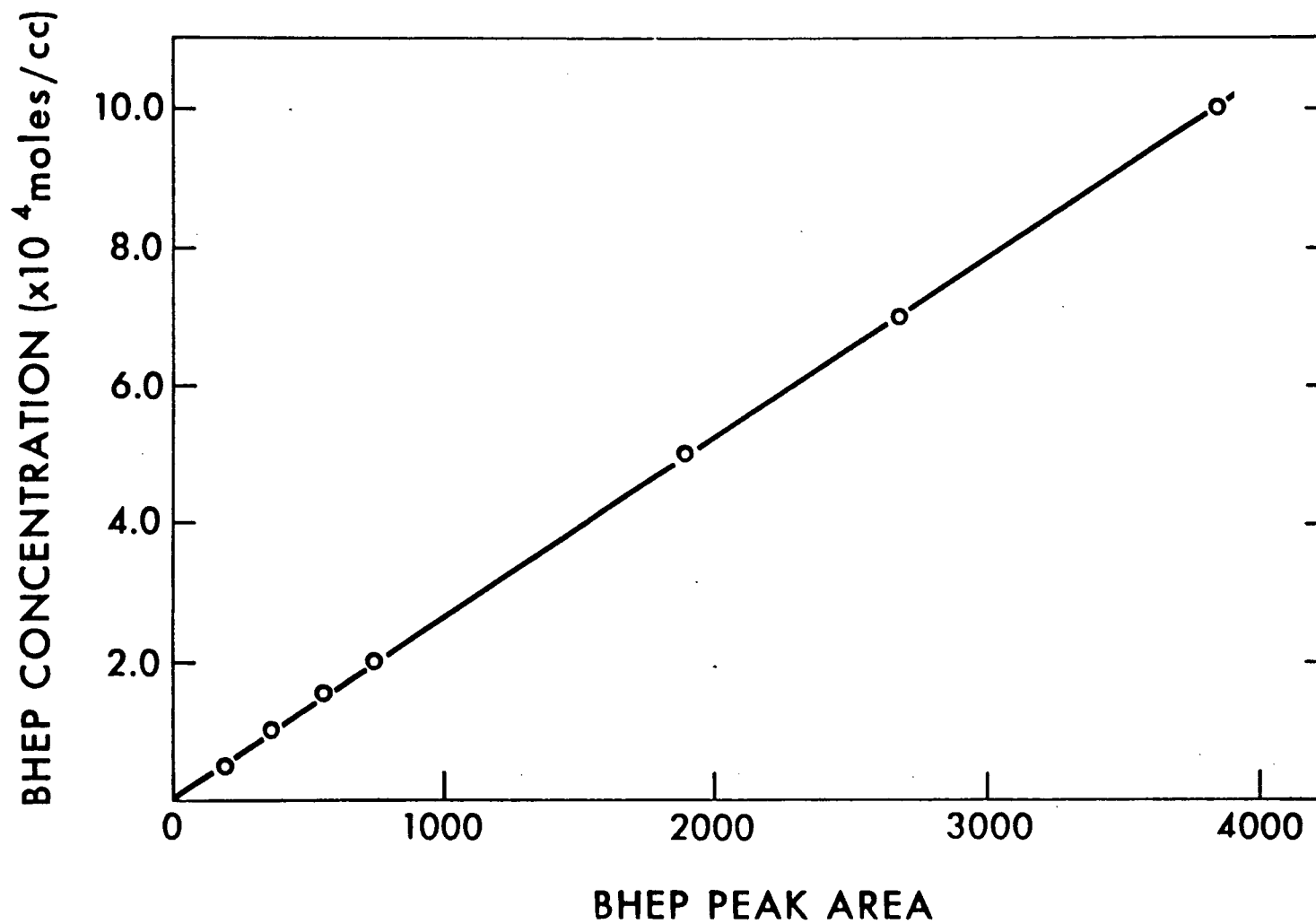


Figure 3.5 Calibration plot for BHEP

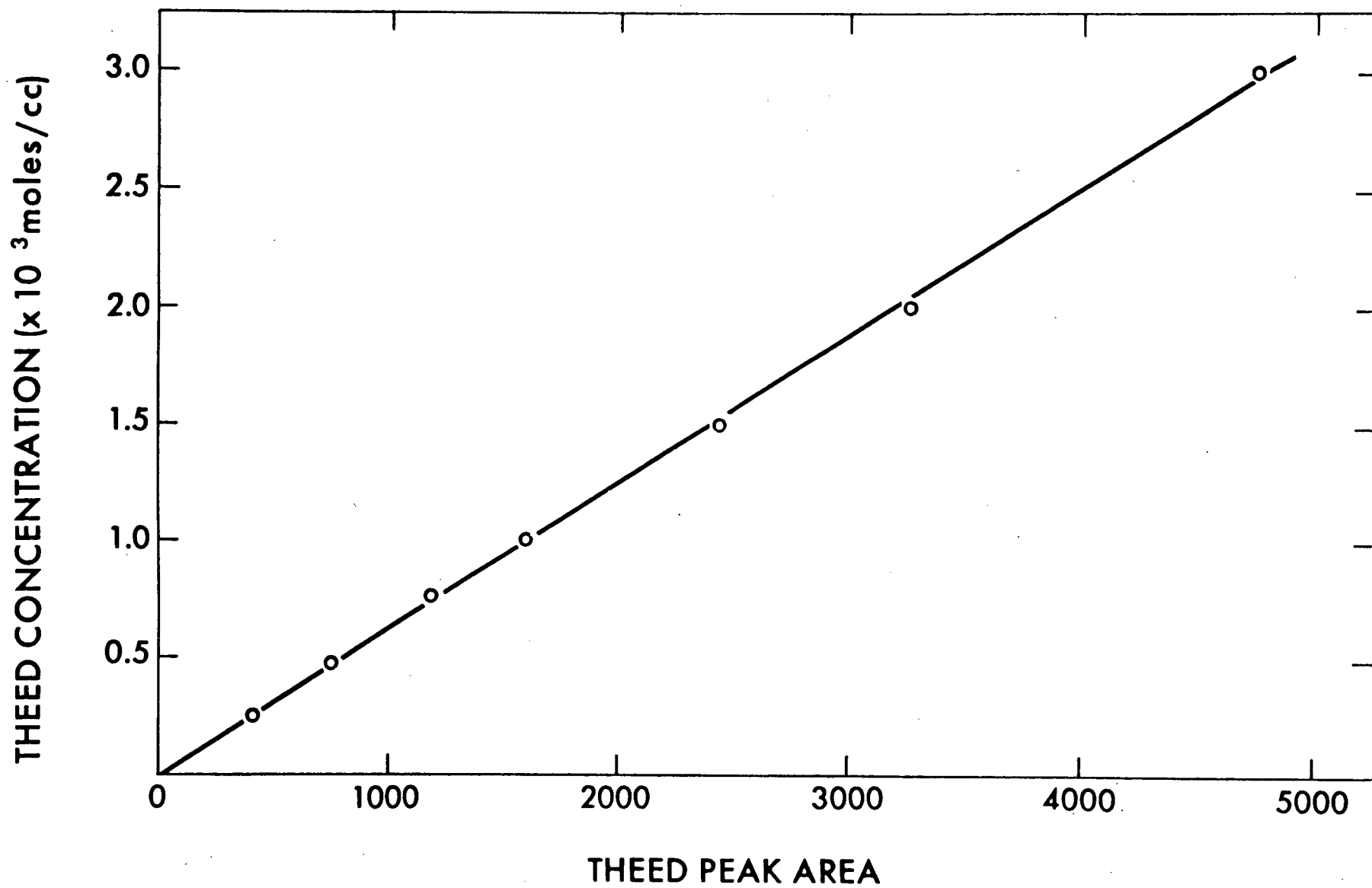


Figure 3.6 Calibration plot for THEED

of Freon 113 flame ionization detector cleaner (purchased from Supelco, Inc.) with equipment operating under normal conditions. Freon elutes from the column and produces hydrogen fluoride as the cleaning agent when burnt in the hydrogen flame.

Since the column does eventually wear out it is considered good practice to check the calibration at least once a month with standard samples. If there is considerable disagreement between the calibration curve and the analysis of the standard samples, then the column should be replaced.

Septa should be replaced at least every 50 injections since they tend to accumulate deposits and eventually begin to leak.

No other routine maintenance is required except keeping the machine clean and free of dust. The grill to the fan which cools the circuit boards may get clogged with dust and restrict the flow of cooling air causing overheating of the circuit boards. Thus the grill must be checked periodically. The printer is generally trouble free requiring only cleaning of the slide rod for the printer head and keeping it free of oil and grease.

3.5 Advantages of the analytical technique

The advantages of the present analytical technique can be summarized as follows.

1. No sample preparation required.
2. Water has no effect on the column.
3. Very simple.
4. Long column life.
5. Small sample required.
6. Reliable and reproducible.

7. Speed, i.e., analysis is completed in less than 35 minutes.
8. Suitability for plant use.

3.6 Errors

The major source of error arises during sample injection. Since direct calibration was used to determine the concentration, then each sample injection had to be as identical as possible. For example, increasing the injection time usually resulted in slightly larger peak areas, since a small volume of liquid, otherwise held in the needle, is partially vapourized and enters the column. Another problem with direct calibration is the sensitivity of the detector is assumed to remain constant from day to day. This assumption is only valid provided the detector is kept clean. Another source of error is changes in the flow of carrier gas. As the column becomes clogged, the flow tends to fall unless adjusted. Therefore, it is best to check the flow of carrier gas daily.

The only other noticeable error is concerned with the calculation of the peak areas which the chromatograph performs automatically. As long as the peaks are sharp and symmetrical and there is little baseline drift, there is usually no problem. If the peaks tend to tail or bunch, the automatic integrator may make small errors in deciding where to begin and end integration. In general, this form of error is minor compared to that produced by sample injection.

3.6.1 Accuracy. The accuracy of the technique can be simply calculated using the relative standard deviation σ_R .

$$\sigma_R = \frac{\sigma}{\bar{x}} = \frac{\sqrt{\frac{\sum (x - \bar{x})^2}{N - 1}}}{\bar{x}}$$

where N = number of measurements

x = measured value

\bar{x} = arithmetic mean

σ = standard deviation

For example, for the analysis of a sample of DEA the following six concentrations were recorded for a sample of aqueous DEA of known concentration 3.5×10^{-3} moles/cc.:-

3.54×10^{-3} , 3.45×10^{-3} , 3.52×10^{-3} , 3.51×10^{-3} , 3.55×10^{-3} ,
 3.43×10^{-3}

$\bar{x} = 3.5 \times 10^{-3}$

$\sigma = 2.19 \times 10^{-5}$ $\sigma_R = 6.3 \times 10^{-3}$

Similarly the following five concentrations were recorded for a sample of aqueous DEA of known concentration 0.95×10^{-3} moles/cc.:-

9.25×10^{-4} , 9.75×10^{-4} , 1.01×10^{-3} , 9.81×10^{-4} , 9.35×10^{-4}

$\bar{x} = 9.652 \times 10^{-4}$

$\sigma = 1.745 \times 10^{-5}$ $\sigma_R = 1.81 \times 10^{-2}$

There is of course one final source of error and that occurs when reading the calibration curves. Therefore considering all the error sources and the relative standard deviation, the accuracy of the analytical technique has been found to be $\pm 5\%$.

3.7 Units of DEA concentration

DEA concentration is, throughout this study, expressed in units of wt % or moles/cc. It should be noted that since the molecular weight of DEA is 105, the concentration expressed as moles/cc can roughly be converted to wt % by multiplying by 10^4 ; e.g., 1.5×10^{-3} moles/cc is roughly equivalent to 15 wt %.

CHAPTER 4

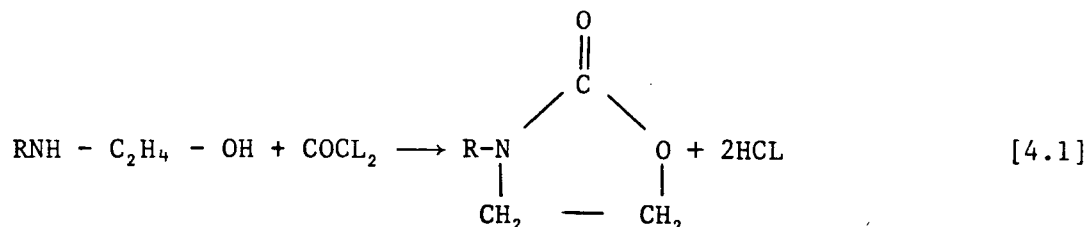
SYNTHESIS OF SELECT DEGRADATION COMPOUNDS FOR CALIBRATION OF THE GAS CHROMATOGRAPH

In order to study DEA degradation quantitatively it is necessary to measure the concentration of DEA and its major degradation products in solution. In order to calibrate the chromatograph, standards of the various degradation compounds had to be obtained. From previous studies the major degradation compounds were thought to be HEOD, THEED, and BHEP. Unfortunately, only BHEP was available commercially. HEOD could only be obtained from ICN Pharmaceuticals, Inc. but its purity was found to be too low for calibration. It is likely that HEOD reverts slowly to DEA and this is discussed further in chapter 11. THEED was unavailable from any commercial source. It was, therefore, decided to synthesize both HEOD and THEED in the laboratory.

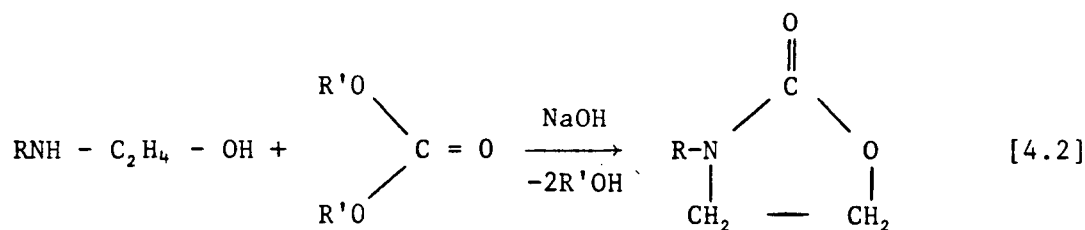
4.1 Synthesis of HEOD

A thorough search of the literature, back to 1920, revealed only the following methods for synthesizing 2-oxazolidones:

- a) From alkanolamines and phosgene.⁶¹ The alkanolamine is reacted with phosgene in chloroform in the presence of lead carbonate which neutralizes the hydrochloric acid produced in the reaction.

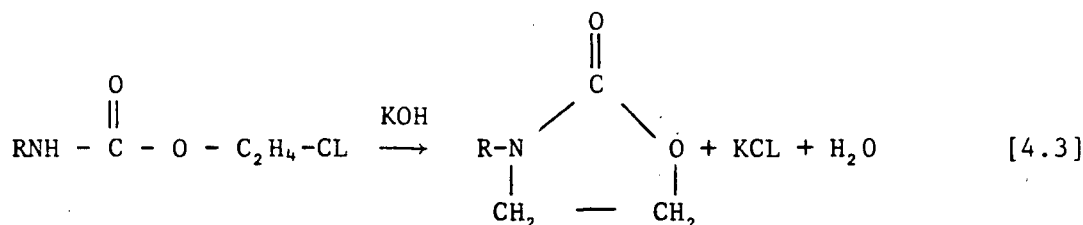


b) From alkanolamines and dialkyl carbonate.^{62,63}

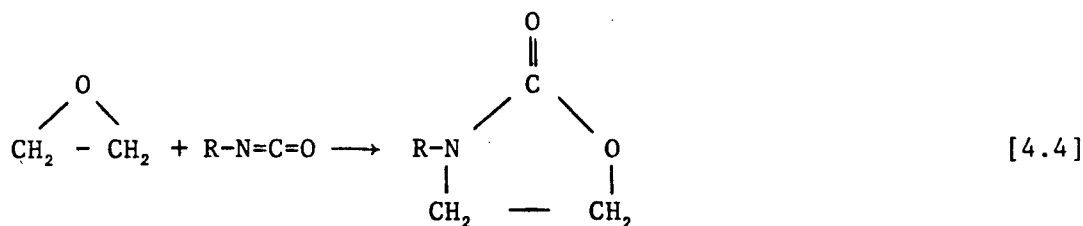


NaOH acts as a basic catalyst.

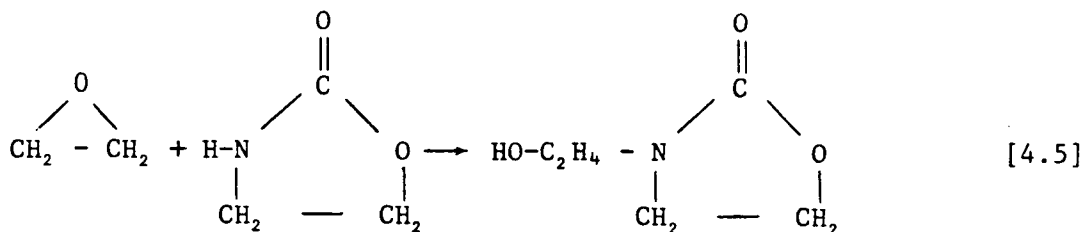
c) From β halogenalkyl carbamate.⁶⁴ The carbamate is boiled in an aqueous KOH solution.



d) From ethylene oxide (EO) and a hydroxyl alkyl isocyanate.⁶⁵ The oxide is heated with the isocyanate in the presence of potassium iodide or lithium chloride, which act as catalysts.



e) From ethylene oxide (EO) and 2-oxazolidone (OZD).⁶⁶ Equal amounts of ethylene oxide and oxazolidone are heated in the presence of a trace amount of water.



With the exception of (e) the methods were non-specific for the production of HEOD. Furthermore complete details of the reaction conditions were not stated.

Methods (b) and (e) were attempted with partial success. Using method (b) the following synthesis was performed. Equal amounts of ethyl carbonate and diethanolamine were mixed and 15g charged to a 25ml. pressure reactor together with about 5g of 1N sodium hydroxide. The reactor was sealed and pressured to about 689.5 kPa (100 psi) with nitrogen. The reactor was then placed in a water bath and heated to about 50°C for one hour. The results of this experiment were rather disappointing. HEOD was produced only in low amounts since there were many side reactions taking place. It was felt that purification would prove difficult as well as time consuming and therefore method (e) was tried.

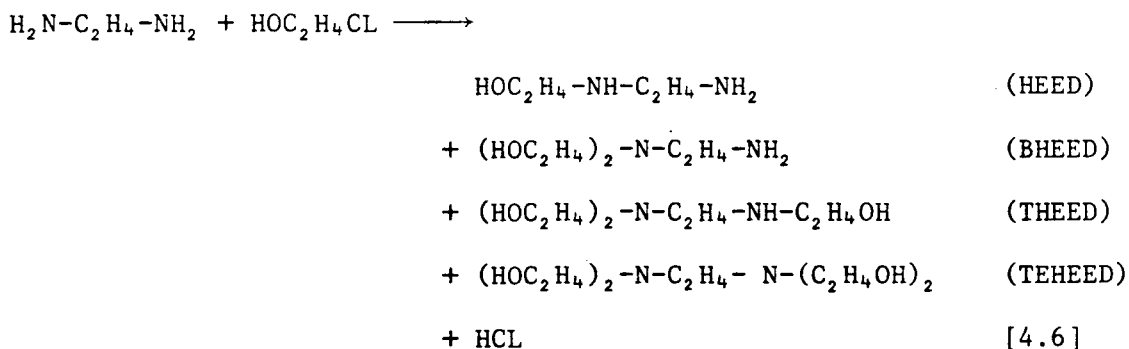
Equal amounts of ethylene oxide and oxazolidone were mixed and 15g charged to the 25 ml. pressure reactor before adding about 1g of water. The reactor was sealed and pressurized to about 689.5 kPa (100 psi) with nitrogen. The reactor was placed in a water bath and heated to 70°C for about eight hours. HEOD conversions of about 70% were achieved with MEA and DEA being the main impurities. However, further purification proved once again to be very difficult. Several methods were tried such as distillation; solvent extraction with chloroform, acetonitrile and pyridine; and gel chromatography. None of these approaches were

very successful. Since HEOD was required in a purity of at least 95%, for calibration of the chromatograph, it was decided to enlist the help of a small firm specializing in custom synthesis of rare chemicals (Synthecan Lab., Inc., Vancouver). A pure 50g sample was purchased and used for the calibration.

4.2 THEED synthesis

Information with regards to synthesis of THEED proved very difficult to find and a thorough literature survey revealed only one relevant reference.⁶⁷ Three different methods were tried for the synthesis of THEED and are summarized below.

a) From ethylenediamine (ED) and chloroethanol. The reaction was expected to produce the following compounds:-



The reaction was initially performed by mixing ethylenediamine with chloroethanol, in the molar ratio of 1:3, in a glass beaker and heating the mixture to about 100°C. Unfortunately the reaction was found to be highly exothermic and a very viscous yellow substance was produced. Analysis showed that no THEED was produced. A similar experiment conducted at 50°C resulted in no reaction taking place.

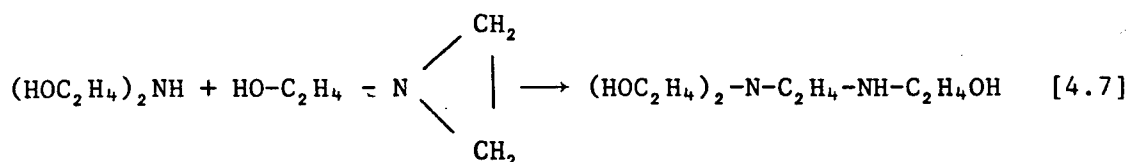
A more controlled experiment was performed where 15 cc. of the reaction mixture was placed in the 25 ml. pressure reactor and the reactor pressurized to about 689.5 kPa (100 psi) with nitrogen. The reactor

was then heated to 90°C in a water bath for about 1 hr. The reaction produced numerous compounds one of which may have been THEED. Purification would have been too difficult and therefore other methods were tried.

b) From ethylenediamine and ethylene oxide. This reaction was far less exothermic and easier to control. The expected products were similar to those stated in Eq. 4.6.

15g of a mixture containing 3 moles of ethylene oxide to one mole of ethylenediamine were charged to the 25 ml. pressure reactor. About 1g of water was added as a catalyst.⁶⁸ The reactor was sealed and pressurized to 689.5 kPa (100 psi) with nitrogen and heated to about 50°C in a water bath for one hour. Five distinct compounds were produced (see Fig. 4.1). Two of the peaks corresponded to the two isomers of BHEED, namely $(\text{HOC}_2\text{H}_4)_2\text{-N-C}_2\text{H}_4\text{-NH}_2$ and $(\text{HOC}_2\text{H}_4)\text{-NH-C}_2\text{H}_4\text{-NH-(C}_2\text{H}_4\text{OH)}$. The substituted ethylene diamines were produced in the following amounts: HEED 17.7%, BHEED 32.4%, THEED 35.8%, and TEHEED 14.1%. Since all these compounds had similar characteristics it was felt once again that purification would present problems especially since THEED was present in only 36% purity. Thus a third method was tried.

c) From diethanolamine and N-(2-hydroxyethyl)ethylenimine (HEM). The following reaction was expected to occur:-



Approximately 200 cc. of an equimolar solution of DEA and HEM was charged to a 600 ml. stirred autoclave (details of the autoclave are given in chapter 6). The 600 ml. autoclave was used so the reaction could be followed more closely by removing samples while the reaction

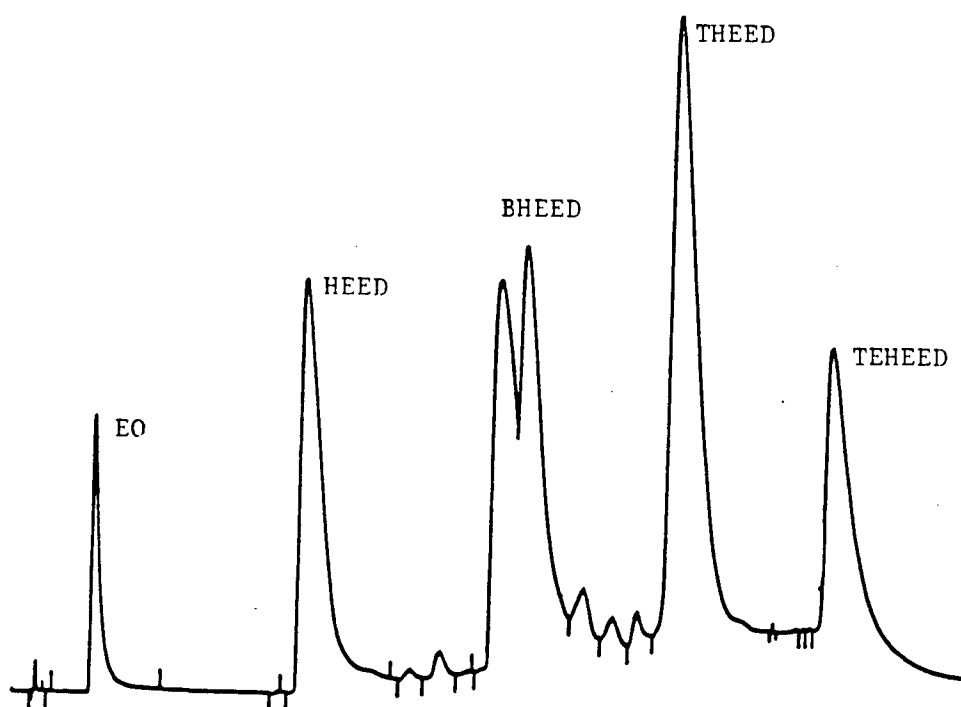


Figure 4.1 Chromatogram of substituted ethylenediamines

was still being carried out. About 5g of aluminium chloride were added to the reaction mixture. The autoclave was sealed and pressurized to 689.5 kPa (100 psi) with nitrogen and heated to 120°C for about eight hours. THEED was produced at about 78% purity, the major impurity being DEA. However, even this concentration was not sufficiently high for calibrating the gas chromatograph. After trying several methods of purification it was found that gel chromatography was most suitable and it was possible to produce THEED of 95% purity. A 2 cm. diameter, 40 cm. long glass column was used for the gel chromatography. The column was packed with 60-200 mesh silica gel. Since THEED and DEA are both soluble in water, water was used as the solvent. A trace of ammonium hydroxide was found to aid separation. 10cc. samples of impure THEED were charged to the column and an elution rate of about 1cc. per 10 minutes was established. Fractions were collected and analysed for THEED content. When sufficient THEED had been collected the samples were concentrated by boiling off the water thereby leaving a viscous colourless liquid of THEED.

CHAPTER 5

IDENTIFICATION OF DEGRADATION COMPOUNDS

5.1 Identification using the gas chromatograph

Before proceeding to the study of degradation reactions the compounds responsible for the peaks on chromatograms had to be identified. For a typical run (i.e., run number 3, where 30 wt % DEA was degraded for eight hours under 4137 kPa (600 psi) CO₂ at 205°C) over 20 peaks were observed. To identify these peaks where possible the following method was used. If a compound was suspected of being produced (based on information from the literature or otherwise), then it was either purchased or synthesized in the laboratory (see chapter 4). A known concentration of the compound was injected into the chromatograph and its retention time noted. This retention time could then be compared with the elution times of the degraded sample of DEA. If a degradation compound produced a peak with the same retention time as that of the standard compound it could be inferred that the degradation compound and standard compound were the same. However, this method does not give a completely reliable identification of a compound since there can be more than one compound with the same retention time. For example, a peak occurred after about 12 minutes which is also the retention time for TEA. It is unlikely, however, that TEA is a degradation product and it is probable that the peak is caused by another compound. TEA does exist as an impurity of

1-2 wt % in the DEA solution. However, the peak area is usually much greater than that produced by TEA in the concentration range of 1-2 wt %.

Thus further information is required for the positive identification of a degradation compound. It was found that using a gas chromatograph and a mass spectrometer (GC/MS) was best suited for this task.

5.2 Identification using a GC/MS

The mass spectrometer simply vapourizes a compound and produces ions from the neutral molecules by bombarding the vapour with electrons. The ions are formed into a beam and accelerated through the field of a powerful electromagnet. The ions are forced into a circular path and become separated according to their mass to charge ratio. The different ions are detected by an electrometer which measures the charge collected on current carried by the ions. Recording the changes in charge a spectrograph is produced of ion current versus mass number. Thus each peak on the spectrograph corresponds to a different ion. Since the molecule fragments in the same manner under similar conditions, the mass spectrograph provides a characteristic "thumbprint" for each compound. The use of a gas chromatograph with the mass spectrometer makes the GC/MS a very useful tool.

Samples of the degraded DEA solution were injected into the GC which separated the compounds. Then each compound flowed into the MS and produced a mass spectrograph corresponding to each peak on the chromatograph.

A Hewlett Packard GC/MS (Model 5985B) was used to produce mass spectrographs of all suspected compounds. Only the mass spectrographs of MEA, DEA, and TEA could be found in the available registries of mass spectral data. Therefore, standard mass spectrographs were made from

pure samples of DEA degradation compounds. These standard mass spectrographs are given in Appendix F.

Samples of degraded DEA solutions could then be analysed using the GC/MS. The resulting spectrographs were compared with the standard spectrographs enabling a positive identification of a degradation compound. For example it was suspected the compound producing the peak marked by the arrow in Figure 5.1 was HEOD.

The mass spectrographs for HEOD and the unknown compound are shown in Figs. 5.2 and 5.3. As can be seen they are very similar. The most notable similarity being the two peaks of masses 100 and 101, which are characteristic of HEOD. Therefore HEOD could be positively identified.

5.3 Identified degradation compounds

Using the methods previously described it was possible to identify 14 compounds in degraded DEA solutions (e.g., Fig. 5.4 shows a typical chromatograph of a degraded DEA solution). Many other compounds were detected, but since their concentrations were extremely low their identification was considered not worth pursuing.

Table 5.1 is a summary of the compounds detected with their retention times using the Tenax G.C. column and conditions described in chapter 3. Mass spectrographs for these compounds are found in Appendix F. Possible mechanisms for their production will be discussed in chapter 11.

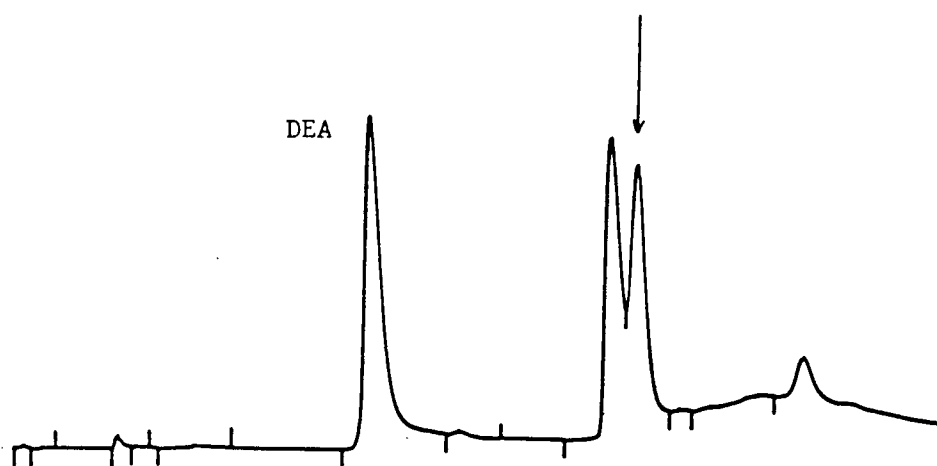


Figure 5.1 Chromatogram showing peak of unknown compound

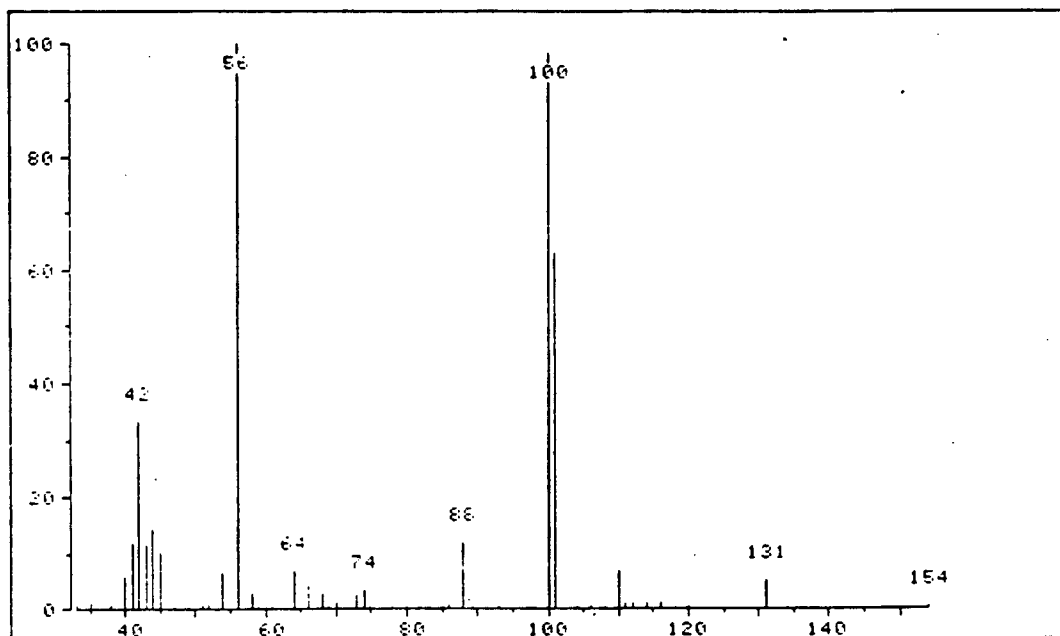


Figure 5.2 Mass spectrum of HEOD

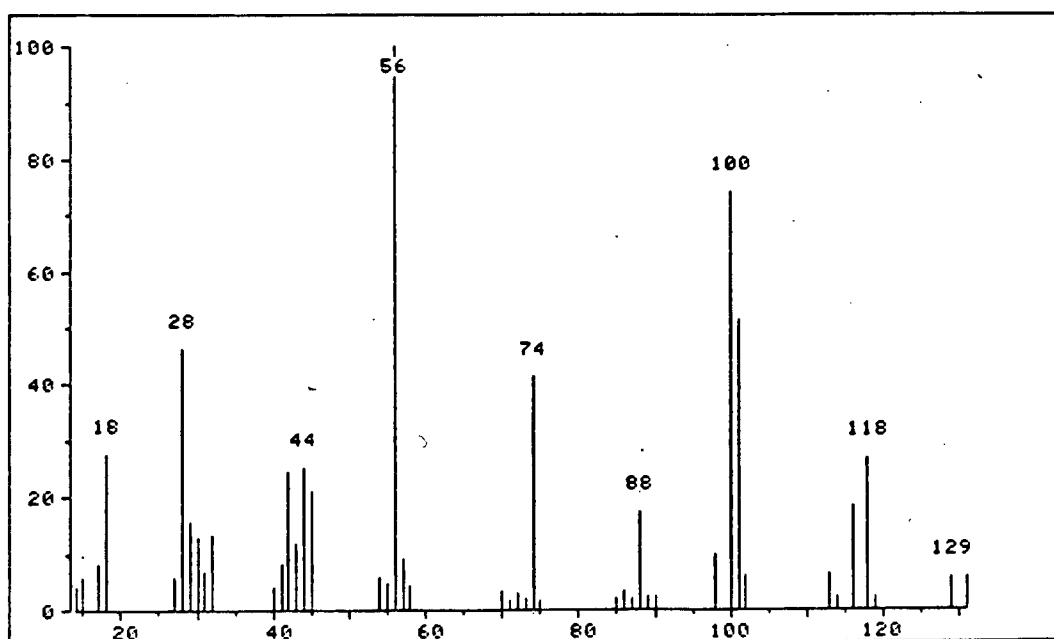


Figure 5.3 Mass spectrum of unknown compound

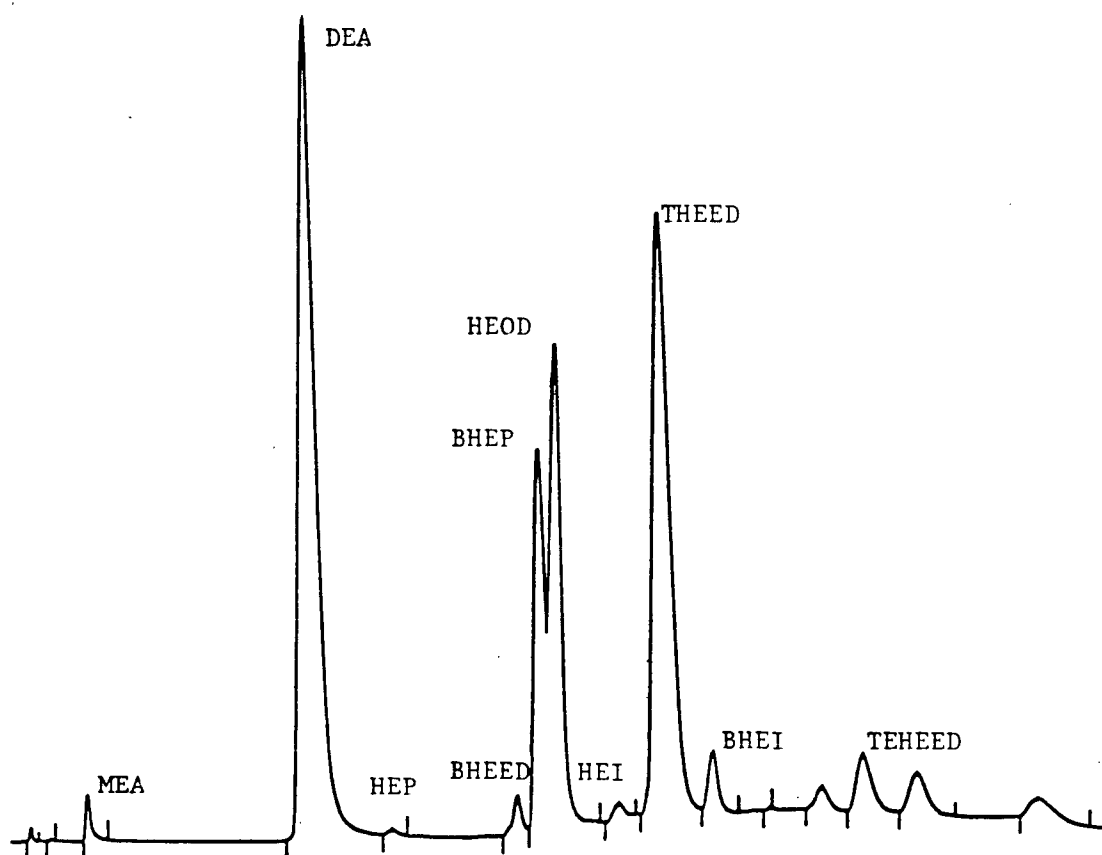


Figure 5.4 Typical chromatogram of a degraded DEA solution

Table 5.1 Compounds found in degraded DEA solutions

Compound	Retention time min.*
MEA	1.4-1.5
HEM	3.1-3.5
HEED	6.8-7.2
DEA	7.4-8.0
HEP	9.8-10.2
OZD	10.4-10.6
TEA	12.0-12.5
BHEED	12.8-13.2
BHEP	13.0-13.6
HEOD	13.4-14.0
HEI	15.5-16.0
THEED	17.2-17.4
BHEI	18.2-18.5
TEHEED	20.4-20.6

*This will vary slightly according to the concentration of the compound present in the sample and the age of the column.

CHAPTER 6

EXPERIMENTAL EQUIPMENT AND PROCEDURE FOR THE CONTROLLED DEGRADATION OF DEA

6.1 600 ml. autoclave

Since DEA degradation is rather complex, the experiments had to be performed under carefully controlled conditions. In particular, it was necessary to keep the temperature and pressure constant for the full duration of a run.

The main component of the experimental equipment was a 600 ml. stainless steel autoclave supplied by the Parr Instrument Company, Ill. (Model 4560). The autoclave could be operated from room temperature up to 400°C at pressures ranging from atmospheric to 13.79 MPa (2000 psi). The principle features of the reactor (see Fig. 6.1) are summarized below.

1. Variable speed stirrer, 0-600 r.p.m., driven by a drive assembly that could be easily disconnected and swung aside to allow full access to the autoclave head fittings.
2. Valves for adding gas, removing gas, and withdrawing liquid samples during runs.
3. A 0-2000 psi pressure gauge, accurate to within ± 5 psi.
4. A safety rupture disc.
5. A close fitting, quartz fabric heating mantle in an insulated aluminium housing. The heater could be easily lowered from the autoclave

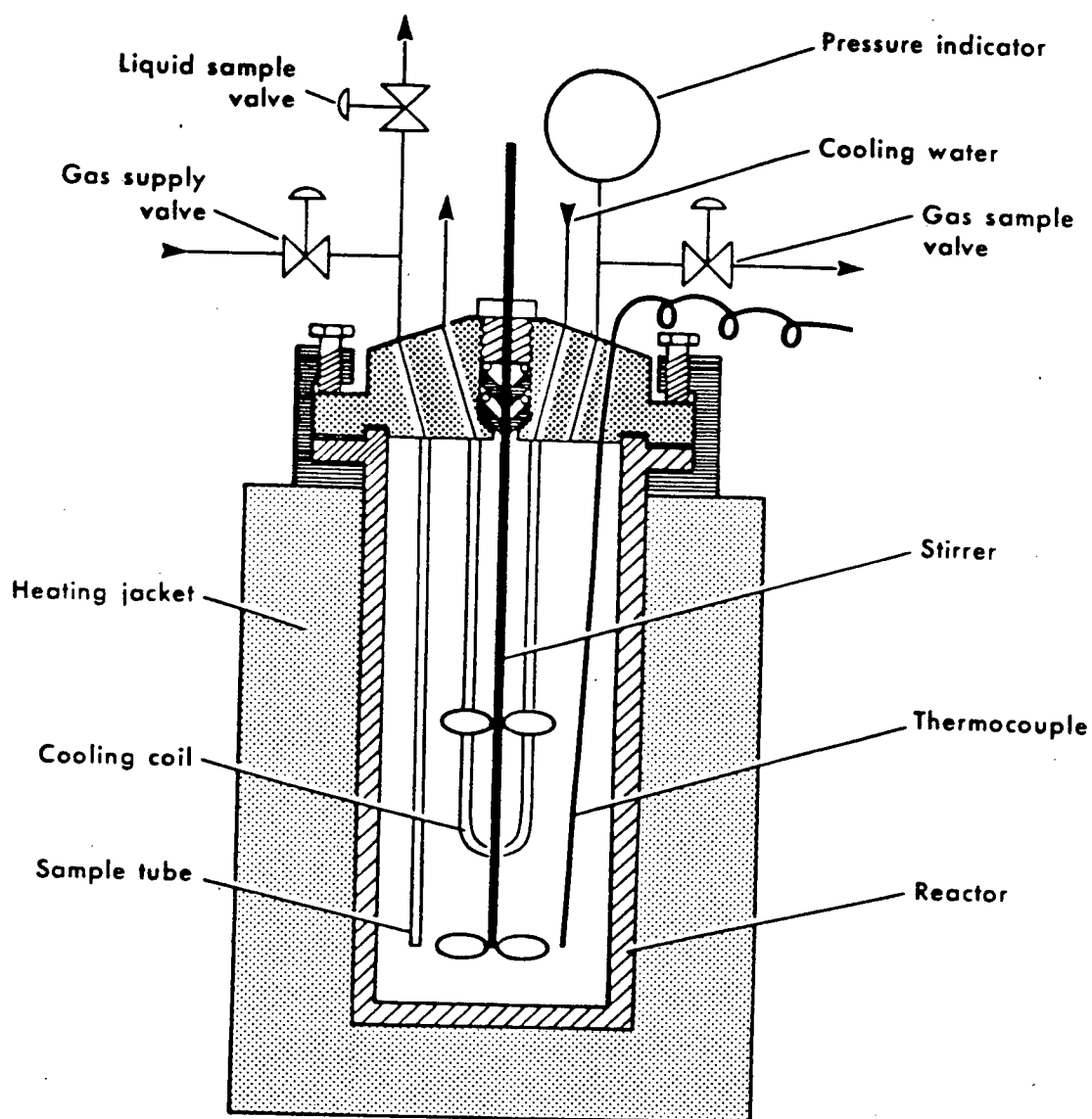


Figure 6.1 Sketch of 600 ml. autoclave

without disturbing the stirrer or affecting any of the head connections.

6. A J-type thermocouple in a stainless steel well placed within the autoclave for measuring the reaction temperature.
7. An automatic temperature controller (Parr, Model 4831EB) whose output is monitored by a digital thermometer (Doric, Series 400A, Model 410A) and recorded on a strip chart recorder (Corning, Model 840). The controller was capable of holding the temperature to within $\pm 0.5^{\circ}\text{C}$ of the desired value for an indefinite period (experiments lasting up to 30 days were performed).
8. An internal cooling coil, which was useful for controlling exothermic reactions and for rapid cooling at the end of a run.
9. The autoclave could be fitted with a pyrex liner so that experiments could be performed without the reactants coming into contact with the metal surface of the autoclave.

6.2 Loading the autoclave

It was desirable to inject the aqueous DEA solution into the autoclave, which had been raised to the desired operating temperature. This measure minimized the problem of accounting for the time required to heat the autoclave and feed at the beginning of a run. A modified 500 ml. pressure sampling cylinder was used for the injection (see Fig. 6,2). The cylinder was first purged with CO_2 or N_2 depending on the type of run being conducted. The purging was necessary to remove any oxygen which could react with DEA forming heat stable salts. The cylinder was then filled with about 250 ml. of aqueous DEA solution and pressurized with CO_2 or N_2 to the operating pressure. The contents of the cylinder were then discharged into the autoclave which was at operating

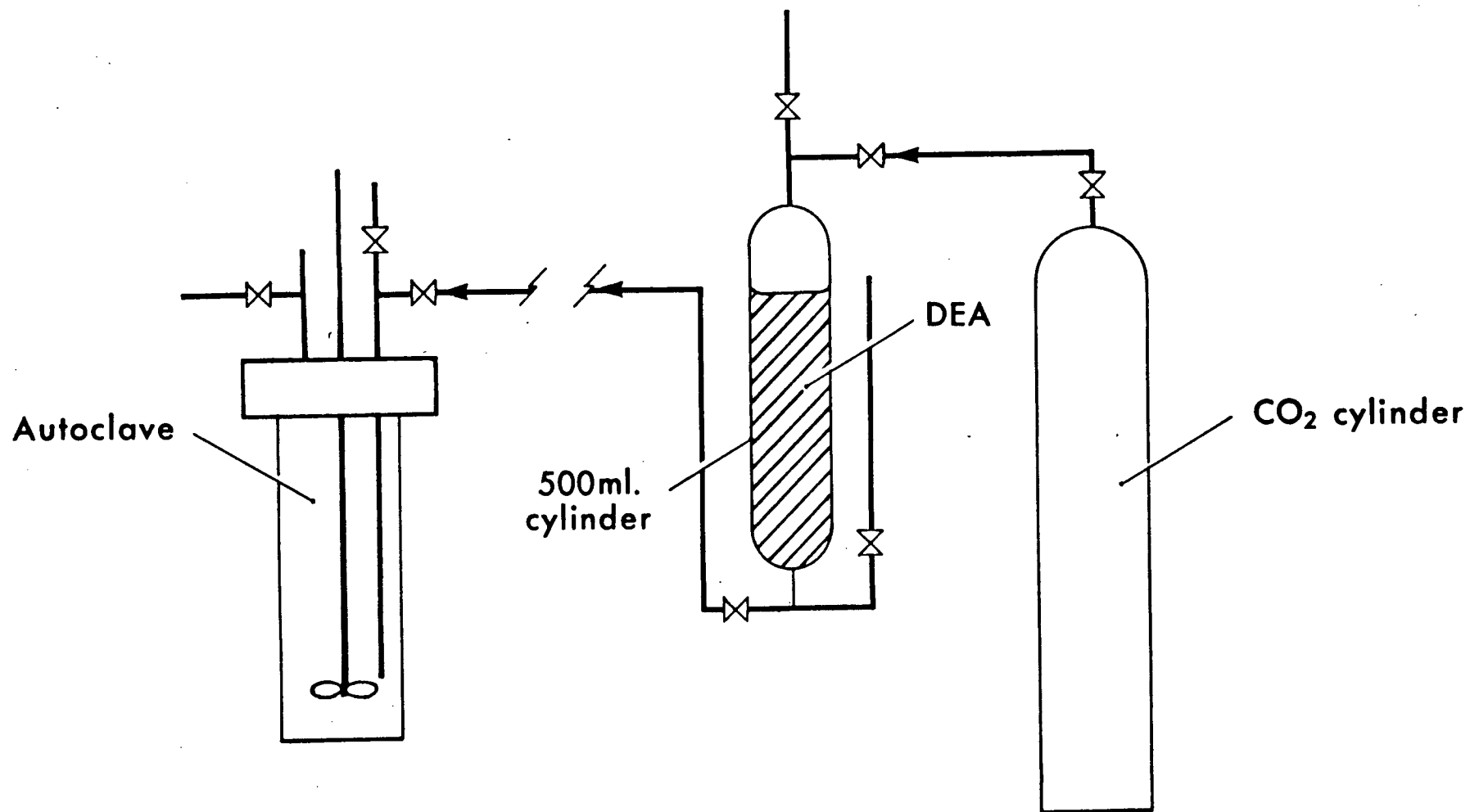


Figure 6.2 Sketch of the autoclave loading system

temperature. A short amount of time (5-10 min.) was then required for the temperature and pressure to level off.

6.3 Sampling

Sampling was done at the operating temperature and pressure by means of a 5 ml. coiled sample tube fitted with an inlet and outlet valve. The sample tube could be easily fitted and removed from the liquid sample port of the autoclave during a run.

The following method was used for obtaining a sample from the reaction mixture. The sample tube was first connected to the autoclave sample port. The autoclave sample valve was opened with the sample tube inlet and outlet valves closed. The sample tube inlet valve was then opened and a liquid sample was forced into the tube under the reactor pressure. The outlet valve was then opened slightly to bleed off a little sample. All the valves were then shut and the sample tube removed and placed in water for rapid cooling. The sample was then removed from the tube and stored in a glass sample bottle under a blanket of nitrogen for later use.

6.4 Analysis of the liquid samples

The samples for the runs were stored in 7 ml. glass bottles with screw tops. 1 μ l. samples were then injected into the gas chromatograph under the conditions described in chapter 3. When the 30 minute analysis was complete the peak areas and retention times of the major peaks of the chromatogram were recorded. Using the calibration curves (see Figs. 3.3-3.6) the concentrations of DEA and its major degradation products could be determined. Using these data, curves of concentration versus time could be plotted and studied.

6.5 Analysis of the gas phase

The degradation of DEA by CO_2 did not result in the production of measurable amounts of gaseous degradation products. Aqueous samples of degraded DEA, which had been removed from the autoclave at various times during a run, were analysed for carbon, hydrogen, oxygen, and nitrogen. The concentration of each element in the liquid phase did not change during the runs. This indicates that no gaseous products were formed in the DEA degradation. Therefore, analysis of the gas phase was considered unnecessary.

6.6 Experimental procedure

A typical controlled degradation run involves reacting an aqueous DEA solution with CO_2 at a desired temperature and pressure for a specific length of time. Samples were removed at regular intervals throughout the run. The subsequent procedure was followed.

1. The autoclave was first sealed empty.
2. The autoclave and modified sampling cylinder were then purged with CO_2 .
3. The autoclave was heated to the desired operating temperature.
4. About 250 ml. of fresh aqueous DEA solution of known concentration was charged to the modified sampling cylinder.
5. The aqueous DEA was injected under pressure into the autoclave.

The stirrer speed was set at about 150 r.p.m. and several minutes were allowed for the temperature and pressure to settle down.

Initially the CO_2 was absorbed by the DEA and the autoclave pressure had to be checked regularly over the first half hour of the run.

CO_2 was added when necessary to keep the operating pressure constant.

Also, since the absorption of CO_2 is an exothermic reaction, water

was passed through the cooling coil to maintain the operating temperature. After about 30 min. the temperature and pressure became steady and required no further attention. (Usually much less than half an hour was required, depending on operating temperature, pressure, and DEA concentration.)

6. Samples were removed at regular intervals during the run using the sampling tube. After the sample had been transferred to the sampling bottle the sampling tube was thoroughly cleaned with distilled water and dried with air.
7. When the run was completed, the heating jacket of the autoclave was switched off and removed. Water was then passed through the cooling coil and the autoclave and contents rapidly cooled to room temperature.
8. When the autoclave was at room temperature the pressure was reduced to atmospheric and the autoclave opened. Once the contents had been removed the autoclave was thoroughly cleaned with distilled water.

Most runs were conducted with 250 ml. of solution in the 600 ml. autoclave. This volume of solution was considered sufficient so that the removal of several samples did not have a significant effect on the reactant volume. Also the reactant volume was not too large to limit the availability of CO_2 . It was hoped that CO_2 would be in excess for all the runs. A pressure of 600 psi, used in most runs, was chosen partly to compare the results of this work with other studies^{34,41} and partly because it is close to pressures used industrially. The duration of the experiment depended simply on how long it took for significant degradation to take place.

6.7 Maintenance and performance

The main problem with the autoclave was gas leakage around the stirrer shaft. There is a short hose nipple, which can be used to monitor the packing gland to detect any leakage as the packing elements and stirrer shaft become worn. Repacking, therefore, had to be carried out periodically. The frequency with which the gland was repacked depended on operating temperature and pressure, nature of the reactants, and the state of repair of the other various elements of the stirrer assembly. However, as a rule, the packing elements were usually replaced after 200 to 300 hours of service. On several occasions the stirrer shaft, in the vicinity of the packing, became worn and had to be replaced. Other than leakage, the autoclave was relatively trouble free. Perhaps the only other problem was cleaning. Usually flushing the equipment with water was sufficient. However, a slow build-up of a thick viscous residue occurred and, periodically, the whole equipment had to be dismantled and thoroughly cleaned using water.

6.8 Sources of errors

It is possible that a sample may have a composition slightly different from the composition of the solution in the autoclave. When a sample is removed from the autoclave it undergoes temperature and pressure changes which may cause the equilibria set up in the bulk liquid to change. Slight errors could also occur in recording the time of sample removal. However this error becomes insignificant for runs of over eight hours.

The temperature controller operates using a simple on/off control. This caused the temperature to oscillate between $\pm 1^{\circ}\text{C}$ at 205°C . Again this error is minimal and, due to the regular oscillation, is averaged out.

Other small errors occur in the reading of the pressure gauge and loss of CO₂ through sampling and minor leaks.

CHAPTER 7

PRELIMINARY EXPERIMENTS AND DEVELOPMENT OF THE EXPERIMENTAL PROGRAMME

7.1 Use of high temperatures for the degradation runs

Since the degradation reaction under plant operating conditions is extremely slow it was decided to conduct the majority of experiments in the temperature range of 175°-205°C. In this range it is possible to achieve significant degradation in a matter of hours rather than weeks. However, it had to be established that the degradation products produced at elevated temperatures were similar to those produced under plant conditions. This was done by first comparing the results of degrading 30 wt % DEA with 4137 kPa (600 psi) CO₂ at 205°C and 120°C (see runs 3 and 11, details of which can be found in Appendix B). Secondly, degraded samples of DEA produced in the laboratory were compared with samples obtained from industrial DEA gas treating units.

7.1.1 Temperature comparisons. Figure 7.1 shows the chromatogram of a degraded solution of DEA whose initial concentration was 3×10^{-3} moles/cc (~30 wt %) and had been degraded with CO₂ at 205°C for one hour. Figure 7.2 shows the chromatogram of a similar sample which was contacted with CO₂ at 120°C for 150 hr.

In both cases the DEA had degraded from 3×10^{-3} moles/cc to about 2.1×10^{-3} moles/cc, and three main degradation products were formed

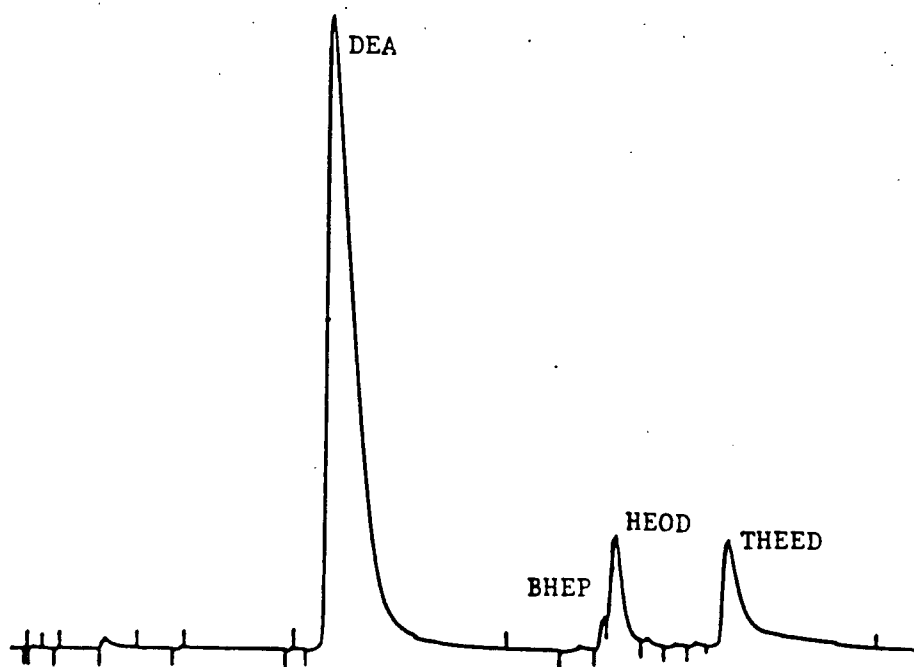


Figure 7.1 Chromatogram of a 30 wt % DEA solution degraded at 205°C under 4137 kPa CO₂ (time--1 hr.)

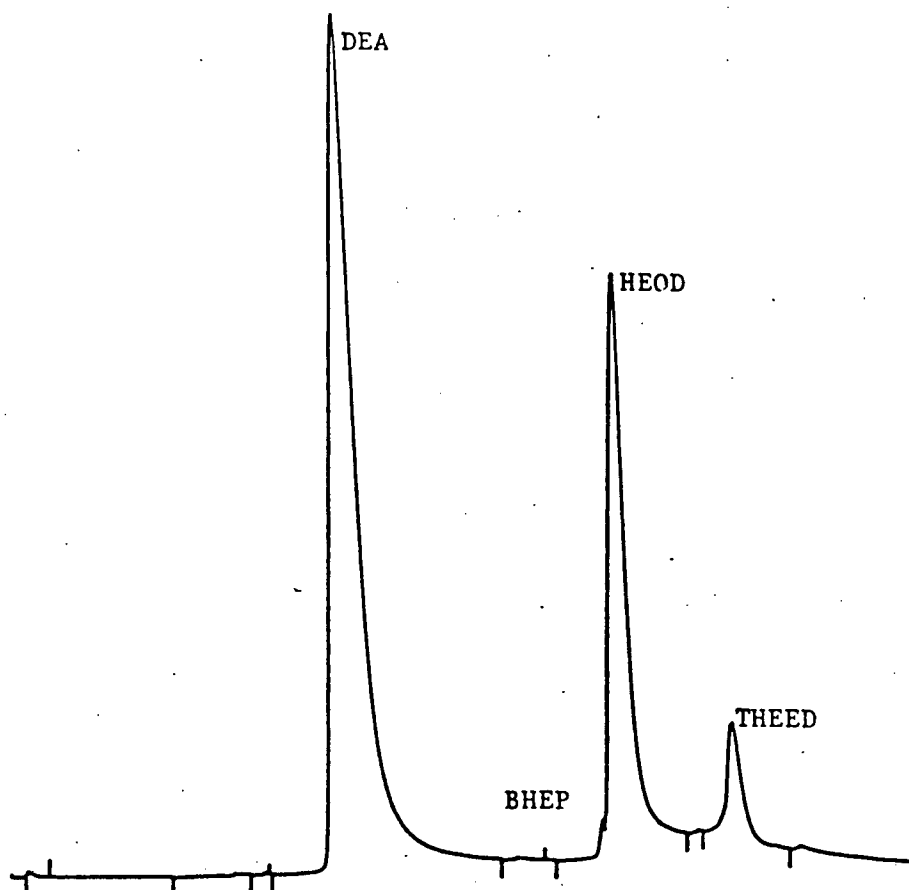


Figure 7.2 Chromatogram of a 30 wt % DEA solution degraded at 120°C under 4137 kPa CO₂ (time--150 hr.)

although in different amounts. These compounds were identified as HEOD, BHEP, and THEED. The reason for the difference in concentration of these compounds will be discussed in chapter 11.

7.1.2 Comparison with industrial samples. Figures 7.3 and 7.4 show chromatograms of DEA treating solutions supplied by Aquitaine Canada Ltd. and Hudson's Bay Oil and Gas Company Ltd. Peaks of HEOD, BHEP, and THEED are evident. A fourth peak is present in the industrial samples which is probably TEA, since industrial DEA solutions contain significant quantities of TEA compared with reagent grade DEA.

From Figs. 7.1-7.4 it is seen that there are strong similarities between the composition of DEA solutions degraded under laboratory conditions at high and low temperatures and those degraded under industrial conditions. It may, therefore, be concluded that DEA undergoes essentially the same kind of reaction in each case.

7.1.3 Thermal degradation. It is known that DEA can undergo thermal decomposition at its boiling point.⁵ Therefore, it had to be determined whether thermal degradation was significant at 205°C. A simple test was conducted in which a 30 wt % solution of DEA was heated to 205°C for 8 hr. under 4137 kPa (600 psi) of nitrogen (run 53). No significant change in the DEA concentration or the formation of degradation compounds were noted. However, in a similar test which lasted 200 hours (run 54), measurable quantities of BHEP and THEED were produced. Since all the runs conducted at elevated temperatures lasted only eight hours, thermal degradation was not considered to be significant.

7.1.4 Justification for the use of elevated temperatures. Experiments conducted at temperatures well above the operating temperature of an industrial gas treating unit is justified for the following reasons.

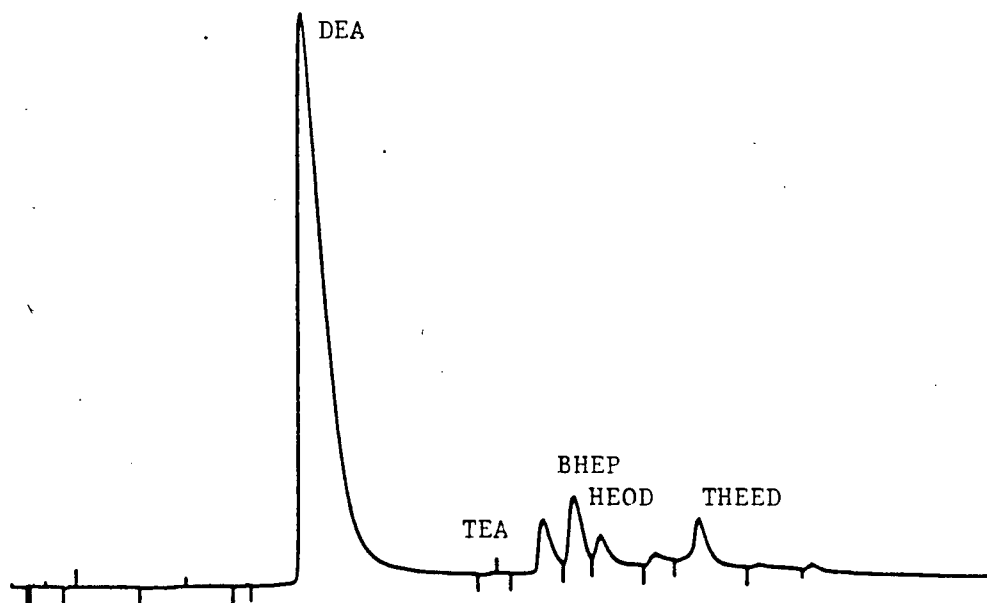


Figure 7.3 Chromatogram of a degraded DEA solution from a gas sweetening unit operated by Aquitaine Canada Ltd.

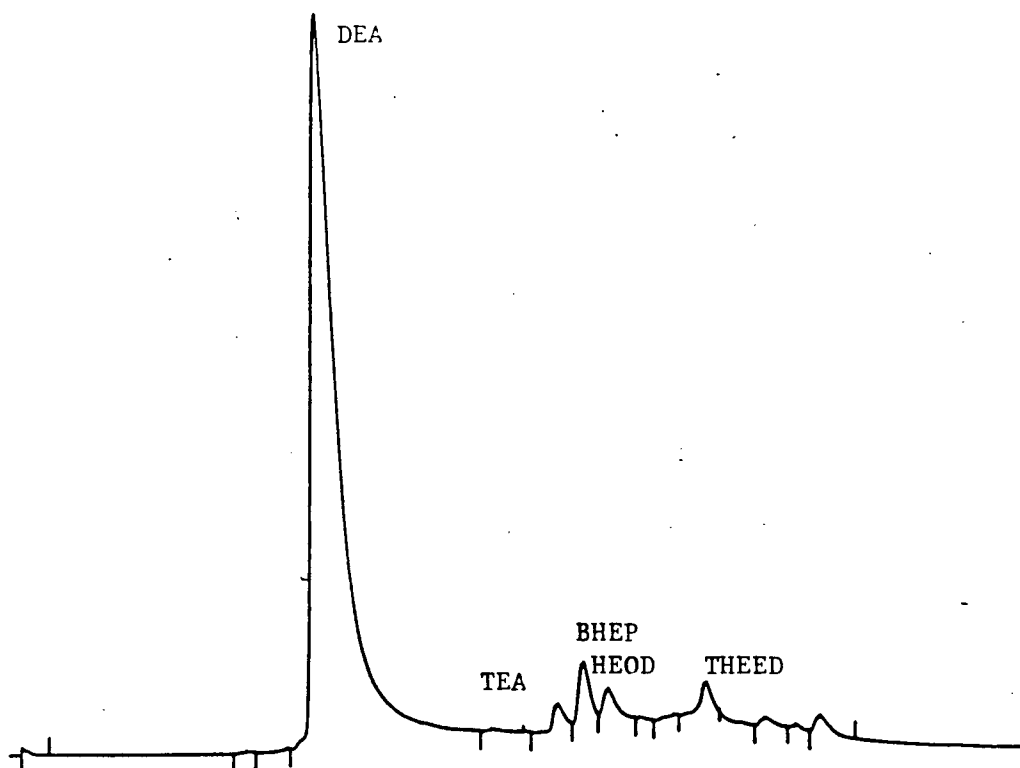


Figure 7.4 Chromatogram of a degraded DEA solution from a gas sweetening unit operated by Hudson's Bay Oil and Gas Co. Ltd.

1. Elevated temperatures accelerate the DEA degradation and make it possible to complete tests in hours rather than weeks.
2. Degradation products formed at elevated temperatures are quite similar to those produced under plant conditions.
3. Temperatures experienced by DEA in operating plants may, at certain points, be much higher than expected. For example, the surface temperature of the heating tubes in the stripper reboiler can be considerably higher than the bulk DEA temperature.
4. Thermal degradation of DEA is not a problem at temperatures up to 205°C.

7.2 Effect of metal surfaces

It has been reported that the presence of metal ions may affect degradation.^{11,16} Therefore, to determine the influence of the stainless steel surface of the autoclave, several runs were conducted using a pyrex liner in the autoclave. The results of these runs were compared with those from identical runs where the liner was absent. No significant change was noted and therefore subsequent runs did not use the pyrex liner.

7.3 Effect of stirrer speed and reactant volume

Various stirrer speeds in the range of 10-150 r.p.m. and reactant volumes in the range of 50-450 ml were used. The purpose of these runs was to determine if the mass transfer of CO₂ from the atmosphere above the solution to the DEA was affected by stirrer speed and/or volume of available CO₂. No significant effects were noted. This was probably due to the fact that the degradation reaction is extremely slow in comparison to CO₂ dissolving into the DEA solution (see chapter 2). Hence the DEA solution is saturated with CO₂ before any significant degradation

takes place and changes such as stirrer speed, have little effect.

7.4 Reproducibility

7.4.1 Samples. Degraded samples of DEA were, in general, very stable at room temperature. Analysis of samples over a two year period were found to be virtually identical. This not only demonstrated the stability of the samples but also the reliability of the analytical procedure.

7.4.2 Runs. Several runs were repeated over a two year period and were found to agree well within $\pm 5\%$. For example, Table 7.1 shows the concentration of DEA versus time for three different runs where a 3×10^{-3} moles/cc DEA solution was degraded at 175°C under 4137 kPa (600 psi) CO_2 . Run C was conducted two years after runs A and B.

Table 7.1 Comparison of reproducibility of degradation runs

Sample Hours	Concentration of DEA moles/cc		
	Run A	Run B	Run C
0	3.00×10^{-3}	3.085×10^{-3}	3.1×10^{-3}
1	2.67	2.85	2.76
2	2.36	2.39	2.43
3	1.988	2.13	2.19
4	1.84	1.87	1.9
5	1.58	1.63	1.7
6	1.44	1.45	1.45
7	1.24	1.23	1.3
8	1.08	1.17	1.12

7.5 Experimental programme

Having established a simple experimental procedure to observe the degradation of DEA under controlled conditions, it was attempted to devise an experimental programme which could produce sufficient information to develop a kinetic model for the reactions. Experiments were therefore conducted to observe the effect of temperature, total pressure and initial DEA concentration. Table 7.2 summarizes the runs carried out.

Table 7.2 Summary of experiments performed with CO₂ at 4137 kPa (600 psi)

Initial DEA Concentration wt %	Temperature °C											
	250	220	205	195	185	175	162	150	145	140	120	90
100			x			x					x	
80			x									
60			x			x		x				
40			x									
30	x	x	x	x	x	x	x	x	x	x	x	x
20			x			x		x			x	
15			x			x		x				
10			x			x		x				
5			x									

A subsequent series of experiments degraded 30 wt % DEA at 195°C under the following pressures of CO₂:- 6895(1000), 5516(800), 4137(600), 3448(500), 2758(400), 2067(300), 1517(220) kPa (psi).

The results of all these sets of experiments are tabulated in Appendix B.

It was later discovered that these experiments were not sufficient to explain fully the degradation mechanism although they could be used

as the basis for developing a kinetic model of the reactions. Therefore, further runs were performed to study the degradation mechanism and are described in chapters 9 and 10. For this reason the chapter on experimental results and discussion has been split into three chapters. Chapter 8 discusses experiments designed to study the kinetics, chapter 9 discusses experiments designed to study the degradation mechanism, and chapter 10 discusses experiments designed to study the behaviour of the major degradation compounds and feed impurities.

CHAPTER 8

RESULTS AND DISCUSSION OF EXPERIMENTS DESIGNED TO STUDY THE KINETICS OF THE DEGRADATION REACTION

The results of the degradation runs are tabulated in Appendix B in the form of concentration of DEA and its main degradation products versus time. Figure 8.1 shows typical chromatograms of a DEA solution degraded under lab conditions (run 3) corresponding to samples taken at 2 hour intervals. Three major degradation peaks produced by BHEP, HEOD, and THEED are evident. The MEA peak is an impurity in the initial solution. The HEOD and THEED peaks increase sharply at first and then either remain constant in size or decrease. This suggests that both HEOD and THEED are intermediate degradation compounds. The DEA peak decreases progressively whereas the BHEP peak grows.

It was observed that the DEA solution slowly darkened with the colour changing from a light yellow to a dark brown as degradation progressed. Also there was a change in odour with the solution becoming more pungent.

Although many other degradation compounds were detected especially at high temperatures, it is believed that it was only necessary to record, in full, data on DEA, BHEP, HEOD, and THEED. This conclusion was reached because the other minor degradation compounds existed generally in very low concentrations and, probably, had little effect on the kinetic model.

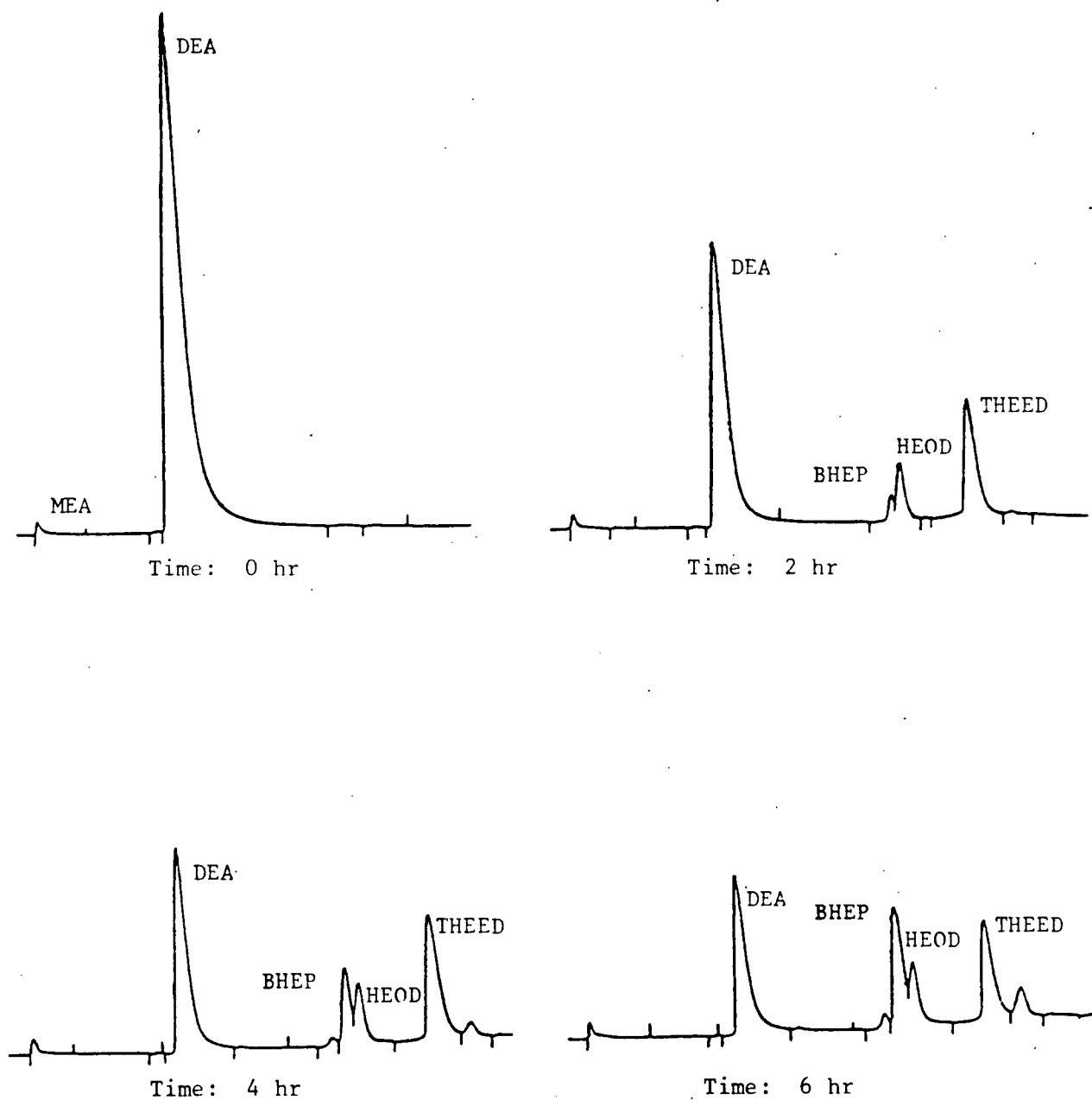


Figure 8.1 Typical chromatograms of a 30 wt % DEA solution degraded at 205°C under 4137 kPa CO₂

8.1 Effect of temperature

Figures 8.2 and 8.3 show the change of DEA concentration with time when a solution consisting initially of about 30 wt % DEA is subjected to CO₂ at a pressure of 4137 kPa (600 psi) and temperatures ranging from 90-250°C (runs 1-12). The results have been plotted on semi-logarithmic scales. The reason for this is that earlier work^{34,41} suggested the initial degradation of DEA to be governed by a first order reaction. Hence, when CO₂ is in excess, DEA was thought to degrade according to the following equations:-



$$\text{then} \quad \frac{d[\text{DEA}]}{dt} = -k_{\text{DEA}} [\text{DEA}]_t \quad [8.2]$$

where $[\text{DEA}]_t$ = concentration of DEA at time t

t = time

k_{DEA} = overall reaction rate constant

The integrated form of Eqn. 8.2 is:-

$$\log [\text{DEA}]_t = \log [\text{DEA}]_0 - \frac{k_{\text{DEA}} t}{2.303} \quad [8.3]$$

If the degradation of DEA is first order then a semi-logarithmic plot of $[\text{DEA}]$ versus t should be a straight line.

Examination of Figs. 8.2 and 8.3 indicates that the data fall on straight lines especially at low temperatures. However, at high temperatures, the degradation rate slows perceptibly after about 5 hours. In an extended run (run 32, Fig. 10.2) where 30 wt % DEA was degraded under 4137 kPa (600 psi) CO₂ at 205°C for 50 hours, the DEA concentration approached a nearly constant value of about 2 wt %. This suggests that the reaction is more complicated than initially suspected. It is possible

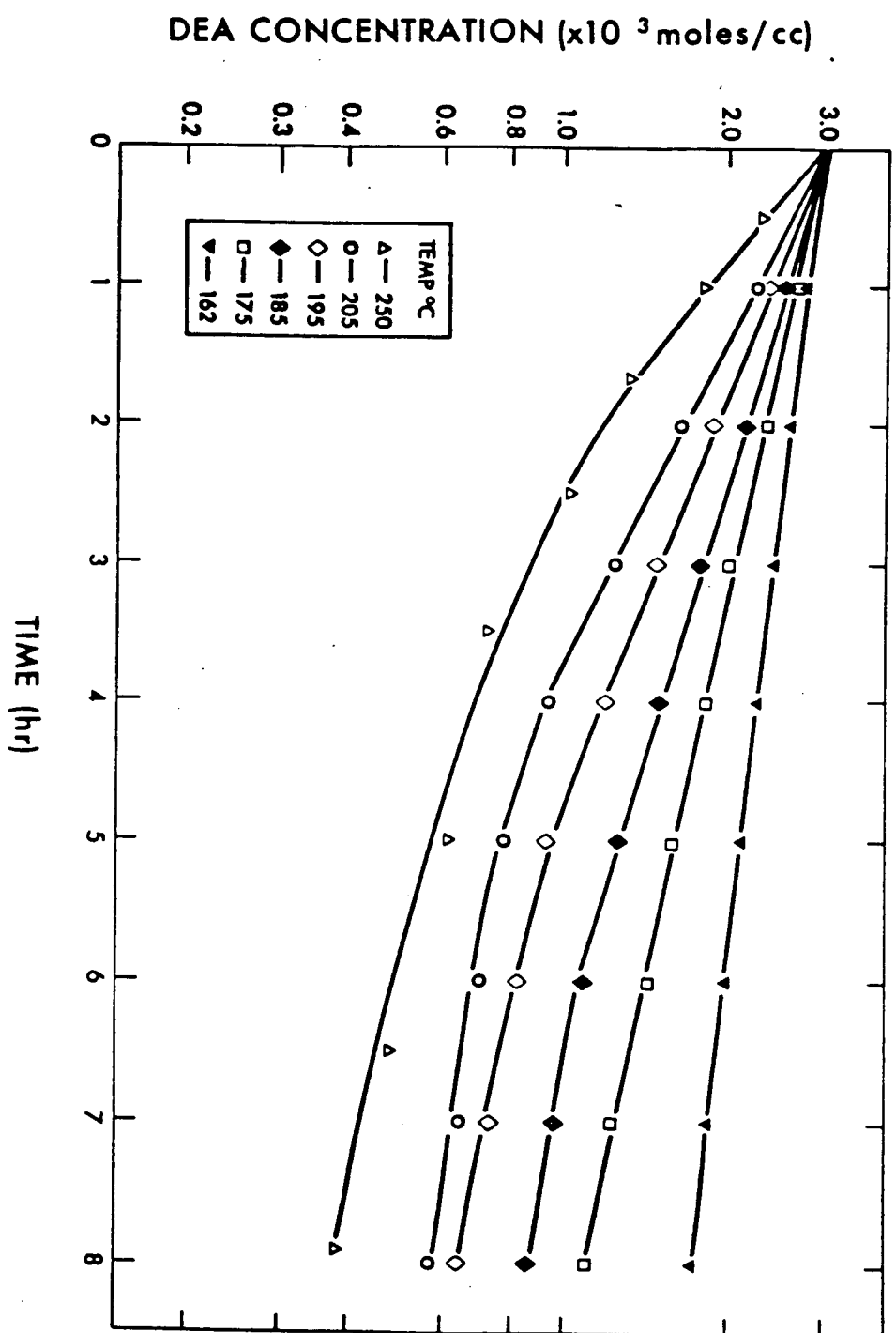


Figure 8.2 DEA concentration as a function of time and temperature (4137 kPa CO₂, 205-162°C)

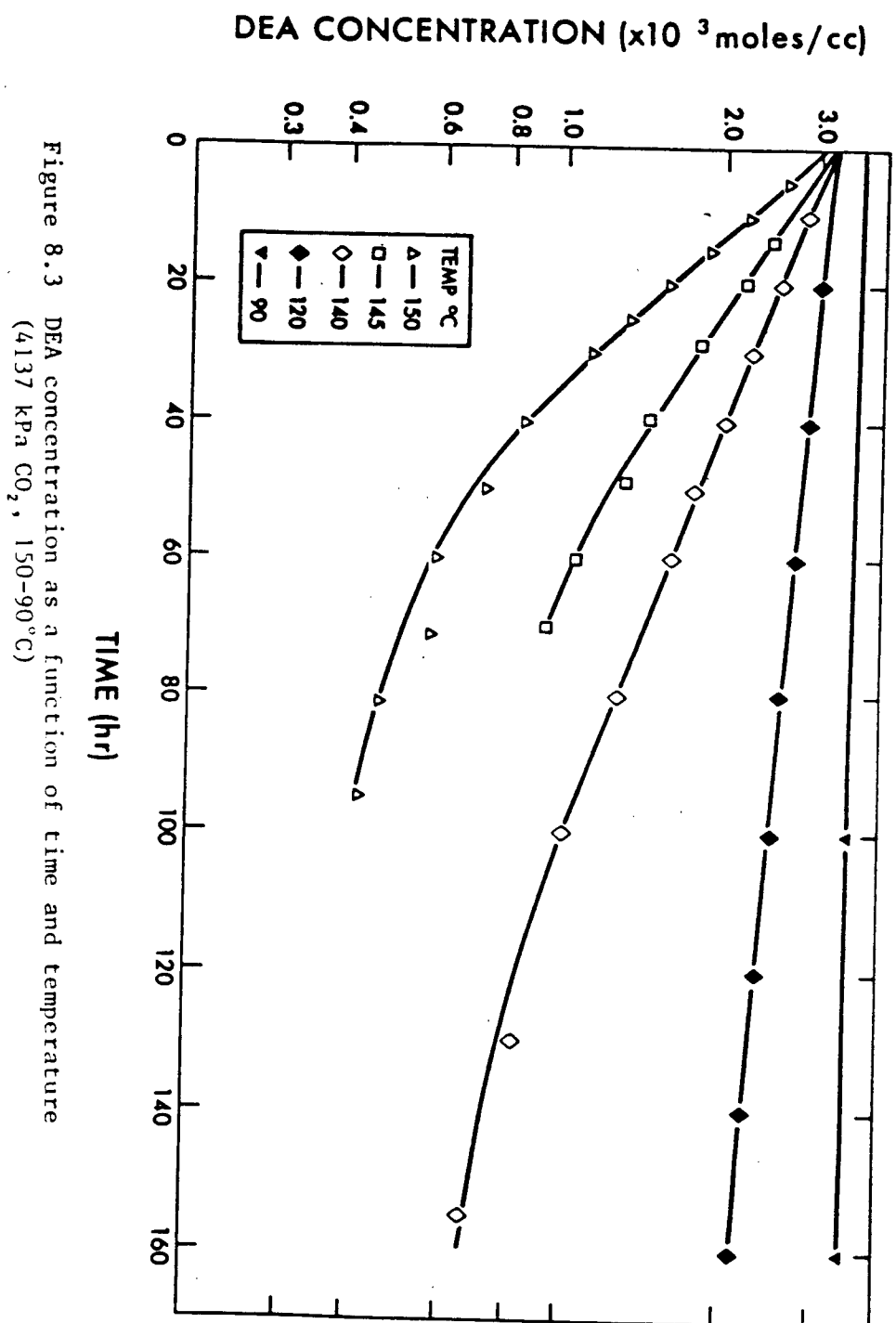


Figure 8.3 DEA concentration as a function of time and temperature (4137 kPa CO₂, 150-90°C)

that CO_2 may cease to be in excess as the run proceeds, or the degradation products themselves may inhibit the degradation or the degradation reactions are reversible. These possibilities will be discussed later in chapter 11.

Since it was not clear whether the initial degradation was governed by a first order reaction, further confirmation was sought. Using Levenspiel's technique⁶⁹, the reaction order was obtained from studying initial degradation rates. Assuming CO_2 is in excess the general degradation reaction is of the form:-



$$\text{Hence} \quad \frac{d [\text{DEA}]}{dt} = - k_{\text{DEA}} [\text{DEA}]^a \quad [8.5]$$

$$\text{or} \quad \log\left\{-\frac{d [\text{DEA}]}{dt}\right\} = \log\{k_{\text{DEA}}\} + a \log \{[\text{DEA}]\} \quad [8.6]$$

Therefore, if the log of initial degradation rate is plotted against log of the initial concentration, then a straight line should be produced with a slope equivalent to the reaction order. The initial degradation rates were calculated from runs of varying initial DEA concentration (runs 13-29) at 205, 175, and 150°C. The results are tabulated in Tables 8.1 to 8.3. Figure 8.4 shows the corresponding plots.

Table 8.1 Initial DEA concentration and initial DEA degradation rates at 205°C

Run No.	Initial concentration moles/cc	Initial degradation rate moles/cc.hr.
13	10×10^{-3}	2.2×10^{-3}
14	8	2
15	6	1.4
16	4	1.18
3	3	0.85
17	2	0.5
19	1	0.26

Table 8.2 Initial DEA concentration and initial DEA degradation rates at 175°C

Run No.	Initial concentration moles/cc	Initial degradation rate moles/cc.hr.
21	10×10^{-3}	11×10^{-4}
22	6	6
6	3	3.8
23	2	2.2
24	1.5	1.65
25	1	0.91

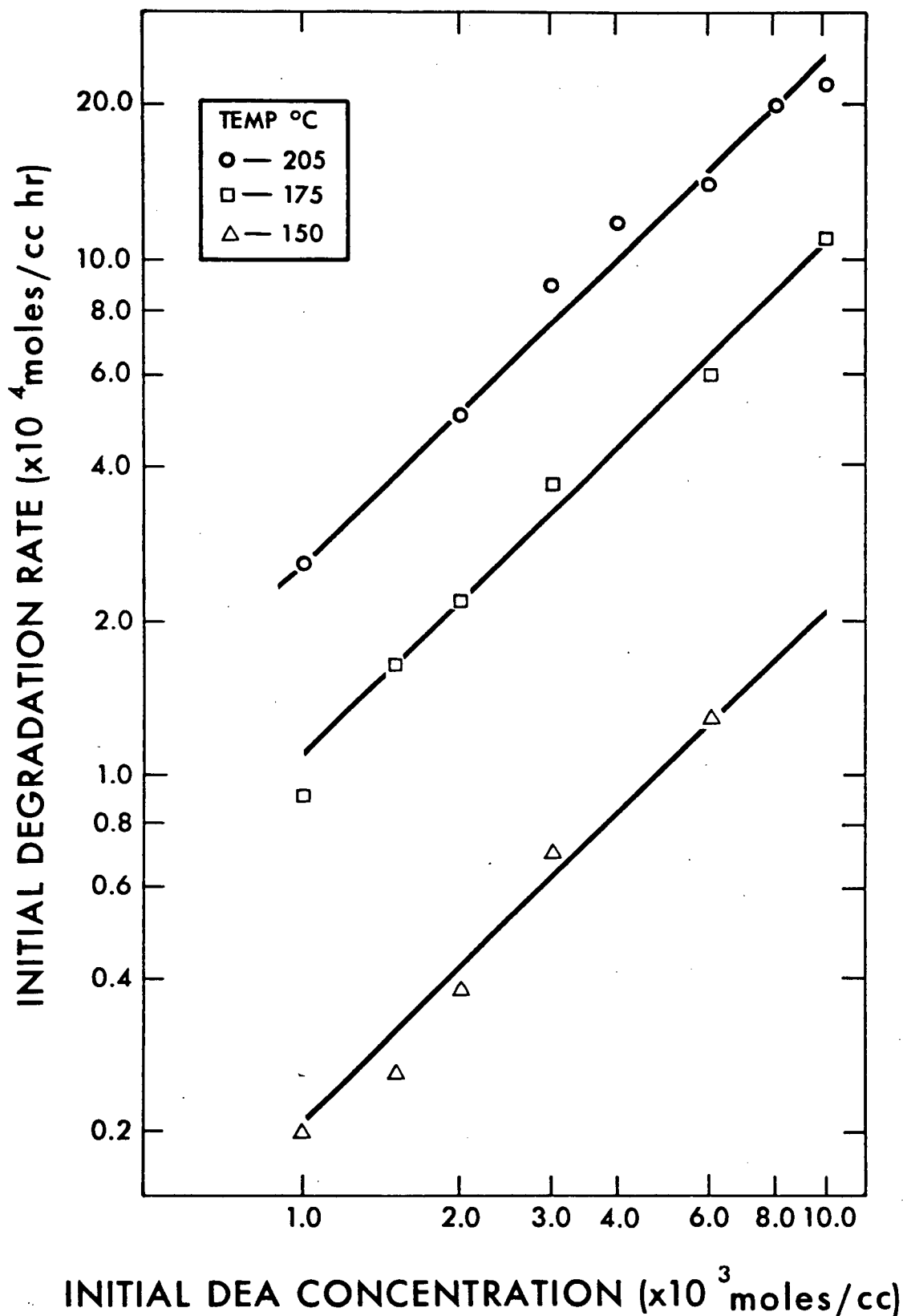


Figure 8.4 Initial degradation rate as a function of initial DEA concentration and temperature

Table 8.3 Initial DEA concentration and initial DEA degradation rates at 150°C

Run No.	Initial concentration moles/cc	Initial degradation rate moles/cc.hr.
26	6×10^{-3}	12.9×10^{-5}
8	3	7.1
27	2	3.8
28	1.5	2.6
29	1	2.0

Using the method of least squares lines were fitted to the plots of $\log(-\frac{d[\text{DEA}]}{dt})$ versus $\log [\text{DEA}]$. The slopes of the lines were found to range from 1.025 to 0.996. Thus it can be assumed the initial degradation reaction is first order.

A further check is provided by an Arrhenius plot based on the relationship:-

$$k_{\text{DEA}} = A \exp. \{-E/RT\} \quad [8.7]$$

$$\text{or} \quad \log k_{\text{DEA}} = \log A - \frac{E}{2.303R} \cdot \frac{1}{T} \quad [8.8]$$

where A = frequency factor

E = activation energy

R = universal gas constant

T = absolute temperature

If the data, when plotted as $\log k_{\text{DEA}}$ vs. $1/T$, fall on a straight line then the first order hypothesis is confirmed. Figure 8.5 is an Arrhenius plot where k_{DEA} is calculated from the initial slopes of the curves in Figs. 8.1 and 8.2. As can be seen, the plot is linear at temperatures

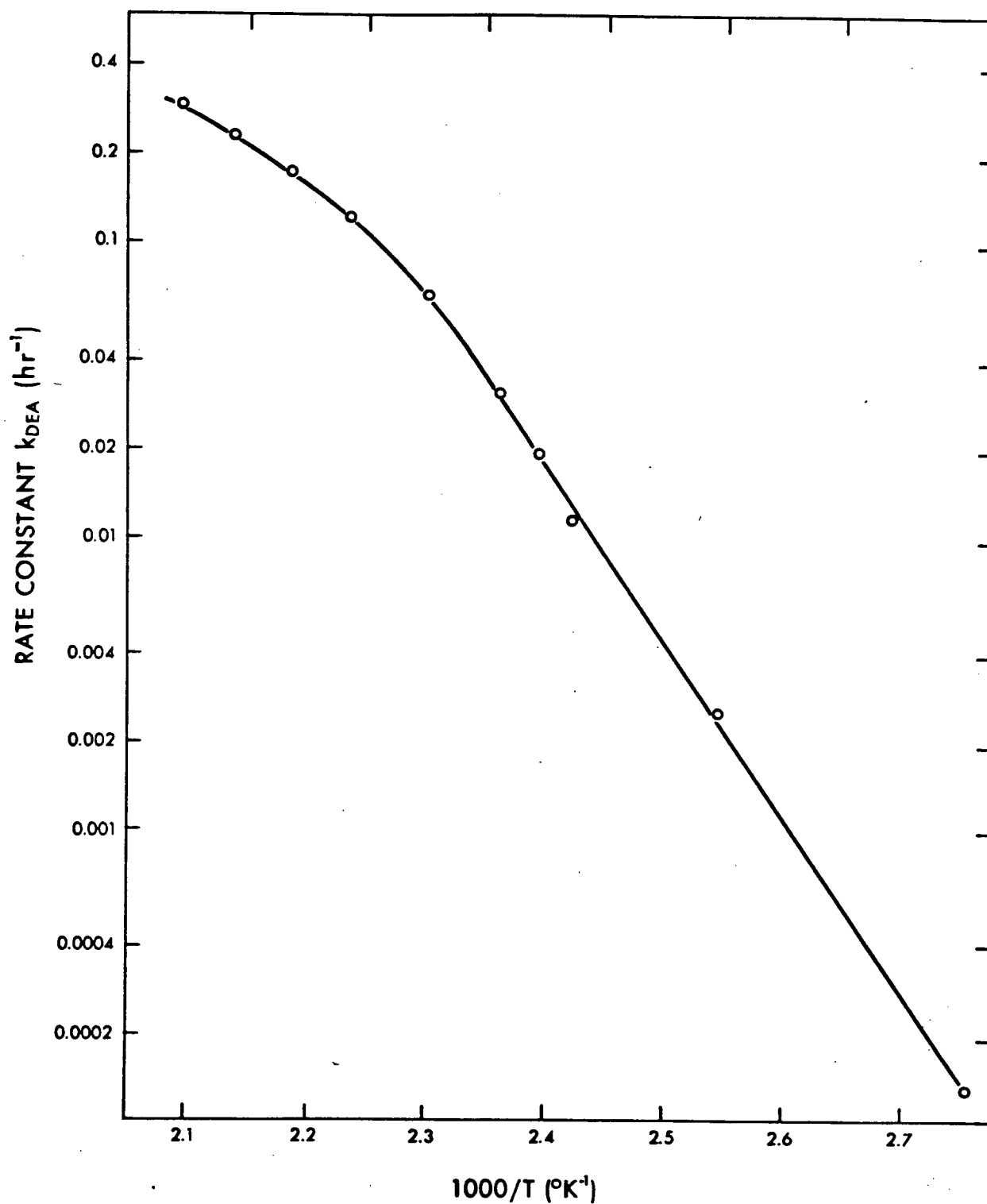


Figure 8.5 Arrhenius plot for a 30 wt % DEA solution degraded with CO_2 at 4137 kPa

ranging from 90-170°C. However, at higher temperatures, there is a departure from the straight line behaviour, once again indicating that more complex reactions are taking place. It is likely that the first order behaviour is only apparent, i.e., there may be several consecutive reactions taking place which are affected differently by temperature. What can be concluded, however, is that the reaction is highly sensitive to temperature. The initial degradation rate increases by nearly a factor of 3000 as the temperature is raised from 90 to 205°C.

8.1.1 Degradation products. Figures 8.6 to 8.11 show plots of HEOD, THEED, and BHEP concentration versus time. Solid lines are drawn through the experimental data points to indicate any observable trends.

8.1.1.1 HEOD. It can be seen from Figs. 8.6 and 8.7 that there is a rapid production of HEOD which levels off. The initial rate increases with temperature although the overall amount of HEOD produced decreases. HEOD does not appear, therefore, to act as an intermediate of the type suggested by the mechanism of Polderman and Steele.³⁴ It may be possible for HEOD to be a final product of DEA degradation, which is thermally unstable. This point will be discussed further in chapter 11.

8.1.1.2 THEED. Figs. 8.8 and 8.9 show that the THEED concentration increases with time at a slightly lower rate than the HEOD concentration, reaching a maximum value before decreasing again. The time required to reach the maximum concentration decreases with increasing temperature. THEED appears to behave more like an intermediate than HEOD.

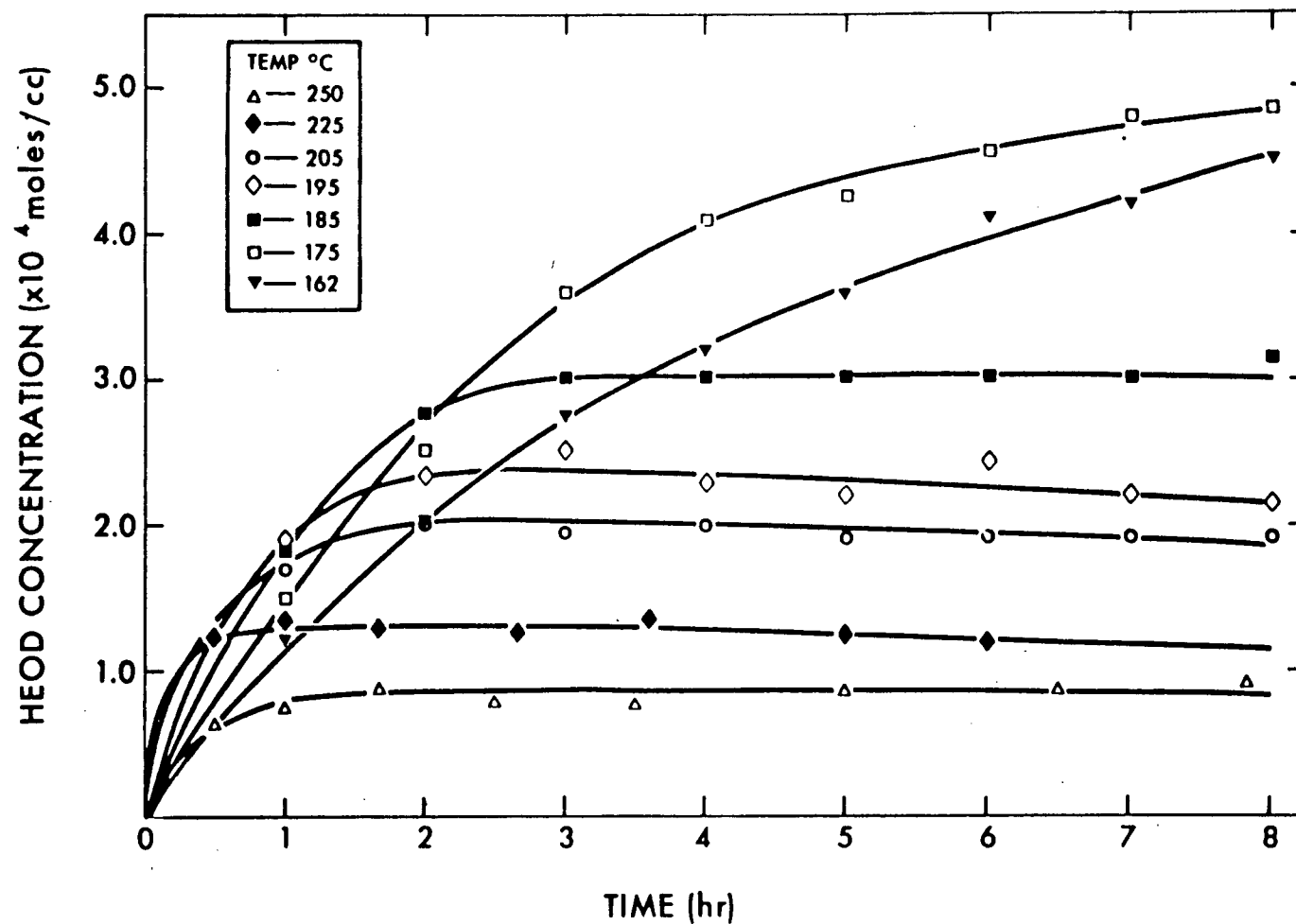


Figure 8.6 HEOD concentration as a function of time and temperature
(30 wt % DEA, 4137 kPa CO₂, 205–162 °C)

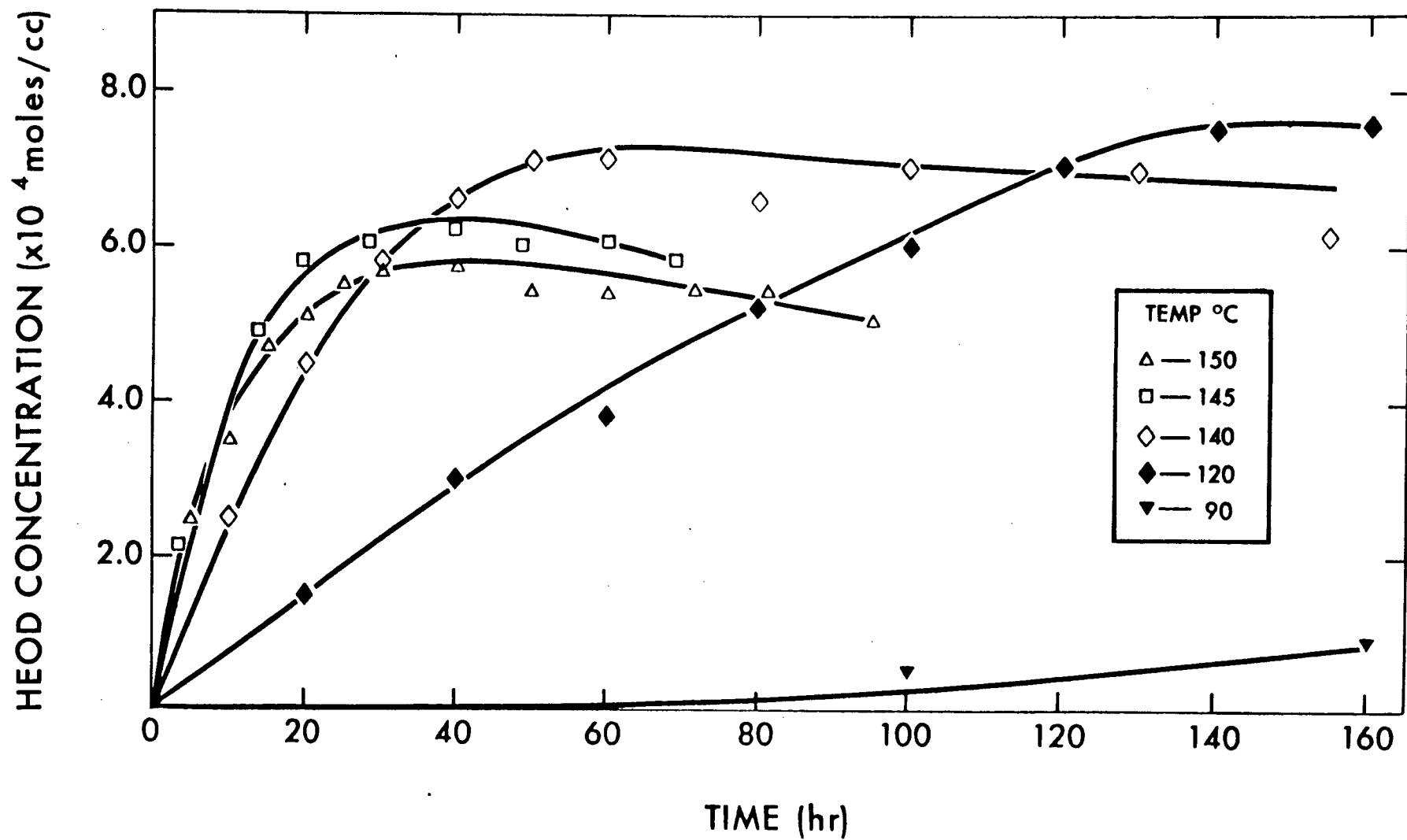


Figure 8.7 HEOD concentration as a function of time and temperature
(30 wt % DEA, 4137 kPa CO₂, 150–90°C)

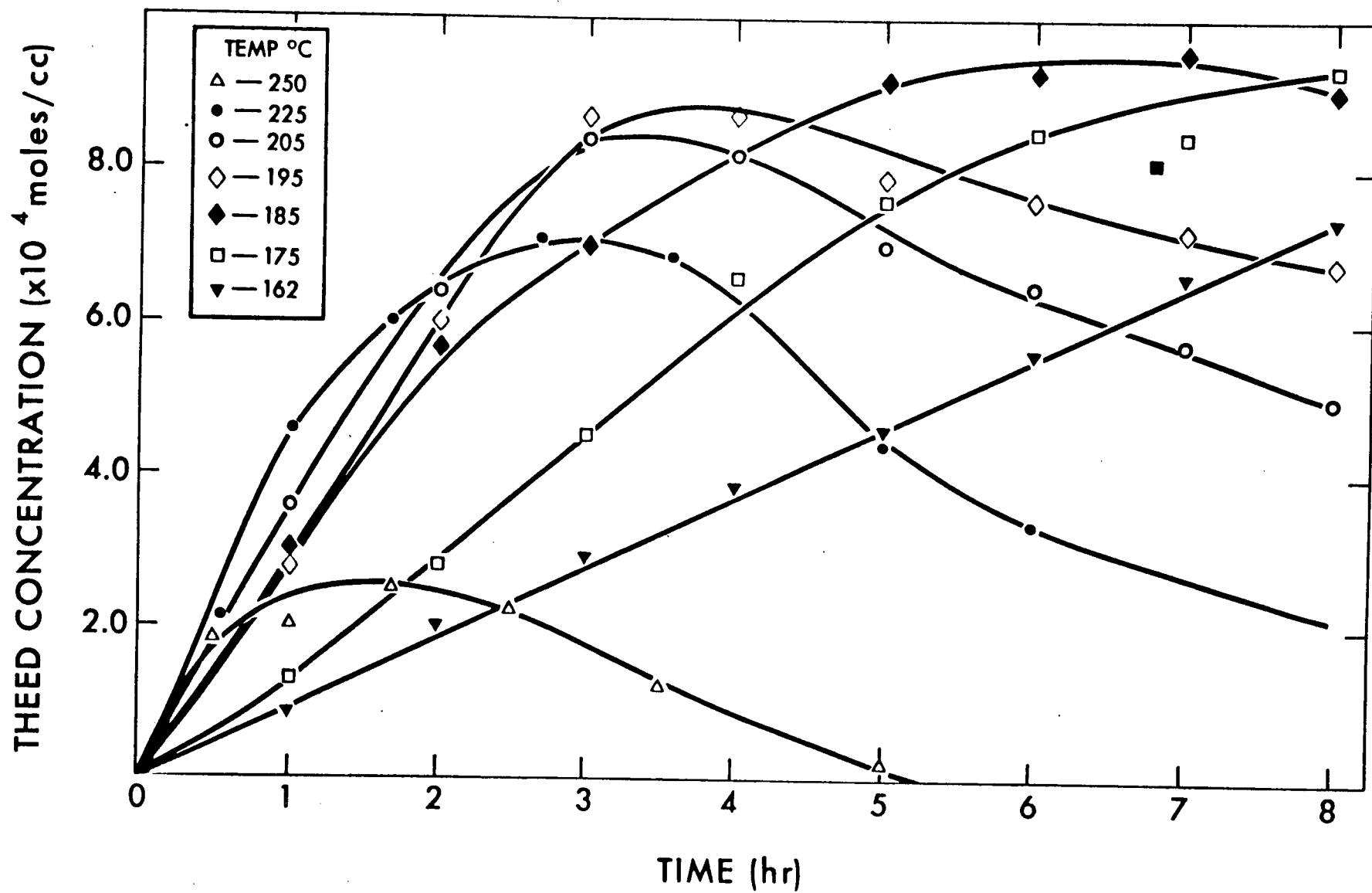


Figure 8.8 THEED concentration as a function of time and temperature (30 wt % DEA, 4137 kPa CO₂, 205-162°C)

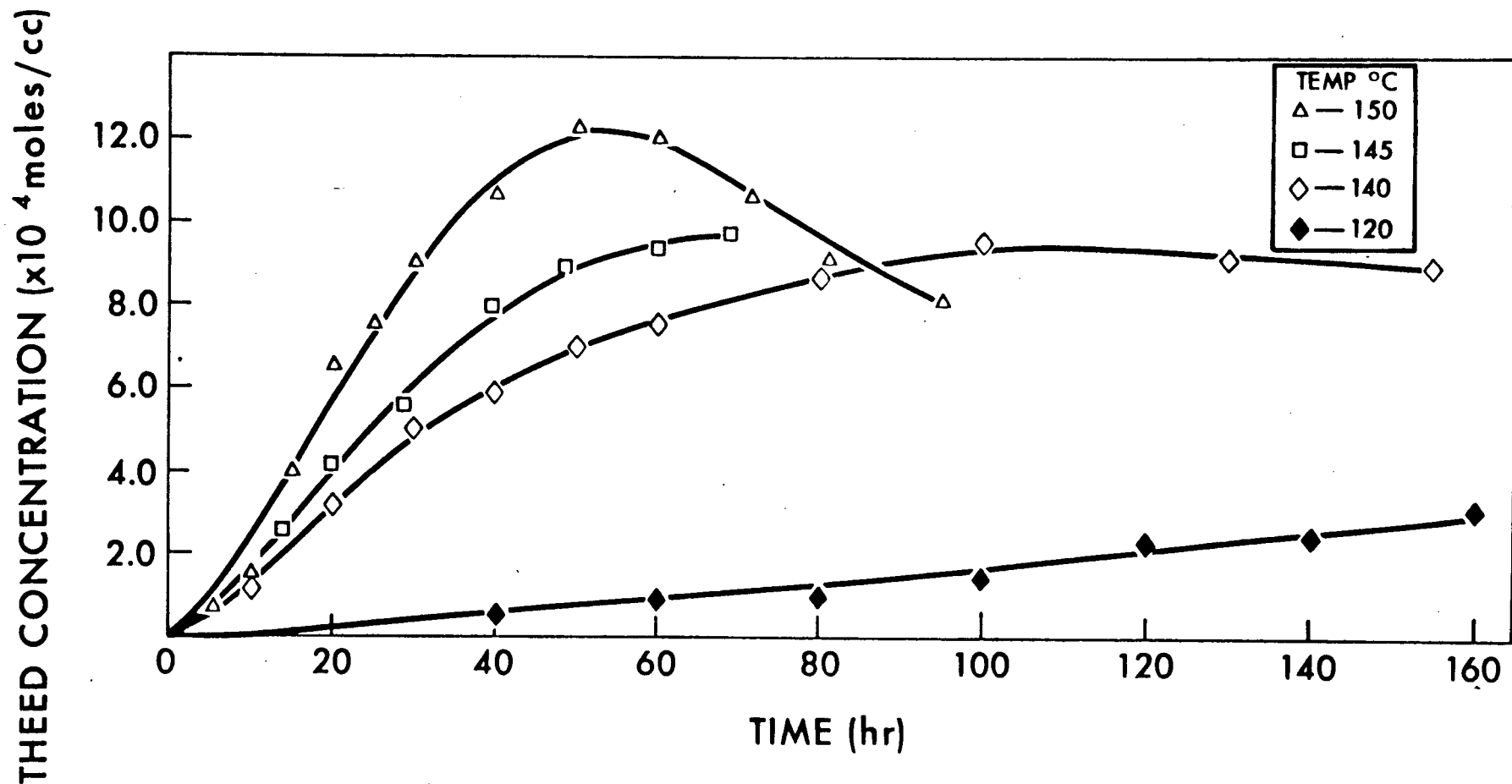


Figure 8.9 THEED concentration as a function of time and temperature
(30 wt % DEA, 4137 kPa CO₂, 150–90°C)

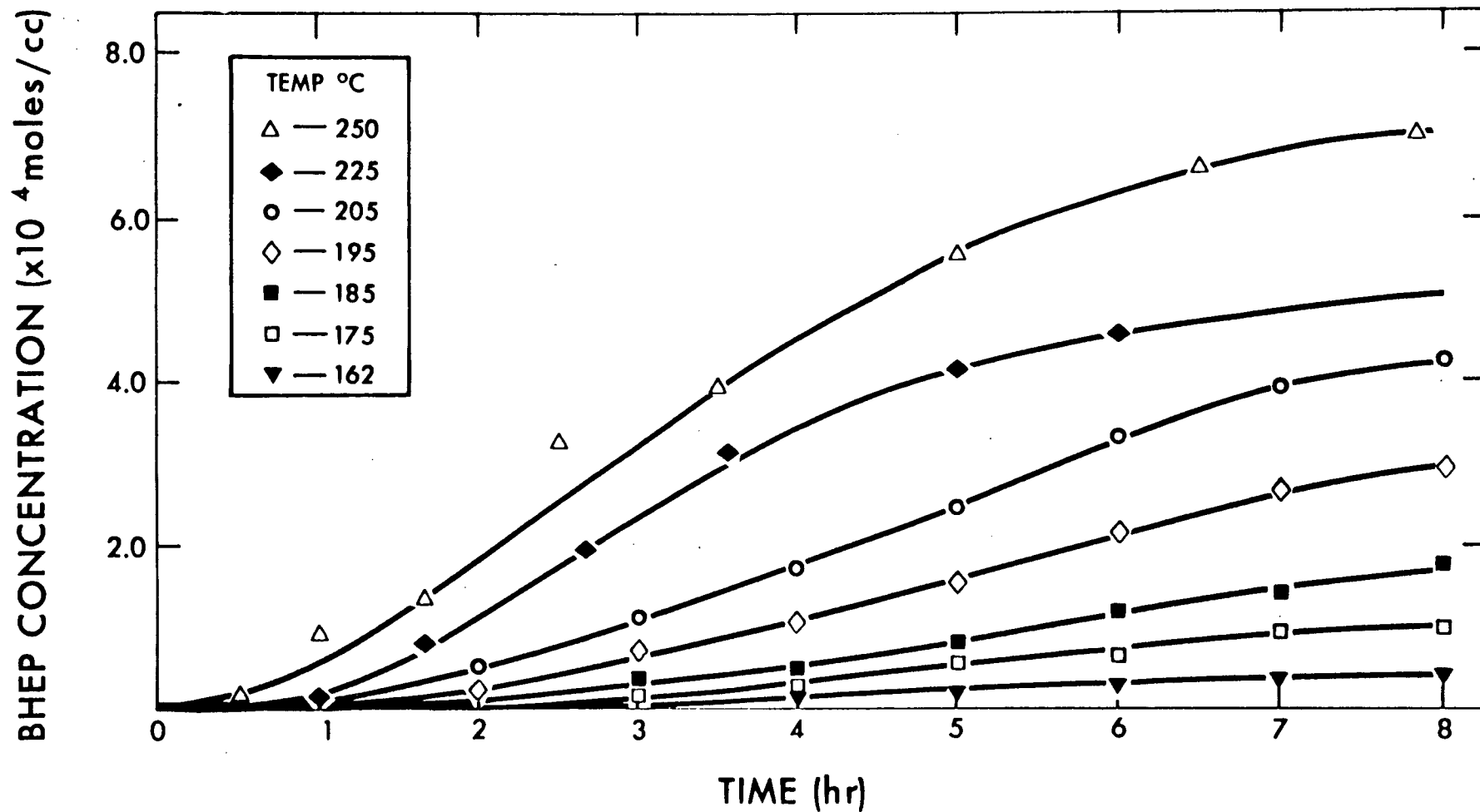


Figure 8.10 BHEP concentration as a function of time and temperature
(30 wt % DEA, 4137 kPa CO₂, 206-162°C)

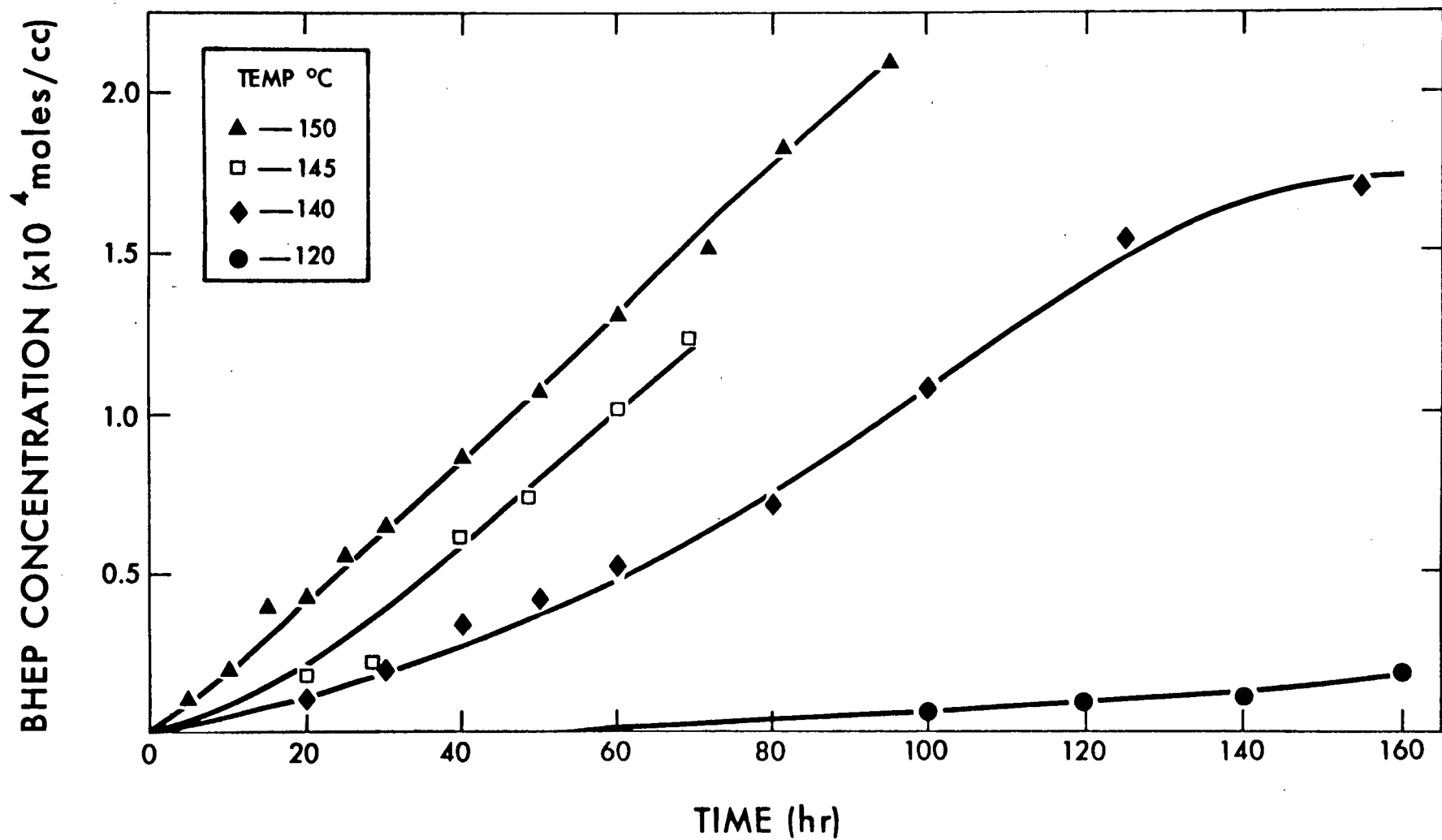


Figure 8.11 BHEP concentration as a function of time and temperature
(30 wt % DEA, 4137 kPa CO₂, 150- 90°C)

8.1.1.3 BHEP. Figures 8.10 and 8.11 show that the concentration of BHEP rises steadily with time. The overall production of BHEP increases rapidly with temperature. At temperatures greater than about 185°C, the production of BHEP (i.e., the slope of the BHEP concentration versus time curve) starts to fall slightly after several hours and this implies that the concentration of a certain intermediate is falling. HEOD cannot be this intermediate since its concentration remains relatively constant after an initial period and this would result in the production of BHEP becoming constant. THEED is more likely to be the intermediate responsible for the formation of BHEP. THEED's concentration falls after reaching a maximum and this would cause the production of BHEP to fall as observed in Figs. 8.10 and 8.11. This will be discussed further in chapter 11.

8.2 Effect of initial DEA concentration

The results of degradation experiments conducted by using different initial DEA concentration were rather confusing. Figures 8.12 to 8.14 show the change in DEA concentration with time for varying solution strengths at temperatures of 205°C, 175°C, and 150°C. Again, the plots tend to deviate from the straight line behaviour at high temperatures. If it is assumed that the initial degradation rate is first order, then k_{DEA} should be independent of the initial DEA concentration. However this is clearly not the case as shown by Fig. 8.15, which is a plot of k_{DEA} versus initial DEA concentration. It appears there are three regimes:-

1. 0-10 wt % where the degradation rate constant of DEA is constant at a low value.
2. 10-30 wt % where the rate constant rapidly increases with increasing

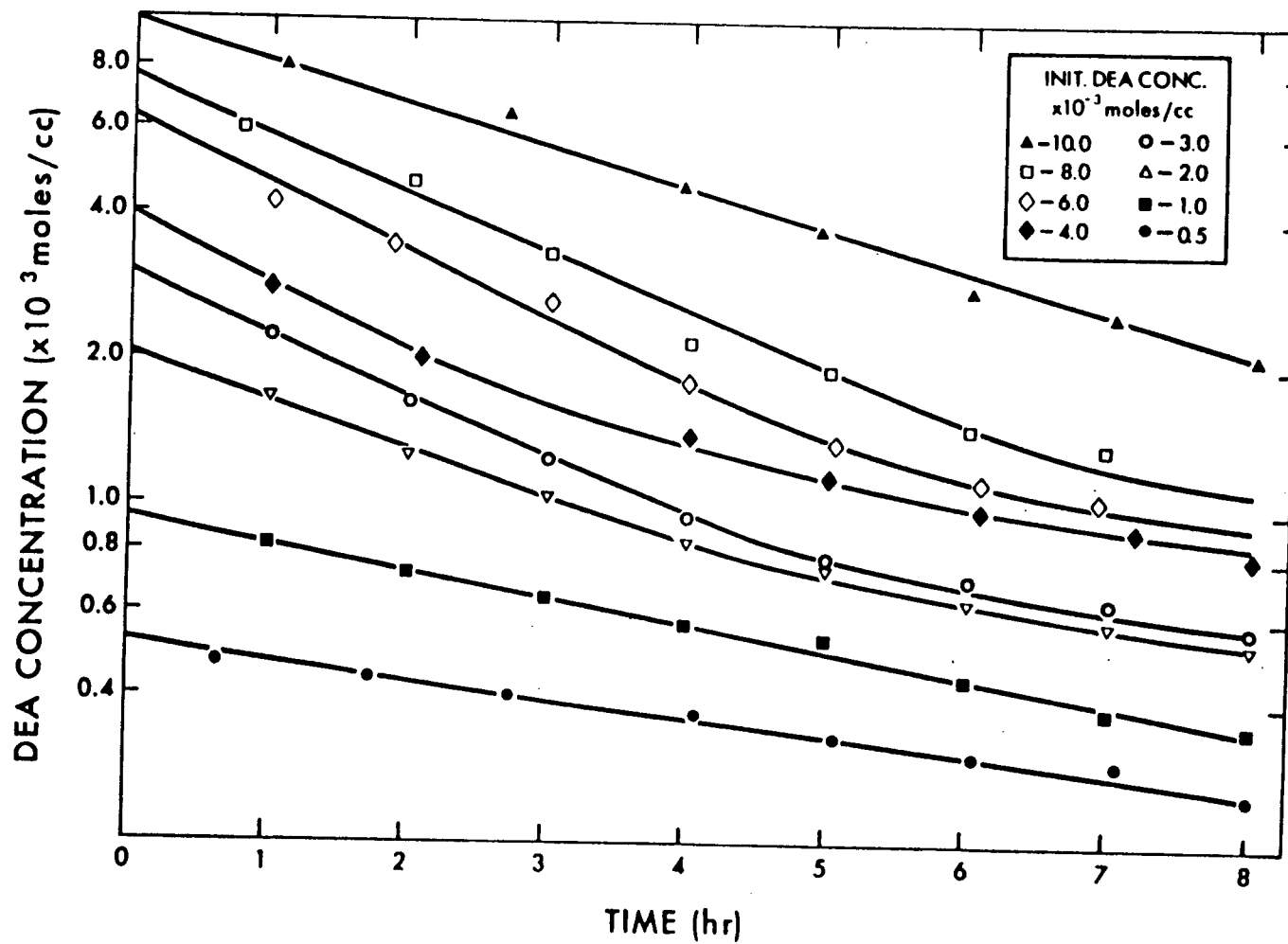


Figure 8.12 DEA concentration as a function of time and initial DEA concentration (4137 kPa CO₂, 205°C)

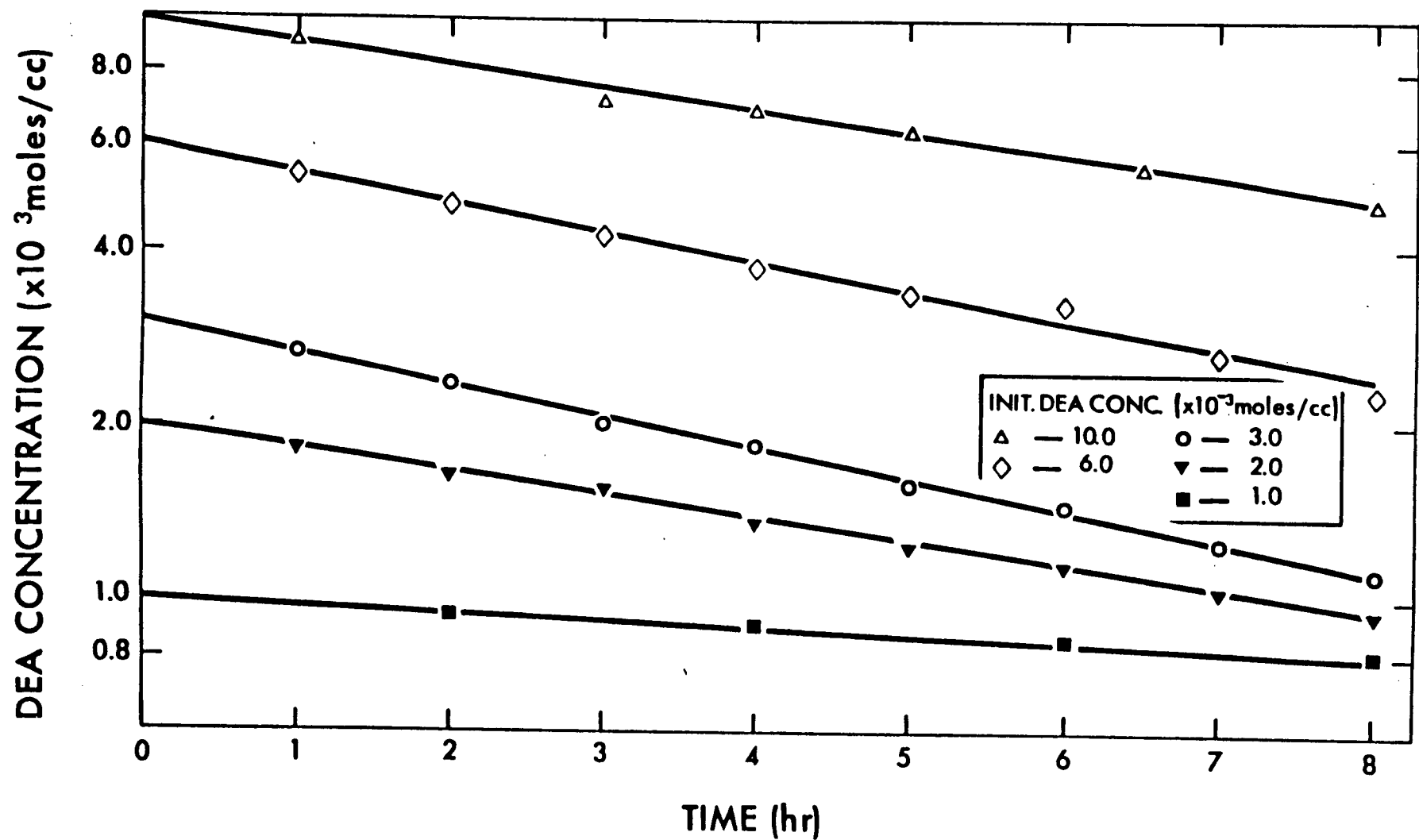


Figure 8.13 DEA concentration as a function of time and initial DEA concentration
(4137 kPa CO₂, 175°C)

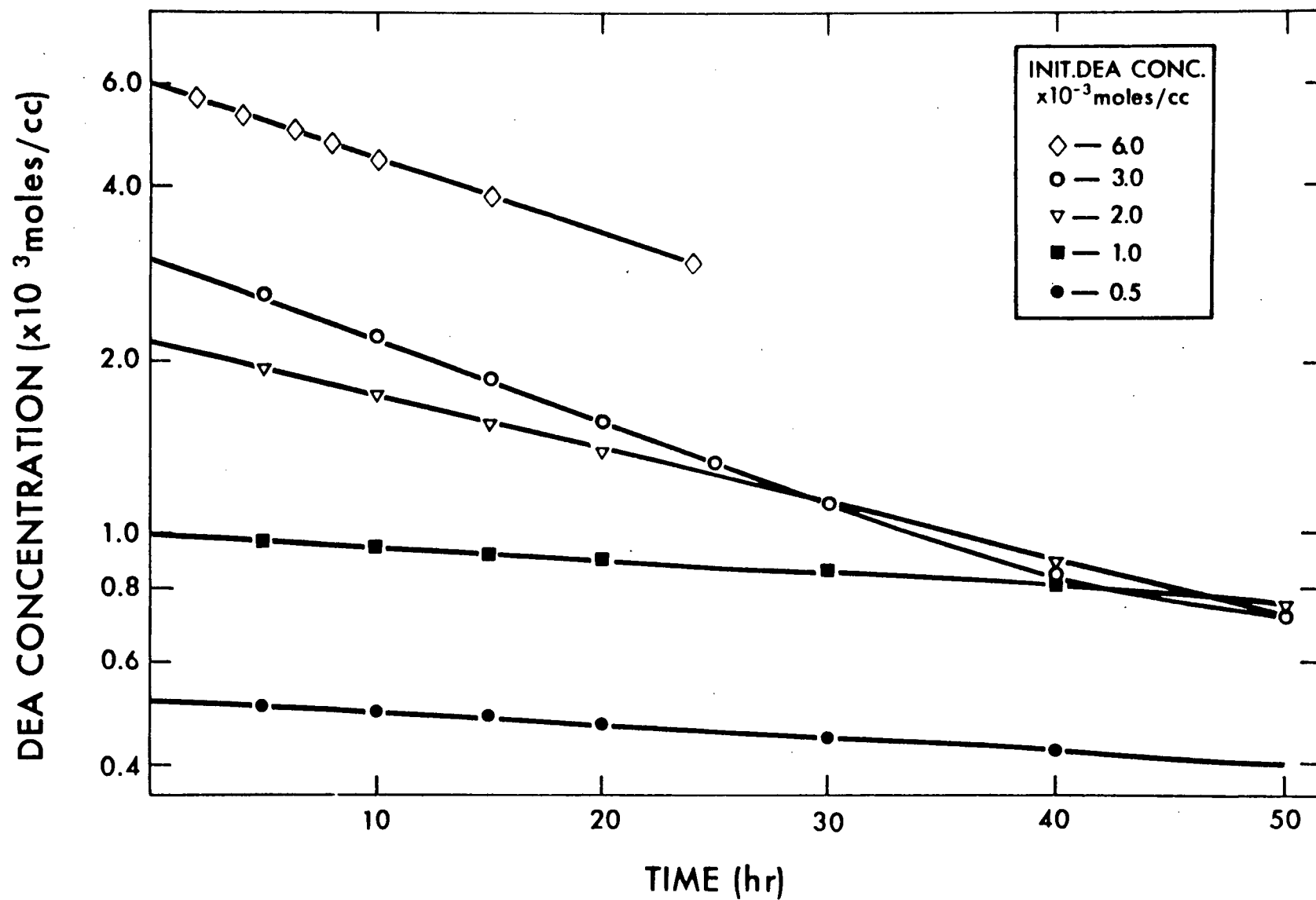


Figure 8.14 DEA concentration as a function of time and initial DEA concentration (4137 kPa CO₂, 150°C)

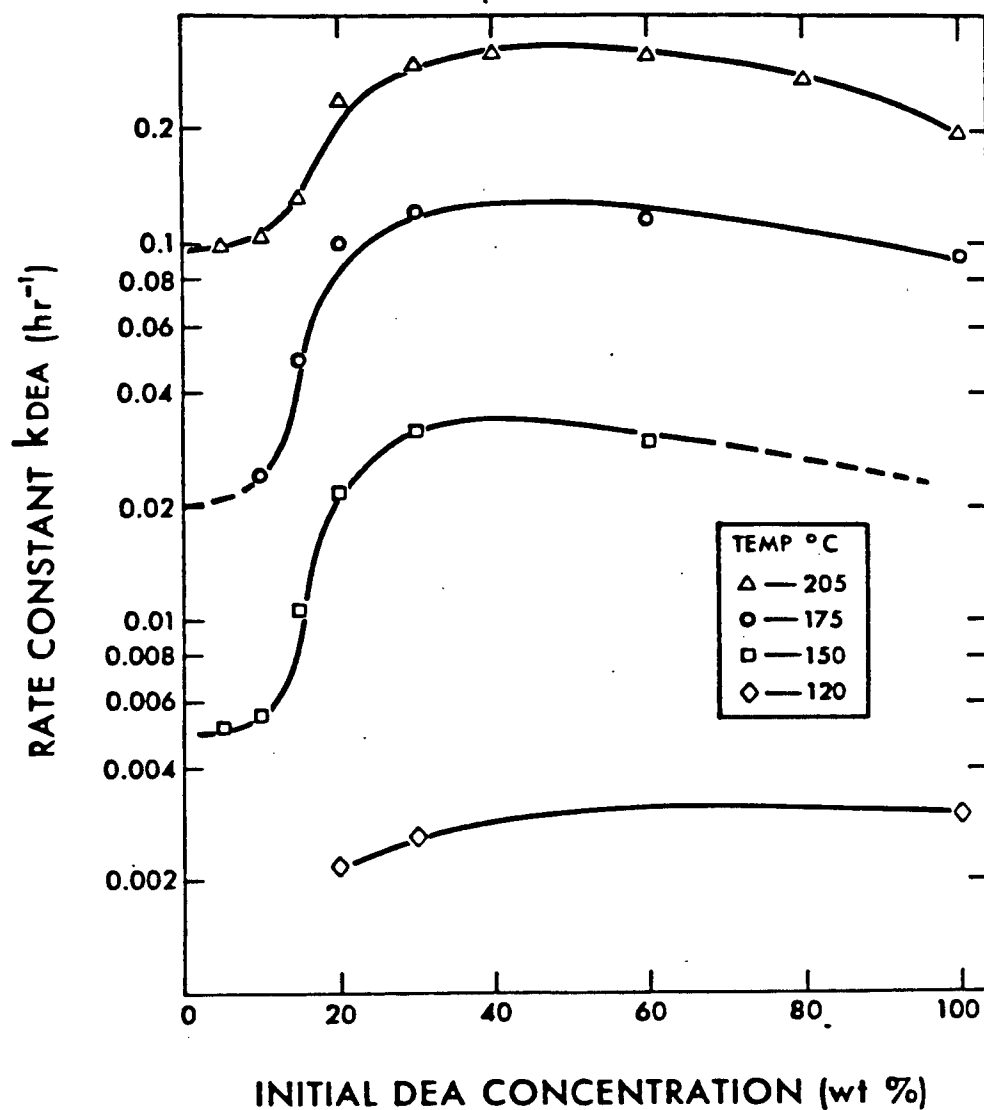


Figure 8.15 k_{DEA} as a function of initial DEA concentration and temperature (4137 kPa CO_2)

initial DEA concentration.

3. 30-100 wt % where the rate constant is high and relatively constant, decreasing slightly as the initial DEA concentration nears 100 wt %.

Figure 8.16 shows the Arrhenius plot for various initial DEA concentrations. Again the three regions can clearly be seen.

At this stage it was not possible to explain this behaviour. Thus more experiments had to be conducted and these are reported in chapters 9 and 10.

Figures 8.17 to 8.19 show typical plots of HEOD, THEED, and BHEP concentrations versus time as a function of initial DEA concentration at 205°C. As before the HEOD concentration rises rapidly and then levels off, whereas THEED tends to a maximum concentration before falling again (especially at high initial DEA concentrations). BHEP once again appears to be produced from THEED rather than HEOD. It is interesting to note that the production of BHEP and HEOD are both lower at an initial DEA concentration of 100 wt % than at 80 wt %. This is reflected in the k_{DEA} values being lower at 100 wt % than 80 wt %. This behaviour indicates that water may play a significant role in the overall degradation. Initially, at 100 wt % DEA, the only water present is in the form of a trace impurity in the DEA feed. As the degradation reaction proceeds water is produced as a degradation product (see chapter 2, Eq. 2.17).

8.3 Effect of pressure

Typical plots of changes in DEA concentration versus time as a function of overall pressure are shown in Figure 8.20. These experiments were conducted at 195°C. At this temperature the water in the 30 wt % DEA solution exerts a considerable pressure of about 1202 kPa (174.3 psi). Therefore, it must be noted that the partial pressure of CO₂

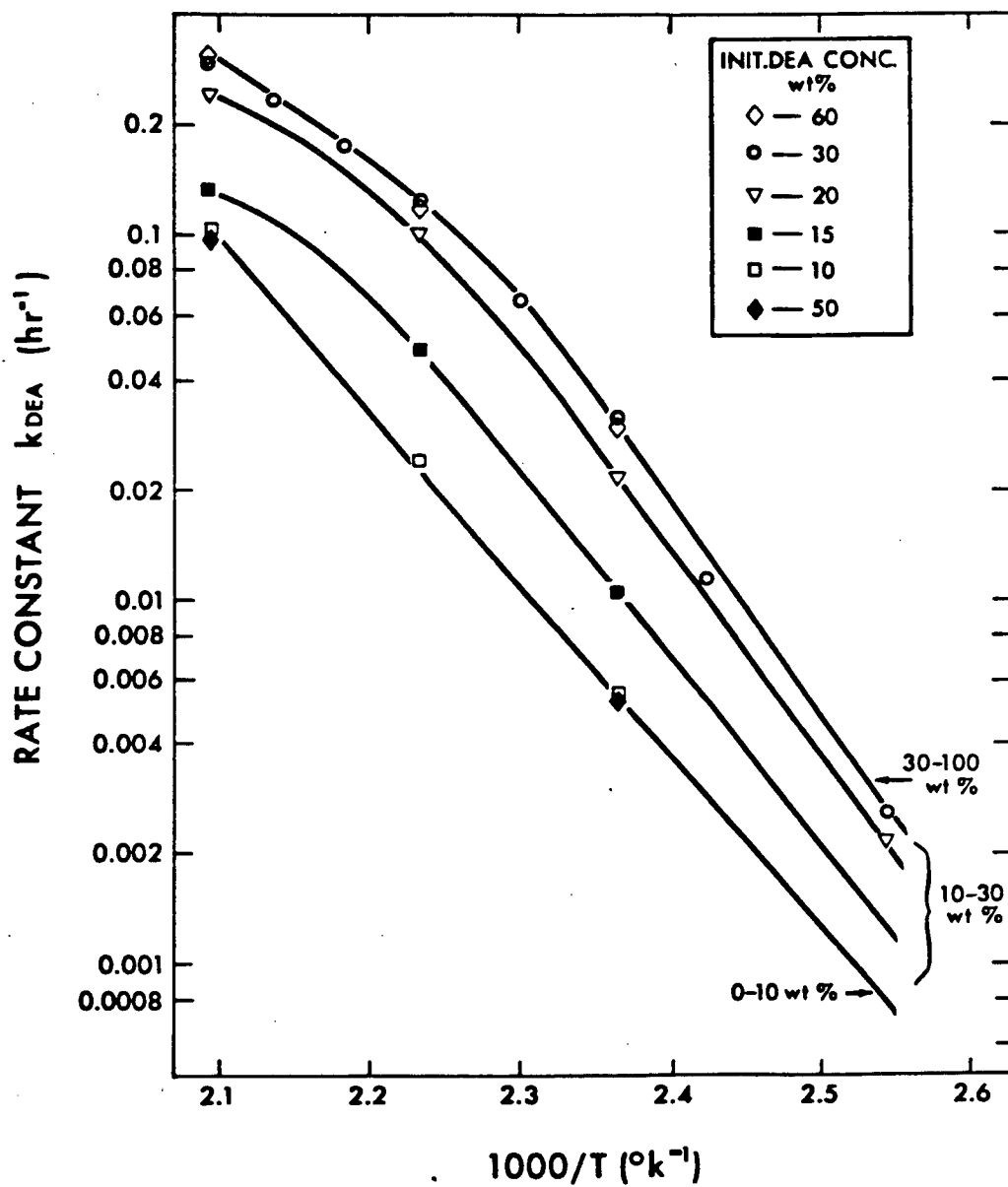


Figure 8.16 Arrhenius plot for varying DEA solution strengths degraded with CO_2 at 4137 kPa

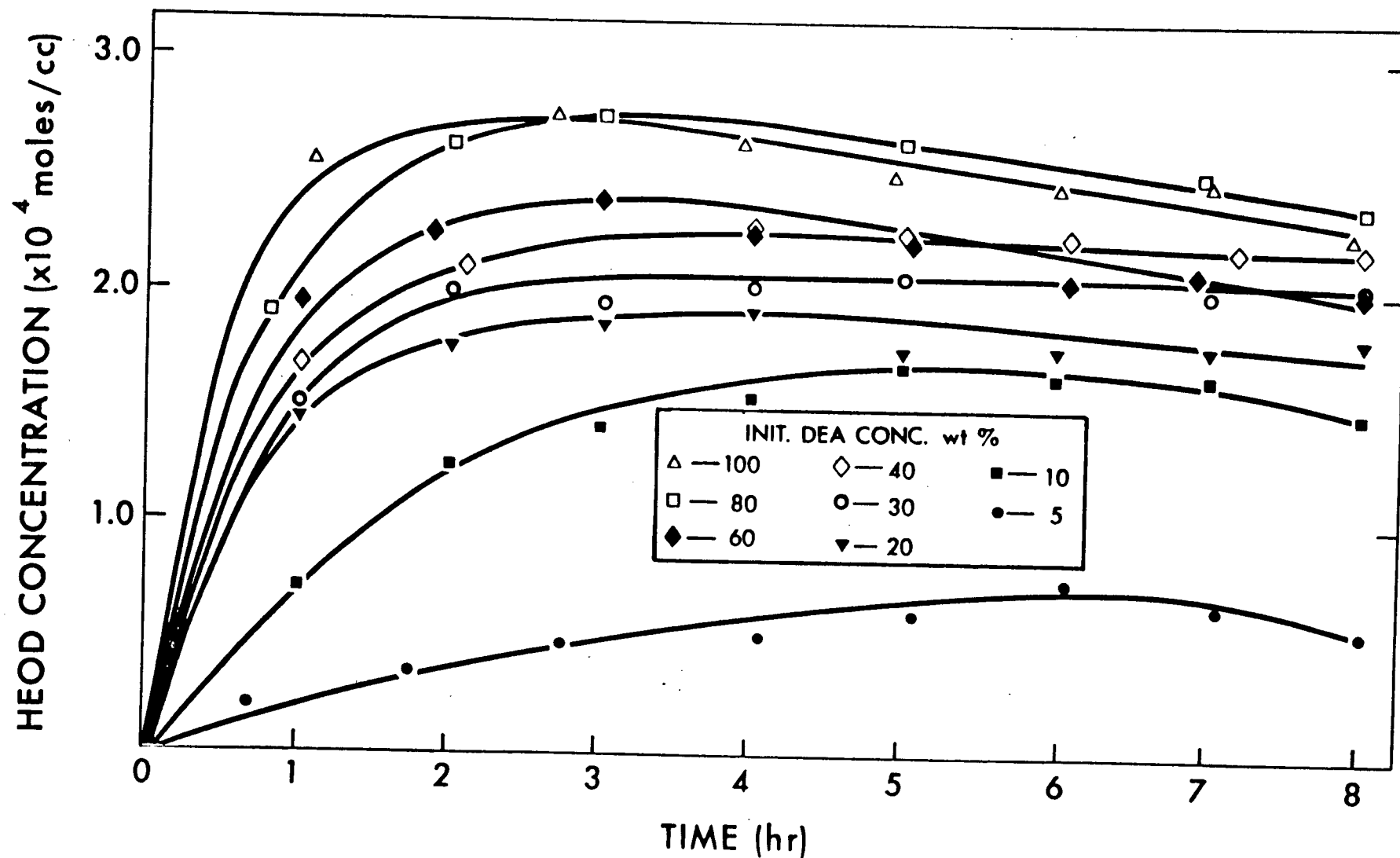


Figure 8.17 HEOD concentration as a function of time and initial DEA concentration (4137 kPa CO_2 , 205°C)

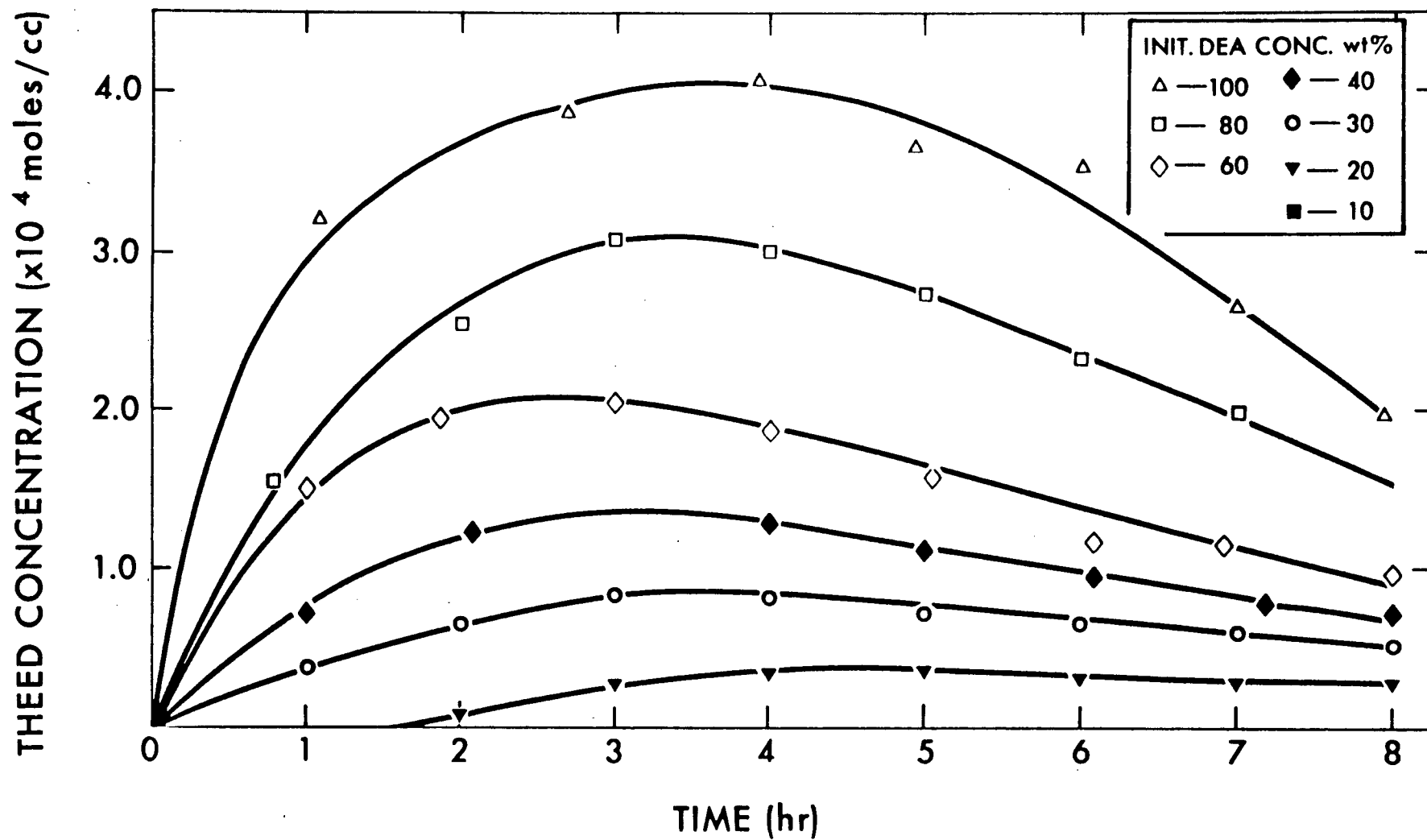


Figure 8.18 THEED concentration as a function of time and initial DEA concentration (4137 kPa CO_2 , 205°C)

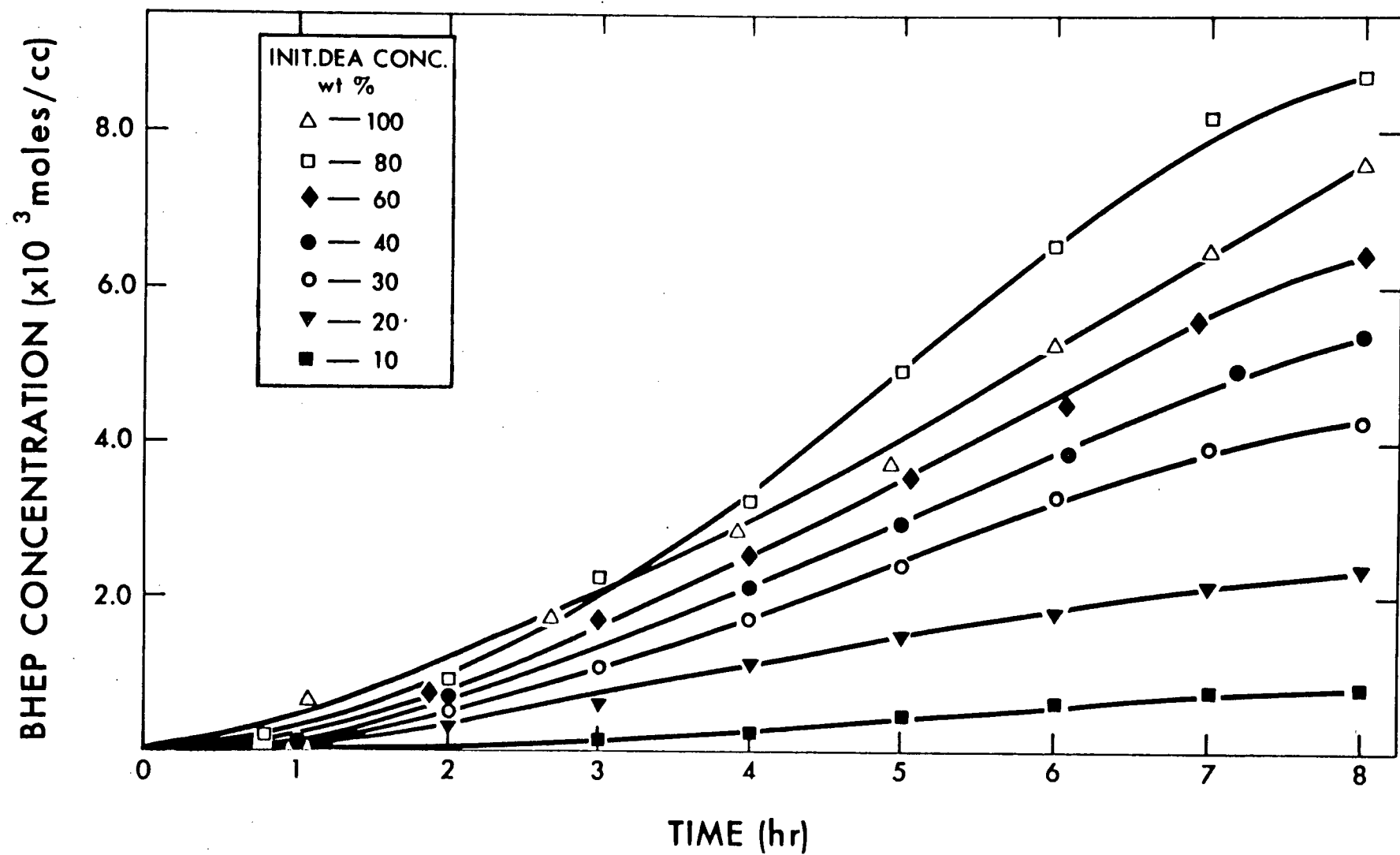


Figure 8.19 BHEP concentration as a function of time and initial DEA concentration (4137 kPa CO₂, 205°C)

is considerably less than the total pressure. From Fig. 8.20 it can be seen that degradation increases with increasing pressure up to about 4137 kPa (600 psi) total pressure; above that pressure little change is noted. Figure 8.21 shows the initial k_{DEA} values as a function of total pressure when a solution containing initially 30 wt % DEA is degraded at 195°C. Both Figs. 8.20 and 8.21 imply that CO_2 is limiting at pressures below 4137 kPa (600 psi). Therefore, it was necessary to determine the solubility of CO_2 in DEA solutions at these overall pressures. Using these concentrations it could then be determined whether or not industrial units were operating under CO_2 limiting conditions and how to relate the results of this study to industrial units. Unfortunately, high temperature data on CO_2 solubility in DEA solutions were not available in the open literature. Hence solubility experiments were performed to obtain these data and are discussed in chapter 9 and Appendix C.

Figures 8.22 to 8.24 show plots of HEOD, THEED, and BHEP concentration versus time as a function of overall reaction pressure at 195°C.

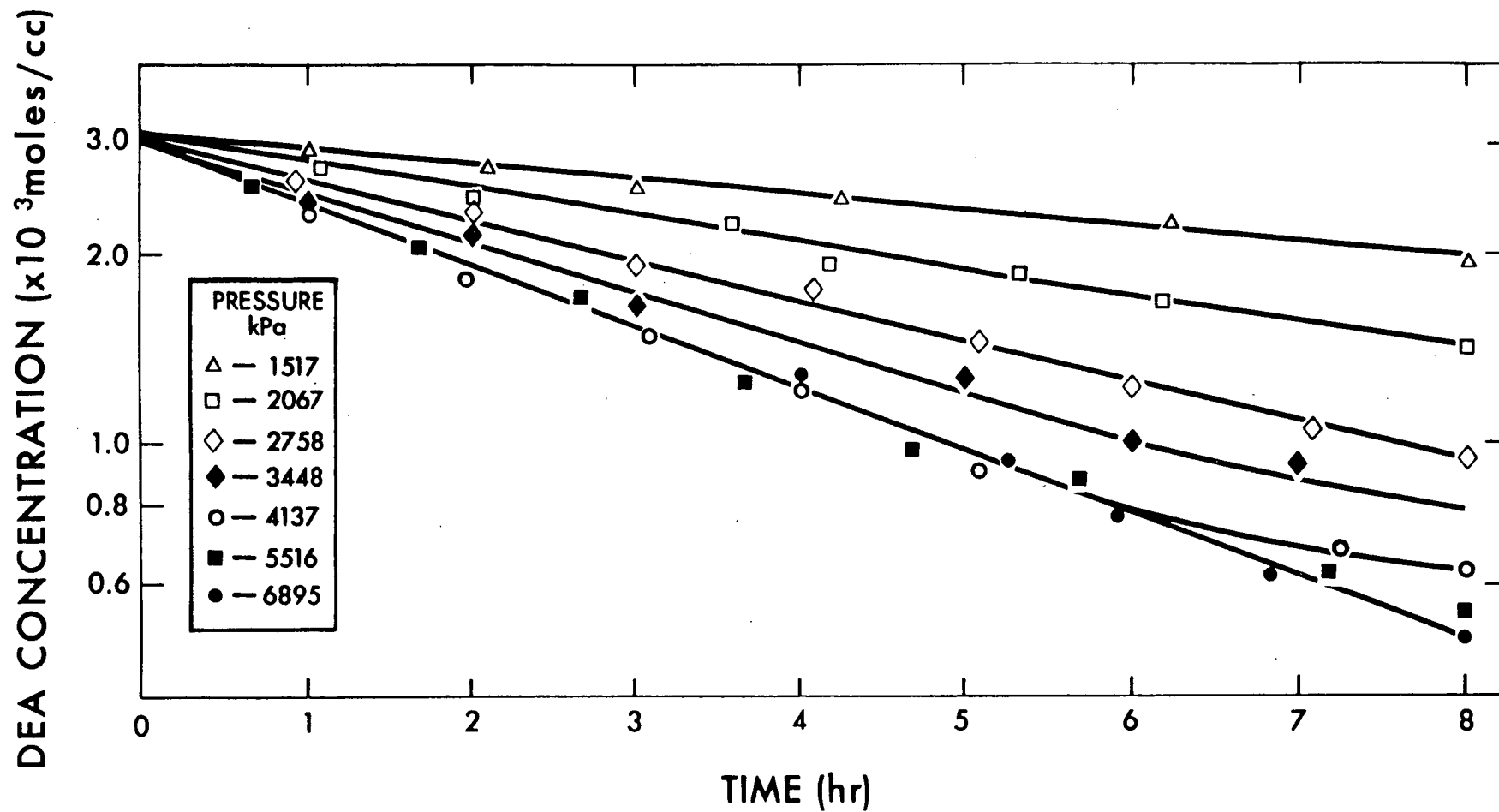


Figure 8.20 DEA concentration as a function of time and pressure
(30 wt % DEA, 195°C)

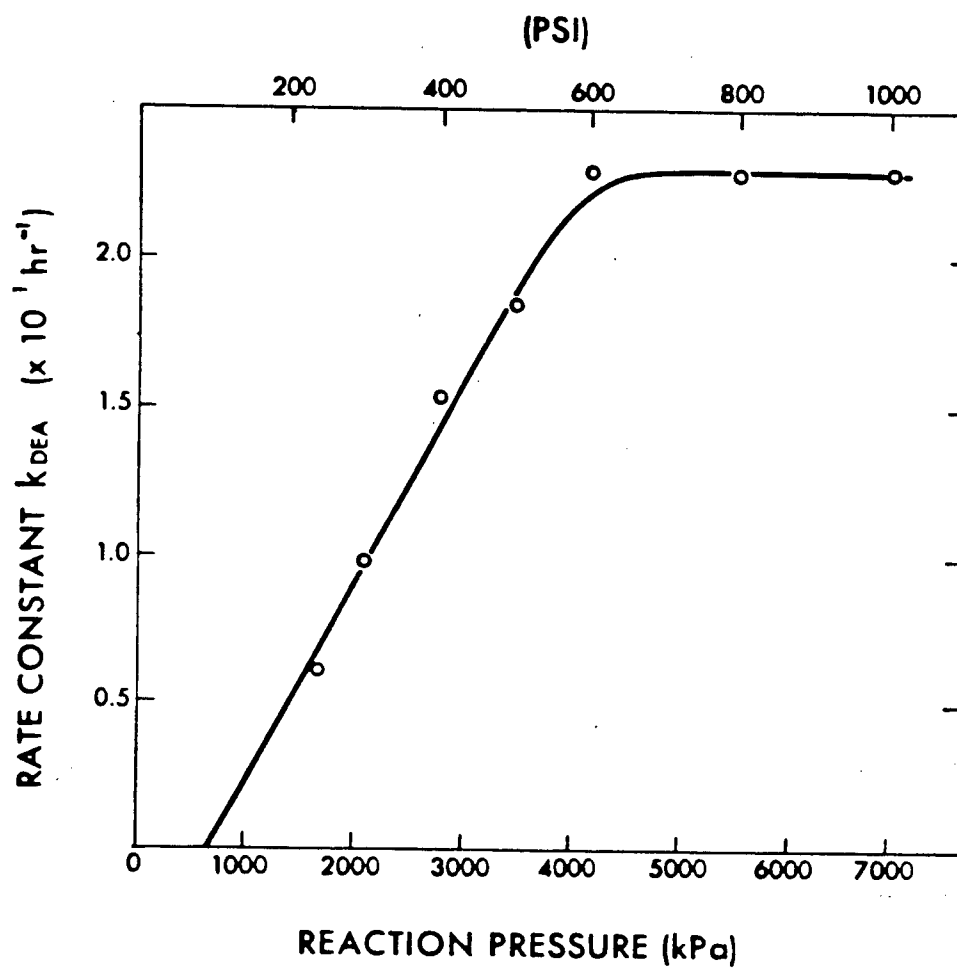


Figure 8.21 k_{DEA} as a function of reaction pressure.
(30 wt % DEA, 195°C)

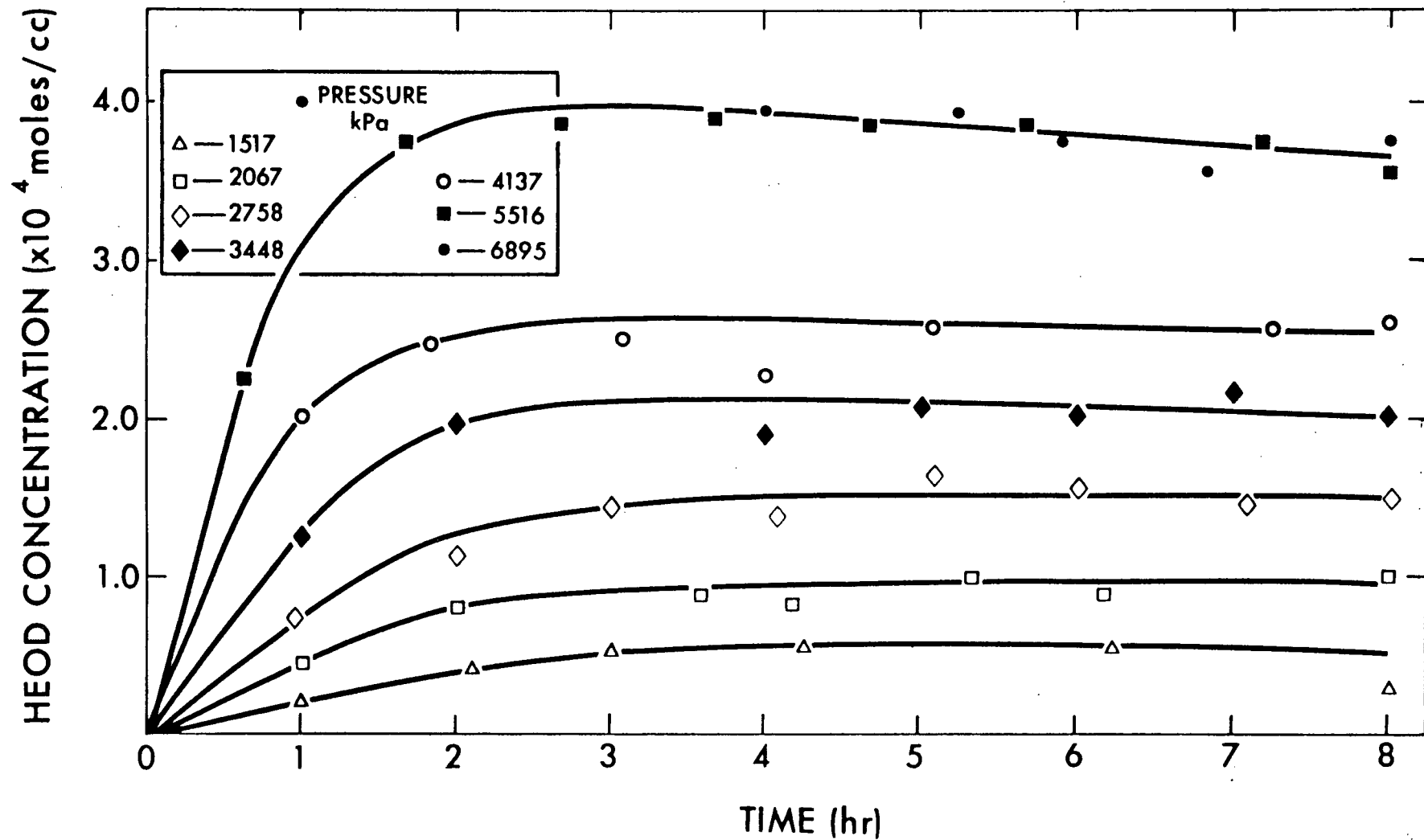


Figure 8.22 HEOD concentration as a function of time and pressure
(30 wt % DEA, 195°C)

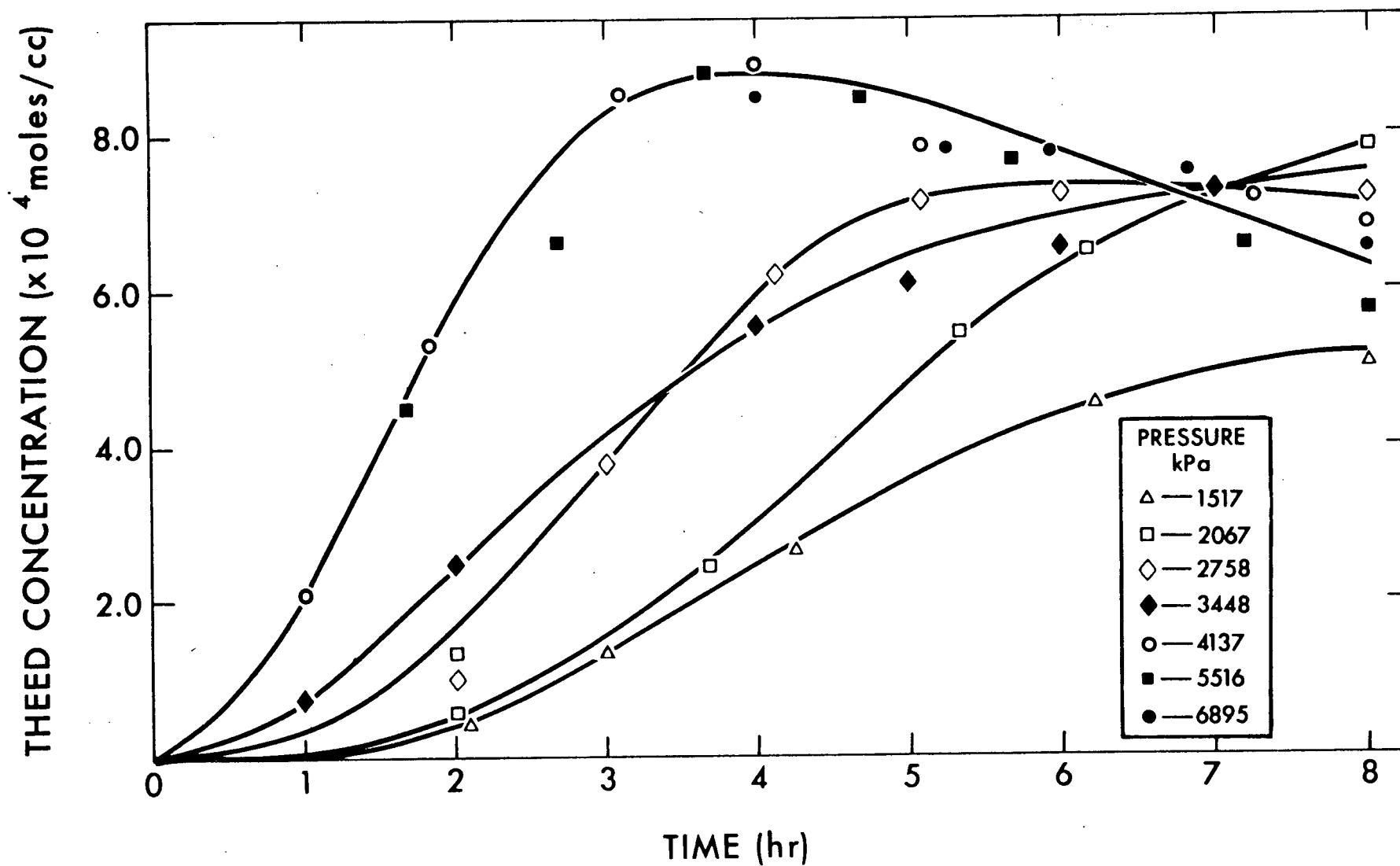


Figure 8.23 THEED concentration as a function of time and pressure (30 wt % DEA, 195°C)

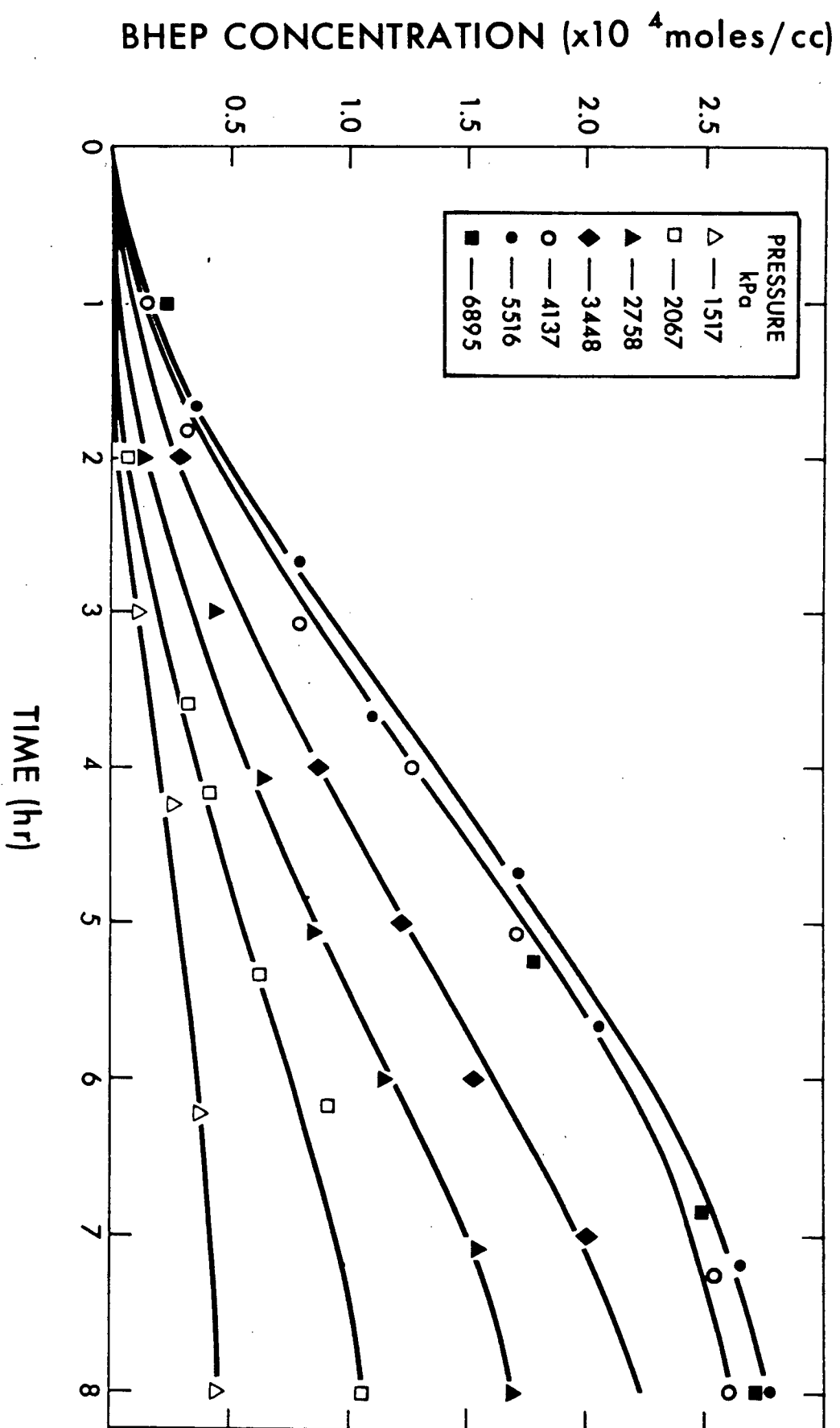


Figure 8.24 BHEP concentration as a function of time and pressure
(30 wt % DEA, 195°C)

CHAPTER 9

EXPERIMENTS DESIGNED TO ELUCIDATE THE DEGRADATION MECHANISM

Before a kinetic model could be devised it was necessary to gain insight into the degradation mechanism. The experiments described in chapters 7 and 8 gave some idea of the mechanism but they also generated many questions which needed to be answered such as, "why does the initial DEA concentration affect the reaction rate?" and "why do the plots of $\log [\text{DEA}]$ vs. time deviate from the linear behaviour at high temperatures?" Therefore, the following studies were conducted in order to explain the questions posed by chapters 7 and 8 and to develop a comprehensive model of the degradation of DEA.

9.1 Effect of pH

Since the DEA solutions are complex mixtures of ionized species, it is highly likely that changes in pH will affect the equilibrium and, in turn, the overall degradation reaction.^{11,16} DEA itself tends to make the solution alkaline whereas the dissolved CO_2 tends to render the solution acidic. Runs were carried out where the DEA feed was made more alkaline or acidic by adding NaOH or HCL respectively (runs 41 to 43). The effect of these changes in pH can be seen in Fig. 9.1 where DEA concentration is plotted as a function of time for different initial solution pH measured at room temperature and at atmospheric pressure. It must be realized that the pH of the reaction mixture under operating

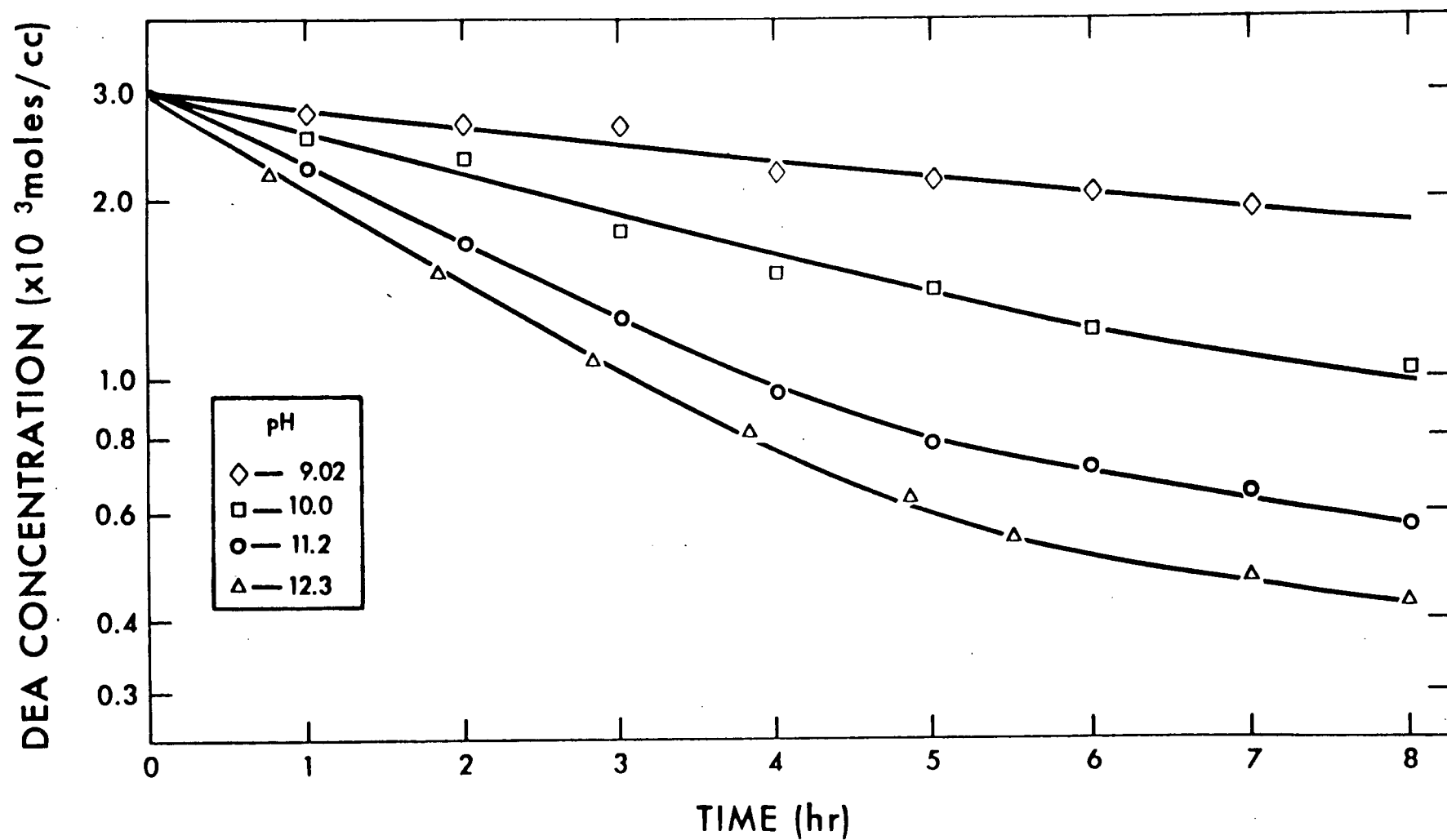


Figure 9.1 DEA concentration as a function of time and solution pH
(30 wt % DEA, 4137 kPa CO₂, 205°C)

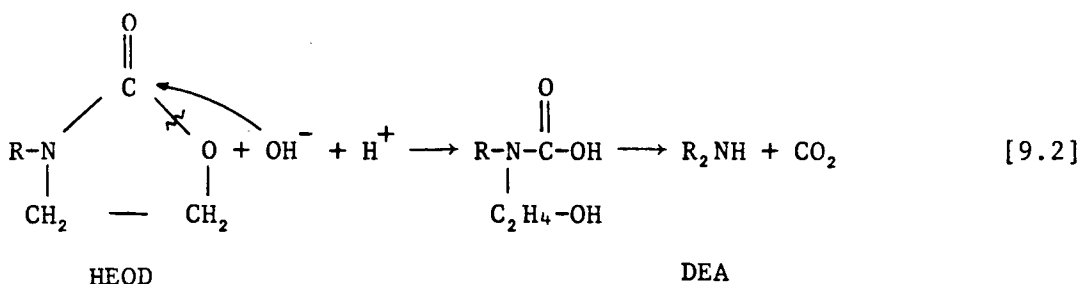
conditions will be different to that at room temperature. However, it was not possible to measure the solution pH under operating conditions with the equipment available. An aqueous solution containing 30 wt % DEA has a pH of about 11.2 at room temperature. Therefore, the run at a pH of 11.2 in Fig. 9.1 (run 3) can be considered the reference experiment.

As seen from Fig. 9.1, lowering the pH reduces the degradation rate. By changing the initial solution pH from 12.24 to 9 the degradation rate is reduced by a factor of over 5. The effect of pH can be linked with the solubility of CO_2 in the DEA solution. The solubility of CO_2 being increased by the action of hydroxyl ions:-



At low pH the solubility of CO_2 is greatly reduced and hence the degradation rate is lower.

Further studies revealed that, when NaOH is added to HEOD in solution most of the HEOD is converted to DEA. This indicates that the HEOD ring is unstable. It appears that the electron deficient carbonyl atom of the ring is attacked by OH^- , resulting in ring opening.⁷⁰



At present, it is not possible to explain why a reduction in HEOD concentration increases DEA degradation. This will be investigated further in chapter 11.

9.2 Effect of bicarbonate and carbonate ions

DEA treating solutions with dissolved CO_2 contain various ionic and molecular compounds such as: R_2NH , R_2NH_2^+ , R_2NCOO^- , HCO_3^- , CO_3^{--} , and CO_2 . Since the pH has such a strong effect on degradation, it is likely that degradation involves some ionic compounds. Therefore, tests were conducted where DEA was reacted with potassium carbonate (K_2CO_3) and potassium bicarbonate (KHCO_3) under 4137 kPa (600 psi) of nitrogen. Thus initially the reaction mixture contained CO_3^{--} or HCO_3^- and no free CO_2 . Under these highly alkaline conditions it is virtually impossible for HCO_3^- or CO_3^{--} to directly revert to free CO_2 .

For these runs the molar concentrations of CO_3^{--} and HCO_3^- were made equivalent to that of CO_2 dissolved in DEA under normal reaction conditions. This was to ensure that any changes noted in the degradation reaction were not due to differences in the amount of CO_2 in the reaction mixture either as free CO_2 or HCO_3^- or CO_3^{--} . Unfortunately the open literature did not provide data on CO_2 solubility in DEA under the reaction conditions of this study. Therefore, a series of solubility experiments had to be performed to produce the necessary data.

9.2.1 CO_2 solubility data. A simple method for determining the solubility of CO_2 in DEA solutions under high temperature and pressure was developed. Details of the method used are given in Appendix C.

Solubilities were determined for the following conditions:-

DEA concentration - 30, 20, and 10 wt %

Temperature - 205 to 100°C

Overall pressure - 413.7 to 4137 kPa (60 to 600 psi)

It must be noted that the overall pressure in the autoclave was made up from CO_2 and water vapour from the aqueous DEA solution (and

to a small extent from DEA itself). For example at 205°C the vapour pressure of a 30 wt % DEA solution is 1503 kPa (218 psi). Figures 9.2 to 9.4 summarize the results of the solubility experiments.

It is realized that the method used for determining the CO₂ solubility was very simple and probably not very accurate. However the purpose of these experiments was only to obtain approximate solubilities to within $\pm 10\%$. To check the accuracy of the method, the solubility results were compared to those in the literature where the data overlapped. The comparisons are shown in Table 9.1.

Table 9.1 Comparison of CO₂ solubilities in DEA solutions

DEA Conc wt %	Temp °C	CO ₂ partial pressure		CO ₂ concentration g CO ₂ /g DEA		% Difference	Reference
		psi	kPa	This study	Literature		
20	100	100.0	689.5	0.272	0.27	0.74	71
20	120	100.0	689.5	0.238	0.212	12.26	71
20	140	100.0	689.5	0.204	0.186	7.53	71
20	100	316.0	2178.8	0.366	0.348	5.17	71
20	120	316.0	2178.8	0.331	0.294	12.58	71
20	140	316.0	2178.8	0.29	0.25	16.00	71
25	107	85.8	591.6	0.22*	0.218	0.92	72
25	107	317.0	2185.7	0.31*	0.287	8.01	72
25	121	48.7	335.8	0.165*	0.143	15.38	72
25	121	230.0	1585.9	0.275*	0.248	10.90	72
25	121	402.0	2771.2	0.33*	0.3	10.00	72

Av = 9.04

*Extrapolated results from Figs. 9.2 and 9.3

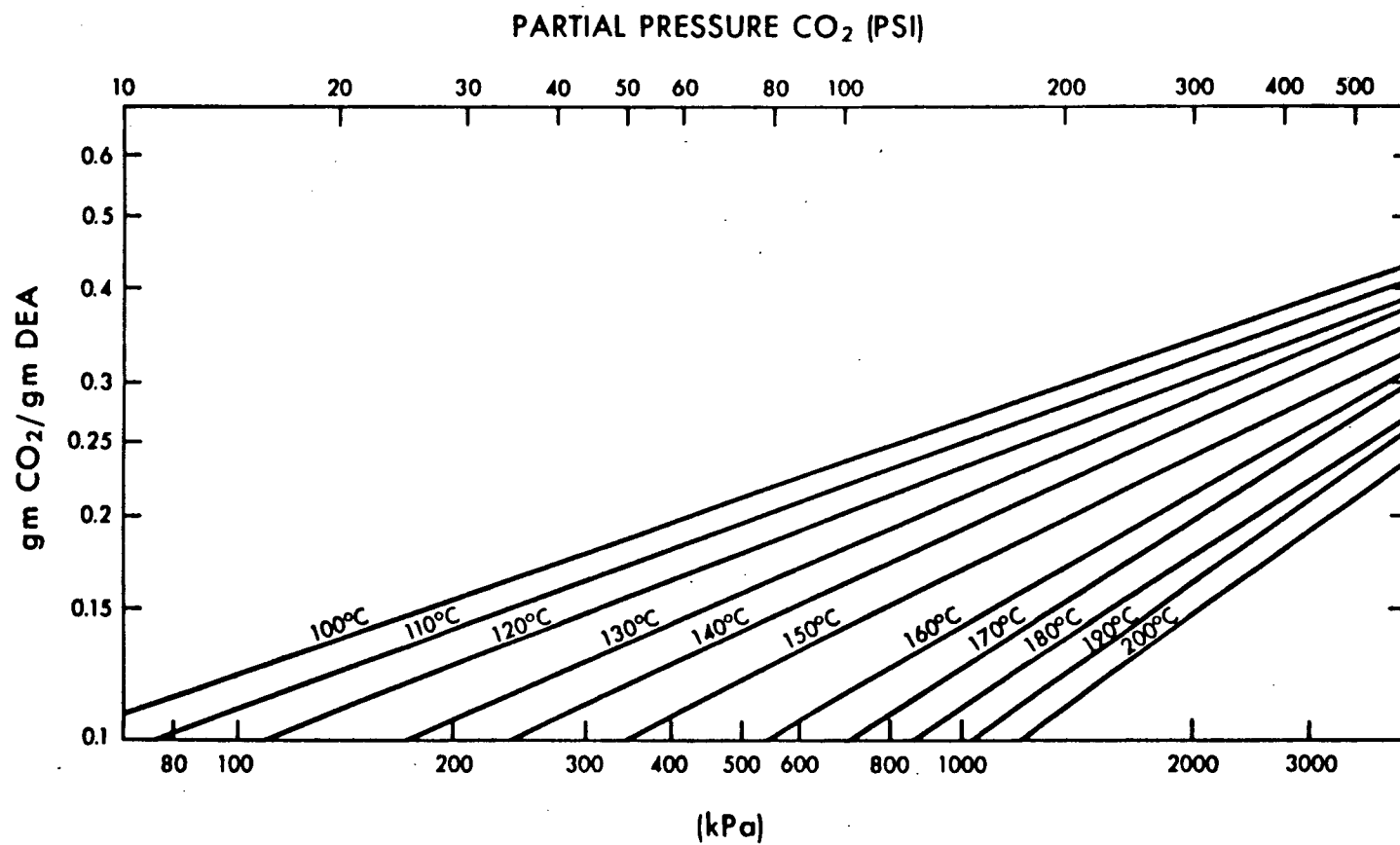


Figure 9.2 Solubility of CO₂ in 30 wt % DEA

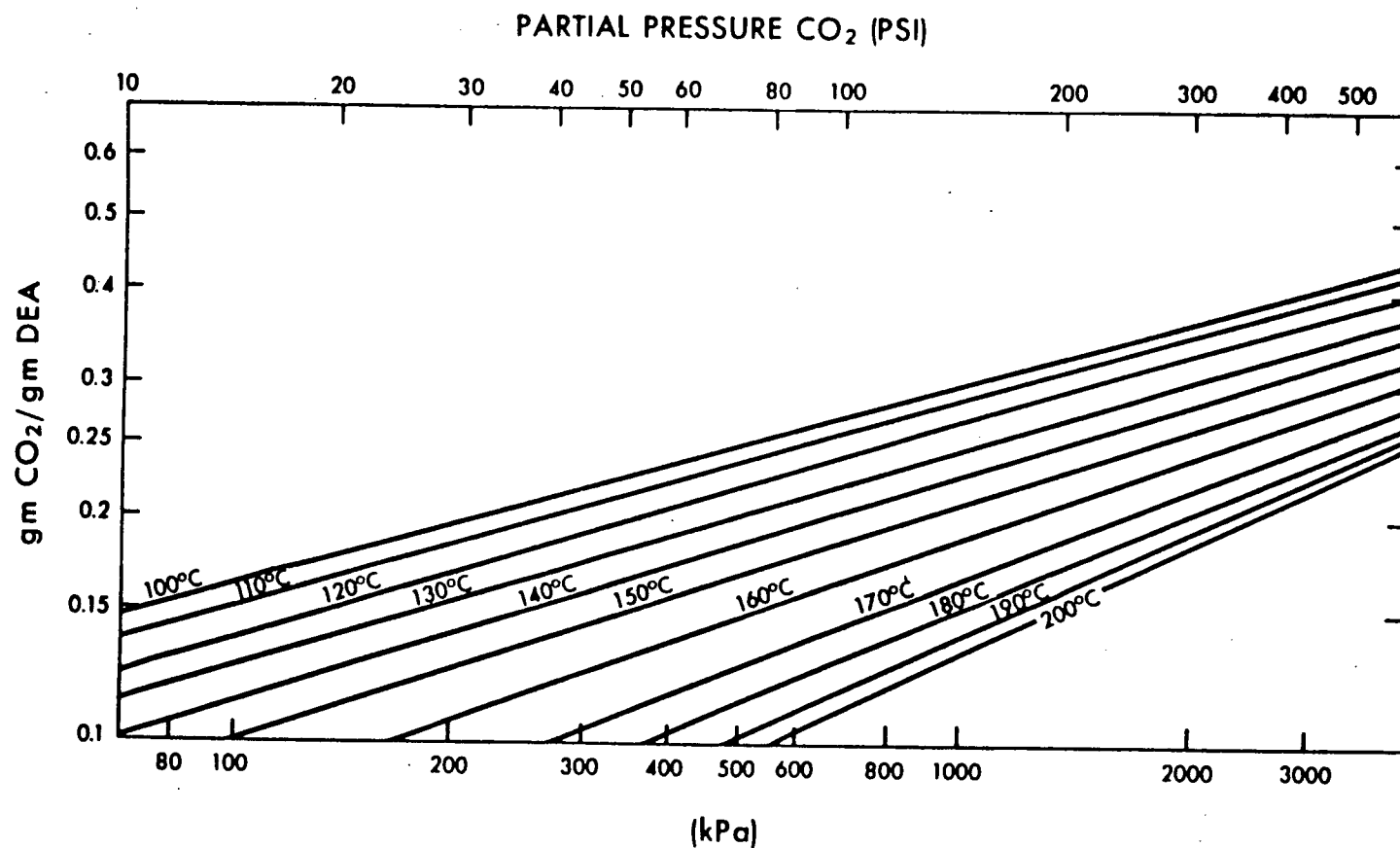


Figure 9.3 Solubility of CO₂ in 20 wt % DEA

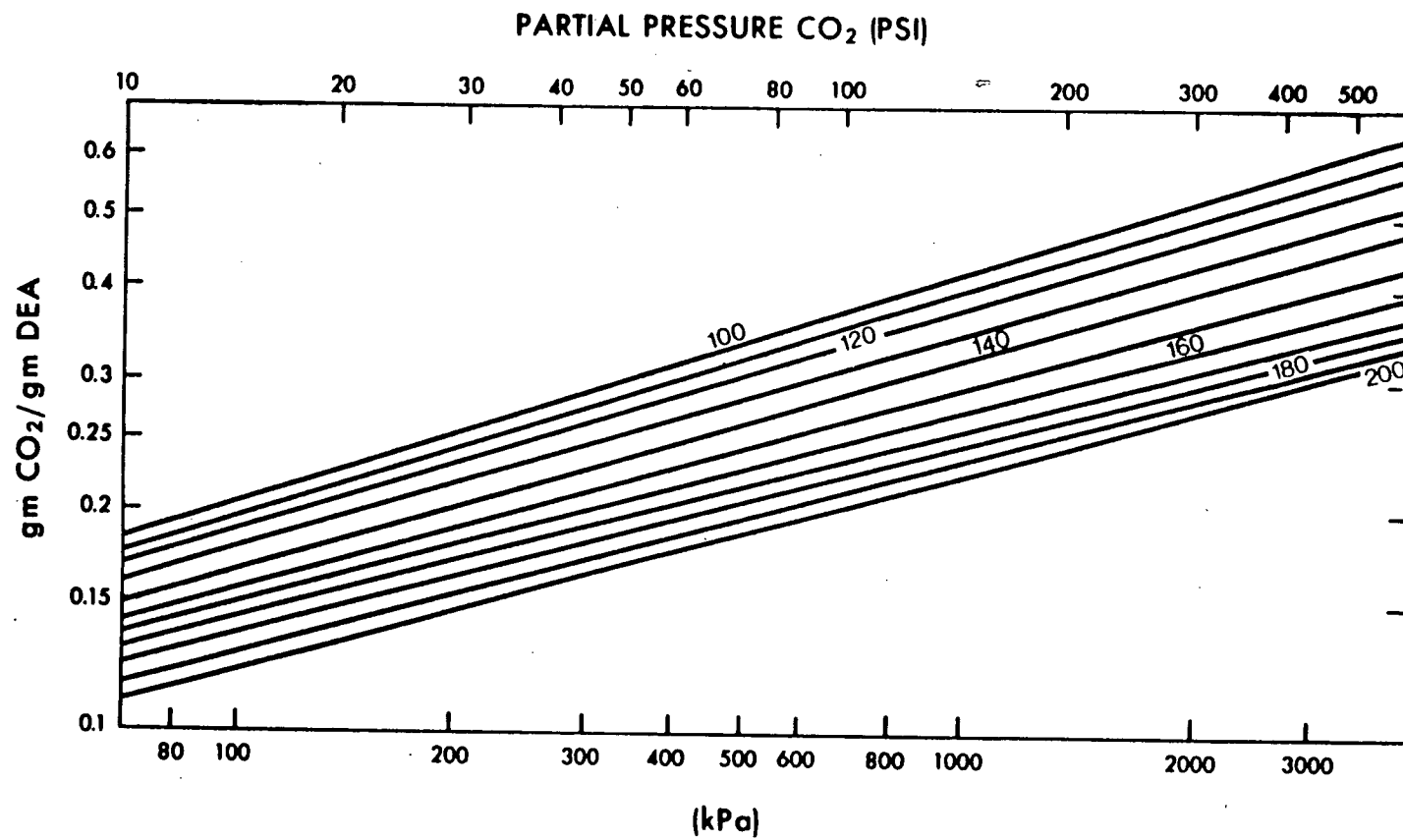


Figure 9.4 Solubility of CO₂ in 10 wt % DEA

9.2.2 Runs using HCO_3^- and CO_3^{--} instead of CO_2 . The runs performed are summarized in Table 9.2.

Table 9.2 Summary of HCO_3^- and CO_3^{--} runs

Run No.	DEA Conc wt %	Temp °C	Nitrogen Pressure		Ion*	Run time hr.
			psi	kPa		
44	30	205	600	4137	CO_3^{--}	8
45	30	205	600	4137	HCO_3^-	30
46	30	175	600	4137	HCO_3^-	24
47	30	150	600	4137	HCO_3^-	50

*The amount of the salt used was calculated by the following method:
For example using run 41 the solubility of CO_2 under operating conditions $\approx 0.17 \text{ g CO}_2/\text{g DEA}$

Wt. of DEA solution	= 300 g	MW of CO_2	= 44
Conc. of DEA	= 30 wt %	MW of KHCO_3	= 100
Weight of DEA	= 90 g		
Required CO_2	= $90 \times 0.17 = 15.3 \text{ g}$		
Required KHCO_3	= $15.3 \times 100/44 = 34.8 \text{ g}$		

Run 44 using K_2CO_3 resulted in no degradation. Therefore CO_3^{--} can be considered to play no part in the degradation of DEA. Since the solution was highly alkaline due to the presence of both DEA and HCO_3^- , it was assumed that CO_2 was only present in the carbonate form.

Figure 9.5 shows DEA concentration as a function of time for runs 45 to 47 in which KHCO_3 was used. The plots are linear up to about 0.9×10^{-3} moles/cc DEA. Figures 9.6 to 9.8 show the corresponding plots for the degradation products. The degradation appears similar to that observed by using pure CO_2 but the rates are very much lower. For example, the degradation products formed at 205°C (run 45) are produced in similar amounts to an equivalent run using CO_2 (run 3, Fig. 8.2) instead of KHCO_3 . Table 9.3 shows the k_{DEA} values for the KHCO_3

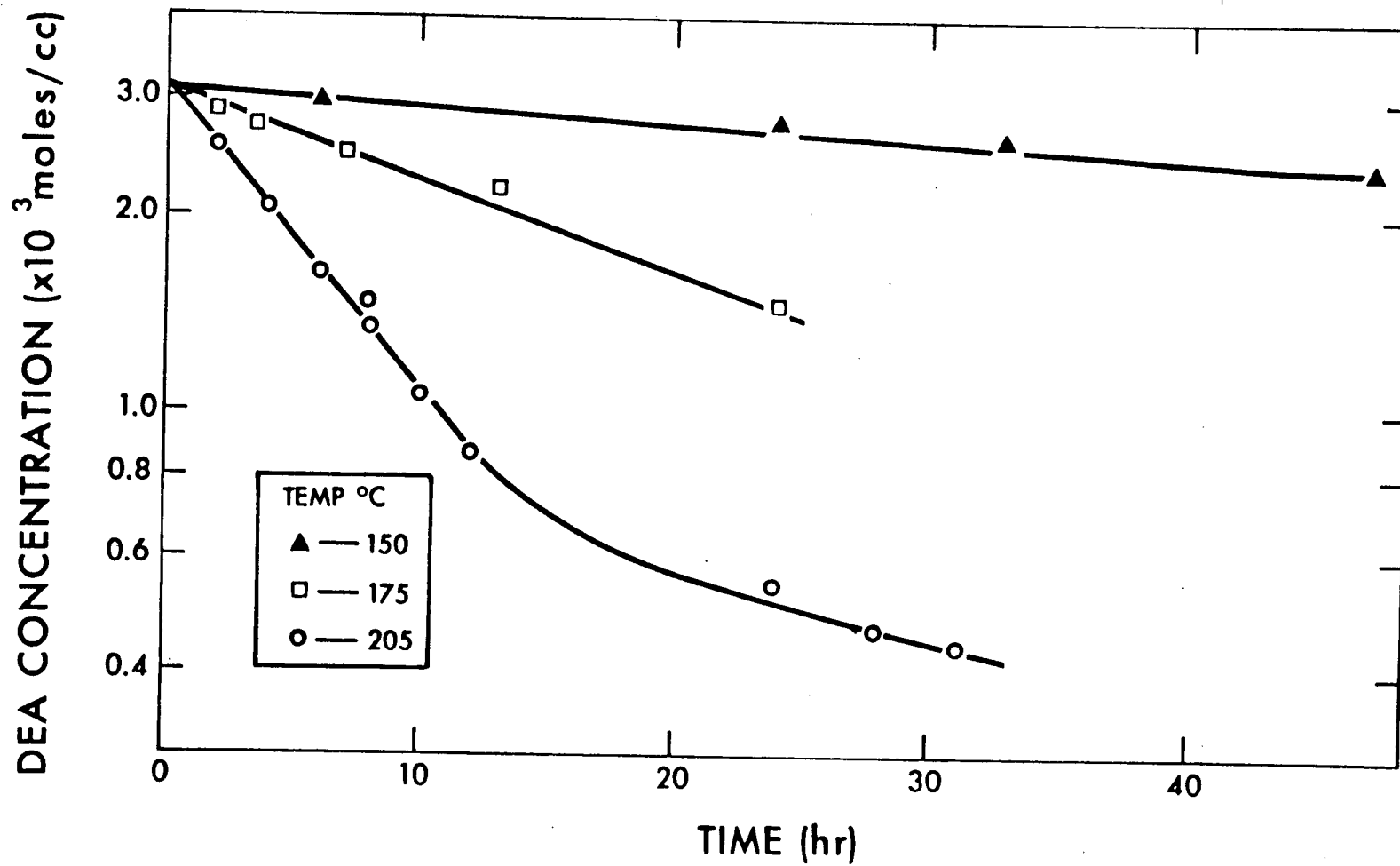


Figure 9.5 DEA concentration as a function of time and temperature
(using KHCO_3 , 30 wt % DEA, 4137 kPa N_2)

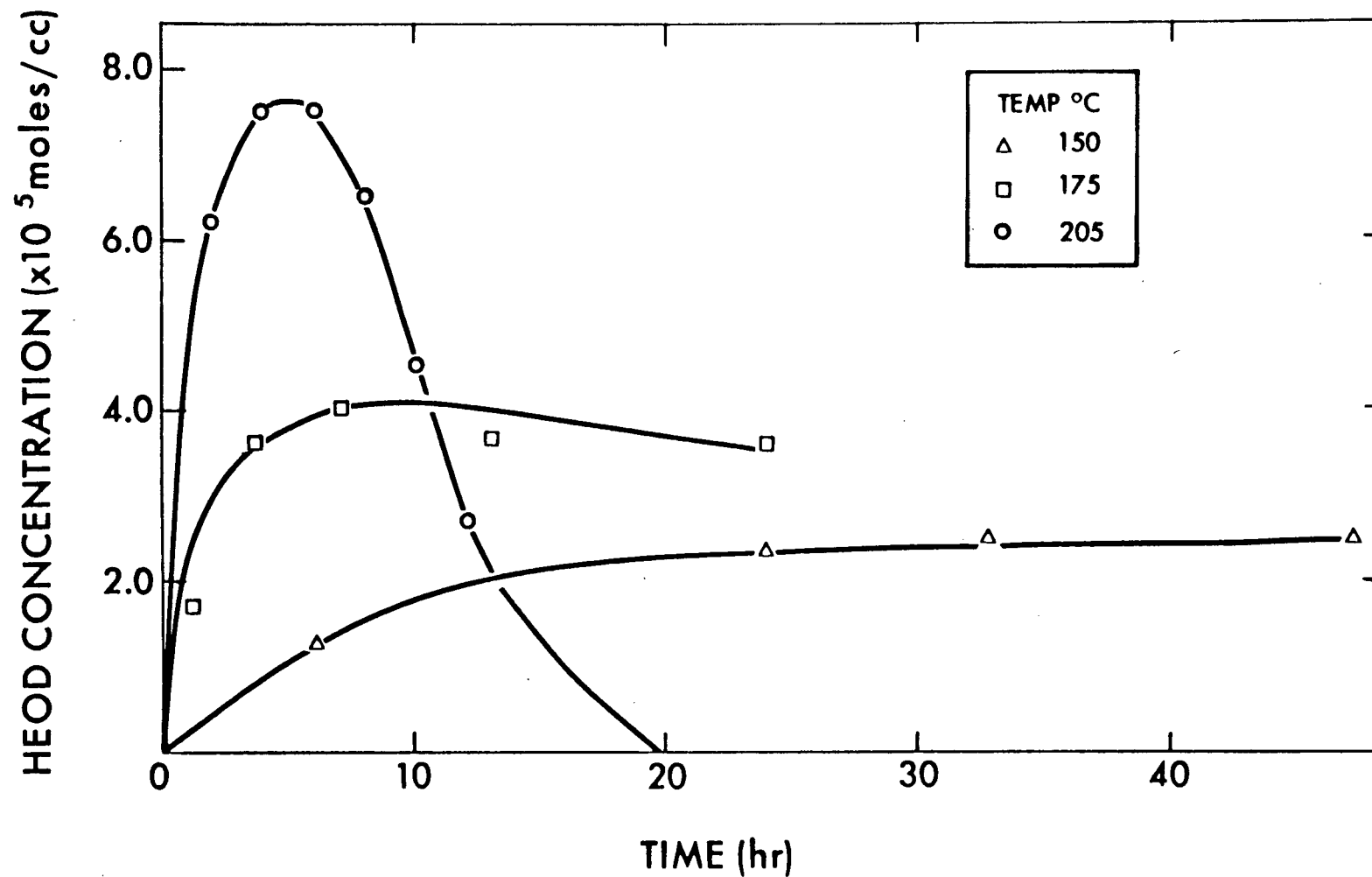


Figure 9.6 HEOD concentration as a function of time and temperature
(using KHCO_3 , 30 wt % DEA, 4137 kPa N_2)

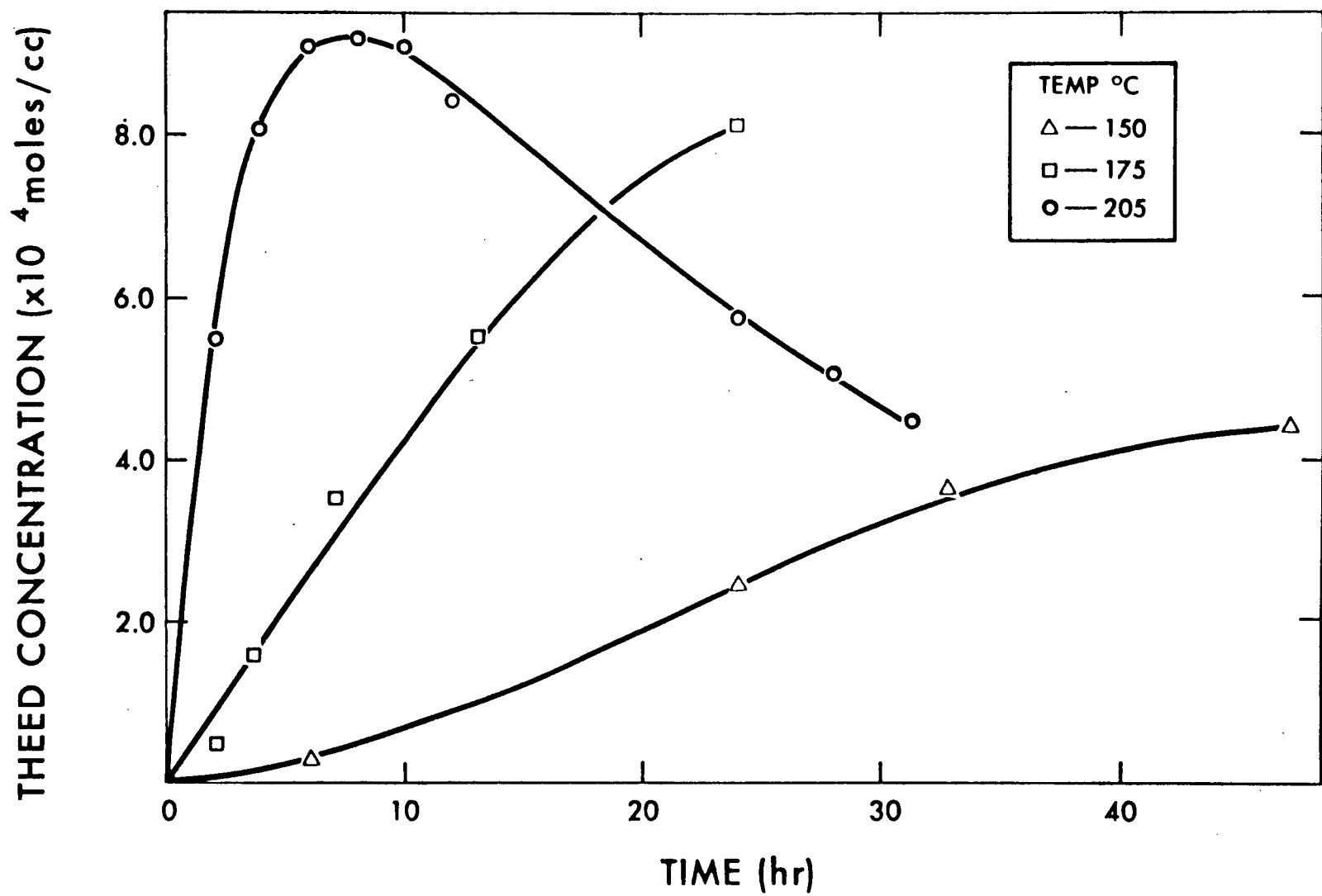


Figure 9.7 THEED concentration as a function of time and temperature (using KHCO_3 , 30 wt % DEA, 4137 kPa N_2)

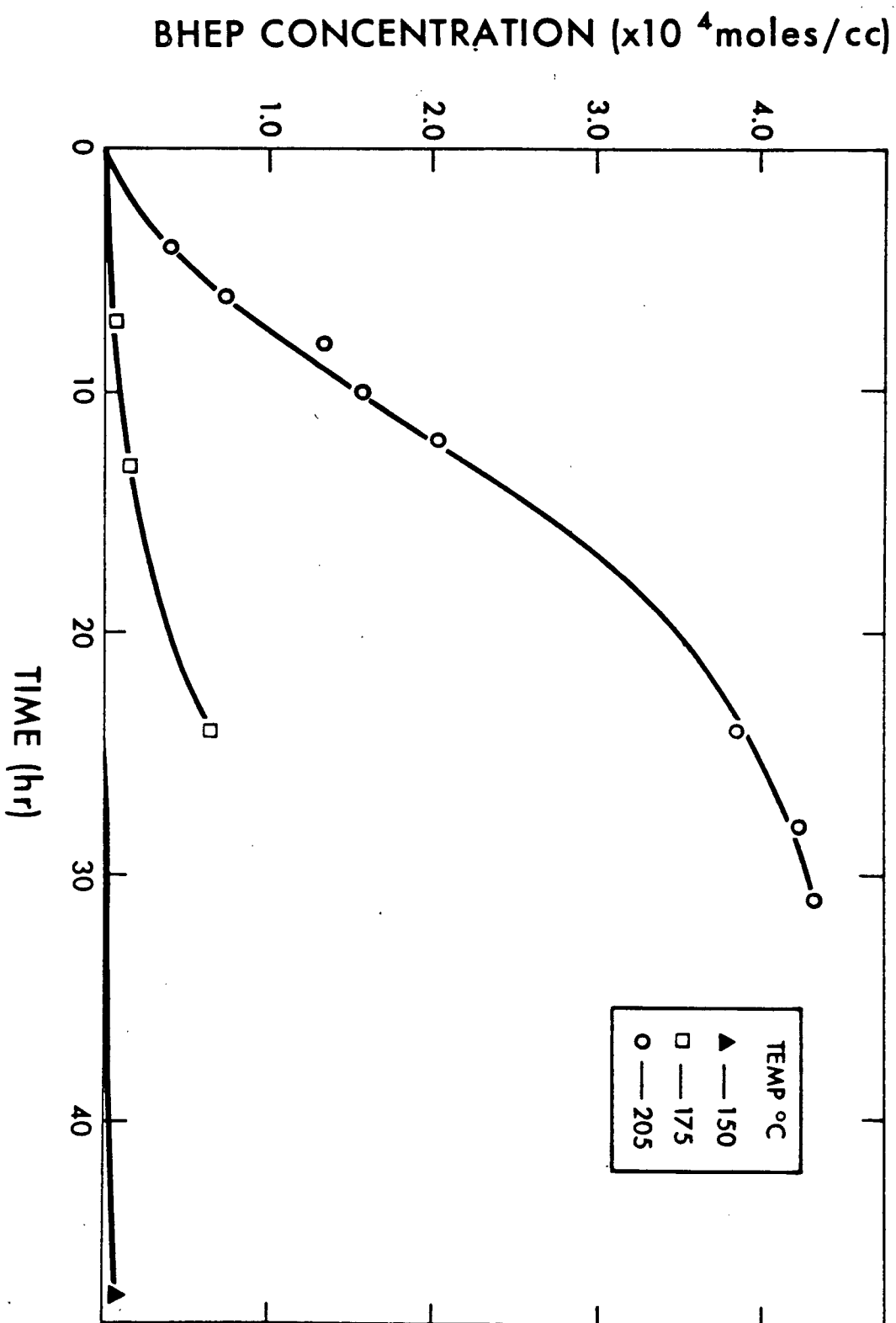


Figure 9.8 BHEP concentration as a function of time and temperature
(using KHCO_3 , 30 wt % DEA, 4137 kPa N_2)

runs and equivalent CO_2 runs. Also, the k_{DEA} values for runs where 10 wt % DEA is degraded under CO_2 are listed. The close similarity between the k_{DEA} values for the ionic runs and the CO_2 runs at 10 wt % DEA is noteworthy.

Table 9.3 Comparison of k_{DEA} values for runs conducted with KHCO_3 and CO_2

Temp °C	k_{DEA} (hr^{-1})		
	30 wt % ionic (KHCO_3 Runs)	30 wt % standard (CO_2 Runs)	10 wt % standard (CO_2 Runs)
205	0.104	0.29	0.101
175	0.026	0.121	0.0242
150	0.0053	0.031	0.0055

The major difference between the ionic runs and the standard CO_2 runs is the production of HEOD. Very little HEOD is produced using KHCO_3 . The lower production of HEOD could be linked with the fact that the solution is more basic than under standard conditions (KHCO_3 being more basic than DEA). As mentioned previously, increasing the alkalinity causes HEOD to break down and to inhibit the production of HEOD.

From these results it can be concluded that DEA degradation can be caused by HCO_3^- . However, other reactions must also take place since the degradation increases when pure CO_2 is used.

9.3 Effect of water

To investigate degradation by other than ionic routes, degradation experiments were conducted with CO_2 in the absence of water. This was achieved by diluting DEA with methyldiethanolamine, MDEA. MDEA is similar to DEA but relatively inert to CO_2 and does not react with DEA under

operating conditions (see run 53). Since water was absent from the reaction mixture, ions could not be formed and hence degradation could only be caused by CO_2 reacting directly with DEA. Since no ions are present, these runs are called "molecular runs". It must be remembered that the reactions producing HEOD, THEED, and BHEP all are accompanied by the production of water. However water is never in excess as in the standard runs performed with aqueous DEA solutions. The runs performed are summarized in Table 9.4.

Table 9.4 Summary of the molecular runs

Run No	DEA conc wt %	Temp °C	Pressure of CO_2 psi	kPa
48	66.7	205	600	4137
49	40	205	600	4137
50	30	205	600	4137
51	30	175	600	4137
52	30	150	600	4137

Figures 9.9 to 9.12 show the results of the runs at 205°C. Once again the three major degradation products are formed in relatively the same amounts as in the standard runs; however, the rate is slower and k_{DEA} decreases slightly with initial DEA concentration.

Thus it appears that DEA can degrade by two parallel reaction paths, one involving pure CO_2 and the other HCO_3^- . Table 9.5 gives the values of k_{DEA} for the molecular runs and compares them with those for the ionic runs and standard runs.

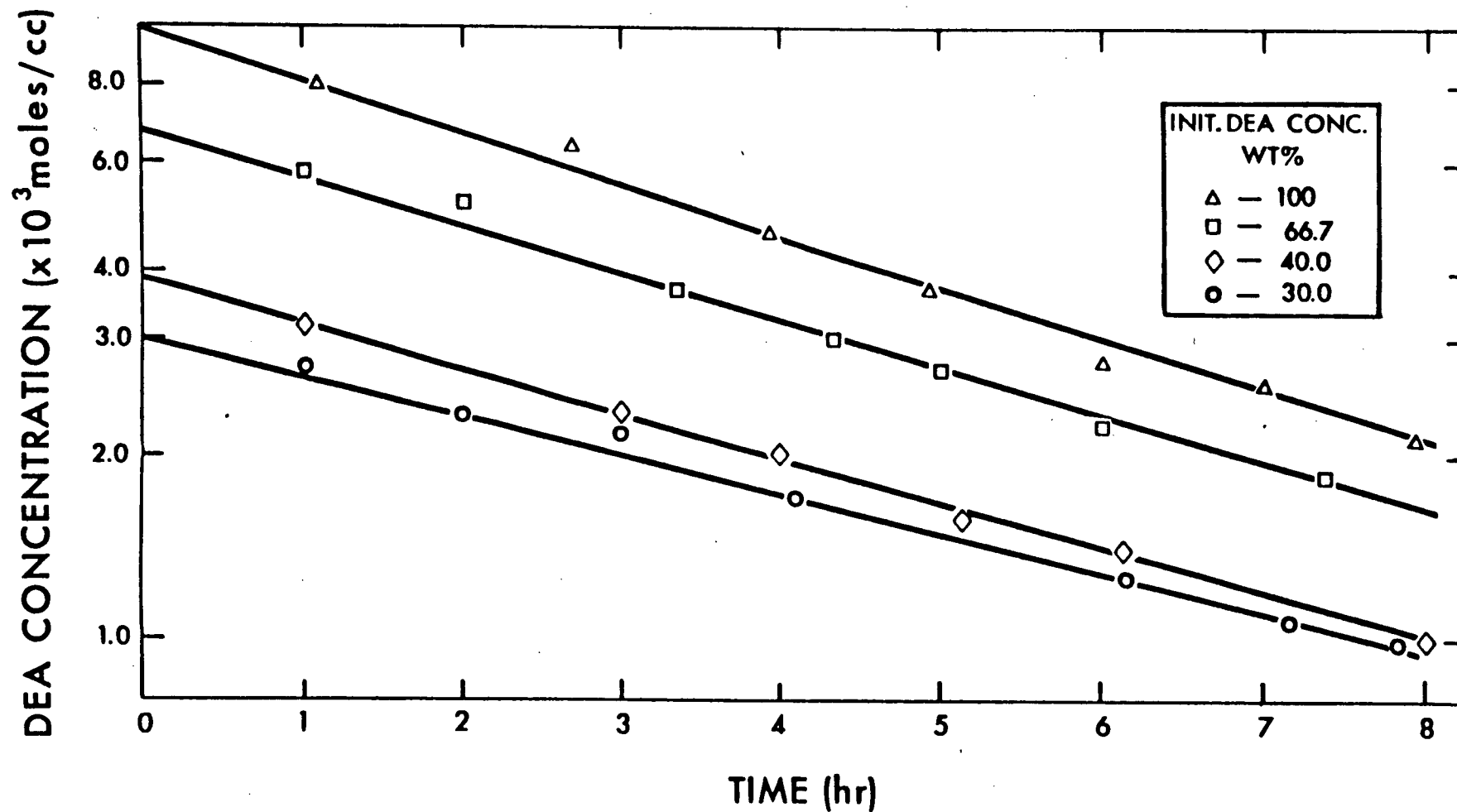


Figure 9.9 DEA concentration as a function of time and initial DEA concentration (no water present, 4137 kPa CO₂, 205°C).

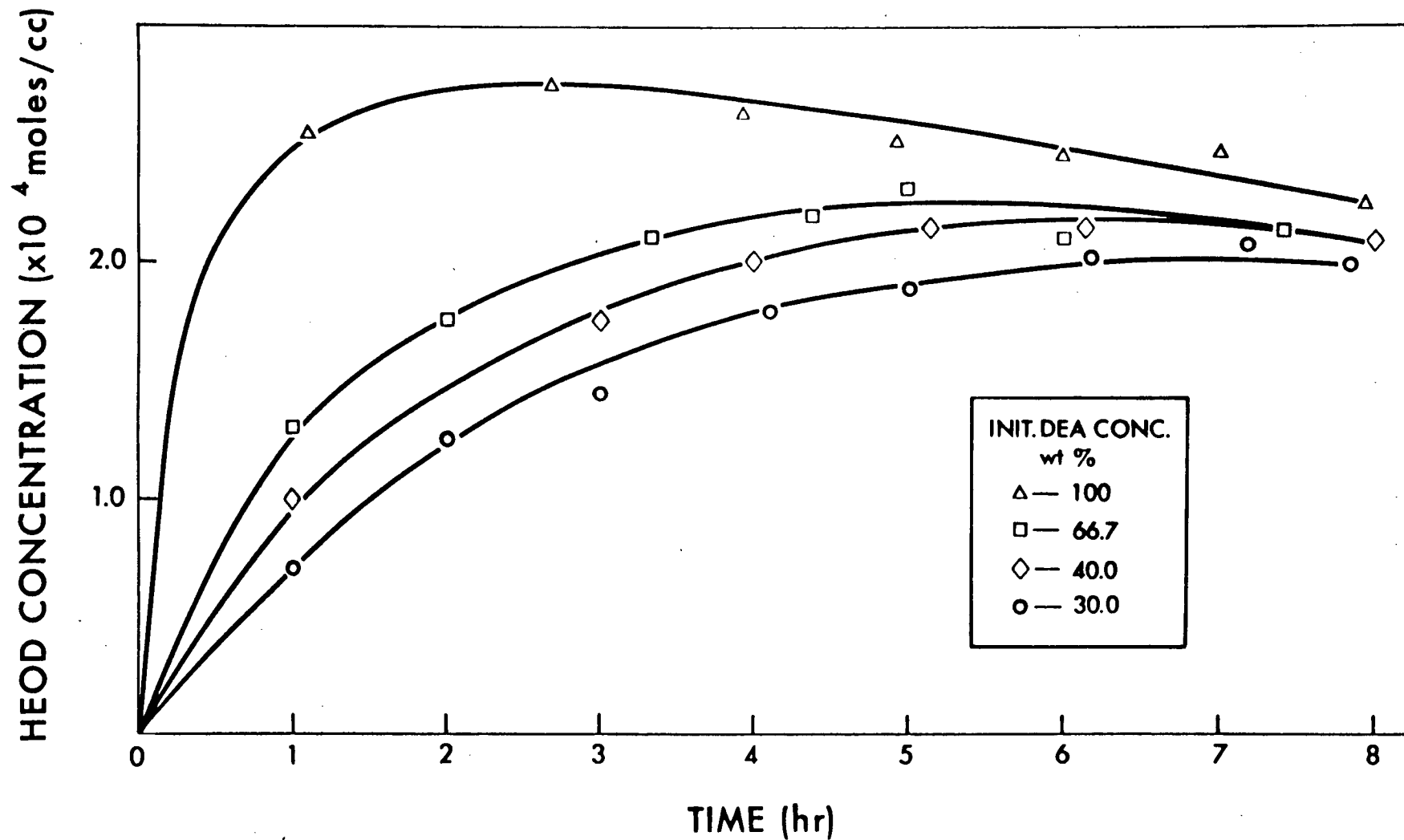


Figure 9.10 HEOD concentration as a function of time and initial DEA concentration (no water present, 4137 kPa CO₂, 205°C)

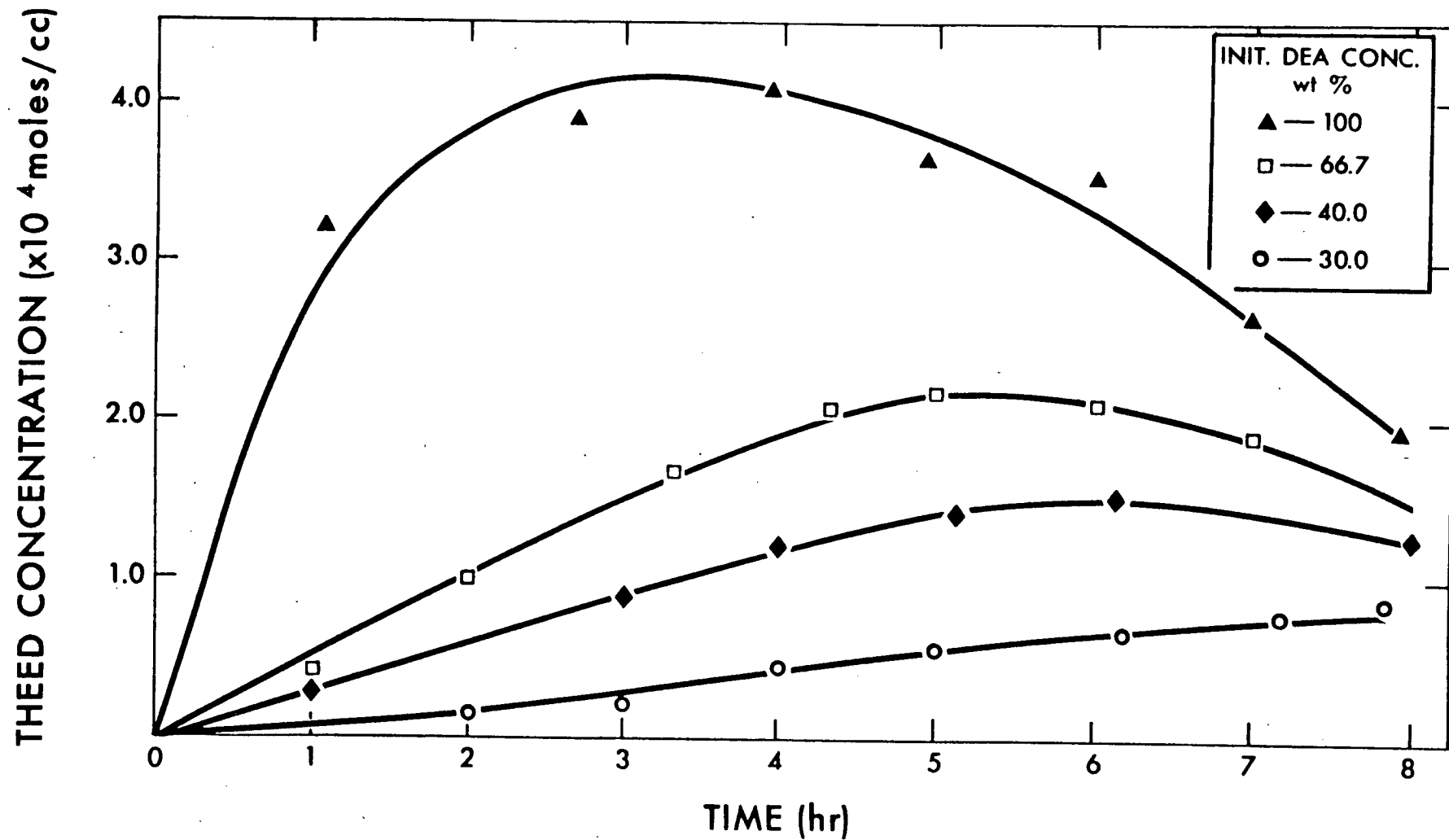


Figure 9.11 THEED concentration as a function of time and initial DEA concentration (no water present, 4137 kPa CO_2 , 205°C)

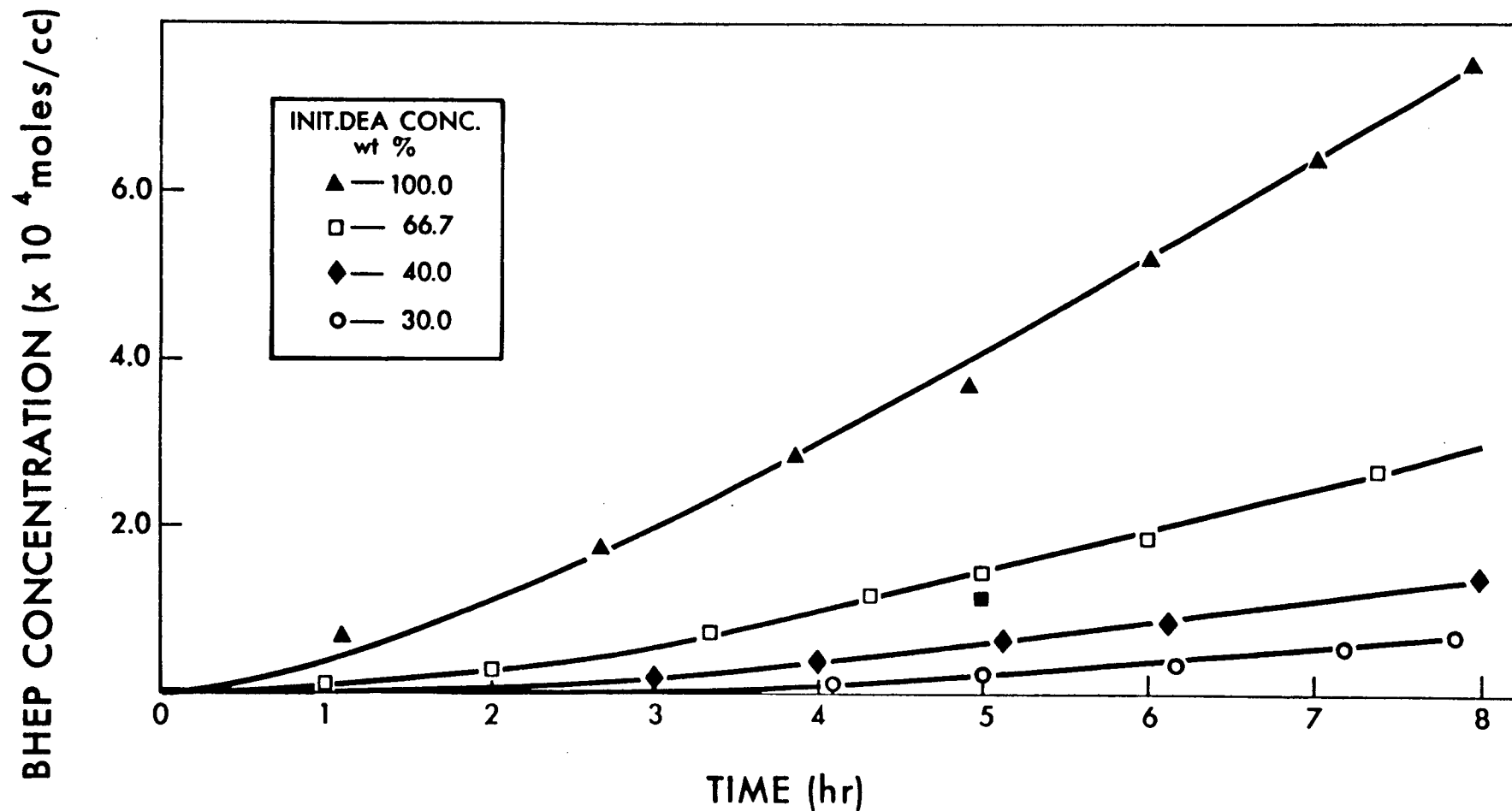


Figure 9.12 BHEP concentration as a function of time and initial DEA concentration (no water present, 4137 kPa CO_2 , 205°C)

Table 9.5 Comparison of k_{DEA} for molecular, ionic, and standard runs

DEA conc wt %	Temp °C	k_{DEA} (hr^{-1})			
		Molecular	Ionic	Standard	Molecular + Ionic
100	205	0.195	-	0.195	-
66.7	205	0.175	-	0.3	-
40	205	0.168	-	0.32	-
30	205	0.14	0.104	0.29	0.244
30	175	0.075	0.025	0.121	0.10
30	150	0.0203	0.0053	0.031	0.0253

Assuming there are two parallel reactions degrading DEA then basic kinetic theory indicates that the overall degradation rate is the sum of the rates for the two parallel reactions, i.e.,

$$(k_{\text{DEA}})_{\text{overall}} = (k_{\text{DEA}})_{\text{ionic}} + (k_{\text{DEA}})_{\text{molecular}} \quad [9.3]$$

Referring to Table 9.5, it can be seen that the sum of the k values for the two degradation routes is close to the k values for the standard run. In all cases the sum the rate constants is lower than the standard value and this is probably due to the fact that the molecular runs exclude water. In a normal run water is always present and it seems likely that water may help the molecular route hence increasing k_{DEA} for the molecular runs. Table 9.5 also shows that the k_{DEA} for the molecular runs decreases slightly with decreasing concentration. A possible reason is that another degradation product is water. At high concentrations of DEA, more water is produced which can aid the overall degradation.

The implications of the possibility of two degradation routes will be discussed further in chapter 11 and an attempt will be made to explain why the initial DEA concentration affects the overall rate constant k_{DEA} (see Fig. 8.15).

9.4 Thermal degradation

One of the reasons for the difficulty in purifying degraded DEA solutions is the fact that DEA breaks down at its boiling point. A simple test where DEA was boiled at atmospheric pressure under nitrogen for about 30 minutes resulted in 20% degradation producing THEED and BHEP. It was, therefore, decided to investigate the thermal degradation of 30 wt % DEA under operating conditions. Two runs were carried out under conditions summarized in Table 9.6.

Table 9.6 Summary of thermal runs

Run No	Initial DEA Conc wt %	Pressure (Nitrogen) psi	kPa	Temp °C	Duration of run hr.
54	30	600	4137	205	200
55	30	600	4137	250	25

Figure 9.13 shows plots of DEA concentration as a function of time. They are both linear on semi-logarithmic scales indicating a first order reaction with the reaction rate being about one hundredth of that under standard conditions at 205°C (see Table 9.7).

Table 9.7 Comparison of k_{DEA} for thermal and standard runs

DEA conc wt %	Temp °C	k_{DEA} (hr ⁻¹)	
		Thermal	Standard
30	205	0.00365	0.29
30	250	0.033	0.69

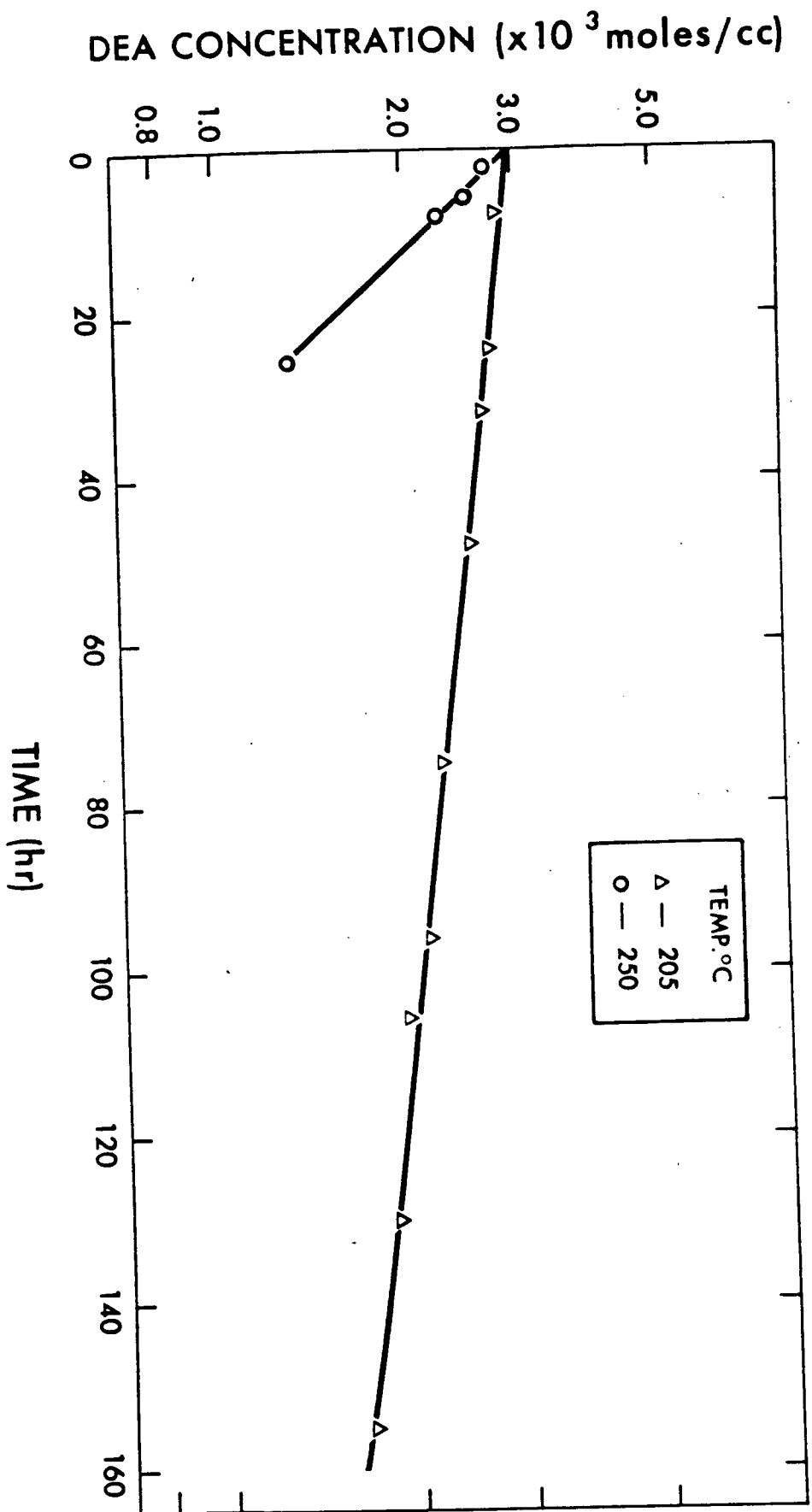
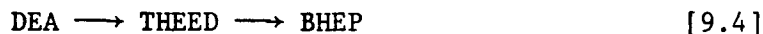
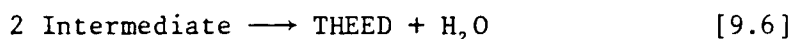


Figure 9.13 DEA concentration as a function of time and temperature
(no CO₂ present, 30 wt % DEA, 4137 kPa N₂)

BHEP and THEED were the major degradation products. Figures 9.14 and 9.15 show plots of concentration versus time. The plots tend to indicate that a series reaction is taking place, i.e.,



The second reaction is more temperature sensitive than the first. Although the thermal degradation of DEA appears first order, it does not agree with the stoichiometric equations, where two molecules of DEA are required to produce one molecule of THEED or BHEP. Therefore the reaction is not as simple as it appears. It is possible that an intermediate is slowly produced from DEA via a first order reaction, which is rapidly consumed to produce THEED. For example:-



What the results show is that BHEP can be produced from THEED which does not agree with the mechanism proposed by Polderman and Steele.³⁴ Hence, thermal degradation represents a third route for the degradation of DEA although its contribution is insignificant at low temperatures.

The major degradation products BHEP and THEED are produced in similar amounts in the thermal runs under nitrogen to the standard runs under CO_2 although at a vastly decreased rate. It is possible, therefore, that CO_2 is just acting as a catalyst. In a typical run and even for runs of over 200 hr (e.g., run 10) CO_2 is neither produced nor consumed which tends to confirm the possibility that CO_2 is acting as a catalyst.

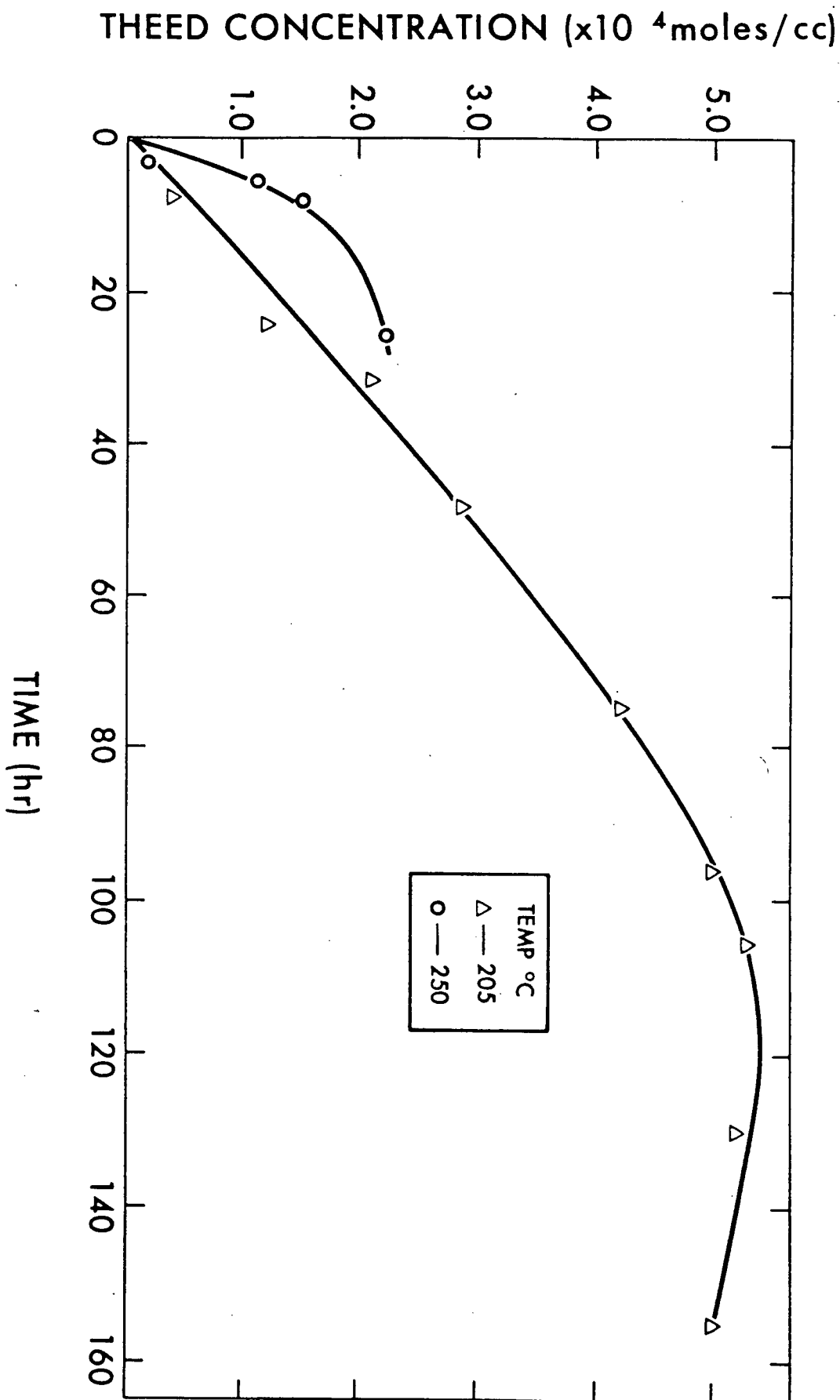


Figure 9.14 THEED concentration as a function of time and temperature
(no CO₂ present, 30 wt % DEA, 4137 kPa N₂)

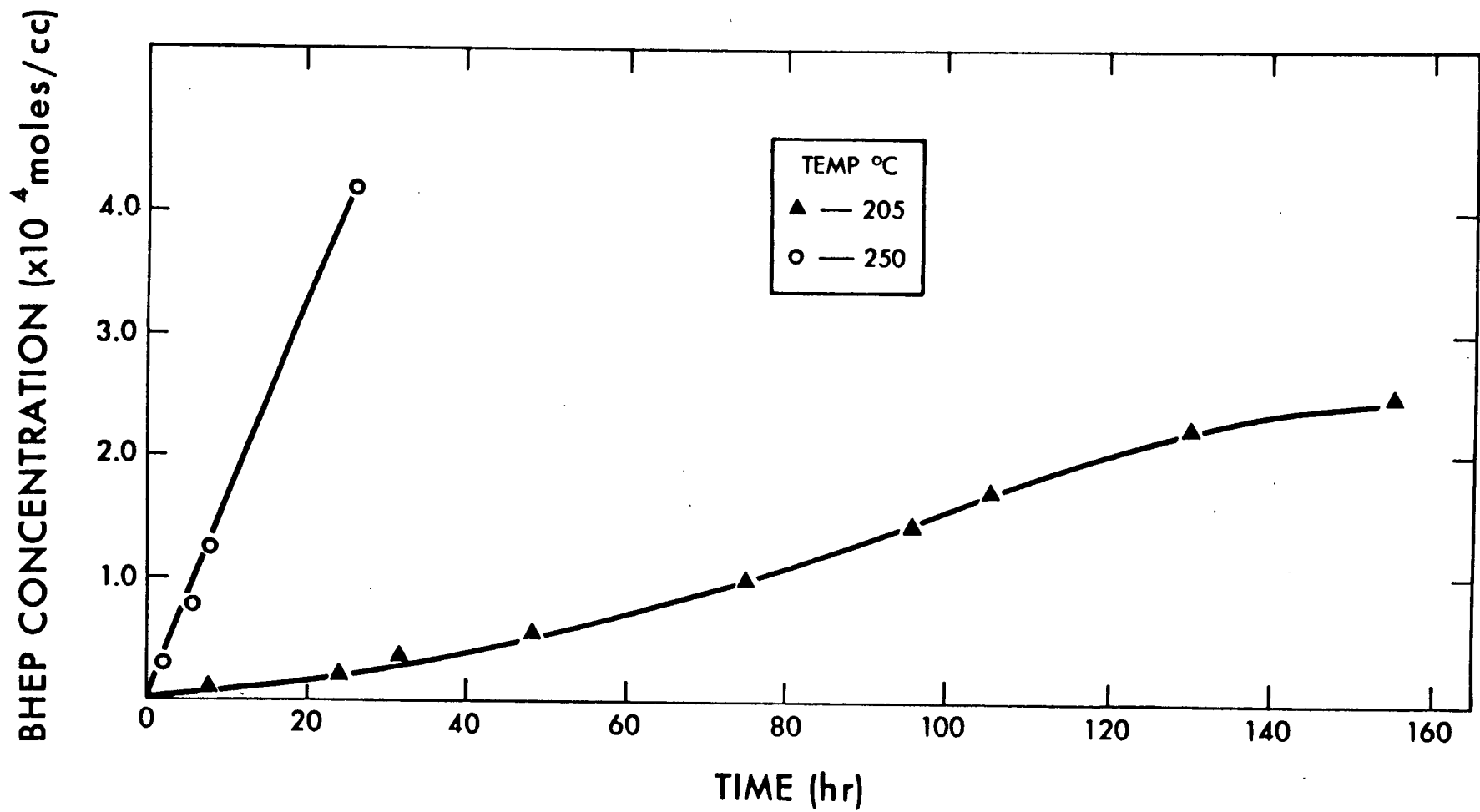


Figure 9.15 BHEP concentration as a function of time and temperature
(no CO_2 present, 30 wt % DEA, 4137 kPa N_2)

9.5 CO₂ solubility studies

It was assumed that CO₂ would be in excess for all the experiments and therefore could be neglected in devising a kinetic model. However, referring to Fig. 8.21, chapter 8, it was noted that the total reaction pressure affected the degradation rate up to about 4137 kPa (600 psi). Using Fig. 9.2 it was possible to plot k_{DEA} as a function of CO₂ concentration in DEA (see Table 9.8 and Fig. 9.16).

Table 9.8 Overall k_{DEA} as a function of CO₂ solubility for degradation runs of 30 wt % DEA at 195°C

Total Pressure psi	Total Pressure kPa	Partial Pressure of CO ₂ psi	Partial Pressure of CO ₂ kPa	Solubility g CO ₂ /g DEA	k_{DEA} hr ⁻¹
1000	6895	825.7	5693.2	0.312	0.23
800	5516	625.7	4314.2	0.259	0.23
600	4137	425.7	2935.2	0.196	0.23
500	3448	325.7	2245.7	0.165	0.185
400	2758	225.7	1556.2	0.127	0.154
300	2069	125.7	866.7	0.08	0.098
220	1517	45.7	315.1	0.043	0.061

From Fig. 9.16 it appears that if the CO₂ concentration falls below approximately 0.2 g CO₂/g DEA, then CO₂ becomes limiting and must be included in the degradation model.

It was found that at high temperatures the concentration of CO₂ is very close to 0.2 g CO₂/g DEA in a 30 wt % DEA solution under 600 psi CO₂. At 195°C the CO₂ concentration falls below the 0.2 level (see Table 9.9).

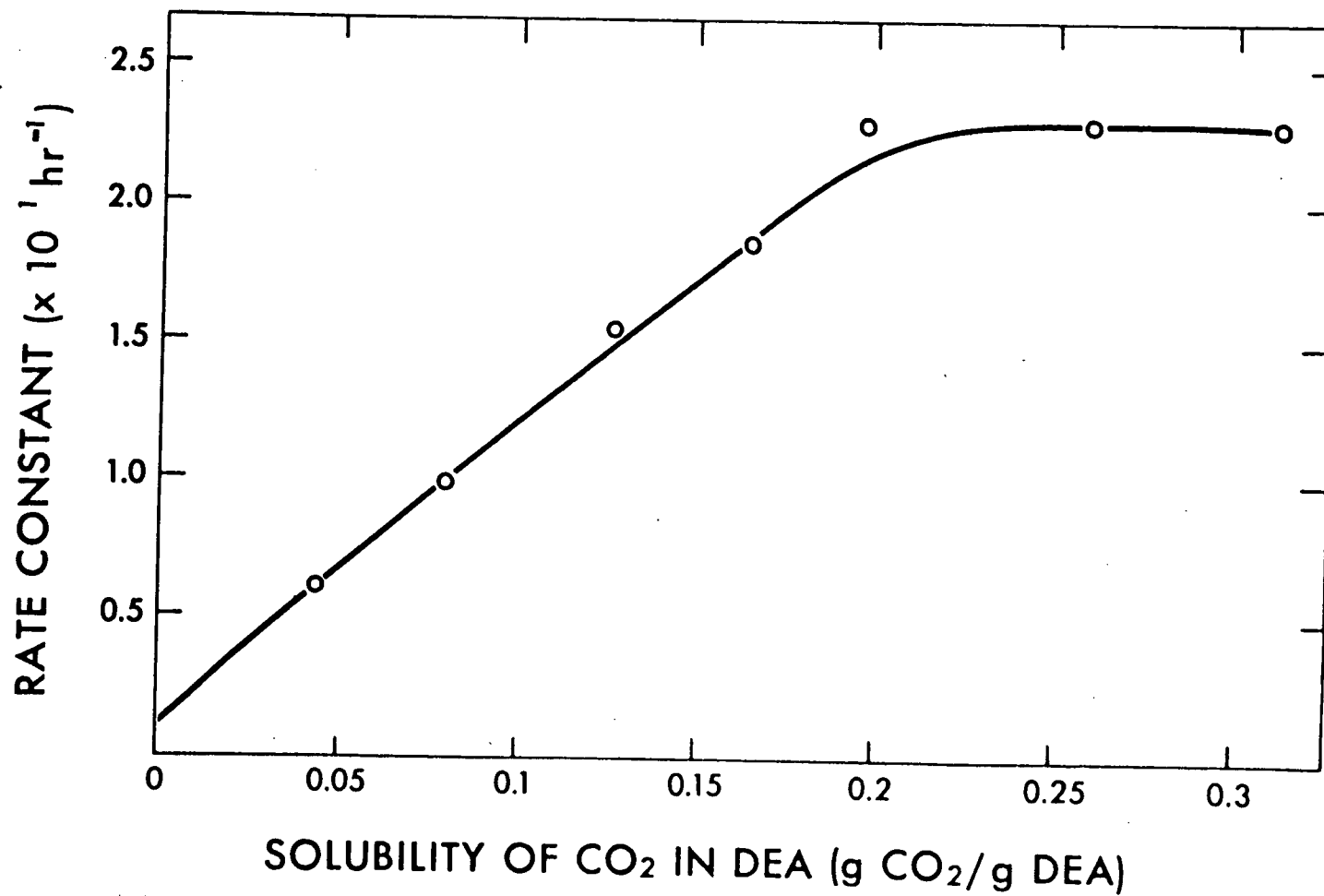


Figure 9.16 k_{DEA} as a function of CO₂ concentration
(30 wt % DEA, 195°C)

Table 9.9 CO₂ solubility as a function of temperature in a 30 wt % DEA solution under a total pressure of 4137 kPa (600 psi)

Temperature °C	Partial Pressure of CO ₂		Solubility of CO ₂ g CO ₂ /g DEA
	psi	kPa	
205	381.4	2629.8	0.168
195	425.7	2935.2	0.194
185	461.4	3181.4	0.221
175	494.1	3406.8	0.245
150	544.3	3752.9	0.32
120	575.4	3967.4	0.38

Also increasing the concentration of DEA tends to reduce the ratio of CO₂ to DEA as shown in Table 9.10.

Table 9.10 CO₂ solubility as a function of DEA concentration for solutions at 205°C under a total pressure of 4137 kPa (600 psi)

Concentration of DEA wt %	Partial pressure of CO ₂		Solubility of CO ₂ g CO ₂ /g DEA
	psi	kPa	
30	381.4	2629.8	0.168
20	370.0	2551.2	0.196
10	358.0	2468.4	0.28

Therefore, it can be concluded that for runs at high DEA concentration and high temperatures, the concentration of CO₂ will be very close to if not below the value of 0.2 g CO₂/g DEA. Thus a possible explanation for the deviation from the straight line behaviour observed in certain DEA concentration versus time plots could be due to changes in the CO₂ concentration in the reaction mixture. Although it appears that no

CO₂ is consumed during a reaction (i.e., there is no change in pressure during a run) it is possible that CO₂ is being converted to a form which reacts slower with DEA (i.e., see the ionic runs discussed in section 9.1) or the CO₂ becomes tied up in some manner with the degradation compounds (see the BHEP runs discussed in section 10.2).

Referring to Fig. 8.20, it can be seen that, as the pressure is increased beyond 4137 kPa (600 psi) the deviation of the plot from the linear form decreases, although the initial k_{DEA} remains the same. This indicates, for example, that for the 6895 kPa (1000 psi) run (run 33) the concentration remains above 0.2 g CO₂/g DEA for the entire run.

A run (run 55) was performed where 30 wt % DEA was degraded at 205°C under twice the usual CO₂ pressure, i.e., 8275 kPa (1200 psi). Figure 9.17 shows a comparison of the results of the run at 8275 kPa (1200 psi) (run 56) with a standard run at 4137 kPa (600 psi) (run 3). The plot of log [DEA] versus time is completely linear at 8275 kPa (1200 psi) whereas the standard run starts to deviate after only 2 hours of reaction time. This clearly demonstrates that, at high temperatures, CO₂ limitation affects the rate of degradation. This will be further discussed in chapter 11.

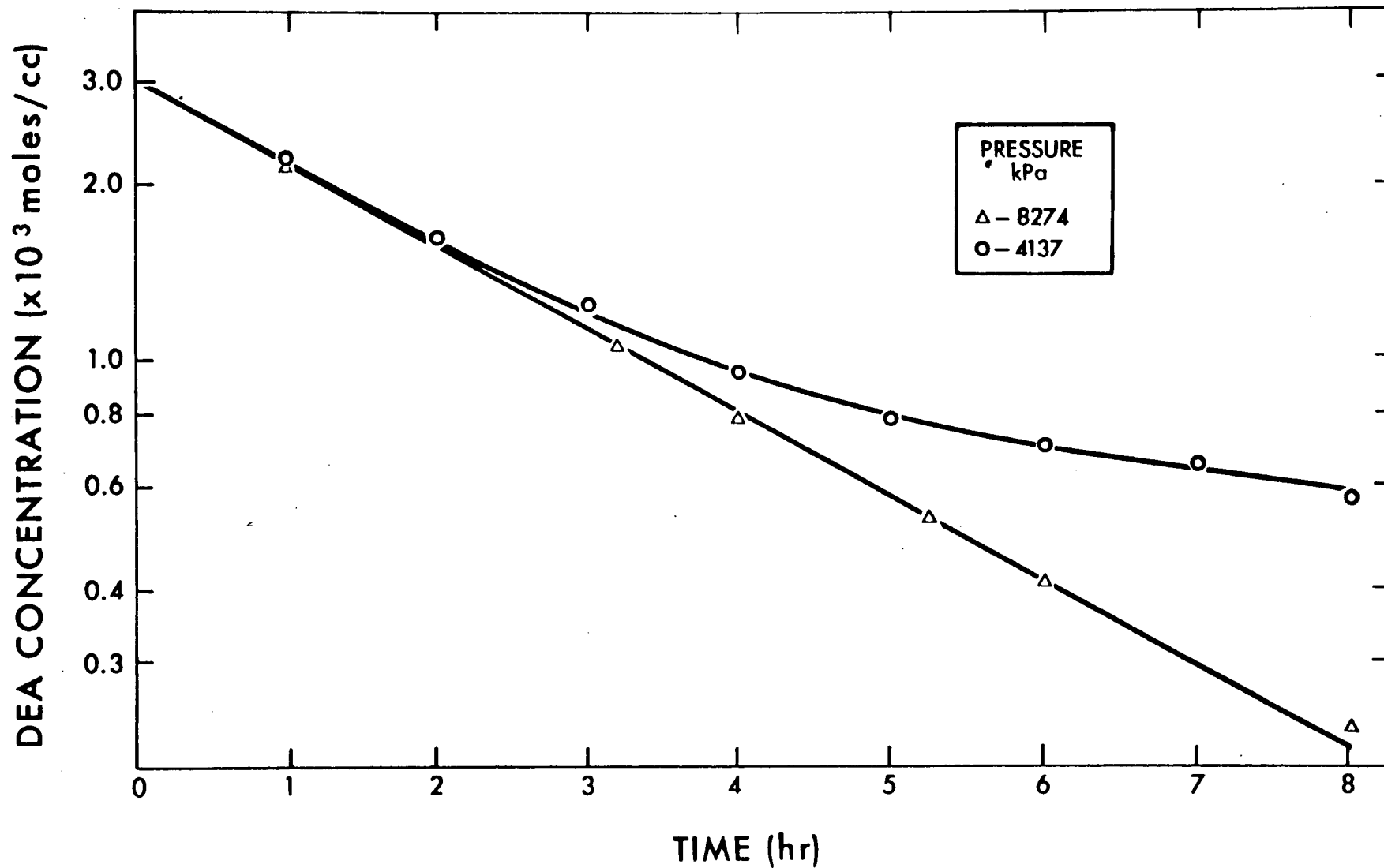


Figure 9.17 DEA concentration as a function of time and CO₂ pressure
(30 wt % DEA, 205°C)

CHAPTER 10

EXPERIMENTS DESIGNED TO STUDY THE BEHAVIOUR OF THE MAJOR DEGRADATION COMPOUNDS AND IMPURITIES IN THE DEA FEED

In general, the degradation of DEA and production of its degradation compounds can be summarized by the qualitative plots shown in Fig. 10.1. The plots suggest that BHEP is produced in a series reaction from DEA via THEED. This hypothesis needed to be confirmed and, also the role of HEOD needed to be understood. Furthermore, it was necessary to determine whether any equilibrium reactions played a role in DEA degradation. To answer these questions, the following tests were performed (see Table 10.1).

10.1 Long term run

Figure 10.2 shows a plot of concentration versus time for DEA, HEOD, THEED, and BHEP. As can be seen, DEA, HEOD, and THEED all tend to zero. BHEP appears to be the main degradation compound. However, under these extreme conditions many other compounds are produced and BHEP accounts for only about 50% of the DEA lost. It is possible that under these conditions high molecular weight polymers are produced which may not be detected by gas chromatography. The conclusion from this run is simple, overall there is no equilibrium between DEA and its degradation products.

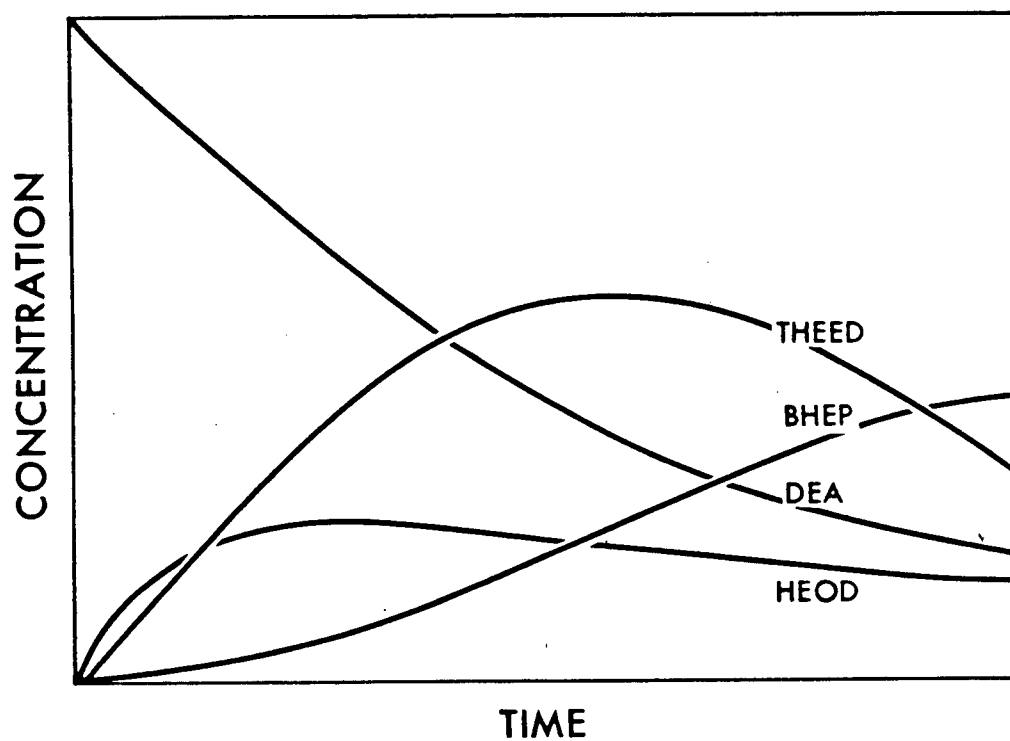


Figure 10.1 Typical plots of concentration as a function of time for DEA and its degradation products

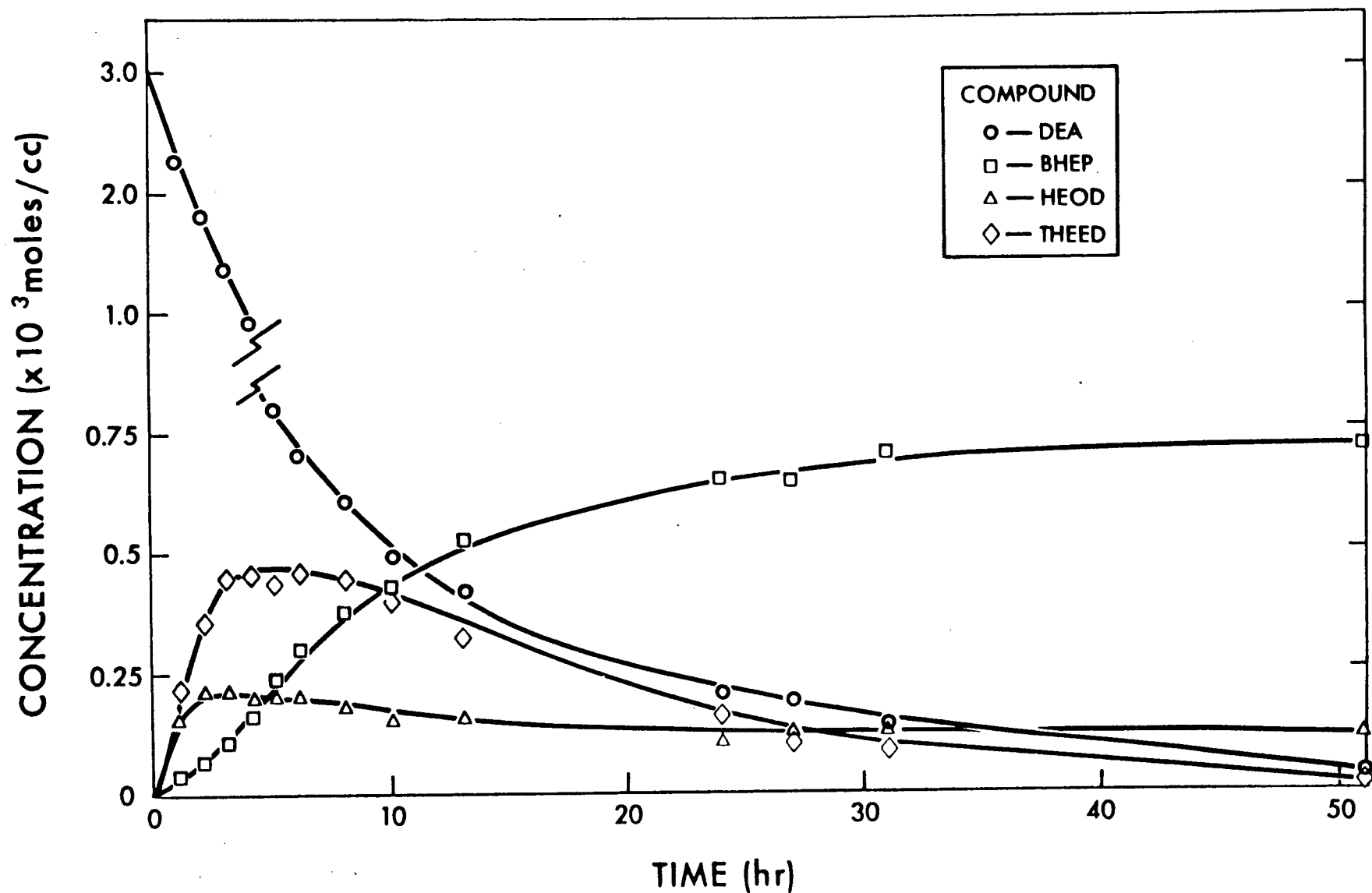


Figure 10.2 Concentration of DEA, HEOD, THEED, and BHEP as a function of time (30 wt % DEA, 4137 kPa CO₂, 205°C)

Table 10.1 Summary of runs to study the behaviour of the major degradation compounds

Run No.	DEA	Feed Concentration moles/cc			Temp °C	Gas	Run Time hr.	Comments
		HEOD	THEED	BHEP				
33	3×10^{-3}	-	-	-	205	CO ₂	50	long term run
57	-	-	-	5×10^{-4}	205	CO ₂	8	BHEP studies
58	3×10^{-3}	-	-	5×10^{-4}	205	N ₂	8	"
59	3×10^{-3}	2.7×10^{-4}	3.3×10^{-4}	3.55×10^{-4}	205	CO ₂	8	"
60	3×10^{-3}	-	-	4.7×10^{-4}	205	CO ₂	50	"
61	3×10^{-3}	-	-	4.7×10^{-4}	150	CO ₂	60	"
62	-	3×10^{-3}	-	-	205	N ₂	1	HEOD studies
63	1.0×10^{-3}	4.24×10^{-4}	-	-	205	N ₂	8	"
64	1.5×10^{-3}	4×10^{-4}	9.7×10^{-4}	0.28×10^{-4}	175	CO ₂	8	"
65	1.5×10^{-3}	4×10^{-4}	9.7×10^{-4}	0.28×10^{-4}	175	N ₂	8	"
66	-	-	2.6×10^{-3}	-	205	CO ₂	1	THEED studies
67	-	-	2.6×10^{-3}	-	205	N ₂	1	"
68	1.2×10^{-3}	-	2.6×10^{-3}	-	205	N ₂	8	"
69	1.2×10^{-3}	-	2.6×10^{-3}	-	205	CO ₂	8	"

All the runs were performed at 4137 kPa (600 psi)

10.2 BHEP runs

The stability of BHEP was first tested in run 57 and it was found that BHEP did not undergo any form of degradation. In run 58 BHEP was mixed with DEA and pressured to 4137 kPa (600 psi) of nitrogen to see whether BHEP would react with DEA. Again, no reaction was observed to take place. Thus it can be concluded that BHEP is a final degradation product and that, overall, DEA is slowly converted to BHEP by a slow complex series of degradation reactions.

Run 59 was carried out to determine whether the presence of BHEP and other degradation products had any effect on the overall degradation.

The feed was made up from a mixture of degraded DEA solution and fresh DEA to give an overall DEA concentration of about 30 wt %. A similar run was performed where 30 wt % DEA was degraded in the presence of only BHEP (run 60). Figure 10.3 compares the degradation of DEA for runs 59 and 60 with a standard run (run 3). As can be seen, the DEA degradation appears to be inhibited by the presence of degradation products, especially BHEP. A possible explanation for this behaviour is that degradation products (and/or BHEP) are tying up some of the available CO_2 dissolved in the reaction mixture. This may then cause the ratio of available CO_2 to DEA to fall below 0.2 g CO_2 /g DEA and therefore reduce the rate of degradation. Run 60 was extended to 50 hours after which the reaction mixture was virtually identical to that of the standard long term run (run 33).

In a similar experiment to run 60 where the reaction was performed at 150°C instead of 205°C (see run 61) no inhibiting effect due to BHEP was observed. Thus it appears as if the presence of BHEP or degradation products tends to slow down the rate of degradation only in situations where the concentration of CO_2 is very close to or below the limiting value of 0.2 g CO_2 /g DEA. Also run 60 shows that the addition of BHEP to the reaction mixture has no effect on the overall production of BHEP from DEA. Therefore, it can be concluded that BHEP is not in equilibrium with DEA or other degradation products.

10.3 HEOD runs

An aqueous solution of HEOD was heated to 205°C for one hour under nitrogen (run 62). DEA, THEED, and a trace of BHEP were produced. This indicated that there must be some form of equilibrium between HEOD and DEA. It is unlikely that there is any equilibrium between HEOD and

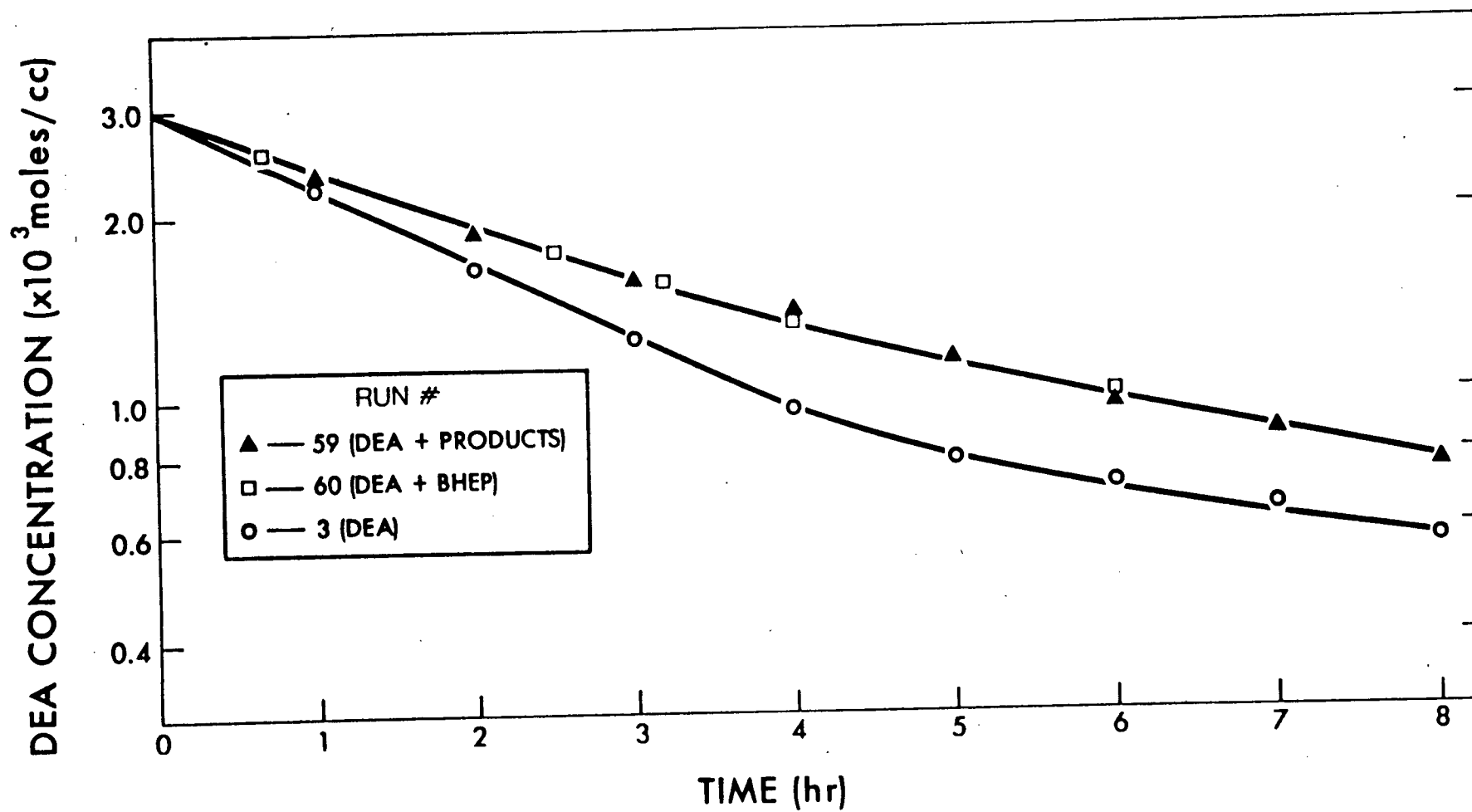


Figure 10.3 DEA concentration as a function of time and degradation products
(30 wt % DEA, 4137 kPa CO₂, 205°C)

THEED since THEED is unable to form HEOD (see run 66 or 67). However, it was not possible at this stage to confirm whether THEED and BHEP were being produced from HEOD or DEA.

Figure 10.4 shows the concentration versus time curves for the degradation of a mixture of HEOD and DEA under nitrogen (run 63). As can be seen, the HEOD is mainly converted to THEED and a trace of BHEP; the DEA loss is fairly small.

The feed used in runs 64 and 65 were produced by degrading a 30 wt % DEA solution at 175°C under 4137 kPa (600 psi) of CO₂ for 6 hr. The product was removed from the autoclave and heated to drive off any dissolved CO₂.

Run 64 is an extended standard run (see run 6) and, in run 65 the mixture is degraded under nitrogen instead of CO₂. Figures 10.5 to 10.8 compare the results of the two runs. For run 64 it appears that HEOD is playing virtually no part in the degradation of DEA and its concentration remains nearly unchanged. THEED increases then falls slightly whereas the BHEP concentration increases steadily. When the same reaction is carried out under nitrogen (run 65) some major differences are noted. The rate of DEA degradation is less than that of the run under CO₂, but it is still quite significant. Since it was established earlier (section 9.4) that DEA does not degrade noticeably at 175°C under nitrogen, it is clear that the CO₂ and/or HCO₃⁻ are provided either by the breakdown of HEOD to DEA or the formation of THEED. It can be seen from Fig. 10.6 that HEOD does not break down completely but its concentration levels off after sharply falling. This indicates some form of equilibrium has been established between HEOD and its breakdown products or DEA.

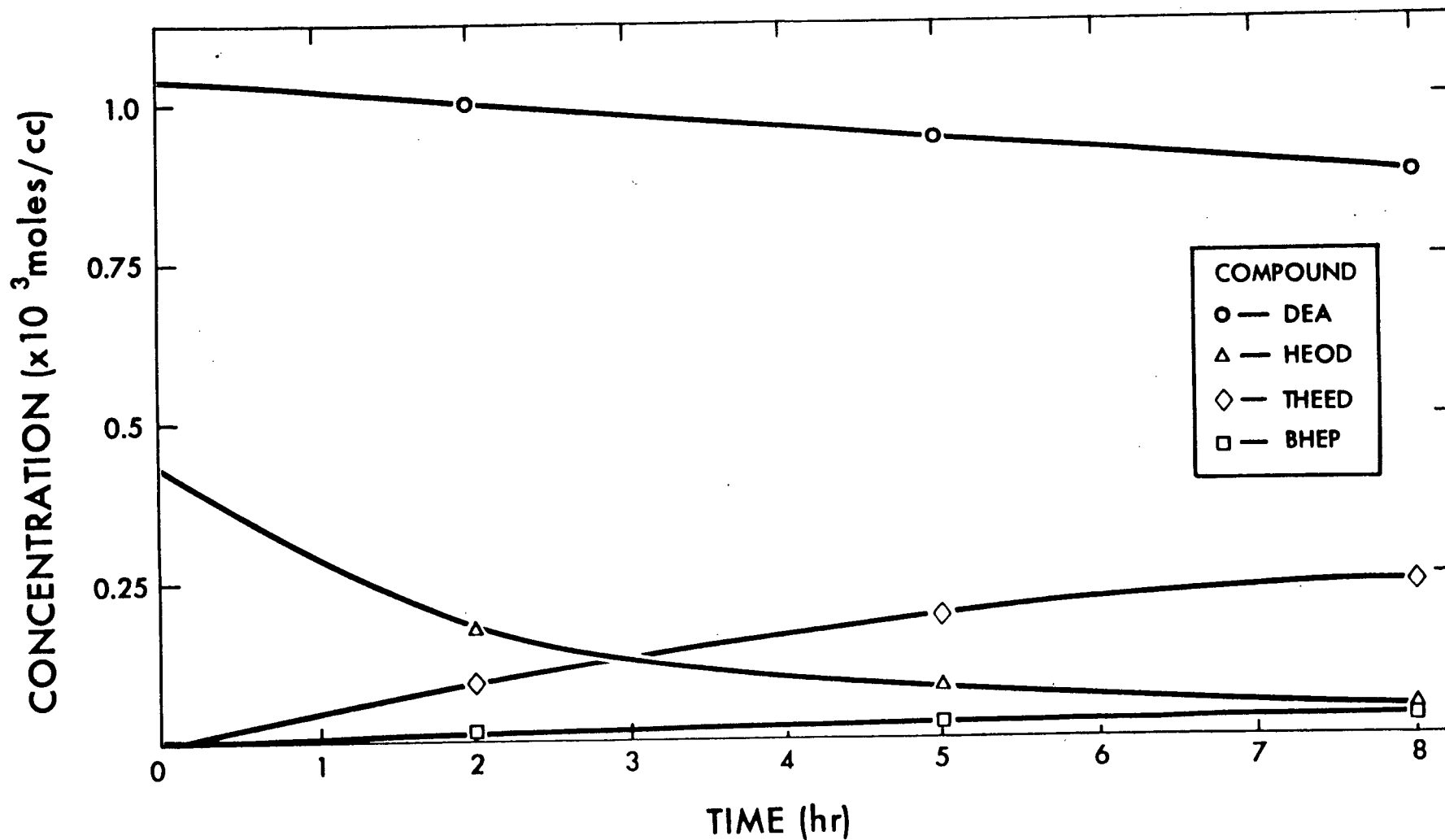


Figure 10.4 Concentration of DEA, HEOD, THEED, and BHEP as a function of time (reactants--DEA and HEOD, 4137 kPa N_2 , 205°C)

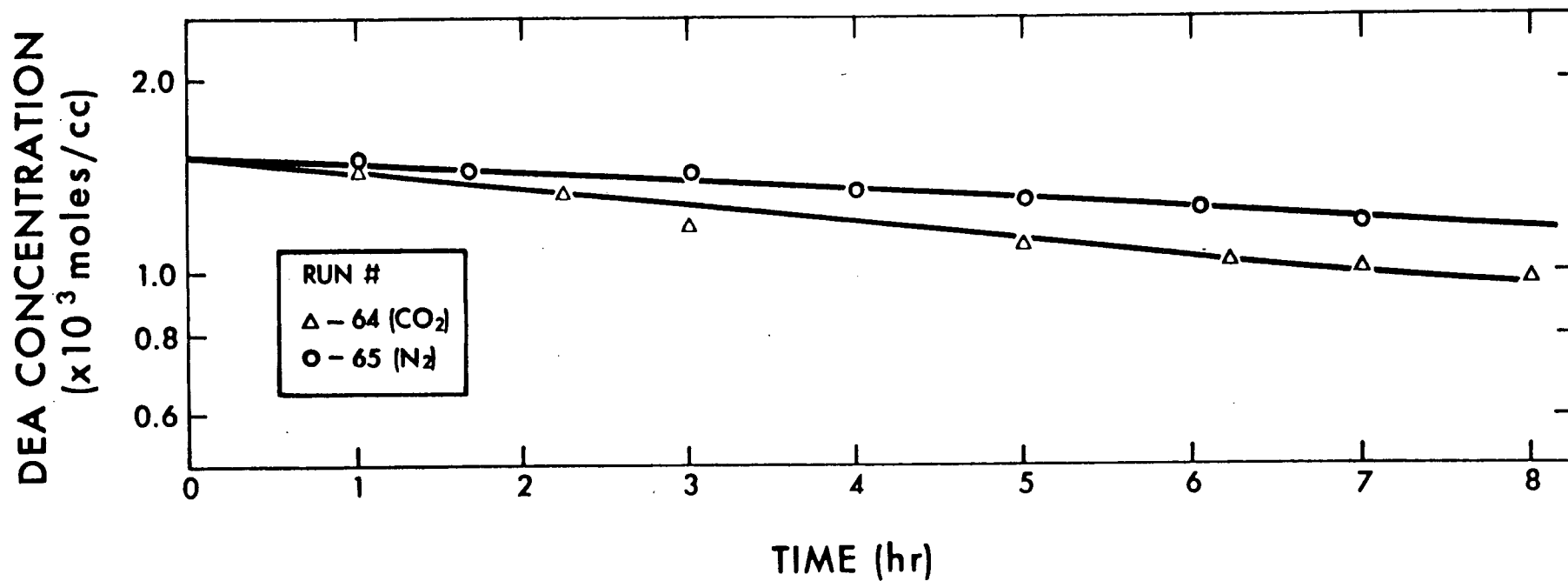


Figure 10.5 DEA concentration as a function of time
(reactants--degraded DEA solution, 4137 kPa CO₂ or N₂, 175°C)

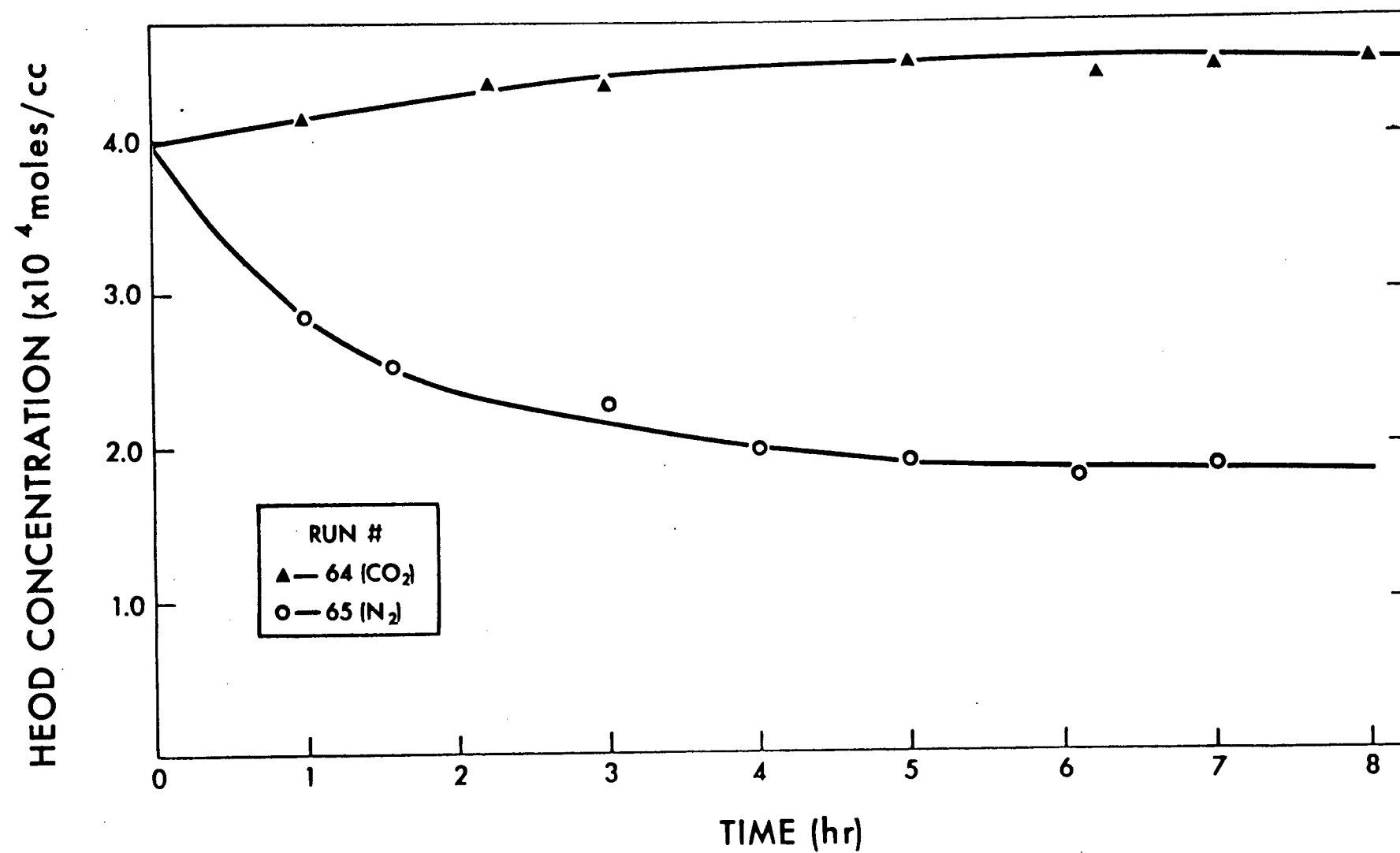


Figure 10.6 HEOD concentration as a function of time
(reactants--degraded DEA solution, 4137 kPa CO₂ or N₂, 175°C)

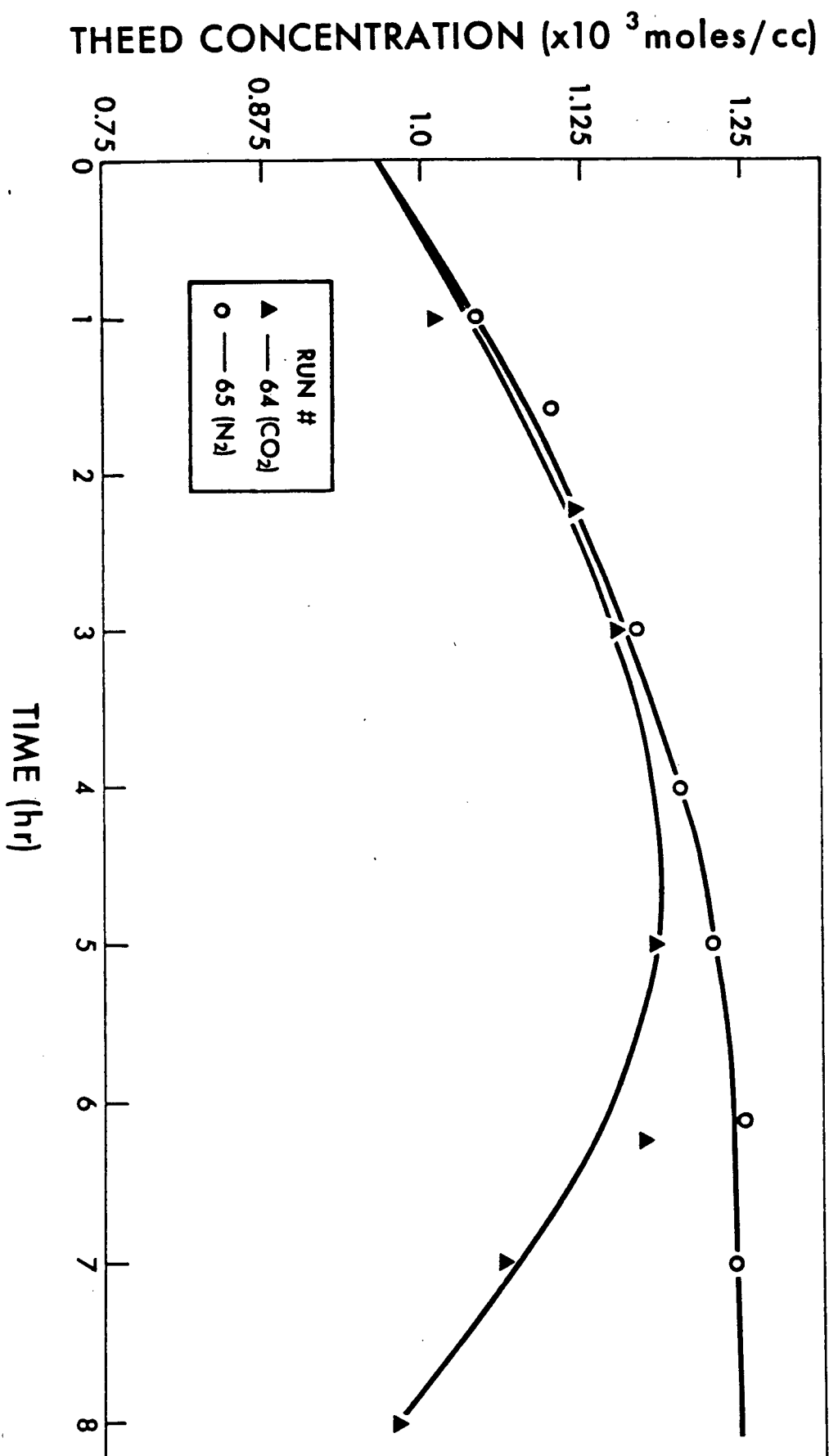


Figure 10.7 THEED concentration as a function of time
(reactants--degraded DEA solution, 4137 kPa CO_2 or N_2 , 175°C)

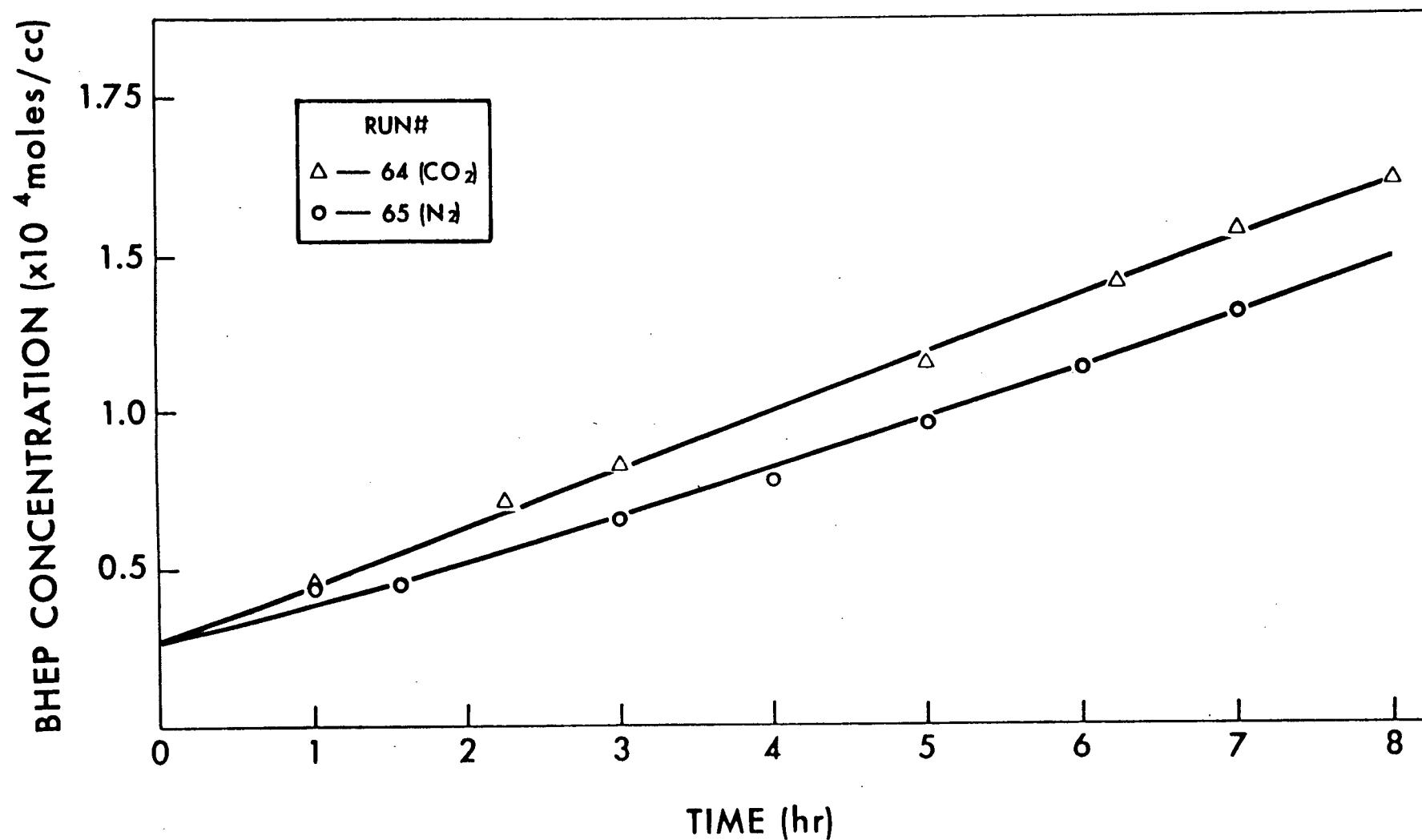


Figure 10.8 BHEP concentration as a function of time
(reactants--degraded DEA solution, 4137 kPa CO₂ or N₂, 175°C)

What appears to be taking place is that HEOD reacts to form either DEA or THEED and HCO_3^- . The bicarbonate ion then reacts with DEA to produce either more HEOD or other degradation products. In the case of run 65 it seems that DEA just degrades to THEED and BHEP once sufficient HCO_3^- has been produced from the breakdown of HEOD. In the case of run 64 it appears that HEOD need not undergo any breakdown since the solution has sufficient HCO_3^- or CO_2 provided by the CO_2 atmosphere.

In summary the following points can be made:-

1. DEA can degrade to HEOD in the presence of CO_2 .
2. HEOD can break down to DEA.
3. HEOD does not break down in the presence of DEA and CO_2 .
4. HEOD partially breaks down in the presence of DEA and N_2 .

Points 1 to 4 imply that HEOD may be involved in a reversible reaction with DEA. However, it is not a straightforward equilibrium and it is possible that HEOD is in equilibrium with a degradation product of DEA which is in turn in equilibrium with DEA. This intermediate product, if it exists, is not detected by gas chromatography or is not produced in sufficient quantities to measure.

10.4 THEED runs

An aqueous solution of THEED was heated to 205°C under 4137 kPa CO_2 for one hour (run 66). The only product produced was BHEP. A similar run under 4137 kPa (600 psi) nitrogen (run 67) also produced BHEP but in a much smaller quantity. It, therefore, appears that BHEP can be directly produced from THEED with CO_2 acting like a catalyst. Runs 68 and 69 were conducted to determine the effect of DEA on the reaction of THEED. Figure 10.9 shows the plots of concentration versus time for run 68. The concentration of DEA remains unchanged for the

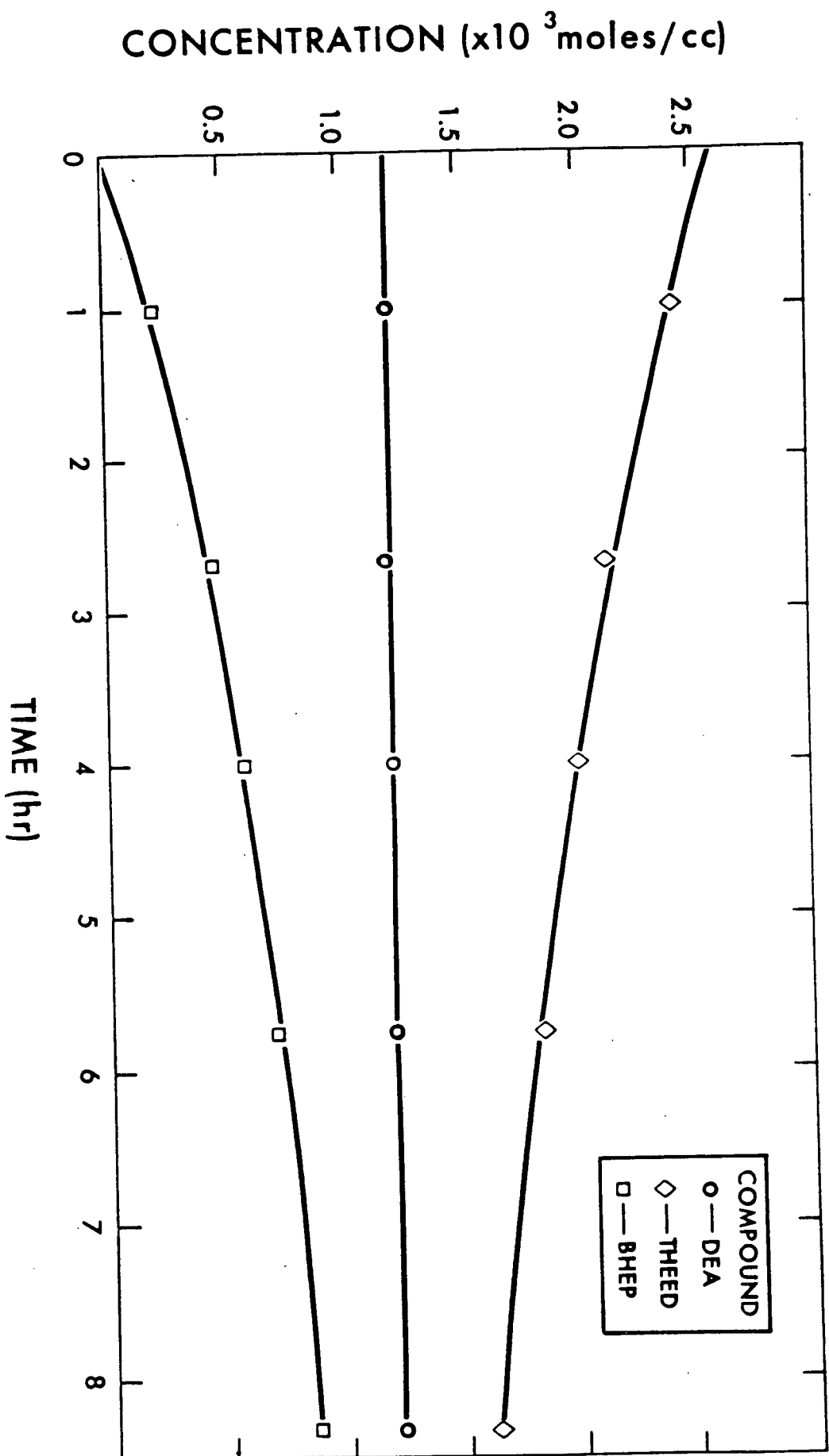


Figure 10.9 Concentration of DEA, THEED, and BHEP as a function of time
(reactants--DEA and THEED, 4137 kPa N₂, 205°C)

8 hour run. This indicates that DEA and THEED do not react. Figure 10.9 also shows that, as the THEED concentration decreases the BHEP concentration increases proportionately. This indicates a stoichiometric relationship between the two compounds.

Figure 10.10 shows the effect of CO_2 which speeds up the conversion of THEED to BHEP (run 69). DEA degrades slightly due to the presence of CO_2 . It is interesting to note that the degradation of the 12 wt % DEA in this run is much slower than it would have been if the THEED were not present. It appears that THEED, like BHEP, is able to reduce the availability of CO_2 and HCO_3^- for DEA attack.

Figure 10.11 shows plots of the THEED concentration versus time for the two runs. The curves are initially linear and indicate a first order reaction of THEED forming BHEP. The asymptotic behaviour exhibited by the THEED concentration in run 69 is probably due to the fact that additional THEED is formed from the DEA degradation. The effect of CO_2 causes the k_{THEED} to increase about five-fold. Table 10.2 shows the values of k_{THEED} obtained from Fig. 10.11. It is interesting to note that the value of k_{THEED} under 4137 kPa (600 psi) CO_2 at 205°C is very close to that obtained from the kinetic model of the degradation of DEA which will be developed in chapter 12.

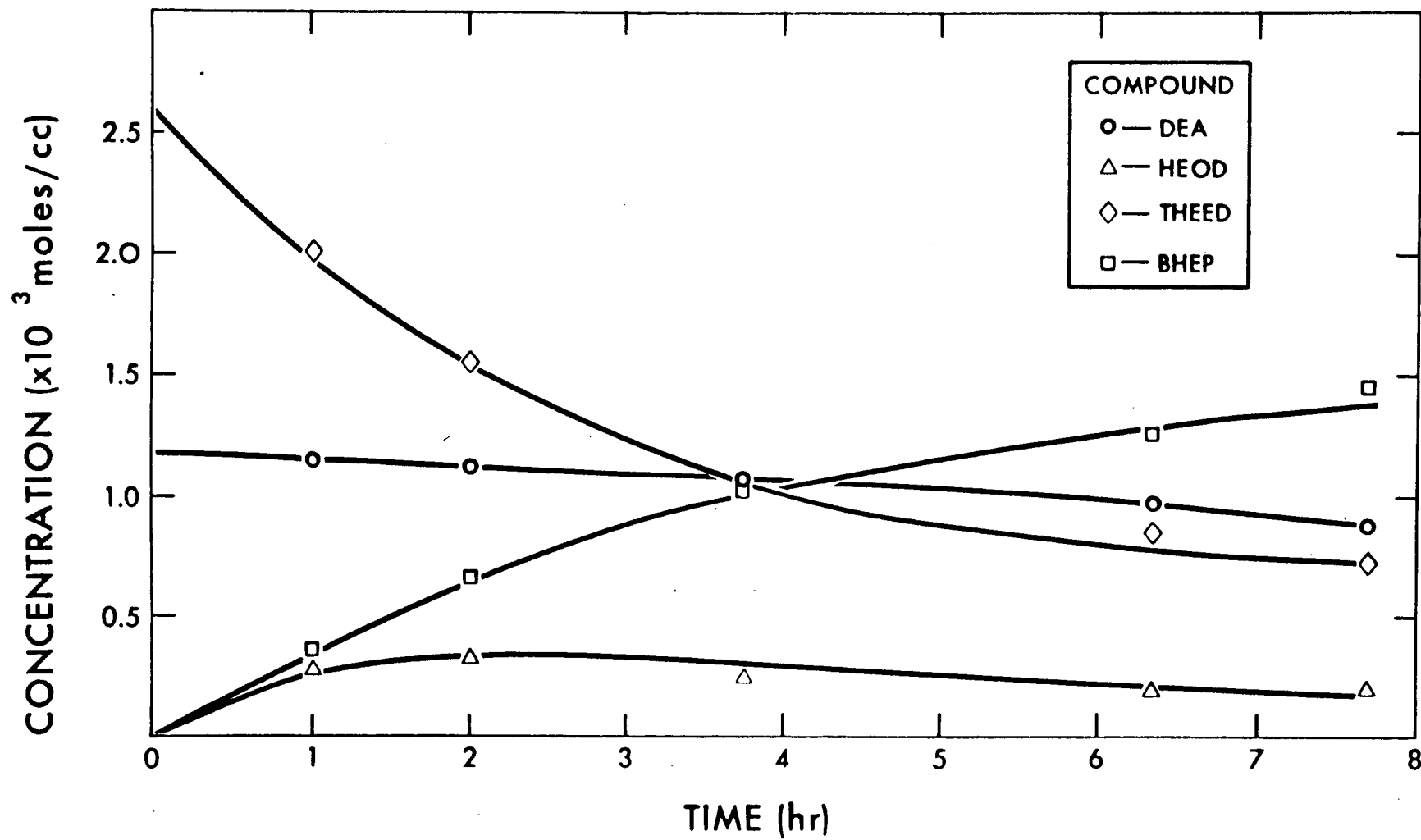


Figure 10.10 Concentration of DEA, HEOD, THEED, and BHEP as a function of time (reactants--DEA and THEED, 4137 kPa CO₂, 205°C)

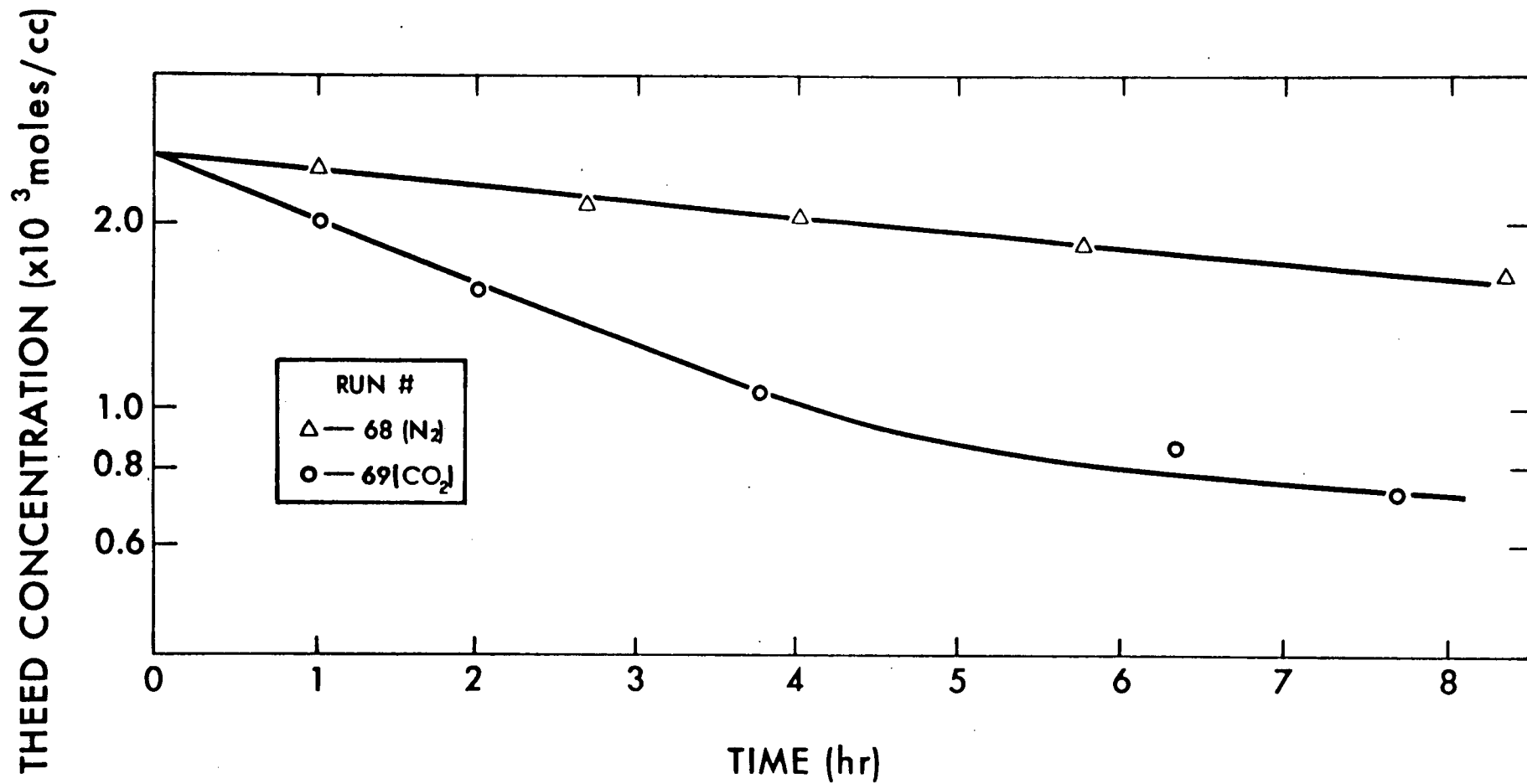


Figure 10.11 $\log[\text{THEED}]$ as a function of time
(reactants--DEA and THEED, 4137 kPa CO₂ or N₂, 205°C)

Table 10.2 k_{THEED} for reactions under CO_2 and N_2

Run No.	Gas	Pressure		k_{THEED} hr^{-1}	k_{THEED} model hr^{-1}
		psi	kPa		
68	CO_2	600	4137	0.25	0.26
69	N_2	600	4137	0.057	-

10.5 Experiments to study the effect of impurities in the DEA feed

The main impurities in the DEA feed are MEA and TEA. Four runs were carried out to determine whether these impurities degrade and whether they react with DEA to form any other degradation compounds. Table 10.3 summarizes the conditions of the runs performed.

Table 10.3 Experimental conditions of runs performed to determine the effects of DEA feed impurities

Run No.	Concentration			Temperature $^{\circ}C$	CO ₂ Pressure	
	MEA	Wt % TEA	DEA		psi	kPa
70	30	-	-	205	600	4137
71	-	30	-	205	600	4137
72	10	-	20	205	600	4137
73	-	10	20	205	600	4137

The degradation of MEA produced mainly HEI with small amounts of OZD and HEED. It was also noticed that samples of degraded MEA solutions which had been stored at room temperature for several months, smelt of ammonia. TEA was unaffected by CO_2 and no degradation compounds were detected.

When DEA was degraded in the presence of MEA (run 72) several

new peaks were detected on the chromatogram. Figure 10.12 is a typical chromatogram from run 72, with all the major peaks labelled.

The major degradation compounds produced as a result of the reaction between DEA and MEA under 4137 kPa (600 psi) CO₂ were found to be HEP, BHEED, and BHEI.

Run 73, where DEA was degraded in the presence of TEA, produced little change from that using pure DEA. However a small peak was detected with a retention time of 20.6 minutes. This was identified to be TEHEED.

The mechanism for the production of these new degradation compounds will be discussed in chapter 11.

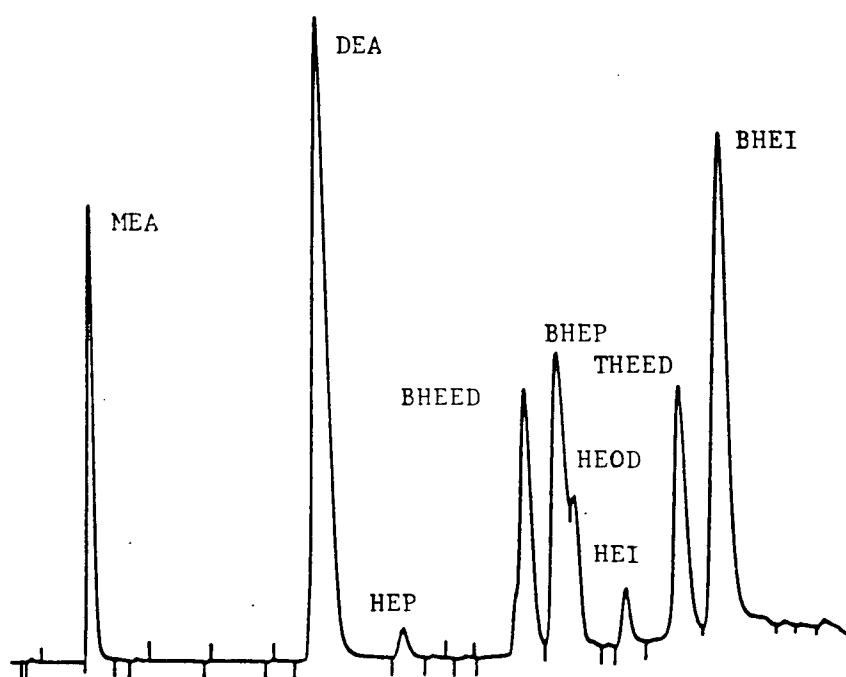


Figure 10.12 Typical chromatogram of a degraded solution of DEA and MEA

CHAPTER 11

DEVELOPMENT OF A MECHANISM FOR DEA DEGRADATION

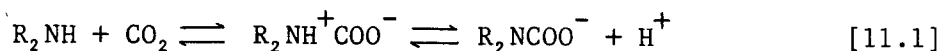
In this chapter, the results of the experiments will be discussed and an attempt will be made to explain the observed phenomena. The overall purpose of this chapter is to develop a model for the degradation of DEA by CO_2 . Reaction mechanisms are proposed which may explain the production of the compounds detected in the degraded DEA solutions. Certain reaction steps are, however, not fully confirmed since, in some cases, there was no way of testing their validity within the scope of this work. Thus certain aspects of the mechanisms remain proposals for explaining experimental observations.

The chapter is split up into five sections. The first section deals with the formation and reactions of HEOD, THEED, and BHEP. In the second, the concept of three degradation routes (i.e., ionic, molecular, and thermal) is developed. The third section contains an explanation of observations which are at variance with the concepts proposed in the first two sections. The fourth section provides an explanation of the production of minor degradation compounds. In the fifth section the conclusions of this chapter are summarized and an overall model of DEA degradation is presented.

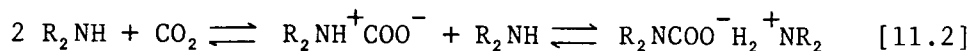
11.1 Formation and reactions of the major degradation compounds

11.1.1 Formation of HEOD. Referring to chapter 2 the following set of equilibria were established between CO_2 and DEA.

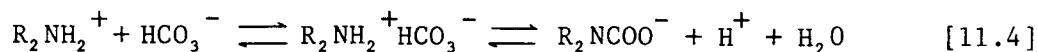
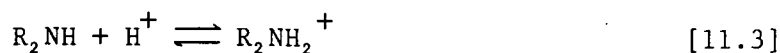
Aqueous conditions:



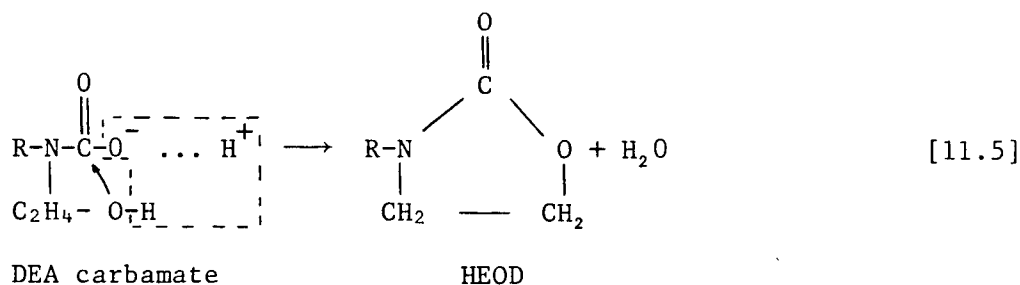
Non-aqueous conditions or high DEA concentrations:



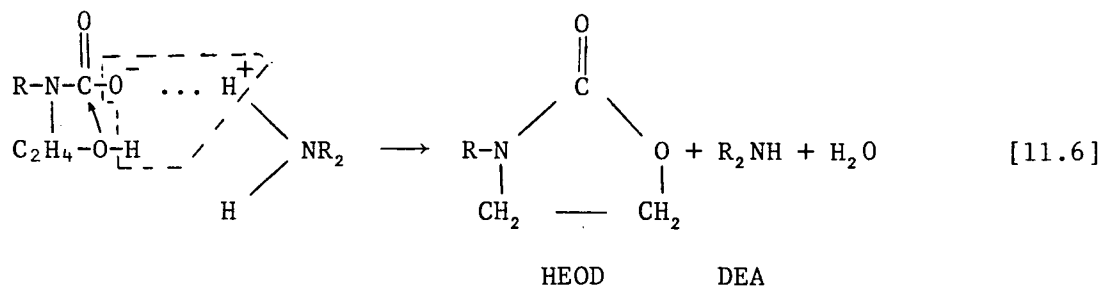
Also DEA is able to react with the bicarbonate ion in the following manner:-



In each case the amine carbamate ion is formed, R_2NCOO^- linked either with H^+ or H_3O^+ or R_2NH_2^+ . By internal dehydration of the carbamate, HEOD can be produced:-



or, at high DEA concentrations:-



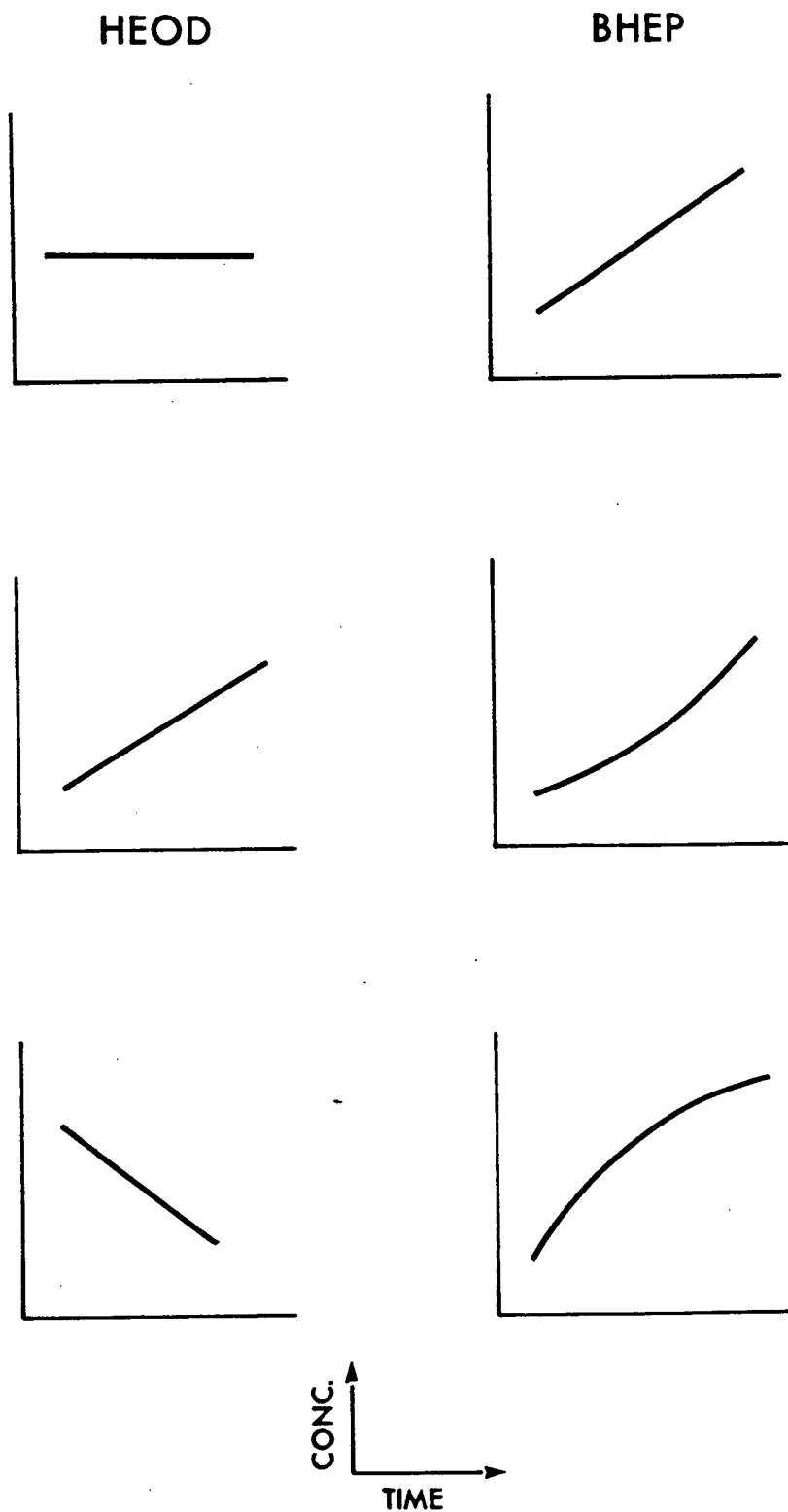


Figure 11.1 Qualitative plots of concentration versus time, showing the possible relationships between HEOD and BHEP

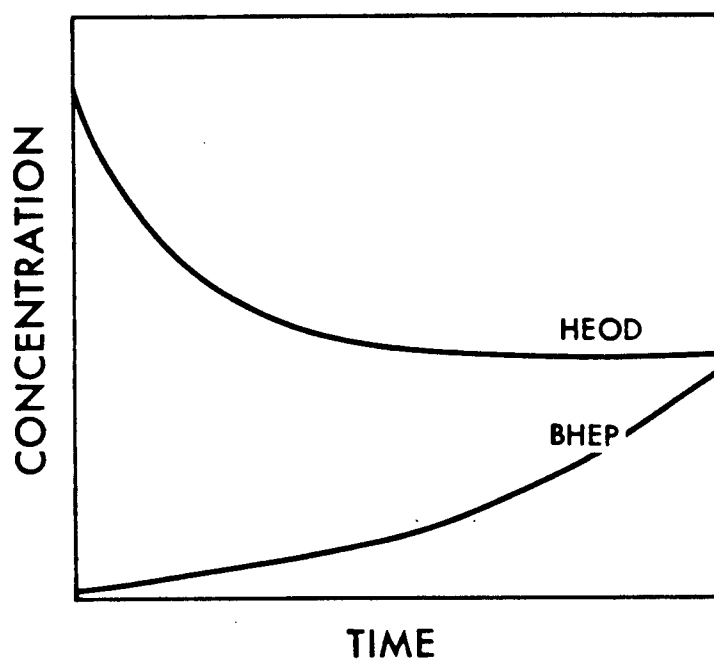


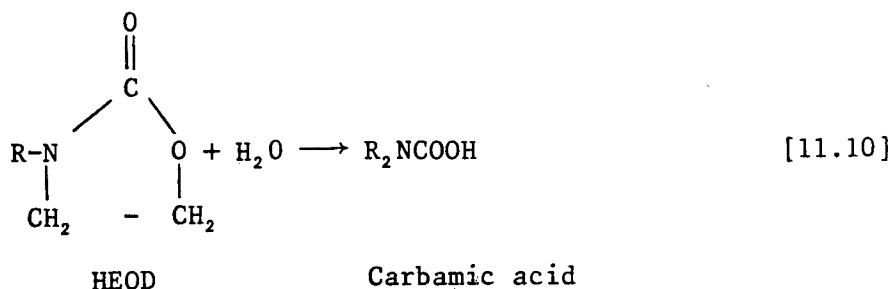
Figure 11.2 Sketch of the concentration of HEOD and BHEP as a function of time for run 65

and 150°C (see runs 10 and 8). Here the concentration of HEOD reaches a maximum then falls, whereas the BHEP concentration rises with increasing rate (see Fig. 11.3).

Similarly, the runs using KHCO_3 instead of CO_2 (i.e., the ionic runs section 9.2) provide convincing proof that BHEP is not produced from HEOD. Again, in these runs the concentration of HEOD rises to a maximum and then falls, whereas the concentration of BHEP increases with increasing rate. Also in these runs the production of HEOD is much lower when using KHCO_3 instead of CO_2 , but the production of BHEP is unaffected. What appears likely is that BHEP is being produced from THEED rather than HEOD.

Finally when the long term run (see section 10.1, Fig. 10.2) is studied, it can be seen that the concentration of BHEP levels off. The only possible ways for BHEP to level off are either that BHEP comes to equilibrium with an intermediate (which has been shown not to take place, see section 10.2), or that the concentration of the intermediate falls to zero. The concentration of HEOD after a run time of 50 hr. is about 1.15×10^{-4} moles/cc and therefore unlikely to be the intermediate whereas the concentration of THEED has dropped virtually to zero.

11.1.2.2 Equilibrium between HEOD and DEA carbamate. Blanc et al.³⁶ suggested that HEOD is attacked by water which breaks the ring to form carbamic acid. The acid then reacts with a molecule of DEA to form THEED.



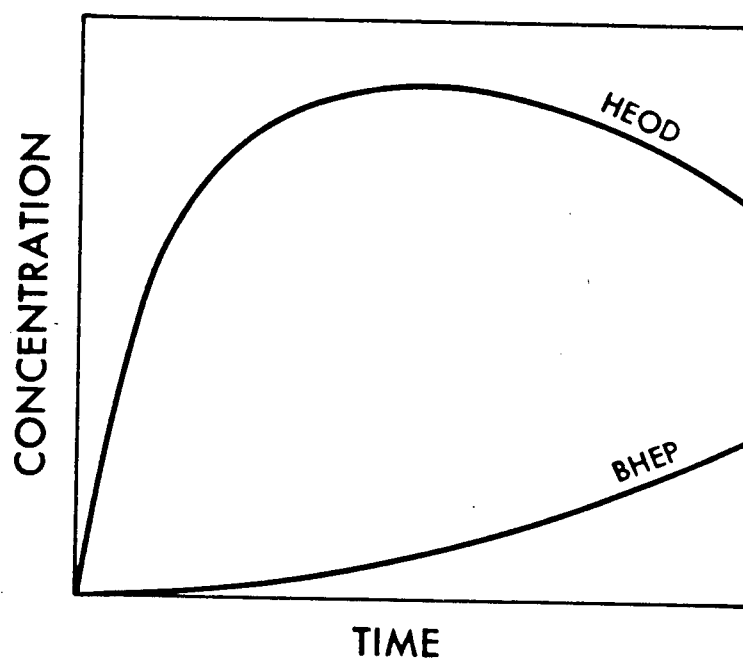
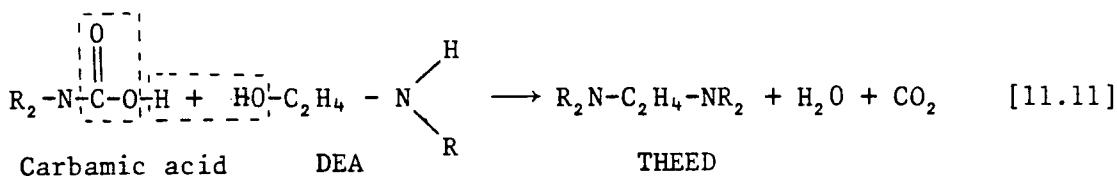
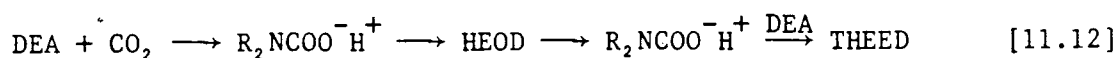


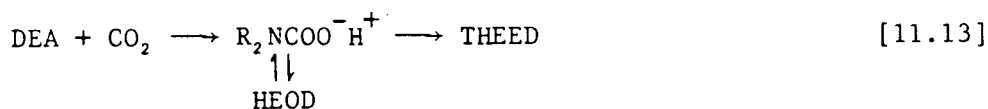
Figure 11.3 Sketch of the concentration of HEOD and BHEP as a function of time for runs 8 and 10



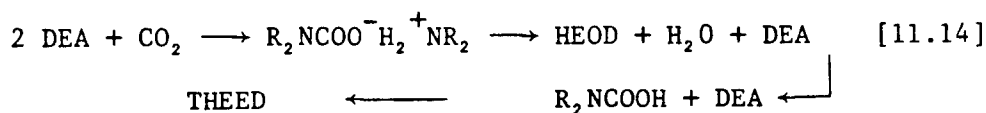
The problem with this proposal is that the carbamic acid is highly unstable and exists in aqueous solutions only as the carbamate ion R_2NCOO^- . Since HEOD is formed from the carbamate ion, it seems unlikely that the next stage of degradation is for HEOD to revert back again to the carbamate ion. This can be seen in Equation 11.12 below.



What actually appears to be happening is that HEOD is in equilibrium with the carbamate ion and is not an intermediate in the production of THEED or BHEP. See Equation 11.13 below:



When there is a limited amount of water (i.e., at high DEA concentrations), it may be possible for HEOD to become an intermediate according to the following equation.



In the absence of water the carbamate can link with a molecule of DEA. Carbamic acid may then be formed from HEOD and react with DEA to form THEED. However, in the normal situation (i.e., DEA concentration < 40 wt %), HEOD is unlikely to be an important intermediate in the formation of either THEED or BHEP.

11.1.2.3 Proof that THEED is not produced directly from HEOD.

Referring to run 65 where HEOD and DEA are reacted in the absence of CO_2 , it is observed that the concentration of HEOD falls sharply then levels off (Fig. 10.6). If HEOD were just an intermediate its concentration would tend to fall to zero. If it is assumed that THEED is produced from HEOD, then the kinetic relationship follows from the reaction:-

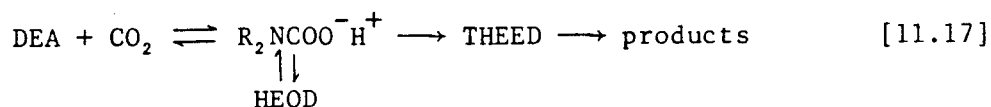


$$\frac{d[\text{THEED}]}{dt} = k_a [\text{HEOD}]^2 - k_b [\text{THEED}] \quad [11.16]$$

The product $k_a [\text{HEOD}]^2$ becomes constant when the concentration of HEOD becomes constant. When $k_b [\text{THEED}]$ equals $k_a [\text{HEOD}]^2$, the concentration of THEED must level off since $\frac{d[\text{THEED}]}{dt}$ becomes zero. This is clearly not the case as can be seen from Fig. 11.4, which shows the general plot of THEED and HEOD concentrations versus time for the temperature experiments (runs 1 to 12).

11.1.3 Proposed model for the production and reactions of HEOD.

It has been shown that BHEP and THEED are not directly produced from HEOD. However, run 62 indicated that HEOD can react to form DEA, BHEP, and THEED. These observations may be explained by referring to the following model in which HEOD is in equilibrium with the DEA carbamate ion and this is, in turn, in equilibrium with DEA:-



According to this scheme, heating HEOD causes it to first break down to the carbamate which, in turn, either reverts to DEA or reacts with itself or DEA to produce THEED. THEED can then in turn produce BHEP.

Using this scheme is it possible to explain the behaviour of HEOD

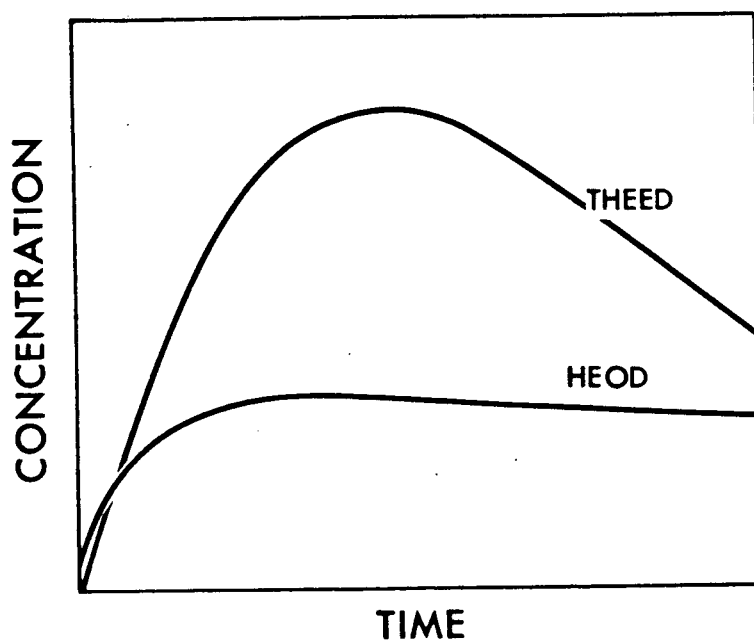
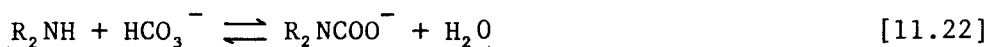


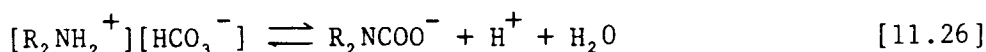
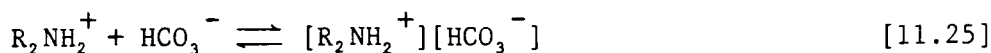
Figure 11.4 Sketch of the concentration of HEOD and THEED as a function of time for runs 1 to 12

under various operating conditions? An equilibrium is first established (very quickly) between DEA, CO_2 , and $\text{R}_2\text{NCOO}^-\text{H}^+$. Next, a second equilibrium is established between $\text{R}_2\text{NCOO}^-\text{H}^+$ and HEOD at a much slower rate. At the same time $\text{R}_2\text{NCOO}^-\text{H}^+$ is slowly removed by further degradation. Therefore, the concentration of HEOD should initially rise rapidly until an equilibrium level is established with R_2NCOO^- and then start to fall as the level of R_2NCOO^- falls. In some cases this was observed experimentally. However, at high temperatures the concentration of HEOD was observed to rise rapidly and then level off or in some cases fall very slowly.

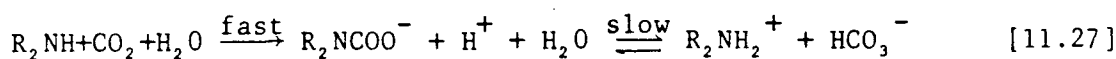
Thus the above scheme is too simplistic and needs refinement. First, consider the equilibrium reactions between DEA, CO_2 , and water. All of the equilibria are established rapidly in comparison with the degradation reactions:-



Since the deprotonation of the zwitterion (Eqn. 11.24) is practically instantaneous²⁶, the formation of the carbamate from CO_2 and DEA can be considered irreversible (Eqns. 11.23 and 11.24). The bicarbonate and the protonated DEA are able to form the amine bicarbonate which can establish a further equilibrium reaction with the carbamate (Eq. 11.26).



The last reaction (Eqn. 11.26) is considered to be much slower than the other reactions. This is based on the fact that in the ionic reactions (sect. 9.2), DEA degrades at a slower rate than normal. (This is discussed in sect. 11.2.1.) All these equations (Eqns. 11.18-11.26) can be simplified to the following relationship.



It needs to be remembered that the solubility of CO_2 for most high temperature runs lies between 0.2-0.3 g CO_2 /g DEA or about 0.45-0.7 moles CO_2 /moles DEA. Therefore, DEA will initially be in excess for the high temperature runs. The reaction mixture will consist essentially of DEA either in the free or protonated form and CO_2 is tied up either as the bicarbonate or carbamate ion.

Degradation appears to begin with the carbamate ion dehydrating to form HEOD and slowly an equilibrium is set up between HEOD and R_2NCOO^- . If no additional degradation were to take place, then the HEOD concentration would level off. However, R_2NCOO^- further reacts slowly to form THEED. Since the concentration of R_2NCOO^- falls it would be expected that HEOD would also decrease. This does not occur and thus some mechanism must be keeping the concentration of R_2NCOO^- constant. Since it is assumed that all the CO_2 is tied up either as HCO_3^- or R_2NCOO^- , the extra R_2NCOO^- is not being produced from the reaction between CO_2 and DEA. The formation of THEED, however, produces bicarbonate ions. These ions will then upset the right hand side of the equilibria, Eqn. 11.27, causing more R_2NCOO^- to be produced from the HCO_3^- reacting with the excess DEA. This process restores the level of R_2NCOO^- to its original

value and keeps the HEOD concentration constant. What actually happens is that the excess DEA is slowly converted to THEED via the formation of R_2NCOO^- from $R_2NH_2^+$ and HCO_3^- (Eqn. 11.26). When no more free DEA is available, the concentration of R_2NCOO^- starts to fall and so will HEOD. Figure 11.5 summarizes the proposed mechanism.

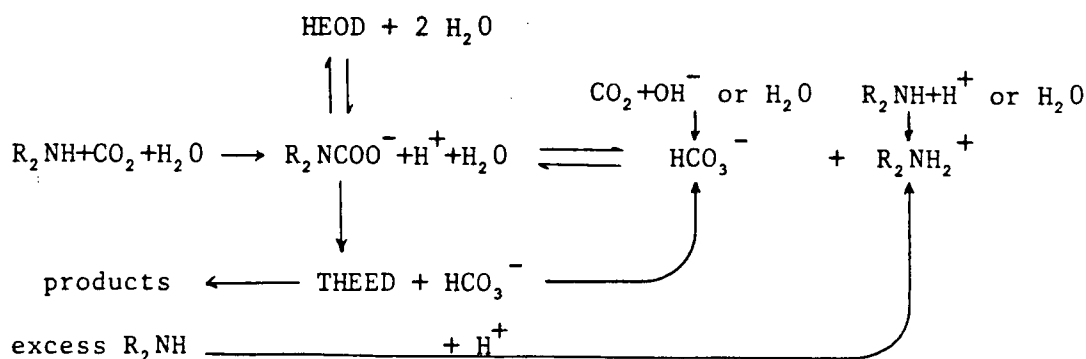


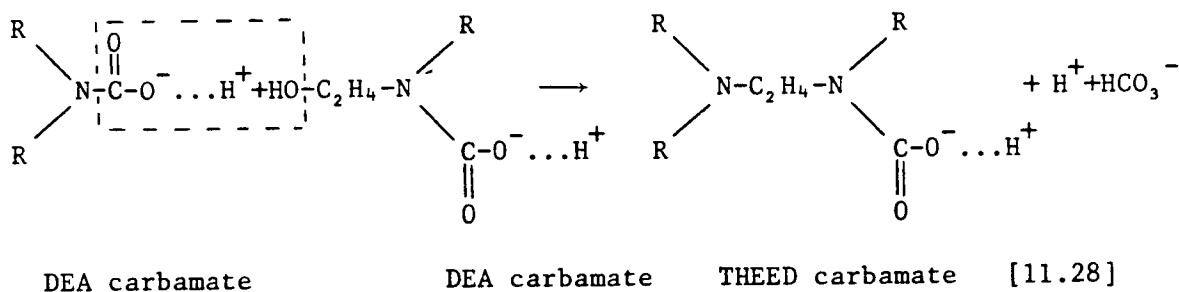
Figure 11.5 Schematic diagram of degradation of DEA.

It must be remembered that the chromatographic analysis is unable to differentiate between R_2NH , $R_2NH_2^+$, and R_2NCOO^- . This causes difficulties in confirming the above mechanism and therefore it must remain for the present only a theory based on inference.

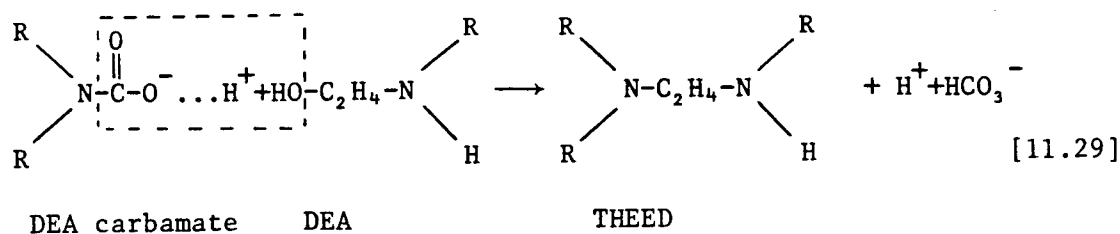
11.1.4 Effect of temperature on the production of HEOD. As pointed out in section 8.1.1.1, the maximum concentration of HEOD falls with increasing reaction temperature. There are possibly two reasons for this. The first is simply that the solubility and hence concentration of CO_2 in the reaction mixture falls with increasing temperature. Therefore the levels of R_2NCOO^- and hence HEOD also fall. The second reason is more subtle and may be due to the fact that the reaction forming THEED is more temperature sensitive than the reaction forming HEOD. Thus at high temperatures the formation of THEED from R_2NCOO^- is increasingly favoured. This was confirmed by the kinetic model developed in chapter 12 (see Figs. 12.4 and 12.7).

11.1.5 Reaction of HEOD and DEA under N_2 . Using the proposed model it is possible to explain the results of run 65 (see Figs. 10.5 to 10.8). Initially the concentration of HEOD will fall rapidly as the carbamate is formed. However, as the equilibrium is established the concentration of HEOD levels off. At the same time equilibria are established between R_2NCOO^- , $R_2NH_2^+$, and HCO_3^- (see Eqn. 11.26). Then R_2NCOO^- slowly reacts to form THEED and HCO_3^- . Thus a cycle is set up where the DEA feed is able to combine with the HCO_3^- produced by the formation of THEED, to form more R_2NCOO^- . Therefore DEA is slowly consumed forming THEED with the concentrations of HEOD, R_2NCOO^- , and HCO_3^- all remaining relatively constant.

11.1.6 Formation of THEED. It seems unlikely that THEED is produced from HEOD as proposed by Blanc et al.³⁶ What is suggested here is that the carbamate ion reacts either with itself or a molecule of DEA to form THEED in the following manner.



or

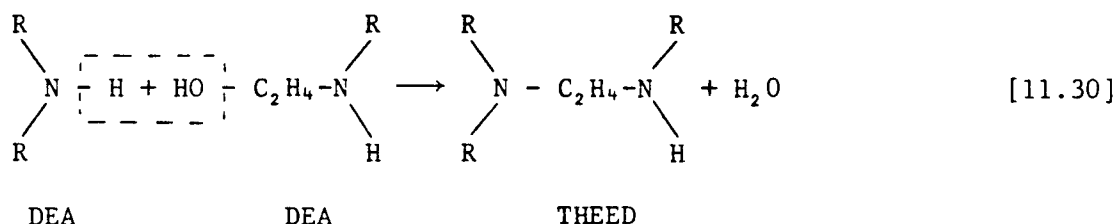


In reaction 11.28 a carbamate ion is formed similar to the DEA carbamate ion. This THEED carbamate ion may then revert to THEED or

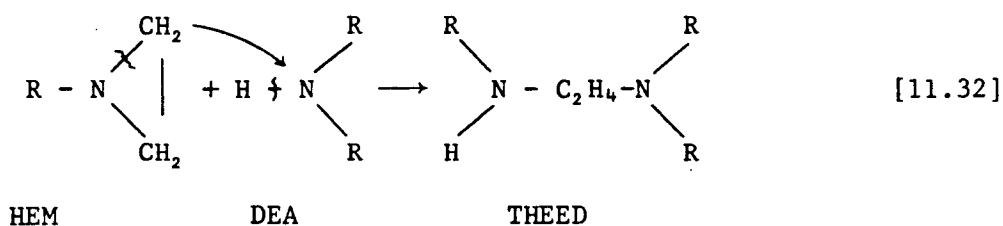
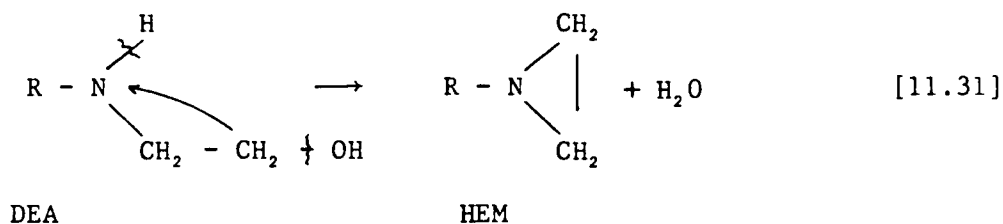
react further to form BHEP (discussed in section 11.1.7).

In the absence of water or at high DEA concentrations it appears that HEOD may act as an intermediate in the formation of THEED as proposed by Blanc et al.³⁶ (see Eqns. 11.10 and 11.11).

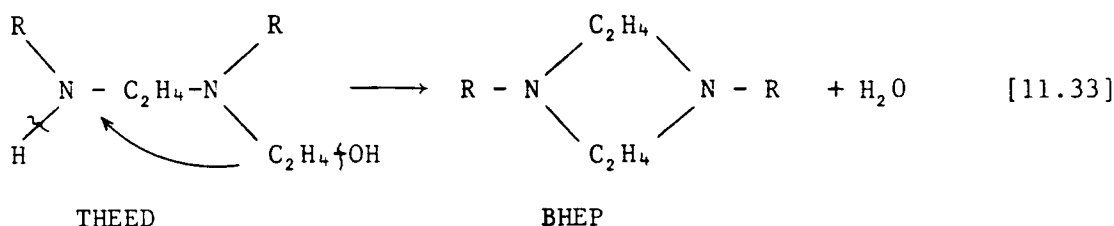
THEED can also be produced directly from DEA by the dehydration of two molecules of DEA. This reaction can be considered the 'thermal degradation' of DEA (see section 9.4).



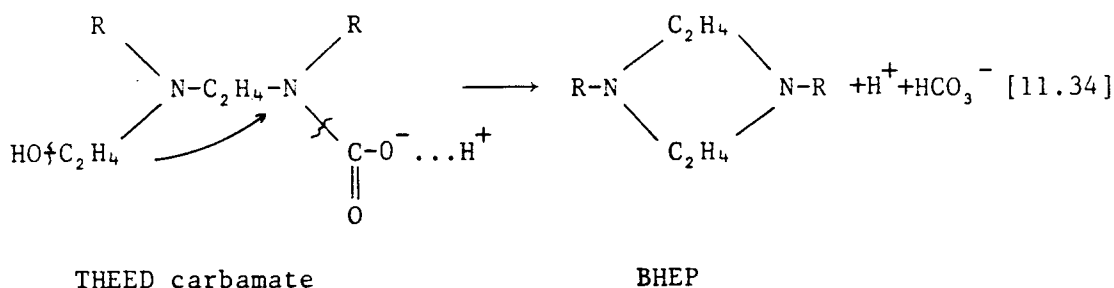
A third possible route, which can also be considered a thermal degradation route (see section 4.2) is where DEA loses a molecule of water to form an imine (HEM). The imine can then react with another molecule of DEA producing THEED.



11.1.7 Formation of BHEP. After studying the various plots of concentration versus time, it became evident that BHEP was not produced from HEOD as suggested by Polderman and Steele³⁴. What is proposed here is that THEED dehydrates to form BHEP.



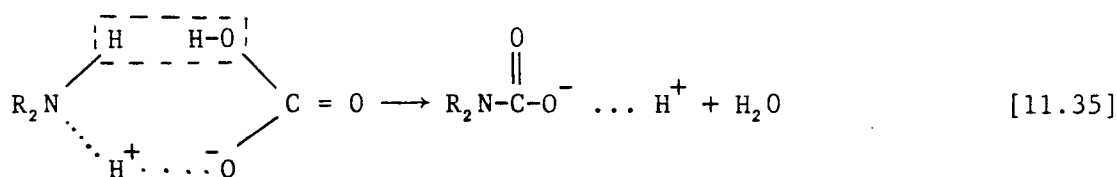
It was observed from the experiments (see sect. 10.4) that the rate of this reaction was increased considerably by the presence of CO_2 and HCO_3^- . It seems likely that CO_2 increases the rate of conversion of THEED to BHEP in a similar manner to the degradation of DEA, i.e., via the formation of a carbamate. Thus CO_2 and HCO_3^- not only catalyse the degradation of DEA to HEOD and THEED, but also the degradation of THEED to BHEP.



11.2 Discussion of the degradation routes

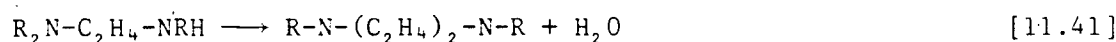
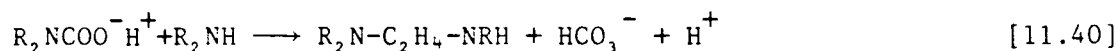
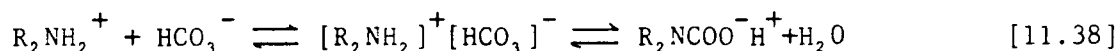
11.2.1 Ionic route. The runs using KHCO_3 yielded similar degradation products to those formed in the normal CO_2 run. This indicates that HCO_3^- aids the degradation of DEA in a similar way to CO_2 . However, the rate of degradation due to HCO_3^- is considerably lower and only small amounts of HEOD are produced. The reason for the lower rate of reaction is the fact that the amine salt (i.e., $\text{R}_2\text{NH}_2^+ \text{HCO}_3^-$)

must break down to form the amine carbamate.



Under normal conditions the carbamate can be produced quickly by free CO_2 reacting with DEA.

The proposed ionic route may be summarized by the following equations.

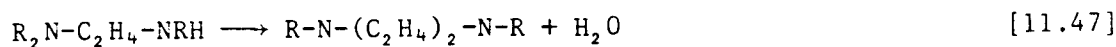
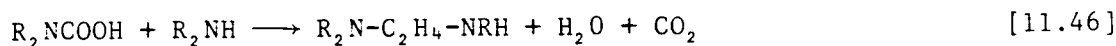
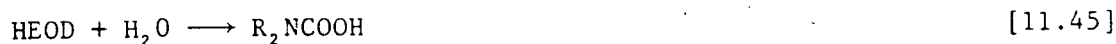
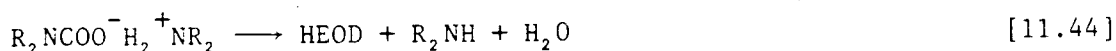
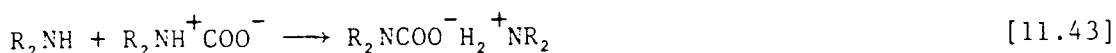


The low concentration of HEOD produced in the runs using KHCO_3 can be explained simply by the fact that the presence of KHCO_3 tends to increase the solution alkalinity as opposed to CO_2 which decreases the solution alkalinity. Under alkaline conditions HEOD becomes more unstable (see sect. 9.1). Therefore HEOD will exist at lower concentrations in alkaline solutions, i.e., there is a shift in the equilibrium from HEOD towards the carbamate.

Referring to Table 9.3 in section 9.2, it was noticed that the initial rate constants (k_{DEA}) for the ionic runs were virtually identical to those where solutions of 10 wt % DEA and lower were degraded with CO_2 . From this it can be concluded that, at low concentrations of DEA the favoured degradation route is the ionic route. It must be remembered that the proportion of R_2NH_2^+ to the total DEA concentration is at its maximum at low DEA concentrations.

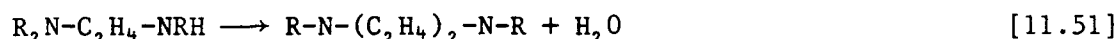
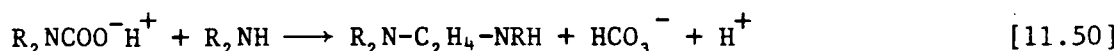
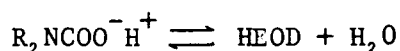
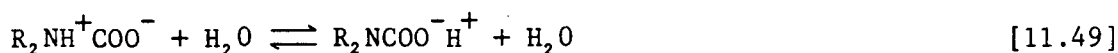
11.2.2 Molecular route. Before discussing this route a distinction must be made between the so called "molecular runs" and the "molecular route." The molecular runs involved degrading DEA with CO_2 in the absence of water. The rate of degradation was slower than normal due to the fact that water was unable to aid the degradation. The "molecular route" denotes the route where DEA reacts directly with CO_2 in aqueous solutions to form the carbamate ion. This is comparable to the ionic route where the carbamate is produced from the ions R_2NH_2^+ and HCO_3^- .

11.2.2.1 Molecular runs. It was observed that DEA could degrade in the absence of water to produce HEOD, THEED, and BHEP. The proposed route is as follows:-

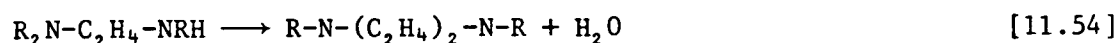
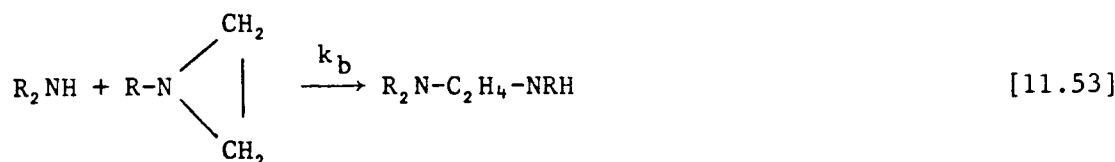


The overall reaction rate is much lower than that observed under normal conditions because more steps are involved and reaction 11.45 requires water to attack the HEOD ring structure. Water is present in the DEA feed only as a trace impurity, but, with the water produced in reaction 11.44, there is sufficient water to begin the degradation. As the degradation proceeds, more water is formed.

The following equations summarize the molecular route under normal reaction conditions where water is present in excess.



11.2.3 Thermal route. The third route for the degradation of DEA consists of DEA reacting with itself to produce THEED. This implies that the reaction should be second order with respect to DEA. However, the experimental results indicate that a first order reaction (see sect. 9.4) is taking place. Thus DEA may first be degrading to an intermediate, which then reacts with DEA to give THEED. A possible intermediate could be HEM as mentioned in sect. 11.1.6. The proposed thermal degradation route becomes:-



The rate of DEA degradation becomes:-

$$-\frac{d[DEA]}{dt} = (k_a + k_b[HEM])[DEA] \quad [11.55]$$

The chromatographic analysis did not positively detect HEM in the degradation mixture. If HEM was being produced it may be assumed that its concentration is very small and relatively constant. Thus the formation of HEM becomes rate controlling and the degradation of DEA becomes a pseudo first order reaction, i.e.,

$$-\frac{d[\text{DEA}]}{dt} = k'[\text{DEA}] \quad [11.56]$$

11.3 Discussion of anomalous experimental observations

11.3.1 The relationship between initial k_{DEA} and DEA concentration.

Figure 11.6 is a typical sketch of initial k_{DEA} versus DEA concentration.

Three distinct regions are observed:

Region I (0-10 wt % DEA)

In this region the main degradation route appears to be the ionic route (see sections 9.2 and 11.2.1).

Region II (10-30 wt % DEA)

As the concentration increases, the proportion of DEA existing as R_2NH_2^+ falls and the degradation route becomes a combination of the ionic and molecular routes with the molecular route gaining dominance. The overall k_{DEA} therefore becomes the sum of the k values for the two parallel degradation reactions.

$$k_{\text{DEA}} = (k_{\text{DEA}})_{\text{ionic}} + (k_{\text{DEA}})_{\text{molecular}} \quad [11.57]$$

Since the thermal route is so much slower than either the ionic or the molecular route its contribution to degradation should be negligible.

Region III (30-100 wt % DEA)

As the concentration of DEA continues to rise the concentration of water falls. Thus the reaction becomes limited by water and the rate decreases until, at 100%, the degradation becomes that proposed for the molecular runs, i.e., Eqns. 11.42 to 11.47.

11.3.2 Arrhenius plot. Referring to the Arrhenius plot in Fig. 8.5, it was observed that, at high temperatures, the data tended to deviate from the linear form and the measured rate constants (k_{DEA}) became much smaller than the predicted ones. One reason for this deviation could

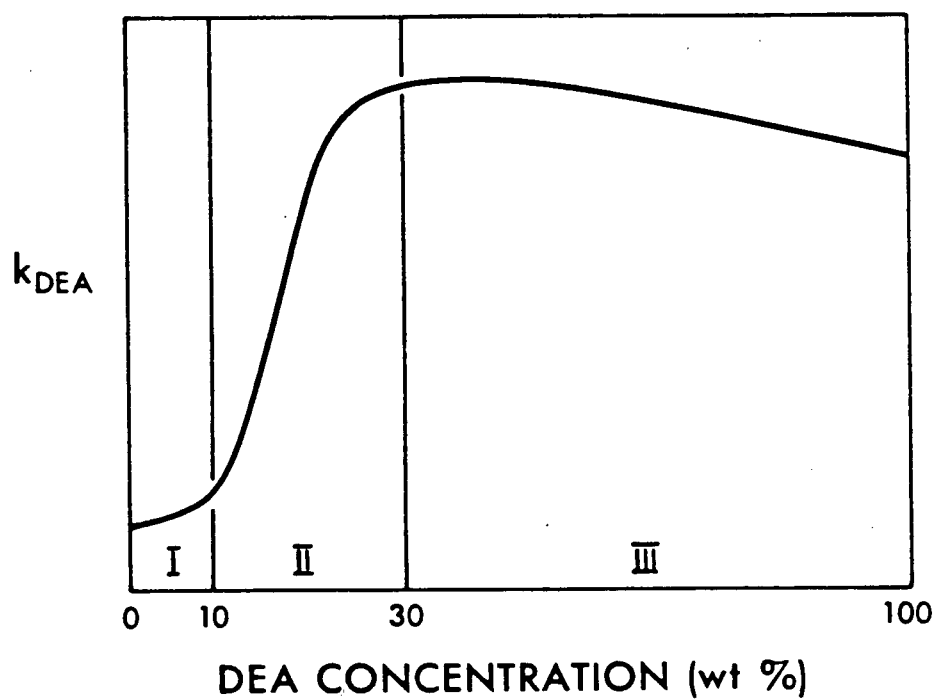
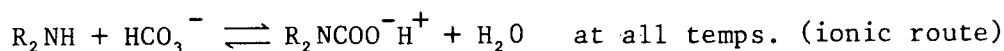
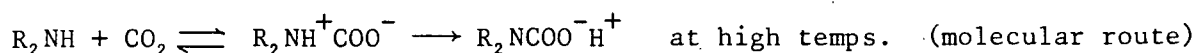
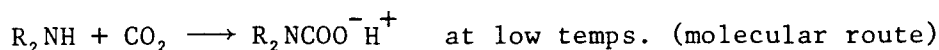


Figure 11.6 Sketch of k_{DEA} as a function of initial DEA concentration

be simply that, at high temperatures, the CO_2 solubility decreases and the CO_2 concentration becomes limiting. Another possible reason is that the ionic route becomes increasingly important with rising temperature. This can be seen in the following sketch (Fig. 11.7) of the Arrhenius plots comparing ionic and molecular runs with standard runs.

What seems to be occurring is the amount of R_2NCOO^- produced by the molecular route falls with increasing temperature. This could be due to the zwitterion being converted back to DEA before it is deprotonated to form the carbamate. Therefore the overall production of R_2NCOO^- falls with increasing temperature and inhibits the overall degradation.

In summary the formation of the carbamate ion becomes:-



11.3.3 Log [DEA] versus time plots. At high temperatures it was observed that the semi-logarithmic plots of DEA versus time were linear only for a few hours and then began to deviate. This indicates that the initial pseudo first order degradation reaction of DEA became inhibited as the reaction progressed. This inhibition could be the result of the following.

1. At high temperatures the concentration of CO_2 is very close to the critical value of 0.2 g CO_2 /g DEA. Any reduction in this level will cause the degradation rate to fall.
2. It has been shown that the presence of degradation compounds (especially BHEP) inhibits degradation at high temperatures by tying up some of the available CO_2 .
3. As the degradation proceeds, the CO_2 is converted to HCO_3^- via the

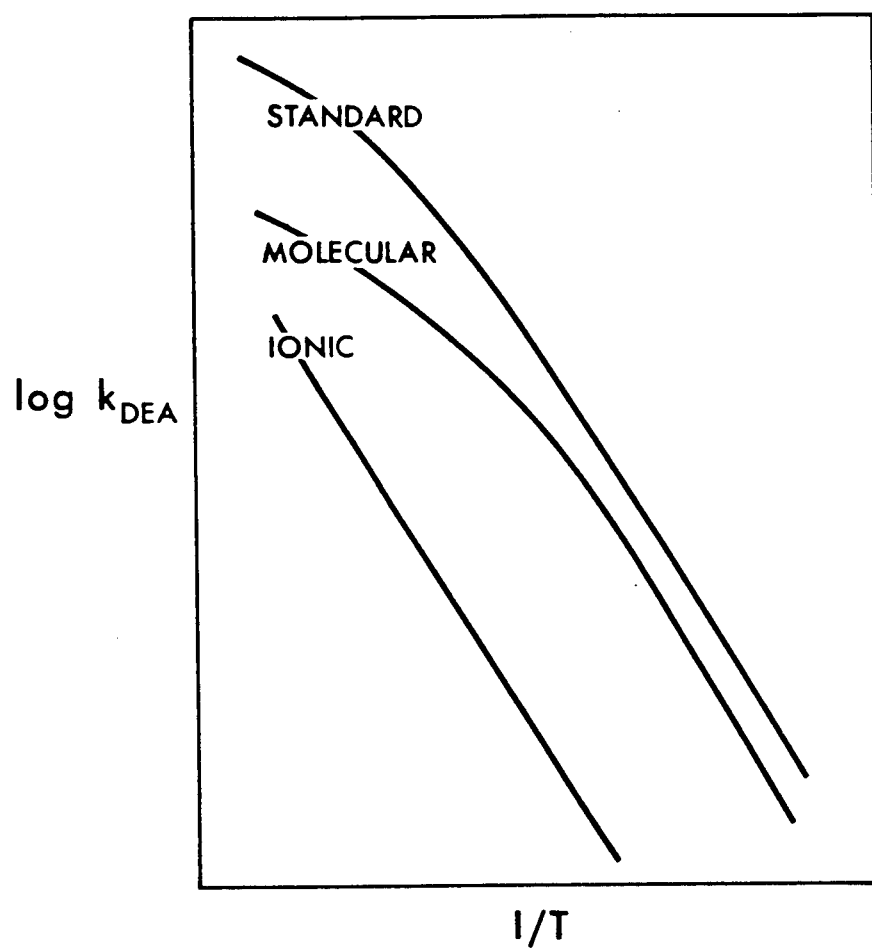


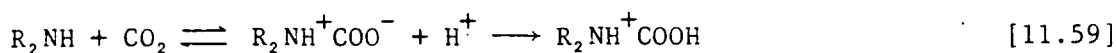
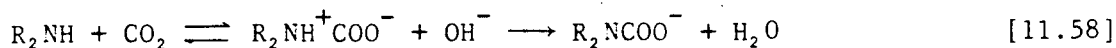
Figure 11.7 Sketch of the Arrhenius plots for ionic, molecular, and standard runs

formation of the degradation products and R_2NCOO^- . Therefore the production of additional R_2NCOO^- must proceed through the ionic route which is slower than the overall rate. Thus the overall degradation rate will tend to fall.

4. As the reaction proceeds the mixture becomes more acidic due to CO_2 and the reduction of DEA. (Although BHEP and THEED are alkaline, two moles of DEA are required to produce each mole of THEED and BHEP; hence the number of moles of alkaline species falls.) Experiments have shown that reducing the pH reduces the degradation rate.

11.3.4 Explanation of the effect of pH. The experimental results show that increasing the pH increases the rate of degradation and reduces the production of HEOD. This can be explained as follows.

1. Increasing the alkalinity tends to aid the deprotonation of the zwitterion formed by CO_2 reacting with DEA, whereas acid conditions tend to stabilize the zwitterion.



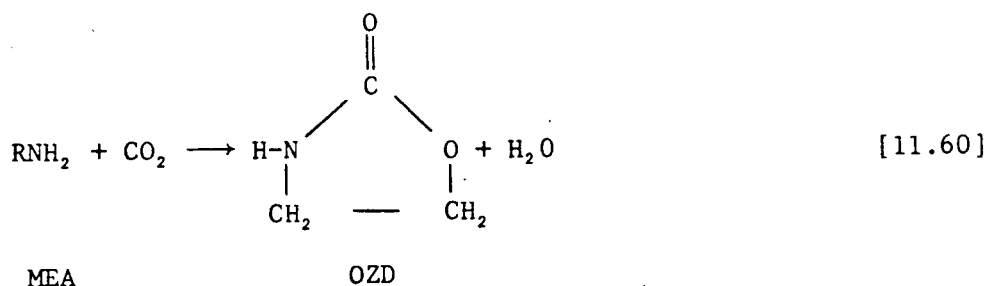
Therefore increasing the pH tends to increase the level of carbamate and hence degradation.

2. Increasing the alkalinity increases the solubility of CO_2 via the bicarbonate formation. This increase in CO_2 availability will, under conditions where CO_2 is limiting, increase the degradation.
3. HEOD is attacked by hydroxyl ions, reacting to form the carbamate. Thus an increase in pH reduces the stability of HEOD and hence the concentration of HEOD.

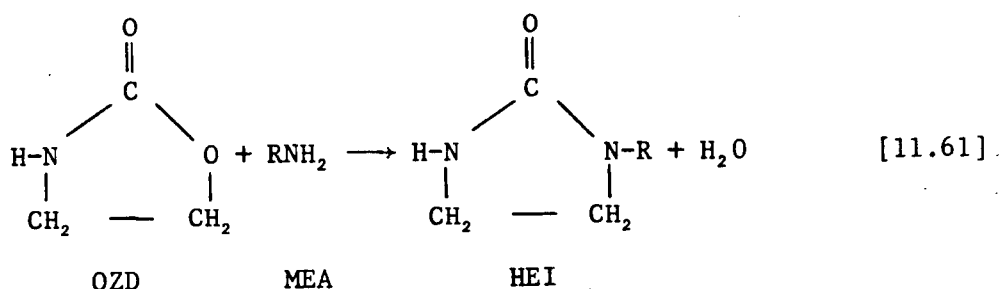
11.4 The formation of minor degradation compounds

Besides the production of the major degradation compounds HEOD, BHEP, and THEED, many other compounds have been detected by the chromatographic analysis and mass spectrometry. These "minor" degradation compounds are produced in low amounts and may be ignored when developing the kinetic model of the degradation. These compounds may result from the reaction of DEA with impurities in the feed and various thermal routes.

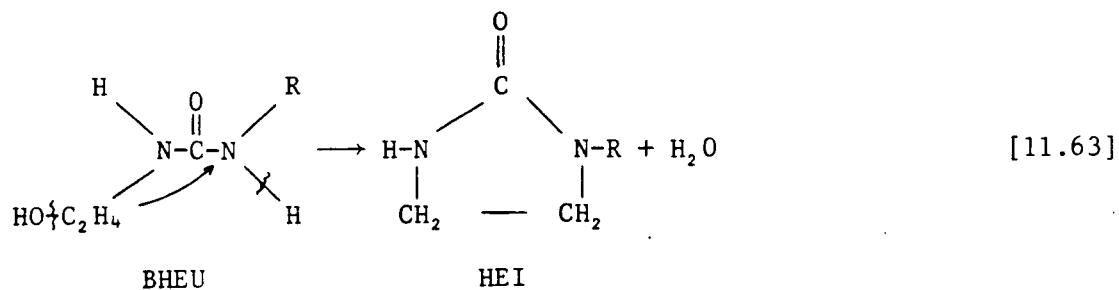
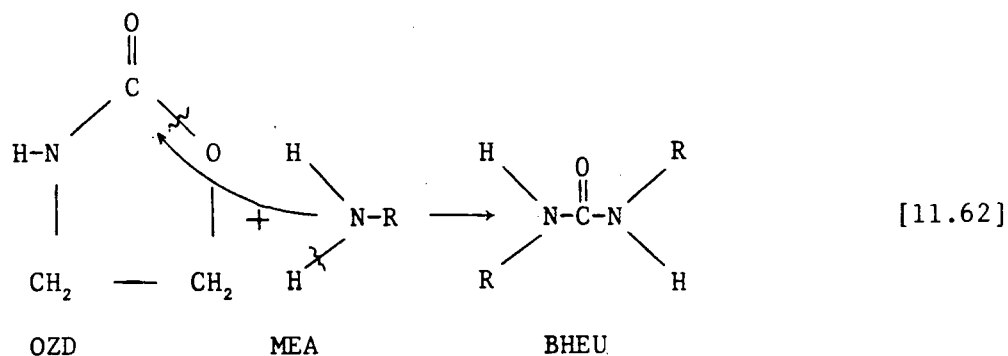
11.4.1 MEA degradation. Probably the major impurity in the DEA feed is MEA which undergoes degradation when subjected to CO₂ under high temperature and pressure. The degradation has been fairly well documented. According to Polderman et al.³⁸ MEA first degrades to OZD, probably via the formation of MEA carbamate (RNHCOO⁻).



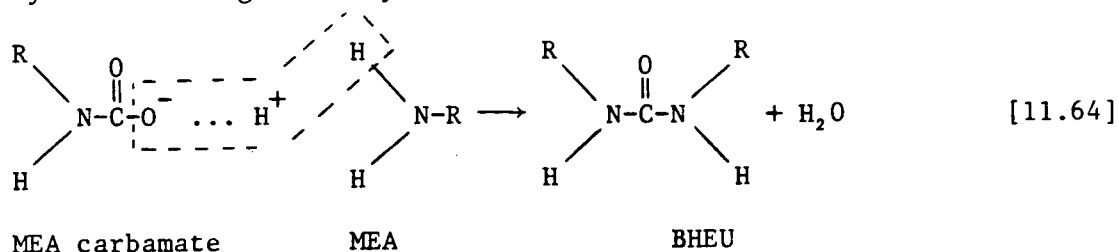
OZD then reacts with another MEA molecule to form HEI.



This route was later shown by Yazvikova et al.⁴⁰ to consist of two stages. The OZD reacts with MEA to form the urea, BHEU. BHEU then undergoes dehydration to form HEI.

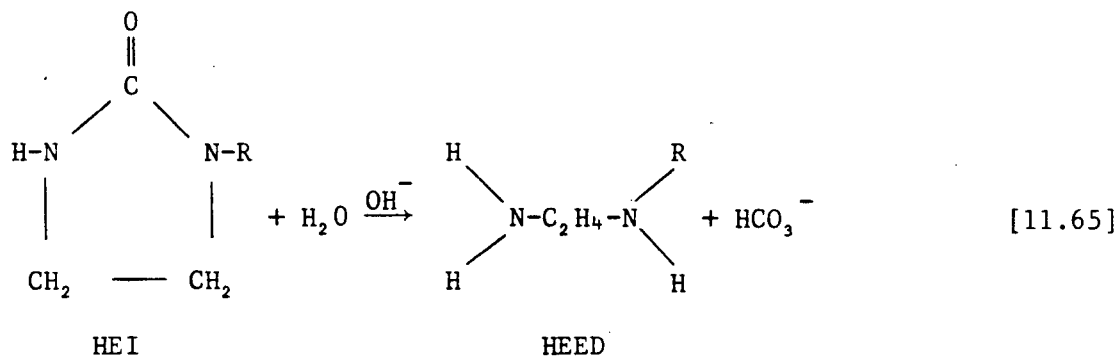


The lone pair of electrons from the nitrogen atom of the basic MEA molecule attack the electron deficient carboxyl atom in the OZD ring and open it up to produce BHEU. If the ring is opened by OH^- a carbamate is formed and it is possible that an equilibrium is set up between OZD and MEA carbamate. This equilibrium is equivalent to that proposed in this work between HEOD and DEA carbamate. BHEU may also be formed by MEA reacting directly with the MEA carbamate in the following manner.

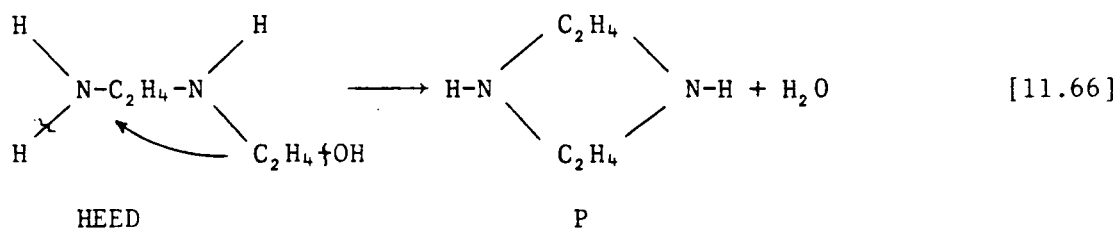


The BHEU can then undergo dehydration to form HEI as in Eqn. 11.63.

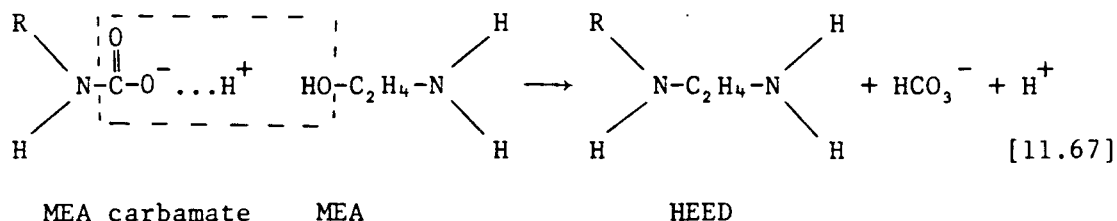
The next stage of the degradation is the hydrolysis of HEI to form HEED in the presence of OH^- ions.



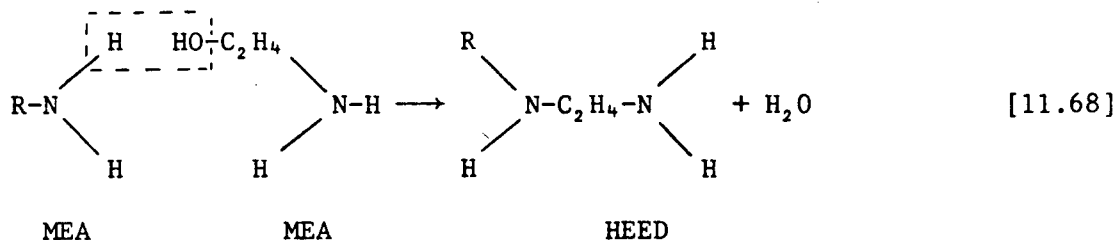
The final stage is the dehydration of HEED to form piperazine or P.



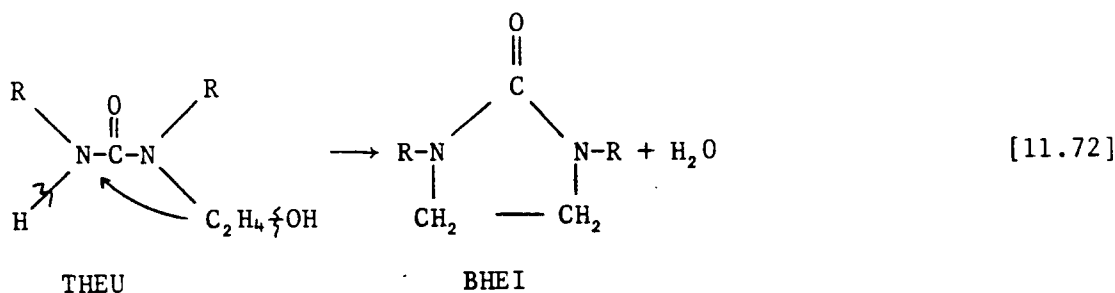
HEED can also be formed directly by MEA reacting with MEA carbamate. (This is similar to DEA reacting with DEA carbamate to form THEED.)



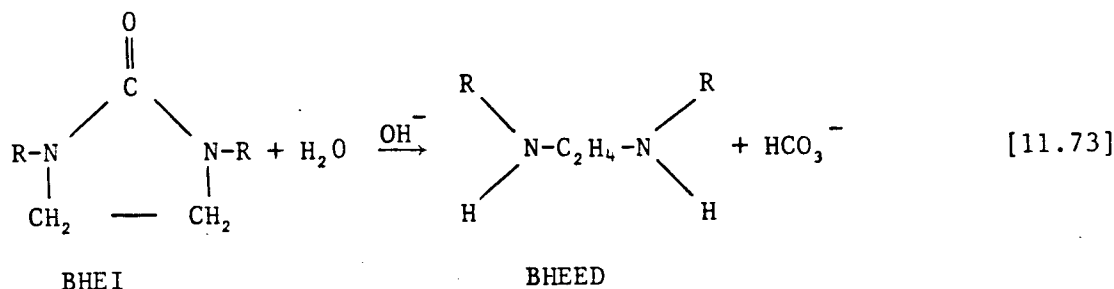
Finally HEED may be formed by the thermal degradation of MEA.



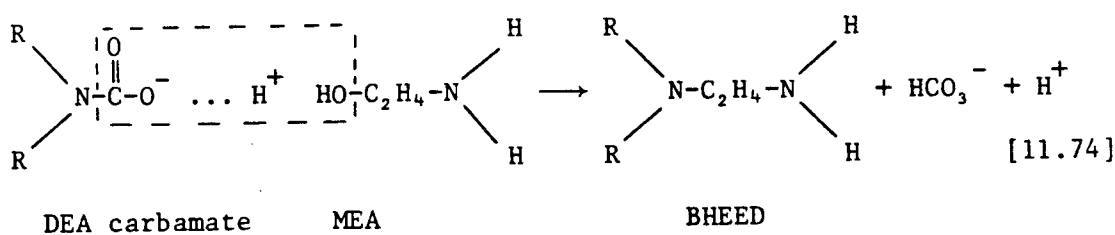
The chromatographic analysis of a degraded MEA solution only indicated the formation of OZD, HEI, HEED, and P. However, it failed to reveal BHEU. It was also not possible to analyse for urea and other substituted ureas. Either the ureas broke down in the chromatographic



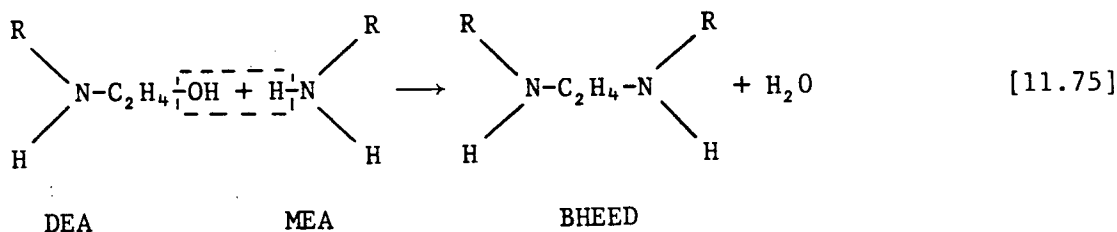
Hydroxyl ions can then catalyse the hydrolysis of BHEI to form NN-bis(hydroxyethyl) ethylenediamine or BHEED.



The compounds THEU, BHEI, BHEED, and HEP may all be produced by reactions similar to Eqns. 11.67 to 11.73, which are initiated by IEA carbamate reacting with MEA. The only difference being the direct formation of BHEED from DEA carbamate and MEA where another isomer of BHEED is formed.

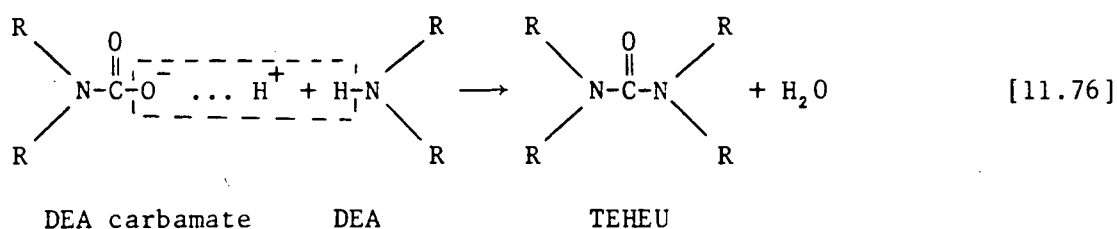


There is one further route leading to the formation of BHEED, i.e., the direct reaction between DEA and MEA.



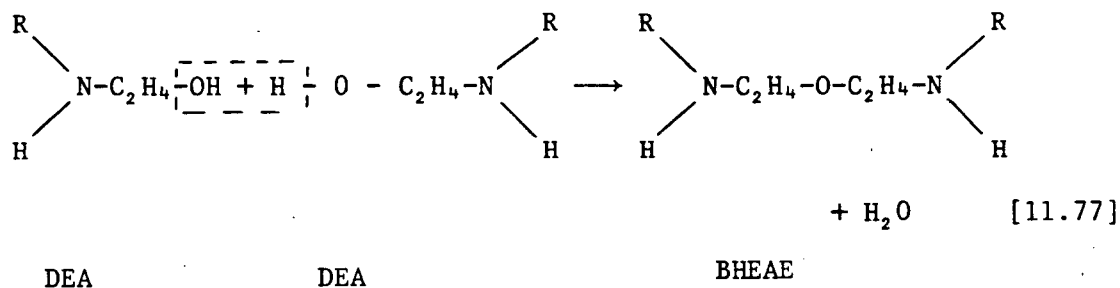
BHEI, BHEED, and HEP were all detected in small amounts in degraded solutions of DEA. The formation of THEU is only suspected since this compound could not be detected with the present analytical technique.

11.4.3 Minor degradation compounds produced from DEA. Since BHEU can be formed from MEA and CO₂,⁴⁰ it seems likely that N,N,N,N'-tetra(hydroxyethyl) urea or TEHEU may be formed from DEA and CO₂. The proposed route is:-



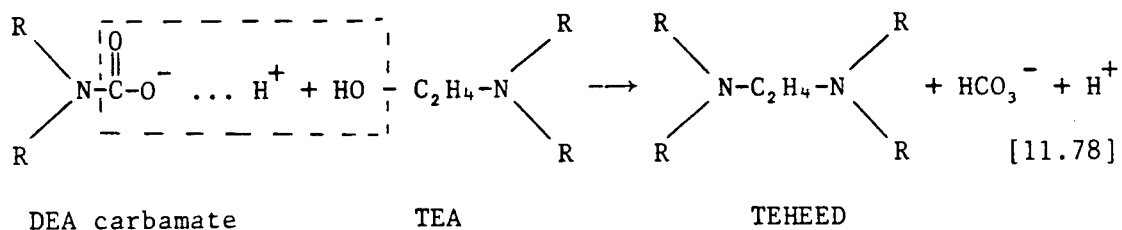
TEHEU is unlikely to undergo further degradation since it has no labile hydrogen (i.e., free hydrogen) attached to the nitrogen atom. Again the production of this compound is only proposed since it could not be detected.

One other degradation route between two molecules of DEA was proposed by Blanc et al.³⁶ They suggested that two molecules of DEA react forming N,N'-bis(hydroxyethyl amino ethyl) ether or BHEAE with the loss of water.

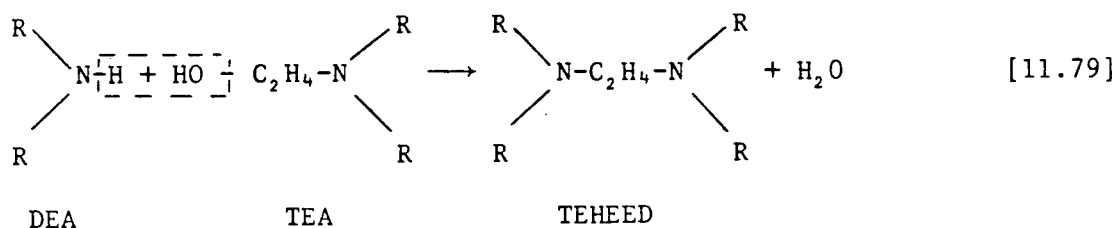


No standards for this compound could be obtained and therefore it could not be determined whether it was produced during the degradation of DEA.

11.4.4 The reaction between DEA and TEA. TEA itself does not undergo any measurable degradation. However, it is able to react with DEA to form NNNN-tetra(hydroxyethyl)ethylenediamine or TEHEED. Two routes are possible, one involving DEA carbamate the other pure DEA.



or



TEHEED was the heaviest compound detected in the analysis of degraded DEA solutions.

11.5 Summary

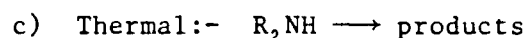
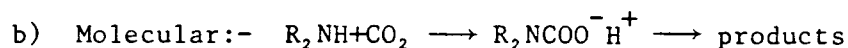
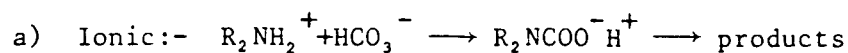
The following section summarizes the principle conclusions of this chapter.

11.5.1 Conclusions of the degradation experiments. Table 11.1 gives the main degradation routes for the range of operating conditions studied.

Table 11.1 Principal DEA degradation routes under various conditions

Temp °C	DEA	Total pressure		Route ¹	Limiting compounds
	Concentration Wt %	psi	kPa		
90-175	0-10	600	4137	Ionic	-
90-175	10-30	600	4137	Ionic+Molecular	-
90-175	30-100	600	4137	Mainly molecular	H ₂ O
175-250	0-10	600	4137	Ionic+Thermal ²	-
175-250	10-30	600	4137	Ionic+Molecular+Thermal	CO ₂
175-250	30-100	600	4137	Ionic+Molecular+Thermal ³	CO ₂ +H ₂ O

¹The routes are:-

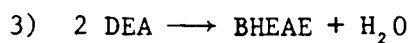
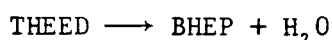
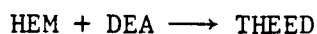
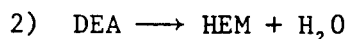
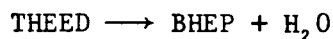
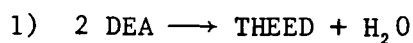


²At high temperatures the thermal route will start to contribute to the degradation, although only to a small extent.

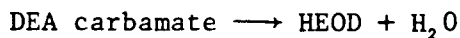
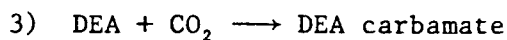
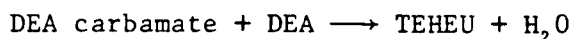
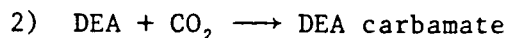
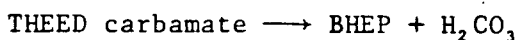
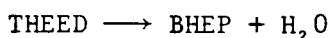
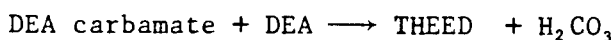
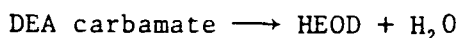
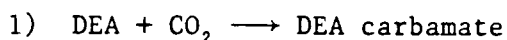
³At high temperatures and DEA concentrations (> 30 wt %), the ionic route contributes more to the degradation than at lower temperatures where the molecular route is responsible for most of the degradation. This is probably due to the reduction in the formation of the carbamate via the molecular route, because the zwitterion reverts back to DEA faster than it is deprotonated to form the carbamate.

11.5.2 Summary of the degradation reactions

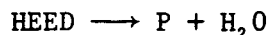
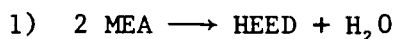
11.5.2.1 Reactions involving DEA.



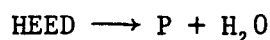
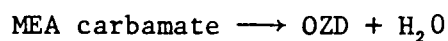
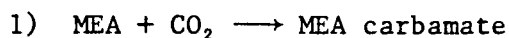
11.5.2.2 Reactions involving DEA and CO₂.



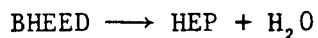
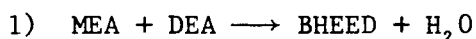
11.5.2.3 Reactions involving MEA.



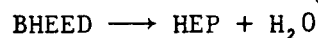
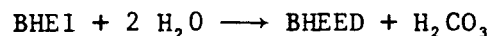
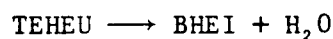
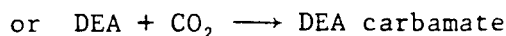
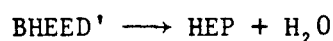
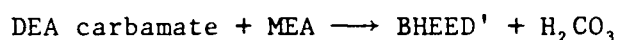
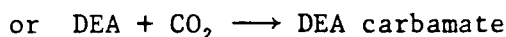
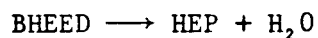
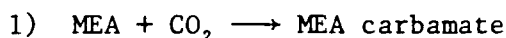
11.5.2.4 Reactions involving MEA and CO₂.



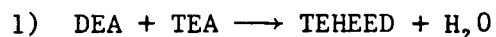
11.5.2.5 Reactions involving MEA and DEA.



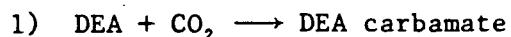
11.5.2.6 Reactions involving MEA, DEA, and CO₂.



11.5.2.7 Reactions involving DEA and TEA.



11.5.2.8 Reactions involving DEA, TEA, and CO₂.



Note: Wherever the carbamate is used the ion is being referred to.

Also H_2CO_3 exists under operating conditions as HCO_3^- and H^+ .

11.5.3 The degradation mechanism. Figure 11.8 shows the major reactions responsible for the degradation of DEA with CO_2 .

CHAPTER 12

KINETIC STUDIES

12.1 Development of a kinetic model

The purpose of the model is to predict, quantitatively, the degradation of DEA and the production of its degradation compounds. At times a model can be based on the stoichiometric equations of the reaction. Unfortunately in the case of DEA the degradation reaction is extremely complex involving several equilibria, parallel and series reactions. Therefore it is necessary to simplify the scheme as presented in chapter 11, Fig. 11.8.

From the experiments it was established that the initial degradation of DEA was pseudo first order with the Arrhenius relationship being obeyed up to about 175°C. Above 175°C the Arrhenius plot deviated from the linear form. A simple kinetic model based on initial k_{DEA} values could not predict this. Since, under industrial conditions it is unlikely that temperatures ever exceed 150°C, a kinetic model need only be applicable up to about 175°C. Above this, the predictions of the model may severely disagree with measurements.

The model may also be simplified by removing the effect of CO_2 . This can be done by assuming that the CO_2 concentration is constant or not limiting. This occurs when the CO_2 concentration is greater than 0.2 g CO_2 /g DEA, i.e., at low temperatures and high total reaction

pressure. Thus the ranges of conditions covered by the following model

Temp: 90-175°C

DEA conc: 0-100 wt %

CO₂ loading: > 0.2 g CO₂/g DEA

Under these conditions the Arrhenius plots can be considered linear and the effect of CO₂ ignored.

Finally the model has to deal with the effect of initial DEA concentration on k_{DEA} . Based on the assumption that DEA degradation was governed by a pseudo first order reaction, experiments showed that k_{DEA} was not independent of the initial DEA concentration (see Fig. 8.15). The figure shows three distinct regions 0-10, 10-30, and 30-100 wt % DEA. The simplest way for the model to deal with this effect is to produce a series of Arrhenius plots similar to Fig. 8.16, which cover the DEA concentration range for each reaction of the kinetic model. The plots could be used to obtain the k value of each reaction at any given set of operating conditions.

12.1.2 Simplified degradation mechanism. The equilibrium reactions between CO₂ and DEA and the formation of R_2NCOO^- is established within a matter of seconds. Therefore, these initial fast reactions may be ignored, when compared to the slow degradation reactions, since they are not rate controlling.

For simplicity the model will consider R_2NCOO^- as DEA. Also, since the ionic and molecular routes both result in identical degradation products they will be considered as one route. The thermal route can be ignored since it is much slower than the normal degradation. Thus the model can be simplified into the following set of equations.



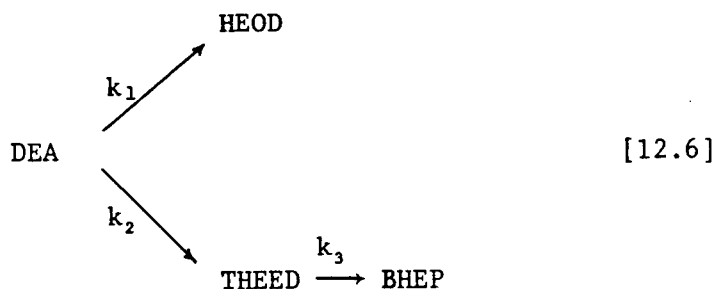
These equations still present a problem. It has been shown that the initial DEA degradation is governed by a pseudo first order reaction. Therefore the rate of DEA degradation should be represented by an equation of the form:-

$$-\frac{d[\text{DEA}]}{dt} = k[\text{DEA}] \quad [12.4]$$

Unfortunately the Eqns. 12.1 to 12.3 do not show this, instead they suggest an equation of the form:-

$$-\frac{d[\text{DEA}]}{dt} = (k+k'')[\text{DEA}] - k'[\text{HEOD}] \quad [12.5]$$

To deal with this it was decided to make the production of HEOD an irreversible reaction. This could be justified since, at low temperatures the equilibrium between R_2NCOO^- and HEOD is established slowly and the plots of concentration of HEOD versus time do not level off. Furthermore, the concentration of HEOD when compared to that of DEA is very much smaller and slight errors in the prediction of the concentration of HEOD should not affect the overall model. Thus, the degradation mechanism can be simplified as follows:-



It must be realized that this is not a stoichiometric relationship but a kinetic relationship, which can be reduced to a model for predicting the degradation of DEA.

12.2 Theory

Using Eqn. 12.6 it is possible to write equations for the rate of change of the various compounds, i.e.:-

$$\frac{d[\text{DEA}]}{dt} = -k_1[\text{DEA}] - k_2[\text{DEA}] \quad [12.7]$$

$$\frac{d[\text{HEOD}]}{dt} = k_1[\text{DEA}] \quad [12.8]$$

$$\frac{d[\text{THEED}]}{dt} = k_2[\text{DEA}] - k_3[\text{THEED}] \quad [12.9]$$

$$\frac{d[\text{BHEP}]}{dt} = k_3[\text{THEED}] \quad [12.10]$$

As shown in Appendix D, these equations can be solved to give:-

$$[\text{DEA}]_t = [\text{DEA}]_0 e^{-(k_1+k_2)t} \quad [12.11]$$

$$[\text{HEOD}]_t = [\text{DEA}]_0 \frac{k_1}{k_1+k_2} (1 - e^{-(k_1+k_2)t}) \quad [12.12]$$

$$[\text{THEED}]_t = [\text{DEA}]_0 \frac{k_2}{k_3-(k_1+k_2)} (e^{-(k_1+k_2)t} - e^{-k_3t}) \quad [12.13]$$

$$[\text{BHEP}]_t = [\text{DEA}]_0 \frac{k_2}{k_2+k_1} \left(1 - \frac{k_3}{k_3-(k_1+k_2)} e^{-(k_2+k_1)t} - \frac{k_1+k_2}{k_3-(k_1+k_2)} e^{-k_3t} \right) \quad [12.14]$$

Since in many cases the plots of THEED concentration versus time go through a maximum (Fig. 12.1), relationships can be derived for relating k_1, k_2 and k_3 using t_{max} and $[\text{THEED}]_{\text{max}}$. Again details are given in Appendix D.

$$t_{\text{max}} = \frac{\ln(k_3/k_2+k_1)}{k_3-(k_2+k_1)} \quad [12.15]$$

$$\frac{[\text{THEED}]_{\text{max}}}{[\text{DEA}]} = \frac{k_2}{k_2+k_1} \left(\frac{k_2+k_1}{k_3} \right)^{\frac{k_3}{k_3-(k_1+k_2)}} \quad [12.16]$$

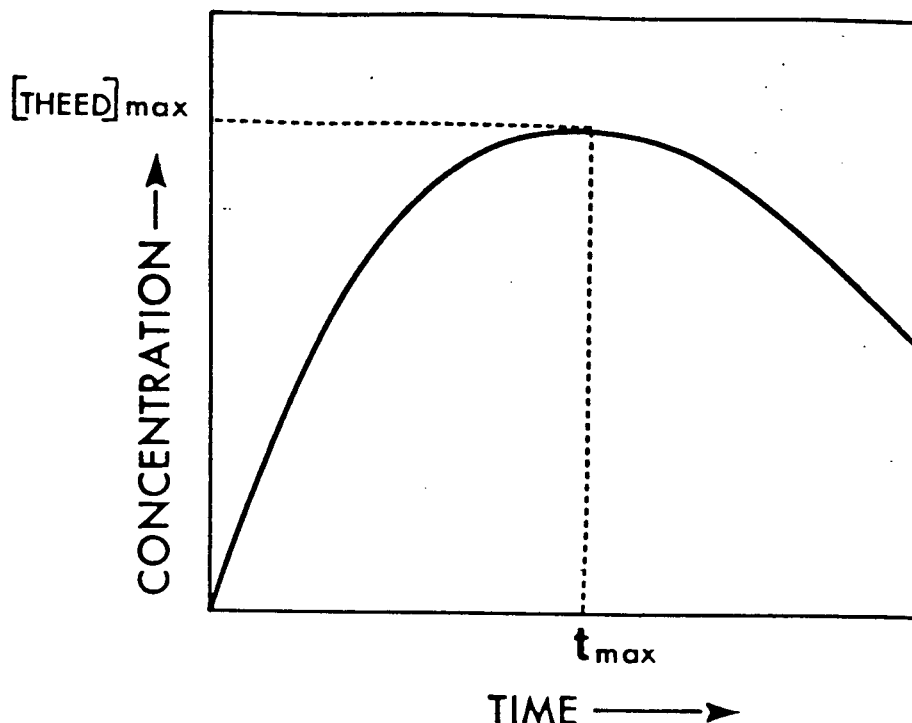


Figure 12.1 Typical plot of [THEED] versus time

In addition,

$$k_{\text{DEA}} = k_1 + k_2 \quad [12.17]$$

12.3 Calculation of the k values

Using the experimental data of DEA, HEOD, THEED, and BHEP concentrations versus time and equations 12.7 to 12.17, the following methods were used to calculate k_1 , k_2 , and k_3 .

12.3.1 Method (A)--The plot of [THEED] vs. t goes through a maximum.

1. From the linear plots of $\log[\text{DEA}]$ versus time, an initial k_{DEA} was calculated from the slope of the plot.
2. Using the results of HEOD concentration versus time and Eqn. 12.12, it was possible to calculate a value of k_1 . Several values of k_1 could be calculated for different times and concentrations and then averaged. Alternatively a plot of

$$[\text{HEOD}] \text{ vs. } \frac{[\text{DEA}]_0}{(k_1 + k_2)} (1 - e^{-(k_1 + k_2)t})$$

could be made; the slope of this line is k_1 .

3. Using Eqn. 12.17, k_1 and k_{DEA} ; k_2 could be calculated.
4. Using the determined values of t_{max} and $[\text{THEED}]_{\text{max}}$, and Eqns. 12.15 and 12.16, it was possible to calculate k_3 . Trial and error were used to solve each equation and the value of k_3 was optimized between both equations.
5. Using the values of k_1 , k_2 , and k_3 with Eqns. 12.11 to 12.14 theoretical values of DEA, HEOD, THEED, and BHEP concentrations could be calculated.

Figure 12.2 shows a typical plot of the model predictions (dashed lines) compared with the experimental results (points) using method (A) (see run 6).

12.3.2 Method (B)--The plot of $[\text{THEED}]$ vs. t does not go through a maximum. Steps (1)-(3) are identical to those for method (A).

4. k_3 may be calculated using the differential Eqn. 12.10. The rate of BHEP production can be determined from the slope of $[\text{BHEP}]$ versus time at various times. By plotting $(d[\text{BHEP}]/dt)_t$ against $[\text{THEED}]_t$ a straight line should be obtained whose slope will give k_3 . Alternatively k_3 may be calculated directly from Eqn. 12.10 at various times and the results averaged. This method of calculating k_3 may be used as a check on the value of k_3 calculated by method (A).

Figures 12.3 shows a typical plot of the model predictions compared with the experimental results for run 23.

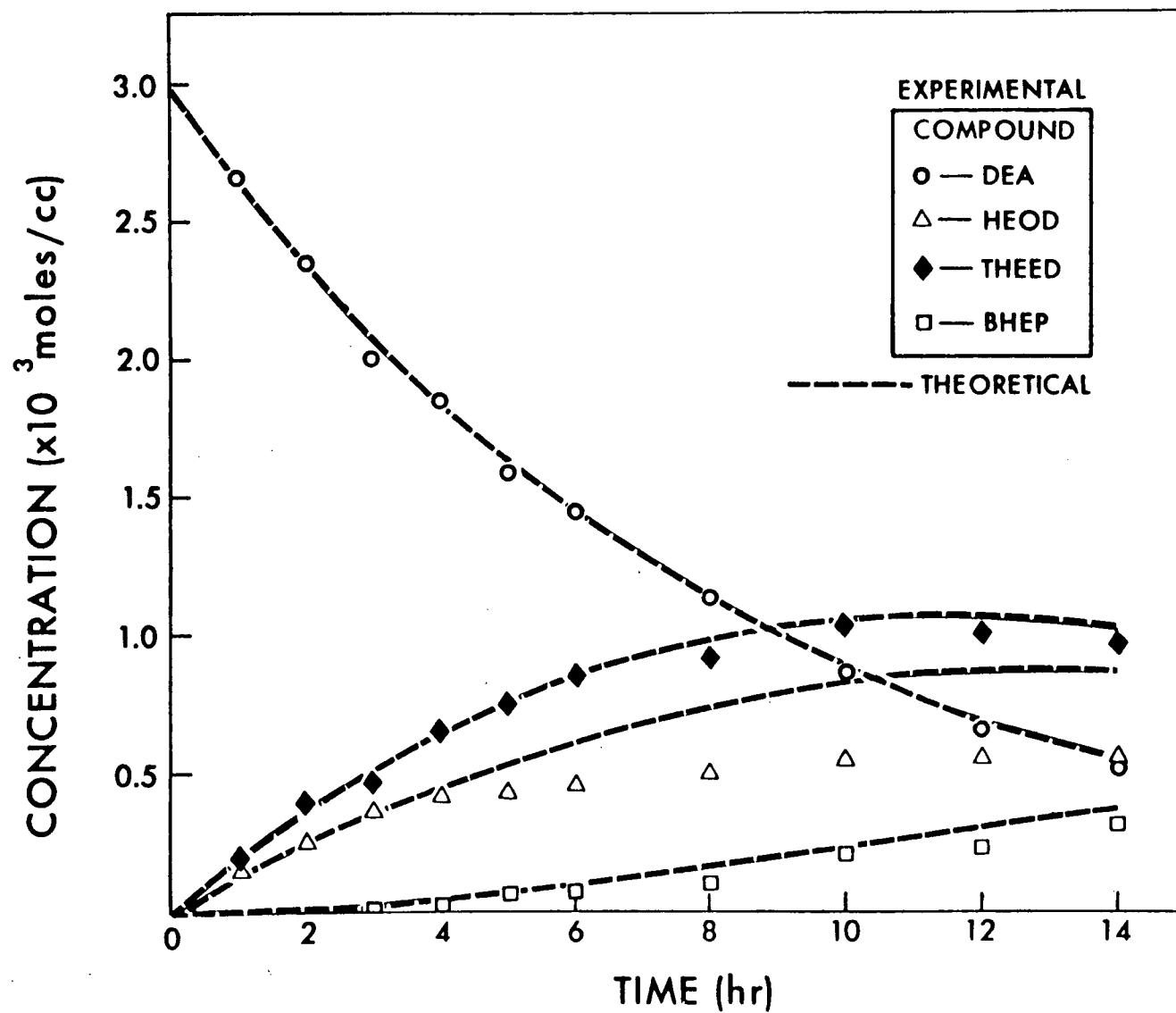


Figure 12.2 Comparison between the experimental and theoretical values of DEA, HEOD, THEED, and BHEP concentrations as a function of time (run 6)

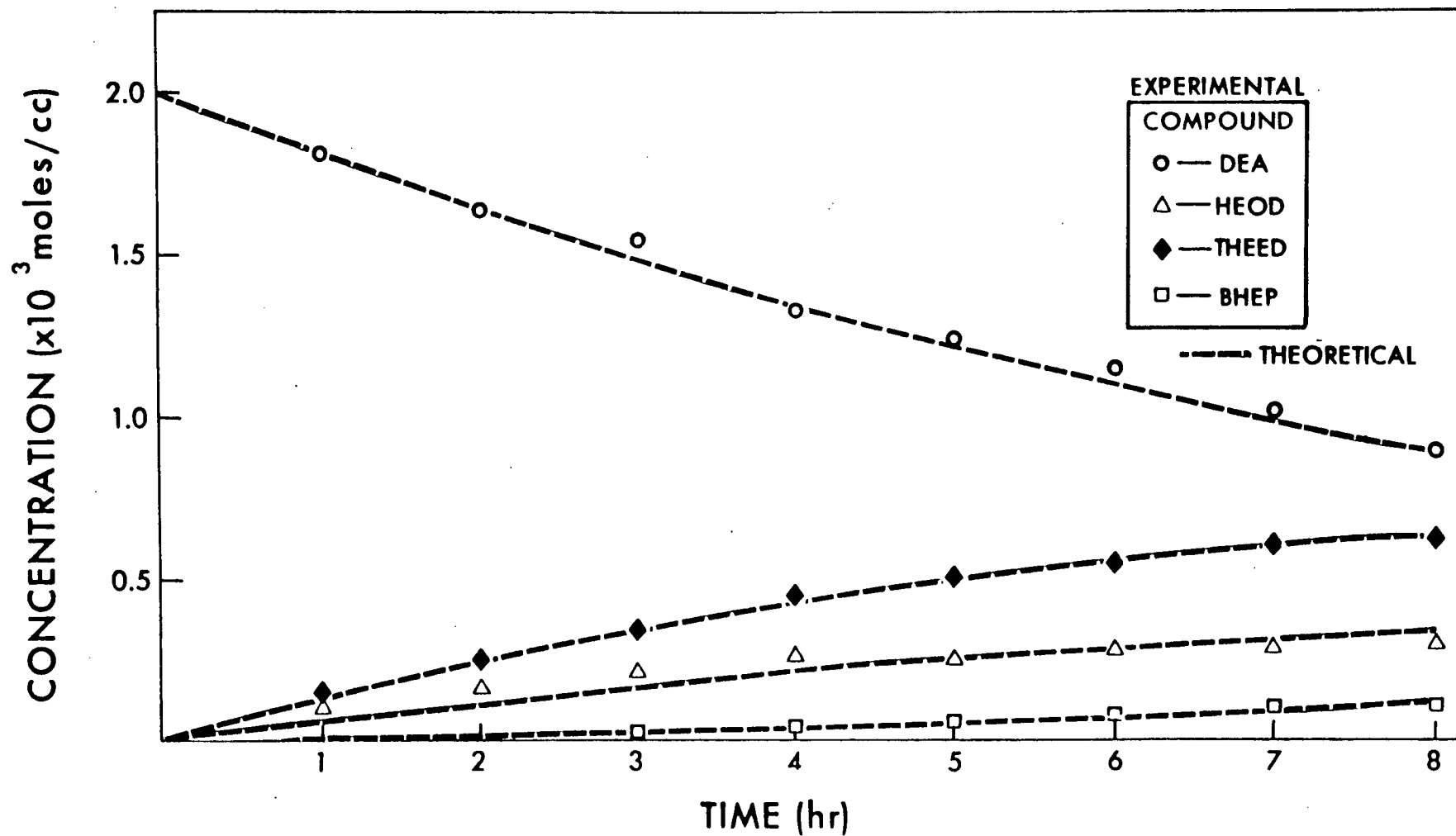


Figure 12.3 Comparison between the experimental and theoretical values of DEA, HEOD, THEED, and BHEP concentrations as a function of time (run 23)

12.4 Comparison of the experimental results with the predictions of the model

Tables of experimental results versus predicted results are presented in Appendix E. The model gave a very good prediction of the concentrations of DEA, THEED, and BHEP for various reaction times (see Figs. 12.2 and 12.3). In the case of HEOD, the model tended to over-predict the concentration after a certain reaction time. This was to be expected since the model did not account for the reversible reaction between HEOD and DEA (or more correctly R_2NCOO^-).

12.5 Application of the model

Figures 12.4 to 12.6 show Arrhenius plots for k_1 , k_2 , and k_3 . The values of the k 's were determined from the experimental data using method (A) or (B). The plots for k_1 and k_2 both conform to the three concentration regimes observed in the Arrhenius plot for k_{DEA} (see Fig. 8.16). In general the lower curve covers concentrations ranging from 0 to 10 wt % DEA and the upper curve covers concentrations between 30 to 100 wt % DEA. For concentrations in the range of 10 to 30 wt % DEA there can be considered a series of curves between the two extremes. (See Fig. 12.7, which shows an example of finding the k value at 140°C for a 17 wt % DEA solution.)

The Arrhenius plot for k_3 (Fig. 12.6) is unaffected by DEA concentration and tends to confirm the fact that BHEP is produced from THEED. Also this plot is a straight line even at high temperatures. It is interesting to note that if this plot is extrapolated to 205°C the k value obtained agrees very closely with the value of 0.25 hr^{-1} calculated from the results of run 69 (section 10.4) where THEED was degraded under CO_2 to BHEP.

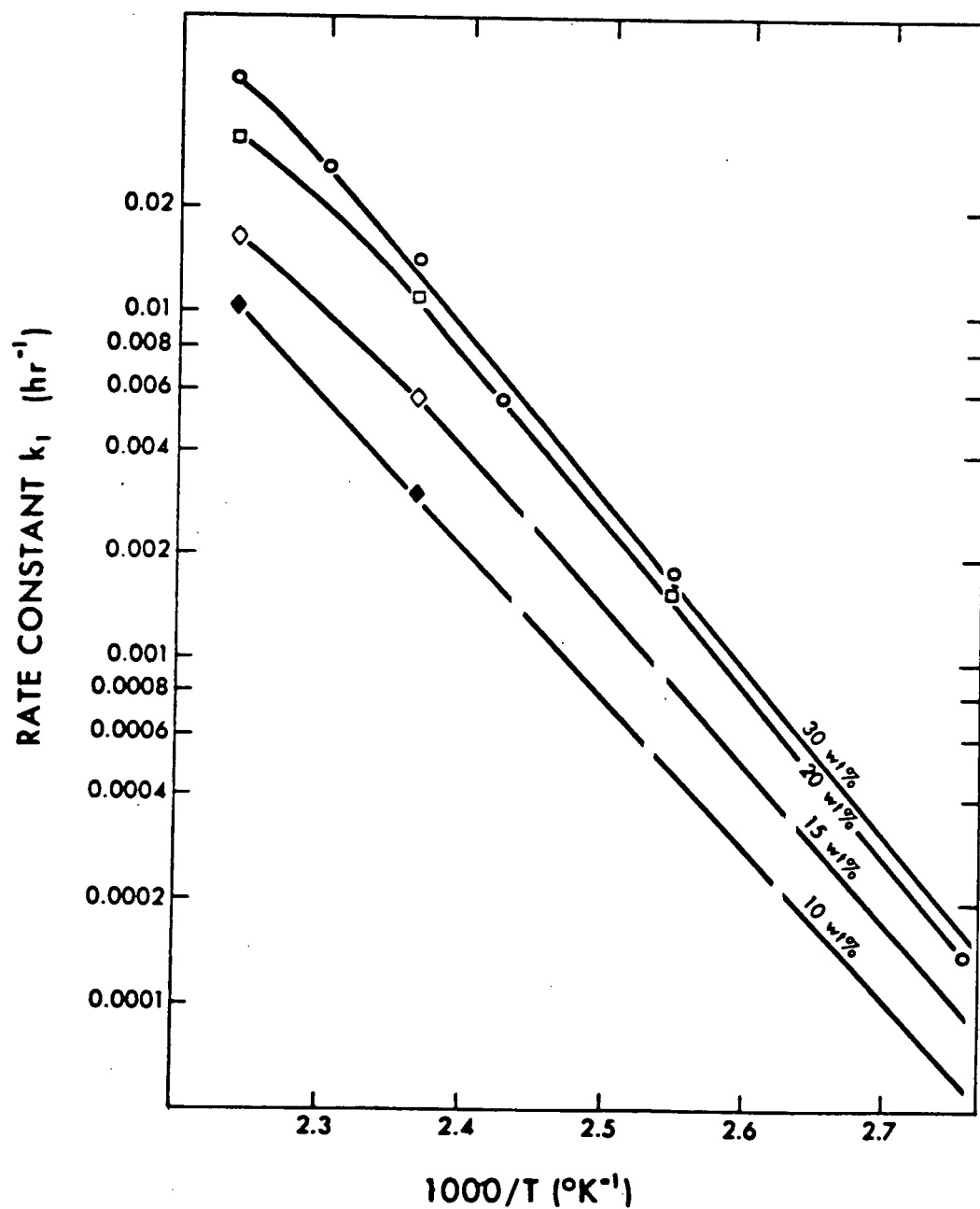


Figure 12.4 Arrhenius plots for k_1 at various initial DEA concentrations
 (DEA $\xrightarrow{k_1}$ HEOD)

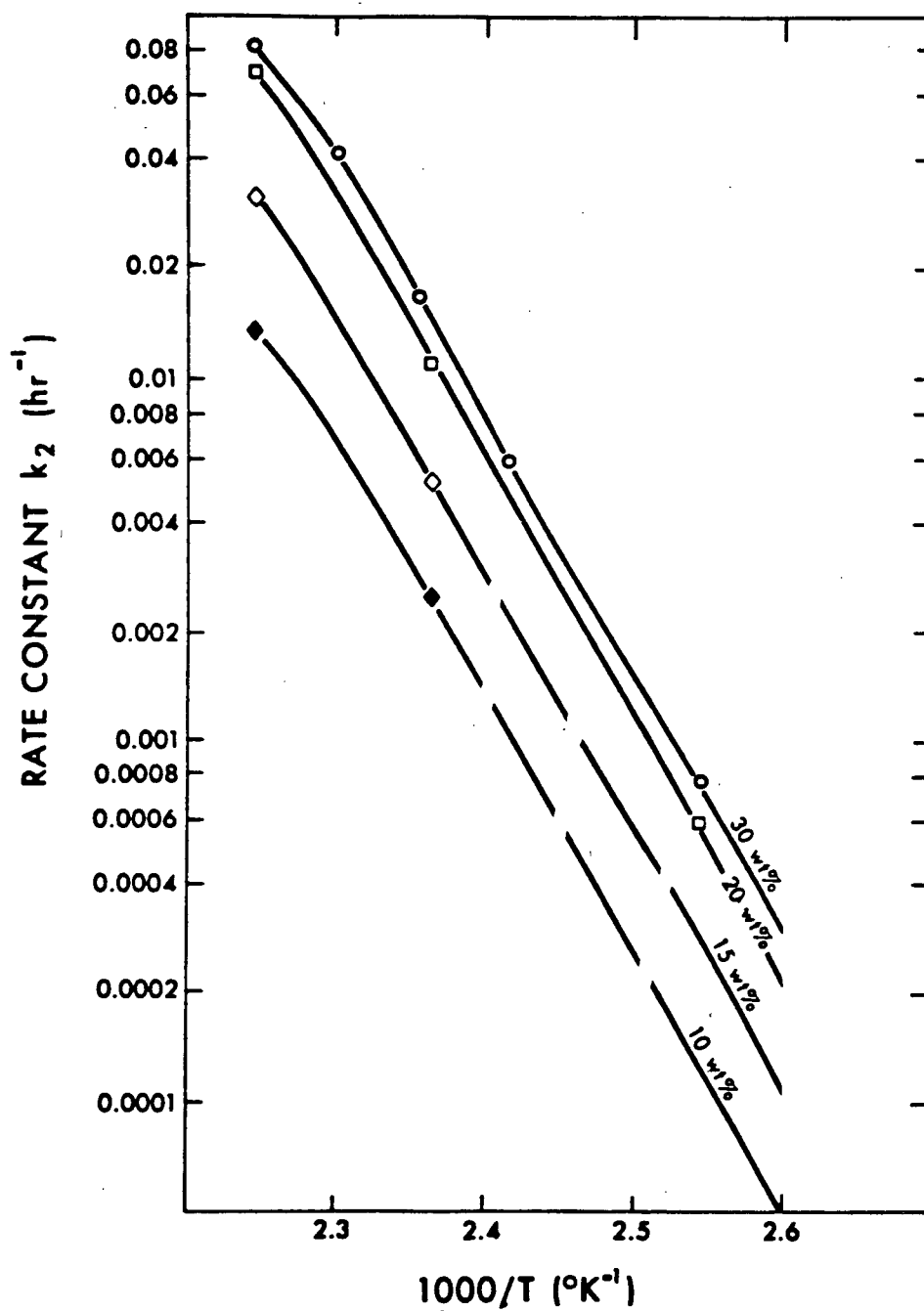
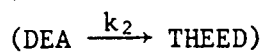


Figure 12.5 Arrhenius plots for k_2 at various initial DEA concentrations



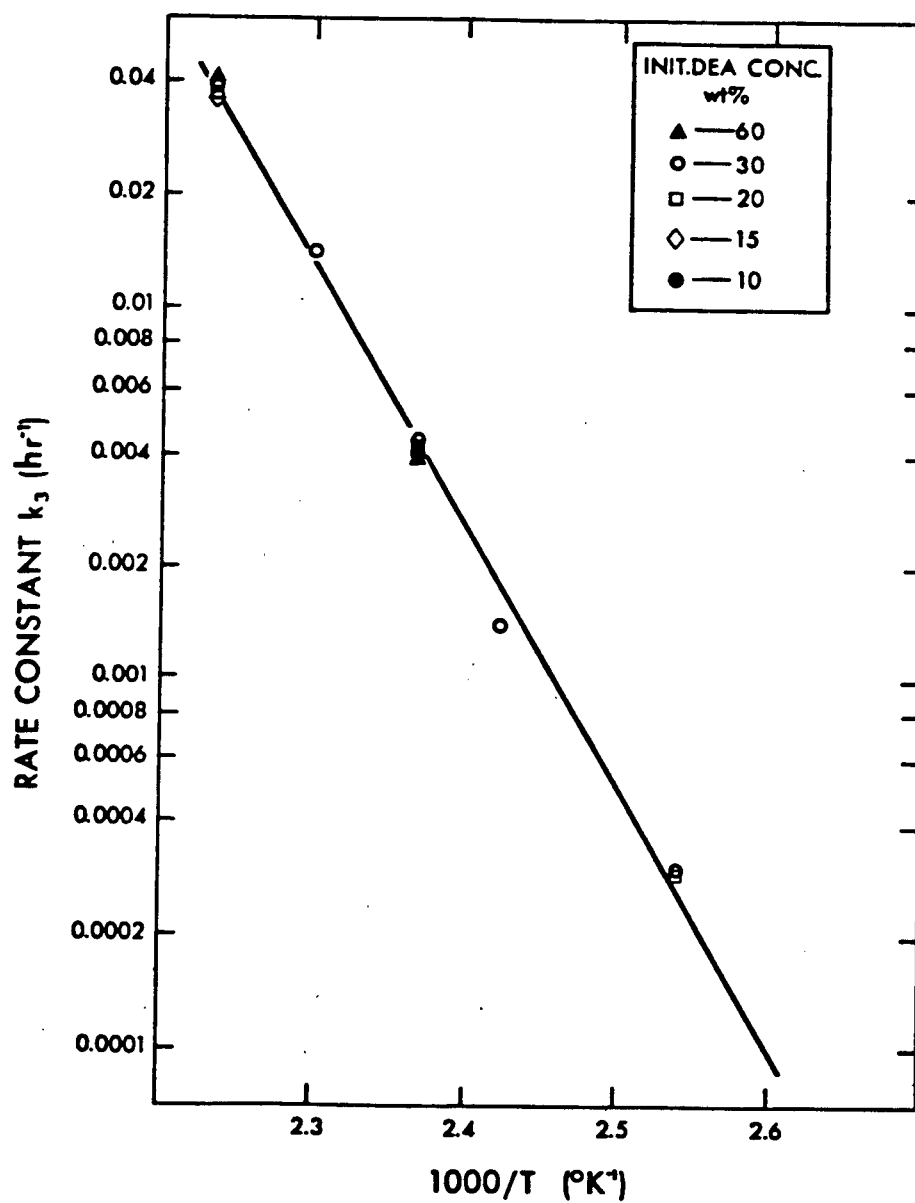


Figure 12.6 Arrhenius plot for k_3 at various initial DEA concentrations
(THEED $\xrightarrow{k_3}$ BHEP)

To predict the degradation of a given DEA solution under a specified set of conditions, the method is illustrated by means of a numerical example. Let 17 wt % DEA be absorbing CO_2 at 140°C at a total pressure of 4137 kPa (600 psi).

1. First determine the values of k_1 , k_2 , and k_3 from the Figs. 12.4 to 12.6. For k_1 and k_2 estimate the value of the 17 wt % Arrhenius plot which lies between the 10 wt % and 30 wt % to curves and read off the corresponding k value for the given temperature, i.e., 140°C (see Fig. 12.7).
2. Using these values of k_1 , k_2 , and k_3 and Eqns. 12.11 to 12.14 the concentrations of DEA, HEOD, THEED, and BHEP can be calculated for any desired time.

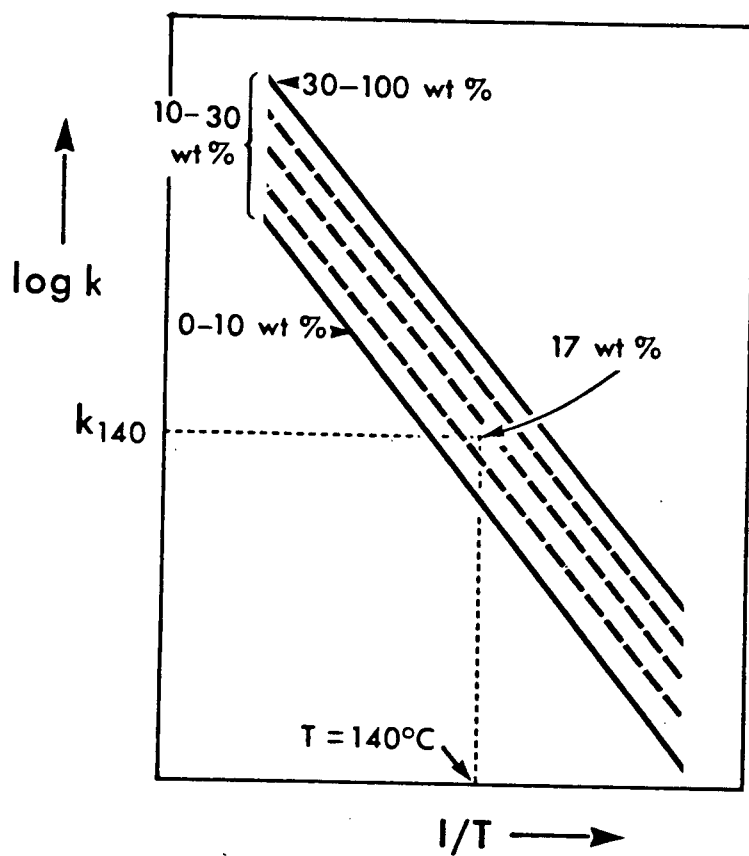


Figure 12.7 Sketch of Arrhenius plots for k_1 and k_2 at various initial DEA concentrations

CHAPTER 13

PURIFICATION OF DEGRADED DEA SOLUTIONS

It is not possible to purify DEA by standard means such as distillation since DEA and its degradation products have similar vapour pressures. Also at atmospheric pressure, DEA degrades near its boiling point. In addition some of the degradation compounds distil over a range of boiling temperatures, which rules out the possibility of vacuum distillation.

13.1 Use of activated carbon

Activated carbon filters have been used in several natural gas treating units to purify degraded DEA solutions. Usually a 5-10% slipstream of the DEA solvent is passed continually through an activated carbon filter. Although it has been claimed by some that the filters are very successful,^{1,11} their general effectiveness has yet to be proven. It appears that the activated carbon absorbs surface active compounds, which may be the cause of foaming, and may remove some dissolved heavy hydrocarbons and possibly some of the heat stable salts. There is however little evidence to date that the filters are able to remove any of the degradation compounds.

In order to determine whether activated carbon can remove degradation compounds, samples from industrial filter units were tested and a series of experiments were conducted in the laboratory.

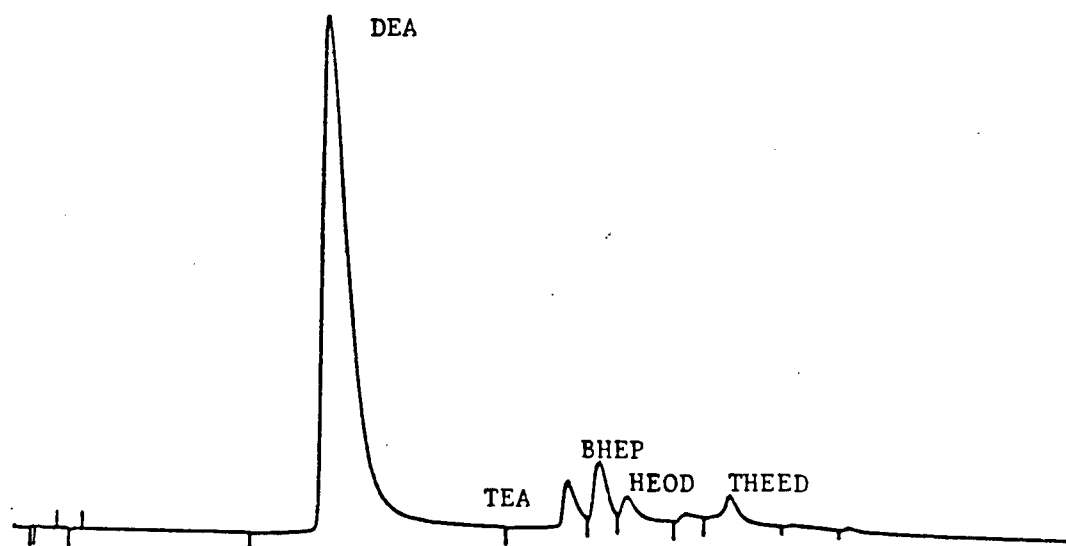
Figure 13.1 shows two typical chromatograms obtained from samples taken upstream and downstream of an activated carbon filter in a large gas plant. The similarity between the chromatograms clearly indicates that the filter was ineffective for removing degradation compounds.

Samples of DEA solutions degraded in the laboratory were contacted with activated carbon for periods ranging from a few hours to a few weeks at room temperature as well as at 50°C. In none of these experiments was the activated carbon found to change significantly the concentration of the degradation compounds. An example of the results can be seen in Fig. 13.2.

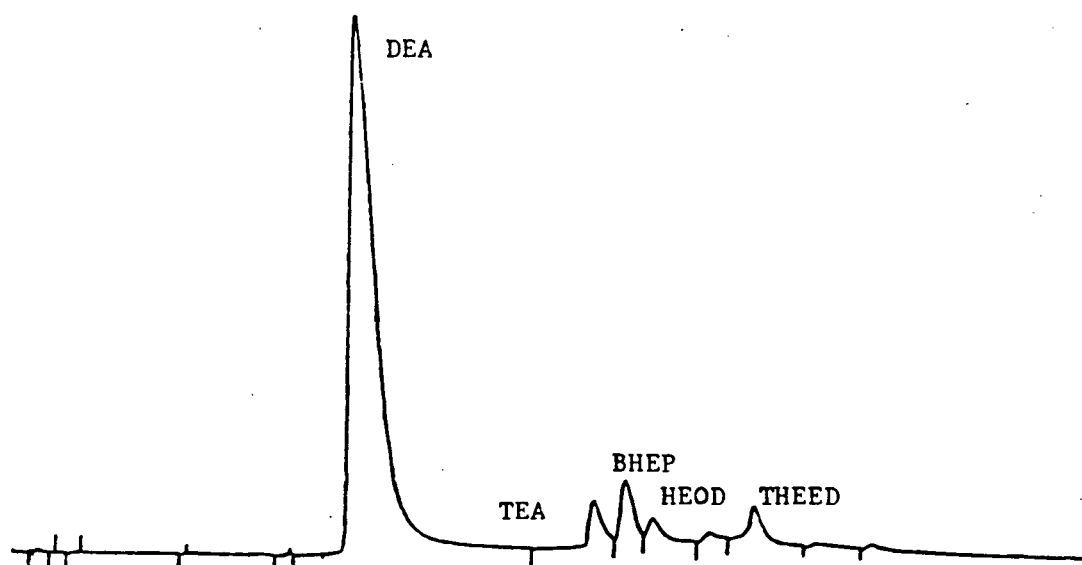
Although none of the major degradation compounds were removed, the degraded DEA solutions did change from a dark brown colour to a light yellow. It therefore seems that activated carbon is unable to remove HEOD, THEED, or BHEP from degraded DEA solutions.

13.2 Use of solvents

Several experiments were conducted to find a solvent in which DEA was soluble and its major degradation compounds were not or vice versa. If a successful solvent is found then a possible purification method could be developed. Unfortunately the tests were generally unsuccessful. Either DEA and its degradation compounds were all soluble or all were insoluble. The results are tabulated in Table 13.1.

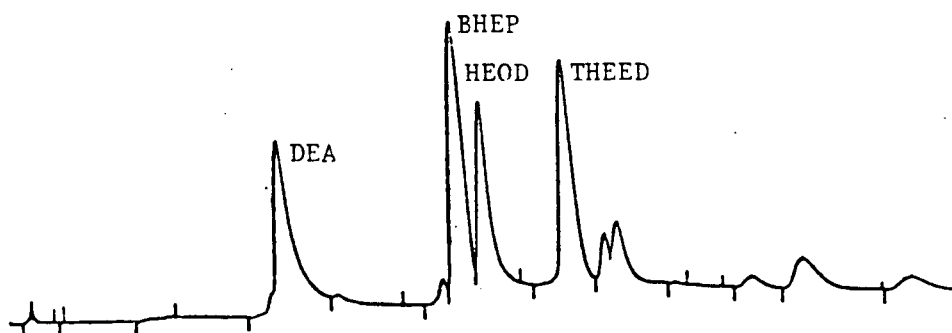


a) Sample taken upstream of filter

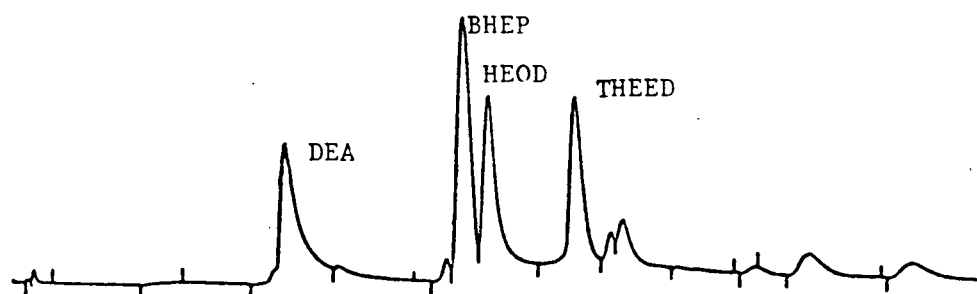


b) Sample taken downstream of filter

Figure 13.1 Typical chromatograms of partially degraded DEA solutions taken upstream and downstream of an activated carbon filter located in a large gas plant



a) Sample before contact with activated carbon



b) Sample after contact with activated carbon

Figure 13.2 Typical chromatograms of partially degraded DEA solutions under laboratory conditions; before and after contact with activated carbon

Table 13.1 Effect of various solvents on degraded DEA solutions

Solvent	Comments
Acetonitrile CH_3CN	DEA and degradation compounds insoluble. Water soluble.
Furan $\text{C}_4\text{H}_4\text{O}$	DEA and degradation compounds partially soluble.
Pyridine $\text{C}_5\text{H}_5\text{N}$	DEA and degradation compounds soluble.
Chloroform CHCl_3	DEA, HEOD, THEED soluble, BHEP partially soluble. Water soluble.
Ethyl alcohol $\text{C}_2\text{H}_5\text{OH}$	DEA and degradation compounds partially soluble.
N-propyl alcohol $\text{C}_3\text{H}_7\text{OH}$	DEA and degradation compounds partially soluble.

13.3 Removal of BHEP

When most of the water is stripped off from a degraded DEA solution with a high BHEP concentration (i.e., $\sim > 5 \cdot 10^{-4}$ moles/cc), BHEP starts to crystallize out at room temperature. It is useful to keep a small amount of water in the solution since it prevents DEA from solidifying (the melting point of DEA is $27\text{--}30^\circ\text{C}$). The crystals of BHEP can then be removed by vacuum filtration. The crystals usually have some viscous DEA adhering to them which can be washed off with propyl alcohol.

13.4 Removal of HEOD

HEOD is easily attacked by OH^- ions to give R_2NCOO^- . Therefore, a simple way to recover DEA from HEOD would be to add NaOH to the degraded DEA solution and apply heat to drive off CO_2 from the carbamate. However a further problem may result from the fact that addition of NaOH increases the CO_2 solubility, which may in turn increase the degradation

(see pH experiments, section 9.1).

13.5 Conclusion

In conclusion, the present purification experiments met with little success. It is recommended that natural gas processing plants try to operate under conditions which minimize degradation, rather than try to purify heavily degraded solutions.

CHAPTER 14

CONCLUSIONS AND RECOMMENDATIONS

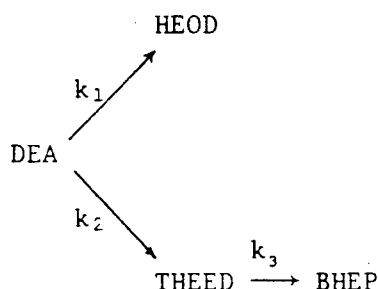
1. The overall reaction between CO_2 and DEA consists of two stages.
The first stage is the rapid establishment of a complex equilibrium between DEA, CO_2 , HCO_3^- , OH^- , R_2NH_2^+ , and R_2NCOO^- . The second stage, called the degradation reaction, is very much slower and DEA is converted irreversibly to degradation compounds.
2. The degradation reaction between DEA and CO_2 is complex and cannot be described by a simple stoichiometric equation.
3. The major degradation compounds are HEOD, THEED, and BHEP.
4. Minor degradation compounds which were detected, are HEED, HEP, OZD, BHEED, HEI, BHEI, and TEHEED. Some of these compounds were produced by the reaction of DEA with impurities in the feed such as MEA and TEA.
5. The degradation reaction proceeds via the formation of the DEA carbamate ion (R_2NCOO^-). The carbamate can be produced by two routes:-
 - a) 'The molecular route', where CO_2 reacts directly with DEA to form the carbamate.
 - b) 'The ionic route' where CO_2 , in the form of HCO_3^- , reacts with DEA in the form of R_2NH_2^+ to give a salt. The salt can then degrade to give the carbamate.
6. DEA can also degrade without the presence of CO_2 forming THEED and BHEP. This reaction is very much slower than the normal

degradation reaction involving CO_2 . It appears that CO_2 acts as a catalyst, with CO_2 being neither produced nor consumed.

7. The carbamate is able to either form HEOD and set up an equilibrium or react with itself or a molecule of DEA to form THEED.
8. Finally THEED can degrade to form BHEP. This reaction also appears to be catalysed by CO_2 .
9. The overall initial rate of DEA degradation is governed by a pseudo first order reaction.
10. The rate of DEA degradation is strongly affected by temperature. The Arrhenius plot confirms this. However at temperatures greater than 175°C , the plot deviates from the straight line behaviour. This was explained by
 - a) CO_2 becoming limiting and b) the molecular route becoming modified at high temperatures.
11. The rate constant (k_{DEA}) is also strongly affected by initial DEA concentration. Three regions can be defined:
 - a) 0-10 wt % DEA, where the main degradation route is ionic.
 - b) 10-30 % DEA, where the k_{DEA} sharply increases as the degradation is a combination of molecular and ionic.
 - c) 30-100 wt % DEA, where the main degradation route is molecular.

The rate slowly falls as water becomes limiting.
12. The degradation rate is unaffected by CO_2 pressure provided the CO_2 concentration in the reaction mixture is greater than about 0.2 g CO_2/g DEA.
13. The degradation rate increases with increasing pH. This is probably due to a) increased CO_2 solubility and b) an increase in the concentration of the carbamate.

14. The degradation rate is inhibited by the presence of degradation products, especially BHEP, at high temperatures. This is probably due to CO_2 being tied up with the degradation products, which reduces the concentration of available CO_2 for DEA degradation to less than 0.2 g CO_2 /g DEA.
15. Using a simplified degradation model



it was possible to develop equations for predicting the degradation of DEA and production of degradation compounds. The model covered the ranges of 90-175°C, 0-100 wt % DEA for CO_2 concentrations greater than 0.2 g CO_2 /g DEA.

16. Activated carbon was found to be incapable of removing any of the major degradation compounds.
17. BHEP can be partially removed by drying degraded DEA solutions and allowing BHEP to crystallize out.
18. DEA can be recovered from HEOD by adding NaOH to the degraded DEA solution and applying heat.

14.1 Practical implications of the present study

a) The effect of temperature. The design and operation of DEA units must avoid the creation of elevated temperatures throughout the plant. The heat transfer surfaces of the stripper reboiler (especially when gas fired) are particularly prone to the formation of localized hot spots. To prevent such hot spots in operating plants, the DEA

circulation through the stripper reboiler should be kept high and the steam or gas temperatures kept low. If, for some reason, the DEA circulation should decrease, immediate action must be taken to reduce the steam pressure or fuel gas flow. There are two other sites where major degradation may take place. The first is within the heat exchanger that heats the rich amine stream with the lean amine stream. In some cases the temperature of the rich amine stream may be as high as 125°C.¹³ The second site is at the base of the absorber. If the CO₂ content of the raw natural gas is high the temperature of the rich amine at the base of the absorber may rise to 110-120°C.

In many DEA units only the bulk solution temperatures are measured. It must be remembered that the skin temperatures of heat transfer surfaces can be very much higher, particularly during process upsets. Reliance on bulk temperatures is therefore inadequate.

b) Effect of pressure. The partial pressures of CO₂ should be kept as low as possible in order to minimize DEA degradation. Although it is not usual to exercise control over the CO₂ content of the raw gas entering a plant, it may be possible to dilute the raw gas with some purified natural gas thus diluting the overall CO₂ content. This dilution would not only reduce the degradation rate, it would also reduce the heat of absorption when CO₂ is absorbed into DEA. This would help to keep the overall temperature in the absorber low.

c) Effect of DEA concentration. Ideally the plants should try to operate with low DEA solution strengths (if possible well below 20 wt %). However, limitations are imposed by the desired plant capacity. Future design of gas treating plants should consider larger equipment for operation with dilute solutions of DEA and dilute raw gas feed.

Again a dilute solution of DEA would reduce local increases in temperature, due to the CO₂ absorption. However, studies would have to be made to determine the cost effectiveness of these measures.

d) Effect of activated carbon filters. Although the activated carbon appears unable to remove the major degradation products, it is not recommended to remove the filters from existing plants. The filters may serve other useful functions such as removing surfactants which can cause foaming, heat stable salts which may cause corrosion and they can act as a means for removing fine particulates.

e) Purification of degraded DEA solutions. Since purification of DEA solutions is very difficult it is recommended that rather than provide equipment to purify the solutions the plant should be built and operated in such a way so as to minimize degradation.

f) Analytical technique. The chromatographic analytical technique developed in this study is ideally suited for plant use. The method is simple and relatively fast with no sample preparation required. Using this method, it is possible to monitor DEA streams regularly. If degradation occurs, it is easy to detect and appropriate action can quickly be taken to minimize the DEA losses.

14.2 Experimental recommendations

a) Measurement of pH. DEA degradation appears to be affected by solution pH measured at room temperature. It would, therefore, be useful to measure pH at the high temperature and pressure of a typical degradation experiment.

b) Measurement of DEA carbamate concentration. The proposed degradation of DEA appears to proceed via the production of DEA carbamate. To further clarify the degradation mechanism it would be useful to determine

the concentration of the DEA carbamate. However, using the existing chromatographic analytical technique it is impossible to detect the carbamate since it is unstable and reverts back to DEA. Silylation may stabilize the carbamate sufficiently to allow its concentration to be determined using chromatography.

NOMENCLATURE

<u>Symbol</u>	<u>Explanation and typical units</u>
A	Frequency factor in the Arrhenius Eq. 8.7 (hr^{-1})
BHEAE	Bis(hydroxyethylaminoethyl) ether
BHEED	N,N-Bis(hydroxyethyl) ethylenediamine
BHEI	N,N-Bis(hydroxyethyl) imidazolidone
BHEP	N,N-Bis(hydroxyethyl) piperazine
BHEU	N,N-Bis(hydroxyethyl) urea
BHG	N,N-Bis(hydroxyethyl) glycine
DEA	Diethanolamine
DEEA	Diethyl ethanolamine
E	Activation energy in the Arrhenius Eq. 8.7 (Cal/g mol)
ED	Ethylenediamine
EO	Ethylene oxide
GC/MS	Gas chromatograph with mass spectrometer
HEED	N-(hydroxyethyl) ethylenediamine
HEI	N-(hydroxyethyl) imidazolidone
HEM	N-(hydroxyethyl) ethylenimine
HEOD	3-(hydroxyethyl)-2-oxazolidone
HEP	N-(hydroxyethyl) piperazine
k	Reaction rate constant
k_{DEA}	Overall reaction rate constant for the degradation of DEA, (hr^{-1})
k_1, k_2, k_3	Rate constants used in the kinetic model of the degradation of DEA, Eqns. 12.7-12.17, (hr^{-1})
MDEA	Methyldiethanolamine
MEA	Monoethanolamine

OZD	Oxazolidone
P	Piperazine
R-	$-C_2H_4OH$
T	Absolute temperature ($^{\circ}K$)
t	Time (hr)
TEA	Triethanolamine
TEHEED	N,N,N,N-Tetra(hydroxyethyl) ethylenediamine
TEHEU	N,N,N,N-Tetra(hydroxyethyl) urea
THEED	N,N,N-Tris(hydroxyethyl) ethylenediamine
THEU	N,N,N-Tris(hydroxyethyl) urea
[]	Denotes concentration (g mol/cc)
[] _t	Denotes concentration at time t (g mol/cc)

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APPENDIX ASources of Equipment and Chemicalsa) Equipment

<u>Item</u>	<u>Supplier</u>	<u>Model</u>
<u>Chromatograph</u>		
Gas Chromatograph	Hewlett Packard, Alvondale, PA.	5830
Syringe	Hamilton Co., Reno, Nev.	701
Septa	Supelco Inc., Bellefonte, Penn.	Microsep F-174
Column	Supelco Inc., Bellefonte, Penn. ^o	Tenax G.C.
<u>Mass spectrometer</u>	Hewlett Packard, Vancouver	5985 B
<u>Autoclave</u>		
Reactor	Parr Instrument Co., Ill.	4560
Temperature controller	Parr Instrument Co., Ill.	4831 EB
Digital thermometer	Doric Instruments, Que.	Series 400A, No. 410A
Chart recorder	Corning	840

b) Chemicals

<u>Chemical</u>	<u>Supplier</u>
Acentonitrile	Mallinckrodt Ltd., Paris, Kentucky
BHG	BDH Biochemicals Ltd., Poole, England
BHEED	ICN Pharmaceuticals Inc., Plainview, N.Y.
BHEI	Frinton Laboratories, Vineland, N.J.
BHEP	Aldrich Chemical Co., Milwaukee, Wis.
CO ₂	Union Carbide, Vancouver, B.C.
Chloroethanol	Aldrich Chemical Co., Milwaukee, Wis.
Chloroform	Caledon Laboratories Ltd., Georgetown, Ont.
DEA	Matheson Coleman and Bell, Norwood, Ohio
DEEA	Aldrich Chemical Co., Milwaukee, Wis.
ED	Aldrich Chemical Co., Milwaukee, Wis.
EO	Matheson of Canada Ltd., Whitby, Ont.
Ethyl alcohol	Mallinckrodt Chemical Works, St. Louis, Mo.
Ethyl carbonate	Eastman Kodak Company, Rochester, N.Y.
Furan	Aldrich Chemical Co., Milwaukee, Wis.
HCL	Allied Chemicals Canada Ltd., St. Claire, Quebec
HEED	Aldrich Chemical Co., Milwaukee, Wis.
HEI	Frinton Laboratories, Vineland, N.S.
HEOD	Synthecon Laboratories, Vancouver, B.C.
HEM	Aldrich Chemical Co., Milwaukee, Wis.
HEP	Aldrich Chemical Co., Milwaukee, Wis.
MEA	Malinckrodt, St. Louis, Mo.

Appendix A (cont.)

Chemical	Supplier
MDEA	Aldrich Chemical Co., Milwaukee, Wis.
NaOH	Fisher Scientific Co., Fairlawn, N.J.
OZD	
Potassium bicarbonate	Mallinckrodt Chemical Works, St. Louis, Mo.
Potassium carbonate	Mallinckrodt Chemical Works, St. Louis, Mo.
Pyridine	
N-propyl alcohol	Mallinckrodt Inc., Paris, Kentucky
Silica gel	Anachemia Chemicals Ltd., Toronto
TEA	Aldrich Chemical Co., Milwaukee, Wis.
TEHEED	ICN,K and K Laboratories Inc., Cleveland, Ohio

APPENDIX BExperimental results for the degradation of DEA by CO₂

Although certain other degradation compounds were detected in degraded solutions of DEA, only data on DEA, BHEP, HEOD, and THEED are recorded here. This was because the other minor degradation compounds and certain feed impurities, such as MEA, existed in very low concentrations and, therefore, they could be ignored when developing the kinetic model.

TABLE B.1

RUN 1 : 30 WT% DEA, 250C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.00	-	-	-
0.50	2.32	0.016	0.063	0.180
1.00	1.81	0.091	0.073	0.200
1.67	1.37	0.131	0.088	0.250
2.50	1.04	0.323	0.075	0.220
3.50	0.72	0.391	0.085	0.120
5.00	0.62	0.553	0.085	0.020
6.50	0.48	0.663	0.086	-
7.83	0.38	0.695	0.091	-

$$k_{\text{DEA}} = 0.691 \text{ hr}^{-1}$$

TABLE B.2

RUN 2 : 30 WT% DEA, 225C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.00	-	-	-
0.58	2.38	-	0.125	0.210
1.00	2.24	0.019	0.140	0.460
1.67	1.76	0.080	0.135	0.600
2.67	1.44	0.195	0.125	0.710
3.58	1.05	0.311	0.135	0.700
5.00	0.82	0.412	0.125	0.441
6.00	0.68	0.459	0.120	0.335
8.75	0.57	0.541	0.118	0.171

$$k_{\text{DEA}} = 0.399 \text{ hr}^{-1}$$

TABLE B.3

RUN 3 : 30 WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.02	-	-	-
1.00	2.24	0.010	0.170	0.360
2.00	1.63	0.051	0.200	0.640
3.00	1.26	0.111	0.195	0.840
4.00	0.95	0.170	0.203	0.820
5.00	0.78	0.245	0.203	0.700
6.00	0.71	0.332	0.208	0.650
7.00	0.65	0.396	0.208	0.576
8.00	0.57	0.423	0.208	0.500

$$k_{\text{DEA}} = 0.291 \text{ hr}^{-1}$$

TABLE B.4

RUN 4 : 30 WT% DEA, 195C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.14	-	-	-
1.00	2.30	-	0.188	0.280
2.00	1.89	0.025	0.233	0.610
3.00	1.47	0.071	0.250	0.870
4.00	1.21	0.104	0.228	0.870
5.00	0.91	0.156	0.220	0.790
6.00	0.82	0.215	0.243	0.760
8.00	0.74	0.256	0.220	0.720
8.00	0.63	0.292	0.215	0.680

$$k_{\text{DEA}} = 0.23 \text{ hr}^{-1}$$

TABLE B.5
 RUN 5 : 30 WT% DEA, 185C, 4137 kPa (600 psi) CO2

SAMPLE hr	DEA	CONC. MOLES/CC BHP	HEOD X10-3	THEED
0.00	3.08	-	-	-
1.00	2.60	-	0.180	0.300
2.00	2.18	-	0.275	0.575
3.00	1.78	0.0175	0.301	0.700
4.00	1.48	0.0325	0.300	0.820
5.00	1.28	0.0830	0.301	0.920
6.00	1.11	0.1190	0.300	0.930
7.00	0.98	0.1410	0.301	0.960
8.00	0.88	0.1790	0.315	0.902

KDEA = 0.173 hr-1

TABLE B.6
 RUN 6 : 30 WT% DEA, 175C, 4137 kPa (600 psi) CO2

SAMPLE hr	DEA	CONC. MOLES/CC BHP	HEOD X10-3	THEED
0.00	3.04	-	-	-
1.00	2.67	-	0.150	0.130
2.00	2.36	-	0.250	0.280
3.00	2.00	0.015	0.360	0.450
4.00	1.84	0.028	0.410	0.660
5.00	1.58	0.058	0.425	0.760
6.00	1.44	0.062	0.460	0.850
7.00	1.24	0.092	0.480	0.840
8.00	1.11	0.098	0.485	0.910
10.00	0.86	0.206	0.540	1.050
12.00	0.65	0.220	0.550	0.990
14.00	0.52	0.284	0.540	0.960

KDEA = 0.121 hr-1

TABLE B.7

RUN 7 : 30 WT% DEA, 162C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.000	-	-	-
1.00	2.803	-	0.105	0.090
2.00	2.620	-	0.200	0.200
3.00	2.450	0.0101	0.275	0.290
4.00	2.280	0.0150	0.320	0.388
5.00	2.137	0.0201	0.364	0.460
6.00	2.000	0.0254	0.412	0.561
7.00	1.870	0.0350	0.420	0.653
8.00	1.744	0.0420	0.425	0.731

$$k_{\text{DEA}} = 0.0678 \text{ hr}^{-1}$$

TABLE B.8

RUN 8 : 30 WT% DEA, 150C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.000	-	-	-
5.00	2.600	0.0098	0.250	0.075
10.00	2.200	0.0210	0.350	0.150
15.00	1.860	0.0380	0.470	0.400
20.00	1.560	0.0425	0.510	0.652
25.00	1.310	0.0550	0.550	0.751
30.00	1.110	0.0640	0.570	0.900
40.00	0.840	0.0860	0.570	1.075
50.00	0.710	0.1060	0.542	1.225
60.00	0.580	0.1300	0.540	1.200
71.40	0.570	0.1500	0.541	1.060
81.10	0.455	0.1860	0.540	0.910
95.00	0.420	0.2100	0.500	0.810

$$k_{\text{DEA}} = 0.0316 \text{ hr}^{-1}$$

TABLE B.9

RUN 9 : 30WT% DEA, 145C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.200	-	-	-
3.25	3.000	-	0.215	-
13.75	2.430	-	0.488	0.250
19.75	2.160	0.0173	0.580	0.403
28.50	1.740	0.0210	0.600	0.551
39.50	1.430	0.0620	0.621	0.790
48.50	1.360	0.0740	0.600	0.881
60.00	1.050	0.1040	0.605	0.925
69.00	0.920	0.1240	0.580	0.944

$$k_{\text{DEA}} = 0.0195 \text{ hr}^{-1}$$

TABLE B.10

RUN 10 : 30WT% DEA, 140C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.000	-	-	-
10.00	2.850	-	0.250	0.120
20.00	2.540	0.0120	0.450	0.320
30.00	2.260	0.0210	0.575	0.504
40.00	2.000	0.0330	0.660	0.581
50.00	1.754	0.0415	0.710	0.700
60.00	1.605	0.0510	0.710	0.751
80.00	1.270	0.0700	0.660	0.863
100.00	1.010	0.1050	0.700	0.950
130.00	0.830	0.1550	0.700	0.910
154.80	0.670	0.1700	0.610	0.892
178.00	0.560	0.2060	0.580	0.810
201.00	0.530	0.2560	0.575	0.754

$$k_{\text{DEA}} = 0.0115 \text{ hr}^{-1}$$

TABLE B.11

RUN 11 : 30WT% DEA, 120C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.150	-	-	-
20.00	3.000	-	0.150	-
40.00	2.900	-	0.300	0.056
60.00	2.800	-	0.380	0.089
80.00	2.650	-	0.525	0.100
100.00	2.500	0.0060	0.600	0.140
120.00	2.340	0.0084	0.705	0.225
140.00	2.244	0.0100	0.751	0.240
160.00	2.131	0.0180	0.760	0.313
180.00	2.000	0.0250	0.770	0.345
200.00	1.905	0.0310	0.780	0.375

$$k_{\text{DEA}} = 0.0026 \text{ hr}^{-1}$$

TABLE B.12

RUN 12 : 30WT% DEA, 90C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.530	-	-	-
100.00	3.500	-	0.050	-
160.00	3.420	-	0.090	-
300.00	3.455	-	0.155	-
441.00	3.403	-	0.191	-
511.00	3.361	-	0.216	0.014
631.00	3.310	-	0.250	0.048
700.00	3.280	-	0.290	0.060

$$k_{\text{DEA}} = 0.000142 \text{ hr}^{-1}$$

TABLE B.13

RUN 13 : 100WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	10.00	-	-	-
1.08	8.00	0.069	0.255	3.200
2.67	6.41	0.172	0.275	3.860
3.92	4.60	0.282	0.263	4.070
4.92	3.71	0.370	0.250	3.645
6.00	2.84	0.524	0.245	3.540
7.00	2.56	0.643	0.247	2.650
7.93	2.12	0.754	0.225	1.958

$$k_{\text{DEA}} = 0.195 \text{ hr}^{-1}$$

TABLE B.14

RUN 14 : 80WT% DEA , 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	7.80	-	-	-
0.78	5.98	0.0224	0.190	1.525
2.00	4.62	0.0960	0.265	2.535
3.00	3.31	0.2220	0.275	3.070
4.00	2.20	0.3260	0.248	3.000
5.00	1.93	0.4980	0.263	2.725
6.00	1.48	0.6560	0.240	2.340
6.95	1.34	0.8200	0.250	1.980
8.58	1.09	0.8700	0.235	1.258

$$k_{\text{DEA}} = 0.277 \text{ hr}^{-1}$$

TABLE B.15

RUN 15 : 60WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	6.18	-	-	-
1.00	4.18	0.0425	0.195	1.500
1.87	3.42	0.0800	0.225	1.950
3.00	2.68	0.1710	0.240	2.030
4.00	1.80	0.2560	0.225	1.834
5.05	1.36	0.3580	0.222	1.560
6.08	1.15	0.4490	0.205	1.168
6.92	1.06	0.5620	0.210	1.169
8.00	0.95	0.6370	0.200	0.954

$$k_{\text{DEA}} = 0.314 \text{ hr}^{-1}$$

TABLE B.16

RUN 16 : 40WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	4.000	-	-	-
1.00	2.800	0.0100	0.170	0.720
2.08	2.000	0.0720	0.210	1.230
4.00	1.410	0.2090	0.228	1.268
5.00	1.180	0.2900	0.225	1.093
6.08	1.000	0.3850	0.225	0.946
7.17	0.921	0.4860	0.220	0.760
8.08	0.804	0.5400	0.220	0.718

$$k_{\text{DEA}} = 0.320 \text{ hr}^{-1}$$

TABLE B.17

RUN 17 : 20WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	2.050	-	-	-
1.00	1.680	0.0050	0.153	-
2.00	1.280	0.0363	0.176	0.060
3.00	1.050	0.0621	0.186	0.252
4.00	0.858	0.1140	0.193	0.326
5.00	0.770	0.1500	0.175	0.350
6.00	0.658	0.1780	0.175	0.291
7.00	0.588	0.2150	0.176	0.278
8.00	0.538	0.2400	0.181	0.265

$$k_{\text{DEA}} = 0.241 \text{ hr}^{-1}$$

TABLE B.18

RUN 18 : 15WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	1.500	-	-	-
0.50	1.333	-	0.045	-
1.00	1.212	0.0025	0.065	0.018
2.00	1.161	0.0108	0.105	0.043
3.00	0.984	0.0280	0.125	0.186
4.00	0.810	0.0480	0.151	0.242
5.50	0.735	0.0845	0.152	0.272
6.25	0.650	0.1130	0.150	0.261
7.56	0.615	0.1280	0.113	0.229

$$k_{\text{DEA}} = 0.131 \text{ hr}^{-1}$$

TABLE B.19

RUN 19 : 10WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	0.935	-	-	-
1.00	0.820	-	0.073	-
2.00	0.735	0.0080	0.125	-
3.00	0.643	0.0145	0.140	0.009
4.00	0.575	0.0250	0.153	0.021
5.00	0.540	0.0495	0.169	0.031
6.00	0.448	0.0650	0.163	0.040
7.00	0.387	0.0793	0.130	0.046
8.00	0.358	0.0838	0.115	0.046

$$k_{\text{DEA}} = 0.104 \text{ hr}^{-1}$$

TABLE B.20

RUN 20 : 5 WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	0.520	-	-	-
0.66	0.470	-	0.020	-
1.75	0.440	-	0.035	-
2.75	0.406	0.0025	0.048	0.015
4.08	0.371	0.0049	0.050	0.028
5.08	0.334	0.0105	0.061	0.044
6.08	0.311	0.0190	0.074	0.068
7.08	0.300	0.0228	0.063	0.063
8.00	0.260	0.0300	0.055	0.062

$$k_{\text{DEA}} = 0.098 \text{ hr}^{-1}$$

TABLE B:21

RUN 21 : 100WT% DEA, 175C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.0	10.00	-	-	-
1.0	9.0	0.020	0.315	0.810
3.0	7.10	0.092	0.445	2.545
4.0	6.90	0.130	0.435	2.960
5.0	6.30	0.174	0.415	3.410
6.5	5.50	0.272	0.416	3.050
8.0	4.80	0.334	0.403	2.550

$$k_{\text{DEA}} = 0.092 \text{ hr}^{-1}$$

TABLE B.22

RUN 22 : 60WT% DEA, 175C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.0	6.00	-	-	-
1.0	5.35	-	0.190	0.300
2.0	4.81	0.035	0.360	0.940
3.0	4.25	0.065	0.450	1.400
4.0	3.74	0.092	0.450	1.660
5.0	3.38	0.115	0.450	1.840
6.0	3.21	0.180	0.420	1.914
7.0	2.65	0.206	0.431	1.980
8.0	2.25	0.250	0.398	2.046

$$k_{\text{DEA}} = 0.118 \text{ hr}^{-1}$$

TABLE B.23

RUN 23 : 20WT% DEA, 175C, 4137 kPa (600 psi) CO2

SAMPLE hr	DEA	CONC. MOLES/CC X10-3 BHEP	HEOD	THEED
0.0	2.02	-	-	-
1.0	1.81	-	0.100	0.150
2.0	1.66	-	0.170	0.250
3.0	1.55	0.024	0.210	0.320
4.0	1.35	0.036	0.250	0.440
5.0	1.24	0.054	0.250	0.500
6.0	1.15	0.074	0.260	0.540
7.0	1.03	0.096	0.270	0.590
8.0	0.96	0.105	0.290	0.615

kDEA = 0.101 hr-1

TABLE B.24

RUN 24 : 15WT% DEA; 175C, 4137 kPa (600 psi) CO2

SAMPLE hr	DEA	CONC. MOLES/CC X10-3 BHEP	HEOD	THEED
0.0	1.50	-	-	-
1.0	1.42	-	0.026	-
2.0	1.37	-	0.050	0.050
3.0	1.31	0.006	0.076	0.100
4.0	1.24	0.013	0.093	0.120
5.0	1.18	0.020	0.118	0.170
6.0	1.12	0.028	0.131	0.172
8.0	1.08	0.049	0.160	0.225
10.0	1.01	0.058	0.171	0.250

kDEA = 0.049 hr-1

TABLE B.25

RUN 25 : 10WT% DEA, 175C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	1.010	-	-	-
2.0	0.940	-	0.020	-
4.0	0.900	-	0.040	-
6.0	0.855	-	0.060	0.048
8.0	0.810	0.0080	0.080	0.068
10.0	0.770	0.0175	0.090	0.060
15.0	0.680	0.0400	0.100	0.100
20.0	0.610	0.0460	0.106	0.142

$$k_{\text{DEA}} = 0.0242 \text{ hr}^{-1}$$

TABLE B.26

RUN 26 : 60WT% DEA, 150C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	6.00	-	-	-
2.0	5.66	-	0.110	0.210
4.0	5.30	-	0.230	0.400
6.0	5.00	0.009	0.382	0.650
8.0	4.71	0.011	0.460	0.850
10.0	4.46	0.021	0.541	1.000
15.0	3.83	0.043	0.625	1.380
24.0	2.95	0.110	0.550	1.520

$$k_{\text{DEA}} = 0.0297 \text{ hr}^{-1}$$

TABLE B.27

RUN 27 : 20WT% DEA, 150C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	2.16	-	-	-
5.0	1.92	-	0.100	0.120
10.0	1.72	-	0.210	0.210
15.0	1.54	-	0.330	0.300
20.0	1.39	0.020	0.390	0.380
30.0	1.12	0.033	0.440	0.481
40.0	0.89	0.045	0.470	0.561
60.0	0.65	0.077	0.520	0.632
71.5	0.61	0.089	0.425	0.551
80.0	0.55	0.097	0.440	0.540
97.5	0.53	0.100	0.410	0.410

$$k_{\text{DEA}} = 0.022 \text{ hr}^{-1}$$

TABLE B.28

RUN 28 : 15WT% DEA, 150C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	1.51	-	-	-
5.0	1.45	-	0.040	0.024
10.0	1.35	-	0.082	0.063
15.0	1.29	0.0040	0.120	0.100
20.0	1.21	0.0060	0.151	0.132
30.0	1.09	0.0150	0.215	0.181
40.0	0.98	0.0220	0.221	0.238
50.0	0.92	0.0311	0.225	0.275

$$k_{\text{DEA}} = 0.0104 \text{ hr}^{-1}$$

TABLE B.29

RUN 29 : 10WT% DEA, 150C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	1.000	-	-	-
5.0	0.978	-	-	-
10.0	0.946	-	0.027	-
15.0	0.921	-	0.046	-
20.0	0.896	-	0.058	-
30.0	0.848	0.004	0.086	0.055
40.0	0.803	0.008	0.110	0.085
50.0	0.715	0.012	0.125	0.092

$$k_{\text{DEA}} = 0.0055 \text{ hr}^{-1}$$

TABLE B.30

RUN 30 : 5WT% DEA, 150C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	0.520	-	-	-
5.0	0.500	-	-	-
10.0	0.488	-	0.0142	-
15.0	0.482	-	0.0200	-
20.0	0.471	-	0.0294	0.021
30.0	0.440	0.0041	0.0421	0.035
40.0	0.413	0.0053	0.0541	0.039

$$k_{\text{DEA}} = 0.00518 \text{ hr}^{-1}$$

TABLE B.31

RUN 31 : 100WT% DEA, 120C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.00	10.0	-	-	-
19.67	9.54	-	0.580	-
43.70	8.77	-	0.992	1.160
67.70	7.98	0.0180	1.063	2.610
91.70	6.95	0.0425	1.094	3.050
120.70	5.01	0.0738	1.171	3.351
163.70	3.71	0.0975	1.170	3.548
187.70	3.21	0.1340	1.164	3.544
211.41	2.78	0.1610	1.171	3.320
236.44	2.41	0.1800	1.175	3.030

$$k_{\text{DEA}} = 0.003 \text{ hr}^{-1}$$

TABLE B.32

RUN 32 : 20WT% DEA, 120C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.0	2.150	-	-	-
20.0	2.070	-	0.060	-
40.0	2.040	-	0.150	0.050
60.0	1.930	-	0.210	0.066
80.0	1.850	-	0.275	0.104
100.0	1.710	0.0018	0.330	0.121
140.0	1.650	0.0033	0.430	0.154
160.0	1.538	0.0043	0.450	0.170
180.0	1.551	0.0056	0.470	0.180
200.0	1.510	0.0066	0.460	0.210

$$k_{\text{DEA}} = 0.0022 \text{ hr}^{-1}$$

TABLE B.33

RUN 33 : 30WT% DEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.050	-	-	-
1.0	2.290	0.0375	0.150	0.221
2.0	1.810	0.0510	0.210	0.354
3.0	1.370	0.1060	0.210	0.460
4.0	0.940	0.1560	0.190	0.461
5.0	0.760	0.2320	0.200	0.440
6.0	0.710	0.2950	0.200	0.460
8.0	0.600	0.3710	0.175	0.450
10.0	0.490	0.4252	0.150	0.400
13.0	0.410	0.5250	0.150	0.321
24.0	0.203	0.6151	0.100	0.154
27.0	0.200	0.6500	0.121	0.110
31.0	0.136	0.7000	0.125	0.091
51.0	0.075	0.7150	0.115	0.008

kDEA = 0.3 hr⁻¹

TABLE B.34

RUN 34 : 30WT% DEA, 195C, 6895 kPa (1000 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.02	-	-	-
1.00	2.38	0.021	0.400	0.205
4.00	1.28	0.131	0.395	0.850
5.25	0.95	0.179	0.394	0.780
5.93	0.77	0.221	0.375	0.780
6.83	0.62	0.249	0.355	0.750
8.00	0.56	0.272	0.375	0.654

kDEA = 0.23 hr⁻¹

TABLE B.35

RUN 35 : 30WT% DEA, 195C, 5156 kPa (800 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.00	3.00	-	-	-
0.67	2.71	0.0275	0.225	0.150
1.67	2.05	0.0353	0.375	0.450
2.67	1.71	0.0800	0.388	0.668
3.67	1.26	0.1110	0.390	0.881
4.67	0.98	0.1710	0.384	0.849
5.67	0.89	0.2060	0.384	0.765
7.17	0.64	0.2660	0.375	0.651
8.00	0.51	0.2752	0.355	0.575

$$k_{\text{DEA}} = 0.23 \text{ hr}^{-1}$$

TABLE B.36

RUN 36 : 30WT% DEA, 195C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.00	3.040	-	-	-
1.00	2.380	0.015	0.202	0.210
1.83	1.950	0.031	0.247	0.531
3.08	1.480	0.080	0.250	0.850
4.00	1.205	0.126	0.228	0.891
5.08	0.907	0.155	0.258	0.785
7.25	0.689	0.254	0.258	0.714
7.92	0.638	0.267	0.260	0.681

$$k_{\text{DEA}} = 0.23 \text{ hr}^{-1}$$

TABLE B.37

RUN 37 : 30WT% DEA, 195C, 3448 kPa (500 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.000	-	-	-
1.0	2.438	0.0055	0.128	0.076
2.0	2.188	0.0288	0.198	0.250
4.0	1.630	0.0865	0.190	0.560
5.0	1.275	0.1220	0.208	0.609
6.0	1.000	0.1560	0.200	0.660
7.0	0.935	0.2030	0.215	0.786
8.8	0.775	0.2420	0.202	0.761

$$k_{\text{DEA}} = 0.185 \text{ hr}^{-1}$$

TABLE B.38

RUN 38 : 30WT% DEA, 195C, 2758 kPa (400 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.030	-	-	-
0.92	2.610	-	0.075	0.074
2.00	2.380	0.0135	0.115	0.100
3.00	1.940	0.0475	0.145	0.380
4.08	1.780	0.0640	0.138	0.620
5.08	1.450	0.0840	0.165	0.714
6.00	1.220	0.1150	0.155	0.721
7.08	1.050	0.1560	0.145	0.691
8.17	0.985	0.1700	0.148	0.720

$$k_{\text{DEA}} = 0.154 \text{ hr}^{-1}$$

TABLE B.39

RUN 39 : 30WT% DEA, 195C, 2069 kPa (300 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.00	3.13	-	-	-
1.08	2.75	-	0.045	-
2.00	2.48	0.0090	0.081	0.051
3.58	2.24	0.0323	0.088	0.247
4.17	1.91	0.0404	0.082	0.384
5.33	1.88	0.0617	0.099	0.545
6.17	1.69	0.0910	0.088	0.650
8.00	1.41	0.1060	0.098	0.785

kDEA = 0.098 hr⁻¹

TABLE B.40

RUN 40 : 30WT% DEA, 195C, 1517 kPa (220 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.00	3.10	-	-	-
1.00	2.94	0.0030	0.020	0.021
2.09	2.73	0.0080	0.041	0.043
3.00	2.55	0.0138	0.053	0.145
4.25	2.45	0.0275	0.054	0.265
6.23	2.25	0.0374	0.053	0.451
8.00	1.96	0.0428	0.025	0.498

kDEA = 0.061 hr⁻¹

TABLE B.41

RUN 41 : 30WT% DEA, 205C, 4137 kPa (600 psi) CO₂
pH adjusted to 12.3

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.000	-	-	-
0.75	2.210	0.0425	0.180	0.248
1.83	1.500	0.1080	0.164	0.650
2.83	1.060	0.1610	0.171	0.750
3.83	0.815	0.2150	0.158	0.630
4.83	0.630	0.2640	0.138	0.710
5.50	0.540	0.3480	0.125	0.680
7.00	0.478	0.4020	0.078	0.650
8.00	0.428	0.4280	0.071	0.640

$$k_{\text{DEA}} = 0.366 \text{ hr}^{-1}$$

TABLE B.42

RUN 42 : 30WT% DEA, 205C, 4137 kPa (600 psi) CO₂
pH adjusted to 10.0

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	2.93	-	-	-
1.0	2.53	-	0.150	0.135
2.0	2.35	0.0485	0.195	0.293
3.0	1.78	0.1040	0.263	0.504
4.0	1.50	0.1450	0.258	0.485
5.0	1.41	0.2020	0.242	0.381
6.0	1.19	0.2411	0.245	0.364
8.4	1.02	0.3980	0.175	0.228

$$k_{\text{DEA}} = 0.157 \text{ hr}^{-1}$$

TABLE B.43

RUN 43 : 30WT% DEA, 205C, 4137 kPa (600 psi) CO₂
pH adjusted to 9.0

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.0	3.02	-	-	-
1.0	2.78	-	0.160	0.094
2.0	2.70	0.0125	0.204	0.193
3.0	2.68	0.0425	0.284	0.261
4.0	2.21	0.0925	0.280	0.340
5.0	2.16	0.1300	0.284	0.300
6.0	2.04	0.1950	0.288	0.280
7.0	1.92	0.2150	0.304	0.225

$$k_{\text{DEA}} = 0.0675 \text{ hr}^{-1}$$

TABLE B.44

RUN 44 : 30 WT%DEA, 205C, 4137 kPa (600 psi) N₂
0.14 g/cc K₂CO₃

No degradation took place.

TABLE B.45

RUN 45 : 30WT% DEA, 205C, 4137 kPa (600 psi) N₂
0.1227 g/cc of KHCO₃

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.0	3.10	-	-	-
2.0	2.50	-	0.062	0.550
4.0	2.02	0.0413	0.075	0.806
6.0	1.61	0.0750	0.075	0.910
8.0	1.35	0.1350	0.065	0.922
10.0	1.05	0.1560	0.045	0.910
12.0	0.86	0.2010	0.025	0.840
24.0	0.55	0.3860	-	0.571
28.0	0.47	0.4240	-	0.502
31.0	0.44	0.4322	-	0.446

$$k_{\text{DEA}} = 0.109 \text{ hr}^{-1}$$

TABLE B.46

RUN 46 : 30WT% DEA, 175C, 4137 kPa (600 psi) N₂
0.1334 g/cc of KHCO₃

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.12	-	-	-
1.0	3.00	-	0.018	0.012
2.0	2.88	-	0.031	0.048
3.4	2.76	0.0035	0.036	0.156
7.0	2.48	0.0075	0.040	0.350
13.0	2.18	0.0148	0.037	0.550
24.0	1.46	0.0650	0.036	0.810

kDEA = 0.0245 hr⁻¹

TABLE B.47

RUN 47 : 30WT% DEA, 150C, 4137 kPa (600 psi) N₂
0.218 g/cc of KHCO₃

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.10	-	-	-
6.0	2.98	-	0.0123	0.030
24.0	2.80	-	0.0231	0.246
32.8	2.61	0.0028	0.0250	0.261
47.0	2.38	0.0073	0.0250	0.440

kDEA = 0.0054 hr⁻¹

TABLE B.48

RUN 48 : 66.7WT% DEA in MDEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	6.67	-	-	-
1.00	5.80	0.010	0.130	0.410
2.00	5.20	0.028	0.175	1.000
4.33	3.10	0.114	0.218	2.060
5.00	2.79	0.143	0.230	2.180
7.37	1.86	0.268	0.213	2.100
8.75	1.42	0.296	0.210	1.910

kDEA = 0.1733 hr⁻¹

TABLE B.49

RUN 49 : 40WT% DEA in MDEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.92	-	-	-
1.0	3.26	-	0.100	0.302
3.0	2.34	0.0175	0.175	0.880
4.0	2.03	0.0398	0.201	1.210
5.1	1.58	0.0605	0.214	1.418
6.1	1.41	0.0825	0.216	1.510
8.0	1.00	0.1390	0.210	1.290

$$k_{\text{DEA}} = 0.169 \text{ hr}^{-1}$$

TABLE B.50

RUN 50 : 30WT% DEA in MDEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.10	-	-	-
1.00	2.80	-	0.070	0.036
2.00	2.34	-	0.125	0.151
3.00	2.20	-	0.141	0.212
4.10	1.71	0.0125	0.178	0.460
5.00	1.62	0.0215	0.188	0.571
6.16	1.28	0.0363	0.202	0.684
7.16	1.09	0.0563	0.208	0.775
7.84	1.03	0.0704	0.200	0.860

$$k_{\text{DEA}} = 0.145 \text{ hr}^{-1}$$

TABLE B.51

RUN 51 : 30 WT% DEA in MDEA, 175C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.000	-	-	-
2.0	2.580	-	0.091	0.100
4.0	2.214	-	0.201	0.210
6.0	1.911	0.0263	0.271	0.490
8.0	1.614	0.0514	0.304	0.580

$$k_{\text{DEA}} = 0.076 \text{ hr}^{-1}$$

TABLE B.52

RUN 52 : 30WT% DEA in MDEA, 150C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.09	-	-	-
5.0	2.82	-	0.040	-
27.3	1.96	-	0.125	0.146
51.5	1.32	0.0213	0.238	0.520

$$k_{\text{DEA}} = 0.0204 \text{ hr}^{-1}$$

TABLE B.53

RUN 53 : 30WT% DEA in MDEA, 205C, 4137 kPa (600 psi) N₂

No degradation took place over a period
of 8 hr.

TABLE B.54

RUN 54 : 30WT% DEA, 205C, 4137 kPa (600 psi) N2

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	2.96	-	-	-
7.50	2.83	0.008	-	0.040
24.00	2.77	0.018	-	0.120
31.50	2.66	0.033	-	0.210
48.00	2.52	0.053	-	0.288
74.50	2.23	0.090	-	0.420
96.00	2.14	0.140	-	0.500
105.55	1.95	0.167	-	0.530
130.05	1.85	0.220	-	0.520
155.00	1.66	0.247	-	0.500
168.50	1.60	0.283	-	0.481
179.00	1.56	0.305	-	0.440
199.04	1.50	0.345	-	0.400

kDEA = 0.00365 hr⁻¹

TABLE B.55

RUN 55 : 30WT% DEA, 250C, 4137 kPa (600 psi) N2

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	3.00	-	-	-
2.00	2.74	0.030	-	0.020
5.50	2.55	0.075	-	0.113
7.83	2.31	0.122	-	0.154
25.33	1.31	0.492	-	0.221

kDEA = 0.058 hr⁻¹

TABLE B.56

RUN 56 : 30WT% DEA, 205C, 8382 kPa (1200 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10 ⁻³			
	DEA	BHEP	HEOD	THEED
0.00	3.00	-	-	-
1.00	2.16	0.0198	0.201	0.530
3.17	1.08	0.1600	0.280	0.604
4.00	0.79	0.2060	0.261	0.531
5.25	0.53	0.3252	0.275	0.441
6.00	0.41	0.3440	0.280	0.380
7.00	0.31	0.4080	0.228	0.330
8.50	0.23	0.4963	0.223	0.275

kDEA = 0.328 hr⁻¹

TABLE B.57

RUN 56 : 5X10⁻⁴ MOLES/CC BHEP, 205C, 4137 kPa (600 psi) CO₂

No degradation observed over a period of 8 hr.

TABLE B.58

RUN 58 : 30WT% DEA + 5X10⁻⁴ MOLES/CC BHEP, 205C, 4137 kPa
(600 psi) N₂

No degradation observed over a period of 8 hr.

TABLE B.59

RUN 59 : 30WT% DEA + DEGRADATION PRODUCTS, 205C, 4137 kPa
(600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.08	0.355	0.275	0.330
1.0	2.34	0.386	0.283	0.810
2.0	1.88	0.518	0.315	1.160
3.0	1.55	0.535	0.301	1.131
4.0	1.38	0.645	0.273	0.861
5.0	1.12	0.754	0.272	0.856
6.0	0.95	0.780	0.253	0.801
7.0	0.86	0.801	0.263	0.850
8.0	0.75	0.836	0.235	0.605

kDEA = 0.26 hr⁻¹

TABLE B.60

RUN 60 : 30WT% DEA + 5X10-4 MOLES/CC BHEP, 205C, 4137 kPa
(600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.0	3.050	0.466	-	-
0.7	2.520	0.481	0.238	0.131
2.5	1.762	0.576	0.252	0.531
3.2	1.580	0.607	0.253	0.551
4.0	1.350	0.654	0.233	0.652
6.0	1.000	0.721	0.225	0.509
9.0	0.790	0.794	0.211	0.400
22.5	0.363	0.953	0.134	0.202
26.0	0.265	1.048	0.143	0.051
29.6	0.205	1.054	0.108	0.010
49.0	0.141	1.171	0.084	-

kDEA = 0.219 hr⁻¹

TABLE B.61

RUN 61 : 30WT% DEA + 5×10^{-4} MOLES/CC BHEP, 150C, 4137 kPa
(600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC $\times 10^{-3}$			
	DEA	BHEP	HEOD	THEED
0.0	3.000	0.466	-	-
10.0	2.230	0.501	0.368	0.171
25.0	1.301	0.523	0.541	0.754
40.0	0.881	0.556	0.560	1.042
60.0	0.572	0.584	0.534	1.021

$$k_{\text{DEA}} = 0.0301 \text{ hr}^{-1}$$

TABLE B.62

RUN 62 : 3×10^{-3} MOLES/CC HEOD, 205C, 4137 kPa (600 psi) N₂

After 1 hr the analysis showed the presence of
HEOD, DEA, THEED, and a trace of BHEP.

TABLE B.63

RUN 63 : 10WT% DEA + 0.425×10^{-3} MOLES/CC HEOD, 205C, 4137 kPa
(600 psi) N₂

SAMPLE hr	CONC. MOLES/CC $\times 10^{-3}$			
	DEA	BHEP	HEOD	THEED
0.0	1.040	-	0.425	-
2.0	1.000	0.0113	0.178	0.091
5.0	0.938	0.0235	0.083	0.187
8.0	0.825	0.0275	0.040	0.238

TABLE B.64

RUN 64 : 15WT% DEA + DEGRADATION PRODUCTS, 175C, 4137 kPa
(600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	1.42	0.0275	0.398	0.970
1.00	1.44	0.0463	0.413	1.011
2.23	1.31	0.0701	0.435	1.118
3.00	1.19	0.0825	0.434	1.150
5.00	1.10	0.1160	0.450	1.181
6.23	1.04	0.1400	0.442	1.171
7.00	1.00	0.1580	0.444	1.063
8.00	0.97	0.1740	0.448	0.984

TABLE B.65

RUN 65 : 15WT% DEA + DEGRADATION PRODUCTS, 175C, 4137 kPa
(600 psi) N₂

SAMPLE hr	CONC. MOLES/CC X10-3			
	DEA	BHEP	HEOD	THEED
0.00	1.52	0.0275	0.398	0.970
1.00	1.50	0.0428	0.285	1.041
1.57	1.46	0.0450	0.253	1.101
3.00	1.43	0.0664	0.235	1.160
4.00	1.32	0.0780	0.201	1.202
5.00	1.29	0.0963	0.193	1.225
6.12	1.24	0.1130	0.180	1.250
7.00	1.20	0.1311	0.188	1.244
8.42	1.18	0.1580	0.191	1.252

TABLE B.66

RUN 66 : 2.6×10^{-3} MOLES/CC THEED, 205C, 4137 kPa (600 psi) CO₂

After 1 hr the only product produced was BHEP
($\sim 0.6 \times 10^{-3}$ moles/cc).

TABLE B.67

RUN 67 : 2.6×10^{-3} MOLES/CC THEED, 205C, 4137 kPa (600 psi) N₂

After 1 hr a trace amount of BHEP was produced
($\sim 0.12 \times 10^{-3}$ moles/cc).

TABLE B.68

RUN 68 : 12WT% DEA + 2.6×10^{-3} MOLES/CC THEED, 205C, 4137 kPa
(600 psi) N₂

SAMPLE hr	CONC. MOLES/CC $\times 10^{-3}$			
	DEA	BHEP	HEOD	THEED
0.00	1.210	-	-	2.580
1.00	1.200	0.210	-	2.450
2.67	1.204	0.440	-	2.160
4.00	1.212	0.565	-	2.080
5.75	1.208	0.670	-	1.860
8.33	1.211	0.861	-	1.630

TABLE B.69

RUN 65 : 12WT% DEA + 2.6×10^{-3} MOLES/CC THEED, 205C, 4137 kPa
(600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC $\times 10^{-3}$			
	DEA	BHEP	HEOD	THEED
0.00	1.180	-	-	2.580
1.00	1.151	0.371	0.285	2.021
2.00	1.111	0.673	0.330	1.560
3.75	1.068	1.018	0.233	1.061
6.33	0.971	1.260	0.185	0.860
7.67	0.875	1.450	0.203	0.731

TABLE B.70

RUN 70 : 30WT% MEA, 205C, 4137 kPa (600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC $\times 10^{-3}$		
	MEA	HEI*	HEED*
0.0	5.490	-	-
1.0	4.689	80.6	1.3
2.0	4.115	441.6	10.5
3.0	3.689	556.1	12.5
4.0	3.230	698.8	37.7
5.0	2.670	850.4	40.5
6.0	2.246	1028.0	44.8
7.0	2.082	1283.0	83.8
8.0	1.705	1233.0	110.4

*Conc. as peak area

Trace amounts of ozd detected

TABLE B.71

RUN 71 : 30WT% TEA, 205C, 4137 kPa (600 psi) CO₂

No degradation observed over a period
of 8 hr.

TABLE B.72

RUN 72 : 10WT% MEA + 25WT% DEA, 205C, 4137 kPa(600 psi) CO₂

SAMPLE hr	CONC. MOLES/CC X10-3				
	MEA	DEA	BHEP	HEOD	THEED
0.0	1.639	2.540	-	-	-
0.5	1.540	2.520	-	0.063	-
1.0	1.210	2.050	0.015	0.101	0.108
2.3	0.967	1.700	0.043	0.124	0.203
3.0	0.803	1.480	0.136	0.145	0.400
4.0	0.672	1.200	0.202	0.125	0.400
5.0	0.541	1.060	0.281	0.125	0.401
6.0	0.451	0.841	0.318	0.120	0.379
7.0	0.410	0.800	0.374	0.120	0.362
23.5	0.230	0.530	0.389	0.095	0.188

hr	HEP*	BHEEP*	HEI*	BHEI*
0.0	-	-	-	-
0.5	-	104.7	-	-
1.0	-	355.0	-	-
2.3	3.3	497.3	49.0	21.0
3.0	37.2	656.2	72.7	141.0
4.0	40.0	617.1	91.0	182.0
5.0	51.5	580.9	127.0	108.0
6.0	63.0	502.3	120.0	137.0
7.0	64.9	487.3	129.0	164.4
23.5	89.0	282.7	193.6	192.0

*Conc. as peak area

TABLE B.73

RUN 73 : 10WT% TEA + 20WT% DEA, 205C, 4137 kPa(600 psi) CO2

SAMPLE hr	CONC. MOLES/CC X10-3					
	TEA	DEA	BHEP	HEOD	THEED	TEHEED*
0.0	0.671	2.00	-	-	-	-
2.0	0.670	1.08	-	0.133	0.230	10.0
4.0	0.662	0.84	0.113	0.135	0.510	21.1
6.0	0.654	0.47	0.250	0.134	0.433	35.0
8.0	0.649	0.41	0.282	0.131	0.301	51.4

*Conc. as peak area

APPENDIX C

The solubility of CO₂ in DEA solutions at high temperature and pressure

Some knowledge of the solubility of CO₂ under operating conditions was required in order to carry out the ionic experiments in section 9.2.

Unfortunately the open literature did not provide the required information. Therefore, a series of simple solubility experiments were performed to provide the necessary data.

C.1 Experimental method

Essentially the method consisted of:

1. Filling a 2 L high pressure bomb to 5156 kPa (800psi) with CO₂ and then weighing the bomb and CO₂. The scales were accurate for changes of down to 0.2 g.
2. The 600 ml autoclave (see sect. 6.1) was charged with 450 ml of a specified aqueous DEA solution and sealed. The autoclave was then heated to the required temperature with the stirrer in operation at about 150 r.p.m.
3. The bomb was then connected to the autoclave and CO₂ was fed into the autoclave to the required pressure. After equilibrium had been reached the bomb was disconnected.
4. The bomb was then reweighed and the weight of CO₂ fed to the autoclave noted.
5. The above procedure was repeated many times to cover the following range of conditions:
 - a) DEA concentration:- 30, 20, and 10 wt %
 - b) Temperature:- 205-100°C
 - c) Overall pressure: 413.7-4137 kPa (60-600 psi)

It should be noted that overall pressure in the autoclave was made up

from the partial pressure of CO_2 and the vapour pressure of the water vapour from the aqueous DEA solution and to a very small extent from the DEA itself. For example at 205°C the vapour pressure of pure water is 1700 kPa (246.6 psi) and the vapour pressure of DEA is 8.6 kPa (1.25 psi). Therefore to determine the partial pressure of CO_2 in the autoclave a knowledge of the vapour pressure of the aqueous DEA solution was required. To determine the vapour pressure the following simple experiments were performed. A specified concentration of DEA was charged to the autoclave. The autoclave was heated to a specified temperature and the pressure noted. The temperature was then raised and the pressure noted again. This was repeated up to 205°C . Table C.1 gives the results which are plotted in Figure C.1.

Table C.1 Vapour pressure of DEA solutions as a function of temperature

Temp. $^\circ\text{C}$	Vapour pressure psi							
	DEA conc. wt %							
	0		10		20		30	
	psi	kPa	psi	kPa	psi	kPa	psi	kPa
100	14.69	101.3	14.69	101.3	14.69	101.3	14.69	101.3
120	29.40	202.7	28.69	197.8	27.0	186.2	24.43	168.4
140	54.96	379.0	52.57	362.5	49.1	338.5	43.57	300.4
160	92.50	637.8	88.14	607.7	82.29	567.4	71.93	496.0
180	148.96	1027.1	142.86	985.	133.29	919.0	121.43	837.3
200	227.50	1568.6	221.29	1525.8	214.29	1477.5	196.14	1352.4
210	285.9	1971.3	273.43	1885.3	259.71	1790.7	243.29	1677.5

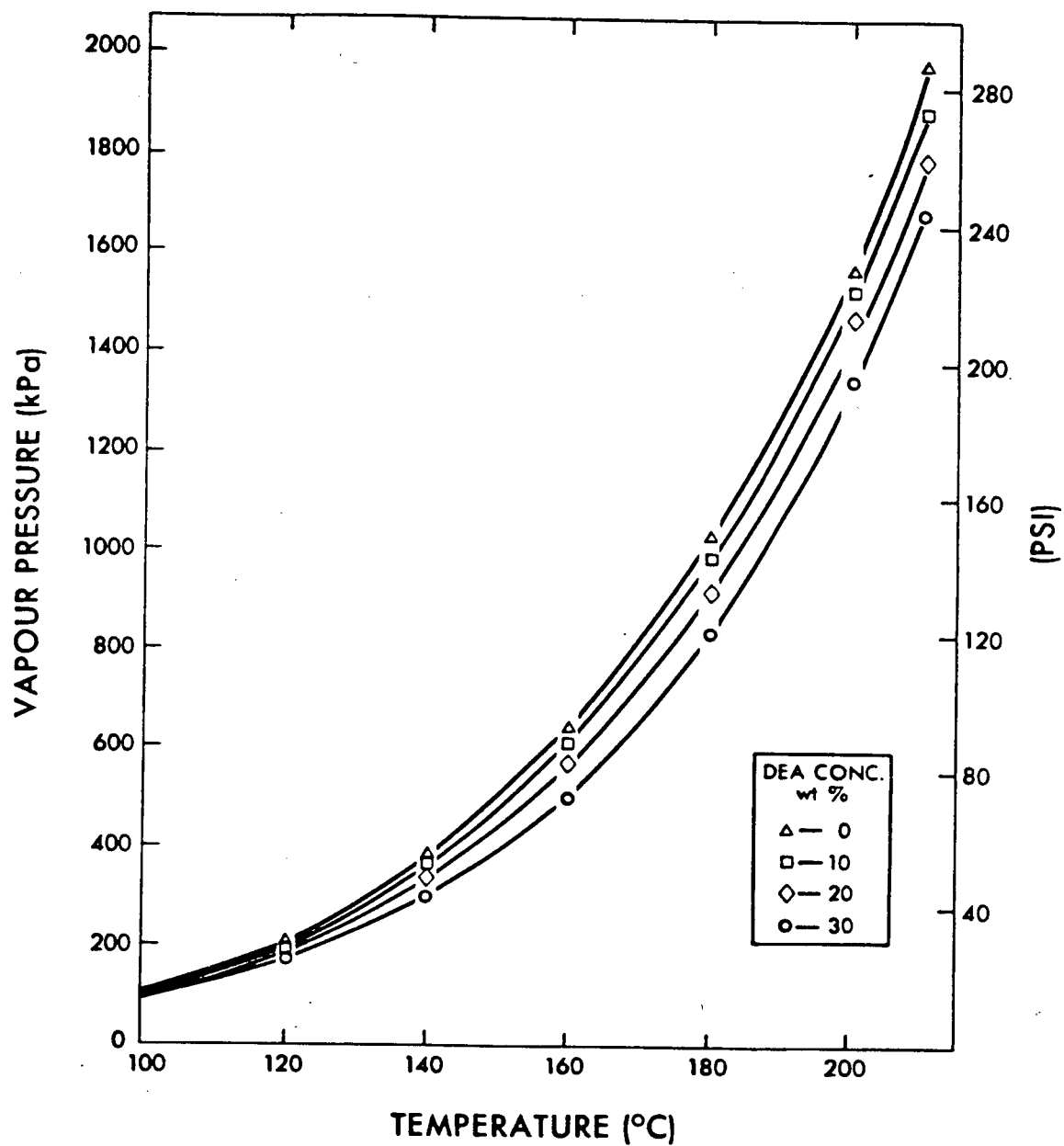


Figure C.1 DEA solution vapour pressure as a function of temperature and DEA concentration

C.2 Calculation of CO₂ solubility

From the knowledge of the total weight of CO₂ used, total pressure in reactor, vapour pressure of aqueous DEA solution, temperature and concentration of DEA, the solubility of CO₂ was calculated as g of CO₂/g of DEA using the following method.

The main problem was to determine the mass of CO₂ in the vapour phase. It was first assumed the mixture of CO₂, water vapour, and DEA vapour was ideal and the partial pressure of each component was proportional to its molar concentration. Therefore to determine the partial pressure of CO₂ in the vapour phase the vapour pressure of the aqueous DEA solution was simply subtracted from the total pressure, i.e.,

$$P.P.CO_2 = P_{total} - V.P.DEA \text{ solution} \quad [C.1]$$

Knowing the partial pressure of CO₂, the volume of the vapour phase (i.e., 600-450 ml = 150 ml) and the temperature; the number of moles of CO₂ could be calculated using an equation of state. Since for the range of conditions studied the compressibility factor for CO₂ lay in the range 0.99-0.92 it could be assumed CO₂ existed as an ideal gas. The Van der Waals equation of state was used to calculate the number of moles.

$$\left(P + \frac{n^2 a}{V^2}\right) (V - nb) = nRT \quad [C.2]$$

Although there are more accurate equations of state available, the Van der Waals relation is still useful for providing an approximate yet simple, analytical representation of the behaviour of a gas.

Once the number of moles of CO₂ in the vapour phase had been determined the mass of CO₂ in the DEA solution could simply be obtained by subtracting the vapour phase mass of CO₂ from the total mass of CO₂ fed to the autoclave, i.e.,

$$\begin{aligned}
 &\text{Mass of CO}_2 \text{ dissolved in DEA solution} \\
 &= \text{total mass of CO}_2 \text{ fed to autoclave} \\
 &\quad - \text{mass of CO}_2 \text{ in vapour phase}
 \end{aligned}
 \tag{C.3}$$

From the mass of CO₂ dissolved in the aqueous DEA solution the solubility of CO₂ as g CO₂/g DEA could be easily calculated.

C.3 Example

The following shows how the solubility of CO₂ in a 30 wt % DEA solution at 205°C under a total pressure of 4137 kPa (600 psi) was calculated.

Total weight of CO₂ fed to autoclave = 31.5 g

Volume of Reactor = 625 cc

Volume of Solution = 410 cc

Volume of CO₂ = 215 cc

Density of 30 wt % DEA = 1.088

Wt of DEA in solution = 133.9 g

a) At 205°C the vapour pressure of 30 wt % DEA = 1510 kPa (219 psi)

the partial pressure of CO₂ in the vapour phase

$$= 4137 - 1510$$

$$= 2627 \text{ kPa (381 psi)}$$

b) 2627 kPa (381 psi) of CO₂ at 205°C in a volume of 215 cc corresponds to a mass of n moles using Eqn. C.2.

$$P = 2627 \text{ kPa (381 psi)} = 25.94 \text{ atm}$$

$$V = 0.215 \text{ L}$$

$$T = 205^\circ\text{C} = 478^\circ\text{K}$$

$$R = 0.082055 \text{ L atm/}^\circ\text{K mole}$$

For CO₂ :-

$$a = 3.59 \text{ L}^2 \text{ atm/mole}^2$$

$$b = 0.0427 \text{ L/mole}$$

Eqn. C.2 becomes

$$\begin{aligned} (25.94 + \frac{n^2 \cdot 3.59}{(0.215)^2}) (0.215 - n(0.0427)) \\ = n \times 0.082055 \times 478 \end{aligned}$$

$$n = 0.151 \text{ moles}$$

$$= 6.47 \text{ g}$$

c) The mass of CO₂ dissolved in the DEA solution is:

$$31.5 - 6.47 = 25.03 \text{ g}$$

d) Therefore the solubility of CO₂ is:-

$$\frac{25.03}{133.9} = 0.187 \text{ g CO}_2/\text{g DEA}$$

It is realized that the calculation of the mass of CO₂ in the vapour phase may be somewhat inaccurate. However, when it is noted that the mass of CO₂ in the vapour phase is usually less than 30% of the CO₂ dissolved in the liquid phase then errors of about $\pm 24\%$ in the vapour phase CO₂ mass will only cause an error of about $\pm 10\%$ in the calculation of solubility. An accuracy of $\pm 10\%$ is considered suitable for these studies.

C.4 Results

The following tables give the solubility of CO₂ in DEA solutions at varying temperature and total pressure as a function of CO₂ partial pressure in the vapour phase. Figures 9.2 to 9.4 in section 9.2 summarize these tabulated results.

TABLE C.2
SOLUBILITY OF CO₂ IN 30WT% DEA

TEMP. C	TOTAL PRESSURE		PARTIAL PRESSURE OF CO ₂		SOLUBILITY OF CO ₂ gCO ₂ /gDEA
	psi	kPa	psi	kPa	
200	550.0	3793.3	400.7	2762.9	0.183
"	405.0	2792.5	208.7	1439.0	0.114
"	275.0	1896.1	78.7	542.6	0.089
190	470.0	3240.7	375.3	2587.7	0.190
"	350.0	2413.3	194.3	1340.0	0.120
"	236.0	1627.2	80.3	553.7	0.081
180	400.0	2758.0	350.6	2417.4	0.192
"	295.0	2034.0	173.6	1197.0	0.123
"	196.0	1351.4	74.6	514.4	0.090
170	520.0	3585.4	427.1	2945.0	0.236
"	338.0	2330.5	310.1	2138.2	0.202
"	245.0	1689.3	152.1	1048.7	0.128
"	160.0	1103.2	67.1	462.7	0.090
160	452.0	3136.5	379.7	2618.0	0.240
"	290.0	2000.0	250.7	1728.6	0.200
"	195.0	1334.5	122.7	846.0	0.132
"	132.0	910.1	59.7	411.6	0.094
150	600.0	4137.0	543.4	3746.7	0.312
"	360.0	2482.2	301.4	2078.2	0.240
"	250.0	1723.8	193.4	1333.5	0.195
"	152.0	1048.0	95.4	657.8	0.137
"	105.0	723.9	48.4	333.7	0.104
140	508.0	3502.7	464.6	3203.4	0.328
"	291.0	2006.4	247.6	1707.2	0.248
"	220.0	1516.9	176.6	1217.7	0.209
"	118.0	813.6	74.6	514.4	0.141
"	83.0	572.3	39.6	273.0	0.106
130	445.0	3068.3	412.7	2845.6	0.330
"	240.0	1654.8	207.7	1432.1	0.249
"	177.0	1220.4	145.0	999.8	0.210
"	90.0	620.6	57.0	393.0	0.144
"	65.0	448.2	32.7	225.5	0.111
120	555.0	3826.7	530.7	3659.2	0.376
"	410.0	2826.9	385.7	2659.4	0.330
"	200.0	1379.0	175.7	1210.1	0.248
"	140.0	965.3	115.7	797.8	0.212
"	68.0	468.9	43.7	301.3	0.147
"	45.5	313.7	21.2	146.7	0.111
110	510.0	3516.5	491.4	3388.2	0.381
"	390.0	2689.1	371.4	2560.8	0.344
"	170.0	1172.2	151.4	1043.9	0.256
"	119.0	820.5	100.4	692.3	0.215
"	53.0	365.4	34.4	237.2	0.149
"	32.6	224.8	14.0	96.5	0.108
100	475.0	3275.1	461.6	3182.7	0.392
"	355.0	2447.7	341.6	2355.3	0.355
"	150.0	1034.3	136.6	941.9	0.264
"	89.0	613.7	75.6	521.3	0.217
"	40.0	275.8	26.6	183.4	0.149
"	24.0	165.5	10.6	73.1	0.108

TABLE C.3
SOLUBILITY OF CO2 IN 20WT% DEA

TEMP. C	TOTAL PRESSURE		PARTIAL PRESSURE OF CO2		SOLUBILITY OF CO2 gCO2/gDEA
	psi	kPa	psi	kPa	
200	560.0	3861.2	353.3	2436.0	0.198
"	405.0	2792.5	198.3	1367.3	0.152
"	307.0	2116.8	100.3	691.6	0.112
190	503.0	3468.2	338.2	2331.9	0.200
"	342.0	2358.1	183.2	1263.2	0.154
"	246.0	1696.2	87.2	601.2	0.115
180	436.0	3006.2	305.0	2103.0	0.205
"	286.0	1972.0	155.1	1069.4	0.159
"	214.0	1475.5	83.1	573.0	0.123
170	552.0	3806.0	450.5	3106.2	0.255
"	378.0	2606.3	276.5	1906.5	0.211
"	238.0	1641.0	136.5	941.2	0.162
"	180.0	1241.1	78.5	541.3	0.129
160	489.0	3371.7	410.0	2827.0	0.270
"	314.0	2165.0	235.0	1620.3	0.226
"	190.0	1310.1	111.0	765.3	0.168
"	140.0	965.3	61.0	420.6	0.142
150	600.0	4137.0	538.5	3713.0	0.315
"	426.0	2937.3	364.5	2513.2	0.280
"	256.0	1765.1	194.5	1341.1	0.236
"	150.0	1034.3	88.5	610.2	0.183
"	108.0	744.7	46.5	320.6	0.144
140	525.0	3619.9	477.7	3293.7	0.330
"	364.0	2509.8	316.7	2182.7	0.290
"	217.0	1496.2	169.7	1156.3	0.240
"	115.0	792.9	67.7	466.8	0.177
"	82.0	565.4	34.7	239.3	0.146
130	469.0	3233.8	433.7	2990.4	0.339
"	301.0	2075.4	265.7	2521.5	0.295
"	186.0	1282.5	150.7	1039.1	0.248
"	86.0	593.0	50.7	349.6	0.183
"	61.0	420.6	25.7	177.7	0.148
120	516.0	3557.8	490.0	3378.6	0.381
"	410.0	2827.0	384.0	2647.7	0.351
"	266.0	1834.1	240.0	1654.2	0.306
"	156.0	1075.6	130.0	896.4	0.257
"	68.5	472.3	42.5	293.0	0.185
"	47.0	324.1	21.0	144.8	0.150
110	470.0	3240.7	450.5	3106.2	0.391
"	367.0	2530.5	347.5	2396.0	0.357
"	220.0	1516.9	200.5	1382.5	0.315
"	137.0	944.6	117.5	810.2	0.270
"	54.5	375.8	35.0	241.3	0.190
"	35.0	241.3	15.5	106.9	0.153
100	414.0	2854.5	400.2	2759.4	0.404
"	327.0	2254.7	313.2	2159.5	0.365
"	199.0	1372.1	185.2	1276.9	0.318
"	113.8	784.6	100.0	689.5	0.275
"	42.0	289.6	28.2	194.4	0.197
"	27.0	186.2	13.2	91.0	0.156

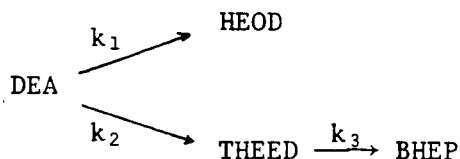
TABLE C.4
SOLUBILITY OF CO₂ IN 10WT% DEA

TEMP. C	TOTAL PRESSURE		PARTIAL PRESSURE OF CO ₂		SOLUBILITY OF CO ₂ gCO ₂ /gDEA
	psi	kPa	psi	kPa	
200	555.0	3826.7	337.9	2329.8	0.279
"	418.0	2882.1	200.9	1385.2	0.246
"	275.0	1896.0	70.9	488.9	0.185
190	495.0	3413.0	321.3	2214.7	0.290
"	363.0	2502.9	189.2	1303.2	0.249
"	238.0	1641.0	64.2	442.7	0.189
180	431.0	2971.7	290.5	2003.0	0.295
"	310.0	2137.5	169.5	1168.7	0.257
"	198.0	1365.2	57.5	369.5	0.191
170	555.0	3826.7	444.9	3067.6	0.338
"	380.0	2620.1	269.9	1861.0	0.300
"	262.0	1806.5	151.9	1047.4	0.262
"	163.0	1123.9	52.9	364.7	0.193
160	482.0	3323.4	396.2	2731.8	0.352
"	332.0	2289.1	246.2	1697.5	0.316
"	218.0	1503.1	132.2	911.5	0.270
"	130.0	896.4	44.2	304.8	0.196
150	600.0	4137.0	533.5	3678.5	0.423
"	416.0	2868.3	349.5	2409.8	0.376
"	281.0	1937.5	214.5	1479.0	0.334
"	181.0	1248.0	114.5	789.5	0.279
"	103.0	710.2	36.5	251.7	0.200
140	533.0	3675.0	481.9	3322.7	0.464
"	360.0	2482.2	295.9	2040.2	0.396
"	232.0	1599.6	180.9	1247.3	0.349
"	147.0	1013.6	95.9	661.2	0.287
"	80.0	551.6	28.9	199.3	0.200
130	478.0	3295.8	439.6	3031.0	0.482
"	312.0	2151.2	273.6	1886.5	0.408
"	193.0	1330.7	154.6	1066.0	0.355
"	123.4	850.8	85.0	586.1	0.292
"	62.0	427.5	23.6	162.7	0.205
120	566.0	3902.6	538.3	3711.6	0.558
"	435.0	2999.3	407.3	2808.3	0.510
"	266.0	1834.1	238.3	1645.1	0.430
"	163.0	1123.9	135.3	932.9	0.370
"	98.0	675.7	70.3	484.7	0.300
"	47.0	324.1	19.3	133.1	0.200
110	510.0	3516.5	489.6	3375.8	0.580
"	392.0	2702.9	371.6	2562.2	0.530
"	226.0	1558.3	205.6	1417.6	0.435
"	136.0	937.7	115.6	797.1	0.376
"	81.0	558.5	60.6	417.8	0.303
"	38.0	262.0	17.6	121.4	0.207
100	463.0	3192.4	448.7	3093.8	0.598
"	353.0	2434.0	338.7	2334.4	0.540
"	192.0	1324.0	177.7	1255.2	0.450
"	120.0	827.4	105.7	728.8	0.382
"	65.0	448.2	50.7	349.6	0.305
"	29.0	200.0	15.3	105.5	0.208

APPENDIX D

Derivation of the kinetic model

Using the simplified degradation route developed in section 12.1,
i.e.,



the following equations were derived for the rate of change of the various compounds.

$$\frac{d[\text{DEA}]}{dt} = -k_1[\text{DEA}] - k_2[\text{DEA}] \quad [\text{D.1}]$$

or
$$\frac{d[\text{DEA}]}{dt} = -k_{\text{DEA}}[\text{DEA}] \quad [\text{D.2}]$$

where
$$k_{\text{DEA}} = k_1 + k_2 \quad [\text{D.3}]$$

$$\frac{d[\text{HEOD}]}{dt} = k_1[\text{DEA}] \quad [\text{D.4}]$$

$$\frac{d[\text{THEED}]}{dt} = k_2[\text{DEA}] - k_3[\text{THEED}] \quad [\text{D.5}]$$

$$\frac{d[\text{BHEP}]}{dt} = k_3[\text{THEED}] \quad [\text{D.6}]$$

Integrating Eqn. D.1 yields

$$[\text{DEA}]_t = [\text{DEA}]_0 e^{-(k_1+k_2)t} \quad [\text{D.7}]$$

Equation D.4 was then integrated:

$$\begin{aligned}
 \frac{d[\text{HEOD}]}{dt} &= k_1[\text{DEA}]_t = k_1[\text{DEA}]_0 e^{-(k_1+k_2)t} \\
 [\text{HEOD}]_t &= k_1[\text{DEA}]_0 \left[-\frac{1}{k_1+k_2} e^{-(k_1+k_2)t} \right]_0^t \\
 [\text{HEOD}]_t &= [\text{DEA}]_0 \frac{k_1}{k_1+k_2} (1 - e^{-(k_1+k_2)t}) \quad [\text{D.8}]
 \end{aligned}$$

Equation D.5 was integrated as follows:

$$\frac{d[\text{THEED}]}{dt} + k_3[\text{THEED}]_t = k_2[\text{DEA}]_0 e^{-(k_1+k_2)t}$$

This is a first-order linear differential equation which can be multiplied by the integrating factor $e^{k_3 t}$.

$$\begin{aligned}
[\text{THEED}]_t e^{k_3 t} &= k_2 [\text{DEA}]_0 \int_0^t e^{(k_3 - (k_1 + k_2))t} dt \\
&= k_2 [\text{DEA}]_0 \left[\frac{1}{k_3 - (k_1 + k_2)} e^{(k_3 - (k_1 + k_2))t} \right]_0^t \\
[\text{THEED}]_t &= [\text{DEA}]_0 \frac{k_2}{k_3 - (k_1 + k_2)} (e^{-(k_1 + k_2)t} - e^{-k_3 t}) \quad [\text{D.9}]
\end{aligned}$$

Equation D.6 was then solved.

$$\begin{aligned}
\frac{d[\text{BHEP}]}{dt} &= k_3 [\text{THEED}]_t = k_3 [\text{DEA}]_0 \frac{k_2}{k_3 - (k_1 + k_2)} (e^{-(k_1 + k_2)t} - e^{-k_3 t}) \\
[\text{BHEP}]_t &= [\text{DEA}]_0 \frac{k_2 k_3}{k_3 - (k_1 + k_2)} \left[-\frac{1}{(k_1 + k_2)} e^{-(k_1 + k_2)t} + \frac{1}{k_3} e^{-k_3 t} \right]_0^t \\
&= [\text{DEA}]_0 \frac{k_2 k_3}{k_3 - (k_1 + k_2)} \left[\frac{(k_1 + k_2) e^{-k_3 t} - k_3 e^{-(k_1 + k_2)t}}{k_3 (k_1 + k_2)} \right]_0^t
\end{aligned}$$

This simplifies to:

$$[\text{BHEP}]_t = [\text{DEA}]_0 \frac{k_2}{k_1 + k_2} \left(1 - \frac{k_3}{k_3 - (k_1 + k_2)} e^{-(k_1 + k_2)t} + \frac{k_1 + k_2}{k_3 - (k_1 + k_2)} e^{-k_3 t} \right) \quad [\text{D.10}]$$

In many cases the plots of [THEED] versus time pass through a maximum. The location of this maxima can be found by differentiating Eqn. D.9 and setting $d[\text{THEED}]/dt = 0$. The time at which the maximum concentration of THEED occurs is thus:

$$\begin{aligned}
\frac{d[\text{THEED}]}{dt} &= \frac{[\text{DEA}]_0 k_2}{k_3 - (k_1 + k_2)} (-(k_1 + k_2) e^{-(k_1 + k_2)t} + k_3 e^{-k_3 t}) = 0 \\
\therefore \frac{e^{-(k_1 + k_2)t} \max}{e^{-k_3 t} \max} &= \frac{k_3}{(k_1 + k_2)} \\
t \max &= \frac{\ln(k_3 / (k_1 + k_2))}{k_3 - (k_1 + k_2)} \quad [\text{D.11}]
\end{aligned}$$

The maximum concentration of THEED can be found by combining Eqns. D.9 and D.11:

$$[\text{THEED}]_{\max} = \frac{[\text{DEA}]_0 k_2}{k_3 - (k_1 + k_2)} \left[e^{-\frac{(k_2 + k_1)}{k_3 - (k_2 + k_1)} \cdot \ln\left(\frac{k_3}{k_2 + k_1}\right)} - e^{-\frac{k_3}{k_3 - (k_2 + k_1)} \cdot \ln\left(\frac{k_3}{k_1 + k_2}\right)} \right]$$

This simplifies to:

$$\frac{[\text{THEED}]_{\max}}{[\text{DEA}]_0} = \frac{k_2}{k_2 + k_1} \left(\frac{k_2 + k_1}{k_3} \right)^{\frac{k_3}{k_3 - (k_1 + k_2)}} \quad [\text{D.12}]$$

APPENDIX EComparison between the experimental results and the prediction of the kinetic model

The following tables compare the experimentally measured values of DEA, BHEP, HEOD, and THEED concentrations with the values predicted by the kinetic model developed in chapter 12. For all the tables the concentration in moles/cc and all k values are given in hr^{-1} . For each case the total operating pressure is 4137 kPa (600 psi).

TABLE E.1

COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 60WT% DEA DEGRADED AT 175C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	6.000	6.000	-	-
1.0	5.350	5.330	-	0.0080
2.0	4.810	4.741	0.0350	0.0321
3.0	4.250	4.211	0.0651	0.0678
4.0	3.741	3.740	0.0920	0.1161
5.0	3.380	3.330	0.1150	0.1718
6.0	3.210	2.960	0.1800	0.2360
7.0	2.650	2.630	0.2060	0.3060
8.0	2.251	2.334	0.2511	0.3820

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
1.0	0.190	0.205	0.300	0.454
2.0	0.360	0.380	0.940	0.842
3.0	0.451	0.550	1.400	1.171
4.0	0.450	0.670	1.661	1.453
5.0	0.440	0.822	1.840	1.682
6.0	0.420	0.935	1.914	1.870
7.0	0.431	0.950	1.980	2.030
8.0	0.398	1.010	2.150	2.150

$k_{DEA} = 0.118$
 $k_1 = 0.0363$
 $k_2 = 0.0817$
 $k_3 = 0.0360$

TABLE E.2

COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 60WT% DEA DEGRADED AT 150C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	6.000	6.000	-	-
2.0	5.660	5.650	-	-
4.0	5.300	5.330	-	-
6.0	5.000	5.022	0.0090	0.0076
8.0	4.710	4.730	0.0110	0.0101
10.0	4.460	4.460	0.0210	0.0200
15.0	3.830	3.240	0.0430	0.0430
24.0	2.950	2.940	0.1100	0.1010

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
2.0	0.110	0.127	0.210	0.218
4.0	0.230	0.247	0.400	0.422
6.0	0.383	0.359	0.650	0.612
8.0	0.460	0.466	0.850	0.790
10.0	0.541	0.566	1.000	0.956
15.0	0.625	0.792	1.380	1.320
24.0	0.550	1.120	1.520	1.840

kDEA = 0.0297

k1 = 0.0109

k2 = 0.0188

k3 = 0.0040

TABLE E.3
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 30WT% DEA DEGRADED AT 175C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	3.040	3.040	-	-
1.0	2.670	2.660	-	-
2.0	2.360	2.360	-	0.0139
3.0	2.000	2.051	0.0150	0.0350
4.0	1.840	1.849	0.0280	0.0500
5.0	1.580	1.610	0.0580	0.0611
6.0	1.440	1.450	0.0620	0.1030
8.0	1.110	1.130	0.0980	0.1700
10.0	0.860	0.895	0.2060	0.2370
12.0	0.651	0.702	0.2200	0.3120
14.0	0.520	0.550	0.2840	0.3810

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
1.0	0.150	0.134	0.130	0.200
2.0	0.250	0.253	0.280	0.380
3.0	0.360	0.358	0.450	0.525
4.0	0.410	0.451	0.660	0.650
6.0	0.425	0.534	0.760	0.750
8.0	0.485	0.729	0.910	0.970
10.0	0.541	0.825	1.050	1.044
12.0	0.550	0.850	0.990	1.066
14.0	0.540	0.870	0.960	1.025

kDEA = 0.1210

k1 = 0.0474

k2 = 0.0736

k3 = 0.0350

TABLE E.4
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS:
FOR 30WT% DEA DEGRADED AT 162C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	3.000	3.000	-	-
1.0	2.803	2.800	-	-
2.0	2.620	2.610	-	-
3.0	2.450	2.410	0.0101	0.0073
4.0	2.280	2.240	0.0150	0.0126
5.0	2.137	2.120	0.0201	0.0194
6.0	2.000	1.975	0.0254	0.0270
7.0	1.870	1.880	0.0350	0.0354
8.0	1.744	1.720	0.0420	0.0460

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
1.0	0.105	0.075	0.090	0.120
2.0	0.200	0.146	0.200	0.230
3.0	0.275	0.212	0.290	0.330
4.0	0.320	0.273	0.388	0.426
5.0	0.364	0.330	0.460	0.513
6.0	0.412	0.385	0.561	0.591
7.0	0.420	0.435	0.653	0.663
8.0	0.450	0.482	0.731	0.730

kDEA = 0.0678

k1 = 0.0260

k2 = 0.0418

k3 = 0.0140

TABLE E.5
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 30WT% DEA DEGRADED AT 150C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	3.000	3.000	-	-
5.0	2.600	2.600	0.0098	0.0024
10.0	2.200	2.200	0.0210	0.0100
15.0	1.860	1.881	0.0380	0.0190
20.0	1.560	1.610	0.0425	0.0322
25.0	1.310	1.380	0.0550	0.0480
30.0	1.110	1.180	0.0640	0.0652
40.0	0.840	0.868	0.0860	0.0980
50.0	0.710	0.637	0.1060	0.1090
60.0	0.580	0.480	0.1300	0.1490

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
5.0	0.250	0.197	0.075	0.231
10.0	0.350	0.366	0.150	0.424
15.0	0.470	0.501	0.400	0.560
20.0	0.510	0.640	0.652	0.719
25.0	0.550	0.740	0.751	0.830
30.0	0.570	0.830	0.900	0.920
40.0	0.570	0.980	1.075	1.059
50.0	0.542	1.050	1.225	1.132
60.0	0.540	1.070	1.200	1.189

$k_{DEA} = 0.0316$
 $k_1 = 0.0142$
 $k_2 = 0.0168$
 $k_3 = 0.0040$

TABLE E.6
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 30WT% DEA DEGRADED AT 140C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	3.000	3.000	-	-
10.0	2.850	2.850	-	-
20.0	2.540	2.500	0.0120	0.0042
30.0	2.260	2.200	0.0210	0.0110
40.0	2.000	2.000	0.0330	0.0180
50.0	1.754	1.745	0.0415	0.0370
60.0	1.605	1.560	0.0510	0.0480
80.0	1.270	1.240	0.0700	0.0650
100.0	1.010	0.980	0.1050	0.0890

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
10.0	0.250	0.171	0.120	0.176
20.0	0.450	0.322	0.320	0.330
30.0	0.575	0.460	0.504	0.466
40.0	0.660	0.576	0.581	0.584
50.0	0.710	0.700	0.700	0.700
60.0	0.710	0.780	0.751	0.775
80.0	0.660	0.940	0.863	0.921
100.0	0.700	1.060	0.950	1.031

$k_{DEA} = 0.01150$
 $k_1 = 0.00563$
 $k_2 = 0.00587$
 $k_3 = 0.00140$

TABLE E.7
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 30WT% DEA DEGRADED AT 120C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	3.150	3.150	-	-
20.0	3.000	2.990	-	-
40.0	2.900	2.840	-	-
60.0	2.800	2.702	-	-
80.0	2.650	2.560	-	-
100.0	2.500	2.430	0.0060	0.0033
120.0	2.340	2.306	0.0084	0.0041
140.0	2.244	2.200	0.0100	0.0063
160.0	2.131	2.080	0.0180	0.0088
180.0	2.000	1.970	0.0250	0.0121
200.0	1.905	1.870	0.0310	0.0151

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
20.0	0.150	0.120	-	-
40.0	0.300	0.218	0.056	0.093
60.0	0.380	0.318	0.089	0.125
80.0	0.525	0.414	0.100	0.175
100.0	0.600	0.505	0.140	0.213
120.0	0.705	0.590	0.225	0.250
140.0	0.751	0.673	0.240	0.280
160.0	0.760	0.750	0.313	0.313
180.0	0.770	0.824	0.345	0.343
200.0	0.780	0.894	0.375	0.371

$k_{DEA} = 0.00260$
 $k_1 = 0.00182$
 $k_2 = 0.00078$
 $k_3 = 0.00030$

TABLE E.8
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 30WT% DEA DEGRADED AT 90C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	3.580	3.580	-	-
100.0	3.520	3.533	-	-
160.0	3.420	3.487	-	-
300.0	3.455	3.441	-	-
441.0	3.403	3.378	-	-
511.0	3.361	3.346	-	-
631.0	3.310	3.300	-	-
700.0	3.280	3.264	-	-

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
100.0	0.050	0.046	-	-
160.0	0.090	0.092	-	-
300.0	0.155	0.137	-	0.0181
441.0	0.191	0.199	0.018	0.0302
511.0	0.216	0.230	0.024	0.0348
631.0	0.250	0.282	0.048	0.0427
700.0	0.290	0.310	0.060	0.0507

$k_{DEA} = 0.000142$
 $k_1 = 0.000140$
 $k_2 = 0.000002$
 $k_3 = -$

TABLE E.9
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 20WT% DEA DEGRADED AT 175C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	2.020	2.020	-	-
1.0	1.810	1.810	-	-
2.0	1.660	1.640	-	-
3.0	1.550	1.480	0.024	0.025
4.0	1.350	1.340	0.036	0.038
5.0	1.240	1.210	0.054	0.046
6.0	1.150	1.090	0.074	0.050
7.0	1.030	0.986	0.096	0.082
8.0	0.910	0.890	0.105	0.112

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
1.0	0.100	0.061	0.150	0.129
2.0	0.170	0.115	0.250	0.241
3.0	0.210	0.165	0.320	0.336
4.0	0.250	0.210	0.440	0.419
5.0	0.250	0.250	0.500	0.489
6.0	0.260	0.286	0.540	0.548
7.0	0.270	0.319	0.590	0.598
8.0	0.290	0.339	0.615	0.638

$k_{DEA} = 0.1010$
 $k_1 = 0.0318$
 $k_2 = 0.0692$
 $k_3 = 0.0390$

TABLE E.10
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 20WT% DEA DEGRADED AT 150C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	2.160	2.160	-	-
5.0	1.920	1.940	-	-
10.0	1.720	1.730	-	-
15.0	1.540	1.553	-	-
20.0	1.390	1.390	0.020	0.016
30.0	1.120	1.120	0.033	0.033
40.0	0.890	0.896	0.045	0.055
60.0	0.650	0.580	0.077	0.096

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
5.0	0.100	0.112	0.120	0.110
10.0	0.210	0.213	0.210	0.219
15.0	0.330	0.304	0.300	0.294
20.0	0.390	0.384	0.380	0.368
30.0	0.440	0.522	0.481	0.488
40.0	0.470	0.570	0.561	0.577
60.0	0.520	0.791	0.632	0.686

kDEA = 0.022

k1 = 0.011

k2 = 0.011

k3 = 0.004

TABLE E.11
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 20WT% DEA DEGRADED AT 120C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	2.150	2.150	-	-
20.0	2.070	2.057	-	-
40.0	2.040	1.970	-	-
60.0	1.930	1.880	-	-
80.0	1.850	1.800	-	-
100.0	1.710	1.725	0.0018	0.0020
140.0	1.650	1.580	0.0033	0.0033
160.0	1.538	1.513	0.0043	0.0045
180.0	1.551	1.450	0.0056	0.0053
200.0	1.510	1.390	0.0066	0.0063

SAMPLE hr	DEA		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
20.0	0.060	0.067	-	0.025
40.0	0.150	0.132	0.050	0.049
60.0	0.210	0.195	0.066	0.072
80.0	0.275	0.252	0.104	0.088
100.0	0.330	0.309	0.121	0.114
140.0	0.430	0.415	0.154	0.152
160.0	0.450	0.460	0.170	0.170
180.0	0.470	0.510	0.180	0.181
200.0	0.460	0.557	0.210	0.202

$$k_{\text{DEA}} = 0.0022$$

$$k_1 = 0.0016$$

$$k_2 = 0.0006$$

$$k_3 = 0.0003$$

TABLE E.12
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 15WT% DEA DEGRADED AT 175C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	1.500	1.500	-	-
1.0	1.420	1.436	-	-
2.0	1.370	1.369	-	-
3.0	1.310	1.294	0.0060	0.0040
4.0	1.240	1.241	0.0130	0.0120
5.0	1.180	1.176	0.0200	0.0208
6.0	1.120	1.125	0.0280	0.0320
8.0	1.080	1.020	0.0490	0.0487
10.0	1.010	0.930	0.0580	0.0618

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
1.0	0.026	0.025	-	-
2.0	0.050	0.050	0.050	0.067
3.0	0.076	0.073	0.100	0.100
4.0	0.093	0.940	0.120	0.122
5.0	0.118	0.118	0.170	0.146
6.0	0.131	0.135	0.172	0.167
8.0	0.160	0.172	0.225	0.204
10.0	0.171	0.205	0.250	0.234

$k_{DEA} = 0.0490$
 $k_1 = 0.0173$
 $k_2 = 0.0317$
 $k_3 = 0.0400$

TABLE E.13
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 15WT% DEA DEGRADED AT 150C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	1.510	1.510	-	-
5.0	1.450	1.420	-	-
10.0	1.350	1.346	-	0.0016
15.0	1.290	1.274	0.0040	0.0038
20.0	1.210	1.212	0.0060	0.0060
30.0	1.090	1.085	0.0150	0.0130
40.0	0.980	0.974	0.0220	0.0218
50.0	0.920	0.874	0.0340	0.0324

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
5.0	0.040	0.042	0.024	0.055
10.0	0.082	0.081	0.063	0.071
15.0	0.120	0.118	0.100	0.100
20.0	0.151	0.154	0.132	0.132
30.0	0.215	0.219	0.181	0.183
40.0	0.221	0.278	0.238	0.227
50.0	0.225	0.330	0.275	0.263

kDEA = 0.0108

k1 = 0.0057

k2 = 0.0051

k3 = 0.0043

TABLE E.14
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 10WT% DEA DEGRADED AT 175C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	1.010	1.010	-	-
2.0	0.940	0.953	-	-
4.0	0.900	0.900	-	-
6.0	0.855	0.865	-	-
8.0	0.810	0.824	0.0080	0.0141
10.0	0.770	0.780	0.0175	0.0196
15.0	0.680	0.696	0.0400	0.0400
20.0	0.610	0.610	0.0460	0.0648

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
2.0	0.020	0.020	-	-
4.0	0.040	0.040	-	-
6.0	0.060	0.059	0.048	0.070
8.0	0.080	0.077	0.068	0.090
10.0	0.090	0.094	0.060	0.101
15.0	0.100	0.133	0.100	0.131
20.0	0.106	0.168	0.142	0.151

$k_{DEA} = 0.0242$
 $k_1 = 0.0106$
 $k_2 = 0.0136$
 $k_3 = 0.0340$

TABLE E.15
COMPARISON BETWEEN EXPERIMENTAL AND PREDICTED CONCS.
FOR 10WT% DEA DEGRADED AT 150C

SAMPLE hr	DEA		BHEP	
	EXP	CALC	EXP	CALC
0.0	1.000	1.000	-	-
5.0	0.978	0.974	-	-
10.0	0.946	0.940	-	-
15.0	0.921	0.920	-	-
20.0	0.896	0.894	-	0.0018
30.0	0.848	0.850	0.0040	0.0040
40.0	0.803	0.804	0.0080	0.0071
50.0	0.715	0.760	0.0120	0.0106

SAMPLE hr	HEOD		THEED	
	EXP	CALC	EXP	CALC
0.0	-	-	-	-
5.0	-	-	-	-
10.0	0.027	0.029	-	-
15.0	0.046	0.043	-	-
20.0	0.058	0.057	-	0.0456
30.0	0.086	0.083	0.0550	0.0600
40.0	0.110	0.108	0.0851	0.0827
50.0	0.125	0.131	0.0920	0.0987

kDEA = 0.0055

k1 = 0.0030

k2 = 0.0025

k3 = 0.0040

APPENDIX F

Mass spectra of DEA and related degradation compounds

The following is basically a library of mass spectra for DEA and its degradation compounds. Out of the 16 compounds analysed only spectra for MEA, DEA, and TEA could be found in existing mass spectra libraries.

F.1 Mass spectra of DEA and its degradation compounds

Figures F.1 to F.4 show the mass spectra of DEA, BHEP, HEOD, and THEED.

F.2 Mass spectra of minor degradation compounds

Figures F.5 to F.11 show the mass spectra of BHEED, HEED, HEI, HEM, HEP, OZD, and TEHEED.

F.3 Mass spectra of impurities in the DEA feed

Figures F.12 and F.13 show the mass spectra of MEA and TEA.

F.4 Mass spectra of associated compounds

Figures F.14 to F.16 show the mass spectra of BHG, DEEA, and MDEA.

BHG or bis-(hydroxyethyl) glycine has been considered to be a degradation compound by some authors.² However, no trace of BHG was found in the degraded DEA solutions and no mechanism seems feasible for its production under present experimental conditions.

DEEA or diethylethanolamine is a tertiary amine with one hydrogen substituted with a hydroxyethyl group and the other two hydrogens substituted with ethyl groups.

F.5 Summary

Table F.1 gives the molecular formula and the mass of the ions producing the major peaks in the mass spectra of each compound analysed.

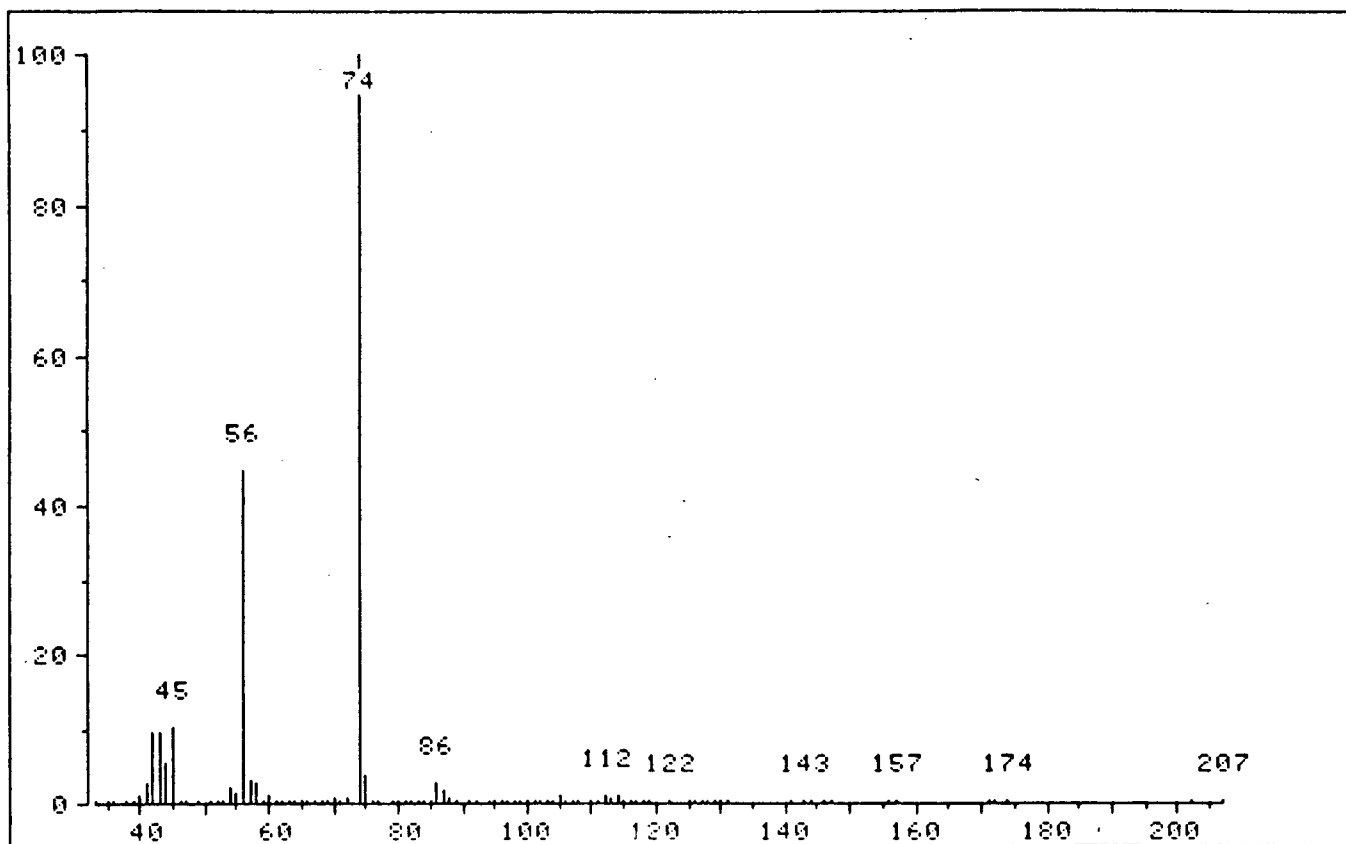


Figure F.1 Mass spectrum of DEA

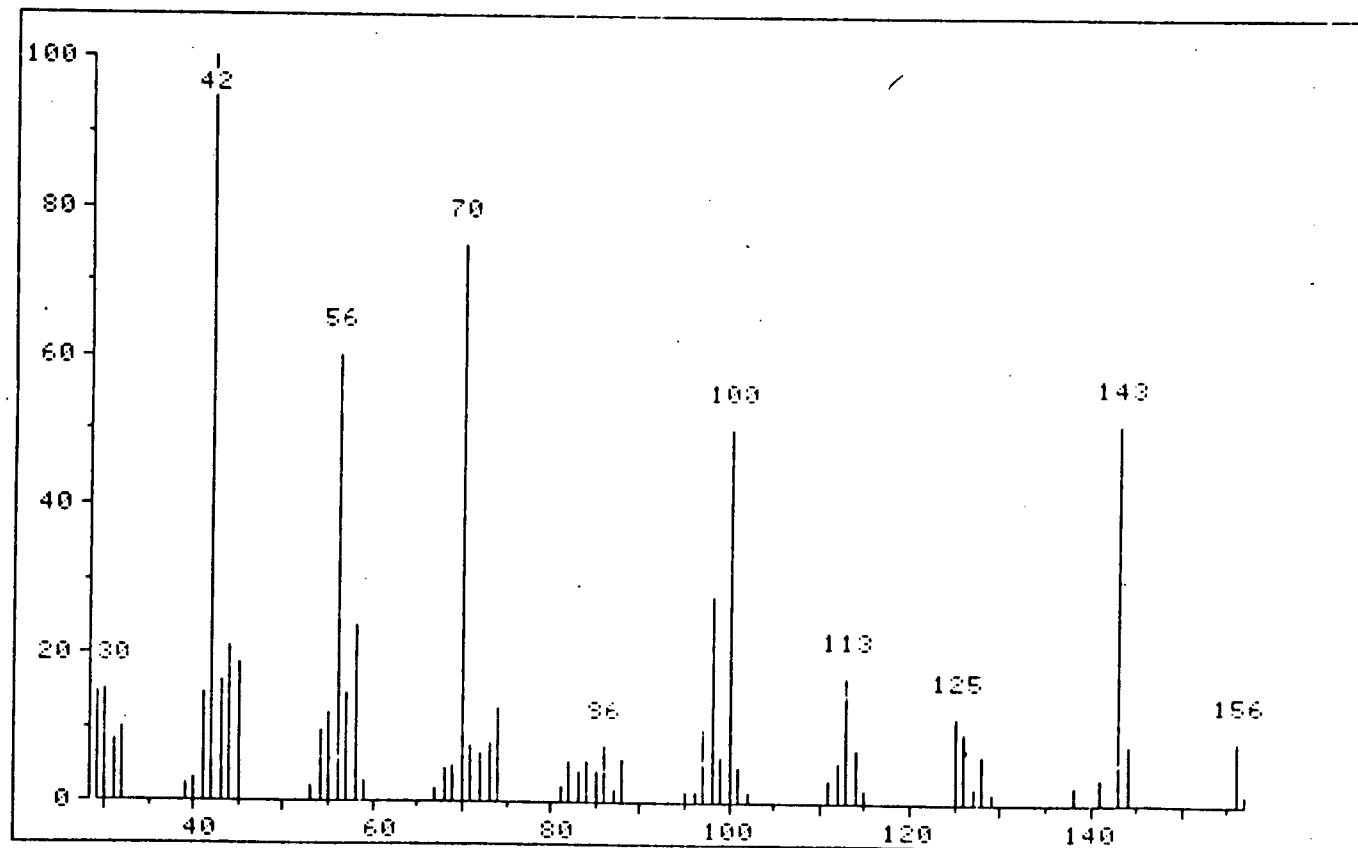


Figure F.2 Mass spectrum of BHEP

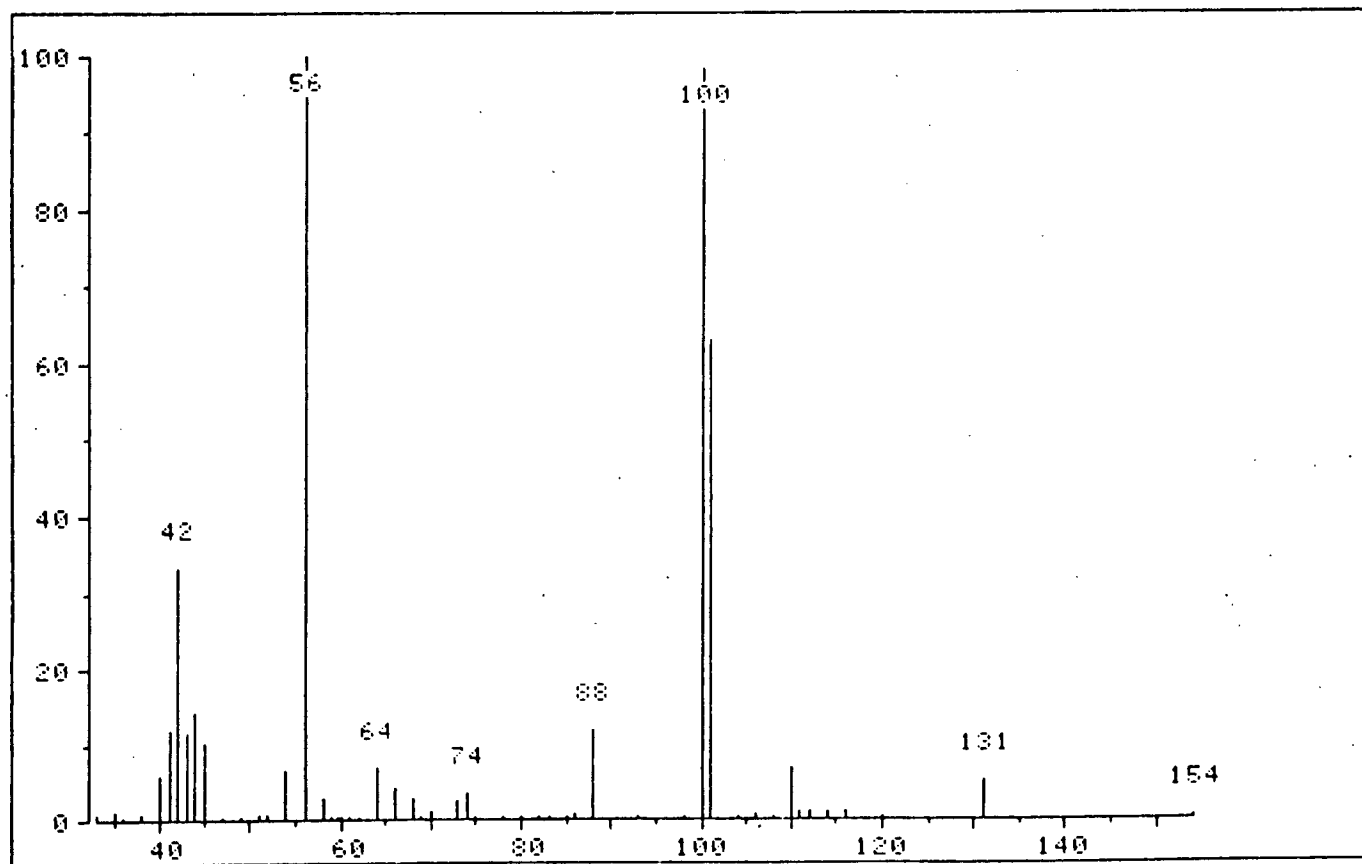


Figure F.3 Mass spectrum of HEOD

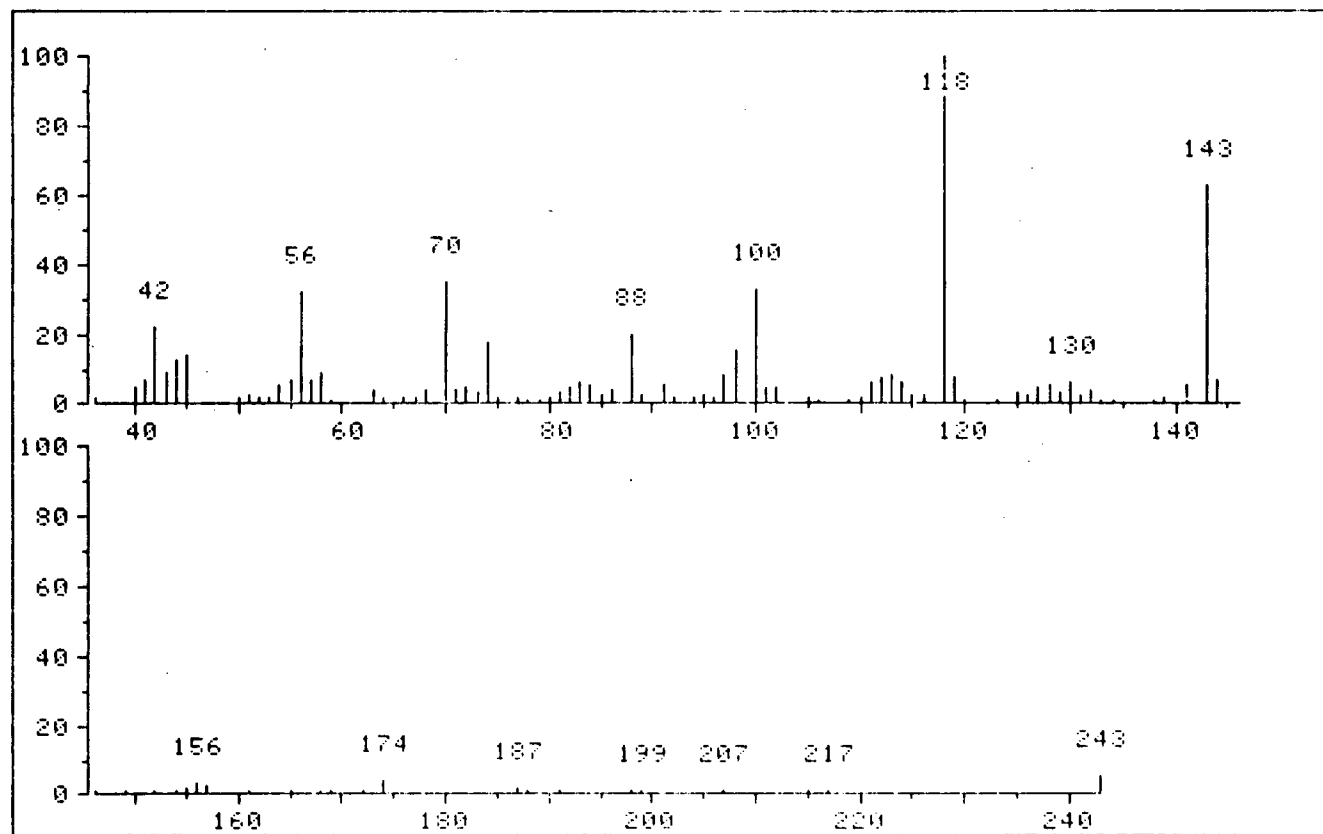


Figure F.4 Mass spectrum of THEED

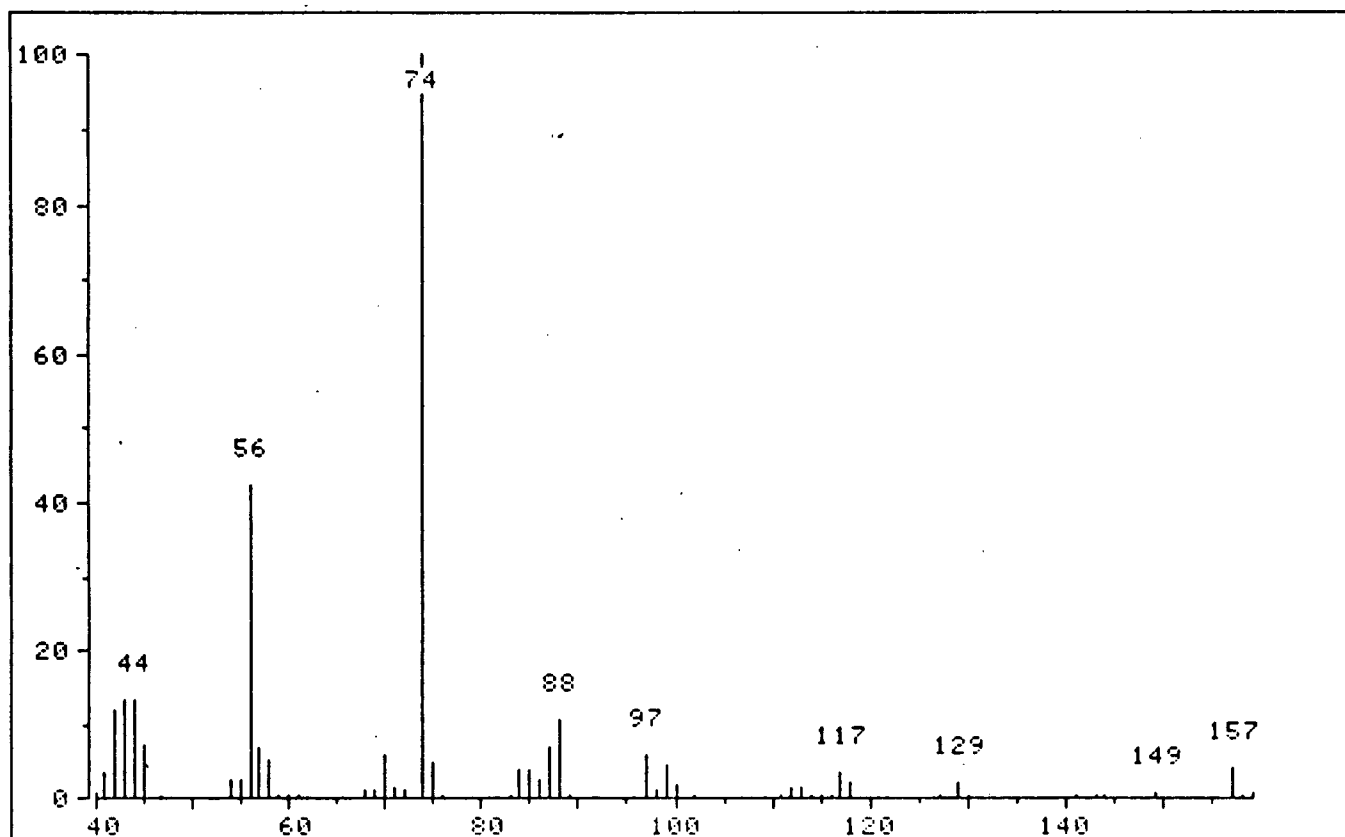


Figure F.5 Mass spectrum of BHEED

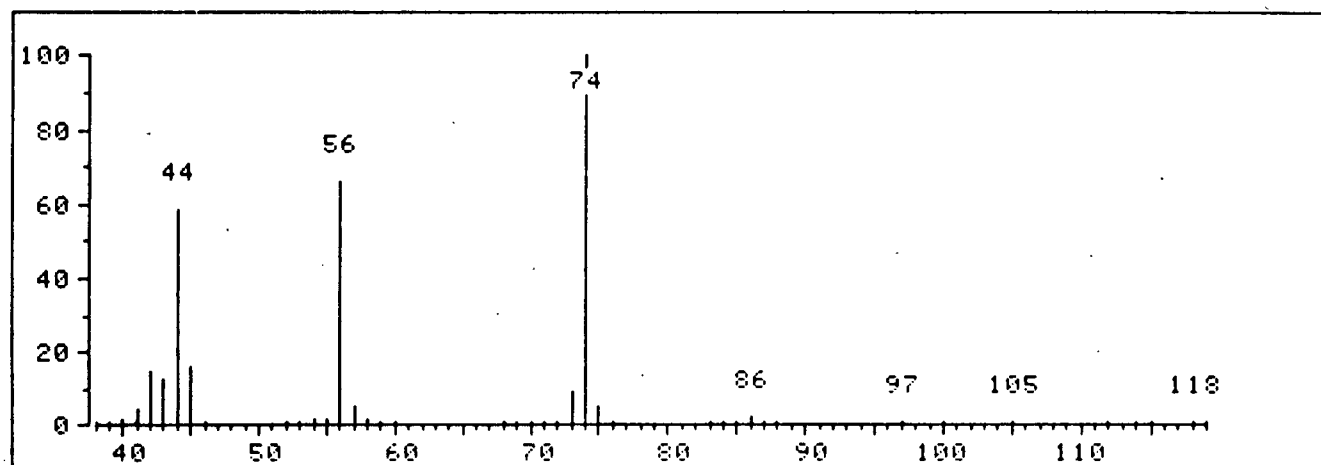


Figure F.6 Mass spectrum of HEED

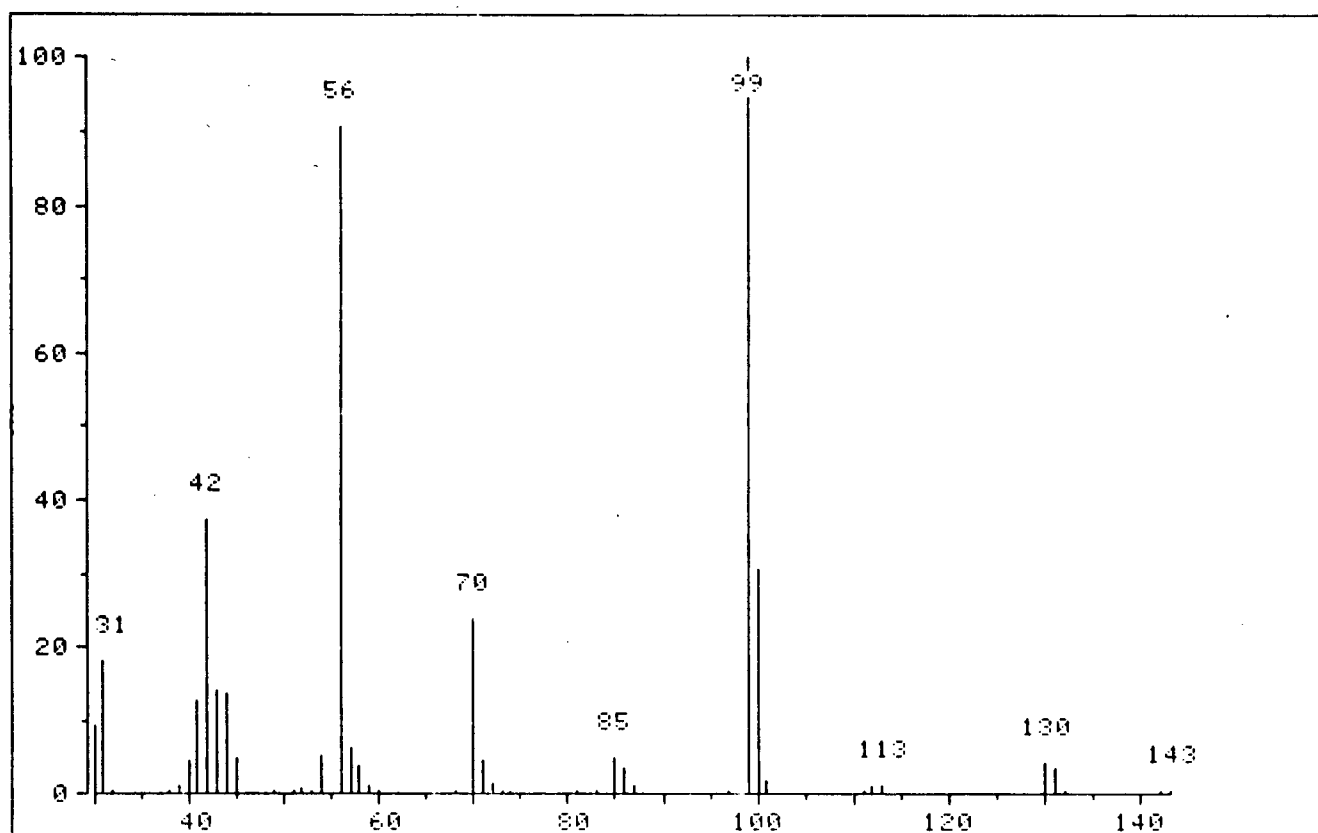


Figure F.7 Mass spectrum of HEI

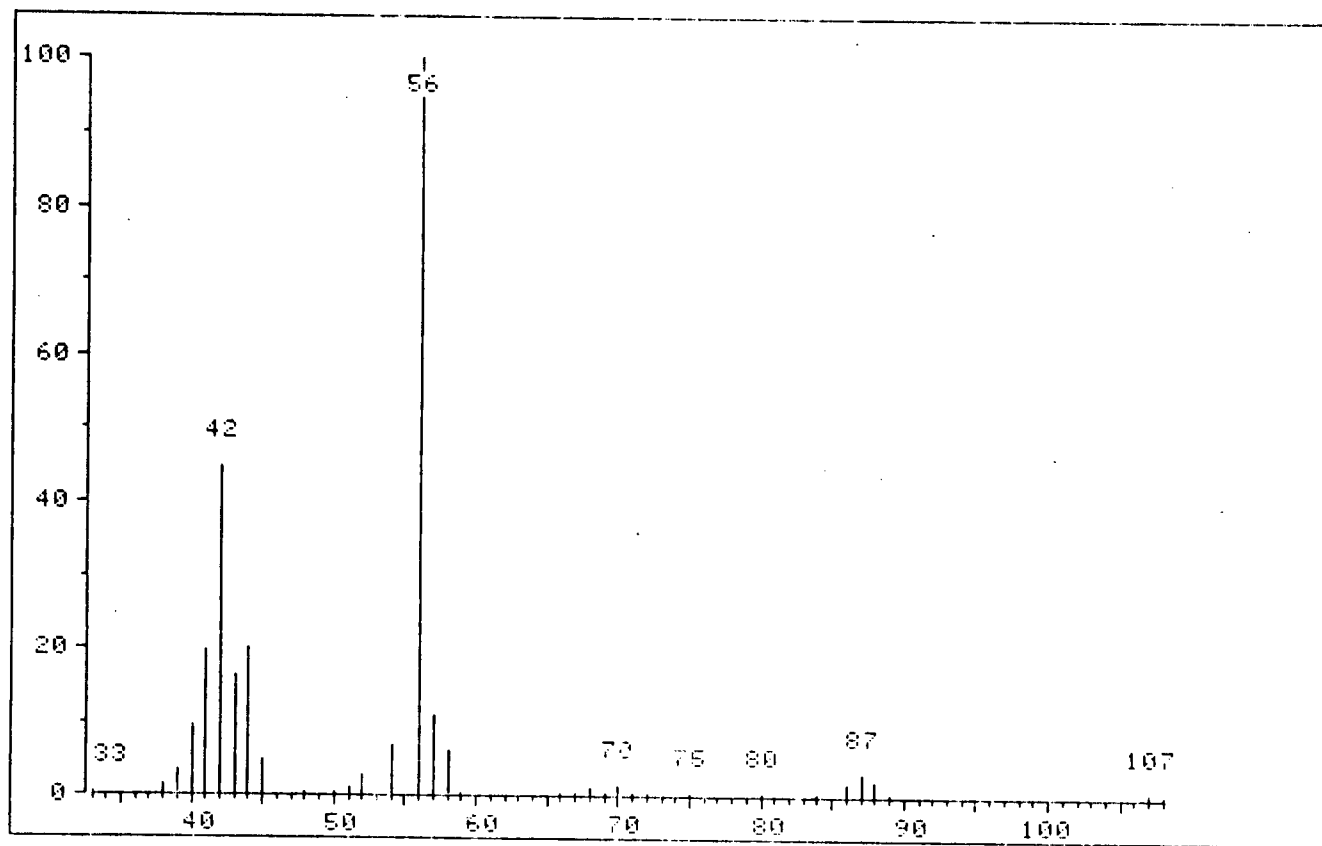


Figure F.8 Mass spectrum of HEM

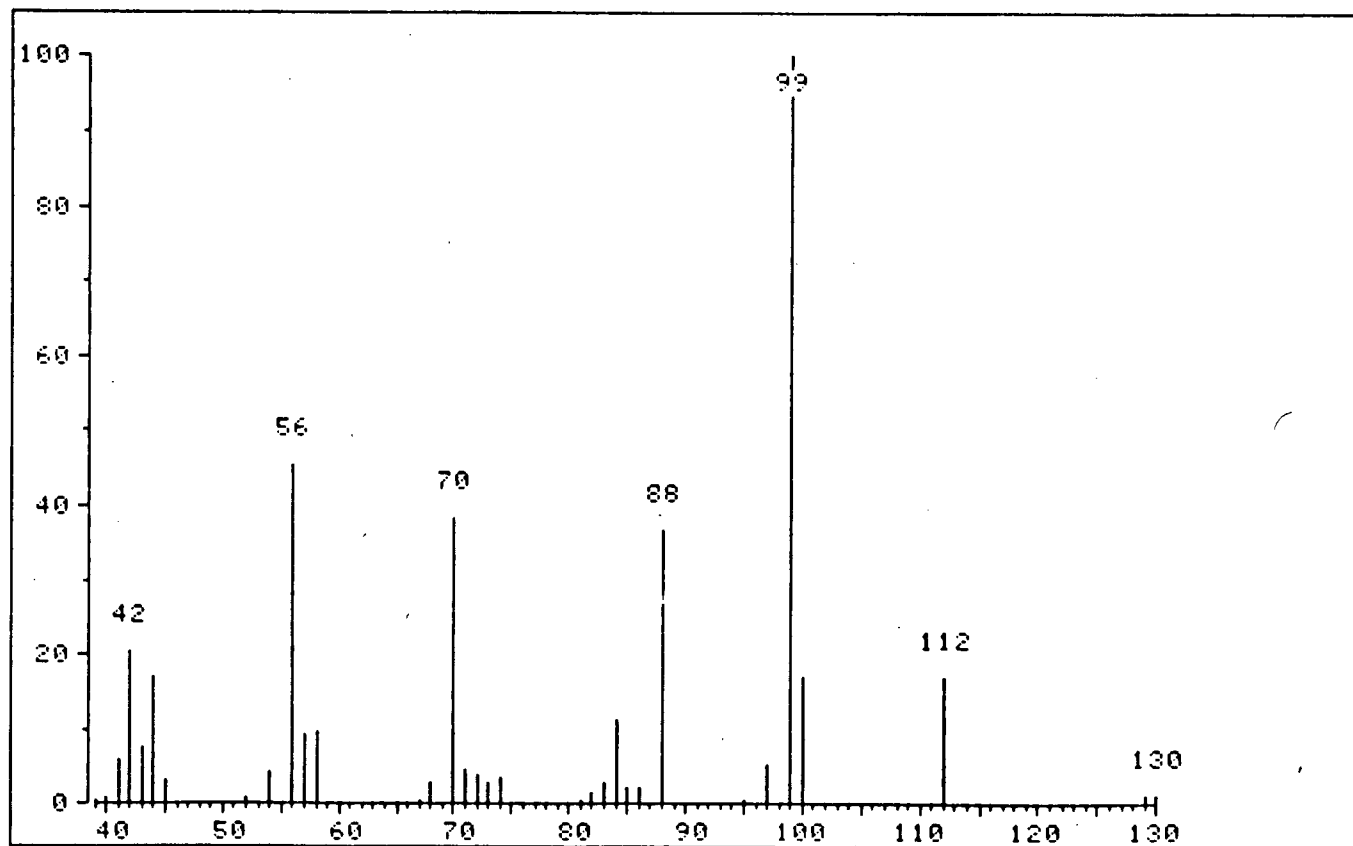


Figure F.9 Mass spectrum of HEP

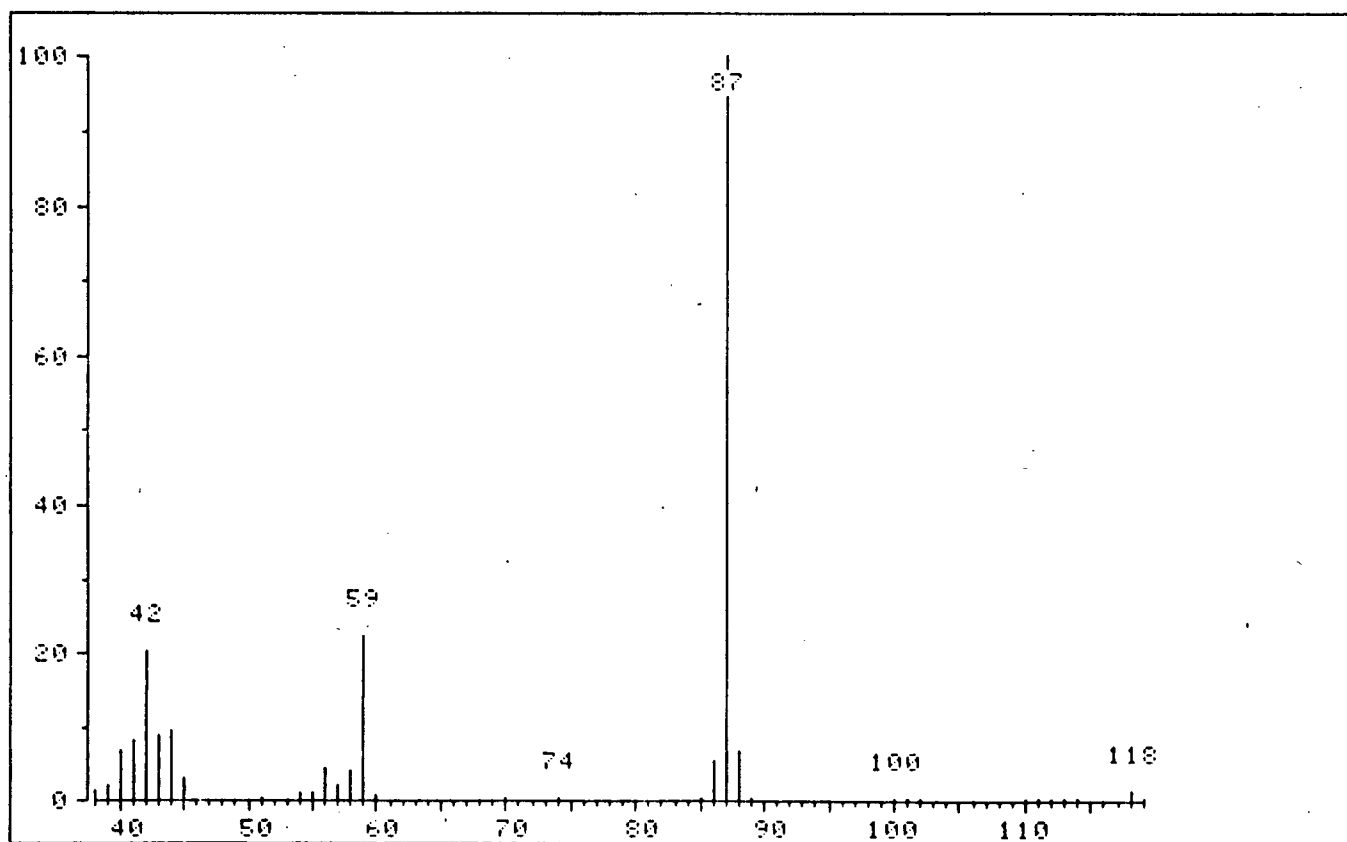


Figure F.10 Mass spectrum of OZD

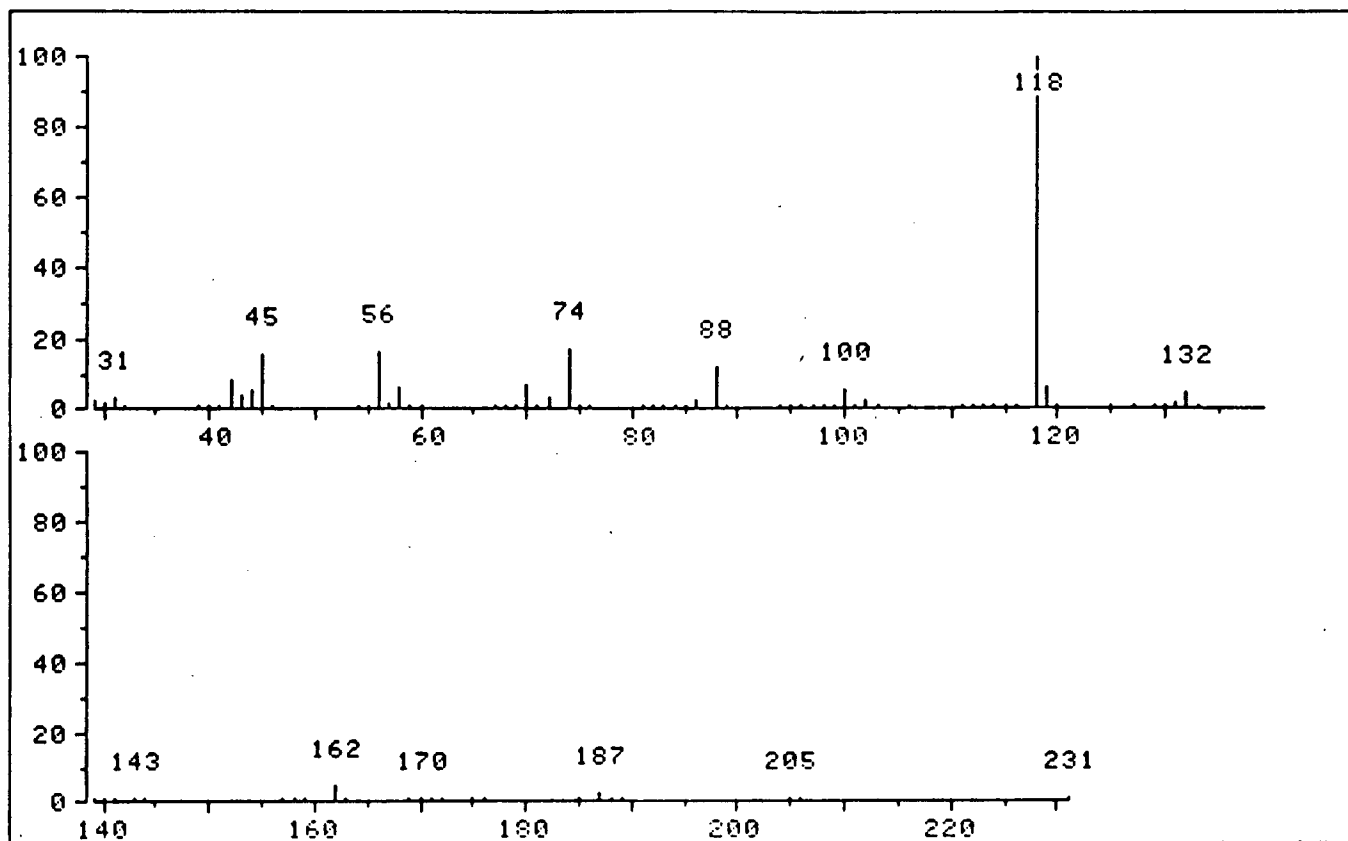


Figure F.11 Mass spectrum of TEHEED

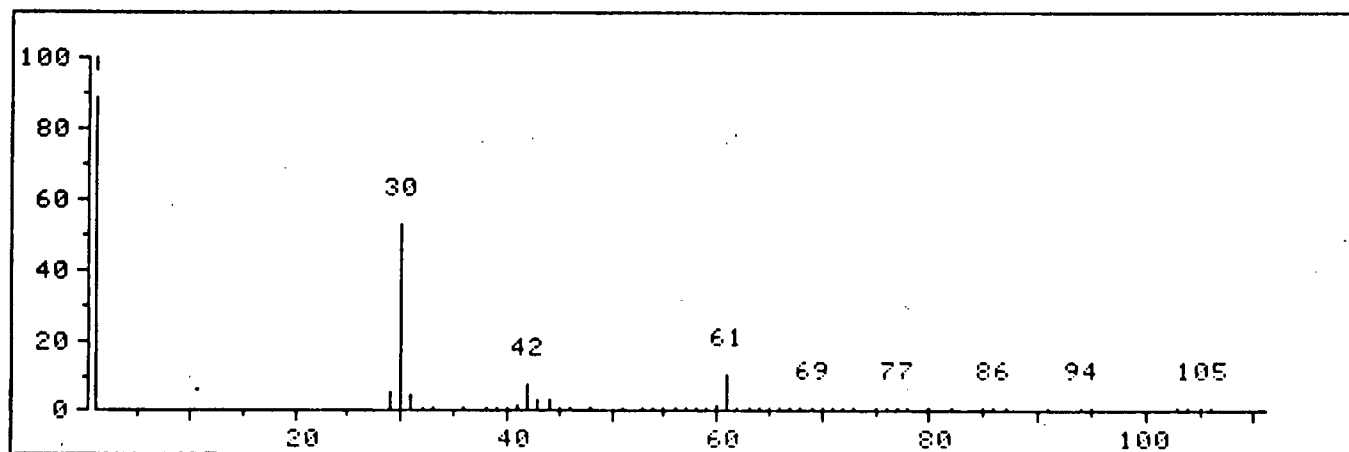


Figure F.12 Mass spectrum of MEA

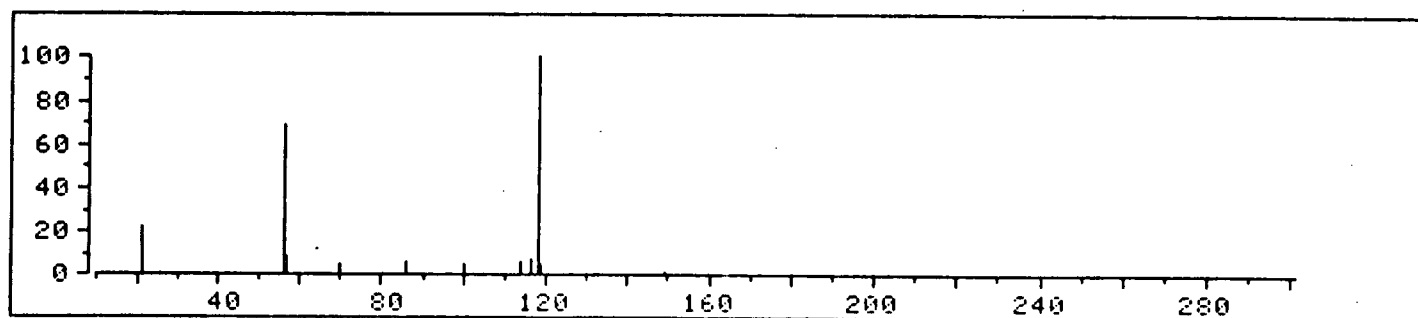


Figure F.13 Mass spectrum of TEA

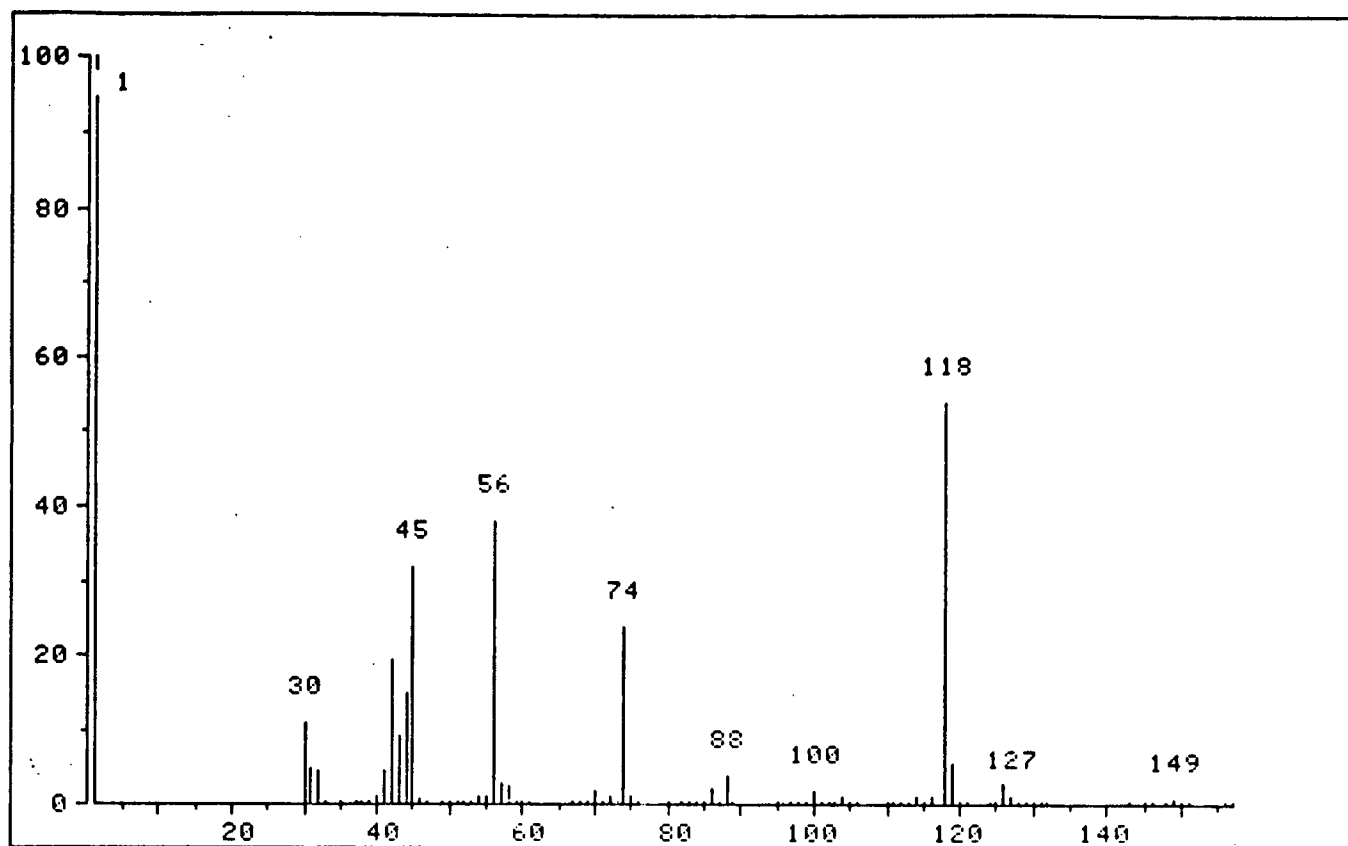


Figure F.14 Mass spectrum of BHG

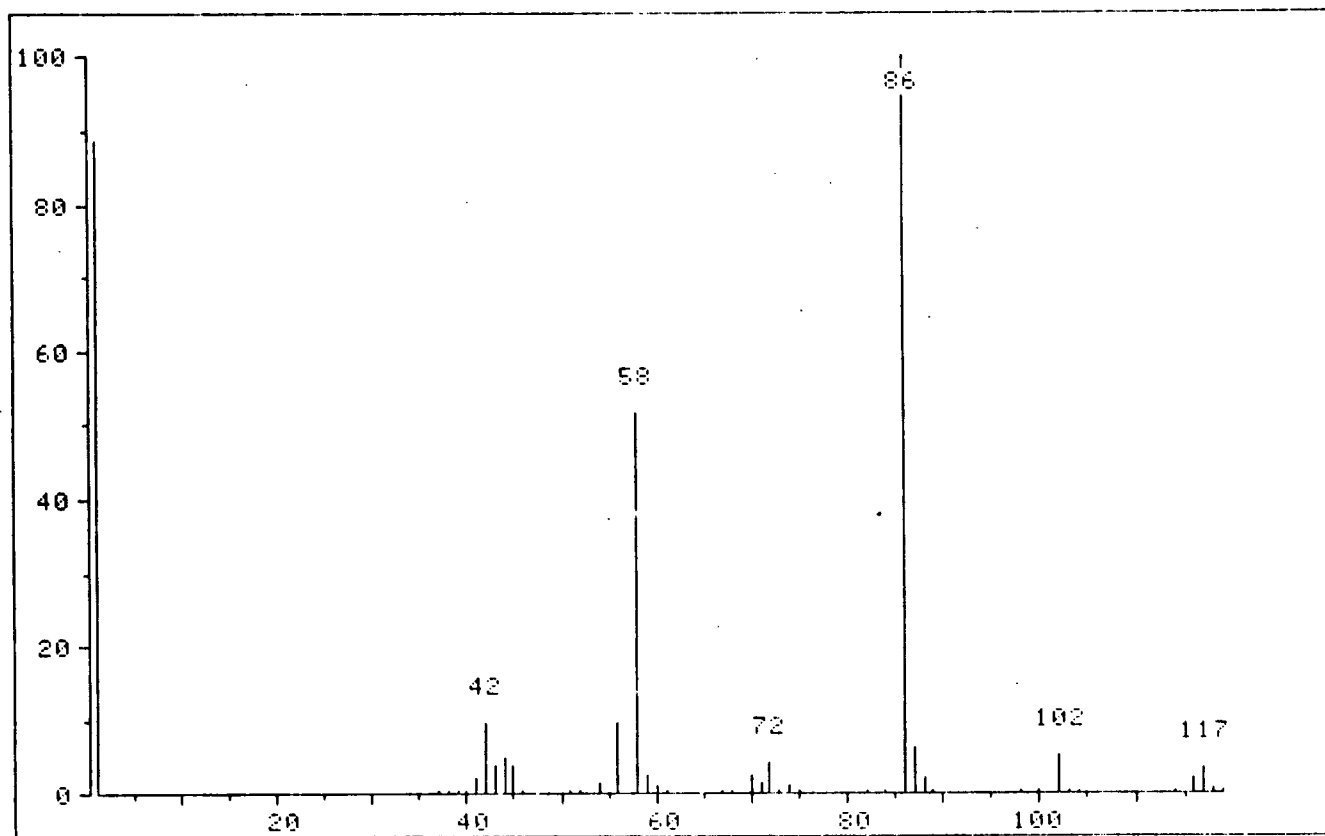


Figure F.15 Mass spectrum of DEEA

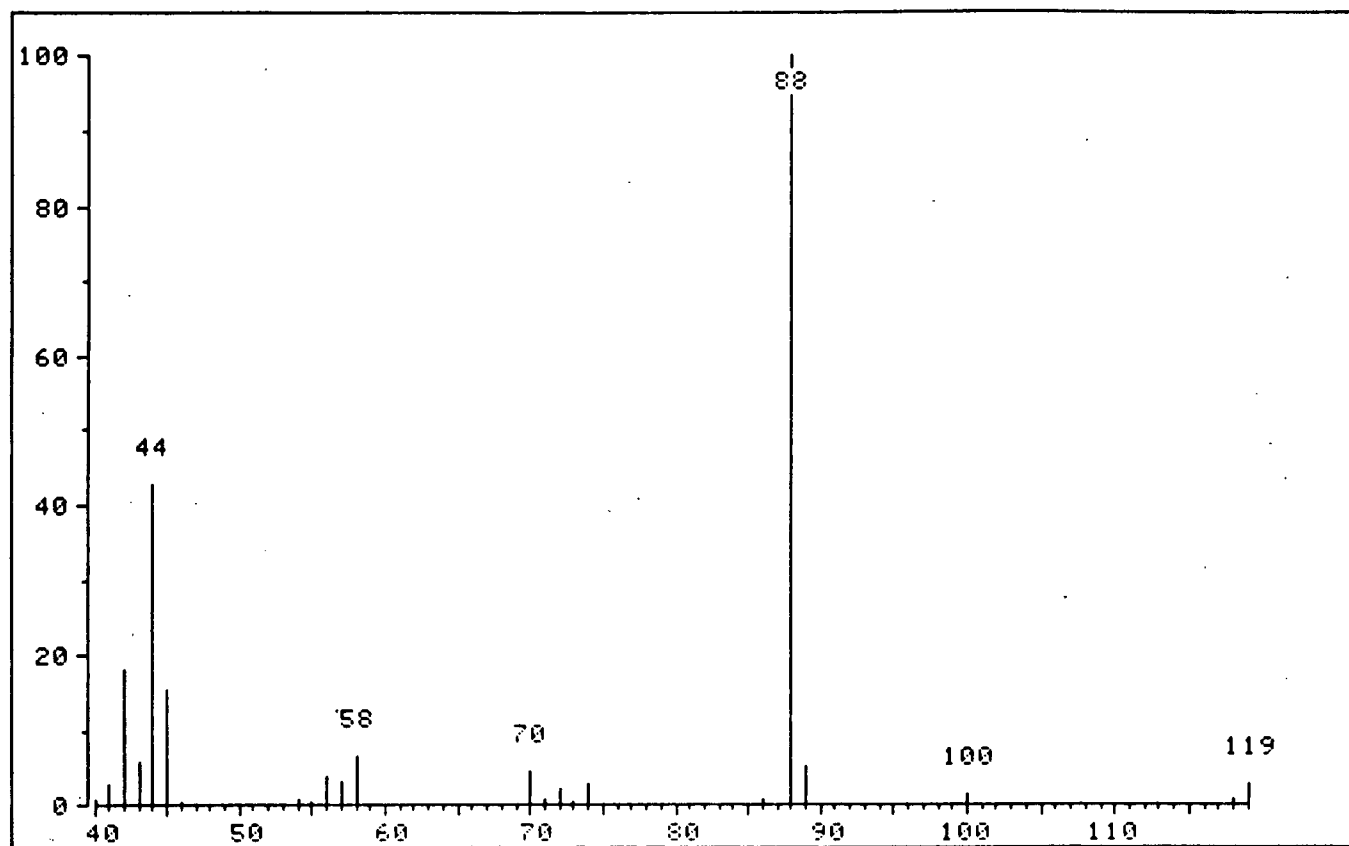


Figure F.16 Mass spectrum of MDEA

Table F.1 Molecular formula and major peaks of mass spectra of compounds studied

Compound		M.W.	Major Peaks	Parent ion
BHEED N,N-bis-(hydroxyethyl) ethylenediamine	$ \begin{array}{c} \text{HO}-\text{C}_2\text{H}_4 \quad \text{C}_2\text{H}_4-\text{OH} \\ \diagdown \quad \diagup \\ \text{N}-\text{C}_2\text{H}_4-\text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \quad \text{H} \end{array} $	148	<u>74</u> , 56, 44	-
BHEP N,N-bis-(hydroxyethyl) piperazine	$ \begin{array}{c} \text{C}_2\text{H}_4 \\ \diagup \quad \diagdown \\ \text{HO}-\text{C}_2\text{H}_4-\text{N} \quad \text{N}-\text{C}_2\text{H}_4-\text{OH} \\ \diagdown \quad \diagup \\ \text{C}_2\text{H}_4 \end{array} $	174	156, 143, 125, 113, 100, 98, 70, 56, <u>42</u>	-
BHG N,N-bis-(hydroxyethyl) glycine	$ \begin{array}{c} \text{HO}-\text{C}_2\text{H}_4 \quad \text{O} \\ \diagdown \quad \parallel \\ \text{N}-\text{CH}_2-\text{C}-\text{OH} \\ \diagup \\ \text{HO}-\text{C}_2\text{H}_4 \end{array} $	163	<u>118</u> , 74, 56, 45	-
DEA Diethanolamine	$ \begin{array}{c} \text{HO}-\text{C}_2\text{H}_4 \\ \diagdown \\ \text{N}-\text{H} \\ \diagup \\ \text{HO}-\text{C}_2\text{H}_4 \end{array} $	105	<u>74</u> , 56, 45	-

Table F.1 (cont.)

Compound		M.W.	Major Peaks	Parent ion
DEEA Diethylethanolamine	$ \begin{array}{c} \text{C}_2\text{H}_5 \\ \diagdown \\ \text{N}-\text{C}_2\text{H}_4-\text{OH} \\ \diagup \\ \text{C}_2\text{H}_5 \end{array} $	117	<u>86</u> , 58, 42	✓
HEED N-(hydroxyethyl) ethylenediamine	$ \begin{array}{c} \text{HO}-\text{C}_2\text{H}_4 \quad \text{H} \\ \diagdown \quad \diagup \\ \text{N}-\text{C}_2\text{H}_4-\text{N} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array} $	104	<u>74</u> , 56, 44	-
HEI N-(hydroxyethyl) imidazolidone	$ \begin{array}{c} \text{O} \\ \\ \text{C} \\ \diagup \quad \diagdown \\ \text{HO}-\text{C}_2\text{H}_4-\text{N} \quad \text{N}-\text{H} \\ \quad \quad \\ \text{CH}_2 \quad \text{CH}_2 \end{array} $	130	100, <u>99</u> , 70, 56, 42	✓
HEM N-(hydroxyethyl) ethylenimine	$ \begin{array}{c} \text{CH}_2 \\ \diagup \quad \\ \text{HO}-\text{C}_2\text{H}_4-\text{N} \\ \diagdown \quad \\ \text{CH}_2 \end{array} $	87	<u>56</u> , 42	✓

Table F.1 (cont.)

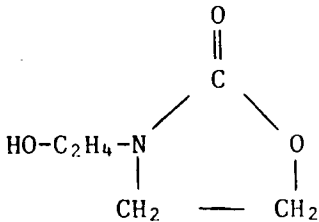
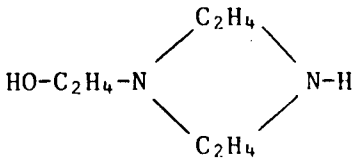
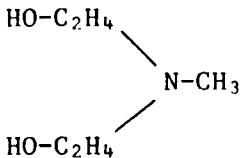
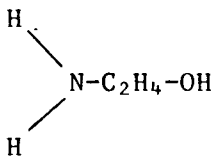
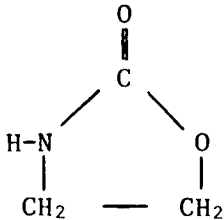
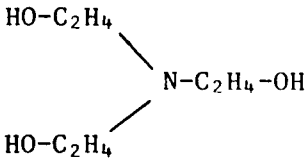
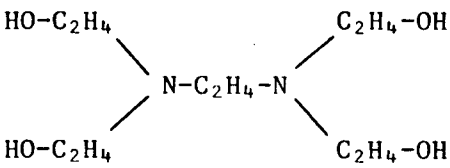
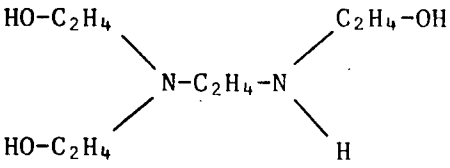
Compound		M.W.	Major Peaks	Parent ion
HEOD 3-(hydroxyethyl)-2-oxazolidone		131	<u>101</u> , 100, <u>56</u> , 42	✓
HEP N-(hydroxyethyl) piperazine		130	112, <u>99</u> , 88, 70, 56, 42	✓
MDEA Methyldiethanolamine		119	<u>88</u> , 44	✓
MEA Monoethanolamine		61	<u>61</u> , 30	✓

Table F.1 (cont.)

Compound		M.W.	Major Peaks	Parent ion
OZD Oxazolidone		87	87, 59, 42	✓
TEA Triethanolamine		149	<u>118</u> , 56, 31	-
TEHEED N,N,N,N-tetra-(hydroxyethyl) ethylenediamine		236	<u>118</u> , 100, 88, 75, 56, 45	-
THEED N,N,N-tris-(hydroxyethyl) ethylenediamine		192	143, <u>118</u> , 100, 88, 70, 56, 42	-

Note: The underlined major peaks represent the ion with the relative abundance of 100%.

Publications:

1. Kennard, M.L. and Meisen, A., "Aerosol Collection in Granular Beds" The 2nd World Filtration Congress, 1979, London, pages 229-238.
2. Kennard, M.L. and Meisen, A., "Degradation of Diethanolamine Solutions", paper presented at the Annual Meeting of the Canadian Gas Processors Association, 1979, Calgary.
3. Kennard, M.L. and Meisen, A., "Control DEA Degradation", Hydrocarbon Processing, April 1980, pages 103-106.
4. Meisen, A. and Kennard, M.L., "Practical Aspects of DEA Degradation Studies", paper presented at the 3rd Quarterly Meeting of the Canadian Gas Processors Association, Calgary, 1981.
5. Meisen, A. and Kennard, M.L., "DEA Degradation Mechanism", Hydrocarbon Processing, Oct. 1982, pages 105-108.