
PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE TECHNISCHE WETENSCHAPPEN AAN DE TECHNISCHE HOGESCHOOL DELFT, OP GEZAG VAN DE RECTOR MAGNIFICUS, IR. H.B. BOEREMA, HOOGLEERAAR IN DE AFDELING DER ELEKTRO–TECHNIEK, VOOR EEN COMMISSIE AANGEWEZEN DOOR HET COLLEGE VAN DEKANEN, TE VER–DEDIGEN OP WOENSDAG 9 JULI 1975 TE 16.00 UUR.

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SUMMARY

The background information and research work described in this dissertation centers about the study of an alternative method, the hot gas recirculation process (HGRP), for the synthesis of urea. For the realization of this process knowledge concerning phase equilibria and corrosion are of fundamental importance. For this reason the bulk of the research work is directly related to these two topics.

In the first chapter the fundamentals of urea technology are presented so that the reader can better judge the HGRP in relation to the other urea processes. A sketch of some economic aspects of urea production and the urea market are also presented as general, but also relevant information, and a brief sketch is given of the development of the urea technology and its possible future trends.

Originally to determine the optimum reactor conditions for the HGRP over a large range of temperature and composition conditions an extensive study was made of the bubble point pressures of $\text{NH}_3$-$\text{CO}_2$-$\text{H}_2\text{O}$-urea mixtures at complete equilibrium. Simultaneously, a theoretical phase model was developed which described the gas-liquid equilibrium conditions in a urea reactor as a part of a newly formulated ternary phase model for the $\text{NH}_3$-$\text{H}_2\text{O}$-$\text{CO}_2$ system at complete equilibrium in the range of $140 \leq T \leq 220^\circ\text{C}$ and $20 \leq P \leq 1000$ atm. This experimental and theoretical work proceeded so well that it, to a certain extent, became an end in itself. Characteristic of this phase model is its reciprocal salt-pair nature and the occurrence of a ternary azeotropic point of the saddle-type. This new model provides a great insight into the inter-relation between composition, temperature, bubble- and dew-point pressure, critical phenomena and the behaviour of the tie-lines; the relation of this model and information to the urea technology is explained. These results and discussion are presented in Chapter II.

In order to quantitatively describe this new phase model a simple, empirical thermodynamic model was developed; this work is presented in Chapter III. The empirical model is based on the assumption of the occurrence of the reactions:

$$\text{(NH}_3\text{)}_3^G \leftrightarrow \text{(NH}_3\text{)}_3^L$$  (1)
$$\text{(CO}_2\text{)}_2^G \leftrightarrow \text{(CO}_2\text{)}_2^L$$  (2)
$$\text{(H}_2\text{O)}_G \leftrightarrow \text{(H}_2\text{O)}_L$$  (3)
$$2 \text{(NH}_3\text{)}_3^L + \text{(CO}_2\text{)}_2^L \leftrightarrow \text{(NH}_4\text{OCONH}_2\text{)}_L$$  (4)
The model consists of the equilibrium relations of reactions (1), (2) and (6), which have been empirically determined and described by modified versions of, respectively Raoult's law, Henry's law and a log K versus 1/T relation (for (3) Raoult's law is assumed). The equilibrium conversion of carbon dioxide to urea, as a function of composition and temperature, is also a necessary part of the model; this information is obtained from the published conversion formula of Mavrovic (1972). On the basis of this model the gas-liquid equilibrium values (tie-lines) may be accurately calculated at conditions of operation of the urea synthesis reactor and, increasingly qualitatively, calculated in the concentration zones approaching the NH$_3$-H$_2$O and CO$_2$-H$_2$O systems and the urea-rich areas. Very importantly, the form of the ternary phase model presented in Chapter II also follows from the calculations of the empirical thermodynamic model, and this latter model can even be used to calculate the conditions and composition of the ternary saddle-azeotropic point. This model also helps explain the effect of excess ammonia and water on the equilibrium urea concentration and provides insight into the effect of temperature on the conversion to urea in the liquid phase.

In the following chapters more attention is placed on questions directly relevant to the realization of the HGRP.

In Chapter IV the measurement of the physical dew-points of NH$_3$-H$_2$O-CO$_2$ mixtures at HGRP conditions is described. Since the liquid phase (condensate) is extremely corrosive to practically all compressor materials (a turbo-compressor forms the heart of the HGRP) it is imperative that condensation be avoided and therefore that the condensation temperatures be known as a function of composition and pressure. For this purpose a unique method and apparatus were developed. Due to experimental difficulties, however, only qualitative results could be obtained. It is nevertheless clear that the most important factors effecting low temperature condensation (beneficial for the HGRP) are low water concentrations and, less importantly, high CO$_2$-concentration in the recycle gas stream. An initial attempt is also made to calculate the NH$_3$-CO$_2$-H$_2$O dew-points.

Since the technical feasibility of the HGRP has often been doubted on the basis of the belief that the high temperature CO$_2$-H$_2$O-NH$_3$ recycle gas stream would present insurmountable corrosion problems, a study of gas phase corrosion at HGRP conditions of typical compressor materials was also made. This work is described in Chapter V. This chapter also contains an extensive literature
search concerning the above mentioned problem. From this search it may be con-
ccluded that nitrogen- and hydrogen-attack are probably the most serious poten-
tial sources of corrosion and that these dangers may be minimized by using high
nickel and high chromium steels, employing pre-oxidation of the alloys and
adding oxidizing gases (O₂) to the recirculation gases. The experimental pro-
gram, conducted in cooperation with the Dept. of Metallurgy of the University,
involved a number of low and high pressure tests, some static, some dynamic, in
an effort to approach the sum of the conditions existing in a HGRP turbo-com-
pressor. As expected, nitrogen attack was observed. The degree of this attack
decreased to insignificant levels with significant (> 8%) nickel concentrations.
It appears that a semi-austenitic precipitation hardened chrome (14%) - nickel
(8%) steel is sufficiently resistant to attack by NH₃-CO₂-H₂O gases at HGRP con-
ditions. An unanswered question, however, remains the eventual corrosion resis-
tance in entrainment containing recycle gas.

In the last chapter a HGRP process itself is discussed. A detailed litera-
ture search of this process is presented, and the fundamental design criteria
become obvious. For a presented design, a mass and energy balance are prepared,
making use of previously presented methods and information. Special attention
is given to the heart of the HGRP, the HGR turbo-compressor and inter-stage
coolers. These results enable the utilities costs to be estimated. From a com-
parison with these utilities costs with those of the DSM CO₂-stripping process,
currently the most successful urea process, it appears that the HGRP may well
be the more economical process. As conclusion it is proposed that further
detailed economic study of the HGRP is certainly warranted.

In the appendices a number of specific topics are discussed in more detail. Appendix 1 illustrates the use of the ternary model, in which water can exist in
a negative concentration area, by means of examples. Appendix 2 discusses the
phase equilibria of the NH₃-CO₂ system. This discussion is presented because of
its importance to the urea technology and because of the fact that in spite of
this importance no systematic study of this system as an entity has as yet been
published. In Appendix 3 the quantitative analysis of urea synthesis gas, air-
CO₂-NH₃-H₂O, is discussed, as this topic formed a significant experimental pro-
blem which had to be solved. In order to acquaint the reader with the actual
calculational methods involved in employing the empirical thermodynamic model,
Appendix 4 presents a typical computer program in which most aspects concerning
the use of the model are illuminated. Finally, Appendix 5 presents a list of the
literature used in this dissertation and some related articles.
CHAPTER I
INTRODUCTION

1.1. Some remarks concerning economic aspects of urea production.

Perhaps the most characteristic aspect of the history of urea production has been its phenomenally rapid growth since the 1950's and its corresponding increasing share in the - also rapidly growing - world nitrogen fertilizer market (see Fig. I-1). One cornerstone of this growth has been the correspondingly huge increase of ammonia production and, simultaneously, the availability of large quantities of almost costless carbon dioxide, the latter available from the production of hydrogen (the raw material for ammonia synthesis) via the CO-shift reaction:

\[ \text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2 \]  \hspace{1cm} (I-1)

Since urea is commercially synthesized from ammonia and carbon dioxide via the overall reaction:

\[ 2 \text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \]  \hspace{1cm} (I-2)

the stimulating effect of burgeoning ammonia manufacture is obvious.

A second cornerstone of the rapid growth of urea manufacture is the fact that urea contains the highest weight percentage nitrogen of any commercially available solid fertilizer (namely 46.6% versus 21% for ammonium sulfate and 34% for ammonium nitrate), a factor which correspondingly reduces transportation, storage and distribution costs per unit nitrogen. Other favourable qualities for fertilizer use include good agronomic characteristics, \(^1\), suitability for combination with other materials to form complex solid N-P-K fertilizers\(^4\), \(^5\), \(^6\), \(^7\) and suitability for application in the form of a liquid fertilizer (usually combined with ammonium nitrate\(^8\)). Urea is also of increasing importance as an industrial intermediate, particularly for the manufacture of urea-formaldehyde and melamine-based resins.\(^9\) Furthermore, urea is winning increasing popularity as a protein supplement in animal feed, in which it can provide part of the nitrogen requirement of ruminant animals, thus reducing needs for much more costly natural proteins.\(^10\) With the specter of large-scale famine never far removed, however, the bulk of urea production (from 61% in 1956 to 87% in 1970) is required for fertilizer use, and this trend will continue in the future (in spite of ecological objections to widespread fertilizer use\(^11\)).

The development of the urea market can be briefly sketched as follows (for a very detailed analysis of the urea market and economics see the publications
of The British Sulfur Corporation and their bi-monthly magazine, "Nitrogen"). The beginning stages (around 1950) of large scale urea production were plagued by serious technical problems (poor product quality, corrosion, frequent plant shut-downs) and doubts concerning the agronomic effectiveness of urea. Only when these problems and doubts had been resolved did production begin to increase rapidly, and it soared in the 1960's (Fig. I-1).

![Fig. I-1. Growth of urea production capacity and growth of urea's share of the world nitrogen fertilizer market.
(Sources: See references 1, 4, 12, 20 and publications of the British Sulfur Corporation.)](image)

In the early stages of growth the production sector was dominated by American, Western European and Japanese manufacturers. The late 1960's, however, witnessed a number of fundamental changes. The Eastern European nations erected enormous production facilities (larger even than those of Western Europe) as this area put more emphasis on its agricultural sector and also came to realize the political usefulness of large scale fertilizer shipments to underdeveloped nations. Similarly, some (now many) of the oil producing nations became increasingly interested in urea manufacture as their interest in down-stream petroleum products increased. Furthermore, many of these countries, particularly those along the Persian Gulf, are in a better geographic position than the Western nations relative to the large importing nations of the Far East (India, China, Indonesia etc), and countries such as Kuwait, Saudi Arabia and Iran have invested heavily in large urea plants. At the same time some of the large importing countries, particularly India, were also busy implementing their own ambitious plans for greatly increased urea production. These developments led to the situation of the late 1960's and early 1970's in which the
urea market lost its balance, and production began to so outstrip demand that urea prices declined significantly. Whereas in the middle 1960's, for example, urea prices of about US $ 80-95 per ton f.o.b. were normal, in 1969 f.o.b. distress prices as low as US $ 33 per ton were being quoted.  

As a result of this oversupply many Western and Japanese manufacturers postponed building their projected new urea facilities. Because of this decrease in investment in new plants and because of serious "teething problems" associated with the coming on-stream of a new generation of large, turbo-compressor equipped ammonia plants, the surplus in urea production lasted only until about 1971/2.  

Due to crop failures in some large countries, which led to increased food production and fertilizer consumption in the United States, the urea market became increasingly tighter. These developments were enormously compounded by the energy crisis and the quadrupling of the oil price. Since 1972 the urea trade has become a seller's market. At the time of this writing urea prices have reached values of US $ 300-400 per ton (leading to further problems in the already seriously strained agricultural sector of many underdeveloped countries), although there are signs that the fertilizer prices may have stabilized temporarily.  

Presently - and in the near future - it appears that urea production capacity is significantly larger (by at least 30%) than demand; the bottleneck in urea manufacture appears to be an acute shortage of ammonia related to a shortage of on-stream production facilities and the high costs, or even non-availability, of hydrocarbon feedstocks. As for the future it is probably to be expected that in spite of high prices nitrogen fertilizer demand will remain high due to the high market value of crops, and shortages will exist well into the 1970's, even in the U.S.  

In the light of rapidly expanding world population the importance of adequate fertilizer supplies cannot be overestimated, and large scale investment in nitrogen fertilizer plants continues in Asia (China), the Middle East and Canada. In these developments urea plays an important role: by the middle or late 1970's urea will have become the most important nitrogenous fertilizer.

1.1.1. Cost factors in the production of urea.  

In order to obtain some insight into the economics of urea manufacture an analysis of the total manufacturing costs of urea is given in Table I-1. The very close relation between the price of urea to that of ammonia is evident; since the largest cost factor in producing ammonia is the feed stock price, the direct correlation between hydrocarbon and urea prices is also obvious. Further items of importance are utilities and investment. A factor of
Table I-1. Analysis of total manufacturing costs for urea.

<table>
<thead>
<tr>
<th>Item</th>
<th>Percent of total costs</th>
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<tbody>
<tr>
<td>Raw materials</td>
<td>79.5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>79.5</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>0.0</td>
</tr>
<tr>
<td>Utilities</td>
<td>10.60</td>
</tr>
<tr>
<td>Electricity</td>
<td>4.39</td>
</tr>
<tr>
<td>Steam</td>
<td>4.67</td>
</tr>
<tr>
<td>Cooling water</td>
<td>1.53</td>
</tr>
<tr>
<td>Direct costs</td>
<td>2.23</td>
</tr>
<tr>
<td>Labour and supervision</td>
<td>0.35</td>
</tr>
<tr>
<td>Maintainance</td>
<td>0.77</td>
</tr>
<tr>
<td>Overheads</td>
<td>1.12</td>
</tr>
<tr>
<td>Fixed costs</td>
<td>7.67</td>
</tr>
</tbody>
</table>

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great importance not shown is plant reliability. Low on-stream time and frequent plant shut-downs and start-up lead to severe financial losses.

1.2. Basic facts underlying the urea technology.

Urea is commercially synthesized from ammonia and carbon dioxide via two reversible consecutive reactions. In the first reaction ammonium carbamate is formed:

\[ 2\left(\text{NH}_3\right)_G + \left(\text{CO}_2\right)_G \stackrel{\text{\textit{RH}}}{\rightarrow} \left(\text{NH}_4\text{OCONH}_2\right)_L \]  

The formation of ammonium carbamate is strongly exothermic (\(\Delta H_{\text{RH}} \approx -28 \text{ Kcal/mole}^{24}\)). This reaction proceeds to completion and is kinetically practically instantaneous as long as the reaction heat is removed rapidly enough to maintain a temperature at which the reaction pressure is equal or greater than the dissociation pressure (see Appendix 2 for a discussion of the properties of ammonium carbamate and its part in the \(\text{NH}_3-\text{CO}_2\) system.)

At temperatures above its melting point (\(T \approx 153^\circ\text{C}\)) ammonium carbamate reacts in the liquid phase more or less rapidly to form urea and water:

\[ \left(\text{NH}_4\text{OCONH}_2\right)_L \stackrel{\text{\textit{R}}}{{+}} \left(\text{NH}_2\text{CONH}_2\right)_L + \left(\text{H}_2\text{O}\right)_L \]  

The kinetics of the ammonium carbamate dehydration have been studied by a number of authors.\textsuperscript{25} An impression of the reaction time as a function of the degree of conversion and temperature is given in Fig. I-2, as calculated on the basis of the studies of Kucheryavyi et al.\textsuperscript{26} Because of the relative speed of
reaction I-4 at reactor temperatures (170 °C < T < 210 °C), catalysts are not applied commercially, being furthermore impracticable due to the highly corrosive nature of the synthesis solution and the danger of product contamination. The overall kinetics of the ammonium carbamate dehydration are influenced by the NH₃/CO₂ and H₂O/CO₂ ratios in the feed and also by the mass transfer rate of the gas-liquid reactions between ammonia and carbon dioxide.²⁵,²⁷ The rate of these gas-liquid reactions is influenced by the hydrodynamics in the urea reactor, which, of course, is affected by reactor design; modern urea reactors contain baffles or sieve-plates so that plug-flow conditions are approached.²⁴,²⁸,²⁹

In contrast to its formation, the dehydration of ammonium carbamate does not proceed to completion. The degree of conversion of ammonium carbamate to urea is a function of initial NH₃/CO₂ and H₂O/CO₂ ratio and reaction temperature; the equilibrium conversion has also been studied by a number of researchers.³⁰,³¹,³²,³³,³⁴

Since the dehydration reaction is endothermic, the conversion of ammonium carbamate to urea is favoured by high temperatures.³⁵ The conversion is also favoured by an excess quantity of ammonia (initial NH₃/CO₂ > 2) and the absence of water in the initial feed (see further sections 3.6 and 3.7 for a discussion of the effect of temperature and composition on the conversion).

At the conditions of the commercial urea synthesis conversions of carbamate to urea in the range of 50 to 80% are obtained. The relatively large amounts of unconverted carbamate are separated from the urea-water solution and recycled back to the reactor. Indeed, the separation and recirculation steps constitute the chief characteristics of urea process technology and form the major points of difference between the various commercial process routes.

An undesirable side-reaction occurring during the synthesis of urea is the formation of biuret:

Fig. I-2. Degree of conversion of ammonium carbamate to urea and water as a function of time at various temperatures.
For certain agricultural applications a biuret concentration below 1-2% is necessary, and the biuret concentration of fertilizer grade urea is usually kept at < 0.7-0.8 wt-%. The formation of biuret, being an endothermic reaction, is favoured by high temperatures. As seen from its reaction scheme (I-5), low NH₃-concentration also favours biuret formation, particularly at long contact times at high temperatures. The kinetics of biuret formation and its equilibrium concentration have been fairly well studied; recent review articles discuss the process technology for reducing the concentration of biuret in finished urea.

Since, for practical purposes, the urea reaction occurs in the liquid phase only, and since the liquid phase is rather volatile due to the presence of ammonium carbamate and dissolved ammonia and carbon dioxide, the urea synthesis requires high pressures, namely 150 to 250 atm, depending on temperature and NH₃-CO₂-H₂O feed ratios (see section 2.4.1.); the vapour pressure of the liquid phase increases roughly exponentially with temperature. The liquid phase is furthermore extremely corrosive necessitating the use of special stainless steels in combination with oxygen passivation, or such relatively exotic metals as titanium or zirconium; the corrosive action of the liquid phase increases greatly with temperature. The rate of urea formation increases exponentially with temperature, and, as already has been mentioned, the equilibrium conversion to urea also increases with temperature. The urea synthesis conditions of the various commercial processes (170 < T < 210°C, 150 < P < 250 atm, 2.4 < NH₃/C O₂ < 4.3, 0.15 < H₂O/C O₂ < 0.65) represent a compromise between a reasonable pressure level and an acceptable corrosion rate against a suitable reaction rate and degree of conversion.

All of the above mentioned factors - the removal and optimum use of the large reaction heat, the necessity of substantial recirculation of unconverted reactants, the high pressures involved, the danger of excessive biuret formation, and the extreme corrosiveness of the liquid phase - have necessitated a much more sophisticated technology for the production of urea than for the production of other nitrogenous fertilizers. In general, the development of the urea process technology has been marked by the improvement of the recirculation step. The developments have centered about reducing the energy and cooling water requirements (by obtaining the heat of ammonium carbamate formation at as high a temperature as possible and by utilizing this heat within the process to the greatest possible extent), reducing the amount of water being recirculated back to the reactor (reduces conversion, thus increases recycle load; furthermore, extra water must eventually be evaporated from the urea solution,
increasing steam requirements), reducing the amount of equipment required (lower investment), increasing plant reliability and on-stream time, reducing corrosion and improving product quality. Another characteristic of the development of urea technology has been the tremendous scale-up of plant size, made possible by improved plant technology and stimulated by increasingly larger ammonia plants. Whereas in the 1950's factories of 50 tons/day were not unusual, today single-stream plants of 1700 tons/day are being constructed, and single-stream plants of 2000 tons/day are considered to be possible.

1.3. A very brief sketch of the history of the urea technology.

Urea was first commercially produced in the 1920's by I.G. Farben in Germany. In the early stages of production a once-through process was used: by heating the reactor effluent under atmospheric pressure the unconverted reactants were separated from the urea-water solution in the form of a gaseous NH$_3$-CO$_2$-H$_2$O mixture. This gas was contacted with sulfuric or nitric acid in order to absorb the NH$_3$. Such a process is quite simple, but suffers from the serious drawback that large quantities of by-products are necessarily produced. The once-through process is now obsolete.

In the late 1930's I.G. Farben developed a process by which the unreacted NH$_3$ and CO$_2$, obtained by pressure reduction and heating, were recycled back to the reactor in the form of a hot gaseous mixture; before entering the reactor the gases were condensed at reactor pressure and process steam was generated. This process, called the hot gas recirculation process (HGRP), is in principle a simple total recycle system. In practice, however, the process suffered from severe corrosion problems in the compressor and was not viable technically. (See Chapter VI for a detailed discussion of this process.)

In the 1930's Dupont developed a urea process with liquid recycle of unconverted reactants. In this process the NH$_3$-CO$_2$-H$_2$O gas stream, formed by pressure reduction and heating of the reactor effluent, was condensed by indirect contact with cooling water, dissolved in a small amount of water (to prevent crystallization) and pumped back to the reactor as an ammonium carbonate solution. This process is referred to as the solution recycle process.

With the advent of large scale urea production in the 1950's, the solution recycle process was continually improved, although the general principles developed by Dupont remained unchanged. Variations of the solution recycle process were offered by the various urea producers, such as Stamicarbon (DSM), Chemical Construction Corporation (Chemico), Mitsui Toatsu and others. Designers of these solution recycle processes strove to reduce the amount of recycled water and improve the heat recovery.
While the solution recycle process is losing ground relative to the newer stripping processes (see below), new plants of this type are still being built. A modern solution recycle process is offered by Mitsui Toatsu of Japan; a simplified scheme of one of their processes is presented in Fig. I-3 and is explained as follows. Carbon dioxide gas, recycle carbamate solution (26) and liquid ammonia (31) enter the reactor (1), which operates at about 190-200°C and 230-250 atm. The reactor feed ratios are \( \text{NH}_3/\text{CO}_2 = 4-4.3 \) and \( \text{H}_2\text{O}/\text{CO}_2 = 0.4-0.6 \); the conversion of ammonium carbamate to urea is about 65-70%. The reaction products (2) urea, carbamate, water and excess ammonia, flow through the let-down valve (3) to the high pressure decomposer (6), which operates at 150-160°C and 15-20 atm. In this first decomposer most of the carbamate decomposes into \( \text{CO}_2 \) and \( \text{NH}_3 \) gas (35). The resulting solution (33) is further reduced in pressure to 1-2 atm (gauge) and about 130°C, at which more carbamate decomposes. The effluent solution (34) of this second stage decomposer (7) flows to the last stage decomposer (8) operating at atmospheric pressure and \(+ 120°C\). Here the remaining carbamate decomposes, and the resulting urea-water solution flows out for evaporation and processing to prills. The gases (10) from the last stage decomposer are condensed by means of cooling water in the low pressure condenser (11) and pumped, as (12), by means of carbamate (solution) pump (13) to the condenser (15) of the second stage decomposer. Here (15) the condensate (14) is mixed with the off-gases (36) of the second stage decomposer; condensation is effected by means of cooling with cooling water. The resulting solution (16) is pumped by means of a carbamate pump (17) to the high pressure absorber (19); in this absorber the recycle liquid (18), which is ammonia-rich, contacts the ammonia-rich gases (35) rising up from the high pressure decomposer (6). The effluent gas (21) is nearly pure \( \text{NH}_3 \), and this is condensed by cooling water and thereupon recycled to the reactor (1) by means.
of an ammonia pump (28) and via an ammonia heater (30). The liquid (20) leaving the high pressure absorber, consisting of a concentrated NH$_3$-CO$_2$ solution in water, is pumped back to the reactor by means of the high pressure carbamate pump (25).

The solution recycle process described above suffers from a number of shortcomings. The most important of these relate to the heat economy. The heat of condensation of ammonium carbamate is obtained at low pressure, hence low temperatures, and cannot be usefully employed; on the contrary, it requires cooling water for its dissipation. Only in the high pressure absorber is the pressure at such a level that condensation occurs at a useful temperature, and the heat so obtained can be used to heat the mother liquor stream, thus providing heat for evaporation of the urea solution. Another problem associated with the solution recycle process is low reactor efficiency and large recycle sections. Due to the relatively high initial H$_2$O/CO$_2$ ratio in the reactor feed a high reactor NH$_3$/CO$_2$ ratio is necessary to obtain reasonable conversions. This excess NH$_3$ necessitates a relatively large reactor, and the excess NH$_3$ must furthermore be recirculated back to the reactor, requiring large recycle sections. The excess water must also be evaporated, increasing steam requirements. Other utility losses involve the condensation of the recycle of ammonia with cooling water in (22) and its subsequent heating in (30). Also, the carbamate decomposers all require import steam. The highly concentrated carbamate solution must necessarily be kept at a high temperature to prevent crystallization, and at these conditions the solution is very corrosive towards the carbamate pump (25). These pumps, usually of the reciprocating type, are also prone to stress corrosion.  

The solution recycle process is still undergoing improvement. The most recent and sophisticated processes of this type is the Mavrovic-Technip "heat recycle" process, which, as its name implies, has been developed with the intention of making maximum and optimal use of the heat of formation of carbamate. In principle, however, the "heat recycle" process does not differ greatly from the above sketched process. For more details the reader is referred to the literature describing this process.

With the rapid increase in plant size, a further general improvement in urea plant technology has been the gradual replacement of reciprocating compressors by turbo-compressors for compression of the CO$_2$-feed. Turbo-compressors offer the advantages of compactness, lower installation and maintenance costs, greater reliability and less vibration, relative to reciprocating compressors, and these advantages become greater with larger gas volumes (i.e., larger plants). The carbamate pumps are also undergoing improvement.
Other processes were developed simultaneously with the improved recycle processes. These alternative processes included recycle of the carbamate as a slurry in oil or in the NH₃-feed and processes in which the carbamate gas recirculation was, in principle, simplified by separating the NH₃ from the CO₂ by means of a selective solvent, recycling the NH₃ back to the reactor and regenerating the solvent. The first process experienced oil decomposition problems, the second never passed the pilot-plant stage and the third type was characterized by very large recycle sections and unfavourable utilities costs. No new processes of these types are being built, although processes of the third type are still in operation.

The middle-1960's saw the introduction of a new generation of urea processes, the so-called stripping processes. In these processes the decomposition of ammonium carbamate is effected at the urea synthesis pressure itself by contacting the reactor effluent with either CO₂ or NH₃ gas (the stripping agent) at high temperatures in a steam heated vertical wetted-wall heat exchanger; the stripping gas reduces the partial pressure of, respectively, NH₃ or CO₂ in the liquid mixture leading to the decomposition of the carbamate; the decomposition mechanism of the carbamate is clearly described in the literature.

The DSM CO₂-stripping process will be described, as this is presently the leading synthesis process, representing 60-70% of the new urea plants now being constructed; a simplified scheme is presented in Fig. 1-4. The reactor (7) operates at a temperature of 185°C, a H₂O/CO₂ ratio of about 0.3-0.4, a NH₃/CO₂ ratio of 2.85 and a pressure of only 140 atm; the NH₃/CO₂ ratio chosen results in a minimum vapour pressure of the liquid phase (bubble-point) at the chosen temperature (see section 2.4.1. for a further discussion of this phenomenon). Upon leaving the reactor the liquid effluent (8) flows, at reactor pressure, into the stripper (2), which is heated with steam at 25 atm (225°C). In contact with CO₂ gas (1), which enters at the bottom of the stripper (2), the liquid flows as a thin film along the heated stripper tubes. At these conditions about 85% of the original carbamate decomposes; any substantial further carbamate decomposition is accompanied by unacceptable rates of biuret formation and urea hydrolysis in this hot, CO₂-rich environment. The resulting NH₃-CO₂ gas ((15), containing some water vapour formed by evaporation) flows to the high pressure condenser (14) where it largely condenses; being at a high pressure and the azeotropic composition (assured by shunting part of the NH₃-feed into the condenser; see further Appendix 2) the condenser produces valuable low pressure steam (at 4.8 atm; 150°C) which is later used in the process for distillation and evaporation. The liquid leaving the stripper is reduced in pressure via let-down valve (3) to about 3 atm and flows to a rectifier (21) and
absorber section where the remaining carbamate is separated from the urea solution by means of distillation, the resulting NH₃-CO₂-H₂O gases (17) being condensed (18) and pumped back to the high pressure condenser by means of a carbamate pump (19).

The NH₃-feed stream and gas-liquid effluent (29) from the condenser enter the reactor, which consists of a number of compartments separated by sieve plates, so that operation approaches a cascade of stirred tanks and thus plug-flow. The heat necessary to effect the endothermic urea reaction is provided by the condensation of NH₃ and CO₂ and the exothermic carbamate reaction. The phase theory underlying this autothermic reactor operation has been described by Kaasenbrood and is also briefly discussed in section 2.1. For more details concerning the DSM CO₂-stripping process the reader is referred to the literature.

The SNAM NH₃-stripping process works rather analogously to the DSM process. The reactor operates at a higher pressure (+150 atm) and, of course, a higher NH₃/CO₂ ratio (≈3.5-4.0). The stripper, operating in an NH₃-rich atmosphere, can dissociate up to 98% of the carbamate without danger of biuret formation. Because of the very high solubility of NH₃ in the urea synthesis solution (relative to CO₂) the low pressure recirculation system is more extensive and requires somewhat higher utilities costs than its counterpart in the DSM process. For a detailed economic comparison of these two processes see the work of Elkin.

The advantages of the strip processes center around the fact that the heat of carbamate dissociation is obtained at synthesis pressure and at azeotropic composition, hence at the highest attainable temperature and thus at maximum utility. Correspondingly, cooling water requirements are greatly reduced. The
reactor $H_2/O/CO_2$ feed ratio is relatively low enabling a low $NH_3/CO_2$ feed ratio to be used. This results in a smaller reactor. The recycle sections of the plant are also smaller and simpler than in the solution recycle process. The troublesome carbamate pump has been either eliminated (SNAM process) or replaced by a much smaller pump (DSM process) working at much milder temperature and composition condition. Because most of the carbamate dissociation occurs at high pressures, relative to the solution recycle process, the amount of recycled water is also lower. The strip processes also operate at considerably lower pressures than the solution recycle process.

The stripping processes are still being improved. Recently DSM developed a high pressure variant of its highly successful process, although this new process is not as yet operating on a commercial scale.\(^{88}\)

1.4. New developments and trends in the urea technology.

As already mentioned, the stripping processes, particularly the DSM $CO_2$-stripping process, are clearly winning the urea market. There are indications, however, that the future may witness the introduction of a new type of urea process technology, probably in the form of completely integrated ammonia-urea plants, possibly in the form of the hot gas recirculation type process.

The importance and volume of urea as a finished product have reached such high levels that, increasingly, the production of ammonia may be seen as an intermediate step in the production of urea. For this reason and because of the manifest relation between the urea and ammonia cost price it is interesting to investigate the possibilities for an integrated ammonia-urea plant. A number of obvious points for integration are (for a discussion of ammonia processes see the general industrial chemistry literature\(^{89}\), or more specialized literature\(^{90}\)):

1. The removal of $CO_2$ from the converted gas.
2. The removal of $NH_3$ from the $N_2-H_2-NH_3$ gaseous effluent from the ammonia reactor.
3. The compression of $CO_2$ to urea synthesis pressure.

A large number of patents exists discussing integrated $NH_3$-urea processes, and many of the leading development companies of urea processes have operated pilot-plants of their version of such processes. Indeed, for many years urea experts have been heralding the imminent construction of integrated plants, but their forecasts remained unfulfilled. Recently, however, SNAM caused some excitement by announcing the sale of the world's first integrated $NH_3$-urea plant, to be built in the USSR.\(^{91}\)

The process (see Fig. 1-5 for a simplified scheme)\(^{92,93}\) is based upon the
SNAM NH₃-stripping process and a SNAM NH₃-separation process in which ammonia is removed from the ammonia reactor effluent gases by means of contact with water and the wet gas dehydrated by means of cooling with liquid ammonia. The process is described as follows. Converted gas (stream (1); the preparation of the converted gas is conventional) is compressed from 30-35 to 180-200 atm by means of compressor (2) and flows to a falling film absorber (3) in which CO₂ is absorbed by a concentrated ammonia solution (5) to produce carbamate solution (4). The converted gas sensible heat content and the heat of formation of ammonium carbamate (the latter being formed at high pressure, hence high temperature) are used to produce steam later used in the process for urea solution distillation and NH₃-recovery (not shown in Fig. I-5) and recycle NH₃ preheating. The entering ammonia solution (5) is highly concentrated (about 80 wt-% NH₃), and the effluent solution (4) is a highly concentrated carbamate solution at 130-140°C; this solution flows to the urea reactor (6). The CO₂-free effluent gas stream (7) is sent to the methanation unit (8) for removal of CO and then, as (9), joins the ammonia synthesis reactor effluent (10) in the ammonia absorption vessel (11). Here the ammonia is almost completely removed from this gas stream by absorption in water (12). The resulting NH₃-solution (5) flows to the CO₂-absorber (3), and the exit gas from (11) is split into a purge gas side stream (26) while the major part (13) is dehydrated in (24) by quenching and scrubbing with a part (14) of the liquid ammonia from the ammonia recycle (15) stream. Dehydrated gas (16) is recycled to the ammonia synthesis reactor (17). A part (18) of the recycle ammonia and the recycle carbamate solution (19) from the urea purification section (not shown) are sent to the urea reactor (6). The reactor effluent (20) flows to a stripper (21) in which most of the carbamate is dissociated by contact with hot NH₃ gas (22). The
stripper effluent (23) is sent to the low pressure recycle section (not shown) for NH$_3$ and carbamate recirculation. The gaseous NH$_3$–CO$_2$ effluent (25) from the stripper flows directly to the reactor where condensation and reaction provide the necessary heat for the endothermic urea reaction. In order to compensate for the large amount of recycle water in the reactor feed ($H_2O/CO_2 = 1-2$) a large excess of ammonia ($NH_3/CO_2 \gtrsim 7$) is used.

SNAM claims that ammonia-urea integration will lead to substantial savings in investment (20%) and production (16%) costs.

In spite of the theoretical advantages of an integrated process a number of possible problems is obvious. Neither ammonia nor urea manufacture are simple processes, and down-periods of a month per year are usual for both types of plants. The coupling of such complicated and vulnerable processes increases the risk of the occurrence of serious disturbances with resultant plant shut-down and large production losses. Furthermore, while the ammonia synthesis and the $NH_3$-stripping urea process have been optimized individually, optimizing the combined processes entails considerable development work.

Come what may, however, the experience of this new integrated plant will be viewed as a test case for the eventual emergence of a new generation of urea plant technology.

1.5. Concerning general and patent literature.

The literature concerning urea technology and its scientific background is extensive. The author presents a representative - though by no means exhaustive - collection of pertinent literature in Appendix 5. So far the literature mentioned has usually referred to specific processes. Good review articles of the general urea technology also exist.

The patent literature concerning the urea synthesis technology is also extensive. This patent literature, however, has not been systematically studied in the literature, although most of the more important patents are mentioned in the articles dealing with the respective processes. One article reviews a large number (173) of patents and one book simply presents the complete specifications of a number (130) of patents; both works are, however, superficial concerning the principles underlying the patents.

The chemical properties of urea are discussed by Berliner and other literature already mentioned.
References and footnotes.


5. European Chemical News, December 1, 1972, 22; February 15, 1974, 32.


10. See reference 1, p. 8.


15. The national and international news media have described the dismal relation between high fertilizer prices and large scale undernutrition. See, for example, James Reston, The International Herald Tribune, July, 8, 1974, p. 8, Time, November 11, 1974, p. 18 and Nitrogen, March/April, 1974, p. 5-7.


17. European Chemical News, April 12, 1974, 32 and April 26, 1974, 8. The two cited articles represent optimistic and pessimistic view points.

18. For recent detailed estimations of the world's future fertilizer requirements and production, see, for example, United Nations Studies, such as that presented the UNIDO in Chem. Age India, December, 1971, p. 881-903. See also the work of R.A. Olson (ed.), "Fertilizer Technology and Use," Soil Science Society of America, Inc., Madison, Wisconsin, 1971, 611 pages, Tennessee Valley Authority (TVA), "World fertilizer review and outlook," 1974, 68 pages, and Dorgelo, F., Chem. Week. (The Netherlands), 25 October, 1974, 13. See also ref. 93.

19. In 1974, for example, China purchased 11 1620 ton/day urea plants; see Nitrogen, Sept./Oct., 1974, p. 24. Large ammonia and urea synthesis projects are also currently under construction, near large natural gas supplies, in Canada and Alaska; see European Chemical News, March 22, 1974, p. 32 and May 10, 1974, p. 12. Large urea production facilities are also still being erected in Eastern Europe, particularly in the USSR. See Nitrogen, May/June, 1974, p. 18.


21. From Ref. 3., p. 20, as based on a 1000 ton/day DSM CO₂-stripping process.
22. For more information concerning the economics of urea manufacture see References 1, 3, 12 and Vernede, J., Hydrocarbon Proces., 47(1), 1968, 143. For information concerning the effect of the energy crisis on the costs of urea production see Nitrogen, May/June, 1974, 43. See also ref. 87.

23. Ammonium carbamate is unsuitable as a fertilizer because of its high volatility, hygroscopic nature and poor agronomic properties. It is of no importance commercially.


25. The literature up to 1972-73 concerning the kinetics of the urea synthesis has been studied in our Laboratory by Kalkman, F.C., "Developments in the study of the kinetics of the urea synthesis," 1972, 104 pages and Verbruggen, P., "The Urea Synthesis Reactor: Considerations and Calculations," 1973, 75 pages. The main conclusion of these reports is that while the articles of Kucheryavyi et al (up to 1972) are not completely sound theoretically, his publications provide good order of magnitude descriptions of the kinetics in the ranges studied.


34. Since, for practical purposes, urea is formed in the liquid phase only, in gas-liquid mixtures the degree of conversion of the originally added CO₂ is dependent on the gas-liquid ratio in the reactor, hence dependent on the pressure and thus "loading density", which is the gross density in a batch reactor (total mass (L + G)/total volume (L + G)). At pressures above the bubble-point pressure, at which no gas exists, the conversion is practically independent of pressure (except as critical conditions are approached).

35. At particularly high temperatures (T ≥ 190-200°C) the conversion in the liquid phase decreases due to the liquid phase dissociation of ammonium carbamate and the approach to critical conditions. See further section 3.7.


40. Ref. 3., p. 35.
41. Frejacques, M., Chemie Industrie, 60(1), 1948, 22.
42. Anon., Hydrocarbon Proces., 44(11), 1965, 286.
46. Sen, D., Chem. Age India, 17(12), 1966, 1017.
49. Very qualitatively, A.V. Slack and G.M. Blouin (Chem. Tech., Jan., 1971, p. 32) describe the methods used in the solution recycle process to minimize the amount of recycled water.
50. The fundamental behaviour of the low pressure recirculation stages is based upon the phase equilibria of the NH_3-CO_2-H_2O-urea and NH_3-CO_2-H_2O systems. At our Laboratory the literature concerning these equilibria has been studied by H. Swets, "Methods of measurement and phase equilibria in the ammonia-water-carbon dioxide system at a pressure of one atmosphere and temperatures between 0 and 100^\circ C," 1973, 74 pages, and J.N. Broers, "The phase equilibria of the system ammonia-water-carbon dioxide at pressures above one atmosphere," 1974, 110 pages. The conclusions of these works are that the solid-liquid equilibria in this system are fairly well known (although the relevant literature is very difficult to fathom); the gas-liquid equilibria, on the other hand, are poorly known. Most of the literature describing the phase equilibria of this ternary system has been collected by D. Schmidt, "Enthalpie - Zusammensetzungsdiagramme für Drei-stoffsysteme am Beispiel des Systems Ammoniak-Wasser-Kohlensäure," Ph.D. Dissertation, Braunschweig, W. Germany, 1973.
64. Viti, A., Het Ingenieursblad, (Belgium), 21, 1971, 619.
95. Kaasenbrood, P.J.C., Proces Techniek (The Netherlands), March 15, 1968, 198; March 29, 1968, 225.
CHAPTER II
A NEW PHASE MODEL FOR THE AMMONIA-WATER-CARBON DIOXIDE
SYSTEM AT EQUILIBRIUM AT UREA SYNTHESIS CONDITIONS

2.1. Introduction

The phase equilibria of mixtures of water, ammonia and carbon dioxide and their reaction products have long been of interest because of their relation to the various aspects of urea technology. Scientifically the system is also interesting because it is composed of basic chemical species (H₂O, NH₃, CO₂) and because the system illustrates many complications which can occur in the study of phase equilibria, such as the occurrence of azeotropy, liquid immiscibility, unusual critical behaviour and, particularly, the occurrence of chemical reactions by which various new chemical compounds can be formed, such as ammonium carbamate and urea.

Any discussion of phase equilibria begins with the application of the phase rule:

\[ F = C + 2 - P \]  

where \( F \) is the number of intensive thermodynamic properties necessary and sufficient to describe the state of the system (degrees of freedom), \( C \) is the number of components and \( P \) is the number of phases. In applying this rule the problem is often that of determining the number of components. For a system with chemical reaction it can be shown that:

\[ C = C' - R - Q \]  

where \( C' \) is the number of chemical substances present in the system, \( R \) is the number of independent, reversible chemical reactions occurring between \( C' \), and \( Q \) is the number of restrictive equations.¹ It should be noted that the phase rule, strictly speaking, may only be applied to systems at complete physical and chemical equilibrium.¹

In systems containing ammonia, water and carbon dioxide the following reactions may occur:

\[ 2 \text{NH}_3 + \text{CO}_2 \rightleftharpoons \text{NH}_2\text{OCONH}_4 \]  
\[ \text{NH}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{HCO}_3 \]  
\[ \text{NH}_2\text{OCONH}_4 + \text{H}_2\text{O} \rightleftharpoons (\text{NH}_4)_2\text{CO}_3 \]  
\[ (\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons (\text{NH}_4)_2\text{CO}_3\cdot\text{H}_2\text{O} \]  
\[ \text{NH}_2\text{COONH}_4 \rightleftharpoons \text{NH}_2\text{CONH}_2 + \text{H}_2\text{O} \]
In studying the phase equilibria of mixtures containing some or all of the above mentioned chemical species a primary question is at what condition the system is considered to be at equilibrium, because this condition determines the minimum number of components necessary and sufficient to describe the system. More specifically: which (how many) reactions are assumed to be reversible and in equilibrium \( R \), and which reactions are assumed not to occur?

For example, at low temperatures \( T < 100^\circ \text{C} \) in a system initially composed of \( \text{NH}_3 \) and \( \text{CO}_2 \) only ammonium carbamate is formed. Thus \( C' = 3 \) (\( \text{NH}_3, \text{CO}_2, \text{NH}_2\text{CONH}_2 \)), \( R = 1 \) (equation II-3); then \( C = 2 \): the system is binary. If water is added to the system and the temperature still kept below about \( 100^\circ \text{C} \), then \( C' = 7 \) (\( \text{NH}_3, \text{CO}_2, \text{H}_2\text{O}, \text{NH}_2\text{CONH}_2, (\text{NH}_4)_2\text{CO}_3, (\text{NH}_4)_2\text{CO}_3\cdot\text{H}_2\text{O}, \text{NH}_4\text{HCO}_3 \)), \( R = 4 \) (equations II-3, 4, 5 and 6); then \( C = 3 \): the system is ternary. If urea is also added to this system at the same conditions (reactions II-7, 8 and 10 do not occur at these low temperatures) it is seen that the system becomes quaternary.

If the temperature of the system is now raised to, for example, \( 160-200^\circ \text{C} \), then reactions II-3 to II-10 are all very close to equilibrium within a reasonable observation time (minutes to some hours; see Fig. I-1). Then \( C' = 11 \), \( R = 8 \) and \( C = 3 \): the system is ternary. It is thus seen that two ternary systems exist, one without urea, the other containing equilibrium concentrations of urea.

It is therefore obvious that one of the inherent problems of studying the phase equilibria of systems composed of \( \text{NH}_3, \text{CO}_2, \text{H}_2\text{O} \) and their reaction products at temperatures above \( 100^\circ \text{C} \) is the question of whether the system is really in equilibrium and whether it is binary, ternary or quaternary. For this reason there is often confusion in the literature concerning the system's number of components, particularly at conditions of \( 140-160^\circ \text{C} \), at which reactions II-7, 8 and 10 are rather slow, so that the system is often regarded as quaternary or "quasi-ternary".

With these points clarified a literature review of the relevant systems may be attempted.

A knowledge of the phase equilibria of the binary \( \text{NH}_3-\text{CO}_2 \) and ternary \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) (no urea present) systems is necessary for the optimum operation of the \( \text{NH}_3-\text{CO}_2 \) gas condensers and the \( \text{NH}_3-\text{CO}_2 \) recirculation sections. The phase equilibria of these systems are quite complicated and only partially known; a detailed review of the available literature is presented in Appendix 2. For purposes here
the most important conclusions are that the NH$_3$-CO$_2$ system is characterized by a pressure minimum in the pressure-composition plane (T = constant) due to the formation of ammonium carbamate; at high temperatures (T $\geq$ 145° C.) a minimum pressure azeotrope is formed whose NH$_3$/CO$_2$ ratio increases with increasing temperature. For the NH$_3$-H$_2$O-CO$_2$ system this same tendency, in the liquid + gas region, exists, the NH$_3$/CO$_2$ ratio of the liquidus pressure minimum also increasing with increasing water concentration (T = constant).

A knowledge of the phase equilibria in the NH$_3$-CO$_2$-H$_2$O-urea system at urea synthesis conditions is of importance in choosing the optimum conditions in the carbamate decomposer, the reactor and the stripper. Published information concerning the equilibria of this quaternary system exists only in very small composition areas. Janecke studied various binary and ternary parts of the figure, such as the urea-NH$_3$, water-urea, urea-ammonium carbamate and NH$_3$-H$_2$O-CO$_2$ systems. Frejacques discussed the application of these results to urea process technology. Otsuka et al have studied the gas-liquid equilibria in a very small composition range (typical of a urea process of a given type) at 60-130° C. and 10-20 atm to effect an optimum separation of NH$_3$ from the reactor product. A similar study has also been published by Kucheryavyi et al.

Phase equilibria of mixtures of NH$_3$, CO$_2$, H$_2$O, urea, etc at high temperatures (T $\geq$ 140° C.) have been studied by Kawasumi and Lemkowitz et al. (The work of the latter authors forms the basis of this chapter.) At these conditions the system is ternary, but Kawasumi described it sometimes as if it were quaternary, sometimes as if it were ternary. Since urea and water are always formed on a 1:1 molar basis from NH$_3$ and CO$_2$, and since the gas phase, as an approximation, contains no water, Kawasumi made use of a ternary composition triangle in which NH$_3$, CO$_2$ and urea:water=1:1 (molar) were the three ternary "components." His use of this construction was, unfortunately, not clarifying. His data will be used in this chapter, however.

Recently Kaasenbrood has presented a new version of the quaternary NH$_3$-CO$_2$-H$_2$O-urea system at urea synthesis conditions. As is usual for quaternary systems, the phase equilibria, at constant temperature and pressure, are presented in a tetrahedron whose four corner points represent the four components. At constant temperature and pressure the compositions of the liquid phase at physical equilibrium are described by means of a curved plane in the tetrahedron. At these conditions and at chemical equilibrium the system becomes ternary, and the number of degrees of freedom is reduced by one, so that the equilibrium concentrations of the liquid phase are described by lines in the figure. Kaasenbrood generally applies his model at constant pressure (P = 130 atm, the pressure of the DSM strip process) and varying temperature, which is the situation occurring in
much of the DSM process. At these particular conditions the system is also characterized by a plane of chemical equilibrium compositions. (The intersection of the chemical equilibrium plane \( P = \text{constant}; T \text{ varying} \) with the liquidus plane \( T \text{ and } P \text{ constant} \) form the lines of chemical equilibrium at constant \( T \) and \( P \).) In his article Kaasenbrood provides a number of drawings which help illustrate this difficult material.

Kaasenbrood simplifies his quaternary model into a "quasi-ternary" model by projecting a temperature axis, at constant pressure \( P = 130 \text{ atm} \), vertically from the flat triangular \( \text{NH}_3-\text{CO}_2-(\text{urea:water} = 1:1, \text{ molar}) \) plane of the tetrahedron (see Figures II-1 a and b). This construction is adequate for describing

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**Fig. II-1a.** The quaternary \( \text{NH}_3-\text{CO}_2-H_2O-\text{urea} \) system at constant temperature and pressure. Point 1 is an equimolar solution of urea and water. A flat plane is drawn through the points \( \text{NH}_3, \text{CO}_2 \) and 1. From this plane, at constant pressure, a temperature axis is projected. In this way the quaternary model is formed.

**Fig. II-1b.** The quasi-ternary \( \text{NH}_3-\text{CO}_2-(\text{water-urea}) \) model at constant pressure. The points have the following meaning: 1: an equimolar solution of urea and water. 2 and 3: projections of liquid isotherms on the composition plane; \( T_2 > T_3 \). 4: azeotropic point on the \( \text{NH}_3-\text{CO}_2 \) system. Line 4-5 (solid): the top-ridge line; (dashed): gas-line analogous to the top-ridge line. Points 6, 7, 8 and 9: assumed critical points on the, respectively, \( \text{CO}_2-1, \text{NH}_3-1, \text{NH}_3-\text{CO}_2 \) (\( \text{CO}_2 \)-rich) and \( \text{NH}_3-\text{CO}_2 \) systems. 10-1: projection of the top-ridge line on the composition plane.
the liquid phase occurring in the reactor as reaction proceeds. A characteristic line in this construction is the "top-ridge line," which, approximately speaking, describes the locus of the points of maximum boiling temperature as the urea reaction proceeds at constant pressure. This line begins at the NH$_3$-CO$_2$ system's azeotropic point and, allowing for non-equilibrium conditions, ends at the urea: water = 1:1 point. In practice, however, beginning at the azeotropic point, the top-ridge line can extend only to a point on the equilibrium line representing a maximum boiling point mixture at 130 atm. The top-ridge line's NH$_3$/CO$_2$ ratio and temperature increase with the increasing urea-water concentration associated with the occurrence of the urea reaction.

The great advantage of Kaasenbrood's model is that it, in principle, describes the phase equilibria of the quaternary system, the equilibrium ternary system and the quaternary system as it reacts towards the equilibrium ternary system. As such it describes the working conditions of the reactor, stripper, separation units, etc. It also describes the form of the liquidus and chemical equilibrium planes. For these reasons his model provides new and highly significant insight into the fundamentals of urea process technology.

Kaasenbrood, however, presents rather little quantitative information concerning the above mentioned equilibria. Only the liquidus and chemical equilibrium lines, at constant pressure (P = 130 atm) and varying temperature (160 < T < 200$^\circ$C.) are shown, projected upon the composition triangle of the quasi-ternary system. The projection of the top-ridge line is also shown. (As such the presented projection illustrates the (optimum) working of a urea reactor.) The relation of the interior of the quaternary system to the four ternary systems, which are themselves not discussed (and which are chemically unstable at the above mentioned conditions), is not given. Furthermore, no information concerning the dew-point lines is given. The Kaasenbrood model is further discussed in section 2.5.

In all of the literature reviewed concerning the binary, ternary and quasi-ternary systems a characteristic feature in the composition-pressure plane is the occurrence of a pressure minimum in the NH$_3$-CO$_2$ system or in planes parallel to this system. With increasing temperature, and/or increasing water or urea: water = 1:1 (molar) concentration, this pressure minimum is displaced towards higher NH$_3$ concentrations. It will be seen later that this behaviour is also characteristic of the NH$_3$-H$_2$O-CO$_2$ system at equilibrium at temperatures above 130$^\circ$C.

The purpose of this chapter is to develop, quantitatively describe and apply
a new phase model for the \( \text{NH}_3 - \text{H}_2\text{O} - \text{CO}_2 \) system at complete chemical equilibrium (reactions II-3 to II-10 all in equilibrium) which describes the phase equilibria of any combination of \( \text{NH}_3, \text{CO}_2, \text{H}_2\text{O} \), ammonium carbamate and urea over the temperature range of 140 to 200° C. and a pressure range of about 30 to 300 atm. The relation of the ternary phase behaviour to the phase behaviour of the binary systems will also be shown.

2.2. Theoretical development of the ternary phase model

Because \( \text{NH}_3, \text{CO}_2, \) and \( \text{H}_2\text{O} \) are the three most fundamental chemical substances present in the ternary system, it is useful to choose these substances as the three components. Then:

\[
\text{NH}_4\text{OCONH}_2 = 2 \text{NH}_3 + \text{CO}_2 \\
\text{NH}_2\text{CONH}_2 = 2 \text{NH}_3 + \text{CO}_2 - \text{H}_2\text{O}
\]

It is seen that the formation of urea requires the use of water as a negative component. Because of this the \( \text{NH}_3 - \text{H}_2\text{O} - \text{CO}_2 \) system cannot be constructed making use of an equilateral triangle, as is ordinarily used to represent a ternary system. To prepare a phase model which can represent all combinations of \( \text{NH}_3, \text{CO}_2, \text{H}_2\text{O}, \) and urea it is possible to use a composition model based on a square, three of whose corner points represent \( \text{CO}_2, \text{H}_2\text{O} \) and \( (2\text{NH}_3) \). It can be shown (see Appendix 2) that any point in the square can be fixed by three lines which represent the mole-percentages of the three components, \( \text{CO}_2, \text{H}_2\text{O} \) and \( (2\text{NH}_3) \). The fourth corner point, diagonally opposed to water, represents the composition: \( \text{CO}_2 + (2\text{NH}_3) - \text{H}_2\text{O} = \text{urea} \), and this result is simply the geometric interpretation of equations II-3 and II-7. (If \( \text{NH}_3 \) instead of \( (2\text{NH}_3) \) were chosen as a component, then the corner point diagonally opposed to water would be: \( \text{NH}_3 + \text{CO}_2 - \text{H}_2\text{O} = \text{HNCO}, \) isocyanic acid.) For a drawing of the proposed composition model see Fig. II-3; for a numerical discussion see Appendix 2.

While a description of the urea synthesis solution using a ternary composition square may seem novel, the idea itself is not new and was already suggested in 1955 by Zernike.\(^{16}\) More recently Kucheryavyi et al have also characterized urea-rich solutions using water as a negative component;\(^{17}\) they do not, however, make use of a square composition plane. It should further be noted that the use of a ternary diagram employing a square composition plane is not infrequently encountered to describe reciprocal salt-pair reactions of the type:\(^{16,18}\)

\[
M + N \rightleftharpoons P + Q \tag{II-13}
\]

in which \( C' = 4, R = 1 \), thus \( C = 3 \).

From the phase rule it is seen that a ternary system is thermodynamically
described by \((5 - P)\) degrees of freedom. In the coming discussion the tempera-
ture is generally chosen to be constant, and the system can then be described by
three degrees of freedom, namely pressure and two composition variables. At con-
stant temperature these variables form a three-dimensional pressure-composition
figure which is constructed by projecting a vertical pressure axis perpendicular
to the square composition plane; the spatial figure is a square-based parallelepiped.

In explaining the spatial composition figure it is convenient to "fold open" the
figure and discuss the four binary systems, \(H_2O-(2NH_3)\), \(H_2O-CO_2\), urea-(2NH.)
and \(CO_2\)-urea, as well as the diagonal plane, \((2NH_3)-CO_2\) (see Fig. II-2).

![Fig. II-2. The pressure-composition figure for the NH\textsubscript{3}-H\textsubscript{2}O-CO\textsubscript{2} system folded open at constant temperature (\(T = 160^\circ C\)). The four binary systems and the diagonal (2NH\textsubscript{3})-CO\textsubscript{2} planes are shown. \(K\) represents the critical point.]

The gas-liquid behaviour of the \(NH_3-H_2O\) system is typical of two components
which are chemically and physically similar. Ammonia dissolves well
in water, and the \(\left(\frac{dP}{dX}\right)_{NH_3,T}\) slope of the liquidus line is therefore moderate.
The gas phase, except at critical conditions, is \(NH_3\)-rich since \(NH_3\) is more vola-
tile than \(H_2O\). The critical line begins at the critical point of \(NH_3\) and extends
regularly to the critical point of water.

The system CO$_2$-H$_2$O exhibits unusual phase behaviour characteristic of a system composed of two dissimilar components, one polar (water), the other not. CO$_2$ is relatively poorly soluble in water and the (dP/dX$_{CO_2}$)$_T$ slope of the liquidus line is therefore very steep. At temperatures below about 250° C. the gas phase contains little water even at very high pressures (P > 1000 atm). The behaviour of the critical line is very unusual. Beginning at the critical point of water (T$_c$ = 374° C., P$_c$ = 218 atm) the critical line decreases in temperature towards the critical point of CO$_2$ (T$_c$ = 33° C., P$_c$ = 73 atm). At about 265° C., however, the critical line abruptly reverses direction and heads towards higher temperatures and very high (P > 1000 atm) pressures. Therefore at temperatures below 265° C. (to about 40° C.) no critical behaviour is found. At temperatures less than about 200° C. the gas and liquidus lines remain widely separated and near the CO$_2$ and H$_2$O axes, respectively, even at thousands of atmospheres.

Before discussing the CO$_2$-urea and (2NH$_3$)-urea system it is necessary to describe some of the properties of urea relating to its stability and its relation to water.

At one atmosphere and at temperatures above its melting point (132° C.) urea decomposes via a number of series and parallel reactions to a mixture of ammonium cyanate, biuret, triuret, triazines (ammelide, ammeline, melamine) and poly-triazines (melam, melon, etc.). Under these conditions the reactions are irreversible, and the eventual composition of the reaction products are functions of time, heating rates, catalysts, etc. In the presence of NH$_3$, however, particularly at high pressures, the decomposition of urea is strongly retarded or even reversed, probably because the initial decomposition reactions (reactions II-8 and II-10) are repressed. As will be discussed later, it has been found that urea-ammonia solutions are stable in an atmosphere of NH$_3$ under pressure. In the rest of this paper it is assumed that liquid urea is stable or decomposes so slowly that the decomposition may be neglected.

There are also a number of facts which point to a similarity between water and urea. The heat of solution of urea in water, 3.5 kcal/mole, is almost identical to urea's heat of fusion, 3.6 kcal/mole. Furthermore the activity coefficients of even highly concentrated aqueous solutions of urea are in the order of unity, a fact which points to their near ideality. Liquid urea is also a fairly good solvent for some inorganic compounds, such as alkaline earth and ammonium salts. Other polar liquids chemically similar to urea, such as formamide (NH$_2$COH) are also noted for their water-like properties.

It is therefore to be expected that the systems CO$_2$-urea and (2NH$_3$)-urea will behave analogously to the systems CO$_2$-H$_2$O and (2NH$_3$)-H$_2$O, respectively. Thus the system CO$_2$-urea will be characterized by a very steep liquidus line (CO$_2$
poorly soluble in liquid urea), and the gas phase will consist almost entirely of \( \text{CO}_2 \). It is also to be expected that the system will not become critical, i.e., the gas and liquidus lines will remain far apart even at very high pressures. The \((2\text{NH}_3)\)-urea system, however, will exhibit a moderately sloped liquidus line (\( \text{NH}_3 \) soluble in liquid urea); the gas phase will be \( \text{NH}_3 \)-rich (this last fact has already been reported in the literature\(^3\)). Beginning at the critical point of ammonia, the system should become critical, the critical line extending into regions of higher temperature and pressure with increasing urea concentration.

Concerning the \((2\text{NH}_3)\)-\( \text{CO}_2 \) diagonal plane, the liquidus (bubble-point) line has already been studied by Kawasumi.\(^7\,8\,9\,10\,11\) Characteristic of this line is a sharp pressure minimum. The cause of this pressure minimum is the reaction of \( \text{CO}_2 \) and \( \text{NH}_3 \) to form ammonium carbamate and \( (\text{urea} + \text{water}) \), all of which are much less volatile than \( \text{CO}_2 \) and \( \text{NH}_3 \). Since the urea synthesis solution contains appreciable concentrations of urea and water it is not surprising that the \( \text{NH}_3 \)-side of this minimum exhibits a moderate slope roughly equal to the slope of the liquidus line of the \((2\text{NH}_3)\)-\( \text{H}_2\text{O} \) system. Similarly, the \( \text{CO}_2 \)-side of the minimum is characterized by a very steep slope roughly equal to that of the liquidus line of the \( \text{CO}_2\)-\( \text{H}_2\text{O} \) system. The dew-point line of this diagonal plane is, in contrast to the bubble-point line, poorly known. A few measured values are available,\(^37\,38\) and a calculation method also exists in the literature;\(^39\) the agreement between these two sources is reasonable.\(^13\) It should be stressed that this diagonal plane is not a true binary system, and gas and liquid points in this plane are not in equilibrium. It is known, however, that liquid points on the \( \text{NH}_3 \)-side of the pressure minimum are in equilibrium with an \( \text{NH}_3 \)-rich gas mixture and vice-versa. From Fig. II-2 it is also seen that the slope of the dew-point line near the pressure minimum is much less sharp than that of the liquidus line.

\[ \text{CO}_2 \quad \text{Urea} \]
\[ \text{H}_2\text{O} \quad (2\text{NH}_3) \]

Fig. II-3. The ternary composition square of the \( \text{NH}_3 \)-\( \text{H}_2\text{O}-\text{CO}_2 \) system at complete chemical equilibrium. The point \( A \) represents the composition of the azeotrope at a given temperature.
With the four binary systems and one diagonal plane discussed, the interior of the phase model can be sketched. Let it for the moment be assumed that at the projected point A of Fig. II-3 a ternary azeotrope exists; the azeotrope is slightly water-rich ($< 10\% \text{H}_2\text{O}$) and $\text{NH}_3$-rich ($\text{(2NH}_3)/\text{CO}_2 \sim 1.3$). Two pressure-composition planes are drawn through this azeotrope, one plane parallel to the $(2\text{NH}_3)-\text{CO}_2$ plane, the other parallel to the $\text{H}_2\text{O}$-urea plane.

Beginning with the $(2\text{NH}_3)-\text{CO}_2$ plane it is to be expected that the addition of a small amount of water to compositions on the $(2\text{NH}_3)-\text{CO}_2$ diagonal will not greatly affect the form of the liquidus line. The bubble-point pressure may slightly increase due to the hydrolysis reaction of urea to form ammonium carbamate. Since the minimum point of the liquidus line parallel to the $(2\text{NH}_3)-\text{CO}_2$ plane is azeotropic, the dew-point line must rise from its position in the $(2\text{NH}_3)-\text{CO}_2$ plane and touch the liquidus line at this point, as is sketched in Fig. II-4 (negative azeotrope).

The plane parallel to the $\text{H}_2\text{O}$-urea plane and through the azeotrope is at a $90^\circ$ angle with the plane discussed above. The end points of the liquidus line of this plane are situated near the bubble-points of pure water and urea. Relative to the urea synthesis solution liquid water and urea are hardly volatile. With the addition of water to urea, or vice-versa, however, the bubble-point pressure increases due to the hydrolysis reaction. A maximum pressure value is reached at the azeotropic point.

The gas phase in equilibrium with the water-rich liquid contains $\text{NH}_3$, $\text{CO}_2$, and $\text{H}_2\text{O}$. The gas phase in equilibrium with the urea-rich liquid contains $\text{NH}_3$, $\text{CO}_2$, $\text{H}_2\text{O}$, $\text{HNCO}$ and possibly urea. With increasing concentrations of urea (decreasing water concentrations) it is to be expected that the gas phase will
contain increasing concentrations of HNCO. In the presented phase model HNCO is formulated making use of water as a negative component:

\[ \text{HNCO} = \frac{1}{2}(2\text{NH}_3)+\text{CO}_2 - \text{H}_2\text{O} \]  

(II-14)

For this reason a gas phase containing more HNCO than water is situated in the negative water region. (It should be noted that at low pressures, particularly low partial NH3 pressures, the urea-rich liquid is not stable and is decomposing slowly to biuret and triazines, the latter via irreversible reactions. In the model we assume that the irreversible reactions are so slow that they may be neglected.) At the azeotrope the liquidus and dew-point lines touch, as is sketched in Fig. II-4 (positive azeotrope).

At the ternary azeotropic point the positive and negative azeotropes meet to form what is called a ternary saddle-azeotrope.

On the basis of the above discussion, the entire phase model (at constant temperature) may be described. A very steeply sloped liquidus plane begins at the CO2-H2O system, extends into the figure in the direction of the urea corner, through the (2NH3)-CO2 plane and ends at the CO2-urea system. Points on this liquidus plane are in equilibrium with a gas phase rich in CO2. These equilibrium gas and liquid points remain far separated in composition, except near and at the azeotropic point, and no critical behaviour occurs.

At the (2NH3)-H2O system a much more moderately sloped liquidus plane begins, extends into the system through the (2NH3)-H2O plane and ends at the (2NH3)-urea system. Beginning in the (2NH3)-H2O system critical behaviour is found, and a critical line extends from this system into the figure, through the (2NH3)-CO2 plane ending at the (2NH3)-urea system. Two dew-point planes exist, one beginning at pure H2O and bounded by the dew-points of the (2NH3)-H2O and CO2-H2O systems, the other beginning at pure urea and bounded by the dew-points of

\[ \text{CO}_2 \quad \text{Urea} \]
\[ \text{H}_2\text{O} \quad P \leq P_{\text{AZ}} \quad (2\text{NH}_3) \]

\[ \text{CO}_2 \quad \text{Urea} \]
\[ \text{H}_2\text{O} \quad P = P_{\text{AZ}} \quad (2\text{NH}_3) \]

\[ \text{CO}_2 \quad \text{Urea} \]
\[ \text{H}_2\text{O} \quad P > P_{\text{AZ}} \quad (2\text{NH}_3) \]

Figures II-6a, b and c. Constant temperature-pressure section below, at and above the azeotropic pressure.
the (2NH₃)-urea and CO₂-urea systems. With increasing water, respectively increasing urea concentrations, the two planes rise in pressure meeting at the point of azeotropic composition and pressure: here these planes merge with the bubble-point planes to form the ternary azeotropic point.

The interior of the phase model is illustrated in Fig. II-5, a, b and c, where constant-temperature-pressure sections are drawn under, at and above the azeotropic pressure.

2.3. Experimental

2.3.1. Apparatus

The experiments were performed in two types of apparatus. For lower pressures (P < 175 atm, T < 200° C.) an apparatus built about a Pyrex glass capillary tube, 4 mm x 12 mm x 30 cm. (Cailletet tube) was used; pressure was generated hydraulically using mercury. The NH₃-H₂O-CO₂ samples, about 40-50 mg. per experiment, were prepared gas volumetrically. In some experiments urea was also dosed. The urea was added to the inverted Cailletet tube as a pellet which was freed from air by cyclically melting and recrystallising it (at ~ 135° C.) in the tube under a stream of NH₃; the presence of NH₃ prevented the decomposition of urea. Mixing of the sample was effected using a glass-covered iron stirrer activated magnetically. Using a dead-weight gauge pressure was measured to within ± 0.1 atm. The Cailletet tube (see Fig. II-6) was enclosed in a silicone oil bath, the temperature of which was constant to within ± 0.2° C. and measured to within ± 0.1° C. using a platinum resistance thermometer.

For high pressure work (P < 1000 atm; T < 400° C.) the experiments were performed in a Pyrex glass container enclosed in an autoclave. The NH₃-CO₂-H₂O and NH₃-CO₂-N₂ samples, about 30-40 mg. per experiment, were also prepared gas volumetrically. Urea was dosed as described above, and mixing of the sample in the glass container was also effected magnetically. In the autoclave pressure, which was created hydraulically using silicone oil, was applied to both sides of the glass container. The oil was separated from the sample by means of mercury. The temperature in the autoclave was constant to within 0.4° C. and was measured to an accuracy of 1° C. by means of a calibrated chromel-alumel thermocouple. Pressure was measured using calibrated precision (DIN class 0.6) bourdon manometers accurate to within 0.5% of the indicated values. A schematic drawing of the autoclave is presented in Fig. II-7.

A sketch of the gas-rack, the apparatus with which the Cailletet tubes and glass containers were filled, is shown in Fig. II-8. The error in dosage was dependent upon the size of the samples and the NH₃:CO₂:H₂O proportions. For CO₂
and NH$_3$ this error was about 0.2–0.4 mole-%, for H$_2$O about 0.5–1.0 mole-% and for N$_2$ about 0.005 mole-%. (The error in urea dosage was about 1 mole-%)

The mercury in this apparatus was freed from entrained air by repeatedly allowing it to fall and splash (parts 5 and 15 of Fig. II-8) under vacuum, the pressurizing gas (part 17) being chemically pure CO$_2$. For more detailed descriptions of the Cailletet tube, the autoclave and the filling techniques see References 44 and 45.

2.3.2. Purity of the Materials

The CO$_2$, NH$_3$, and N$_2$ used were Union Carbide high purity (99.99%) gases. The
water used was triple distilled. The CO₂, NH₃, and H₂O were further purified using freezing techniques. The urea was Merck analytical grade. Test bubble-points found for NH₃, CO₂ and H₂O are given in Table II-1.

Table II-1. Test bubble-points for NH₃, CO₂ and H₂O

<table>
<thead>
<tr>
<th></th>
<th>T measured (°C)</th>
<th>P measured (atm)</th>
<th>P literature (atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₃</td>
<td>105.3</td>
<td>68.5</td>
<td>68.5</td>
</tr>
<tr>
<td>CO₂</td>
<td>24.6</td>
<td>65.2</td>
<td>65.0</td>
</tr>
<tr>
<td></td>
<td>25.7</td>
<td>66.7</td>
<td>66.6</td>
</tr>
<tr>
<td>H₂O</td>
<td>162.6</td>
<td>7.1</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>186.0</td>
<td>11.6</td>
<td>11.3</td>
</tr>
</tbody>
</table>


2.3.3. Safety precautions

The mercury used was free of metallic impurities above the 0.1 ppm level.
The use of extremely pure mercury and oxygen-free materials was necessary to prevent the formation of highly explosive Millon's base products on the mercury's surface.

2.3.4. Experimental method

A given mixture was brought to a temperature of about 160°C and a pressure of 150-250 atm. After a period of at least 12 hours, during which complete chemical equilibrium had been reached, the bubble-points were measured, again allowing sufficient time for equilibrium. Bubble-points were measured at roughly 10°C intervals. For measurements in the 140-200°C range the sequence of temperatures was random. For higher temperature measurements the sequence was roughly random, but tending towards higher temperatures up to the critical point; thereafter the sequence was completely random. The measurements were made visually; the bubble-point was found as the minimum pressure, at a given temperature, at which the last gas bubble disappeared. The critical point was found at that temperature and pressure at which the meniscus appeared and disappeared exactly in the middle of the sample's volume. Mixing occurred continuously. The bubble-points could generally be measured with a reproducibility within the experimental error. The critical points were considerably more difficult to measure, and values recorded are subject to an uncertainty of roughly 2-3°C and perhaps 1% of the indicated pressure.

In measuring the dew-points the liquid samples were expanded in the Cailletet tube in steps from the equilibrium bubble-point conditions to gas-liquid mixtures. After each expansion the system's length (thus volume) was measured to 0.02 mm using a cathetometer. Equilibrium was found at that time at which the system's volume was constant with time. The pressure was then decreased and equilibrium awaited, etc. The dew-points were measured as the lowest pressure at which liquid could be observed. Due to the sluggishness of the urea hydrolysis reaction, the experimental procedure was very tedious and slow, and days to weeks were necessary to measure one point. The accuracy varied from about ±0.3 atm at water-rich mixtures to about 5% of the indicated pressure at points near the \((2\text{NH}_3)\text{-CO}_2\) diagonal. The system remained completely reversible during the dew-point measurements: bubble-points measured before and after the dew-points had been measured were identical within the experimental error.

2.4. Experimental results and discussion

2.4.1. Bubble- and critical-points on the \((2\text{NH}_3)\text{-CO}_2\) diagonal plane

These points have been studied in the range of 130 ≤ T ≤ 260°C, 30 ≤ P ≤ 1000 kg/cm² and \(\text{NH}_3/\text{CO}_2\) (molar) = 2 to 100% \(\text{NH}_3\). A number of representative
Fig. II-9. Clapeyron plot of bubble-points of selected NH$_3$-CO$_2$ mixtures. NH$_3$ concentrations (mole-%) are: V, 66.5; ●, 74.0; △, 79.8; O, 90.0. The solid symbols represent measured critical points; the dashed line represents the extrapolated vapour pressure of pure NH$_3$.

points is plotted in a log pressure vs. reciprocal absolute temperature (Clapeyron) graph in Fig. II-9. The great reproducibility of the measurements is evident from the smoothness of the Clapeyron lines. These results indicate that for compositions on the (2NH$_3$)-CO$_2$ plane, at their bubble-point pressures, no irreversible reactions occur even at temperatures of up to 250$^\circ$C.

From Fig. II-9 it is also seen that mixtures rich in NH$_3$ behave similarly to pure NH$_3$: a linear log P vs. 1/T relation parallel to the extrapolated vapour pressure line of NH$_3$ and ending at a critical point is found. Mixtures richer than about 30 mole-% CO$_2$ are characterized by high bubble-point pressures and steep dP/dT slopes. For mixtures of intermediate composition the situation is more complex. At low temperatures their dP/dT slopes are similar to those of the NH$_3$-rich mixtures. With increasing temperature, however, their dP/dT slope increases rapidly. This behaviour is related to the following facts: that the liquidus lines, at constant temperature, on the (2NH$_3$)-CO$_2$ plane are characterized by a minimum pressure point, that the CO$_2$-sides of this pressure minimum are marked by very high pressure values, and that this minimum pressure point is displaced towards higher NH$_3$/CO$_2$ ratios with increasing temperature (see Fig. II-10). (The cause of this displacement of the minimum pressure point is that the volatility of CO$_2$, which is itself much less soluble in the urea synthesis solution than NH$_3$ (hence the high pressure values on the CO$_2$-side of the pressure minimum), increases much more rapidly with temperature than the volatility of NH$_3$. Therefore at higher temperatures a higher concentration of NH$_3$ is necessary to reduce the concentration of free CO$_2$ in the solution by "binding" it in the form of ammonium carbamate. This question is discussed more quantitatively in section 3.3.) Thus a given NH$_3$/CO$_2$ ratio, on the NH$_3$-side of the pressure minimum at low temperatures, may be situated on the CO$_2$-side of the minimum at higher temperatures. As such its pressure must increase rapidly, hence the increasing dP/dT slope.
From Fig. II-9 it is also seen that some mixtures exhibit a negative $\frac{dP}{dT}$ slope in the vicinity of the critical point. Such behaviour is not unusual for multi-component systems and also occurs in the $\text{CO}_2$-$\text{H}_2\text{O}$ system. The cause of this behaviour is that as critical conditions are approached the liquid and gas phases become increasingly similar to one another, and their mutual solubility can actually increase with temperature.

If all the experimental results are plotted on a Clapeyron graph, then composition-pressure-temperature values can be found. In the region of $160 < T < 260^\circ \text{C}$, a pressure-composition graph is presented in Fig. II-10. This graph illustrates the occurrence of a pressure minimum in the bubble-points on the $(2\text{NH}_3)$-$\text{CO}_2$ plane at temperatures below about $235^\circ \text{C}$. As expected, the $\text{CO}_2$ side of this pressure minimum exhibits a much steeper slope than the $\text{NH}_3$-side, and with increasing temperature the minimum pressure composition is displaced towards higher $\text{NH}_3$/$\text{CO}_2$ ratios.

Fig. II-10. Pressure-composition graph of bubble-points on the $(2\text{NH}_3)$-$\text{CO}_2$ plane. The symbols $\circ$, $\bullet$, $\blacksquare$, $\blacksquare$, $\triangle$, $\triangledown$, $\star$, and $\nabla$ refer to, respectively, the temperatures 160, 180, 200, 210, 220, 230, 240 and $250^\circ \text{C}$. $\times$ refers to the critical point at the given temperature.

Fig. II-11. Pressure composition graph of bubble-points on the $(2\text{NH}_3)$-$\text{CO}_2$ plane at $140 < T < 200^\circ \text{C}$. The symbols $\Delta$, $\bullet$, and $\nabla$ refer to 160, 180 and $200^\circ \text{C}$, respectively. The solid symbols represent Ref. 12, the open symbols Ref. 13. Ref. 7-11 at 160 and $180^\circ \text{C}$, Ref. 49 at $200^\circ \text{C}$, Ref. 51 at 160, 180, and $200^\circ \text{C}$, Ref. 15 at 160 and $180^\circ \text{C}$ and Ref. 50 at $200^\circ \text{C}$, are represented, respectively, by the symbols $\times$, $\bullet$, $\star$, $\square$, and the dashed line.
Bubble-point behaviour in the range 140 ≤ T ≤ 200°C is given in Fig. II-11. It is seen that agreement with Kawasumi \(^{7,8,9,10,11}\) and Kaasenbrood \(^{15}\) is excellent but that Wenger \(^{49}\), Nilsen et al \(^{50}\) and Kucheryavyi et al \(^{51}\) present values systematically too high. The cause of this difference is probably the occurrence of very small amounts (<< 1%) of inert gas in these researchers' experimental mixtures.

The effect of small amounts of inert gas (N\(_2\)) on the bubble-point pressures of an NH\(_3\)/CO\(_2\) = 4 (molar) mixture is seen from Fig. II-12. It is seen that even small amounts of inerts lead to large increases in the bubble-point pressure. Interestingly, the relative pressure increasing effect of the inert decreases with higher temperature. The cause of this behaviour is that as the temperature is increased the liquid phase approaches critical conditions, and the solubility of the inert increases in the increasingly "gas-like" liquid phase. That gas solubility in a liquid increases with temperature, as critical conditions are approached, is a general phenomenon. \(^{52}\)

![Fig. II-12. Clapeyron graph of bubble-points of an NH\(_3\)/CO\(_2\) = 4.0 (molar) mixture with various percentages inert-gas (N\(_2\)). The symbols O, □, △, and X represent zero %, 0.088 %, 0.25 % and Ref. 51, respectively.](image)

From Fig. II-12 it can be shown that the pressure increasing effect of inert gas is approximately linear with concentration (Henry's law) and that the presence of 1 mole-% inert in the liquid leads to very large increases of the bubble-point pressure, namely 475, 400 and 315 atm, at 160, 180 and 200°C, respectively, relative to an NH\(_3\)/CO\(_2\) = 4 mixture without inert.

A temperature-pressure-composition projection of the minimum bubble-points and critical points is presented in Fig. II-13. Concerning the former points, it is seen that agreement with Ref. 50 is excellent with respect to the composition. His pressure values are higher, however, probably due to inert gas in his mixtures, since the relative difference decreases with temperature. At about 235°C.
the minimum pressure point line intersects the critical line. The critical line begins at the critical point of NH$_3$ ($T_c = 132^\circ$ C, $P_c = 112$ atm) and extends into higher temperature and pressure regions with increasing CO$_2$/NH$_3$ ratios.

At temperatures slightly above critical conditions retrograde condensation occurred. At temperatures considerably (> 50° C.) above critical conditions super-critical behaviour was observed. That is, no phase change occurred during pressure variation, the mixture remaining in the so-called fluid phase. It was also observed that as the temperature was increased to the vicinity of the cri-
tical temperature the samples' density (d), as measured volumetrically using a calibrated container, decreased sharply. Fig. II-14 illustrates this behaviour for an NH$_3$/CO$_2$ = 2.86 (molar) mixture. This behaviour, the so-called "critical dilation effect," is not unusual for multi-component systems nearing critical conditions.\textsuperscript{53} (At the time of the writing of this work a systematic study of the densities of urea synthesis solutions at equilibrium is being performed. Such information is important for the design of the urea reactor.\textsuperscript{54} The literature discussing liquid densities is either inadequate\textsuperscript{9,10,55} or open to question.\textsuperscript{56,57})

With the occurrence of critical behaviour, very unusual optical effects, the phenomena of critical opalescence,\textsuperscript{58} were also observed. These effects were clearly filmed in colour.

It was also noticed that at a given temperature and pressure the viscosity of the liquid phase clearly increased with decreasing NH$_3$/CO$_2$ ratio, probably due to the decrease in concentration of the gas-like super-critical NH$_3$.

2.4.2. Bubble- and critical-points in the (2NH$_3$)-urea system

A Clapeyron graph of some of these experimental results is presented in Fig. II-15. For the NH$_3$-rich mixtures the measured points are completely reproducible. The measurements lie on a straight line parallel to the extrapolated vapour pressure line of ammonia. This behaviour points to the probability that the gas phase in equilibrium with the liquid phase consists almost entirely of ammonia, as is the case with the NH$_3$-H$_2$O system. Urea-rich mixtures (urea $\geq$ 75 mole-% on a urea-NH$_3$ basis) including pure urea, are not stable and increase progressively in pressure with time, probably via the reaction to biuret (equation II-8), which is slowly reaching equilibrium, and the formation of cyanuric acid:

$$3(\text{NH}_2\text{CONH}_2) \rightarrow (\text{HNCO})_3 + 3\text{NH}_3 \quad \text{(II-15)}$$

which is irreversible at these temperatures\textsuperscript{28,29}. The unstable points are considered to be "metastable," and a line has been drawn through the lowest points on the Clapeyron graph.

From the Clapeyron graph a temperature-pressure-composition figure can be prepared (Fig. II-16). As expected, the bubble-point lines exhibit a moderate slope indicative of the relatively good solubility of NH$_3$ in liquid urea. The slope of the liquidus lines is also similar to that of the liquidus lines, at the same temperatures, in the NH$_3$-H$_2$O system.

The NH$_3$-urea system also becomes critical beginning at the critical point of NH$_3$. Measured critical points for 4.8, 9.3 and 16.0 mole-% urea mixtures are 157$^\circ$ C. and 159 atm, 177$^\circ$ C. and 211 atm and 280$^\circ$ C. and 496 atm, respectively. From these results it is probable that urea can dissolve in super-critical NH$_3$.\textsuperscript{42}
From the critical measurements in the (2NH₃)–CO₂ diagonal it is also probable that urea can dissolve in highly compressed super-critical mixtures of NH₃ and CO₂.

The phase equilibria of the urea–NH₃ system have only been studied in the three phase (solid-liquid-gas) region up to about 120°C by Scholl and Davis and Janecke. The vapour pressure of liquid urea has been measured by a number of authors or can be calculated from their data for the gas-solid equilibria pressures, but the results differ from one another by a factor 10³. The results presented here for pure urea agree best with Matignon and Frejacques, although the results of these authors are lower than results reported here by a factor of 3–4.

In summary it can be said that the (2NH₃)–urea system qualitatively resembles the NH₃–H₂O system.

2.4.3. Bubble-points in the CO₂–urea system

Results of bubble-point measurements of urea–CO₂ mixtures are shown in Fig. II–16. From the figure it is seen that, firstly, the bubble-point pressures are,
as expected, very high relative to similar urea-NH$_3$ mixtures and, secondly, that the measurements are not stable, the pressure values decreasing with time. From the measurements it is seen that CO$_2$ is poorly soluble in liquid urea. No other experimental studies exist concerning the solubility of CO$_2$ in liquid urea. (One work studying the solubility of CO$_2$ at high pressures in liquid melamine, a substance vaguely resembling urea, reported that CO$_2$ was practically insoluble in this liquid$^{62}$). That the bubble-point pressures decrease with time is due to the gradual decrease in the concentration of free CO$_2$ in the mixture via the urea decomposition reactions (equations II-8 and II-15) in which CO$_2$ reacts with the liberated NH$_3$ to form ammonium carbamate. For this reason it is probable that the measured bubble-point values are considerably too low.

A line has been drawn through the highest points of the Clapeyron graph. From this line a number of bubble-point values have been obtained; for comparison similar values in the (NH$_3$)$_2$-urea system are shown (see Table II-2).

Table II-2. Comparison of bubble-points in the CO$_2$-urea and NH$_3$-urea system.

<table>
<thead>
<tr>
<th>$^\circ$C</th>
<th>CO$_2$-urea (10.6 mole-% CO$_2$)</th>
<th>NH$_3$-urea (10.6 mole-% NH$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>434</td>
<td>13</td>
</tr>
<tr>
<td>160</td>
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<tr>
<td>180</td>
<td>697</td>
<td>21</td>
</tr>
</tbody>
</table>
2.4.4. Bubble- and dew-points in the \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) system

In order to determine the form of the \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) system a number of bubble- and dew-point experiments were performed in the positive water (water-rich) and negative (urea-rich) regions of the ternary figure at temperatures of 140° C. to 200° C. As is illustrated in Fig. II-18, bubble-points were measured along four composition lines parallel to the urea-water diagonal; the chosen composition lines intersect the \( (2\text{NH}_3)\text{-CO}_2 \) diagonal at \( (2\text{NH}_3) = 62.50, 60.00, 57.50 \) and \( 53.75 \) mole-%. These compositions were chosen because they are situated around the pressure minima (in planes parallel to the \( (2\text{NH}_3)\text{-CO}_2 \) plane) and because they illustrate the occurrence of a maximum bubble- and dew-point pressure on a plane parallel to the urea-\( \text{H}_2\text{O} \) plane. The point of intersection of the minimum and maximum of these planes is the ternary azeotropic point (see Fig. II-4).

A number of bubble-point results is plotted in a Clapeyron graph in Fig. II-19. It is seen that measurements in both the water-rich and urea-rich regions...
were completely reproducible. The results of the bubble-point measurements are presented in Table II-3. The results of the dew-point measurements are represented in Table II-4.

For a given composition line the bubble-point pressures at various temperatures can be plotted on a plane parallel to the urea-$H_2O$ plane, as is illustrated in Fig. II-20. If the results of the four composition lines are thus plotted, and if the bubble-point pressures are found at constant positive and negative water concentrations (see construction of Fig. II-18) by interpolation, then the bub-
ble-point pressures in planes of constant water concentration (planes parallel to the \((2\text{NH}_3)\)-CO\(_2\) plane) can be found; the \((2\text{NH}_3)\) concentrations of points on these planes can be found as is illustrated in Fig. II-18. The results of such a construction are presented in Fig. II-21 a and b. It is seen that the minimum bubble-point pressure, which existed on the \((2\text{NH}_3)\)-CO\(_2\) plane, extends throughout the entire ternary system. It is also seen that, as expected, the CO\(_2\)-side of the minimum exhibits a steep slope, while the \text{NH}_3-side exhibits a much more gradual slope. It is also seen that at a given temperature the slope of the \text{NH}_3-rich side of the pressure minimum decreases with increasing water or urea concentration. The cause of this decrease in the slope is the decrease in the bubble-point pressure of the H\(_2\text{O}\)-(2\text{NH}_3) or urea-(2\text{NH}_3) system with increasing H\(_2\text{O}\), respectively, urea concentration. Some of the above mentioned conclusions can also be inferred from the results of Kucheryavyi et al, who studied the vapour pressures of water-rich and urea-rich gas-liquid mixtures at constant loading density.\(^{63,64}\)

If the minimum-pressure points of Fig. II-21 a and b are, at given temperatures, projected upon the ternary composition square, then Fig. II-22, a and b, result; the projected line represents the composition of the pressure minima. We call this line the equilibrium-ridge line to distinguish it from the non-equilibrium top-ridge line measured by Kaassenbrood in the \text{NH}_3-CO\(_2\)-(H\(_2\text{O}\)-urea = 1:1) system.\(^{15}\) It is seen that the equilibrium-ridge line begins at the water axis, curves toward higher \text{NH}_3/CO\(_2\) concentrations and proceeds more or less as a straight line along the composition plane; at high negative water concentrations the line bends towards the urea axis, where it ends. With increasing temperatures the equilibrium-ridge line is displaced towards higher \text{NH}_3/CO\(_2\) ratios.

A pressure-composition projection of the equilibrium-ridge line on the urea-H\(_2\text{O}\) plane at 160 and 180° C., along with the dew-point results at these temperatures, is presented in Fig. II-23. The equilibrium-ridge line exhibits a pressure maximum near the \((2\text{NH}_3)\)-CO\(_2\) plane; the slope of this line in the region of the
pressure maximum is, however, so flat that it is not possible to determine whether the maximum exists in the positive or negative water region. But from the dew-points it is clear that the maximum exists in the positive water region.

To find the azeotropic point the intersection of the equilibrium-ridge line with the minimum pressure dew-points must be known. Because of the duration of the dew-point experiments, however (see Table II-4), it was not possible to perform enough experiments to precisely find these minima. It is to be expected, however, that the curvature (on planes parallel to the $(2\text{NH}_3)\text{-CO}_2$ plane) of the dew-point curves in the region of the minima is rather flat (see Fig. II-4) so that the dew-points of line II mixtures may, as a good approximation, be regarded as the minimum pressure dew-points.

The intersection of the dew-point line with the equilibrium-ridge line yields the ternary azeotropic point. These results, with an estimation of the experimental error, are given in Table III-2, (in this Table experimental azeotropic conditions are compared with the calculated azeotrope). It is seen from Table III-2 that the azeotropic NH$_3$/CO$_2$ ratio can be estimated more accurately than the azeotropic water composition.

It may be noted that considerable confusion and contradiction exist in the literature concerning the effect of the addition of water or urea on the equilibrium pressures of mixtures originally situated on the $(2\text{NH}_3)\text{-CO}_2$ plane. The cause of these difficulties is that the above cited researchers studied the pressure of the liquid plus gas system, and they had, furthermore, little or no insight into the form of the phase model. From the present study it is seen that the effect of added water or urea on the equilibrium vapour pressure of the liquid phase is, at a given temperature, completely determined by the point's composition relative to the equilibrium-ridge line, which, at a given water concentration, determines the NH$_3$/CO$_2$ ratio at the point of minimum pres-
**Fig. II-24.** Effect of the addition of water, at constant temperature, on the vapour pressure of a liquid phase originally on the \((2\text{NH}_3)\)-\(\text{CO}_2\) plane. Line ABC: bubble-point line on the \((2\text{NH}_3)\)-\(\text{CO}_2\) plane. Lines B-(\(\text{H}_2\text{O}\)) and D-(\(\text{H}_2\text{O}\)) are the equilibrium-ridge line and its projection on the composition plane, respectively. B: point on the equilibrium-ridge line; C point on the \(\text{NH}_3\)-side of the equilibrium-ridge line. Adding water to point C (path \(E-(\text{H}_2\text{O})\)) reduces the pressure, as the resulting liquid approaches the equilibrium-ridge line. Adding water to point B (path \(D-(\text{H}_2\text{O})\)) increases the pressure, since the resulting liquid's composition is displaced from the equilibrium-ridge line.

sure. Starting from the \((2\text{NH}_3)\)-\(\text{CO}_2\) plane addition of water or urea lowers the vapour pressure of the liquid phase for liquids on the \(\text{NH}_3\)-side of the pressure minimum; the higher the \(\text{NH}_3/\text{CO}_2\) ratio of such points the greater the decrease in vapour pressure. For mixtures at or on the \(\text{CO}_2\)-side of the pressure minimum such additions greatly increase the pressure. This behaviour is clarified by Fig. II-24. In the normal working area of a urea reactor \((2.8 \leq \frac{\text{NH}_3}{\text{CO}_2} \leq 4)\) the addition of small amounts of water, such that the \(\text{H}_2\text{O}/\text{CO}_2\) ratio increases by a few tenths, has little effect on the equilibrium liquid pressure, as Kucheryavyi et al suspected.67

### 2.4.5. Constant temperature and pressure sections in the \(\text{NH}_3-\text{H}_2\text{O}-\text{CO}_2\) system

It is also interesting to construct constant temperature and pressure sections because such figures facilitate the visualisation of the ternary spatial model. Such sections also show the relation of the ternary measurements to the binary boundary systems and can also be used to illustrate and compare the ternary phase measurements of Kawasumi.

In constructing such figures the bubble-point values for the \(\text{NH}_3-\text{H}_2\text{O}\) system were obtained from inter- and extrapolation of the values of References 20 and 22; the dew-points were found by interpolation of the values of Reference 21. For the \(\text{CO}_2-\text{H}_2\text{O}\) system the works of Reference 24 were used. In all cases inter- and extrapolations were achieved by constructing Cox-Othmer plots with water as the reference substance.68

The results of the constant-temperature \((T = 160^\circ \text{C.})\) and -pressure constructions are presented in Figures II-25 a to i. Sub-azeotropie sections are presented in a and b. Two liquid sections, one water-rich, the other urea-rich, are in equilibrium with a gas phase, the one gas phase (as represented by the dew-point line) richer in water than the other. The liquid plus gas areas are separated by a gas region whose narrowness is indicative that these sections are
Fig. II-25a to i. Constant temperature-pressure sections ($T = 160^\circ C.$) below and above the azeotropic pressure. The circles refer to the author's measurements, the triangles to those of Ref. 8, 9, 10 and 11. The solid symbols refer to bubble-points, the open symbols to dew-points. The solid and open squares refer to the bubble- and dew-points, respectively, of the $NH_3-H_2O$ and $CO_2-H_2O$ systems.
only slightly under the azeotropic pressure \( T = 160^\circ \text{C}, \ P_{\text{az}} \approx 71 \text{ atm} \). In Fig. II-25 a \( P = 66 \text{ atm} \) agreement with Kawasumi is poor, but it is certain that Kawasumi's liquid and/or gas analysis is incorrect, since these two points must form a straight tie-line through the gross composition point of the mixture, which, since he started from ammonium carbamate \( (2 \text{NH}_3) : \text{CO}_2 = (1:1) \), is situated at the exact centre of the composition square. At 69 atm the gas area between the liquid plus gas region is even narrower than at 66 atm, as is to be expected. Agreement with Kawasumi's points is better. It should be noted, however, that in the pressure region only slightly under the azeotropic pressure the flatness of the equilibrium-ridge line results in the fact that small errors in pressure \( 2-3 \text{ atm} \) can lead to relatively very large composition errors in the liquidus lines, particularly in those parts of the lines which most closely approach one another.

In the remaining figures (c to i) above-azeotropic pressures are illustrated. It is seen that a single liquid region, widening with increasing pressure, transverses the whole composition section. The gas areas decrease with increasing pressure; the distance separating the dew-point lines, which bend in and approach the liquidus lines, from the liquidus lines increases with pressure. In general agreement with Kawasumi's measurements is excellent. At 136.5 atm (Fig. II-25 g) the \( (2 \text{NH}_3) - \text{H}_2\text{O} \) system becomes critical, and at higher pressures an increasingly large part of the \( \text{NH}_3 \)-rich half of the composition square becomes super-critical i.e., exists in the so-called fluid state. Further pressure increase above 160 atm has little effect on the phase behaviour due to the steepness of the liquidus and dew-point lines in the \( \text{CO}_2 \)-rich regions.

Similar sections can be constructed at temperatures from 140 to 200\(^\circ\text{C}\); qualitatively similar results are found \( (160^\circ \text{C.} \text{ was chosen because almost all of Kawasumi's results are at this temperature).} \)

2.4.6. Ternary critical behaviour

The measurements of the critical points of the binary systems \( (2 \text{NH}_3) \)-urea and \( (2 \text{NH}_3) - \text{H}_2\text{O} \) (the data from the latter system available in Reference 21) and the \( (2 \text{NH}_3) - \text{CO}_2 \) diagonal plane are illustrated in Fig. II-26. In this construction the critical points are projected upon the composition square and their respective critical pressure values are projected upon a plane parallel to the urea-water plane. For the ternary regions this diagram should be viewed as only semi-quantitative since each line is drawn through only three points, themselves interpolated values (the \( (2 \text{NH}_3) \)-urea critical line is the least accurate as only four experimental points are available). The drawing does, however, illustrate that the critical behaviour is (at \( 140 \leq T \leq 220^\circ \text{C.} \)) consistent and in agreement with the theoretical discussion.
Fig. II-26. Pressure- and composition-projections of the ternary critical lines. The symbols A, ■, • , ○ and ▼ refer to the temperatures of 140, 160, 180, 200 and 220°C, respectively. The dashed line illustrates the use of this figure: A mixture consisting originally of 10 mole-% CO₂, 80 mole-% (2NH₂) and 10 mole-% urea has, as its critical conditions, $T_c = 160^\circ$C, and $P_c = 270$ atm. (Note that the given mixture has the following composition, respectively, in terms of the basic components, (2NH₂), CO₂ and H₂O: 90, 20 and -10 mole-%. (See Appendix II for a detailed example of the breakdown of mixtures into their component compositions.)

The occurrence of critical behaviour in the NH₃-H₂O-CO₂ system is perhaps related to the reported decrease in the conversion in the liquid phase at temperatures above 200°C. This problem is discussed in more detail in Chapter III.

2.5. Further discussion and practical applications of the model

The advantage of the proposed model is that it provides a clear insight into the phase behaviour of the entire NH₃-H₂O-CO₂ system at equilibrium at temperatures and pressures of the urea synthesis. Particularly clear is also the relation of the phase behaviour of the ternary compositions to the binary boundary systems.

The model does, however, possess a number of shortcomings, these being:

1. The non-equilibrium (quaternary system) conditions are not described.
2. The chemical concentrations of the actual chemical constituents are unknown.
3. The gas-liquid equilibria (tie-line) compositions are also not known.

Concerning the first point, it should be noted that normally thermodynamics does not describe non-equilibrium conditions, and hence this can not be expected of a phase model, which makes use of the phase rule, itself a thermodynamic law valid only at equilibrium. Together with Kaasenbrood's quaternary model, however, the non-equilibrium temperature-composition path towards an equilibrium point can - in principle - be followed. There are, unfortunately, two problems associated with the use of the quaternary model in this respect. Firstly, and as already mentioned, the amount of published quantitative information concerning the qua-
ternary model is restricted to the liquid phase in the working area of a DSM urea reactor (P = 130 atm, 160 °C < T < 200 °C). Secondly, the ternary boundary systems of the quaternary system are, at temperatures above ~ 180 °C, so unstable that measurement of their physical equilibria would, in the writer's opinion, present extremely difficult problems. For this reason their assumed existence is to a certain extend "unreal", and the relation of the quaternary phase behaviour to that of the ternary boundary systems is obscure.

Concerning the second problem, it can be answered that while the phase model itself does not describe the concentrations of the actual chemical constituents, such as urea or ammonium carbamate, it is possible to calculate these compositions over a wide range of compositions and temperatures using published equilibrium conversion formulas.

As to the last point, the proposed phase model will in Chapter III be enlarged with a quantitative thermodynamic basis by which it becomes possible to calculate gas-liquid equilibrium tie-lines in an area of direct interest to the urea synthesis.

For practical purposes it may be stated that the urea synthesis occurs almost exclusively in the liquid phase. It therefore follows that the operation of a urea reactor which works at or near chemical equilibrium can proceed most economically at a pressure just slightly above the equilibrium bubble-point pressure. Once the choice of temperature (a question of corrosion and conversion considerations) and NHₓ / CO₂ ratio (a more complex question related to the type of process, amount of recycle water entering the reactor, etc.) has been made, the minimum reactor pressure can be found from Figures II-11 and II-13, assuming that no inert gases are present in the feed gases.

For example, the urea reactor of DSM's CO₂-stripping process operates at 180-190 °C. Since CO₂ is the stripping agent, the reactor effluent must be just saturated with CO₂ (no excess NH₃); otherwise part of the stripping agent will dissolve in the urea synthesis solution. The ideal reactor composition therefore lies at the pressure minimum. From Fig. II-13 it is to be expected that the optimum NH₃ / CO₂ ratio be ~ 2.8 (NH₃ = 74 mole-%) and the minimum reactor pressure be about 125 atm; this is indeed the case. For SNAM's NH₃-stripping process the reactor effluent must be located on the NH₃-side of the pressure minimum; otherwise part of the NH₃, which is much more soluble in the urea melt than CO₂, will dissolve into the urea synthesis solution during stripping. For this reason a SNAM reactor must work at a higher NH₃ / CO₂ ratio and hence a higher pressure than a DSM reactor working at the same temperature.

The actual reactor pressure must always be somewhat higher than the equilibrium bubble-point pressure since the feed gases always contain, as impurities,
a few percent inert gases, which are practically insoluble in the urea synthesis solution (see section 2.4.1.). In practice the DSM process works at about 140 atm. The SNAM process, whose bubble-point pressure is about 135 atm \((\text{NH}_3/\text{CO}_2 = 3.5, \ T = 185^\circ \text{C})\), works at about 150 atm. The ideal reactor pressure, as a function of percent inert, is an economic question: increased pressure increases volumetric reactor efficiency, but it also increases investment and operating costs. A qualitative discussion concerning the choice of reactor pressure is given by Reference 50. A quantitative discussion of the detrimental effect of inert on the efficiency of a urea reactor is given by Otsuka.

According to Frejacques it is to be expected that an excess amount of \(\text{CO}_2 ((2\text{NH}_3)/\text{CO}_2 < 1)\) will act to increase the conversion of ammonium carbamate to urea (conversion on \(\text{NH}_3\)-basis). Experimentally, however, this was not found, and Frejacques's explanation was that added excess \(\text{CO}_2\), at a given constant loading density, remained in the gas phase because of its limited solubility. The author believes that this explanation is correct. Excess \(\text{CO}_2\) - in the liquid phase - will indeed increase the conversion of \(\text{NH}_3\) to urea, but in order to force a substantial excess of \(\text{CO}_2\) into the liquid phase pressures of thousands of atmospheres are necessary, as Fig. II-10 illustrates. It is for this reason that all commercial urea reactors operate at the pressure minimum or, more commonly, at a slightly \(\text{NH}_3\)-rich composition relative to this minimum; such compositions are always at a molar \(\text{NH}_3/\text{CO}_2\) ratio significantly greater than two.

Table II-3. Temperature-pressure table of the ternary bubble-points (pressure is given in atm)

<table>
<thead>
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<th>T °C</th>
<th>No. 1</th>
<th>No. 2</th>
<th>No. 3</th>
<th>No. 4</th>
<th>No. 5</th>
<th>No. 6</th>
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43. Private communications with Ir. J.M. Verstegen of the Central Laboratory of
Dutch State Mines, Geleen, the Netherlands.


53. Ibid., p. 432-434.


74. Otsuka, E., Kogyo Kagaku Zasshi (Japan), 63(7), 1208.

CHAPTER III
AN EMPIRICAL THERMODYNAMIC MODEL FOR THE AMMONIA-WATER-CARBON DIOXIDE SYSTEM AT EQUILIBRIUM AT UREA SYNTHESIS CONDITIONS

3.1. Introduction

The first and probably still most widely used thermodynamic model for the ammonia-water-carbon dioxide system at complete chemical equilibrium at urea synthesis conditions was presented in 1948 by Frejacques. In this model the liquid phase is described by one overall reaction:

\[ 2(NH_3)_L + (CO_2)_L \rightleftharpoons (NH_2CONH_2)_L + (H_2O)_L \]  

\[
K_1 = \frac{(X'_{\text{urea}})_L (X'_{H_2O})_L}{(X'_{NH_3})_L (X'_{CO_2})_L} \]  

The terms \((X'_{NH_3})_L\) and \((X'_{CO_2})_L\) refer to \(NH_3\) and \(CO_2\) in the liquid phase not existing as urea; Frejacques assumed, for his model, that the urea synthesis solution contained no ammonium carbamate. Kawasumi also used Frejacques’s model, but found that the \(K_1\) value varied with composition. Very recently Inoue et al. have also found that Frejacques’s \(K_1\) values vary significantly with composition and that the conversions found using his nomogram, in which the \(K_1\) values are used, are systematically too low at temperatures below 190–200°C and systematically too high above these temperatures. Mavrovic, however, using Frejacques’s thermodynamic approach has claimed to have improved the \(K_1\) values so that conversions can accurately be calculated up to about 190–200°C, the region in which most industrial reactors operate. Baranski and Fulinski have also presented a detailed thermodynamic study of the urea synthesis solution and concluded that Frejacques’s model was indeed correct.

There are, however, a number of considerations which question the thermodynamic validity of the Frejacques model. Firstly, thermodynamic calculations point to the association of \(NH_3\) and \(CO_2\) to ammonium carbamate in the liquid phase, as is shown later in this chapter. Furthermore, the occurrence of azeotropy in the \(NH_3\)-\(CO_2\) system, as measured by Kaasenbrood, is also indicative of this pronounced association. Secondly, the use of the Frejacques model leads to a serious thermodynamic contradiction. It can easily be shown that reaction (III-1) is highly exothermic, the enthalpy of reaction at synthesis conditions being about -19 kcal/mole. It is also a well known fact that the conversion to urea in the liquid phase increases with temperature, at least to temperatures of 190–200°C. This fact is reflected in the increase of \(K_1\) with temperature, as is given by
Table II.3 (continued)

**SERIES III**

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Composition in mole-% of the various fillings (for Table II-3).

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</table>

References

Frejacques and Mavrovic. An equilibrium constant which increases with temperature for an exothermic reaction, however, is in contradiction to the rule of Van 't Hoff. Indeed, from Frejacques's and Mavrovic's values for $K_1$ endothermic reaction enthalpies in the order of respectively $+6$ and $+10.7$ kcal/mole are found - and this for a highly exothermic reaction! For the above reasons the one reaction scheme must be rejected as a thermodynamic description.

A second thermodynamic model was presented in 1962 by Effremova and Leontieva. This model assumed that the urea synthesis solution contained appreciable quantities of ammonium carbamate. No free carbon dioxide existed in the liquid phase, however; all of the original carbon dioxide was assumed to be present in the form of ammonium carbamate and urea. Gaseous ammonia and water were in equilibrium with dissolved ammonia and water (equations (III-3) and (III-5) below), but a similar equilibrium reaction for carbon dioxide (equation (III-4) below) was neglected.

In 1969 Nilsen et al presented a model which, in essence, expanded Ref. 10's model to include the $\mathrm{CO}_2$-reaction (equation (III-4) below). The paper described the computational possibilities of the model, which included the description of bubble-point pressures, but was very superficial regarding the development of the model itself.

The purpose of this chapter, which is based on publications of Lemkowitz, de Cooker and van den Berg, is to develop and apply an empirical, thermodynamically consistent model for the water-rich half of the ammonia-water-carbon dioxide system at equilibrium conditions in the range of $140 < T < 200^\circ$C. and $30 \leq P \leq 250$ atm which can quantitatively or semi-quantitatively describe a number of important phenomena at urea synthesis conditions, such as the bubble-points, the gas-liquid equilibrium values, the equilibrium-ridge line and the effect of excess $\mathrm{NH}_3$ and $\mathrm{H}_2\mathrm{O}$ on the conversion of $\mathrm{CO}_2$ to urea. The question of the conversion to urea in the liquid phase at high temperatures ($T \geq 190-200^\circ$C.) is also discussed.

In constructing the model it is necessary to calculate the concentrations of the various chemical substances in the liquid phase; in the water-rich regions ($0 \leq W \leq 1$) this can be done using conversion formulas in the literature. For the urea-rich area no such conversion formulas exist (although Kucheryavyi et al have recently experimentally studied this problem). It is also as yet not possible to develop relations for the equilibrium distribution of isocyanic acid and urea (constituents which will occur in high concentrations in the negative water area) in the liquid and gas phase. For this reasons the model cannot as yet be applied to the negative water region.
3.2. Some general aspects of the model

The model is based on the following assumptions:

1. The liquid phase is an ideal mixture and consists of ammonium carbamate, urea, water and free (unreacted) ammonia and carbon dioxide. The presence of carbonates, bicarbonates, biuret, etc., is neglected. The occurrence of ionization is also neglected. The activities of the constituents are assumed to be equal to their mole fractions.

2. The gas phase is ideal and consists of ammonia, carbon dioxide and water (the gas phase contains neither urea nor isocyanic acid).

3. The equilibrium conversion of carbon dioxide to urea in the liquid phase is found by means of the K-values of Mavrovic who makes use of an equation of exactly the same type as Frejacques (equation (II-2)). Mavrovic's method was chosen because it presents the most recent values for the conversion over a large concentration area.

4. The model consists of the following five reactions:

\[
(NH_3)_G \rightleftharpoons (NH_3)_L \quad (III-3)
\]

\[
(CO_2)_G \rightleftharpoons (CO_2)_L \quad (III-4)
\]

\[
(H_2O)_G \rightleftharpoons (H_2O)_L \quad (III-5)
\]

\[
2(NH_3)_L + (CO_2)_L \rightleftharpoons (NH_2OCONH_4)_L \quad (III-6)
\]

\[
(NH_2OCONH_4)_L \rightleftharpoons (NH_2CONH_2)_L + (H_2O)_L \quad (III-7)
\]

A schematic presentation of the model appears in Fig. III-1.

![Schematic presentation of the model](image)

**Fig. III-1. Schematic presentation of the thermodynamic model for the NH₃-H₂O-CO₂ system at complete chemical equilibrium.**

For calculative purpose it is useful to combine equations (III-6) and (III-7) to obtain the equation:
\[
2(N\text{H}_3)_L + (C\text{O}_2)_L \overset{\Leftrightarrow}{\rightarrow} (N\text{H}_2\text{CONH}_2)_L + (H\text{O}_2)_L
\]  
(III-8)

(Note that the symbols \((N\text{H}_3)_L\) and \((C\text{O}_2)_L\) refer to the \textit{free} \(N\text{H}_3\) and \(C\text{O}_2\) in solution, not the \(N\text{H}_3\) and \(C\text{O}_2\) originally added or existing as urea or ammonium carbamate). The equilibrium constant for this reaction,

\[
K_2 = \frac{(X_{N\text{H}_2\text{CONH}_2})_L (X_{H\text{O}_2})_L}{(X_{N\text{H}_3})_L (X_{C\text{O}_2})_L}
\]  
(III-9)

is given in Fig. III-2 as a function of temperature.

For further calculations it is necessary to know the gas-liquid equilibrium relations for the three constituents of the gas phase, \(N\text{H}_3\), \(C\text{O}_2\) and \(H\text{O}_2\). Since the free ammonia is present in the liquid phase at relatively high concentrations, Raoult's law is used to calculate the partial pressure of ammonia:

\[
P_{N\text{H}_3} = (X_{N\text{H}_3})_L P^{O'}_{N\text{H}_3}
\]  
(III-10)

The value of \(P^{O'}_{N\text{H}_3}\) as a function of temperature is given in Fig. III-3.

Raoult's law behaviour is also assumed for water:

\[
P_{H\text{O}_2} = (X_{H\text{O}_2})_L P^{O'}_{H\text{O}_2}
\]  
(III-11)
Fig. III-4. Values of the Henry coefficient for carbon dioxide as a function of temperature.

For carbon dioxide, which is greatly above its critical temperature ($T_c = 31^\circ C$) and only slightly soluble in the liquid phase, Henry's law is used:

$$P_{CO_2} = (X_{CO_2}) L \cdot H_{CO_2}$$  \hspace{1cm} (III-12)

The value of the Henry coefficient as a function of temperature is presented in Fig. III-4. The linear relation over a limited temperature range is not unusual for a gas only slightly soluble in a given liquid phase. The values of the Henry coefficient for carbon dioxide in the urea synthesis solution are quite similar to the values for this coefficient for carbon dioxide in water at the same temperatures.\(^{15}\)

The values of $K_2$, $P_{NH_3}^{O'}$, and $H_{CO_2}$ have been determined empirically to obtain the best fit between experimental and calculated bubble-points at $W = 0$. The values of $K_2$, $P_{NH_3}^{O'}$, and $H_{CO_2}$ are assumed to be independent of pressure and composition.

From the stoichiometry of the chemical reactions (III-6) and (III-7) the following material balance is valid for the liquid phase at equilibrium (per one mole initial carbon dioxide, $L$ moles initial ammonia and $W$ moles initial water):

- $x$ = moles urea
- $x + W$ = moles water
- $C$ = moles free $CO_2$
- $L - 2 + 2C$ = moles free ammonia
- $1 - x - C$ = moles ammonium carbamate

$$L + x + W + 2C - 1 = \text{total moles}$$

3.3. The calculation of the bubble-points

The bubble-points and minimum pressure conditions are important for the
optimum working of a urea synthesis reactor. The calculations of the bubble-points as a function of temperature and composition has been approached by Kucheryavyi et al. In one article an empirical method is presented.\(^{16}\) It can be easily shown, however, that this method cannot fix a bubble-point pressure within an accuracy of better than about 100 atm, which is unacceptable. In a second article a formula based on thermodynamic reasoning appears.\(^{17}\) This formula is also dubious because it does not cover experimental bubble-points in a previous article by the same authors\(^{18}\), and it fails to predict the occurrence of a pressure minimum in the \(\text{NH}_3-\text{CO}_2\) plane, which is a characteristic feature of this plane, as has been shown in the previous chapter.

Experimentally the bubble-points in the \(\text{NH}_3-\text{CO}_2\) plane have been determined in a wide range of temperature, composition and pressure by Kawasumi\(^2,3,4,19\) and Lemkowitz et al\(^{20,21}\) (see previous chapter). These works form the experimental basis of the calculations presented here.

Using the model presented the bubble-points are calculated in the following way: a temperature, \(\text{NH}_3/\text{CO}_2\) and \(\text{H}_2\text{O}/\text{CO}_2\) ratio are chosen. At the given temperature values of \(K_1\), \(P^{o'}_{\text{NH}_3}\) and \(P_{\text{CO}_2}\) are fixed (see the respective Figures), and the conversion may be calculated using Mavrovic's method. From the material balance \(K_2\) becomes:

\[
K_2 = \frac{(x)(x + W)(L + x + W + 2C - 1)}{(L - 2 + 2C)^2c} \quad (\text{III-13})
\]

in which \(x, W, L\) are now known. The value of free carbon dioxide, \(C\), can be solved numerically from equation (III-3) using the Newton-Raphson technique. With \(C\) known the total number of moles is known, and all of the mole fractions can be calculated.

Since the gas phase is ideal, and using equations (III-10), (III-11) and (III-12), the bubble-point pressure is:

\[
P = P_{\text{NH}_3}^{o'} + P_{\text{CO}_2}^{o'} + P_{\text{H}_2\text{O}}^{o'} = (X_{\text{NH}_3}) L^{o'} P_{\text{NH}_3}^{o'} + (X_{\text{CO}_2}) L^{o'} P_{\text{CO}_2}^{o'} + (X_{\text{H}_2\text{O}}) L^{o'} P_{\text{H}_2\text{O}}^{o'} \quad (\text{III-14})
\]

The results of calculations at \(W = 0\) are presented in Fig. III-5. In the region of \(140 \leq T \leq 200^\circ\text{C}\) and \(2.4 \leq L \leq 6\), which is the region of commercial urea synthesis, the agreement between the calculated and measured bubble-points is very good, i.e. within 0-4%. It is also seen that the calculated lines follow the displacement in the measured bubble-point minima towards higher \(\text{NH}_3\)-concentrations with increasing temperatures very well. The temperature-composition behaviour of the pressure minima is particularly affected by the value of \(K_2\). The values of \(P_{\text{NH}_3}^{o'}\) and \(P_{\text{CO}_2}^{o'}\) determine the absolute pressure values of the calculated bubble-points at the \(\text{NH}_3\)-side and the \(\text{CO}_2\)-side of the pressure minima,
Fig. III-5. Measured and calculated bubble-points on the \( \text{NH}_3-\text{CO}_2 \) plane. The symbols \( \square, \Delta, \bigcirc, \) and \( \nabla \) refer to the temperatures 140, 160, 180 and 200 \( ^\circ \text{C} \). The open symbols refer to Ref. 20 and the closed symbols to Ref. 21. \( \ast \) refers to Ref. 2, 3, 4 and 19. The symbols refer to measured bubble-points. The solid line refers to calculated bubble-points at 140, 160, 180 and 200 \( ^\circ \text{C} \).

The values used for the calculation of Fig. III-5 are presented in Table III-1.

<table>
<thead>
<tr>
<th>( T ) ( ^\circ \text{C} )</th>
<th>( P_{\text{NH}_3} ) ( \text{atm} )</th>
<th>( P_{\text{CO}_2} ) ( \text{atm} )</th>
<th>( K_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>128</td>
<td>1400</td>
<td>215</td>
</tr>
<tr>
<td>160</td>
<td>180</td>
<td>2600</td>
<td>120</td>
</tr>
<tr>
<td>180</td>
<td>240</td>
<td>3800</td>
<td>70</td>
</tr>
<tr>
<td>200</td>
<td>335</td>
<td>5000</td>
<td>40</td>
</tr>
</tbody>
</table>

3.4. Calculations of gas-liquid equilibrium values in the water-rich half of \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) system

The knowledge of gas-liquid equilibria is of great importance for the optimum design and operation of a urea synthesis plant. Gas-liquid equilibria in the \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) system (no urea present) at atmospheric pressure and temperatures of 20-60\( ^\circ \text{C} \) were studied by van Krevelen et al.\textsuperscript{22} This work was of great value because it was the first to attack the problem on the basis of the laws of ionic equilibria. This study was later expanded by Wicar to the quaternary \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2-\text{urea} \) system at pressures of up to about 30 atm and temperatures of 60 to 160\( ^\circ \text{C} \).
The results for calculations of the partial ammonia pressure are fairly accurate in the region of high NH\textsubscript{3}-concentrations (L ≥ 4), which prevailed in the urea processes then common. To describe the gas-liquid phase relations in the NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O-ammonium nitrate system (ammonium nitrate solution was then commonly used to separate NH\textsubscript{3} from CO\textsubscript{2} in the recycle gases) Othmer and Frolich considerably expanded the theoretical and experimental basis of van Krevelen's work. While the above-mentioned works do not describe the phase equilibria of the ternary system at high temperatures at complete chemical equilibrium (urea present) they are nevertheless of considerable interest because the empirical-thermodynamic model presented in this chapter is essentially a highly simplified version (ionizations, ionic interactions and activity coefficients neglected) of the methods presented in these articles.

Another approach in describing the phase equilibria of the ternary system (no urea present) has been to use the van Laar equation. Takahashi used this equation, but it can be shown that this article contains serious miscalculations so that it is of dubious practical use. Very recently Yanagisawa et al have also used the van Laar equation to describe this equilibrium. Because the van Laar method completely neglects the occurrence of chemical reactions, which definitely play a prominent role in the NH\textsubscript{3}-H\textsubscript{2}O-CO\textsubscript{2} system, there are reasons to disapprove of such an approach. Since the equation contains six constants (for a ternary system), which are fitted on the basis of the experiments, it is the writer's opinion that such an approach is basically purely empirical and mathematical (statistical) in nature.

More recently Kucheryavyi et al. have also attempted to describe gas-liquid equilibria in the NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O and NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O-urea systems. In one article an empirical method is presented. It can be shown, however, that this article is not consistent with the phase behaviour of the NH\textsubscript{3}-H\textsubscript{2}O-CO\textsubscript{2} system at equilibrium. A second article, based on a modification of Ref. 10's work, contains a number of serious typographical and/or mathematical errors and inconsistencies, and it can further be shown that use of this article leads to results inconsistent with the phase behaviour of the system.

Using the model presented here, it is possible to calculate gas-liquid tie-lines in the water-rich half of the NH\textsubscript{3}-H\textsubscript{2}O-CO\textsubscript{2} system. Temperature and pressure may be chosen to fix a plane in the ternary (2NH\textsubscript{3})-H\textsubscript{2}O-CO\textsubscript{2} phase prism. With the temperature chosen, values for k\textsubscript{2}, P\textsubscript{NH\textsubscript{3}}\textsuperscript{0}, H\textsubscript{CO\textsubscript{2}}\textsuperscript{0} and P\textsubscript{H\textsubscript{2}O}\textsuperscript{0} are fixed (these values are the same as those used for the bubble-point calculations at W = 0; see Table III-1 and the respective Figures). An initial water concentration, W, is chosen, and the bubble-point pressure is calculated at varying L. The correct value of L is that at which the calculated pressure agrees with the chosen pressure. For
the gas phase the partial pressures of the three components are calculated ac-
cording to the equations (III-10), (III-11) and (III-12).

Although the model was originally based on the bubble-points at \( W = 0 \) it is
interesting to compare the calculated results with the experimental constant-
temperature and -pressure sections discussed in the previous chapter. In Figs.

---

**Figures III-6a to d.** Constant temperature and pressure sections below, at and
above the azeotropic pressure (\( T = 180^\circ \) C.). The crosses represent the author's
bubble-point measurements, the circles the author's calculated bubble- and dew-
points. The triangles represent the measurements of Kawasumi, the open and
solid symbols referring to the dew- and bubble-points, respectively. The author
tie-lines are solid, those of Kawasumi are dashed. The solid and open squares
refer to the bubble- and dew-points, respectively, of the \( \text{NH}_3-\text{H}_2\text{O} \) and \( \text{CO}_2-\text{H}_2\text{O} \) systems.
III-6, a to d, sections at 160° C. under, at and above the azeotropic pressure are shown. In Fig. III-6a a sub-azeotropic section is calculated at 69 atm and 160° C. It is seen that the measured and calculated bubble-point lines agree reasonably well, the measured line being somewhat more NH₃-rich than the calculated line. The calculated dew-point line follows the expected path towards the (2NH₃)₃H₂O and CO₂-H₂O dew-points. Relative to the calculated line, Kawasumi's measured dew-point is water-rich by about 2-3 mole-% absolute; this difference is systematically found in all comparisons with him. In Fig. III-6b the calculated azeotrope is shown. For above azeotropic conditions calculations are presented for 80 and 89 atm in Figs. III-6c and III-6d. Agreement between calculated and measured bubble-points is very good. Kawasumi's dew-points are systematically 2-3 mole-% (absolute) higher in water concentration relative to the calculated points. It is also interesting to see that at low water concentrations in the liquid phase the calculated dew-points tend to concentrate in a small area and turn towards the negative-water area, as is to be expected (see Fig. II-5c).

In Fig. III-7 the azeotropic area is shown in more detail. The peculiar behaviour around the azeotropic point is seen: small changes in the L-ratio of the liquid phase lead to large changes of the L-ratios of the gas phase. It is also interesting to compare the calculated azeotrope with the azeotrope obtained by inter- and extrapolation of the measurements; this is done in Table III-2.

Table III-2. Comparison of calculated and experimentally estimated azeotrope conditions

<table>
<thead>
<tr>
<th>T °C</th>
<th>P atm</th>
<th>P atm</th>
<th>(2NH₃) mole-%</th>
<th>(2NH₃) mole-%</th>
<th>CO₂ mole-%</th>
<th>CO₂ mole-%</th>
<th>H₂O mole-%</th>
<th>H₂O mole-%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>exp.</td>
<td>calc.</td>
<td>exp.</td>
<td>calc.</td>
<td>exp.</td>
<td>calc.</td>
<td>exp.</td>
<td>calc.</td>
</tr>
<tr>
<td>160</td>
<td>71±2</td>
<td>70.6</td>
<td>52.5±2</td>
<td>54.3</td>
<td>40.0±2</td>
<td>42.0</td>
<td>7.5±2</td>
<td>3.7</td>
</tr>
<tr>
<td>180</td>
<td>119±2</td>
<td>119.9</td>
<td>54.0±2</td>
<td>57.1</td>
<td>38.5±2</td>
<td>39.3</td>
<td>7.5±2</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Fig. III-8. Calculated points at and about the azeotropic point.
The agreement between the calculated and experimentally estimated azeotropic \((2\text{NH}_3)\) and \(\text{CO}_2\) compositions is good; that relating to the azeotropic water percentage is poor. It is difficult to decide which result is more reliable: experiments in this region are difficult because of their duration (dew-points) and because the measured differences in bubble-point pressures, in the zero-% water area, are often not much larger than the experimental error. On the other hand, the model makes no mention of negative-water based constituents in the gas phase, a factor which probably affects the accuracy of the calculated results. Since it is possible that with increasing temperature the concentration of \(\text{HNCO}\) and, perhaps, urea in the gas phase increases relative to water, it may be that the water concentration at the azeotrope is displaced towards the negative-water area with increasing temperature.

3.5. Calculations of the equilibrium-ridge and related lines.

Using the values of \(K_2\), \(P_{\text{NH}_3}^\circ\), and \(H_{\text{CO}_2}\) developed for the calculation of the bubble-points on the \((2\text{NH}_3)-\text{CO}_2\) plane, it is also possible to calculate bubble-point lines at constant water concentration, i.e., on planes parallel to the \((2\text{NH}_3)-\text{CO}_2\) plane. By calculating such lines and graphically determining their minimum pressure values and corresponding \((2\text{NH}_3)\) concentrations it is possible
to determine the equilibrium-ridge line. The thus calculated equilibrium-ridge line is compared with the experimental results in Figs. III-8 and III-9. In Fig. III-9, in which the pressure values are projected upon the urea-water plane, it is seen that the calculated and measured equilibrium-ridge lines agree very well at 160° C. up to about 50% H₂O; for 180° C. the agreement becomes less good after about 20% H₂O. Concerning the equilibrium-ridge line compositions, as is illustrated in the projection of Fig. III-8, the calculated and measured values agree well, even at high water concentrations.

It is also possible to calculate the dew-point lines at chemical equilibrium (this is a somewhat more complex calculation than the previous ones, and it is explained in detail in Appendix IV.) Calculations of the dew- and bubble-point lines have been performed for compositions corresponding to series II, for which experimental values are available (see Tables II-3 and II-4). The results are shown in Fig. III-10, a and b. Calculated and measured bubble-points agree fairly well, particularly at low water concentrations. The most interesting result, however, is the occurrence of a distinct pressure maximum in the calculated dew-point lines, as is to be expected due to the occurrence of the azeotrope. The calculated and measured dew-points also agree fairly well, although the values of the calculated maxima are less water-rich than the measured values.

![Graphs showing calculated and measured bubble- and dew-points of series II mixtures. The symbols + and X and Δ and O refer to measured bubble- and dew-points and calculated bubble- and dew-points, respectively.](image)

3.6. The effect of excess NH₃ and H₂O on the conversion in the liquid phase.

That excess NH₃ increases the conversion to urea in the liquid phase and that water decreases this conversion is one of the fundamental facts concerning
the urea synthesis. Frejacques explained this effect on the basis of the law of
mass action, which from equation (III-1) introduces a quadratic conversion
increasing effect for NH$_3$.

Otsuka, however, explained the efficacious effect of excess NH$_3$ on the assumption that it lowered the activity of the water present
in the reaction mixture.

At temperatures below 190-200° C. the concentration of free CO$_2$ is very
small relative to the concentrations of the remaining constituents, i.e., the
dissociation of carbamate may be neglected. At these conditions the conversion
to urea is controlled by equation (III-7). In this equation, however, NH$_3$ does
not occur explicitly.

The effect of excess NH$_3$ must be seen primarily as that of an essentially
inert diluent, as can be shown as follows: If per one mole CO$_2$, L moles NH$_3$ are
introduced, then from equation (III-7) (in which the very small carbamate disso­
ciation is neglected) the expression for the equilibrium constant for reaction
(7) is:

\[
K_3 = \frac{(X_{NH_2CONH_2})_L (X_{H_2O})_L}{(X_{NH_2OCONH})_L} = \frac{(x) (x + W)}{(1 - x) (L + x + W - 1)}
\]  

(III-15)

If, for example, at a given temperature the conversion at L = 4 (and W = 0)
is calculated using Mavrovic's method then $K_3$ may be calculated. Assuming that
$K_3$ is independent of composition, the effect of L on the molar conversion in the
liquid phase, Y, may be calculated from equation (III-15) by solving for x at
constant $K_3$ and varying L. This is done for W = 0 in Fig. III-11 in which the
results are compared with those using Mavrovic's method at various values of L.
The agreement is reasonable.

In Fig. III-12 the results are shown for the effect of varying W at L = 4.
(The value of $K_3$ used is the same as that value used in computing the effect of
NH$_3$.) The agreement between the results using Mavrovic's method and equation (III-
15) is reasonable until about W = 0.5, which is the usual composition range in
which urea is commercially synthesized. The agreement becomes less good at higher
water concentrations probably because of the breakdown of the assumption, at these
water concentrations, that the activities may be replaced by mole fractions. Appr­
ciable quantities of carbamate and carbonate ions may also be formed. It is also
possible that Mavrovic's method is no longer accurate in this area.

The effect of water on the conversion is two sided: On the one hand it
decreases the conversion due to the mass action effect; on the other hand it
increases the conversion due to the dilution effect. Of these two effects the
former is the more important.

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That an inert diluent increases conversion for a reaction in which the number of moles increases (reaction III-7) is a general rule of chemical thermodynamics.\textsuperscript{29} The author does believe, however, that excess NH\textsubscript{3} also serves secondarily to lower the activity of the water present.

3.7. Concerning the conversion to urea in the liquid phase at high temperatures (T > 190\textdegree{}C.)

The question of the conversion to urea in the liquid phase as a function of temperature, particularly at temperatures above 190\textdegree{}C., has received considerable attention in recent years. Frejacques believed that this conversion increased with temperature, assuming the absence of decomposition reactions for urea.\textsuperscript{1} Use of Mavrovic's nomogram also leads to increasing conversion up to about 200\textdegree{}C., the maximum temperature to which the nomogram may be used.\textsuperscript{6} Wenger, on the basis of a careful study of the relevant literature (to 1968) and his own experiments, also concluded that the conversion in the liquid phase increased with temperature.\textsuperscript{30} This researcher also stressed, however, that the overall conversion (conversion to urea based on total initial CO\textsubscript{2} rather than conversion based on CO\textsubscript{2} (in the form of ammonium carbamate and urea) in the liquid phase) could decrease with increasing temperature if the system's pressure fell below the liquid's bubble-point pressure, since at these conditions part of the liquid phase evaporates.
In 1970, however, Yoshimura presented experimental values which showed that for an L = 4 mixture the conversion in the liquid exhibits a maximum value at about 190° C. and decreases with further temperature increase. Recently Inoue et al have also found that the conversion reaches a maximum at temperatures of 190-200° C. and that the higher the NH₃/CO₂ ratio the lower the temperature at which the conversion maximum is reached. Kucheryavyi and Gorlovskii have also developed an empirical conversion formula which predicts the occurrence of a conversion-temperature maximum and that this maximum occurs at lower temperatures as the NH₃/CO₂ ratio is increased; very recently these researchers also published experimental evidence supporting their empirical formula.

From the model presented here, it is to be expected that the conversion in the liquid phase eventually reaches a maximum at a sufficiently high temperature. The conversion of CO₂ to urea in the liquid phase is determined by reactions (III-6) and (III-7). At lower temperatures (T < 190-200° C.), however, reaction (III-6) lies far to the right, and the conversion is determined by reaction (III-7) only. This reaction is weakly endothermic (ΔH = 3.7 kcal/mole), and increasing temperature therefore leads to a slightly increasing conversion. Reaction (III-6), however, is highly exothermic (ΔH = -22 kcal/mole), and increasing temperature leads to a steady and pronounced decrease in the value of the equilibrium constant for this reaction, K₄ (see Fig. III-2). The value for K₄ was found by calculating the value of K₃ at L = 4 and W = 0 and dividing this value into the value of K₂ at given temperatures). Eventually a temperature is reached at which the dissociation of ammonium carbamate in the liquid phase becomes so large that reaction (III-6) becomes controlling, and further increase in temperature leads to a decrease in the conversion.

The above explanation is essentially the same first put forward by Yoshimura and later expanded by Inoue et al. Yoshimura also presented, as an alternative explanation, the hypothesis that reaction (III-7) becomes exothermic at high temperatures. This idea has, however, always been regarded as unlikely, and recently Sarbaev et al have shown experimentally that reaction (III-7) is indeed endothermic to temperatures of at least 220° C. Baranski and Fulinski have also theoretically studied the problem of decreasing urea yield at high temperatures. Their thermodynamic analysis, however, is unfortunately based on Frejacques's one reaction model and must therefore be rejected as a thermodynamic explanation.

While the writer believes that the primary cause of the conversion-temperature maximum is the eventual pronounced dissociation of ammonium carbamate, it is also probable that a related phenomenon, the approach to critical conditions, occurs as a secondary factor. As the concentration of free ammonia and carbon
dioxide in the liquid phase increases, this phase becomes increasingly "gas-like" and all of the system's parameters (K-values, $H_{CO_2}$, etc.) increasingly become functions of pressure as well as temperature. The critical line in the $NH_3-CO_2$ system has been measured, as is discussed in Chapter II (see Fig. II-13), and it has been found that the higher the L-ratio the lower the temperature and pressure at which critical conditions are reached. For this reason it is to be expected that the higher the L-ratio the lower the temperature at which the conversion-temperature maximum is found. This conclusion is in agreement with the empirical conversion formulas of Ref. 5 and Ref. 32 and the experimental results of Ref. 5 and Ref. 33. Interestingly, the relation between the approach to critical conditions and the liquid phase dissociation of ammonium carbamate was already suggested in 1911 by Scheffer. Concerning the decrease in conversion to urea in the liquid phase at high temperatures, Baranski in 1955 suggested that the cause of this phenomenon was the approach to and the occurrence of critical behaviour in the urea synthesis solution.

If the approach to critical conditions at high temperatures ($T \geq 200^\circ C.$) and high $NH_3-CO_2$ ratios does indeed substantially affect the conversion, then it is to be expected that the conversion will become increasingly pressure sensitive as the critical conditions are approached. This is perhaps the reason that one urea process, which operates at the very high temperature of $215^\circ C.$, works at a pressure roughly 100 atm above its bubble-point pressure.

3.8. Limitations of the model

While the presented model can describe a number of important phenomena, there are nevertheless a number of unsolved problems. The equilibrium constant $K_3$, for example, which should be independent of concentration, varies significantly as L and W are varied in the range L = 2-6, W = 0-1. The bubble-point calculations also become inaccurate as critical conditions are approached and, particularly, as the $(2NH_3)-H_2O$ plane is approached.

The most important causes of these inadequacies are the assumption of ideal gas behaviour and the replacement of activities by mole fractions (fugacity and activity coefficients equal to unity), particularly the latter. Experiments in our Laboratory have shown that the gas phase can be described well using a Redlich-Kwong type equation, assuming ideal mixture behaviour, so that the actual fugacity coefficients can be calculated. But the core of the problem is the calculation of the activities in the liquid phase. The complexity of the possible ionic and polar interactions, the fact that the system is often not too far removed from critical conditions (in which all of the parameters become pressure sensitive), and the dearth of experimental information has forced the writer
to choose the simplest possible model.

The fact that this model nevertheless gives a good description of a number of important phenomena lies in the validity of chemical reactions presented, the fact that the model is based on experiments (the bubble-points) and on the fact that the parameters have been chosen so as to achieve the best possible agreement.

References

CHAPTER IV
CONDENSATION OF A GASEOUS MIXTURE OF AMMONIA, CARBON DIOXIDE AND WATER

4.1. Introduction and theory

Because of the severe corrosiveness of liquid carbamate at high temperatures it is imperative that condensation be avoided during compression of a gaseous NH₃–CO₂–H₂O mixture. It is therefore necessary to know the dew-point conditions of this mixture over the range of conditions at which compression can occur. (A knowledge of the dew-points is also important for the operation of carbamate-gas condensers, which operate most effectively at near azeotropic conditions.)

In considering the condensation of NH₃–H₂O–CO₂ gas mixtures it is necessary to define the state of the system at condensation. Assuming that no decomposition of urea occurs, the following reactions may occur at condensation:

\[
\begin{align*}
\text{(NH}_3\text{)}_G \leftrightarrow \text{(NH}_3\text{)}_L \\
\text{(CO}_2\text{)}_G \leftrightarrow \text{(CO}_2\text{)}_L \\
\text{(H}_2\text{O)}_G \leftrightarrow \text{(H}_2\text{O)}_L \\
2\text{(NH}_3\text{)}_L + \text{(CO}_2\text{)}_2 \leftrightarrow \text{(NH}_2\text{CONH}_2\text{)}_4 \\
\text{(NH}_4\text{OCONH}_2\text{)}_4 \leftrightarrow \text{(NH}_2\text{CONH}_2\text{)}_2 + \text{(H}_2\text{O)}_L
\end{align*}
\]

The following equation may be derived from IV-1, 2 and 4:

\[
2\text{(NH}_3\text{)}_G + \text{(CO}_2\text{)}_G \leftrightarrow \text{(NH}_4\text{OCONH}_2\text{)}_4
\]

At condensation we may assume that reactions IV-1 to IV-4 or reactions IV-1 to IV-5 are in equilibrium. The first case we call condensation at "physical equilibrium" (no urea present in saturated liquid phase) and the second case condensation at "chemical equilibrium" (equilibrium concentration of urea in liquid phase). The gas-liquid equilibria of chemical equilibrium dew-points is described by means of the square-based ternary phase diagram discussed in Chapter II. The dew-points at physical equilibrium can be described by means of an ordinary, triangle-based ternary system whose three sides represent the CO₂–H₂O, NH₃–H₂O and CO₂–NH₃ systems. At physical equilibrium this last plane is a true binary system characterized by a pressure minimum azeotrope.

Beginning at the NH₃–CO₂ plane, it is to be expected that dew-points at physical equilibrium will, at a given temperature, be characterized by considerably higher pressures than points at chemical equilibrium since urea and water are much less volatile than ammonium carbamate. With the addition of water, however, the concentration of urea in the system at chemical equilibrium decreases rapidly, and it is to be expected that the two ternary systems rapidly approach
one another in properties with increasing water addition, merging at the water axis. This behaviour is illustrated in Fig. IV-1.

In practice, the actual condensation behaviour may lie between the two cases described above, or this behaviour may be even more complicated if the surface on which condensation occurs is not inert towards the gas mixture. The condensation surface may, for example, be contaminated with urea decomposition and corrosion products, which may well facilitate condensation, so that condensation may occur at even lower pressures, at constant temperatures, than those associated with the chemical equilibrium conditions discussed above.

The literature offers very little data describing the dew-points of NH$_3$-H$_2$O-CO$_2$ gas mixtures at pressures above atmospheric. Kaasenbrood was the first to qualitatively describe the temperature-pressure-composition (T-P-X) diagram of this system at physical equilibrium (see Fig. II-1b in which point 1 may be replaced by water).\(^1\) This researcher also presented a quantitative diagram for the binary NH$_3$-CO$_2$ system at 130 atm.\(^1\) Recently Verstegen has presented the T-P-X values of the NH$_3$-CO$_2$ azeotrope in the range of \(148 < T < 180^\circ\text{C}\) and \(77 < P < 200\text{ atm}\).\(^2\) Kiyama et al measured dew-points of NH$_3$-H$_2$O-CO$_2$ mixtures at or on the way to chemical equilibrium.\(^3,4\) The description of the experimental technique is, however, vague, and the articles are probably of dubious accuracy. Effremova and Leontieva developed a theoretical method to calculate the dew-points at physical and chemical equilibrium.\(^5\) Because this work is also related to the empirical thermodynamic model presented in Chapter III, it is discussed in some detail here.

Effremova and Leontieva based their model on reactions IV-1, 5 and 6. CO$_2$ was assumed to be insoluble in the liquid phase; the H$_2$O equilibrium was also neglected because, by approximation, the H$_2$O concentration in the gas phase in equilibrium with a liquid phase originating from NH$_3$ and CO$_2$ contains only a few percent water. For each reaction an equilibrium reaction was written:

---

Fig. IV-1. Dew-point pressures, at constant temperature, as a function of water concentration in the NH$_3$-H$_2$O-CO$_2$ systems. The top line represents the dew-points at physical equilibrium; the bottom line the dew-points at chemical equilibrium. The planes are drawn at a constant NH$_3$/CO$_2$ ratio through the chemical equilibrium azeotropic point, A.
\[ K_1 = \left( f_{\text{NH}_3} \right) / \left( a_{\text{NH}_3} \right) \] (IV-7)

\[ K_3 = \left( a_{\text{NH}_2\text{CONH}_2} \right) \left( f_{\text{H}_2\text{O}} \right) / \left( a_{\text{NH}_4\text{OCONH}_2} \right) \] (IV-8)

\[ K_6 = \left( f_{\text{NH}_3} \right)^2 \left( f_{\text{CO}_2} \right) / \left( a_{\text{NH}_4\text{OCONH}_2} \right) \] (IV-9)

in which \( f_1 \) and \( a_i \) represent the fugacity and activity, respectively, of constituent i. The fugacities in the gas phase were calculated using the Lewis-Randall rule (ideal gas mixture of non-ideal gases) and the known fugacities of the pure components at the given temperature and pressure.\(^6^,\)\(^7\) The activities were assumed to be equal to the mole fractions. A pressure correction, the simplified Poynting rule,\(^8\) was applied to the activities:

\[
\left( \frac{\partial \ln a_i}{\partial P} \right)_T = \frac{\bar{v}_i}{RT}
\] (IV-10)

in which \( \bar{v}_i \) is the partial molar volume of liquid constituent i. (This correction is superfluous because it is almost certainly overshadowed by variations in the activity caused by varying concentration.) For \( \text{NH}_3 \), \( \text{NH}_4\text{OCONH}_2 \) and \( \text{NH}_2\text{OCNH}_2 \), the authors roughly estimated \( \bar{v}_i \) values, which were assumed to be independent of temperature, pressure and composition. Under these conditions and taking the standard state of the various constituents as the hypothetical liquid phase at 1 atm and T, equation IV-10 can be integrated to:

\[ a_i = X_i \exp \left[ \frac{\bar{v}_i \left( P-1 \right)}{RT} \right] \] (IV-11)

Then equations IV-7 to 9 become:

\[ X_{\text{NH}_3} = \left( a_{\text{NH}_3} \right) / \exp \left[ \frac{\bar{v}_{\text{NH}_3} \left( P-1 \right)}{RT} \right] \] (IV-12)

\[ X_{\text{AC}} = \left( f_{\text{NH}_3} \right)^2 \left( f_{\text{CO}_2} \right) / K_1 \exp \left[ \frac{\bar{v}_{\text{AC}} \left( P-1 \right)}{RT} \right] \] (IV-13)

\[ X_U = X_{\text{H}_2\text{O}} = \sqrt{\frac{k_2 \left( f_{\text{NH}_3} \right)^2 \left( f_{\text{CO}_2} \right)}{k_1 \exp \left[ \frac{\bar{v}_{\text{AC}} \left( P-1 \right)}{RT} \right] \exp \left[ \left( \Delta \bar{v} \right) \left( P-1 \right) / RT \right]}} \] (IV-14)

in which:

\[ \Delta \bar{v} = \bar{v}_U + \bar{v}_{\text{H}_2\text{O}} - \bar{v}_{\text{AC}} \] (IV-15)
and AC = ammonium carbamate and U = urea. The values of the gas-liquid equilibrium concentrations of the various constituents, necessary for the calculation of the equilibrium constants, were taken from the publications of Kawasumi\textsuperscript{9} and Bolotov.\textsuperscript{10} (Plots of \(\ln K\) vs. 1/T for the various K's reveal considerable scatter. This scatter has two causes: the equilibrium concentrations of Bolotov are not very reliable and the K-values vary significantly with concentration.)

At a given temperature the various K-values are fixed. By choosing a given gas composition and pressure, the fugacities are also fixed and, from equations IV-12 to 14 the mole fractions in the liquid phase can be calculated. In a trial and error calculation the pressure can be varied at constant temperature and gas composition until the sum of the calculated mole-fractions is equal to unity; the chosen pressure is the dew-point pressure. For dew-points at physical equilibrium equations IV-12 and 13 are used; for dew-points at chemical equilibrium equations IV-12, 13 and 14 are used.

The results of calculations using this method are illustrated in Figures IV-2a and b. With respect to the chemical equilibrium dew-points (Fig. IV-2a) the agreement between the calculations and measurements of the author is very good. With regard to the physical dew-points, which are, as expected, much higher in pressure (at the same temperature) than the chemical equilibrium dew-points, agreement with Verstegen's measurements is very poor. That the calculated chemical equilibrium dew-points agree much better with the experimental results than the calculated physical dew-points is not surprising since the values of the equilibrium constants of Ref. 5's model are based on the concen-

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{comparison_of_measured_calculated_dew_points}
\caption{Fig. IV-2a. Comparison of measured (the circles; see Table II-4) and calculated (the lines) dew-points at chemical equilibrium on the \(\text{NH}_3\)-CO\(_2\) plane.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{comparison_of_measured_calculated_dew_points}
\caption{Fig. IV-2b. Comparison of measured\textsuperscript{2} (the circles) and calculated (the lines) dew-points at physical equilibrium on the \(\text{NH}_3\)-CO\(_2\) plane.}
\end{figure}
trations at chemical equilibrium. (Effremova and Leontieva present a table of calculated physical dew-points which agree much better with Verstegen's results. The writer, however, has not been able to duplicate the values of this table.)

Recently Kucheryavyi et al.\(^\text{11,12}\) have re-worked the above mentioned article. The various equilibrium constants are presented in analytical form, and the water equilibrium is included. As in many of their previous articles, however, these writers appear to have little physical-chemical insight into the phenomena they are discussing. They make, for example, no distinction between physical and chemical equilibrium dew-points. These works also give rise to suspicion because the values for the same equilibrium constants presented in the two articles differ significantly, and the more recent article does not even refer to the earlier article. In one article\(^\text{12}\) a table of calculated dew-points is presented, but the writer, using these authors' own values and formulas, has calculated dew-points very different from those presented. Kucheryavyi et al.\(^\text{12}\) also presented a simplified formula for the calculation of the condensation point temperature (chemical equilibrium):

\[
T_c = 150.6 + 0.158 P + 93.4 X_{H_2O} + 5.3 X_{NH_3}
\] (IV-16)

where \(T_c\) = the condensation point in °C., \(P\) = the chosen pressure in atm, \(X_{NH_3}\) and \(X_{H_2O}\) the mole fractions of \(NH_3\) and \(H_2O\), respectively. This formula, which is that of a flat plane at constant pressure (or temperature) is in complete disagreement with the curved dew-point surface sketched in Fig. II-1b. The dew-point values calculated using this formula are also in serious disagreement with the table of dew-points presented in the same article and with the dew-point values of Ref. 5.

Because of the dearth of experimental information and the lack of reliable computational methods, it was decided to experimentally measure the physical dew-points of \(NH_3-H_2O-CO_2\) gas mixtures in the range of \(20 < P < 180\) atm, \(130 < T < 180\) °C., \(0.1 < NH_3/CO_2 < 3\) (molar) and \(H_2O = 2-15\) mole-% \(H_2O\).

4.2. Experimental

Normally dew-points are measured in a static method (to insure equilibrium) by analyzing the gas phase in equilibrium with a given liquid phase. For the \(NH_3-H_2O-CO_2\) system at physical equilibrium at high temperatures, however, such a procedure was not possible for the following reasons. Firstly, at high temperatures (\(T > 150\) °C.) the liquid phase is, initially, rapidly reacting towards the chemical equilibrium concentrations. Secondly, at higher temperatures (\(T > 180\) °C...
The liquid phase becomes so corrosive that only special, and expensive, materials (Ti, Zr or Ta) are sufficiently corrosion resistant. For these reasons a new method had to be developed for the measurement of the dew-points; this was done by Walthie. 13

The theory of the experimental method and the work method are illustrated using Figs. IV-3 and IV-4. The experimental method consists basically of the following: A flowing gas mixture of composition Y (Fig. IV-3) is cooled at constant pressure, and a sample of this gas is continually analysed. At slightly under the condensation temperature \( T_c \) a liquid phase \( X_L \) is formed leading to a decrease in the concentration of the least volatile component in the gas phase \( Y_G \). If the temperature is now increased the liquid phase evaporates, and the concentration of the least volatile component, which had decreased with condensation (as measured by the analysis; see Fig. IV-4), suddenly begins to increase to a value larger than its true value in the gas mixture. Since the gas is flowing this concentration eventually decreases to its original value. The temperature and the concentration of the least volatile component (water) are continuously registered by means of a recorder (Fig. IV-4), in which the height of the vertical lines represents the water concentration.

A sketch of the apparatus is presented in Fig. IV-5. A stainless steel 316 10 litre autoclave (1) contains the gas mixture \( (T \sim 300 \text{ °C}) \), which is continually mixed by means of a magnetically operated stirrer (2). The tube containing the mixer's iron core is kept hot using a defroster transformer (7) operating at 2 volts and about 500 amperes. The gas mixture flows to the dew-point apparatus (10), which consists of a SS-316 L capillary, 1 mm. x 3 mm. x 50 cm., that is contained in a thermostat (11). The flow of gas through the capillary is so low \( (\sim 2-4 \text{ litre/hour STP}) \) that the temperature in the capillary is that of the thermostat. The pressure and temperature are measured using a Foxboro pressure

---

**Fig. IV-3.** Condensation of a gaseous binary mixture \( (P = \text{constant}) \).

**Fig. IV-4.** Condensation as registered by the recorder.
Fig. IV-5. The dew-point apparatus.
1: Autoclave. 2: Mixer. 3: Iron core.
4: Magnets. 5: Heating element. 6:
Eccentric for magnets. 7: Defroster
transformer. 8: Pressure seal. 9:
To analysis section. 10: Dew-point
spiral. 11: Thermostat. 12: Heating
oil pump. 13: Heating oil. 14: NH3
or CO2 in. 15: Vent. 16: H2O in.
17: Platform for quickly lowering
(and raising) bottom of thermostat
to change dew-point spiral.

Seal (8) and a chromel-alumel thermocouple, which is attached to the capillary.
From the dew-point apparatus the gas flows to a fine-control valve located in a
separate thermostat (11). This valve reduces the pressure to atmospheric. The
gas then flows to the analysis section (9), which consists of two gas-solid
chromatography units. One analysis unit is for the qualitative analysis of water;
the other is for a quantitative analysis of the mixture. The conditions of the
analysis are given in Table IV-1. (The analysis section is discussed in detail

<table>
<thead>
<tr>
<th>Table IV-1. Specifications of the analysis sections</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Column material</strong></td>
</tr>
<tr>
<td>Stainless steel 321</td>
</tr>
<tr>
<td>4 x 6 x 300 mm.</td>
</tr>
<tr>
<td>Poropak T (80-120 mesh)</td>
</tr>
<tr>
<td>H2; 60 cm.³/min., STP</td>
</tr>
<tr>
<td>130 °C</td>
</tr>
<tr>
<td>200 ma.</td>
</tr>
<tr>
<td>³/₄ cm.³</td>
</tr>
<tr>
<td>8.0 atm. abs.</td>
</tr>
<tr>
<td>1425 mm. Hg. abs.</td>
</tr>
<tr>
<td>Beckman 6-way</td>
</tr>
<tr>
<td>Pneumatic</td>
</tr>
<tr>
<td>1 min.</td>
</tr>
</tbody>
</table>
in Appendix III). All gas lines are kept hot (T \( \geq \) 250-300 °C.) by means of resistance coils ("Pyrotenax").

The experimental method and apparatus were tested by measuring the known dew-points in the \( \text{NH}_3 \)-\( \text{H}_2\text{O} \) system. The measured points agreed with the literature values within 0 to 2 °C.

Measuring the \( \text{NH}_3 \)-\( \text{CO}_2 \)-\( \text{H}_2\text{O} \) system was extremely difficult, however. Local cooling led to condensation, severe corrosion and clogging of the lines. A very serious problem was that residues of urea decomposition products in the capillary also led to positive temperature errors; periodic "cleaning" with steam or \( \text{H}_2\text{O} \)-\( \text{NH}_3 \) mixtures helped reduce this error but could not eliminate it. Recently Bijwaard has improved the technique by replacing the capillary with a new one after each dew-point measurement.\(^{15}\) This is a very tedious procedure, but as will become apparent from the next section it is necessary for more accurate measurements.

Another recent development by Broers has been to measure the dew-points in the Cailletet tube.\(^{16}\) This is done by compressing the gas mixture at constant temperature and measuring its length, hence volume, by means of a cathetometer. A graph of \( 1/P \) versus the volume is plotted. At the condensation point a discontinuity in the plot is found and at slightly higher pressures condensation can often be visually observed. After each dew-point measurement the system’s pressure is reduced to some previously measured value below the dew-point pressure and the volume is measured. When this volume is identical to the previously measured (before condensation) volume, which occurs if the liquid phase has completely evaporated, another dew-point is measured at a different temperature. In the area of positive water concentration so far measured (7.5 and 10 mole-% \( \text{H}_2\text{O} \)) the volume measurements have been completely reproducible. In the plane of 0-% \( \text{H}_2\text{O} \) the evaporation of the liquid phase, which involves the hydrolysis of urea present in this phase, requires days so that experiments in this area were not carried out.

In general the dew-points could be measured most accurately in the area near azeotropic condensation (the area of the pressure minimum, at constant temperature) since condensation was here rather abrupt and accompanied by a large volume change; the resulting discontinuity in the plot was found easily. At high \( \text{NH}_3 \)-concentrations the measurements became increasingly difficult due to the approach of critical conditions. At high \( \text{CO}_2 \)-concentrations the measurements also became increasingly difficult because of the steepness of the bubble-point line (at constant temperature); little condensate was formed even at pressures much higher than the actual dew-point pressure. The measured dew-points were also somewhat dependent on the rate at which the pressure was increased. In the area of steps of 1-2.5 atm/3 min, in discreet steps of 1-2.5 atm, this effect was negligible and experiments were normally carried out at these rates.
As was to be expected the dew-point pressures measured in the Cailletet tube were higher than those measured in the spiral, as is discussed in the next section.

4.3. Results and discussion

A typical Clapeyron graph of results obtained with the dew-point spiral is illustrated in Fig. IV-6. It is seen that at high water concentrations the dew-point line is approximately parallel to the vapour pressure line of water; this behaviour is indicative that the dew-point condensate consists principally of water at this condition. At low water concentrations and, particularly, at high pressures and temperatures, the slope of the Clapeyron lines increases ($|\Delta H|$ increases), a fact which probably indicates that the condensate contains increasing concentrations of ammonium carbamate at these conditions.

From the Clapeyron graph pressure-composition (percent water) figures can be prepared at various temperatures, as is shown in Figures IV-7a and b. In Fig. IV-7a it is seen that the author's measurements form a smooth curve with the dew-points given by Verstegen. Considerable scatter, however, is also apparent. Concerning Fig. IV-7b the most salient features are that the pressure values of this CO$_2$-rich section are very high relative to Fig. IV-7a, which is NH$_3$-rich, and that the dew-point pressures drop sharply with the first small additions of water; this effect is most pronounced at high temperatures. With increasing quantities of water the decrease in condensation pressure becomes increasingly more gradual. The cause of this effect lies in similar behaviour found in the NH$_3$-H$_2$O and CO$_2$-H$_2$O systems, as can be seen from Fig. II-2.

If all the experimental results are plotted in such graphs then pressure-composition figures at constant water concentrations can be prepared. Such graphs are presented in Figures IV-8a to d in which the pressure values are projected upon the NH$_3$-CO$_2$ plane (percentages are molar). At low water concentrations the
Fig. IV-7a. Pressure-mole-% water composition curves of dew-points at \( \text{NH}_3/\text{CO}_2 = 3 \) (molar). The symbols □, ○, and △ refer to 140, 160 and 180 °C., respectively. The solid symbols (0% \( \text{H}_2\text{O} \)) refer to Verstegen's measurements.

Fig. IV-7b. Pressure-mole-% water composition curves of dew-points at \( \text{NH}_3/\text{CO}_2 = 0.2 \) (molar). The symbols ●, □, x, ○, +, and △ refer to 130, 140, 150, 160, 170, and 180 °C., respectively.

Results are particularly clear: a minimum pressure point in the region of \( \text{NH}_3/\text{CO}_2 \approx 2 \) is found. With increasing \( \text{NH}_3 \) and \( \text{CO}_2 \) concentrations the condensation pressure increases. At high temperatures and at high \( \text{CO}_2 \) concentrations this pressure increase is especially evident. There are too few experiments to accurately determine the position of the pressure minimum and the direction of its displacement with increasing water concentration and temperature. From theoretical considerations (analogous to the computational methods of Chapter III) it is to be expected that the pressure minimum will be displaced towards increasing \( \text{NH}_3 \) concentrations with increase in temperature and water concentration. With regard to the effect of temperature, Verstegen has indeed shown that on the \( \text{NH}_3-\text{CO}_2 \) plane the pressure minimum is displaced from about 69.7 mole-% \( \text{NH}_3 \) at 145 °C. to about 70.9 mole-% \( \text{NH}_3 \) at 180 °C.

Concerning the accuracy of the measured dew-points it is, unfortunately, certain that they are too low in pressure, at constant temperature, relative to the real physical dew-points due to the presence of urea decomposition products in the dew-point spiral. This systematic error has been demonstrated by recent dew-point determinations at 10 mole-% \( \text{H}_2\text{O} \) in the Cailletet tube. It is found (see Fig. IV-9) that condensation on clean glass (the Cailletet tube) occurs at consistently higher pressures than that found in the spiral, particularly at high \( \text{CO}_2 \)-concentrations, at which the formation of considerable amounts of decomposition products is to be expected. It has also been found that the condensation
Figures IV-8a to d. Dew-point pressures, at constant temperature and mole-% water concentrations, projected upon the NH\textsubscript{3}-CO\textsubscript{2} plane. The symbols X, •, □, ○, ⋆, and △ refer to 130, 140, 150, 160, 170, and 180 °C., respectively. The lines are dashed to indicate that too few points are available to determine them accurately.

occurs at higher temperatures, at constant pressure, with a spiral which has already been used than with a new spiral. Furthermore, even after one condensation it has been observed that the inside of the spiral is blackened and that after repeated condensations the inside of the spiral tends to become coated with a black amorphous substance, presumably a mixture of urea decomposition and corrosion products. Reproducible dew-points can be consistently obtained only by using a new spiral for each measurement. Unfortunately, it must therefore be concluded that while the form of the NH\textsubscript{3}-H\textsubscript{2}O-CO\textsubscript{2} dew-point plane has been experimentally verified, more measurements are necessary to quantitatively determine this plane.
4.4. Practical applications of the dew-point measurements

Regarding the HGRP a cardinal question is what the condensation conditions will be in practice. It is probable that as long as all of the surfaces along which the gas mixture flows are "clean" (not contaminated with urea decomposition products) no condensation will occur as long as the boundaries of the physical condensation regions are not transgressed. Therefore design calculations may be based on Figures IV-8a to d. These figures even provide for a considerable safety margin, since most of the points are even higher in temperature, at constant pressure, than the dew-points at chemical equilibrium. If, however, condensation occurs locally, it is probable that a sort of autocatalytic reaction can occur: at condensation urea decomposition products can be formed; these products facilitate further condensation so that the area of condensation tends to continuously increase. For this reason it is imperative that no local cold spots occur in a HGRP.

Another possible problem associated with the condensation conditions concerns the necessary cooling area of the interstage coolers, which remove part of the heat generated by compression of the recycle gases. In cooling these gases the coolant's temperature may not be lower than the gases' dew-point temperature. Since at high pressure the recycle gases condense at relatively high temperatures, the temperature difference between coolant and gas cannot be large (as would be the case if cooling water could be used). This fact, already pointed out by Frejacques, can lead to very large cooler surfaces. This question is discussed in more detail in Chapter VI.

The above mentioned problem can be minimized by working in an area of low condensation temperature (high condensation pressure). It is therefore desirable that the recycle gases contain as little water and as much CO₂ as possible. The
former specification is also advantageous with respect to the conversion in the reactor. Cook probably had the second factor in mind when he suggested coupling the HGR compression with the CO\textsubscript{2}-feed.\textsuperscript{18}

4.5. Further discussion of the possibilities for the calculation of the dew-points

As has been discussed in section III-1, the methods available from the literature are not capable of accurately describing the physical dew-points. It is interesting to attempt to describe these points using the empirical-thermodynamic model presented in Chapter III. On the basis of equations IV-1 to 4 and III-10 to 12 and the parameters \( H^\text{CO}_2 \) and \( P_{\text{NH}_3}^0 \) presented in Chapter III it is possible to calculate the dew-point line over the entire \( \text{NH}_3-\text{CO}_2 \) composition area (at a given \( \text{H}_2\text{O} \) concentration) on the basis of one experimental point from which the value of the equilibrium constant \( K_4 \) for reaction IV-4 can be calculated. In the area of 10-60\% \( \text{NH}_3 \) agreement between the calculated and measured dew-points is good. At higher \( \text{NH}_3 \) values, however, the calculated dew-points are systematically lower than the measured values.

In principle, however, it is not to be expected that the empirical thermodynamic model, which was developed for the \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) system at complete chemical equilibrium, should be capable of describing the \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) system at physical equilibrium. This is especially true at the \( \text{NH}_3-\text{CO}_2 \) plane. At the equilibrium situation a liquid situated on the \( \text{NH}_3-\text{CO}_2 \) plane contains appreciable concentrations (\( \approx 40 \text{ mole-\%} \)) of the analogous substances urea and water, and the addition of water to this mixture will not drastically change the nature of the solution. At physical equilibrium, however, the liquid phase consists of liquid ammonium carbamate and dissolved \( \text{NH}_3 \). Solid ammonium carbamate is poorly soluble in liquid ammonia, and it is therefore to be expected that \( \text{NH}_3 \) will be only very poorly soluble in this liquid salt relative to a urea-water solution. Thus the \( P_{\text{NH}_3}^0 \) value of \( \text{NH}_3 \) in liquid carbamate should be much higher than the value for the urea synthesis solution. Since the addition of water to liquid ammonium carbamate significantly changes the solubility of \( \text{NH}_3 \) in the resulting solution, it is also to be expected that the \( P_{\text{NH}_3}^0 \) value should be a strongly dependent function of the water concentration. Similar reasoning holds for the \( H^\text{CO}_2 \) value. Since it is also to be expected that the activity coefficients will vary significantly with composition, \( K_4 \), should also be a strong function of composition (e.g., at \( T = 160 \) °C. and \( L = 3 \), the value for \( K_4 \), as calculated from the dew-point measurements, varies some 600\% as the percent water varies from 1 to 12\%). For these reasons it is probable that a model which describes the phase equilibria of the \( \text{NH}_3-\text{H}_2\text{O}-\text{CO}_2 \) system at physical equilibrium will have to consider the ionic relations and activity coefficients (such models were mentioned in section III-3).
References


CHAPTER V

CORROSION IN A GASEOUS AMMONIA-CARBON DIOXIDE-WATER MIXTURE

AT THE CONDITIONS OF A HOT GAS RECIRCULATION PROCESS

5.1. Introduction.

5.1.1. Corrosion in the liquid phase in the urea synthesis.

One of the key problems which prevented an earlier large scale production of urea was the severe corrosiveness of the urea synthesis solution. A great number of articles and patents exist which describe how these corrosion problems have been overcome or minimized. For reasons of scope and space these articles will not be discussed here, although considerable work has been done at our Laboratory to collect and digest the literature pertaining to corrosion. Excellent reviews of this literature have been prepared by Glaser, Barake, Hoogendijk, Borg and Verhulst. In the general literature reviews by James, Capel and van der Horst, Krystow, Wilnitz, Staukov et al, Otsuka and McDowell are to be recommended. For a more complete list of articles concerning corrosion the reader is referred to Appendix V, which lists a large number of articles relating to the urea synthesis. Because of the very high pressures and temperatures involved in the urea synthesis, electrochemical studies of the corrosion mechanism at process conditions are very difficult, and to date only two works exist which attempt to study this problem theoretically. All of the other articles are more or less empirical studies of the observed corrosion resistance of various alloys. Two possible exceptions are recent articles by van der Horst in which a theory is presented that the mechanism of the corrosion of stainless steels, the most common material for urea plant manufacture, involves the formation of ammonium complexes, in particular, for nickel.

This chapter is devoted to the question of corrosion in a hot gaseous mixture of CO₂-H₂O-NH₃ at the conditions of a HGRP. The results of an extensive literature search are presented as well as the results of some simple, preliminary experiments. The question of liquid phase entrainment corrosion at turbo-compressor conditions is also briefly discussed in this chapter (and also in Chapter VI).

5.1.2. Corrosion in the gas phase - its relation to the HGRP.

The technical feasibility of the HGRP has been doubted on the basis of the belief that compression of a hot gaseous mixture of NH₃, CO₂ and H₂O would present nearly insurmountable corrosion problems. Evidence for this belief was based on the experience of I.G. Farben at Oppau, Germany. At this plant severe corrosion problems in the HGR compressor had eventually forced the plant to be
shut down. Frejacques, Fauser, Kaasenbrood and Tonn also mention the corrosiveness of an NH$_3$-CO$_2$-H$_2$O gas mixture as a serious obstacle to the realization of a HGRP. For this reason it is all the more surprising that while a number of patents and articles have appeared in the last years concerning new versions of the HGRP (see Chapter VI) no researcher has as yet performed a systematic study of possible gas phase corrosion problems.

Before discussing the literature relating to this problem it is clarifying to attempt to specify the types of materials which are most likely to be used in a HGR compressor and to make an important remark concerning the temperature.

5.1.3. The choice of materials for a HGR turbo-compressor.

It is obvious that the material to be chosen for a HGR turbo-compressor must possess both high strength and high corrosion resistance. It should also be, preferably, inexpensive and workable (weldable, machinable).

The strength criterion for the impeller can be quantitatively expressed, as an approximation, by means of the strength requirements for a rotating disc:

\[
\frac{\sigma_{0.2}}{\rho} > \frac{1}{3} \left( \frac{2\pi N}{60} \right)^2 \left( \frac{d}{2} \right)^2
\]

(V-1)

in which \(\sigma_{0.2}\) is the yield strength, N/m$^2$ (in practice kgf/mm$^2$), \(\rho\) is the density in kg/m$^3$, \(N\) is the rotational speed in rpm, \(d\) the diameter in meters. For the maximum operating conditions of the HGR turbo-compressor we assume the following values: \(d = 0.4\) m, \(N = 15000\) rpm (then tip-speed = 314 m/s) and \(T = 300^\circ\)C. Then:

\[
\frac{\sigma_{0.2}}{\rho} > 3.3 \times 10^4 \frac{m^2}{s^2}
\]

(V-2)

The corrosion requirements are more difficult to specify in advance. Since the materials will be exposed to a hot gaseous NH$_3$-CO$_2$-H$_2$O (eventually plus \(\approx 1\%\) air) mixture, possible corrosion reaction will be based upon the decomposition of ammonia (hydrogen- and nitrogen-attack) or possibly oxidation, caused by H$_2$O, CO$_2$ and eventually O$_2$.

On the basis of strength and corrosion requirements it is probable that one of the following types of alloys will be chosen for the HGR turbo-compressor (the materials are listed roughly in order of price and, more roughly, workability):

1. Chromium-based steels (chrome steels)
2. Precipitation hardened (PH) chromium-nickel (Cr-Ni) steels
3. High nickel content Ni-Cr-Fe alloys
4. Titanium (Ti) alloys

A condensed discussion of these alloys follows. For more detailed information the reader is referred to the literature.22,23,24

The characteristics of the chrome steels are determined chiefly by the percentage of chromium, a strong ferrite former, and carbon, a very strong austenite former.25 The chrome steels with a high temperature austenite structure can be transformed into a martensitic structure by means of a suitable heat treatment. The chromium steels are therefore divided into the ferritic and martensitic types.

The ferritic Cr-steels contain 12-18% Cr and < 0.12% carbon. Due to the high chromium and low carbon concentrations these alloys have a relatively high corrosion resistance; the low carbon concentration, however, results in a relatively low yield strength. The martensitic Cr-steels can be divided into a number of groups with roughly increasing Cr and C content. Steels with 12-14% Cr and < 0.15% C are widely used for turbine rotors. Increasing C content results in increasing strength and hardness, but lowered corrosion resistance, but this last factor can be compensated for by increasing the Cr content and adding Ni (2-4%) and Mo (1-2%) to the alloy. Roughly speaking, ferritic and martensitic Cr-steels exhibit approximately similar corrosion resistance. The corrosion resistance increases with increasing Cr, Ni and, to a lesser extent, Mo concentration and decreases rapidly with increasing C concentration. The increase in corrosion resistance effected by chromium is caused by its property of forming an impervious, adherent and inert oxide film on the alloys' surface. Nickel enhances the protective working of the oxide film.

The austenitic Cr-Ni steels, such as the AISI-300 series, are well known for their outstanding corrosion resistance. Unfortunately, however, these alloys are also characterized by relatively low yield strengths. In order to combine the high corrosion resistance of these austenitic Cr-Ni steels with high strength and hardness, the last 25 years has witnessed the development of the so-called precipitation hardened (PH) Cr-Ni steels. These are Cr-Ni steels to which small amounts (< 0.5-4%) of copper, aluminium, titanium and eventually other elements have been added. Following a suitable heat treatment these elements form an intermetallic precipitate which, by reducing the ease with which shear occurs, greatly increases the strength and hardness relative to the ordinary Cr-Ni steels.

The PH Cr-Ni steels may be divided into two classes, namely the martensitic and semi-austenitic types. The martensitic PH steels contain a relatively
small percentage (≤ 4%) of nickel, while the semi-austenitic types contain larger amounts (4-8%) of this element (nickel is a strong austenite former). These two PH alloy types do not differ greatly in strength; in general the semi-austenitic types offer a somewhat greater corrosion resistance than the martensitic types. As a class the PH Cr-Ni steels exhibit significantly better corrosion resistance than the Cr-steels.

The rapid development of the use of titanium alloys in the chemical industry is based upon the great corrosion resistance of these alloys. Like the Cr- and Cr-Ni-steels, the corrosion resistance of Ti-alloys is based upon the protective working of an oxide film. Pure Ti is rather weak, but combined with such elements as Al, Va and Sn, alloys are formed which are approximately as strong as those of the Cr- and PH Cr-Ni steels. Due to their low density (4.5 vs. 7.9 g/cm³ for steel alloys) Ti-alloys are also characterized by an especially high σ₀₂/₀ ratio. For this reason Ti-alloys are popular in the aero-space industry for turbine rotors. Unfortunately, however, these alloys are roughly 5-10 times more expensive than stainless steels and also require more expensive fabrication techniques.

The Ni-based alloys were not studied and will therefore not be further discussed.

Some properties of the materials tested are presented in Table V-1.

As already mentioned the Cr-steels, PH Cr-Ni steels and Ti-alloys are materials whose corrosion resistance is based largely on a protective oxide film which isolates the metal phase from the environment. In discussing the corrosion resistance of these materials it is therefore essential to distinguish as to whether they are exposed to a completely reducing atmosphere, which tends to destroy the oxide film, thus exposing the base metal to attack, or to an atmosphere containing oxidizing agents, which tend to retain the oxide film and thus retard corrosion.

5.1.4. Temperature, the HGR compressor and corrosion in the gas phase.

It is useful to divide the temperature range into two areas, temperatures up to 300°C and temperatures from 300 to about 550°C. This division is based on the following reasons: Firstly, modern turbo-compressors of standard design have, as their maximum operating conditions, temperatures of 250-300°C. Operation at higher temperature is technically possible, but requires special techniques and design, which can drastically increase the cost price. Secondly, it is also probable that the reliability of the standard compressor is also greater than the special types. Thirdly, as will be shown later in this chapter, the rate of corrosion of the materials considered is low at temperatures
Table V-1. Composition and some properties of the alloy types studied.

<table>
<thead>
<tr>
<th>Material</th>
<th>Supplier</th>
<th>Composition, %</th>
<th>Structure</th>
<th>((a_{0.2}/\rho)^1) m/s.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>Cr</td>
<td>Ni</td>
</tr>
<tr>
<td>Cr-steels</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Remanit 1520</td>
<td>D.E.W.(^2)</td>
<td>0.20</td>
<td>13.5</td>
<td>----</td>
</tr>
<tr>
<td>ARZ</td>
<td>Sch. Bl.(^3)</td>
<td>0.20</td>
<td>13.5</td>
<td>----</td>
</tr>
<tr>
<td>ARL</td>
<td>Sch. Bl.</td>
<td>0.22</td>
<td>16.5</td>
<td>1.7</td>
</tr>
<tr>
<td>ARD</td>
<td>Sch. Bl.</td>
<td>0.38</td>
<td>16.5</td>
<td>0.5</td>
</tr>
<tr>
<td>ARW-B</td>
<td>Sch. Bl.</td>
<td>0.10</td>
<td>13.5</td>
<td>----</td>
</tr>
<tr>
<td>Cr-Ni steels</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AISI-316</td>
<td>Sch. Bl.</td>
<td>0.05</td>
<td>17.5</td>
<td>11.0</td>
</tr>
<tr>
<td>PH 17-4</td>
<td>Armco(^4)</td>
<td>0.04</td>
<td>15.5</td>
<td>4.5</td>
</tr>
<tr>
<td>PH 17-7</td>
<td>Armco</td>
<td>0.07</td>
<td>15.2</td>
<td>7.0</td>
</tr>
<tr>
<td>PH 14-8-Mo</td>
<td>Armco</td>
<td>0.03</td>
<td>15.0</td>
<td>8.4</td>
</tr>
<tr>
<td>OFV 520B</td>
<td>F.V.(^5)</td>
<td>0.07</td>
<td>14.0</td>
<td>5.5</td>
</tr>
<tr>
<td>OFV 520S</td>
<td>F.V.</td>
<td>0.05</td>
<td>15.0</td>
<td>5.5</td>
</tr>
<tr>
<td>Remanit 1870</td>
<td>D.E.W.</td>
<td>0.07</td>
<td>17.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Ti-alloys</td>
<td></td>
<td></td>
<td>Sn</td>
<td>V</td>
</tr>
<tr>
<td>Ti-317</td>
<td>I.C.I.(^6)</td>
<td>5</td>
<td>2.5</td>
<td>----</td>
</tr>
<tr>
<td>Ti-318</td>
<td>I.C.I.</td>
<td>6</td>
<td>----</td>
<td>4</td>
</tr>
</tbody>
</table>

1. Values given relate to 300°C. 2. Deutsche Edelstahlwerke (See reference 24 for addresses of suppliers.).
of up to 300°C, but increases rapidly at higher temperatures (for this reason it is desirable to design a HGRP with a maximum compressor temperature below 300°C; this question is further considered in Chapter VI). The high temperature range must also be considered because a number of important patents exists for HGR processes in which the HGR turbo-compressor operates at $300 < T < 550°C$. (These processes are discussed in Chapter VI.)

5.2. The results of a literature search concerning corrosion in a gaseous mixture of ammonia-carbon dioxide-water.

5.2.1. Corrosion in gaseous ammonia.

5.2.1.1. A short discussion of the corrosion mechanism of metals exposed to hot gaseous mixtures containing ammonia.

With the experience gained from the operation of plants for the synthesis of $\text{NH}_3$ via the Haber-Bosch process it is well known that hot, high pressure gaseous mixtures containing $\text{NH}_3$ can severely attack metals. The underlying cause of the corrosiveness of $\text{NH}_3$ is that it decomposes into atomic hydrogen, $\text{H}$, and atomic nitrogen, $\text{N}$, via the catalytic working of metals. $^{27,28}$ (There is a direct correlation between the catalytic activity of metals in decomposing $\text{NH}_3$ and the extent to which these metals are attacked by $\text{NH}_3$. $^{29,30}$) Both $\text{N}$ and $\text{H}$ can simultaneously attack metals in what is called nitrogen- and hydrogen-attack.

Hydrogen attack manifests itself in a physical and chemical form. The basis for both these forms is that the atomic hydrogen, $\text{H}$, can easily diffuse through metals. The source of the $\text{H}$, aside from decomposing $\text{NH}_3$, can be hydrogen molecules, which, adsorbed on a hot metallic surface, dissociate into $\text{H}$. $^{27,28}$ In the physical form the $\text{H}$ is simply dissolved in the metallic lattice; as such it causes brittleness and loss of strength. The higher the temperature the greater the solubility of the hydrogen. This "corrosion" effect is, however, reversible: by slowly cooling the metal hydrogen re-diffuses out, and the metal's original strength characteristics return to normal. Chemical H-attack is much more serious. With steel alloys the $\text{H}$ can react with the carbon present (decarburization) to form methane; this gas cannot diffuse out of the metal, and it accumulates at the crystal boundaries causing severe internal stresses, eventually blistering and rupturing the metal. Chemical hydrogen attack is progressive and permanent.

To prevent H-attack metals are added to the steel which have more chemical affinity for carbon than hydrogen. These are the so-called carbide stabilizing metals. The commonly used metals are chromium, molybdenum and tungsten, which progressively increase resistance to H-attack, and titanium, niobium, vanadium.
and zirconium, which increase the resistance abruptly once the stoichiometric amounts of these metals, relative to the amount of carbon present, have been reached. Extensive studies of H-attack occur in the literature. The reader is referred to the thorough studies of Class, and, especially, to the quantitative studies of Nelson; a more recent study of the mechanism has been published by Molstad and Gunther. For purposes here it is sufficient to state that steels containing \( \approx 12\% \) Cr are very highly resistant to H-attack at temperatures to at least 600°C and \( H_2 \) partial pressures to at least 500 atm.

Absolutely pure titanium reacts rapidly with ammonia to form the brittle hydride and nitride. Normal titanium (oxide film present) can also react with hydrogen; this attack, however, is greatly retarded by traces of oxygen, water or, to a lesser extent, carbon dioxide, which tend to retain the protective oxide film. Towards \( NH_3 \) titanium is a very poor catalyst, even at high temperatures. Therefore it is to be expected that titanium will not be attacked by \( NH_3 \). This will be shown to be the case.

The other form of corrosion caused by decomposing \( NH_3 \), N-attack, is much more difficult to prevent because the very metals, Cr, Mo, Ti and others, needed to prevent H-attack, react strongly with atomic nitrogen to form nitrides. These nitrides are very brittle, and their formation is also accompanied by a significant volume increase relative to the base metal. For example,

\[
\frac{V_{CrN}}{V_{Cr}} \approx 1.5 ; \quad \frac{V_{Fe_4N}}{4 V_{Fe}} \approx 1.2
\]  

 voi(V-3)

(in which \( V_m \) is the specific molecular volume of material \( m \)). For alloys containing elements which react with nitrogen (Mo, Ti and, particularly, Cr) the N-attack is usually gradual and localized to the surface of the metal, at which a nitride layer is formed. This film, if intact, is protective, and the rate determining step in its growth is the rate of diffusion of atomic nitrogen through the film. Due to the brittleness of the nitride film and the volume increase accompanying its formation, a thickening of the film often leads to fissuring and rupturing of the layer, exposing fresh metal to attack; in this case the nitride layer is not protective, and the corrosion rate can actually increase with time.

In considering N-attack the variables alloy composition and gas composition, temperature and pressure, as well as secondary factors, such as surface conditions (oxidized or not, roughness), the occurrence of welds and stress, and the addition of secondary alloying elements must be taken into account. These
factors will be briefly discussed below. (A summary of literature relating to quantitative experimental studies of N-attack in NH$_3$-containing atmospheres is presented in Table V-2, which is placed at the end of this Chapter.) It is difficult to quantitatively compare all of these studies because of the different methods of interpretation used by the various authors to measure the N-attack (weight gain, micro-hardness, loss of strength and ductility, metallographic studies, etc.) and because many authors do not discuss the purity of the NH$_3$ used, in particular, whether it contained traces of oxidizing agents such as O$_2$ and H$_2$O.

5.2.1.2. The effect of alloy composition and gas conditions on the corrosion rate.

Unalloyed steels can be attacked by pure NH$_3$ even at 1 atm and 300°C, $^{29}$, 30,39 (see Table V-2); at 300 atm significant attack by ammonia synthesis gas mixtures begins already at 250°C. $^{31}$ These unalloyed and low-alloy steels exhibit nitriding not as a surface layer but rather as attack throughout the interior of the metal; $^{39,40}$ metallographically this attack manifests itself as needles of iron nitride distributed near the surface. $^{39}$

Concerning the effect of increasing Cr-content, there is disagreement in the literature. Various researchers $^{27,40}$ state that concentrations of Cr above 11-12% lead to increased resistance to nitriding. (The basis of this increased corrosion resistance is, according to Cihal, $^{27}$ that at high Cr-concentrations a Cr-rich carbide, (Fe,Cr)$_{23}$C$_6$, is formed. The Gibbs free energy ($\Delta G_f$) of this carbide is lower than that of the carbide formed at lower Cr-concentrations, Cr$_7$C$_3$, and, more importantly, lower than the $\Delta G$ of chromium nitride.) Increasing Cr-content results in thinner, harder and more protective nitride layers. Other researchers, $^{41,42}$ however, state that increasing Cr-content increases N-attack. In a British patent a maximum Cr-content of 12% is advised. $^{42}$

The contradictory reports concerning the effect of Cr may be related to the occurrence, or non-occurrence, of oxidizing agents, such as O$_2$, H$_2$O and CO$_2$, in the NH$_3$, as is discussed in section 5.2.1.3. The optimum Cr-concentration is probably also related to the amount of nickel present. $^{43}$

Concerning the effect of nickel addition, all of the relevant literature $^{39,41,42,44,45}$ is in agreement that increasing Ni content greatly decreases the nitriding effect of NH$_3$ (see Fig. V-1 and Table V-2, in which the alloys are usually arranged in order of increasing Ni content). The favourable effect of Ni is probably the result of several factors. Firstly, at the conditions being discussed Ni does not readily form a nitride $^{41}$ as does Cr, for example, and therefore hardly reacts with atomic nitrogen, N. Secondly, N is apparently insoluble in Ni. $^{41}$ Ni therefore acts as an effective barrier to N diffusion,
which, as already mentioned, is the rate determining step in the nitriding process. Thirdly, it appears that Ni, which is present as finely divided metallic nickel in the nitride layers of an exposed Cr-Ni steel, reduces the brittleness of this layer and, as such, reduces the tendency of the layer to fissure and blister (a process which greatly accelerates nitriding by exposing fresh metal areas to attack). The beneficial effect of Ni may also be related to its austenite-forming properties (see further section 5.2.1.4.).

For these reasons Cr-Ni steels (8 ≤ Ni ≤ 22%) are much more resistant to N-attack than Cr-steels (see Table V-2), and Cr-Ni steels are therefore extensively applied in the NH₃ synthesis reactor, as long as conditions do not become too extreme (temperatures should remain under roughly 500°C). At these conditions a protective nitride layer is rapidly formed in the early stages of exposure, and this layer grows further only very slowly (< 0.1 mm/year; see the results of McDowell in Table V-2). For more extreme conditions or when only minimum corrosion rates can be tolerated (< 0.1 mm/year), high Ni content alloys 20 ≤ Ni ≤ 80%) have to be used. These alloys are much more expensive and less workable than austenitic Cr-Ni steels.

The corrosion resistance of titanium in low pressure, high temperature NH₃ is excellent (see Table V-2). However, since Ti-alloys are not used in the NH₃ industry little has been published concerning their resistance to higher pres-
sure NH$_3$. Two patents dealing with corrosion in the manufacture of melamine at high pressures report that Ti offers excellent corrosion resistance (corrosion rates < 0.2 mm/year) in NH$_3$-CO$_2$ atmospheres at 400°C and 100 atm - as long as these atmospheres contain small (≤ 0.1 mole-%) amounts of oxygen.\textsuperscript{49,50}

Aside from alloy composition, temperature is also a critical variable. As has already been mentioned, the temperature may be divided into two ranges, temperatures up to 300°C and temperatures from 300 to 600°C. It can be seen from Table V-2 that all of the four types of alloys being discussed are corrosion resistant to temperatures of 300°C, probably because at these temperatures the dissociation rate of NH$_3$ on these alloys is negligible. (This is an important conclusion concerning the HGRP of our design (Chapter VI) because it implies that the HGR turbo-compressor may possibly be constructed from a relatively common and inexpensive compressor alloy type, such as the Cr-steels or, with more assurance, a PH Cr-Ni steel.)

As a first approximation it can be stated that for a given material under given conditions the log of the nitriding rate decreases with increasing reciprocal absolute temperature.\textsuperscript{27} In reality, however, the situation is more complex because in some cases the brittleness of the nitride layer apparently decreases with increasing temperature and thus acts to decrease the corrosion rate by preventing fissuring and cracking of the layer.\textsuperscript{39} As far as the writer knows no researcher has as yet determined an analytical relation between corrosion rate and temperature under the conditions discussed here.

This is also the case with regard to pressure and NH$_3$-concentration. While it has long been known that increasing synthesis gas pressure and NH$_3$-concentrations above the equilibrium value (at the given conditions) increase the corrosion rate,\textsuperscript{51} almost no publications exist which quantitatively study these effects, nor do the relevant publications even differentiate between total pressure and NH$_3$ partial pressure as, for example, Nelson has done with respect to H-attack.\textsuperscript{34} Cihal,\textsuperscript{44} McDowell\textsuperscript{47} and Moran et al\textsuperscript{41} present graphs (summarized in Fig. V-1) in which the corrosion increasing effect of the synthesis gas pressure is apparent. It is seen, however, that the pressure dependency presented by McDowell, relative to the work of Moran et al, is much greater than that presented by Cihal. Cihal, however, reports very much higher corrosion rates than McDowell or Moran et al. Direct comparison is, unfortunately, not possible because neither Cihal nor McDowell report NH$_3$-concentration. Since the corrosion rate of NH$_3$ increases with its increasing tendency to dissociate, it is to be expected that at a given temperature NH$_3$ will be more corrosive at low pressures than at higher pressures.
5.2.1.3. The effect of low concentrations of oxidizing gases \((O_2, H_2O, CO_2)\) on the corrosive effect of \(NH_3\).

As has already been mentioned, Cr-steels, Cr-Ni steels and Ti-alloys are materials whose corrosion resistance is based largely on the existence of a protective oxide film or layer which, once formed, is maintained by oxidizing agents; the presence of small concentrations of \(O_2\), \(H_2O\) and \(CO_2\) can therefore drastically reduce the rate at which these materials are attacked by \(NH_3\). The increased corrosion protection is caused by a number of interrelated factors. The basic factor is that the stability of the oxides of titanium\(^52\) and chromium\(^53\) as judged from their \(\Delta G_f\) values, is much greater than the stability of the respective nitrides. Because of this tendency towards oxidation, nitriding (and reaction with hydrogen\(^44,52\)) of Cr-Ni steels\(^31\) or Ti-alloys\(^52\) in the presence of appreciable concentrations of \(O_2\) is drastically reduced in rate or does not occur at all; the oxides are preferentially formed. These oxides, covering the active metal phase, are furthermore highly tenacious, impervious and protective and therefore seriously impair the catalytic activity of Fe, Cr and Ni towards the association and dissociation of \(NH_3\), \(O_2\), \(H_2O\) and \(CO_2\), for example, poison the Fe-based catalyst used for the \(NH_3\) synthesis;\(^54\) similarly, small concentrations of these oxidizing agents also greatly reduce the rate at which Fe and Cr-Ni-Fe alloys catalyze the decomposition of \(NH_3\).\(^55\)

Aside from the shielding and anti-catalytic effect of the oxide, its presence also favourably influences the mechanical properties of the eventually formed nitride layer. In the presence of low concentrations \((\sim 1\%)\) of oxygen the nitriding rate is reduced, and a mixed oxide-nitride layer is formed.\(^39,55,56\) This mixed layer is apparently less hard and brittle than a purely nitride layer, and it exhibits much less tendency to fissure and spall.\(^39,56\)

Sorokin et al\(^55\) have studied the effect of the addition of \(H_2O\) and \(H_2O-CO_2\) on the corrosion rate and mechanical properties of Cr-Ni steel, titanium, and high Ni-alloys exposed to \(NH_3\) at 1 atm and 500°C (see Table V-2). It is seen that, in particular, the corrosion rate of Cr-Ni steel is drastically reduced (by a factor 50 to 570!) by addition of these oxidizing gases; the corrosion rate of titanium is also greatly reduced and that of the Ni-based alloys either decreases or remains the same (the effect on the mechanical properties is ambiguous). Jäckel and Schwenk\(^39\) studied how the addition of small quantities of oxygen \((0.2\) mole-%) and water \((0.1\) mole-%) to \(NH_3\) at 1 atm and 500°C affected the structure of the nitride film formed. Besides finding a mixed oxide-nitride film, these researchers also found that for a Cr-17 steel the layer's thickness was reduced by a factor 3, relative to the nitride layer formed in pure \(NH_3\), and, very importantly, that the nitride-oxide layer exhibited much less ten-
dency to fissure. For a Cr-Ni steel similar, though less pronounced, effects were observed. These writers suggested that the contradictory findings in the literature concerning the effect of Cr were possibly due to the (unrecorded) presence of small quantities of oxidizing agents in the NH₃.

5.2.1.4. Secondary factors affecting corrosion (surface conditions, the occurrence of welds, stress, secondary alloying elements and structure) of metals by ammonia.

While basic alloy composition, gas composition, temperature and pressure and the occurrence of small concentrations of oxidizing gases are the basic factors affecting corrosion, a number of secondary factors are also of importance. Concerning the surface conditions it is not surprising that an oxidized surface is much more resistant to nitriding (and H-attack) than an unoxidized surface. Moran et al. observed that unoxidized metal samples suffered approximately double the nitriding rate of oxidized samples. Jäkel and Schwenk found that Cr-Ni steel samples whose oxide layer had been reduced in hot H₂ formed much thicker (2x) and much more fissured nitride layers than samples that had been oxidized in air, both samples being exposed to pure NH₃ at 1 atm and 500°C. The favourable effects of an oxidized surface are also discussed by Defranoux.

The occurrence of welds is also of importance in corrosion in a HGR compressor because the impellers are usually of a welded construction. The effects of welding are difficult to study because they are often the result of not easily reproducible factors, such as the skill of the welder and the type of weld and the formation of stress and composition variation caused by the welding action. To the author’s knowledge only Sorokin et al. and Tseitlin et al. have done any study on the effect of welding under the conditions of interest here. The results of welding on the corrosion resistance are ambiguous, and one is inclined to believe that there is no evidence that welding exercises a significant harmful effect. Unfortunately the cited authors simply present their measurements in tables and do not comment on this question.

Stress is also a factor of great importance because, firstly, a turbo-compressor operates under very great centrifugal stress, and, secondly, the nitride layer can be very brittle and thus sensitive to fissuring and spalling. The turbo-compressor is also subject to large temperature effects during start-up and shut-down, and these may also lead to extra stress between the nitride layer and base metal. As far as the author knows no study of this problem in the area of interest here has been made. Only Tseitlin et al. remark that "the stressed loop samples of the tested materials did not differ essentially from
Concerning the effect of secondary alloying elements, niobium and copper have been mentioned in the literature to exert a beneficial effect. Cihal and Defranoux report that small quantities (\(\leq 1\%\)) of Nb can be used to replace Cr to prevent H-attack in NH\(_3\) atmospheres, since Nb forms a highly stable carbide. In combination with Cr (5-12\%) and Ni (17-40\%) it also appears that these concentrations of Nb also enhance the resistance to N-attack. The reason for the beneficial effect of Cu is unknown.

Relating to the structure of the alloy it is well known that, in general, austenitic Cr-Ni steels are more corrosion resistance than the types of another structure (martensitic or ferritic). A British patent reports that high Ni Cr-Ni steels of a ferritic type exhibit very poor resistance to nitriding relative to steels of the same composition but of an austenitic structure. The greater corrosion resistance of the austenitic types may be related to their more homogeneous structure and to the fact that they are usually more easily brought into the passive state than the other structures. The difference in N-diffusion rates may also play a role. It should be further mentioned that an austenitic structure is usually associated with a relatively high Ni-content.

### 5.2.2. Corrosion in gaseous mixtures of carbon dioxide, water and air.

Due to the use of pressurized CO\(_2\) as a cooling agent in nuclear reactors a large amount of literature has appeared in the last fifteen years describing the corrosion of steels and other alloys in CO\(_2\) at 300 \(\leq T \leq 1100\)°C and 1 \(\leq P \leq 60\) atm. The literature concerning the corrosion resistance of iron and low-alloy steels will not be discussed here, as these materials are insufficiently strong and/or resistant to attack to high temperature NH\(_3\). Concerning the high alloy types, all of the four types of materials discussed in this chapter are highly resistant to CO\(_2\), H\(_2\)O, air and mixtures of these gases in the temperature range of interest. The corrosion resistance is based on the formation of a protective oxide film on the materials by these oxidizing gases.

Steels containing \(\geq 12\%\) Cr have been found to be extremely corrosion resistant (corrosion rates \(\leq 0.001\) mm/year) to CO\(_2\) to temperatures of about 600° C. These Cr-steels offer roughly the same resistance towards superheated steam at these conditions. Austenitic Cr-Ni steels are so resistant to oxidation in CO\(_2\) and CO\(_2\)-H\(_2\)O mixtures that they are commonly used in the temperature range of 600 - 1100°C (indeed, information concerning corrosion at lower temperatures hardly exists); in a CO\(_2\) atmosphere at 700° C and 40 atm, for example, corrosion rates in the order of 0.001 mm/year have been found. At these conditions the resistance to superheated steam is also excellent. High Ni Cr-Ni alloys are also very resistant to CO\(_2\), even at temperatures above
600° C, although perhaps not quite so resistant as the high Cr (Cr > 20%) austenitic stainless steels. Concerning Ti-alloys no information exists concerning their corrosion resistance in pure CO₂ at high temperatures, as these alloys are not used at these conditions. Since, however, Ti-alloys are commonly used in jet engine turbines working at 500° C it is probable that these materials are highly resistant to corrosion in CO₂-H₂O mixtures at the temperatures of interest here. All of these alloy types are also highly resistant to air: Ti-alloys to 500° C, the other alloy types to above 600° C.

The resistance towards oxidation of the alloy steels is determined primarily by the Cr-concentration; the protective Cr₂O₃ layer is formed. While this oxide layer is not as brittle as a nitride layer, the oxide is still liable to spalling during temperature cycles. The presence of Ni and, in much smaller amounts (< 1%), ytterbium and cerium, minimize oxide spalling.

In analogy with results found concerning the resistance to attack by NH₃, it has also been found that pre-oxidation in air increases the resistance of Cr-Ni steels to attack by CO₂, the resulting oxide layer being thinner and more compact. For these reasons it would seem advisable to "condition" the HGR compressor by exposing it to a high temperature air or air-steam mixture.

In general it can be concluded that for the four types of alloys mentioned oxidation in the temperature range of 200 < T < 600° C by CO₂, H₂O, air and mixtures of these gases is not likely to be a serious problem - in comparison with attack by NH₃ at these conditions. In the temperature range to 300° C it is to be expected that oxidation will be completely negligible.

5.2.3. Previous studies concerning the corrosion of metals in hot, high pressure ammonia-carbon dioxide-water gas mixtures.

The experimental studies of Sorokin et al. have already been mentioned. These researchers found that the addition of CO₂ and, especially, H₂O, greatly increased the corrosion resistance of Cr-Ni alloys to attack by NH₃ (see Table V-2). Kucheryavyi et al. has also studied the corrosion-erosion resistance of a few Ni-based and Cr-Ni steels (see Table V-2). The purpose of this study was to choose a suitable material for a HGR turbo-compressor. To achieve this end these researchers caused a jet of NH₃-H₂O, CO₂-H₂O or NH₃-CO₂-H₂O to impinge at 300 m/s on stationary metal samples at 300 and 500° C; this high velocity was achieved by allowing the gases to expand from 10 to 1 atm. The experiments lasted only 50 to 250 hours. At 300° C all of the tested materials were corrosion resistant (corrosion rates of 0.0 to 0.2 mm/year); at 500° C the corrosion rate increased to about 0.7 mm/year for the Ni-based alloys and 1.1 to 1.5 mm/year for the Cr-Ni steels. Due to the briefness of this report (nine sentences
plus one small table) no critical analysis can be made. Their general conclusion, however, that the corrosion rate in the gas phase at 300°C is low is in agreement with the previous discussion and with the author's findings. That these authors also found that corrosion increased considerably at 500°C and that the high Ni-alloys were more resistant at these temperatures is also in agreement with the previously discussed literature.

5.3. Experimental.

5.3.1. Goal and types of experiments.

The ideal experimental procedure would be one in which the to be tested materials were subjected to the actual conditions existing in a turbo-compressor, namely very high stress, a highly dynamic gas-metal interface, high temperatures (T < 300°C; eventually T < 550°C), high pressures (20 < P < 150 atm) and, eventually, the occurrence of entrainment (liquid dispersion in the gas phase); these conditions would all exist simultaneously. After the experiments the metallic specimens would be subjected to extensive metallurgical investigations, such as weighing, physical property tests (hardness, strength, ductility, etc.), microscopic and X-ray micro-probe examination, etc. Such an experimental study, which more or less implies the construction and operation of a turbo-compressor, was beyond the technical and financial means of our Laboratory; such an extensive metallurgical investigation was beyond the proficiency of the writer. For these reasons a preliminary study was set up whose goal was, firstly, to decide whether or not the HGRP was technically impossible due to the corrosiveness of the hot gas phase, as had often been stated, and secondly, to select the least expensive types of alloys which might be suitable for use in a HGR compressor.

Since the totality of the corrosive conditions existing under turbo-compressor conditions could not be achieved in a single experimental apparatus, it was decided to "analyze" these conditions into a number of separate, more easily realizable experimental conditions and subsequently to "synthesize" the results of these experiments to an entity which would be "representative" of the conditions in a compressor. These separate experimental conditions to which the alloy samples were exposed were:

Type 1. P = 1 atm, T = 300°C; slowly flowing mixture of NH₃-CO₂-H₂O.

Type 2. P = 100 and 200 atm, T = 250°C; static mixture of NH₃-H₂O, NH₃-CO₂-H₂O in autoclave.

Type 3. P = 1 atm, T = 300 to 350°C. A disc (diameter = 30 cm, thickness = 1 cm) of the material to be tested rotating at 15000 to 18000 rpm in a flowing NH₃-CO₂ gas stream.
Type 4. P = 100 atm, T = 250°C. Slowly flowing NH₃–CO₂ mixture.

Type 5. P = 1 atm, T = 250°C. Samples exposed to a gas phase containing droplets of a urea solution (entrainment experiments).

The experimental conditions are discussed in detail below.

Type 1. The metallic samples, about 20 x 50 x 2 mm, were placed in separate glass containers (to prevent mutual contact); the samples were sometimes mechanically polished. The loaded glass containers were placed in an AISI-316 apparatus which was placed in a thermostat operating at 300°C ± 5°C. The gaseous mixture of NH₃, CO₂, NH₃–CO₂ or NH₃–CO₂–H₂O flowed over the samples at about 8 mm/s. Experiments were carried out continuously for periods of about one month and usually repeated three times.

Type 2. Similar samples, placed individually in glass containers, were placed in an AISI-316 autoclave, which itself was contained in a thermostat. The gases were pumped into the hot autoclave (first the major component was pumped in, then water, then, a day or so later, the last component; such a procedure prevented local condensation of water). The hot autoclave was, before use, checked with helium for leakage. The temperature and pressure of the autoclave remained constant to within about 5°C and 5 to 10 atm within the experimental duration, which was about one month. The pressure and temperature were measured by means of a membrane manometer (Foxboro "pressure seal") and thermometer, respectively.

Type 3. These experiments were carried out in a so-called "turbo-disc" apparatus, a schematic drawing of which appear in Fig. V-2. A most important aspect of this apparatus is that the discs, fabricated of the to be tested material, could be interchanged. This interchangeability was accomplished by mounting each disc on its own (conical) hub. The hub and the disc, plus locking ring and nut, formed an entity which was balanced on a balancing machine. The balanced disc plus hub was then connected to the shaft by means of a double-threaded nut. The plain bearings of the machine were of the oil-film type; in addition to lubrication the oil flow also cooled the bearings and shaft. The oil was prevented from reaching the gaseous mixture by means of the seal gas CO₂ and a spiral-grove seal, which pumped the oil away from the disc area by means of rotation of the shaft relative to the threaded ring. The machine was driven by a 3.7 KW electric motor of the impulse type, power being transmitted to the shaft by toothed pulley-belts. The disc was rotated at 15000 to 18000 rpm (maximum tip-speed = 314 m/s) continuously for periods of one month; each disc was rotated for three months. The temperature was 300 to 350°C; the machine developed so much heat due to the turbulence of the flow (caused by the
Type 4. It was attempted to carry out experiments in which the samples were exposed to a slowly flowing (~ 1 cm/s), high temperature, high pressure \( \text{NH}_3-\text{CO}_2 \) gas stream. These experiments were carried out in the reactor of our HGRP pilot-plant (see Chapter VI). It was not possible to run this pilot-plant automatically, and insufficient personnel was available for continuous manual operation. For these reasons experimental difficulties often arose in the form of local cooling of the gas lines, which led to local condensation and clogging of the lines. These were opened by pumping water through them, a procedure which brought water into the reactor and thus facilitated condensation in the reactor itself. The results are therefore not representative of gas phase corrosion and are included only to qualitatively indicate the devastating effect of corrosion caused by the liquid phase at high temperatures and pressure.

Type 5. In these experiments a \( \text{CO}_2 \) gas stream was blown through a saturated urea-water solution in order to obtain a gas stream containing entrained urea solution; this gas stream containing urea-water droplets was subsequently mixed with an \( \text{NH}_3 \) gas stream and led over the alloy samples contained at 250°C. Here again, unfortunately, experimental difficulties prevailed: at the entrance of the apparatus containing the samples the high temperature caused the urea solution to evaporate and react to solid products, such as biuret and triazines, clogging the entrance. The "corrosion results," which were quite favourable, are therefore not reported as they are not representative of the entrainment which would exist under high pressure conditions, at which the urea solution droplets would be much more stable. Attempts at performing these experiments are mentioned only to indicate the difficulty of achieving them under laboratory conditions.
5.3.2. The materials used.

The CO and NH\textsubscript{3} used were of technical purity and were supplied by the companies Aga, Amsterdam and Hoekloos, Amsterdam, respectively. According to Aga the specifications of the CO\textsubscript{2} were: CO \geq 99.94\%, H\textsubscript{2}O \leq 0.006 - 0.06\%, O\textsubscript{2} \leq 10 ppm, S (in all forms) \leq 1 ppm, oil \leq 1 ppm, hydrocarbons (as CH\textsubscript{n}) \leq 1 ppm, NO \times \leq 2 ppm. Hoekloos gave much more vague specifications, namely NH\textsubscript{3} \geq 99.9\%, H\textsubscript{2}O \leq 0.1\%, oil \leq 5 ppm, O\textsubscript{2} \leq 5 ppm. Our experience was that the gases varied from batch to batch in quality. According to analysis work done at our Laboratory the CO\textsubscript{2} contained as much as 0.2\% N\textsubscript{2} and 0.08\% O\textsubscript{2}; the NH\textsubscript{3} contained up to 1.2\% H\textsubscript{2}O and 0.03\% O\textsubscript{2}. The gases were not purified.

In some cases the metal samples were mechanically polished to 5 ru before use; in most cases, however, the samples were used as received from the suppliers. The samples were washed in mild soap solution, rinsed with distilled water and alcohol and dried with acetone and oil-free air before and after each experiment. Direct finger contact was avoided.

5.3.3. Experimental results.

In the following section the experimental results will be reported in terms of the tests carried out to estimate the degree of corrosion. These tests included weighing, micro-hardness determination and microscopic and X-ray microprobe examination.

5.3.3.1. The results of the weighings of the exposed samples.

The results of Type 1 experiments (1 atm, 300\textdegree C) will be discussed first. These experiments were carried out at various NH\textsubscript{3}-CO\textsubscript{2} ratios and with and without H\textsubscript{2}O (5 mole-%). The results are presented in Table V-3.

The first impression given by this Table is that the corrosion caused by the gaseous phase at these conditions, as judged from the weight increases of the samples, is negligible, namely microns per year. (In general other corrosion tests gave corrosion rates roughly an order of magnitude greater. See the following sections.) A number of other points are also obvious from the Table. As can be seen by comparing the first two columns, the weight gains caused by contact with NH\textsubscript{3} were much greater - a factor 10 to 100 - then those caused by contact with CO\textsubscript{2}; this is particularly clear for the Cr-steels. From the other columns it is seen that, in general, the corrosion rate increases with the NH\textsubscript{3} concentration; this behaviour is illustrated for a number of alloys in Fig. V-3. It also appears that the presence of water decreases the corrosion rate, as can be seen by observing the columns at NH\textsubscript{3}/CO\textsubscript{2} = 1 with and without 5\% H\textsubscript{2}O. It is further seen that the corrosion rate of the various alloys corresponds
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<th>CO₂ 2</th>
<th>NH₃ 1</th>
<th>NH₃ 2</th>
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<th>NH₃:CO₂ = 1:2 2</th>
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<td>7.5</td>
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<td>( -0.45)( -0.04)</td>
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<td>( -0.45)( 2.6)</td>
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</table>

*Note: The numbers in the Table refer to the area weight gain in mg. 10²/cm². The numbers between parenthesis refer to the calculated (based on the density of the alloy itself) corrosion rate in microns per year.*

**Gas composition, mole-% or ratio.**

<table>
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<tr>
<th>Exposure time, months</th>
<th>Material</th>
<th>CO₂</th>
<th>NH₃</th>
<th>NH₃:CO₂ = 1:2</th>
<th>NH₃:CO₂ = 1:1, 5% H₂O</th>
<th>NH₃:CO₂ = 3:1</th>
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<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
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</table>

**Gas composition, mole-% or ratio.**

- NH₃:CO₂ = 1:2
- NH₃:CO₂ = 1:1, 5% H₂O
- NH₃:CO₂ = 3:1
Fig. V-3. The influence of the molar concentration of \( \text{NH}_3 \) in an \( \text{NH}_3-\text{CO}_2 \) gas mixture at 1 atm and 300 °C on the corrosion rate of various alloys. The symbols X, □, ○, and △ refer to Ti-318, ARZ, PH 14-8 Mo and unalloyed steel, respectively.

roughly with the classes into which these alloys fall: unalloyed steel suffers the largest weight gain followed by the Cr-steels, then the Cr-Ni steels and, at a very much lower level (usually within or near the weighing error) the Ti-alloys. (It was also found that the difference in weight increases between polished and unpolished samples was usually within or near the weighing error (± 0.2 mg).)

In general the alloys formed a protective layer with continuing exposure, as can be seen from Table V-3 and Fig. V-4; in the latter an experiment of long duration and varying \( \text{NH}_3/\text{CO}_2 \) ratio is given. It is seen that the corrosion rate is roughly parabolic. The superiority of the Ti-alloys is also apparent.

The experimental results at high pressures (Type 2 experiments) may be divided into three classes: the experiments at 100 atm and ≥ 0% \( \text{H}_2 \text{O} \) (no formation

Fig. V-4. The effect of time on the corrosion rate of alloys in an \( \text{NH}_3-\text{CO}_2 \) atmosphere at \( T = 300^\circ \text{C} \) and \( P = 1 \text{ atm} \). Area 1: \( \text{NH}_3/\text{CO}_2 = 1 \). Area 2: \( \text{NH}_3/\text{CO}_2 = 4 \). Area 3: Pure \( \text{CO}_2 \). The symbols X, △, ○, ▽, □, and ● refer to Ti-317, Ti-318, ARZ, PH 17-4, PH 14-8 Mo and unalloyed steel, respectively.
of solid matter), experiments at 200 atm (formation of solid matter) and experiments at 100 atm with \( \leq 4\% \) \( H_2O \) (formation of solid matter). The experimental values of all of the high pressure experiments are presented in Table V-4.

The results at 100 atm (experiments 2-HP-1 through 2-HP-3) are particularly clear: the corrosion rate, as judged from the weight gain, is negligible, being in the order of \( \leq 0.1 \) micron/year. The weight increase (which was often small as to be near or within the experimental error) is even lower than in the Type 1 experiments, probably because the lower (by 50°C) temperature and much higher pressure reduced the dissociation rate of the \( NH_3 \). The difference between the polished and unpolished samples was also negligible, as was the variation in behaviour caused by the different \( NH_3/CO_2 \) ratios.

The experiments at higher pressures (200 atm) resulted in a most curious phenomenon, namely the formation of a solid phase. In discussing these experiments it is important to attempt to separate the corrosion effects into those caused by contact with the high pressure gas phase and those caused by contact with the solid phase.

Concerning the former it is seen from experiment 2-HP-4 that corrosion caused by the high pressure gas, in the cases in which little or no solid phase was formed, was roughly as insignificant as that caused by the gas at the lower (100 atm) pressure. The Cr-Ni steels, Ti-alloys and monel exhibited negligible corrosion rates. The situation was entirely different, however, in the cases in which significant formation of the solid phase occurred (e.g., experiment HP-5). Here appreciable weight gains were found (serious corrosion was also found, as is discussed in later sections of this Chapter).

Concerning the formation and nature of the solid phase only some general, vague remarks can be made. The temperature of the gas mixture was well above its physical dew-point temperature so that no physical condensation could have occurred. The pressure was also very probably under that of the chemical dew-point conditions (the dew-point pressures are very difficult to estimate at these high temperatures) so that formation via chemical condensation of the liquid phase is also doubtful. From experiment 2-HP-5 it is also seen that the formation of the solid phase occurred preferentially on the unalloyed steel and, to a considerably lesser extent, on the Cr-steels; very little solid formation occurred on the Cr-Ni steels and Ti-alloys. For this reason it is also not probable that chemical condensation occurred. A more probable explanation of the occurrence of the solid phase may be that its formation took place via reactions catalyzed by iron.71

Concerning the appearance of the solid material formed on the unalloyed steel and Cr-steels the following can be said. Directly on the metallic surface
<table>
<thead>
<tr>
<th>Experiment No.</th>
<th>Conditions and remarks</th>
<th>Material</th>
<th>Weight increase, mg.</th>
<th>&quot;Corrosion rate,&quot; micron/year</th>
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</thead>
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<tr>
<td>2-HP-1</td>
<td>T = 250°C, P = 100 atm, NH₃/CO₂ = 2, duration = 31 days.</td>
<td>Steel-37, PH-17-4, PH-17-7, AISI-316, PH-14-8-Mo, Ti-317, Ti-318</td>
<td>0.5, 0.2, 0.1, 0.5, 0.3, 0.2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>2-HP-2</td>
<td>T = 250°C, P = 100 atm, NH₃/CO₂ = 2, duration = 37 days.</td>
<td>Steel-37, Steel-37², ARZ, ARZ², PH-17-4, PH-14-8-Mo, Ti-317, Ti-318</td>
<td>-0.2, 0.2, -0.1, 0.5, 0.5, -0.1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>2-HP-3</td>
<td>T = 250°C, P = 100 atm, duration = 34 days.</td>
<td>Steel-37, ARZ, ARW-B, Re-1520, PH-17-4, PH-14-8-Mo, Ti-317, Ti-318</td>
<td>0.8, -0.4, -0.2, -1.2, 2.7, -0.3, -0.2, 0.2</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>2-HP-4</td>
<td>T = 250°C, P = 200 atm, NH₃/CO₂ = 2, duration = 29 days.</td>
<td>Steel-37, Steel-37², ARZ, ARZ², PH-17-4, PH-14-8-Mo, Ti-317, Ti-318, Monel</td>
<td>&quot;A&quot;, &quot;A&quot;, &quot;A&quot;, &quot;B&quot;, 0.6, 0.2, 0.5, 0.1</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>2-HP-5</td>
<td>T = 250°C, P = 200 atm, NH₃/CO₂ = 2, duration = 40 days.</td>
<td>Steel-37, ARZ, ARD, ARL, ARW-B, AISI-316, PH-14-8-Mo, Ti-317</td>
<td>550.7, 66.9, 77.8, 65.4, 47.5, 3.5, 3.0, 2.3</td>
<td>314, 38, 44, 37, 27, 2, 1.7, 2.3</td>
</tr>
<tr>
<td>2-HP-6</td>
<td>T = 250°C, P = 200 atm, NH₃/CO₂ = 1/5, duration = 36 days.</td>
<td>Steel-37, Steel-37², Re-1520, PH-17-7, AISI-316, Ti-318</td>
<td>3.4, 3.6, 4.0, 1.4, 0.6, -0.8</td>
<td>2.1, 2.3, 2.5, 0.9, 0.4, 0.9</td>
</tr>
</tbody>
</table>
Experiment No. | Conditions and remarks | Material       | Weight increase, mg | "Corrosion rate," micron/year
--- | --- | --- | --- | ---
2-HP-7 | T = 2500°C, P = 100 atm, NH₃/CO₂ = ½, 4% H₂O, duration = 35 days. | Steel-37 | 4.8 | 3.1 |
 | | ARZ | 5.1 | 2.1 |
 | | ARW-B | 2.9 | 1.9 |
 | | Re-1520 | 2.8 | 1.8 |
 | | Re-1520 | 2.8 | 1.8 |
 | | PH-17-6 | 0.2 | 0.1 |
 | | PH-14-8-Mo | 1.6 | 1.0 |
 | | Ti-317 | 0.3 | 0.3 |
 | | Al | 11.6 | 22.4 |

x = polished to 5 ru. "A" = heavily covered with amorphous/crystalline solid phase; "B" = lightly covered with crystals; "C" = large crystals found locally. Steel-37 is unalloyed steel.

transluscet white or coloured crystals were found, and above these crystals a white porous mass, often ± 1 mm thick, of a flaky, apparently amorphous material was formed. A quantitative analysis of the N : C atomic ratio yielded 1.056; analysis for triazines \(^{71}\) yielded a few tenths of a percent ammeline and melamine. For the remainder the composition of the deposited material is unknown. In the author's opinion it is highly doubtful that formation of solids will occur in practice, in which highly dynamic conditions exist. For this reason no further analytical study was made of the solid materials.

At the same temperature and pressure conditions as 2-HP-4 and 5, but at a lower NH₃/CO₂ ratio (experiment 2-HP-6) much less crystals were formed. There was again a preferential formation of crystals on unalloyed steel. An experiment at 100 atm and 4% H₂O (experiment 2-HP-7) also resulted in a small amount of crystals being formed, again preferentially on the unalloyed and Cr-steels.

The results of the experiments with the turbo-discs (Type 3 experiments) are condensed into Table V-5. From this Table it is seen that small, irregular weight variations corresponding to low corrosion rates were found. (The discs were weighed on a Sauter KG 7470 balance with an accuracy of ± 0.1 g (at a max. capacity of 10000 g)). These experiments suggest that the highly stressed conditions of the discs did not result in extra corrosion.

The results of Type 4 experiments are presented in Table V-6. As already mentioned, these experiments were plagued with technical difficulties, and it is certain that the samples came into contact with condensing/condensed liquid phase. The very high calculated corrosion rates are evident, particularly for the unalloyed steel, which had partly corroded away. The differences between the "upper" and "lower" sections of the autoclave are probably caused by the fact that the condensing liquid phase tended to drip down to the autoclave bot-
Table V-5. Results (weighings) of Type 3 (turbo-disc) experiments.

<table>
<thead>
<tr>
<th>Experiment's duration, months</th>
<th>Temperature, °C</th>
<th>Weight increase, g</th>
<th>&quot;Corrosion rate,&quot; micron/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material: FV 520S. Original weight = 4685.3 g. Rotational speed = 15000 rpm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>320 - 350</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>2</td>
<td>340 - 360</td>
<td>1.2</td>
<td>12.9</td>
</tr>
<tr>
<td>3</td>
<td>295 - 310</td>
<td>-0.4</td>
<td>-4.3</td>
</tr>
<tr>
<td>Material: FV 520B. Original weight = 2473.2 g. Rotat. sp. = 14000-14500 rpm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>300 - 320</td>
<td>0.7</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>300 - 310</td>
<td>0.1</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>335 - 360</td>
<td>0.6</td>
<td>6.5</td>
</tr>
<tr>
<td>Material: Armco PH 17-4. Original weight = 5036.7 g. Rotat. sp. = 18000 rpm.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>290 - 310</td>
<td>0.4</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>290 - 310</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>3</td>
<td>290 - 310</td>
<td>0.3^X</td>
<td>3.2</td>
</tr>
</tbody>
</table>

^XAfter two months exposure the surface of this disc was removed by turning (for balancing purposes). This value therefore represented exposure of a fresh surface.

In the presence of liquid phase, electrochemical corrosion occurred, unalloyed steel functioning as the anode. These results have been included only to impress upon the reader the devastating effect of condensing liquid phase, even to Cr-Ni steels and Ti-alloys.81

5.3.3.2. Results of microscopic examination.

The surfaces of all of the samples were viewed with a microscope. Except for the cases in which crystals formed, no exceptional results were observed in any of the samples. Only a preferential tarnishing of the polishing grooves of the samples was noted. For a number of samples sections were prepared by Mr. L. van der Meer of the Department of Metallurgy. (These samples had been exposed to the high pressure conditions (type 2) of experiments 2-HP-1 and 2-HP-5 and to low pressure experimental (type 1) conditions designated by 1-LP-1 (NH3/CO2 = 1/2, duration = 62 days), 1-LP-2 (NH3/CO2 = 1, 111 days; NH3/CO2 = 1/2, 62 days; pure CO2, 70 days) and 1-LP-3 (pure NH3, 90 days); in all of the 1-LP-experiments pressure and temperature were 1 atm and 300°C, respectively. Samples of the alloys exposed to Type 3 (turbo-disc) conditions were also studied.) The
### Table V-6. Results (weighings) of Type 4 (condensation at high pressure) experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Upper section autoclave</th>
<th>Lower section autoclave</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight loss, mg</td>
<td>&quot;Corrosion rate,&quot; micron/year</td>
</tr>
<tr>
<td>PH 17-7</td>
<td>2</td>
<td>1.1</td>
</tr>
<tr>
<td>PH 14-8 Mo</td>
<td>3.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Re-2604-MoS</td>
<td>4.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Ti-317</td>
<td>4.9</td>
<td>4.7</td>
</tr>
<tr>
<td>AISI-316</td>
<td>4.6</td>
<td>2.4</td>
</tr>
<tr>
<td>PH 17-4</td>
<td>3.8</td>
<td>2.0</td>
</tr>
<tr>
<td>Ti-318</td>
<td>204</td>
<td>192</td>
</tr>
<tr>
<td>Steel 37</td>
<td>-1701</td>
<td>-902</td>
</tr>
<tr>
<td>Re 1520</td>
<td>297</td>
<td>158</td>
</tr>
<tr>
<td>PH 15-7</td>
<td>331</td>
<td>176</td>
</tr>
<tr>
<td>ARW B</td>
<td>338</td>
<td>180</td>
</tr>
<tr>
<td>AISI-316</td>
<td>198</td>
<td>105</td>
</tr>
</tbody>
</table>

Conditions: $T = 250 \, ^\circ C; P = 100 \, \text{atm}; \text{NH}_3/\text{CO}_2 = 1.5$; no water and no $O_2$ injections; duration of experiment = 43 days. The experimental samples were no cleaned, as they were covered with a tenacious layer of condensation/corrosion products.

Samples were embedded in reinforced Bakelite and polished with carborundum of increasing fineness and finished with diamond powder (3, 1 and 1/2 micron). The etching agents used were Nital for unalloyed steel, Krolls solution for the Ti-alloys and Kallings solution for the rest of the alloys studied.

In Figures V-5 to V-8 the results of Type 2 experiments are seen for 2-HP-1 conditions. In Fig. V-5 unalloyed steel is shown. A poorly adherent corrosion layer, approximately 30 microns thick, is evident. (This observed depth of corrosion is far deeper than that calculated from the weight increases, a fact which illustrates the importance of examination of sections.) The corrosion layer is probably of an oxide-nitride composition. Careful observation of Fig. V-5 reveals that just under the clearly delineated corrosion layer a second, much lighter and somewhat less thick (+15-20 microns) layer is apparent, characterized by a light gray, "dotted" structure; this area may illustrate a reaction zone preceding the much more serious attack seen at the sample's surface.

A Cr-13 steel, ARZ, is shown in Fig. V-6. It appears that this steel is largely
Fig. V-13. PH 14-8 Mo. 800X.

Fig. V-14. Ti-318. 1000X.

Fig. V-15. Remanit 1620. 320 X.

Fig. V-16. PH 17-4. 320 X.

Fig. V-17. FV 520B. 320 X.

Fig. V-18. FV 520S. 320 X.

Fig. V-24. Unalloyed steel, 880 X, HP-1 conditions. 1: 210. 2: 190. 3: 660.

Fig. V-25. Unalloyed steel, 880 X, HP-5 conditions. 1: 180. 2: 470-770. 3: 1370.
Fig. V-26. Cr-13 steel ARZ, 880 X. 2-HP-5 conditions. 1: 210. 2: 190. 3: 660.

Fig. V-28. FV 520B, 880 X. Type 3 (turbo) conditions. 1: 470. 2: 1050-1200. 3: 1130-1150.

Fig. V-29. FV 520S, 880 X. Type 3 (turbo) conditions. 1: 350. 2: 410-720.

Fig. V-30. Unalloyed steel, 2-HP-5 conditions, 250 X. Example of X-ray micro-analysis scan.

Figures V-24 to V-29 are photographs of Micro-Vickers hardness determinations of some previously presented samples. Compare, respectively, Figures V-5, V-9 and 10, V-11, V-13, V-17 and V-18. The first numbers (1 to 3) refer to the zone indicated in the figure; the second number refers to the corresponding measured Micro-Vickers hardness. (The smaller the diamond-shaped indentation, the greater the value of the measured hardness.)
resistant to attack, as only isolated patches of corrosion, not more than 3-4 microns thick, are seen. Similar favourable results were found for the PH 17-4 and PH 17-7 steels, although, in general, these steels exhibited increasing corrosion resistance with increasing Ni-content. With a Ni-content of 8%, PH 14-8-Mo exhibited complete corrosion resistance (Fig. V-7). Ti-317 (Fig. V-8) and Ti-318 also exhibited perfect resistance to attack.

The results of experiments performed under high pressure conditions at which formation of solid phase occurred, however, gave a rather different picture, as photos of samples exposed to 2-HP-5 conditions illustrate. Unalloyed steel (Figures V-9 and 10) was very seriously attacked to a depth of about 300 microns by the condensation product. The corrosion consisted partly of a gross attack (the black areas in the figures). The gray zones surrounding the black areas may be braunite, a eutectoid of iron and iron nitride. The dark "needles" originating at the edges of the gray zones are almost certainly iron nitride needles. Cr-13 steel ARZ is also heavily attacked (Fig. V-11) by the solid phase. Careful examination of Fig. V-11 reveals that under the dark areas of gross corrosion, roughly 10, locally as much as 40 microns thick (under the precipitate the corrosion was the deepest), a second, much lighter zone is apparent, which follows the contours of the dark corrosion area. This lighter zone, roughly 15 microns thick, blends gradually into the normal interior of the metal. The lightness of this zone, even relative to the base metal, is probably due to the absence of chromium carbide particles, which appear as dark coloured "dots" in the normal matrix of this alloy. Similar results were also found with the other Cr-steels. The steels with a high Ni-content, however, such as PH 14-8-Mo, exhibited excellent corrosion resistance, as Fig. V-12 illustrates. (As already mentioned, condensation occurred preferentially on steel and Cr-steel, and little or no deposit was found on the Cr-Ni and Ti-alloys.) It was nevertheless observed that a thin layer, 2-4 microns thick, was formed on this material's surface, as a photograph at high magnification reveals (Fig. V-13). Close examination of this layer which closely follows the surface, reveals that it actually consists of two layers. Furthermore, it is sharply defined (ends abruptly), as if it functions as an impenetrable barrier to further attack. Ti-alloys were also completely resistant to attack; even at high magnification no traces of corrosion can be seen (Fig. V-14).

Examination of sections of samples exposed to Type 1 conditions also revealed signs of attack. With regard to experiments 1-LP-1 it was found that unalloyed steel was the most seriously attacked metal and exhibited braunite areas and nitride needles; attack was deep, namely to 100-150 microns. As usual, the corrosion resistance increased with increasing Ni-concentration. The PH
Cr-Ni steels were visibly attacked to a depth of only 5 to 15 microns. Not surprisingly, PH 14-8-Mo exhibited exceptional resistance, visible attack being less than 2 microns. For experiment 1-LP-2 somewhat greater attack was found. Unalloyed steel was attacked heavily to about 12 microns, and nitride needles were found as deep as 150 microns. The Cr-steels were also more severely attacked, visible attack occurring to about 50 microns. Again, with increasing Ni-content the visible corrosion attack decreased: PH 17-4 and PH 14-8-Mo exhibited a visible corrosion depth of, respectively, about 25 and 10 microns. The Ti-alloys exhibited no trace whatsoever of corrosion. For the 1-LP-3 experiment, in which the samples were exposed to pure NH₃, roughly similar behaviour was found. Unalloyed steel exhibited visible attack to about 35 microns; nitride needles were also observed under the corrosion zone. The Cr-steels, however, were surprisingly good, exhibiting visible attack to only 8 to 10 microns. PH 17-4 was attacked to about 25 microns, PH 14-8-Mo only to about 8-12 microns. The Ti-alloys were completely free of visible corrosion.

Concerning the turbo-disc (Type 3) experiments, examination of the discs' surfaces revealed only a heavy tarnishing, particularly towards the edge of the disc, at which the rotational speed is the greatest. Sections of the turbo-discs are presented in Figures V-15 to V-18. Surprisingly, the Cr-steel Remanit 1620 exhibited no attack. The PH 17-4 steel also exhibited practically no attack, but this may be due to the fact that the surface of this disc was removed by turning after two months exposure (for reasons of balancing), and the section shown is that exposed to only 30 days instead of the usual 90. The Firth Vickers PH Cr-Ni steel FV 520B exhibited attack to a depth of about 30 microns, which manifests itself as an occasional dark area at the surface under which a lighter layer is evident (possibly due to the absence of chromium carbides). The FV 520 S seems to have undergone less serious attack, only a light surface layer, about 15 microns thick, being found in this material.

5.3.3.3. Results of the hardness tests.

Since metallic nitrides are, in general, very hard and brittle, their presence at a metallic surface can be inferred from micro-hardness tests, in which the hardness can be measured in a very small (\(< 4 \text{ microns}^2\)) area. By plotting the hardness as a function of distance from the sample's surface, an idea of the degree of penetration of the nitriding attack can be found. In the experiments discussed, a micro-hardness apparatus of the type Leitz Duriment was used, usually with a 15 gram load; the values presented in the graphs represent the average of 3 to 5 measurements.

In Fig. V-19 a and b the results of experiment 2-HP-1 are shown. It is
Micro-Vickers hardness as a function of the distance from the surface for a number of alloys exposed to 2-HP-1 conditions (see Table 4). In Figures V-19 to V-22 the symbols □, X, △, *, ●, ■, △, ▽, ▽, +, ◊, and ○ refer to the alloys ARZ, Ti-317, PH 14-8 Mo, Ti-318, PH 17-4, PH 17-7, monel, ARW, AISI-316, ARL, PH 17-5 Mo and unalloyed steel, respectively.

Micro-Vickers hardness as a function of the distance from the surface for a number of alloys exposed to 2-HP-5 conditions (see Table V-4).
Micro-Vickers hardness as a function of the distance from the surface for a number of alloys exposed to 1-LP-1 conditions.

Micro-Vickers hardness as a function of the distance from the surface for a number of alloys exposed to 1-LP-3 (pure NH₃) conditions.
seen that, aside from unalloyed steel, no significant hardening has occurred. Apparently, at these high pressures NH₃ has little tendency to dissociate. The gas phase itself is not corrosive to the alloyed steels. These results are in agreement with the weighing results and microscopic examinations. For samples exposed to the conditions of experiment 2-HP-5, however, Figures V-20 a and b show that significant hardening occurred in the unalloyed and, particularly, in the Cr-steels. ARL, with a relatively high Cr-content (16.5%) exhibits the greatest hardness and depth of hardening. The depth of hardness increase is about 50 microns for the ARL and 20 to 30 microns for the other Cr-steels and the unalloyed steel. The beneficial effect of Ni is exhibited in the results of PH 14-8-Mo; both the depth (+ 10 microns) and the degree of hardening are significantly less than in the other steel alloys. In agreement with the microscopic examination, the Ti-alloys show no increase in hardness at all.

For the low pressure (Type I) experiments roughly similar results were found, although the intensity of the attack was greater, both with regard to depth of attack and, particularly, hardness, probably because of the increased tendency of NH₃ to dissociate at these conditions of higher temperature and much lower pressure. In Figure V-21 a and b the results of exposure of samples to the conditions of experiment 1-LP-2 are shown. High Cr-percentages correspond with great hardness increase over a depth of more than 100 microns; the low Ni PH 17-4 exhibits a greater hardness but a considerably shallower (< 50 microns) penetration depth. Unalloyed steel shows no sharp hardness increase, but rather a deep penetration (> 100 microns) into the metal itself. The favourable effects of Ni are apparent in the relatively low hardness increase and penetration depth (< 20 microns) in PH 14-8-Mo. As usual, Ti-alloys exhibit no hardening at all. Similar behaviour is shown in Fig. V-22 a and b for samples exposed to pure NH₃ for 90 days.

Fig. V-23 illustrates the hardness measurements of the turbo-discs (Type 3 experiments). All of the metals tested showed a considerable hardness increase. The striking difference in behaviour between the PH Cr-Ni 520B and 520S is apparent. The lower hardness and depth of attack of the latter may be related to its semi-austenitic structure (FV 520B has a martensitic structure). The behaviour illustrated by PH 17-4 is too favourable, relative to the other alloys, as the values for 17-4 refer to only a 30 day exposure.

In order to obtain a better impression of the relation between the hardness and the structure of the corroded areas, a number of photographs of sections were prepared after hardness tests had been carried out; the results are presented in Figures V-24 to V-29. These photographs, all taken at 160 X magnification, were photographically enlarged by a factor 5.5. (NOTE: All of the
Fig. V-23. Micro-Vickers hardness as a function of the distance from the surface for alloys exposed to Type 3 (turbo) experiments. The symbols O, □, △, and ● refer to, respectively, the alloys Remanit 1620, FV-620B, FV-520S and Armco 17-4 PH.

photographs presented in this work have been reduced 25% in size by the reproduction process involved in printing this dissertation; hence, a photograph at, for example, 100 X magnification, appears as 75 X in the presented figure.)

5.3.3.4. Results of the X-ray micro-analysis examinations.

In order to obtain a better insight into the nature of the corrosion products studies using X-ray micro-analysis were performed on sections. In this preliminary study qualitative determinations were carried out for nitrogen and oxygen. Samples of unalloyed steel, Cr-13 steel ARZ, and the PH steels PH 17-4 and 18-8-Mo were studied; these samples had been exposed to the conditions of Type 1 and 2 experiments. The surface of the section were given an electrolytically applied Ni coating to prevent dispersion of the electron beam in the region of the sample's edge. The X-ray micro-probe measurements were carried out by Ir. D. Schalkoord and Mr. E.J.A. van Dam of the Department of Metallurgy.

Fig. V-31. Qualitative determination by means of X-ray micro-analysis of nitrogen and oxygen as a function of distance from the surface for PH 17-4 exposed to 1-LP-2 conditions.
using two X-ray micro-analyzers, one of the Applied Research Laboratory (ARL), model EMX, the other of the Japanese Electro-Optical Laboratory (JEOL), model JXA-50A. A photograph of a "scanned" sample is shown in Fig. V-30.

Concerning unalloyed steel in the high pressure experiment 2-HP-5 it was found that the dark corrosion areas (see Figures V-9 and 10) were rich in both oxygen and nitrogen, suggesting that this corrosion zone may be of a nitride-oxide composition. The gray areas adjacent to the heavily corroded dark areas contained significant amounts of nitrogen but no oxygen, suggesting that these areas contained braunite. The "needles" were also scanned and showed sharp peaks for nitrogen, so that it is more or less certain that they are iron nitride needles, as their characteristic shape suggests. In a scan from deep in the material to the surface it was found that the oxygen concentration line exhibited a sharp increase very near and at the surface, while that of nitrogen showed a much more gradual increase from the interior of the material (> 50 microns) to the surface. These results can be interpreted in the light that an oxide zone forms on the surface while nitride formation occurs via nitrogen atoms which have diffused deep into the interior of the metal.

Roughly similar results were obtained for the other materials. For illustration two experimental results (micro-analysis graphs) are presented. For PH 17-4 exposed to 1-LP-2 conditions Fig. 31 shows the sharp oxygen peak at the surface and the "peakless," gradually rising nitrogen line. For PH 14-8-Mo exposed to LP-3 conditions rather more favourable behaviour is apparent. It is seen from Fig. V-32 that the nitrogen concentration line exhibits a peak form of roughly 15 microns thickness; it appears that this Ni-containing steel forms a protective nitride barrier which protects the interior of the metal from attack.

5.4. Conclusions, criticisms and suggestions for further work.
In general the experimental results are in agreement with the expectations suggested from the literature survey. The corrosive action of an $\text{NH}_3\text{-H}_2\text{O-CO}_2$ gas mixture is essentially caused by the corrosiveness of dissociating $\text{NH}_3$, which, for alloys protected from H-attack by Cr-addition, manifests itself largely as N-attack. Unalloyed steel is strongly attacked, and an apparently porous, poorly adherent layer, probably of a nitride-oxide composition, is formed. Cr-based steels which have not undergone passivation and are not continuously exposed to oxidizing gases, such as oxygen and water vapour, also experience significant N-attack. The layer formed on these alloys is much harder and much more adherent than that formed on unalloyed steel. Increasing concentrations of Ni increase the resistance of Cr-containing steels to attack by $\text{NH}_3$, as is apparent from studies of the PH Cr-Ni steels. The depth of nitriding attack is considerably reduced, and the hardness of the layer formed is usually lower than that of the Cr-steels containing no Ni. The favourable effects of Ni are probably the result of a combination of properties of this metal itself and its action as an austenite forming element. Of the PH Cr-Ni steels, PH 14-8-Mo, with a relatively high Ni/Cr ratio and a semi-austenitic structure, exhibited by far the best corrosion resistance. Of especial excellence were the Ti-alloys, which suffered no corrosion at all.

From the experiments it appears that $\text{NH}_3\text{-H}_2\text{O-CO}_2$ gas mixtures are less corrosive under high than under low pressures, probably because of the lesser tendency of $\text{NH}_3$ to dissociate under high pressure conditions. In general, for the alloyed steels at low pressures the materials appear to form a self-protective layer, and the nitriding rate decreases with time. Such behaviour is also to be expected at higher pressures. The depth of attack varies from zero for the Ti-alloys to - roughly speaking - 5 to 15 microns for the PH 14-8-Mo, 20 to 25 microns for the other PH Cr-Ni steels and > 50 microns for the Cr-steels.

At high pressures and at static conditions it appears that $\text{NH}_3$ and $\text{CO}_2$ can combine, probably via a reaction catalyzed by unalloyed steel and, to a lesser extent, by Cr-steels, to form a solid C-N-O containing product, possibly of a condensed triazine composition. This product is extremely corrosive to unalloyed steel, very corrosive to Cr-steels and practically not corrosive to PH Cr-Ni and Ti-alloys; furthermore, the precipitate hardly forms on these latter two alloy sorts. It is the author’s opinion that under the highly dynamic conditions found in practice such solid formation will not occur.

Judging from the turbo-disc experiments, stress does not appear to adversely affect the corrosion resistance.

Concerning the HGRP the general conclusion is that a hot gaseous $\text{NH}_3\text{-H}_2\text{O-CO}_2$ mixture is much less corrosive than has been suggested in the literature
discussing this process. The most probable alloy types for use in a HGR turbo-compressor are PH Cr-Ni steels with a relatively high Ni-Cr ratio. Ti-alloys are also suitable, but, of course, much more expensive.

For the sake of completeness a number of critical remarks must be made. The corrosion investigation was begun on the basis of an inadequate literature study, and only in the later stage of the experimental study was a comprehensive literature search performed. For this reason the corrosion experiments overlooked the probable occurrence of N-attack as well as the probable protection afforded by pre-oxidation and the addition of air and water vapour to the NH$_3$-CO$_2$ gas mixture. For this reason also, Ni-based alloys were not tested. Furthermore, it was later found that a number of alloys tested, including PH 14-8-Mo, had not been given the necessary hardening treatment (the samples had been purchased from the suppliers under the assumption of a proper heat treatment). That the heat treatment conditions of the samples were not checked beforehand represents a serious oversight, as this treatment affect the structure, and thus the corrosion resistance, of the alloy.

On the basis of these comments and criticisms the basis for further study is obvious. Most importantly, corrosion and metallographic tests should be carried out with pre-oxidised samples in NH$_3$-CO$_2$-$H_2O-O_2$ mixtures ($H_2O$ and air are normally present in the recycle gases of a HGRP). Such treatment and conditions may cause the Cr-steels to be sufficiently corrosion resistant. Since turbo-impellers fabricated from Cr-steels are only about half as expensive as those of PH 14-8-Mo, such a finding could be quite important.

Further tests should involve the effect of a flowing high pressure NH$_3$-$H_2O$-CO$_2$-air mixture at turbo-compressor temperatures and pressures. Such experiments are very difficult to achieve in a laboratory and may best be carried out in a heated section of a gas stream of an industrial urea process (e.g., the gas stream flowing to the high pressure condensor in the DSM CO$_2$ strip process; see Fig. 1-4).

Another extremely important question is the possible problem of entrainment in the gas phase flowing to the HGR compressor. Because practical conditions representative of this problem are extremely difficult to define, being influenced by the efficiency of demisters, flow and temperature patterns, etc., an experimental simulation is correspondingly difficult. Probably the only realistic method of investigating this (possible) problem is to construct a HGR turbo-compressor and to place this in a gas recycle loop following liquid expansion to a gas-liquid mixture. Since no existing urea processes are characterized by large gas recirculation volumes, such tests more or less entail the construction of a HGRP in order to test its own feasibility.
Table V-2. A list of condensed results of studies of the attack of metals in hot NH₃- containing atmospheres

<table>
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<tr>
<th>Author(s)</th>
<th>Gas composition, mole-%</th>
<th>Exposure duration hours</th>
<th>Pressure, atm.</th>
<th>Temperature ºC</th>
<th>Alloys tested</th>
<th>% Cr</th>
<th>% Ni</th>
<th>Corrosion rate reported</th>
<th>Extrapolated corrosion rate mm/year</th>
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<td>NiMo16CrW</td>
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<td>Kucheryavyi et al, 1972</td>
<td>NH₃,CO₂,H₂O</td>
<td>120</td>
<td>10+1 in all cases</td>
<td>EI-437B</td>
<td>1.20 g/m² h</td>
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<td>EI-395</td>
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<td>EI-417</td>
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<td>0.45 g/m² h</td>
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<td>29164</td>
<td>360</td>
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<td>0.023 mm/year</td>
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<td></td>
<td>H₂, 20% H₂,</td>
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<td>8% A</td>
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<td>AIS1 304</td>
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Note: All data is given in millimeters per year (mm/year) and grams per square meter per hour (g/m² h).
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<th>38Ni/18Cr</th>
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<th>12.3</th>
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<td>McDowell, 1962</td>
<td>NH₃=12%</td>
<td>H₂=66%</td>
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<td>3 years</td>
<td>750</td>
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<td>AlSi 446</td>
<td>26.0</td>
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<td>1.059 mm</td>
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<td>British Patent 1074245, 1967</td>
<td>NH₃=12%</td>
<td>H₂=66%</td>
<td>N₂=22%</td>
<td>½ year</td>
<td>290</td>
<td>500</td>
<td>8Cr-30Ni</td>
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<td>30.0</td>
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<td>H₂=67%</td>
<td>N₂=23%</td>
<td>NH₃=10%</td>
<td>4 months</td>
<td>300</td>
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<td>25Cr-2.5Ni-N</td>
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<td></td>
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<td>0.39 &quot;</td>
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</tbody>
</table>
References.

24. For exhaustive information concerning the alloy types under discussion the reader is referred to the enormous number of technical brochures published by the various manufacturers. Of special excellence are the publications of the Armco Steel Corp. (Ti- and PH Cr-Ni steels), Baltimore, Maryland, U.S.A., the Climax Molybdenum Co. (Cr- and PH Cr-Ni steels), New York, New
York, International Nickel Ltd. (Cr-Ni and Ni-based alloys), London, Henry Wiggins & Co., Ltd. (Ni-alloys), Hereford, England, Imperial Metals Industries, Ltd. (Ti-alloys), Birmingham, England, Deutsche Edelstahlwerke Aktiengesellschaft (Cr- and PH Cr-Ni steels and Ti-alloys), Krefeld, Germany, Firth-Vickers (Cr- and PH Cr-Ni steels) and Contimet (Ti-alloys), Krefeld, Germany.

25. For a better understanding of this chapter an elementary knowledge of physical metallurgy is necessary. See, for example, Guy, A.G., "Physical Metallurgy For Engineers," Addison-Wiley, Readings, Mass., U.S.A., 1962.

26. Personal communications with Dr. F. Tavasani and Mr. J. Geitenbeek of, respectively, Nuovo Pignone Compressor Co., Holland, and Demag Compressors, Holland.


32. Class, I., Stahl und Eisen, 80, 1960, 1117.


42. British patent 1074245 (1967).


44. Cihal, V., Chemicky Prumysl. (Czechoslovakia), 15/40(2), 1965, 92.


61. A review of 22 papers concerning corrosion of metals by CO₂ is given by H.C. Cowen and C. Tyzak in the British Corrosion Journal, 3, 1968, p. 220. The papers, unfortunately, were for the most part not published. Abstracts of these papers were, however, published in Brit. Cor. J., 2, 1967, 229.
71. A possible explanation of the occurrence of the solid phase may be that its formation took place via reactions catalyzed by iron or iron oxides. In 1921, for example, Baily\(^2\) found that at atmospheric pressure, high temperatures (500 °C < T < 700°C) and short contact times (4-10 minutes), NH\(_3\) and CO\(_2\), in the presence of quartz or metallic oxides, could react to form ammonium cyanate and urea, which deposited as a solid upon cooling the effluent gases. Most probably the following gross reactions can occur:

\[
\begin{align*}
\text{(NH}_3\text{)}_3 \quad \text{+} \quad \text{(CO}_2\text{)}_2 \quad \text{+} \quad \text{(HNCO)}_g \quad \text{+} \quad \text{(H}_2\text{O)}_g \\
\text{(HNCO)}_g \quad \text{+} \quad \text{(NH}_3\text{)}_3 \quad \text{+} \quad \text{(NH}_4\text{CNO)}_s \quad \text{+} \quad \text{(NH}_2\text{CONH}_2)_s
\end{align*}
\]

(1)

(2)

Under the conditions of the high pressure experiments, in which the temperature is much lower than in Baily's work but the pressure and contact time much greater, reaction 1 may well have occurred. Since urea is unstable at these high temperatures, the isocyanic acid (HNCO) may have reacted further via gross reactions of the type:

\[
3(\text{HNCO})_g + n(\text{NH}_3)_g \rightarrow \text{polytriazines}_s
\]

(3)

in which R = -NH\(_2\) or -OH groups. Thermodynamically the reactions of NH\(_3\) and CO\(_2\) to triazines and polytriazines are highly favourable.\(^7\)


75. See Reference 25, p. 84-86, for example, for an elementary discussion of X-ray microanalysis.

76. Mukaewaki, K., Inagaki, H. and Oshima, N.Io., Tetsu to Hagane (Japan), 53(11), 1967, 1347.

77. In general, proper heat treatment improves the corrosion resistance of PH Cr-Ni steels. See, for example, the technical brochures of Armco, such as "Armco PH 17-4, Product Data (S-9b)," p. 3, 10.


80. This strength/density requirement necessitates yield strengths (at 300°C) for Ti- and Fe-based alloys of 27 kgf/mm\(^2\) and 15 kgf/mm\(^2\), respectively.

81. In general NH\(_3\)-CO\(_2\)-H\(_2\)O condensate formed at a given temperature is much more corrosive than the liquid phase existing at this temperature. See, for example, Nitrogen, Sept./Oct., 1971, p. 36 and reference 6.

82. The "ru" is a Dutch unit for the measure of roughness and is equal to 0.025 micron. For a discussion of the normalized roughness determination involving the ru see the Nedelands Normalisatie-Instituut, NEN 630-I and 630-II.

6.1. Introduction.

While a number of articles and patents exist concerning the HGRP most of them are qualitative in nature and do not discuss the basic design criteria, the method of calculation of the mass and energy balance, utilities costs, etc. The purpose of this chapter is to provide for this missing information.

In the first section of this chapter the literature concerning the HGRP is critically reviewed. In this review the basic design criteria for a HGRP become obvious, and they are presented systematically in the second section. In the third section pilot-plant experience with a HGRP is briefly discussed. In the fourth section an approximate design for a HGRP is presented: heat and mass balances are calculated, with particular attention being given to the specification of the HGR turbo-compressor and the inter-stage coolers, which form the heart of this process. On the basis of the heat and mass balance an estimation of the utilities costs can be made. In order to make these results more meaningful, they are compared with the published values of the DSM CO$_2$-stripping process, presently the most commercially successful urea process. This comparison indicates that the HGRP may well be economically superior to the DSM process.

6.2. A critical review of the literature concerning the HGRP.

The first - and last - commercially operating HGRP was built by I.G. Farben in Germany and produced urea (60 tons/day) in the 1940's.\(^1,2\) Characteristic for operation of this HGRP were severe corrosion problems in the HGR compressor, which was of the plunger type. While the relevant literature does not discuss the cause of this corrosion, a number of thought-provoking remarks are included in these reports. The gaseous recycle stream, for example, contained a relatively high percentage of water (+ 10 mole-%); this resulted in a recycle gas which was prone to condensation, i.e., condensed at high temperatures (see section 4.3.). No information concerning the condensation points is given in the reports, and since the condensation conditions are very difficult to measure it may well have been the case that they were not well known to I.G. Farben. The inter-stage coolers of the HGR compressor were air-cooled; no temperatures are reported. With this type of cooling local undercooling may have occurred with resultant partial condensation, the liquid droplets formed flowing to the following compressor stage. The literature suggests that monel lining was used for the compressor. While monel is resistant to NH$_3$-containing gas mixtures, this alloy is extremely susceptible to attack by the liquid phase.\(^3,4\)
The process was also not equipped with demisters for the removal of eventual entrained liquid in the gas phase.

It is the author's opinion that the corrosion problems in the I.G. Farben HGRP were not caused by gas phase corrosion, but that the high water content of the gas phase facilitated condensation, which may have occurred in the inter-stage coolers, the resulting liquid severely attacking the monel-lined compressor. Entrainment in the gas phase may also have played a role.

Because of this unsuccessful industrial application of a HGRP it was commonly assumed that compression of a hot gaseous $\text{NH}_3 - \text{CO}_2 - \text{H}_2\text{O}$ mixture presented insurmountable corrosion problems. Frejacques saw another potential problem. Because the compression temperature could be neither too high, in connection with compression energy and corrosion considerations, nor too low, in connection with the possibility of condensation, the HGR compressor would have to be cooled with a hot coolant. For these reasons the available $\Delta T$ between gas and coolant could not be large. From the formula for the area necessary for a given heat exchange,

$$A = \frac{\phi_h}{U \ln \left[ \frac{(\Delta T_1 - \Delta T_2)}{(\Delta T_1 / \Delta T_2)} \right]}$$

in which $A$ is the necessary heat exchange area ($\text{m}^2$), $\phi_h$ is the amount of heat exchanged ($\text{Kw}$), $U$ is the overall heat exchange coefficient ($\text{W/m}^2\,\text{C}$) and $\Delta T$ is the difference between the gas and coolant temperature at the begin and end of the cooler, it can be seen that small $\Delta T$'s lead to large areas (of expensive corrosion-resistant materials) for the inter-stage coolers.

Although for some twenty years no commercial interest existed for the HGRP, research was started in the Laboratory of Chemical Technology of the University in 1963. Later, stimulated by the advances in turbo-compressor development, an American design firm specializing in the fertilizer industry, Chemical Construction Corp. ("Chemico"), patented a number of versions of a HGRP. Chemico's three most advanced patents will be briefly discussed here to illustrate the principles underlying design of a HGRP.

The flow chart of a process patented in 1967 is presented in Fig. VI-1. A number of principle characteristics of this process is obvious. Firstly, the small gaseous recycle stream (1), formed in the last carbamate decomposer (3), is added to the feed $\text{CO}_2$ so that compression of the last recycle stream occurs via the much larger volume of the $\text{CO}_2$ feed. Since turbo-compressors operate efficiently only at large gas volumes and since the trend to $\text{CO}_2$ compression via turbo-compressors is manifest in modern urea processes, the advantages of
such a procedure are clear. A second characteristic of this process is that the hot recycle gas streams (33,35) are cooled by contacting them directly with the liquid phase in the higher pressure carbamate decomposers (6,12). This procedure, according to Chemico, eliminates the need for inter-stage compression cooling, facilitates the dissociation of carbamate due to the stripping action of the hot, CO₂-rich recycle gases and slightly reduces the steam requirements for the carbamate decomposers.

The process can be explained in detail (see Fig. VI-1) starting from the small low pressure recycle gas stream (1), which flows from the gas-liquid separator (2) following the low pressure carbamate decomposer (3); this gas stream (1) is mixed with the much larger CO₂ feed stream. This gas mixture (4) is compressed via a HGR turbo-compressor (5) to 10 \( \leq P \leq 40 \) atm, the pressure of the medium pressure carbamate decomposer (6) and then contacted directly with the liquid phase in this decomposer for cooling. The liquid effluent (7) flows from the gas-liquid separator (8) via expansion valve (9) to the low pressure carbamate decomposer (3). The gas phase (10) flows to a second HGR turbo-compressor (11) in which it is compressed to the pressure (50 \( \leq P \leq 110 \) atm) of the high pressure carbamate decomposer (12) and contacted directly with the liquid phase in this apparatus. The gas phase (36) leaving the gas-liquid separator (14) flows to the last stage of the HGR turbo-compressor (15) in which it is compressed to reactor pressure (140 \( \leq P \leq 420 \) atm). The gas stream (16) leaving this compressor is at a very high temperature (300-550°C!) and is cooled in heat exchanger (17), in which pressurized water (18) is converted to saturated steam (19). The cooled recycle stream (20) is further cooled by direct addition of liquid NH₃ (21) via NH₃ pump (22). The resulting stream (23) reacts in the condenser-reactor (24) in which process steam (25)
is generated. The reactor effluent (26) then flows to a scrubber (27) in which the inerts (28) are removed by cooling and venting. The scrubber is cooled with liquid NH$_3$ (29) which is vapourized to gaseous NH$_3$ (30). The liquid effluent (31) is then reduced in pressure via expansion valve (32) and flows to the high pressure carbamate decomposer (12) in which it is contacted directly with hot recycle gas (33) and indirectly heated with steam. The liquid effluent is separated by means of (14) and flows through the pressure reducing valve (34) to the medium pressure decomposer (6), which works analogously to (12).

A slightly more recent (1968) Chemico HGRP patent is presented in Fig. VI-2. This design is somewhat similar to the previous one, the main difference being that direct contact between the recycle gas streams and the liquid phase in the carbamate decomposers does not occur; cooling of the recycle gas streams is effected by mixing these streams with the much cooler gas streams originating in the carbamate decomposers. Somewhat lower maximum compression temperatures ($T \geq 370-380^\circ C$) are also mentioned. (The equipment and stream numbers of Fig. VI-2 are equivalent to those of Fig. VI-1.)

In critically examining these two Chemico processes a number of questionable practices becomes apparent. Firstly, it is seen that in these two patents the maximum compressor temperatures are very high, namely 300 to 550$^\circ C$. In the author's opinion there are a number of serious objections to such high temperature compressor operation. As has already been mentioned in section 5.1.4., turbo-compressors of standard design do not operate at temperatures higher than 250 to 300$^\circ C$. Furthermore, as is also discussed in 5.4., the corrosion due to nitriding increases rapidly above 300$^\circ C$ and very rapidly above 400$^\circ C$, so that high temperature operation necessitates the use of special (expensive) mate-

---

**Fig. VI-2. Chemico HGRP patent from 1968.** See text for explanation.
rial, such as high nickel- or titanium-alloys. Another objection to high tempera
ture operation becomes apparent from the formulas for the energy requirements for a turbo-compressor; these are:

\[
\begin{align*}
H_{ad} &= ZR'T_1 \left( \frac{K}{K-1} \right) \left[ \frac{P_2}{P_1} \right]^{(K-1)/K} (VI-2) \\
P &= \frac{H_{ad} \phi_m}{367200} (VI-3)
\end{align*}
\]

in which \( H_{ad} \) = adiabatic head (m), \( Z \) = compressibility factor (dimensionless), \( R' = \) gas constant/molecular weight (kgf m/kgm \(^0\) K), \( K = \) \( C_p/C_v \) (dimensionless), \( T_1 = \) entrance temperature (\(^0\)K), \( P_1 \) and \( P_2 \) = begin and end pressure, respectively (Kgf/cm\(^2\)), \( P \) = compressor power (Kw), \( \phi_m \) = mass flow rate of gas (kgm/hour) and \( \eta_{ad} \) = adiabatic compression efficiency (dimensionless). It is seen that the required compression power (\( P \)) is directly proportional to the absolute temperature (since \( Z \) increases with increasing temperature the compressor energy increase is even more than directly proportional to increases in the compression temperature). For this reason it is desirable to compress at as low a temperature as possible, the ideal case being low temperature isothermal compression.

That the condenser and reactor are not separated is puzzling; as has been shown in section 1.3., separation of these two pieces of equipment facilitates temperature control in the reactor. It can also be shown that the Chemico reactor does not work at the optimum conditions, i.e., autothermic and along the top-ridge line to a point of composition at a minimum pressure at a given reactor temperature. It is also open to question as to whether the direct contact between the hot CO\(_2\)-rich gas phase and the liquid in the carbamate decomposers is so favourable. The very high temperatures of the gas phase (300 \( \leq T \leq 550^\circ\)C) may well lead to urea hydrolysis and/or biuret formation in the carbamate decomposers. The CO\(_2\) concentration of the incoming gases may also not be high enough to exert a stripping action so that partial condensation may even occur. A further possible difficulty related to the direct contact of recycle gas with the liquid in the decomposers is the occurrence of entrainment in the gas phase, which may be difficult to separate in the high pressure gas-liquid separators. It is surprising that Chemico makes no mention at all of this potential problem.

The most recent (1974) and advanced Chemico patent\(^{14}\) is presented in Fig. VI-3. The improvements of this process relative to the previously discussed patents include the separation of the condenser (14), which operates at azeo-
tropic conditions, from the reactor (20), which, however, does not operate along the top-ridge line, its feed being insufficiently NH₃-rich; the reactor operates autothermally. Another principal improvement is that the formation of ammonium carbamate is effected at high pressure (reactor pressure) so that the formation heat is generated at such a high temperature that it can be directly used to generate process steam (17) in the condenser (14) and, very importantly, be directly employed, via indirect heat exchange, to decompose the carbamate in the urea reactor effluent (29). This carbamate decomposition is effected in a stripper-carbamate decomposer (7), which operates at a pressure considerably lower than reactor pressure; in this stripper the liquid reactor effluent (29) is contacted with the hot, CO₂-rich recycle gases (6) from the first HGR turbo-compressor (5). Another important improvement is that the maxi-

mum compression temperature is about 225°C, which is much lower than that reported in all of the other Chemico patents. (Further information concerning this process is provided in the text accompanying Fig. VI-3.)

It should be remarked that this patent, as presented, is incomplete, as no mention is made of inter-stage cooling for the HGR turbo-compressors. From the information presented in the patent and using equation VI-2 it can easily be shown that inter-stage cooling is necessary to effect such low maximum compression temperatures.

Of all of the articles\textsuperscript{17,18,19,20} concerning the HGRP which have appeared in the general literature, only a study by ECN\textsuperscript{21} has any depth. In this article the advantages and disadvantages of the HGRP are considered. The important point is made that the economics of the HGRP relative to the other processes is dependent on the relative costs, which often vary locally, of steam and electricity. Furthermore, while the HGRP concept is attractive because of its simplicity, the most serious drawback of this process is that it has never been tested in practice, the problem being that a HGR turbo-compressor, being limited to very large gas flows, cannot be scaled down to pilot-plant operation levels. No company has as yet ventured to gamble millions of dollars in an untried design.

6.3. A qualitative design outline for a HGRP.

On the basis of the preceding literature and discussion a qualitative design outline can be presented for the optimization of a HGRP. An optimization process involves the following factors, which obviously must be weighed against one another to reach the most profitable compromise.

I. Minimize compression costs.

A. Keep the \( P_{\text{out}} / P_{\text{in}} \) ratio of the HGR turbo-compressor as low as possible by operating the reactor and stripper-decomposer at as low, respectively, high a pressure as possible.

B. Achieve a high molecular weight in the recycle gases: \( \text{CO}_2 \)-feed via HGR compressor.

C. Keep the compression temperature as low as possible: employ inter-stage coolers (maintain a minimum \( \text{H}_2\text{O} \)-concentration in the recycle gas stream so that this may be cooled to a relatively low temperature) or, eventually, cool by means of gas injection and/or direct contact with the solution in the carbamate decomposers.

D. Maintain a large recycle gas stream (\( \eta_{\text{ad}} \) high): large production units; \( \text{CO}_2 \)-feed via HGR compressor.

II. Minimize investment costs.
A. Keep the $P_{out}/P_{in}$ ratio of the HGR compressor as low as possible (smaller compressor).

B. Minimize or avoid the use of inter-stage coolers, for example, by means of high temperature compression and/or direct cooling with other process streams (see I-C).

C. Minimize the concentration of water in the recycle gases. (Deeper inter-stage cooling is possible, which allows for smaller cooling areas. Lower recycle water concentration also results in lower initial water concentration in the reactor and thus higher conversions; higher conversions lead to a smaller reactor and a smaller recycle section.)

1. Maintain stripper-decomposer pressure as high as possible and its temperature as low as possible.

2. If possible, eventually shunt part of the CO$_2$-feed past the carbamate decomposer directly to the HGR compressor.

D. Minimize the number of carbamate decomposers, e.g., strive to achieve (nearly) complete carbamate decomposition in one low pressure decomposer-stripper (low pressure favours more complete carbamate decomposition).

E. Keep reactor pressure low.

III. Produce steam of high quality (maximum amount at maximum temperature).

A. Strive for azeotropic condensation in the high pressure condenser.

B. Design for high pressure reactor-condenser operation.

C. Compress at as high a temperature as possible (steam from inter-stage coolers).

6.4. Operation of a small HGRP pilot-plant.

In order to gain experience with the actual operation of a HGRP a small (capacity = 25 kg urea/day) pilot plant was built, which is schematically presented in Fig. VI-4. The most important part of the plant is the HGR compressor (9), which consists of a membrane compressor developed in cooperation with the firm Corblin in Paris. The temperature of the compressor was regulated by means of a hot oil circuit. The compressor-house, like the rest of the pilot-plant, is fabricated from AISI-316LC. The membrane is constructed of AISI-316LC or Ti-alloys (IMI-317 or 318); the membrane diameter is 20 cm. Experiments were performed over continuous periods of five days (longer experiments were not possible due to a shortage of personnel). The pilot-plant operating conditions are given in Table VI-1. To minimize corrosion oxygen was added to the system (to a concentration of 0.1-0.5 mole-% of the recycle gas).
The most important experimental finding was that it was possible to operate the plant without difficulties with the compressor. No serious corrosion occurred, as was also shown by the iron content of the urea produced: 1 ppm Fe. This result, together with the results of Chapter V, provide serious indications that the corrosion problems of a HGRP can be kept within acceptable limits.

Table VI-1. Operating conditions of the HGRP pilot-plant.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Temperature, °C</th>
<th>Pressure, atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor</td>
<td>180</td>
<td>140-180</td>
</tr>
<tr>
<td>Carbamate decomposer</td>
<td>130</td>
<td>20</td>
</tr>
<tr>
<td>Gas recycle line</td>
<td>≈225</td>
<td>20 to 140-180</td>
</tr>
<tr>
<td>Compressor-house*</td>
<td>250</td>
<td>20 to 140-180</td>
</tr>
</tbody>
</table>

* Heated by means of circulating hot oil.

6.5. Concerning the design and economics of a HGRP.

6.5.1. The basis of the design.

For a HGRP a design flowsheet (see Fig. VI-5), mass and energy balance and rough economic estimation of the utilities consumption will be presented. Special attention will be given to the critical components of the process, namely the HGR turbo-compressor and inter-stage coolers, particularly their power requirement and, respectively, cooling area and steam production. The calculations will be only sketched here; for more detailed explanation the
reader is referred to the work of Bijwaard and Pingen. It should also be noted that the HGRP layout considered here resembles that presented in a Norsk-Hydro patent (1968), which was later improved in an article.

The mass balance is based on a production rate of 1500 tons urea/day, which is roughly the size of the larger plants being built today using the conventional processes. Based on practical values the NH$_3$ and CO$_2$ are assumed to be 99 and 97.5 mole-% pure, respectively. Oxygen injection occurs via air in the CO$_2$. The NH$_3$ losses are assumed to be 0.5 mole-%.

The heat balance has been based on the studies of Otsuka and Schoondorp for the heat content of the liquid phase and Schröder for the heat content of the gas phase. The heat balance scheme for the liquid phase is given in Fig. VI-6. The ΔH's of the excess NH$_3$ and H$_2$O and free CO$_2$, at the total pressure and temperature of the liquid phase, are given by ΔH$_8$, ΔH$_9$ and ΔH$_{10}$, respectively.

The specific heat of the liquid phase as a function of the composition is

![Diagram](image-url)

unknown. For simplicity Otsuka’s assumption that the specific heat of the process stream is 97.5 kcal/mole, independent of the composition, is used. Furthermore, the heat of condensation of excess NH₃ and water and the heat of mixing of all of the constituents are neglected.

The basis of the enthalpy values of the gas phase are the following empirical formulas obtained by regression analysis to the literature values for NH₃, CO₂, inert, and water. These are:

\[
\begin{align*}
\text{NH}_3 (G), 1 \text{ atm, } 25^\circ C & \quad \text{CO}_2 (G), 1 \text{ atm, } 25^\circ C \\
H_1 = 9377 \quad (\text{ref. 30}) & \quad H_2 = 8495 \quad (\text{ref. 30})
\end{align*}
\]

- Carbamate reaction: \( \Delta H_3 = -38060 \) (ref. 26)
- Carbamate (S), 1 atm, 25°C
- Heating to 150°C, \( P = 1 \) to \( P_{\text{reactor}} \)
- Carbamate (S), reactor pressure, 150°C
  - Melting of carbamate: \( \Delta H_5 = 4850 \) (ref. 26)
  - Carbamate (L), reactor pressure, 150°C
  - Urea reaction: \( \Delta H_6 = 3700 \) (ref. 32)
  - Carbamate + urea + water (L), reactor pressure, 150°C
  - Heating to reactor: \( \Delta H_7 = 97.5 \left(T_{\text{reactor}} - 150\right) \) (ref. 26)

**Fig. VI-6.** Enthalpy model for the liquid phase. The reference temperature is 0°C. All values are in kcal/kmole.
\[ H_{NH_3} = 15.47357 \, T - 0.09172 \, P^2 + 7917.3 \quad (VI-4) \]

(Kcal/Kmole, 127 \( < \) T \( < \) 227\(^\circ\)C, 1 \( < \) P \( < \) 140 atm)

\[ H_{CO_2} = 0.21623 \, T - 0.28143 \, P + 0.00115 \, PT + 188.1 \quad (VI-5) \]

(Kcal/kg, 110 \( < \) T \( < \) 150\(^\circ\)C, 0.5 \( < \) P \( < \) 150 atm)

\[ H_{H_2O} = 0.45823 \, T - 4.13038 \, P + 0.01512 \, PT + 596.3 \quad (VI-6) \]

(Kcal/kg, 150 \( < \) T \( < \) 190\(^\circ\)C, 0.2 \( < \) P \( < \) 4.8 atm)

\[ H_{AIR} = 30.14643 \, T - 2.56272 \, P + 11482.8 \quad (VI-7) \]

(KJ/Kmole, 87 \( < \) T \( < \) 177\(^\circ\)C, 1 \( < \) P \( < \) 100 atm)

(For \( NH_3 \), \( CO_2 \) and air the reference temperature is 0\(^\circ\)K; for water it is 0\(^\circ\)C.)

The conditions used in the calculations were the temperature of the mixture and the partial pressures of the component gases. Since the dissolved \( NH_3 \) and \( CO_2 \) are above their critical conditions in the reactor liquid, these formulas were also used to calculate the enthalpy values of these constituents in the liquid phase, the conditions now being the temperature and total pressure of the system.

The conditions and mass and heat values of the most important streams in Fig. VI-5 are given in Table VI-2 (placed at the end of this chapter).

6.5.2. The individual pieces of equipment.

6.5.2.1. The reactor (13).

In practice the urea reactor reaches approximately 95\% of chemical equilibrium. For calculating the mass balance it is assumed, for simplicity, that complete equilibrium is reached; on this basis the compositions of the gas and liquid streams leaving the reactor can be calculated using the model developed in Chapter III.

The temperature of the reactor is a compromise between the kinetic rate, corrosion rate and bubble-point pressure, particularly the first two variables. A reactor temperature of 185\(^\circ\)C is chosen, as this is normally the highest temperature which AISI 316 LC, a relatively inexpensive reactor lining material, may be used with acceptable corrosion rates. From Fig. II-13 it is seen that at 185\(^\circ\)C the molar ratio corresponding to a minimum bubble-point pressure is 2.85; this minimum bubble-point pressure is 126 atm. Because of the inerts present in the feed gases, however, the actual reactor pressure must be higher than the pressure without inert. From practice, a value of 140 atm is chosen, this value
being a compromise between reactor volumetric efficiency and investment and operating costs, all of which increase with pressure. The construction (a series of compartments separated by sieve plates) and operation (along the top-ridge line) are analogous to those of the DSM CO₂-stripping process reactor.

6.5.2.2. The scrubber (15).

The gas stream (14) leaving the reactor enters the scrubber; this gas stream is assumed to contain all of the inerts of the feed streams. The gases are contacted with water (16) to remove the NH₃ and CO₂ present, and the inerts (17) are vented. The amount of water added to the scrubber should be kept to a minimum for the sake of high reactor conversions; the quantity of stream (16) is dependent on the gas flow and the solubility of NH₃ and CO₂ at the given operating conditions. The scrubber temperature is estimated to be 100°C; this temperature is maintained by cooling with hot water. At these conditions the water flow rate can be estimated, using the solubility diagrams of Frejacques. It is assumed that all of the entering NH₃ and CO₂ are contained in the scrubber effluent (21), which flows to the condenser (12).

6.5.2.3. The carbamate decomposer-stripper (4).

The reactor effluent (18) is expanded via an expansion valve (23) to a flash evaporator and gas-liquid separator (8), the resulting liquid (24) flowing to the carbamate decomposer-stripper (4). (The composition and temperature of the gas (26) and liquid (24) streams leaving the flash evaporator cannot be calculated because the system is quaternary (reaction III-6 does not occur) and therefore beyond the validity of the ternary model presented in Chapter III.)

The stripper pressure is chosen to be 20 atm for the following reasons:

1. In order to keep the compression costs low, the stripper should work at as high a pressure as possible; a high stripper pressure also results in a low water concentration in the recycle gases. On the other hand, the pressure must be low enough to effect an almost complete (≥ 99%) recovery of the total dissolved NH₃, a factor which favours low pressures.

2. The heating of the stripper can be most conveniently achieved using steam which has been produced elsewhere in the process. This maximum steam temperature is approximately 150-160°C. Higher pressures in the stripper require the use of higher temperature steam (e.g., the DSM CO₂-stripper, operating at 140 atm, uses steam at 220-225°C). ⁴⁶

3. The turbo-compressor manufacturers (Nuovo Pignone, for example) supply CO₂ turbo-compressors which reach 20 atm in one casing.
The maximum temperature in the bottom of the stripper is 150°C, using steam at 160°C generated in the compressor inter-stage coolers; the upper part of the stripper, heated with steam at 150°C produced in the condenser, is 130°C.

The composition of the liquid stream (27) leaving the stripper is calculated on the basis that the inlet liquid is for 99.5% stripped of its original NH₃-content. The NH₃ concentration in the combined gas streams (9) leaving the flash evaporator (26) and stripper (5) is calculated on this strip efficiency; the water content is calculated on the basis of the assumption that the gases are at their physical condensation conditions at the given pressure.

The heat required \( (H_{4 dac}) \) for the decomposition of ammonium carbamate in the stripper (4) is calculated by means of the heat balance equation:

\[
\Sigma H_{in} = \Sigma H_{out} + H_{4 dac} + H_{18} + H_2 = H_9 + H_{27} + H_{4 dac} = 3859 \text{ kcal/s (VI-8)}
\]

(In Fig. VI-4 the dotted line indicates that part of the CO₂-feed may be shunted past the stripper because not all of it may be needed to effect the 99.5% carbamate decomposition. Such a shunt procedure is desirable as it would reduce the water content of the recirculation gases.)

6.5.2.4. The compressors (1,10).

The HGRP requires two turbo-compressors, a CO₂ compressor (1) for the compression of the feed CO₂ from 1 to 20 atm (stripper pressure) and a HGR compressor (10) for compression of the recycle gases from stripper pressure to reactor-condenser pressure (140 atm).

At our Laboratory work has been done to estimate the specifications of a HGR turbo-compressor. An accurate design of a turbo-compressor, however, requires the use of specialized information which is specific to a given manufacturer and not available in the general literature. Because of the central importance of the HGR turbo-compressor for the HGRP a compressor calculation as accurate as possible was desired, and experts in the compressor field were contacted. Dr. F. Tavasani of Nuovo Pignone, the largest manufacturer of CO₂-turbo-compressors for urea plants, was kind enough to prepare the specifications (based on the \( Z \) and \( K \) values of the gas mixture as a function of temperature and pressure, which the author provided) for the HGRP presented in Fig. VI-5. The results of his calculations, including the CO₂ turbo-compressor, are given in Table VI-3.

The HGR turbo-compressor consists of two standard Nuovo Pignone casings (a casing is a series of impellers on a single axis). The costs mentioned include the compressor, gears, instruments, lubrication, sealing and anti-surge systems, control panel and base-plate. Installation and piping costs to the
Table VI-3. Specifications of CO₂ turbo-compressor and HGR turbo-compressor for HGRP.

### I. CO₂ compressor

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity:</td>
<td>23,000 NM³/hour</td>
</tr>
<tr>
<td>Number of stages:</td>
<td>2, with 3 and 4 impellers per stage</td>
</tr>
<tr>
<td>Diameter impellers:</td>
<td>600/500 mm</td>
</tr>
<tr>
<td>Inlet conditions:</td>
<td>P = 1 atm, T = 20°C</td>
</tr>
<tr>
<td>Outlet conditions:</td>
<td>P = 20 atm, T = 245°C</td>
</tr>
<tr>
<td>Speed (rpm):</td>
<td>9,000</td>
</tr>
<tr>
<td>Compressor power:</td>
<td>3,600 kwatt</td>
</tr>
<tr>
<td>Rotor and house material:</td>
<td>Cr-13 steel (first two impellers FV-520 S)</td>
</tr>
<tr>
<td>Price (March, 1975):</td>
<td>Dfl. 1,500,000.-- (US $ ~ 625,000.-- )</td>
</tr>
</tbody>
</table>

### II. HGR compressor

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas compressed:</td>
<td>NH₃ = 58.3 mole-%; CO₂ = 37.1 %; H₂O = 4.0 %; inert = 0.6 %</td>
</tr>
<tr>
<td>Capacity:</td>
<td>102,000 NM³/hour</td>
</tr>
<tr>
<td>Stages (4):</td>
<td>I    II    III    IV</td>
</tr>
<tr>
<td>Number of impellers:</td>
<td>3    3    3    3</td>
</tr>
<tr>
<td>Inlet conditions:</td>
<td></td>
</tr>
<tr>
<td>Pressure, atm</td>
<td>20.0 47.10 76.8 107.0</td>
</tr>
<tr>
<td>Temp. °C</td>
<td>127 161 173 187</td>
</tr>
<tr>
<td>Temp. °K</td>
<td>400 434 446 460</td>
</tr>
<tr>
<td>Cp/Cv</td>
<td>1.34 1.4 1.54 1.64</td>
</tr>
<tr>
<td>Z</td>
<td>0.94 0.89 0.825 0.795</td>
</tr>
<tr>
<td>Discharge conditions:</td>
<td></td>
</tr>
<tr>
<td>Pressure, atm</td>
<td>48.45 77.75 112.4 140</td>
</tr>
<tr>
<td>Temp. °C</td>
<td>247 252 257 257</td>
</tr>
<tr>
<td>Temp. °K</td>
<td>520 525 530 530</td>
</tr>
<tr>
<td>Cp/Cv</td>
<td>1.32 1.43 1.53 1.62</td>
</tr>
<tr>
<td>Z</td>
<td>0.93 0.88 0.845 0.80</td>
</tr>
<tr>
<td>Speed (rpm):</td>
<td>9,000</td>
</tr>
<tr>
<td>Compressor power:</td>
<td>11,500 kwatt</td>
</tr>
<tr>
<td>Rotor material:</td>
<td>FV 520 S</td>
</tr>
<tr>
<td>House material:</td>
<td>Cr-13 steel</td>
</tr>
<tr>
<td>Price (March, 1975):</td>
<td>Dfl. 2,600,000.-- (US $ ~ 1,083,000.-- )</td>
</tr>
</tbody>
</table>
inter-stage coolers are not included. The two compressors (CO and HGR), operating at the same speed, are driven by a single electric motor (or steam turbine). For comparison, a CO turbo-compressor for a DSM CO-stripping process (1500 tons urea/day, P = 1 to 140 atm) costs (March, 1975 prices) Dfl. 3,274,000.— (US $ = 1,364,000.—) and requires 7000 kW of power.

6.5.2.5. The inter-stage coolers (not shown in Fig. VI-5).

As with the compressor, the size of the inter-stage coolers was first estimated at our Laboratory. Contact was then sought with the Bronswerk Co., Nijkerk, The Netherlands, in which the heat exchanger specialists, Ir. J.H. Hoogma and Ir. G. van Rees, were kind enough to provide the specifications of the heat exchangers fitting the compressor designed by Dr. Tavasani. The physical property constants of the mixture, necessary for the exchanger calculations, are presented in Table VI-4; they were calculated by Ir. Hoogma and van Rees. The specification of the three inter-stage coolers are presented in Table VI-5.

The heat exchangers consists of bundles of tubes through which the gases flow; pressurized hot water flows around the tubes. Water is chosen as the coolant because it can be used, after expansion to saturated steam, to heat the carbamate decomposer-stripper. In order to prevent local under-cooling and condensation, the temperature of the cooling water must not be lower than the condensation temperature of the gas mixture at the given pressure; this is achieved by adjusting the water flow rate.

The price of the heat exchangers are for about 60% material costs.

The heat obtained from the coolers \( H_{\text{cool}} \) can most accurately be calculated from the relation following from Fig. VI-5 for the combined energy balance over the compressor-inter-stage coolers (in which \( H_{\text{10com}} \) = the compression energy required by the HGR turbo-compressor (10)):

\[
H_{\text{cool}} + H_{\text{11}} = H_{\text{10com}} + H_{9} \rightarrow H_{\text{cool}} = 1573 \text{ kcal/s} \quad \text{(VI-9)}
\]

The water leaving the exchangers is at 204°C; it is expanded to steam and water at 160°C, which is the temperature at which the 1573 kcal/s is obtained. (Note from Table VI-5 the large size of the coolers: diameter = 4.5 m and length = 6.0 to 7.2 m.)

6.5.2.6. The high pressure condenser (12).

The hot gases (11) leaving the HGR turbo-compressor (10) are combined with the liquid (21) leaving the scrubber (15) and flow to the high pressure condenser (12). The basis of condenser operation is azeotropic condensation, and this is assured by adding part of the original NH\textsubscript{3}-feed stream directly to the con-
Table VI-4. Gas mixture properties at inter-stage cooler conditions.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Temperature °C</th>
<th>Viscosity kg sec/m²</th>
<th>Specific heat (Cp) kcal/kg °C</th>
<th>Thermal conductivity kcal/m h °C</th>
<th>Density kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>48.5</td>
<td>170</td>
<td>1.99 \times 10^{-6}</td>
<td>0.43</td>
<td>0.035</td>
<td>38.9</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>2.28 \times 10^{-6}</td>
<td>0.42</td>
<td>0.042</td>
<td>31.3</td>
</tr>
<tr>
<td>77.8</td>
<td>180</td>
<td>2.10 \times 10^{-6}</td>
<td>0.47</td>
<td>0.039</td>
<td>64.7</td>
</tr>
<tr>
<td></td>
<td>260</td>
<td>2.37 \times 10^{-6}</td>
<td>0.44</td>
<td>0.045</td>
<td>50.6</td>
</tr>
<tr>
<td>112.4</td>
<td>190</td>
<td>2.26 \times 10^{-6}</td>
<td>0.54</td>
<td>0.044</td>
<td>97.6</td>
</tr>
<tr>
<td></td>
<td>270</td>
<td>2.48 \times 10^{-6}</td>
<td>0.46</td>
<td>0.049</td>
<td>73.9</td>
</tr>
</tbody>
</table>

Table VI-5. Specifications of the inter-stage coolers

<table>
<thead>
<tr>
<th></th>
<th>Cooler 1</th>
<th>Cooler 2</th>
<th>Cooler 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat transfer area, m²</td>
<td>210</td>
<td>192</td>
<td>230</td>
</tr>
<tr>
<td>Heat exchanged, Kcal/hour</td>
<td>3.96 \times 10^6</td>
<td>4.3 \times 10^6</td>
<td>4.5 \times 10^6</td>
</tr>
<tr>
<td>Tube length, m</td>
<td>6.6</td>
<td>6.0</td>
<td>7.2</td>
</tr>
<tr>
<td>Tube inner and outer diameter, mm</td>
<td>15,19</td>
<td>15,19</td>
<td>15,19</td>
</tr>
<tr>
<td>Cooler diameter, m</td>
<td>4.5</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Number of tubes</td>
<td>268</td>
<td>268</td>
<td>268</td>
</tr>
<tr>
<td>Average gas velocity, m/s</td>
<td>10.2</td>
<td>12.5</td>
<td>8.4</td>
</tr>
<tr>
<td>Coolant velocity, m/s</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Coolant pressure, atm</td>
<td>8.3</td>
<td>12.5</td>
<td>17.5</td>
</tr>
<tr>
<td>Coolant temperature, in and out, °C</td>
<td>160; 174</td>
<td>174; 189</td>
<td>189; 204</td>
</tr>
<tr>
<td>Heat transfer rate, Kcal/m² OC hour</td>
<td>624</td>
<td>871</td>
<td>900</td>
</tr>
<tr>
<td>Price* per cooler, in Dutch guilders</td>
<td>105,000.--</td>
<td>113,000.--</td>
<td>150,000.--</td>
</tr>
</tbody>
</table>

The material in (the coolant) with contact the gas mixture is AISI-316 LC.

The fluid circulated in the shell-side is pressurized water, 275,000 kg/hours.

The fluid entering the tube-side is the HGRP recycle gas mixture, 120,000 kg/hour.

* March, 1975 prices of Bronswerk, Nijkerk, Holland, not including installation.
denser via stream (20) to effect the azeotropic NH₃/CO₂ ratio (This equal 2.4 at 140 atm; Tₐ = 167°C. See Fig. A2-2.) Azeotropic condensation is of great importance because, firstly, the highest possible condensation temperature is reached, which results in high quality steam, and, secondly, because the azeotropic gas mixture condenses like a pure substance, there is no problem of diffusion through an inert gas; thus the condenser size (investment) is at a minimum.

The stream (27) leaving the condenser is a gas-liquid mixture, the proportion of gas being such that the reactor operates autothermically. That is, the exothermic heat of condensation of the gas and the resulting exothermic heat of carbamate formation is just sufficient to compensate for the endothermic heat of formation of urea and the increase in the boiling point temperature resulting from the increase in concentration of the relatively involatile constituents, urea plus water, as the reaction proceeds towards equilibrium. On this basis the heat available for steam production in the condenser, ¹Hₑ₂coₙ, can be calculated from the relation:

\[ H_{28} + H_{16} + H_{11} = H_{12coₙ} + H_{17} + H_{18} + H_{12coₙ} = 9510 \text{ kcal/s} \] (VI-10)

Steam at + 150°C can be produced in the condenser. The gas-liquid ratio of the condenser effluent is controlled by varying the pressure (thus temperature) of the steam being produced in the condenser.

6.5.3. A preliminary economic comparison between a HGRP and the DSM CO₂-stripping process.

Assuming comparable on-stream time, the decisive factor affecting the economic viability of a HGRP will be the operating costs (utilities and direct costs) and the investment costs. The utilities costs of the DSM process have been published;⁴⁶ the utilities cost of the HGRP presented here can be estimated on the basis of the heat and mass balances prepared in the previous sections.

The utilities costs are estimated as follows. The total electricity costs for the HGRP compressor are 3600 + 11500 = 15100 kW. Assuming that the total electricity requirements equal 16500 kW, then the electricity requirements per ton of urea are 264 kWh/ton urea. Concerning the heat production (as steam production) this is:

\[ 1573 + 9510 - 3859 = 7224 \text{ kcal/s} \] (VI-11)

coolers condenser stripper

Of this heat a part must be used to evaporate the water in the urea-water solution. On the basis of a flow of 0.321 kmole H₂O/s and a heat of evaporation of 540 kcal/kg H₂O, this is 3120 kcal/s. The remaining 4100 kcal/s is used to
generate saturated steam at 150°C (4.8 atm). Based on a feed water at 100°C, 0.425 ton steam/ton urea can be exported. Concerning the cooling water requirements, it is certain that the HGRP process, as calculated, requires less than the CO₂-stripping process, as the HGRP requires less energy per ton urea produced than the CO₂-stripping process. For simplicity, however, and because the cooling water costs are relatively small, they have been considered to be equal for both processes.

In Fig. VI-7 the comparative utilities costs of both processes are presented (in which:

\[ \Delta C_u = \text{(Utilities costs DSM CO}_2\text{-stripping - utilities cost HGRP)/ton urea)} \] (VI-12)

as a function of steam and electricity costs. It is seen that the HGRP, as calculated, offers substantial saving in utilities costs relative to the CO₂-stripping process; the cause of this advantage is, as already mentioned, that the former process requires less energy expenditure per ton urea produced.

Fig. VI-7, however, obviously invites a number of critical comments. Most importantly, it should be realized that the CO₂-stripping process utilities consumption are real ones, i.e., based on actual industrial practice, while those presented for the HGRP are based on a calculational model whose accuracy is open to question. On the other hand, while the DSM process has been highly optimized, the HGRP certainly has not been. It is probably, for example, that the economics of this process can be improved by operating the stripper at a somewhat higher pressure than 20 atm, as the various patents suggest. The author therefore concludes this chapter with the statement that the HGRP may well be a potential competitor for the DSM CO₂-stripping process and is certainly worthy of detailed economic evaluation by experts in the field.
<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mass flow kmole/s</th>
<th>Enthalpy kcal/kmole</th>
<th>Enthalpy kcal/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Stream 2. CO₂ feed to carbamate decomposer (P=20 atm, T=150°C)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.289</td>
<td>9608</td>
<td>2777</td>
</tr>
<tr>
<td>inert</td>
<td>0.007</td>
<td>3825</td>
<td>28</td>
</tr>
<tr>
<td><strong>Stream 9. Gas stream to HGR turbo-compressor (P=20 atm, T=130°C)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>0.717</td>
<td>9873</td>
<td>7074</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.455</td>
<td>9910</td>
<td>4512</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.049</td>
<td>11779</td>
<td>576</td>
</tr>
<tr>
<td>inert</td>
<td>0.007</td>
<td>3650</td>
<td>27</td>
</tr>
<tr>
<td><strong>Stream 11. Recycle gas stream leaving HGR turbo-compressor (P=140 atm, T=257°C)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>0.717</td>
<td>10932</td>
<td>7833</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.455</td>
<td>10325</td>
<td>4698</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.049</td>
<td>12475</td>
<td>610</td>
</tr>
<tr>
<td>inert</td>
<td>0.007</td>
<td>4318</td>
<td>32</td>
</tr>
<tr>
<td><strong>Stream 14. Reactor gaseous effluent (P=140 atm, T=185°C)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NH₃</td>
<td>0.083</td>
<td>10104</td>
<td>836</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.029</td>
<td>9812</td>
<td>291</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.003</td>
<td>12181</td>
<td>37</td>
</tr>
<tr>
<td>inert</td>
<td>0.013</td>
<td>4060</td>
<td>54</td>
</tr>
</tbody>
</table>

155
| Stream 16. H₂O-feed to scrubber (P=140 atm, T=100°C) |
|-----------------|-----------------|-----------------|-----------------|
| H₂O             | 0.032           | 414             | 13              |

| Stream 17. Inert leaving scrubber (P=140 atm, T=110°C) |
|-----------------|-----------------|-----------------|-----------------|
| inert           | 0.013           | 2925            | 39              |

| Stream 18. Reactor liquid effluent (P=140 atm, T=185°C) |
|-----------------|-----------------|-----------------|-----------------|
| NH₃             | 0.412           | 8983            | 3701            |
| CO₂             | 0.013           | 9613            | 121             |
| urea            | 0.289           | 5800            | 1676            |
| carbamate       | 0.154           | 2100            | 323             |
| water           | 0.370           | 3393            | 275             |

\[ \text{Total} = 6096 \]

| Stream 21. Liquid effluent leaving scrubber (P=140 atm, T=110°C) |
|-----------------|-----------------|-----------------|-----------------|
| NH₃             | 0.083           |                 |                 |
| CO₂             | 0.029           |                 |                 |
| H₂O             | 0.035           |                 |                 |

\[ \text{Total} = 1192 \]

| Stream 27. Carbamate decomposer liquid effluent (P=20 atm, T=150°C) |
|-----------------|-----------------|-----------------|-----------------|
| urea            | 0.289           | 2388            | 690             |
| water           | 0.321           | 2533            | 81              |

\[ \text{Total} = 771 \]

| Stream 28. NH₃-feed to reactor and high pressure condenser (P=140 atm, T=15°C) |
|-----------------|-----------------|-----------------|-----------------|
| NH₃             | 0.578           | 4226            | 2443            |
| inert           | 0.006           | 2767            | 16              |

\[ \text{Total} = 2459 \]
References.


15. For discussions of these equations and the design of compressors see, for example, Dobson, T., Chemical Age of India, 23(1), 1972, 21; Spiering, M.J., Polytechnisch Tijdschrift (The Netherlands), January 6, 1971, 21; and Fullemann, J. Advances, Petrol.Chem. Ref., 6, 1962, 469. See also the design guides of the various compressor manufacturers, particularly that of Elliot.


28. The heat balance presented in this chapter is, unfortunately, not based on the most recent published values for the various steps of the thermodynamic analysis presented in Fig. VI-6. Study33 of the relevant literature indicates, for example, that the heat of reaction of carbamate to urea plus water ($\Delta H_5$) is approximately +6 kcal/mole rather than 3.7 kcal/mole; the former value is also cited by Bentall.34 The value of the heat of condensation of ammonia, which is a function of temperature, pressure and composition, is approximately $-1.5$ kcal/mole26,32,35 at the conditions of the urea synthesis, i.e., conditions far removed from critical. A more accurate value for the heat of fusion of carbamate ($\Delta H_5 = 6.5$ kcal/mole) is given in a more recent article by Otsuka.36 Furthermore, for the gas phase, it is more accurate to calculate the enthalpies at the total pressure of the mixture rather than at the partial pressures of the components.37 Fairly recent studies of the heat balance of the urea synthesis are given by Kucheryavyi et al35,38 and Pradhan and Rao.39 The reader is also referred to the work of Elkin.48 Calculations being done at the time of the writing of this chapter using the above mentioned values and methods indicate that the amount of low pressure export steam is probably significantly less than the value of 0.425 ton/ton urea mentioned in section 6.5.3. This lower amount of export steam causes the utilities price advantage of the HGRP relative to the DSM CO$_2$-stripping process to be slightly less advantageous than is indicated by Fig. VI-7. The general conclusion indicated in the last paragraph of section 6.5.3., however, remains valid.

41. The Z-value (compressibility factor) can be calculated as a function of temperature and pressure making use of the Law of Corresponding States (as presented in table form by Hougen, Watson and Ragatz\textsuperscript{42}) and using the relation

\[ Z_m = \sum Y_i Z_{ci} \]

in which \( Z_m \) is the critical compressibility of the mixture, \( Y_i \) is the mole fraction of component \( i \) and \( Z_{ci} \) is the critical compressibility of component \( i \). Broers\textsuperscript{43} has shown that calculations on this basis agree well (\( \pm 1\% \)) with those performed on the basis of the Redlich-Kwong equation. Broers\textsuperscript{43} has also shown that calculated and measured Z-values for gaseous mixtures of NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O in the range of interest here are in reasonable (\( \pm 5\% \)) agreement. See Bijwaard\textsuperscript{22} for details of the computer calculations.


43. Broers, J.N., "Studies of the bubble-points, dew-points, density and conversion to urea in the NH\textsubscript{3}-CO\textsubscript{2}-H\textsubscript{2}O system at chemical equilibrium at urea synthesis conditions," Internal Report (as 3), 1974, 144 pages.

44. The K-values were determined on the basis of:

\[ K = \frac{C_p}{C_v}; \quad C_m = \sum Y_i C_i \quad \text{and} \quad C_v = \sum Y_i C_{vi} \]

at the pressure and temperature of the mixture. For NH\textsubscript{3} the data of DIN\textsuperscript{30} is sufficient; for CO\textsubscript{2} one must refer to the data of Vukalovich and Altunin\textsuperscript{30} (The presence of water (present at \( < 5\% \)) was neglected.)


47. According to "The Netherlands Foundation for Apparatus for the Process Industry" (Stichting Nederlandse Apparaten voor de Procesindustrie, Den Haag, Holland), April, 1975 prices for 25 atm saturated steam and electricity (for industrial use) are, respectively, Dfl. 20/ton and Dfl. 0.05/kWh; the cost factor of 25 atm steam to that of 4.8 atm is about 1.2. These prices and factor have been used in preparing Fig. VI-7.

Appendix 1

Use of the ternary phase model.

From Fig. A2-1 it is shown how the \((2\text{NH}_3)\), \(\text{CO}_2\) and \(\text{H}_2\text{O}\) concentrations of a given point can be found by, respectively, noting the lengths of the lines parallel to the \((2\text{NH}_3)\) side and the \(\text{CO}_2\) side (from these sides to the point) and the distance of the point to the \((2\text{NH}_3)\)-\(\text{CO}_2\) diagonal. It can be shown that the sum of these lines is equal to one of the sides of the square, whose length is equivalent to 100%.

A numerical example using one of Kawasumi's experiments is illustrative. In this experiment (Bull. Chem. Soc. Japan, 25(4), (1952), 227) Kawasumi, starting from pure ammonium carbamate, reported the following equilibrium concentrations (at \(T = 160^\circ\text{C}\) and \(P = 69\) atm): Gas phase: \(\text{NH}_3 = 0.537\), \(\text{CO}_2 = 0.398\), \(\text{H}_2\text{O} = 0.065\). Liquid phase: Urea = 0.202, \(\text{H}_2\text{O} = 0.171\), \(\text{CO}_2 = 0.168\), \(\text{NH}_3 = 0.459\). In the model used here: \(1\text{NH}_3 = \frac{1}{2}(2\text{NH}_3)\) and 1 urea = \((2\text{NH}_3) + \text{CO}_2 - \text{H}_2\text{O}\). Then for the gas phase \((2\text{NH}_3) = 0.537/2\). The \(\text{CO}_2\) and \(\text{H}_2\text{O}\) remain unchanged, and the new mole fractions become 0.368, 0.543 and 0.089 for \((2\text{NH}_3)\), \(\text{CO}_2\) and \(\text{H}_2\text{O}\), respectively. For the liquid phase \((2\text{NH}_3) = (0.459/2) + (0.202), \text{CO}_2 = 0.168 + 0.202\) and \(\text{H}_2\text{O} = (0.171) - (0.202)\), and the new mole fractions become 0.560, 0.480 and \(-0.040\) for \((2\text{NH}_3)\), \(\text{CO}_2\) and \(\text{H}_2\text{O}\), respectively. Ammonium carbamate is composed of \(1(2\text{NH}_3)\) and \(1\text{CO}_2\) and is therefore situated at the exact centre of the composition square. A straight tie-line can be drawn through the gross composition point (ammonium carbamate) and the gas and liquid points. This is done in Fig. A2-2.
A Temperature-Pressure-Composition Phase Model for the NH$_3$-CO$_2$ System.

A knowledge of the phase equilibria of the binary NH$_3$-CO$_2$ system is of great importance in choosing the optimum conditions for the recirculation section of the urea synthesis plant. In spite of the technical and scientific importance of this system, however, no systematic study of it as an entity has yet been published, probably because of the difficulty in measuring it, due to the high pressures involved and the occurrence of the urea reaction, which destroys its binary nature. In the following the relatively scarce literature is examined in the light of the theory of phase equilibrium diagrams, and an attempt is made to organize this information into a temperature-pressure-composition model for the entire system. This discussion is based upon the work of Bezemer and, in particular, Broers.

Because of the significant chemical differences of the two components, NH$_3$ being a highly polar substance of basic character and CO$_2$ being non-polar and slightly acidic in character, and because of the large difference in volatility, the system NH$_3$-CO$_2$ exhibits complex phase behaviour, such as:

1. NH$_3$ and CO$_2$ react to form a dissociating compound, ammonium carbamate:

$$2 \text{(NH}_3\text{)}_{\text{G,L}} + \text{(CO}_2\text{)}_{\text{G,L}} \leftrightarrow \text{(NH}_2\text{OCONH}_4\text{)}_{\text{S,L}} \hspace{1cm} \text{(A2-1)}$$

2. The formation of the relatively involatile ammonium carbamate leads to the occurrence of a maximum temperature azeotrope in the liquid (L)-gas (G) planes.

3. In the NH$_3$-rich area (relative to ammonium carbamate) liquid immiscibility occurs.

4. In the CO$_2$-rich area a lower critical end-point is found, i.e., solid ammonium carbamate coexists with super-critical CO$_2$.

In the following these phenomena will be examined in some detail.

The dissociation pressure of ammonium carbamate has been studied by a number of researchers. Gmelin presents a summary of the published results up to about 1936. More recently this compound has been studied by Briggs, Egan, Bennet and Jonich. Egan has shown that up to about 100°C the literature discussing the vapour pressure is in good mutual agreement and can be described by the relation:

$$\log P = -2742/T + 11.1448$$

(P in mm Hg, T in K). Briggs and Swets derived a formula for the pressure-
temperature-composition relation of the condensation pressure (to solid ammonium carbamate) of NH₃-CO₂ gas mixtures, based on the assumption of ideal gas behaviour and the absence of association of NH₃ and CO₂ in the gas phase (this last fact being substantiated by studies reported by Gmelin and, more recently for higher pressures, by Effremova and Leontieva). This formula is:

\[
\log P = -2741.9T + 7.9876 - \frac{1}{3} \log \left[ \frac{Y_{\text{NH}_3}}{Y_{\text{NH}_3}} \right] \quad (A2-3)
\]

in which \( P \) is the condensation pressure in atm, \( T \) is in °K and \( Y_{\text{NH}_3} \) is the gas phase mole-concentration of NH₃.

Ammonium carbamate is a dissociating binary compound and as such its behaviour must be seen as a part of the NH₃-CO₂ system. In general a dissociating compound does not, like a normal pure substance, exhibit a triple point (at a constant \( T \) and \( P \)) but rather a temperature-pressure interval in which solid, liquid and gas can exist simultaneously in mutual equilibrium. The beginning-point of this interval is called the maximum sublimation point and is the maximum temperature and pressure at which gas and solid can coexist in the absence of liquid. The end-point of this interval is called the minimum melting point and is the lowest temperature and pressure at which liquid and solid can coexist in the absence of gas. The maximum sublimation point, often incorrectly referred to in the literature as the melting point, has been measured by a number of researchers, whose results appear below in Table A2-1.

<table>
<thead>
<tr>
<th>Researcher</th>
<th>Temperature, °C</th>
<th>Pressure, atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Briner 14</td>
<td>152</td>
<td>83.4</td>
</tr>
<tr>
<td>Frejacques 15</td>
<td>155</td>
<td>——</td>
</tr>
<tr>
<td>Jänecke 16</td>
<td>153</td>
<td>88</td>
</tr>
<tr>
<td>Terres 17</td>
<td>147 - 150</td>
<td>——</td>
</tr>
</tbody>
</table>

(It should be noted that at higher temperatures (\( T \geq 130^\circ C \)) the study of ammonium carbamate is complicated by the occurrence of the urea reaction.) The values of \( T = 153^\circ C \) and \( P = 87 \) atm are chosen as the values of the maximum sublimation point.

The minimum melting point is unknown (and perhaps does not exist) and is impossible to measure due to the rapid occurrence of the urea reaction at temperatures above the maximum sublimation point. For simplicity the minimum melting point has been arbitrarily chosen as occurring at 156°C and 110 atm.
The NH₃-side (relative to ammonium carbamate) of the NH₃-CO₂ system is fairly well known. Solid ammonium carbamate dissolves poorly in liquid NH₃; therefore the three phase line S₋L₋G is only slightly lower in pressure in the P-T projection than the vapour-liquid line of pure NH₃. The composition of L₂ has been estimated to be 98 mole-% at 116°C, and the solubility of ammonium carbamate is probably even less at lower temperatures; the composition of the gas phase is practically pure NH₃. The quadruple point S₋L₋L₋G of the system has been estimated to occur at 116-120°C and 83 atm, which is just slightly less than that of saturated NH₃ at this temperature. At these conditions a second liquid phase, L₁, is formed whose composition has been estimated to be about 78 mole-% NH₃. As has already been mentioned, L₂ is nearly pure NH₃, and the three phase line L₋L₋G therefore lies only slightly below the L₋G line of pure NH₃. The NH₃-CO₂ system thus exhibits an area of liquid immiscibility (L₁ + L₂). At a given temperature the area of immiscibility in the pressure-composition plane decreases with increasing pressure (as has been found at our Laboratory) and ends at a critical point, L₁ ≡ L₂. The pressure, temperature and composition values of this critical line are unknown and have been drawn arbitrarily in Figures A2-1 and 2. In the projection the quadruple point S₋L₋L₋G has been formed by the intersection of the three phase line S₋L₋G with the three phase line L₋L₋G. It is therefore assumed that with decreasing temperature the critical line L₁ ≡ L₂ intersects a three phase line depicting an area in which a solid phase exists, namely the line S₋L₋L₂. Since L₂ is almost identical to pure NH₃, it is also reasonable to assume that the three phase line L₋L₋G ends at the critical line L ≡ G, which begins at the critical point of NH₃; the P-T point of intersection will be only slightly higher than that of the critical point of NH₃, and the composition at intersection will be very near the NH₃-axis.

For the urea technology the most important line in the NH₃-CO₂ system is the azeotropic line. Operation of the high pressure condenser (see, for example, apparatus numbers 14 and 12 of Figures 1-4 and VI-5, respectively) at azeotropic conditions results in condensation at the highest possible temperature (at a given pressure) leading to the production of the highest quality steam. Since azeotropic condensation occurs without the occurrence of diffusion limitation through a non-condensing gas, the condenser operating at azeotropic conditions is also of minimum size.

The T-P-X values of the azeotropic line have been reported by Verstegen of Dutch State Mines and are incorporated in the Figures below. The azeotropic line begins at 147°C and 70 atm at the three phase line S₋L₋G, which itself begins at the quadruple point. The azeotropic composition becomes increasingly
NH₃-rich with increasing temperature. Because the azeotropic line is, at its begin, tangent to the three phase line $S_{AC}-L_{G}$, and because the pressure value at this point of tangency is lower than that of the begin- and end-point of this three phase line (respectively, the quadruple point and the maximum sublimation point), the $S_{AC}-L_{G}$ line must exhibit a pressure minimum, as is shown in Fig. A2-1.

The CO₂-side of the system (relative to AC) is almost completely unknown. Because of the large temperature difference in the melting points of CO₂ and the maximum sublimation point of AC, and because of the almost complete insolubility of AC in liquid CO₂ a first critical end-point (P) is found nearly at the critical point of CO₂ itself ($T_c = 31.0^\circ$C, $P_c = 75.3$ atm); at this point solid AC is in equilibrium with a critical gas-liquid mixture. The $S_{AC}-L_{G}$ line practically coincides with the vapour pressure line of CO₂, and the gas and liquid phases consist of practically pure CO₂. At temperatures above P, solid AC is in equilibrium with a fluid phase consisting largely of CO₂. The P-T-X values of the second critical end-point (Q) have been arbitrarily chosen. Because of the very large differences in the triple point temperatures of CO₂ (- 56°C) and the maximum sublimation point of ammonium carbamate, it is not improbable that the CO₂-AC area of the NH₃-CO₂ system exhibits behaviour of the type CO₂-diphenylamine, rather than of the type ether-anthraquinone (both these types of behaviour describe systems in which a solid coexists with a fluid phase). Behaviour of the former type implies that the second critical end-point (Q) is likely to occur at very high pressures. The path of the critical line also implies metastable liquid miscibility in this CO₂-rich area. Because of the impossibility of measuring such behaviour (due to the occurrence of the urea reaction and subsequent further decomposition reactions) and its lack of practical importance, no further discussion of this area will be attempted, and ether-anthraquinone behaviour will be assumed for simplicity.

The above-mentioned behaviour is qualitatively presented in Fig. A2-1, in which the P-T-X differences of the three phase lines are exaggerated relative to the phase lines of the pure components for clarity. In Fig. A2-2 a quantitative projection is attempted. In this projection many of the three phase lines simply coincide with the phase lines of CO₂ and NH₃. A beautiful and clarifying three dimensional phase model of this difficult system has been prepared at the Laboratory of General and Inorganic Chemistry of the University by Prof. G.A.M. Diepen, Ir. J.N. Broers and Mr. J. Ruis.
Fig. A2-1. Qualitative temperature-pressure-composition projection for the ammonia-carbon dioxide system.

Fig. A2-2. Attempt at a quantitative temperature-pressure-composition projection for the ammonia-carbon dioxide system.
Literature

15. Frejacques, M., Chim. et Ind., 60, 1948, 22.
Appendix 3

Quantitative analysis of air, carbon dioxide, ammonia and water.

A3-1. Introduction.

Early studies of the quantitative analysis of gaseous mixtures of air, NH₃, CO₂ and H₂O are given by van Krevelen et al and Kawasumi. Ammonia was absorbed in dilute H₂SO₄, carbon dioxide in barium hydroxide or soda-lime and water in concentrated H₂SO₄. These analysis techniques, which involved weighing and titration, are tedious and difficult, and errors of at least 1%, 3% and 5% (probably relative) are reported for the analysis of NH₃, CO₂ and H₂O, respectively.

In 1965 Koran and Andreatch presented a near infrared spectrophotometric method for the determination of NH₃, CO₂ and H₂O gases in situ under conditions of moderate temperatures and pressures (45 < T < 130°C; 500 < P < 5200 mm Hg). The method, however, is not especially accurate (analysis error < 10% per component, relative), and the equipment is complicated.

With the development of gas chromatography relatively simple and accurate methods for the continual routine analysis of these inorganic gases became available. Basically two types of columns are found in the literature: polyethylene glycol on an inert solid carrier and, much more commonly, porous polymer beads, usually coated with an amine for reducing the tailing of ammonia. Hillis et al, for example, analyzed NH₃-H₂O mixtures using the former type of column; no discussion of the accuracy of the analysis is given, however. Quantitative analysis of N₂, O₂, CO, CO₂, H₂S, NH₃, H₂O and C₁ through C₄ using polymer beads (Poropak Q) is discussed by Jones; this researcher used a two column system with back-flushing and temperature programming. Linear calibration lines for each component were obtained. The author claimed that the analysis accuracy was good, i.e., about 0.25% absolute per component. Bethea and Meador also found that air-CO₂-NH₃-H₂O mixtures could be separated using Poropak Q or QS. Ammonia tended to exhibit considerable tailing, however. Whilhite and Hollis, using a column of Poropak Q and R in series and temperature programming separated N₂, O₂, CO₂, NH₃ and H₂O (plus 9 other components), but the NH₃ peak exhibited severe tailing. Mindrup and Taylor developed a method for the quantitative analysis of trace amounts of CO₂ and H₂O in NH₃, special attention being given to reducing the tailing of the ammonia peak and improving the separation of ammonia and water. Two columns were used in series, Poropak R and Poropak R with 10% polyethylenimine. H₂O and CO₂ were determined at different conditions, and the H₂O was completely resolved from the (very slight) tail of the NH₃ peak.
For determination of the dew-points (Chapter IV) it was necessary to quantitatively analyze air-\( \text{CO}_2 \)-\( \text{NH}_3 \)-\( \text{H}_2\text{O} \) mixtures in the range of air: 0 - 5%; \( \text{CO}_2 \): 0 - 100%; \( \text{NH}_3 \): 0 - 100%; and \( \text{H}_2\text{O} \): 0 - 20%. It was also desired to keep the analysis apparatus as simple and reliable as possible, i.e., to use a one column system at constant temperature with no back flushing. Another particular problem was that the analysis apparatus was located in a large pilot-plant hall in which the ambient temperature and pressure varied considerably, namely up to 20°C and 5 cm Hg per day, due to poor heating and extensive ventilation. Since none of the articles mentioned above met these demands it was necessary to develop an analysis system which fitted our specific requirements. This was accomplished largely by Aldorf, upon whose work the following discussion is based.\(^{10}\)

A3-2. Experimental.

In designing the apparatus two factors were central. Firstly, the method of absolute calibration was chosen rather than the method of internal standardization. This choice was made because the sample was gaseous (rendering addition of a marker difficult) and because the various components varied greatly in concentration. Furthermore, the use of the absolute method also provided a check on the accuracy of the analysis, namely that the sum of the components is equal to 100% (for a discussion of the applicability of the two calibration procedures see Willis\(^{11}\)). The use of the absolute method required, however, that the sample size and katharometer response remain highly constant, which was difficult because of the varying ambient conditions. The second factor therefore centered about the design of an analysis system whose stability and accuracy were unaffected by relatively large changes in ambient conditions. Placing most of the components of the apparatus in thermostats largely eliminated the temperature dependency, but reducing the effect of the atmospheric pressure variation was more difficult. In minimizing this pressure effect (and in achieving high stability and accuracy in general) we were very much influenced by the work of Goedert and Guiochon, who performed classic studies of the sources of error in quantitative gas chromatography.\(^{12,13}\) Basically the design of the apparatus was such that the volumetric and mass flow rates of the carrier gas remained constant, in spite of varying ambient conditions, by maintaining constant column beginning and ending pressures and constant temperatures.

The apparatus worked as follows (see Fig. A3-1 for a schematic drawing): High purity (99.99%) \( \text{H}_2 \) (10) enters the system, its pressure being controlled by a pressure controller ((9), Conoflow Flow Controller, Model H-40-XT-HM, 125 psi). After passing through a sintered stainless steel filter (5 micron, (1)),
the H₂ flows through a capillary tube (3), whose dimensions are: length, 9.6 m; internal diameter, 0.2 mm; material, stainless steel 316. The large pressure drop (+6 atm) over the capillary serves to minimize the effect of atmospheric pressure variation on the regulating effect of (9). (For a discussion of this

1 Filter
2 Buffer vat
3 Capillary
4 Catharometer
5 Column
6 Injection valve
— normal flow
--- sample injection
7 Sample loop
8 Pressure gauge
9 Pressure control

10 H₂ in
11 H₂ out (to flow meter)
12 Flow control
13 Hg manometer
14 Control air
15 Sample in
16 Sample out (to rotameter)

— Thermostat

Fig. A3-1. Schematic diagram of the analysis section.

principle of flow control see Rushnik et al. 14) The H₂ gas then passes to the reference channel of the catharometer (4) and thence to a buffer vat (2), volume: 200 cm³, which dampens pressure pulsations caused by sample injection. The H₂ thereupon enters the pneumatically operated injection valve (7), Rattrisch or Beckman 6-port valve), and, under normal conditions, then flows to the column (5). From the column the H₂ flows to the measurement channel of the catharometer and thence to another buffer vat (2). The H₂ leaves the analysis systems via a constant flow valve (12), Brooks Elf Flow Controller, Model 8743, stainless steel, Teflon membrane, No. 1 taper needle; constant up-stream, variable down-stream pressure) and flows, at atmospheric pressure, to a thermostated soap-bubble meter. The sample gas flows via a sintered stainless steel filter (1) to the injection valve (6). The sample normally flows through a sample loop (7), ± ½ cm³ and then, via a precision rotameter (Fischer Porter 08F 1/16-12-4, sapphire float) to purge. The pressure at the analysis entrance is measured to within ±0.05 atm using a precision pressure gauge (8); the pressure at the analysis exit is measured to within 1 mm Hg using an absolute Hg manometer (13). Sections (1) to (7) are enclosed in a thermostat (ΔT < 1°C);
section (8) to (12) are enclosed in another thermostat operating at about 30°C. The rotameter and all of the sample lines are kept at about 120°C to avoid carbamate condensation. Because the ammonia of the samples adsorbs on metal surfaces, the samples had to be injected at precisely regulated time intervals in order to reach a steady-state condition and constant analysis value. For this reason sample injection occurred automatically using a timer mechanism operating micro-switches, which in turn actuated electrically controlled pneumatic valves providing for the operation of the pneumatic sample valve. The automation of the system is similar to that of Hems and Adams. The bridge signal was registered with a Hitachi Perkin Elmer 1 mv recorder and integrated with an Infrotronics digital integrator, model CR 200.

Two satisfactory column materials were found, Poropak T and Chromosorb 104 (See Table IV-4 for the specifications of the Chromosorb 104 column. The specifications for the Poropak column were identical except that it operated at 130°C.) The Poropak T, however, exhibited large variations in quality from batch to batch. (The problem of varying batch quality of porous polymer beads has been discussed in an excellent review article by Hollis.) Many other column materials were tested, including 10% PEG-400 on neutral Teflon mesh (satisfactory for CO₂-NH₃-H₂O separation, unsatisfactory for air-CO₂ separation; exhibits oxidation and aging), Poropak Q (absorbs NH₃ irreversibly), Poropak R, Poropak S, Chromosorb 103 (all unsatisfactory) and 7% polyethylenimine on Poropak Q (probably satisfactory).

In order to calibrate the column, gaseous mixtures of N₂ with NH₃ or CO₂ were made in gas cylinders and analyzed chemically. These gas mixtures, pure NH₃ and CO₂, and ammonium carbamate, which sublimes stoichiometrically (2NH₃ + CO₂) were used to prepare calibration lines. A plot of corrected peak areas vs. mole-concentration yields a straight line for NH₃ and CO₂ (see Figures A3-2 and 3). Since the injection occurred at atmospheric pressure, the peak areas were corrected to standard atmospheric pressure (760 mm Hg) using the formula:

$$ A_{760} = \frac{760}{P_{at}} A_m $$

in which $A_{760}$ = area standardized to 1 atmab., $P_{at}$ = atmospheric pressure in mm Hg at the time of injection and $A_m$ = the measured peak area. For water a calibration line was obtained by injecting saturated mixtures of water vapour in N₂. The N₂ bubbled through a sintered glass plate into ± 10 cm depth of water and flowed thence to a coiled column, ca. 1 by 30 cm, filled with crushed brick. The first part of this brick powder was saturated with liquid water and dark brown in colour. It was necessary that the last part (ca. the last fifth) be dry, as is clearly seen from its light colour. This part of the column,
saturated with respect to water vapour, prevented entrained water droplets from entering the system. The entire water saturater was contained in a constant temperature bath and the percent water calculated from the water vapour pressure, at the given temperature, divided by the atmospheric pressure at that time. Because the water peak sometimes appears on the tail-end of the NH₃ peak, it was found that measurement of peak height gave more constant values than values for peak areas. The water calibration with the saturater exhibited considerable scatter (ca. 10 percent, relative) in the peak values. Recently Bijwaard and Verhoeff greatly improved the calibration by employing binary water-organic azeotropes (constant water concentration). The corrected peak height vs. concentration H₂O is nearly linear in the range of 0-15% H₂O, as is shown in Fig. A3-3.

A3-3. Results.

A typical chromatogram for a mixture is presented in Fig. A3-4. The resolution of air, CO₂ and NH₃ is excellent. The resolution of NH₃ and H₂O, particularly at high NH₃ and low H₂O concentrations is less good, but usable using peak heights for water. Base line stability is also very good, namely ca. 10 microvolt. For a total of 36 air-CO₂-NH₃-H₂O mixtures measured over a period of two years the average sum of the concentrations was 99.8% and the standard
deviation 1.2%. The relative accuracy of the analysis for the various components was about \( \frac{1}{2}-1\% \) for air and \( \text{CO}_2 \), 1-2\% for \( \text{NH}_3 \) and 5\% for \( \text{H}_2\text{O} \).

Fig. A3-4. Typical chromatogram for an air-carbon dioxide-ammonia-water separation on Chromosorb 104.
References.

4. The problem of tailing of the ammonia peak using porous polymer beads was reported early in its use. Even rather recently the problem of ammonia peak tailing is being discussed. See, for example, for early and recent articles discussing this problem, Hollis, O.L. and Hayes, W.V., J. of Gas Chromatog., July, 1966, 235 and Moretti, E. et al, J. Chromatog. Sci., 12, 1974, 64.
Appendix 4

Computer calculations with the empirical thermodynamic model.

In order to acquaint the reader with the use of the empirical thermodynamic model as a calculational tool a computer program is presented. The program discussed (written in the language CPS for use with a terminal) is used to calculate the bubble-point lines parallel to either the \((2\text{NH}_3)\)-CO\(_2\) plane or the H\(_2\)O-urea plane (in the ternary T-X-Y model); the locus of minimum pressure points (at constant temperature) of the former planes forms the equilibrium-ridge line. Examples of the results of these calculations are given, respectively, in Figures III-5, III-10 a and b and III-8 and 9.

The program works as follows. The procedures "newton" and "mavr" are first called up. The former is used to calculate the root of the cubic equation (III-13) for the concentration of free carbon dioxide, c, in the liquid phase, using the iterative Newton-Raphson method. The latter procedure ("mavr") is an analytical representation of the conversion nomogram presented by Mavrovic. After choosing the temperature, the values of the models parameters, \(p_{\text{H}_2\text{O}}^0\), \(K_2\), \(p_{\text{NH}_3}^0\), and \(H_{\text{CO}_2}\), are calculated (the figures III-2, III-3 and III-4 have been represented analytically). A choice is then made as to whether bubble-point lines are calculated on planes parallel to the \((2\text{NH}_3)\)-CO\(_2\) or H\(_2\)O-urea planes. In the former case the H\(_2\)O-concentration is held constant (in terms of \((2\text{NH}_3)\), CO\(_2\) and H\(_2\)O); in the latter case the value of the difference of the CO\(_2\) and \((2\text{NH}_3)\) concentration is held constant. (Geometrically the results of the calculations refer to the \((2\text{NH}_3)\)-CO\(_2\)-H\(_2\)O square. For certain calculations, however, such as the degree of conversion, calculations are performed in terms of NH\(_3\), CO\(_2\) and H\(_2\)O. Hence a number of formulas (e.g., statement 30) are necessary to convert from the one composition system to the other.) The \(L\), \(W\), \(X\) and mole fractions of the constituents of the liquid phase are calculated. Using these concentration values and the values of the parameters, the partial pressures of the three constituents (NH\(_3\), CO\(_2\), H\(_2\)O) of the gas phase may be calculated. The total pressure and molar concentration of the gas phase follow. As already indicated calculations on the liquid phase are expressed in terms of the chemical constituents, in terms of NH\(_3\), CO\(_2\) and H\(_2\)O and in terms of \((2\text{NH}_3)\), CO\(_2\) and H\(_2\)O.

Detailed discussions of computer calculations making use of the model are presented by de Cooker, Kalkman, Verbrugge, Bijwaard and Schröder and Bijwaard.
Computer calculation of bubble-points

1. PUT LIST ('Calculation of bubble-points.');
2. DECLARE newton ENTRY EXT LIB(STPF), mavr ENTRY EXT LIB(STPF);
3. PUT LIST ('Give the temperature.');
4. GET LIST (t);
5. T=t+273;
6. ph2oO=exp(2.303*(5.5233-2051.3/T));
7. K=exp(2.303*(-3.3918+2367/T));
8. pnh3O=exp(2.303*(5.361-1345/T));
9. H=-7000+60*t;
10. PUT LIST ('Bubble-points line // N2H6-CO2 diagonal (1), or // Urea-H2O diagonal (2)?');
11. GET LIST (sw);
12. start: IF sw=1 THEN GO TO h2o;
13. PUT LIST ('Give a = CO2 - N2H6.');</n
14. GET LIST (a);
15. step=.01;
16. stop=(1+a)/(3-a);
17. GO TO door;
18. h2o: PUT LIST ('Give b = fraction H2O.');
19. GET LIST (b);
20. step=.01;
21. stop=(b-1)/(b-3);
22. door: PUT LIST ('');
23. PUT IMAGE(t,K,H,pnh3O)(iml);
24. PUT LIST ('');
25. PUT LIST ('================================================================');
26. PUT LIST ('');
27. PUT LIST ('| L W X P % NH3 | LIQUID | N2H6 CO2 H2O | GAS | N2H6 CO2 H2O | ');
28. PUT LIST ('');
29. DO fco2=.1 BY step TO stop;
30. IF sw=1 THEN fnh3=2*(fco2-1+b)/(b-2); ELSE fnh3=2*(fco2-a)/(1-a);
31. fh2o=1-fnh3-fco2;
32. L=fnh3/fco2;
33. W=fh2o/fco2;
34. procn=100*L/(L+W+1);
35. XO=X;;
36. X=mavr(L,W,XO,t);
37. k=L-2;
38. l=.25*k*k-.5*X*(X+W)/K;
39. w=-.25*(X+W)*(L+W+X-1)*X/K;
40. c0=.1;
41. eps=.00001;
42. CALL newton(k,l,m,c0,eps); smo1=smol=L+W+X-1+2*c;
44. mfco2=c/smol;
45. mfh2o=(X+W)/smol;
46. mfnh3=smol+smol+smol+smol+smol+smol;
47. sum=.5*L+W+1;
48. fnl=.5*L/sum;
49. fcl=1/sum;
50. fh1=W/sum;
51. pn=mfnh3*ph2oO;
52. pc=mfco2*H;
53. ph=mfh2o*ph2oO;
54. phtot=pn+ph+pc;
55. frnh3=pn/phtot;
56. fco2=pc/phtot;
57. frh2o=ph/phtot;

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58. \[ \text{som} = 0.5 \times \text{frnh3} + \text{frco2} + \text{frh2o}; \]
59. \[ \text{fng} = 0.5 \times \text{frnh3}/\text{som}; \]
60. \[ \text{fcg} = \text{frco2}/\text{som}; \]
61. \[ \text{fhg} = \text{frh2o}/\text{som}; \]
62. \[ \text{PUT IMAGE (L,W,100*X,ptot,procn,fnl,fcl,fhl,fng,fcg,fhg)(im2);} \]
63. \[ \text{END}; \]
64. \[ \text{END}; \]
65. \[ \text{PUT LIST ('|')}; \]
66. \[ \text{PUT LIST ('|')}; \]
67. \[ \text{GO TO start;} \]
68. \[ \text{im1: IMAGE}; \]
69. \[ \text{im2: IMAGE;} \]
70. \[ \text{END}; \]

Symbols used in previous program:

t = temperature °C; T = absolute temperature °K; ph2o0 = vapour pressure pure water, atm; K = equilibrium constant K2; pnh30 = extrapolated vapour pressure NH3, atm; H = Henry coefficient CO2, atm; sw = calculation variable; a = constant difference mole-fractions CO2 and NH3; b = constant mole-fraction H2O; step = step size fco2; stop = upper boundary fco2; fco2, fnh3, fh2o = mole-fractions components NH3, CO2, H2O; L = NH3/CO2-ratio; W = H20/CO2-ratio; procn = gross percentage NH3 with NH3, CO2 and H2O components; X = conversion; XO = start value conversion; k, 1, m = coefficients cubic equation; c0 = start value c; c = number of moles free CO2; eps = required degree of accuracy in c; smol = sum number mole of constituents; mfnh3, mfc02, mfh2o = mole fractions; sum = sum of the moles 2NH3, CO2 and H2O components; f = number of moles 2NH3, CO2 and H2O in the gas phase; som = sum number moles 2NH3, CO2 and H2O in the gas phase.

Procedure "newton"

1. \[ \text{newton: PROCEDURE (a,b,c,xO,x,eps);} \]
2. \[ \text{LET F(x)=x*x*x+a*x*x+b*x+c;} \]
3. \[ \text{LET f(x)=3*x*x+2*a*x+b;} \]
4. \[ x=xO; \]
5. \[ \text{weer: x=x-F(x)/f(x);} \]
6. \[ \text{IF abs(F(x)/f(x))>eps THEN GO TO weer;} \]
7. \[ \text{END newton;} \]

Symbols used in "newton" procedure:

newton = procedure name; a, b, c = k, l, m, resp. coefficients of cubic equation; x0 = start value root; x = root to be calculated; F(x) = cubic equation; f(x) = first derivative of the cubic equation; eps = accuracy of determination of the root.
Procedure "mavr"

1. mavr: PROCEDURE (L,W,XO,t);
2. DECLARE newton ENTRY EXT LIB(STPF);
3. Y=.0463+.002722*t;
4. K=.25*Y*Y*(3-Y)/((1-Y)*(1-Y)*(1-Y));
5. a=1L-1;
6. b=(4*L*K+L*K+L*W+L*W+W*W)/(4*K-1);
7. c=-K*L*L/(4*K-1);
8. eps=.0001;
9. CALL newton(a,b,c,XO,X,eps);
10. RETURN (X);
11. END mavr;

Symbols used in "mavr" procedure:

mavr = function procedure; L = NH3/CO2-ratio; W = H2O/CO2-ratio; XO = start value conversion to urea; t = temperature °C; newton = procedure for Newton-Raphson; Y = conversion to urea of pure carbamate; K = equilibrium constant (model Fréjacques); a, b, c = coefficients of cubic equation; eps = necessary calculation accuracy in the conversion value; X = conversion to urea in the liquid phase; P = pressure, atm.

References
Appendix 5

Bibliography

In this Appendix a listing is given of the literature referred to in this thesis. For the reader's convenience some related articles are also included.

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SAMENVATTING

De achtergrondinformatie en het researchwerk van dit proefschrift zijn gericht op de studie van een alternatieve methode voor de synthese van ureum, het hete gas recirculatieproces (HGRP). Kennis van fasenevenwichten en corrosie zijn van fundamenteel belang voor het realiseren van dit proces. Het zwaartepunt van het researchwerk ligt daarom bij deze twee onderwerpen.

In het eerste hoofdstuk worden de fundamentele aspecten van de ureumtechnologie besproken, zodat de lezer zich een oordeel kan vormen over het HGRP in vergelijking met andere ureumprocessen. Ook wordt een schets voorgelegd van enige economische aspecten van de ureumproductie en de ureummarkt als algemene, maar ook relevante informatie. Tevens wordt een korte schets gegeven van de ontwikkeling van de ureumtechnologie tot nu toe en haar mogelijke toekomstige ontwikkelingen.

Om de optimale reactorcondities voor het HGRP over een breed gebied van temperatuur- en samenstellingscondities te bepalen werd aanvankelijk een uitgebreide studie gemaakt van de bubble-pointsdrukken van NH₃-CO₂-H₂O-ureum mengsels bij volledig evenwicht. Tegelijkertijd werd een theoretisch fasenmodel ontwikkeld, dat de gas-vloeistof evenwichtscondities in een ureumreactor beschrijft, als deel van een nieuw ternair fasenmodel voor het NH₃-H₂O-CO₂ systeem bij volledig evenwicht in het gebied 140 < T < 220°C en 20 < P < 1000 atm. Dit experimenteel en theoretisch werk vorderde zo goed, dat het, tot op zekere hoogte, een doel op zich werd. Het karakteristieke van dit fasenmodel is, dat het beschreven kan worden als een reciprook zout-paren systeem en dat er een ternaire zadelazeotroop in voorkomt. Dit nieuwe model verschaf een groot inzicht in de relatie tussen samenstelling, temperatuur, bubble- en dauwpuntsdruk, critische verschijnselen en het gedrag van de nodenlijnen. Ook wordt de relatie besproken tussen dit model en de ureumtechnologie. Deze resultaten en discussie worden voorgelegd in hoofdstuk II.

Om dit nieuwe fasenmodel kwantitatief te kunnen beschrijven, werd een eenvoudig empirisch thermodynamisch model ontwikkeld; dit werk wordt gepresenteerd in hoofdstuk III. Het empirisch model is gebaseerd op het optreden van de volgende reacties:

\[(\text{NH}_3)_G \rightleftharpoons (\text{NH}_3)_L\]  
(1)
\[(\text{CO}_2)_G \rightleftharpoons (\text{CO}_2)_L\]  
(2)
\[(\text{H}_2\text{O})_G \rightleftharpoons (\text{H}_2\text{O})_L\]  
(3)
\[2(\text{NH}_3)_L + (\text{CO}_2)_L \rightleftharpoons (\text{NH}_2\text{COONH}_4)_L\]  
(4)
\[(\text{NH}_2\text{COONH}_4)_L \rightleftharpoons (\text{NH}_2\text{CONH}_2)_L + (\text{H}_2\text{O})_L\]  
(5)
Het model bestaat uit de evenwichtsvergelijkingen van reacties (1), (2), (3) en (6), die worden beschreven door gemaandateerde versies van de wet van Raoult ((1), (3)), Henry ((2)) en een log K versus 1/T vergelijking ((6)). De evenwichtsconversie van koolzuur tot ureum, als een functie van samenstelling en temperatuur, is ook een noodzakelijk deel van het model; deze informatie wordt verkregen uit de gepubliceerde conversieformule van Mavrovic (1972). Op basis van dit model kunnen de gas-vloeistof evenwichtswaarden (nodenlijnen) nauwkeurig worden berekend bij de bedrijfscondities van de ureumsynthese reactor en, steeds meer kwalitatief, in de concentratiezones gaande in de richting van de NH$_3$-$H_2$O en CO$_2$-$H_2$O systemen en de ureum-rijke gebieden. Een belangrijk feit is, dat de vorm van het ternaire fasenmodel, gepresenteerd in hoofdstuk II, ook volgt uit de berekeningen met het empirisch thermodynamisch model, en dat dit laatste model zelfs gebruikt kan worden om de condities en samenstelling van het ternaire zadelazeotropisch punt te berekenen. Dit model draagt tevens bij tot de verklaring van het effect van een overmaat aan ammoniak en water op de evenwichts-ureumconcentratie en geeft inzicht in het effect van temperatuur op de conversie tot ureum in de vloeistoffase.

In de volgende hoofdstukken wordt meer aandacht geschonken aan vragen, die direct verband houden met de realisatie van het HGRP.

In hoofdstuk IV wordt de meting van de fysische dauwpunten van NH$_3$-$H_2$O-CO$_2$ mengsels bij HGR condities beschreven. Daar de vloeistoffase (condensaat) buitengewoon corrosief is voor praktisch alle compressormaterialen (een turbo-compressor vormt het hart van het HGRP), is het noodzakelijk, dat condensatie wordt vermeden en dat daarom de condensatietemperaturen bekend zijn als functie van samenstelling en druk. Voor dit doel werden een unieke methode en apparatuur ontwikkeld. Wegens experimentele moeilijkheden konden echter slechts kwalitatieve resultaten worden bereikt. Niettemin is het duidelijk, dat de belangrijkste factoren die lage temperatuurcondensatie (gunstig voor het HGRP) veroorzaken, lage waterconcentraties zijn en, minder belangrijk, hoge CO$_2$-concentraties in de recycle gasstroom. Ook wordt een eerste poging gedaan om de NH$_3$-CO$_2$-$H_2$O dauwpunten te berekenen.

Daar er vaak getwijfeld is aan de technische uitvoerbaarheid van het HGRP op basis van het geloof, dat de hoge temperatuur CO$_2$-$H_2$O-NH$_3$ recycle gasstroom overkomelijke corrosieproblemen zou geven, werd ook een studie gemaakt van gasfase corrosie van typische compressormaterialen bij HGR condities. Dit werk wordt beschreven in hoofdstuk V. Dit hoofdstuk bevat ook een uitgebreid literatuuronderzoek betreffende de hierboven genoemde problemen. Uit dit literatuuronderzoek
mag geconcludeerd worden, dat stikstof- en waterstofaantasting waarschijnlijk de ernstigste potentiële bronnen van corrosie zijn en dat deze gevaren tot een minimum kunnen worden teruggebracht door staal met een hoog nikkel- en chroomgehalte te gebruiken, pre-oxydatie van de alliages toe te passen en oxyderende gassen toe te voegen ($O_2$) aan de recirculatiegassen. Het experimentele programma, uitgevoerd in samenwerking met de afdeling Metaalkunde van de Technische Hogeschool, bestond uit een aantal statische en dynamische proeven met lage en hoge druk in een ponging de som van de condities, die in een HGR turbo-compressor bestaan, te benaderen. Zoals verwacht, werd stikstofaantasting waargenomen. Bij nikkelgehalten > 8% nam de aantasting tot een te verwaarlozen grootte af. Het blijkt, dat een semi-austenitisch precipitatie-gehard chroom (14%)-nikkel (8%)-staal voldoende resistent is tegen inwerking door $NH_3$-$CO_2$-$H_2O$ gassen bij HGR condities. Een onbeantwoorde vraag blijft echter de eventuele corrosieresistentie tegen synthesevloeistof (nevel) bevattende gasmengsels.

In het laatste hoofdstuk wordt een HGRP zelf besproken. Er wordt een gedetailleerd literatuuronderzoek van dit proces voorgelegd, en de fundamentele ontwerpcriteria worden uiteengezet. Voor een gegeven ontwerp wordt een massa- en energiebalans opgesteld, waarbij gebruik gemaakt wordt van eerder gepresenteerde methoden en informatie. Speciale aandacht wordt geschonken aan het hart van het HGRP, de HGR turbo-compressor en tussenkoelers. Met deze resultaten kunnen de utilities-kosten geschat worden. Vergelijken we deze utilities-kosten met die van het DSM CO$_2$-stripping proces, op dit moment het meest succesvol, dan lijkt het HGRP economischer. Geconcludeerd kan worden, dat verdere gedetailleerde economische studie van het HGRP zeker gerechtvaardigd is.

In de appendices worden een aantal specifieke onderwerpen nader besproken. Appendix 1 illustreert met voorbeelden het gebruik van het ternaire model, waarin water kan voorkomen in negatieve concentraties. Appendix 2 bespreekt de fasen-evenwichten van het $NH_3$-$CO_2$ systeem. Deze bespreking wordt gepresenteerd vanwege het belang voor de ureumtechnologie en wegens het feit, dat er ondanks dit belang tot nu toe nog geen systematische studie van dit systeem als geheel is gepubliceerd. In Appendix 3 wordt de kwantitatieve analyse van het ureumsynthesegas, lucht-$CO_2$-$NH_3$-$H_2O$, besproken, daar dit onderwerp een belangrijk experimenteel probleem vormde, dat opgelost moest worden. Om de lezer bekend te maken met de eigenlijke berekeningsmethoden, die bij het empirisch thermodynamisch model gebruikt worden, geeft Appendix 4 een typisch computerprogramma, waarin de meeste aspecten betreffende het gebruik van het model belicht worden. Tenslotte geeft Appendix 5 een lijst van de literatuur die bij dit proefschrift gebruikt werd en enige andere relevante artikelen.
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STELLINGEN

1. Een duidelijke definitie van azeotropische condities is: de azeotropische condities zijn de temperaturen en drukken, waarbij de coëxisterende gas- en vloeistoffasen dezelfde samenstelling hebben, de laatste uitgedrukt in termen van concentraties van de componenten van het systeem. Het aantal componenten van het systeem is eenduidig te bepalen, gebruik makend van de fasenregel van Gibbs, ook wanneer chemische reacties optreden in dit systeem.


2. Ieder model, ook een grafisch model, is een incomplete weergave van de "realiteit". Een model, dat de metingen goed weergeeft, is een goed model. Omdat het de "realiteit" nooit volledig weergeeft, is het tegelijkertijd een "fout" model.

3. Het verdient aanbeveling de contacten tussen studenten van de Technische Hogeschool in hun afstudeerjaar en de industrie te bevorderen, zij het met behoud van wederzijdse vrijheid.

4. De bewering van Prof. C.N. Parkinson, dat de enigszins gedecentraliseerde federatieve staatsvorm van de Verenigde Staten van Amerika als model moet dienen voor een toekomstige Verenigde Staten van Europa, is niet correct.

   (N.R.C. Handelsblad, 25 maart, 1975, p. 11.)

5. In verband met de waarschijnlijke finlandisering van West-Europa is het gewenst om Russische geschiedenis en taal nu facultatief in het schoolrooster op te nemen.

6. Naast maatschappelijk verantwoordelijkheidsbesef is juist ook inzicht in de samenhang der wetenschappen nodig bij α,γ-onderwijs op de technische hogescholen.

7. De depressie in de bouwwereld is gedeeltelijk te verklaren door de slechte kwaliteit van de nieuwbouwwoningen.

8. Het idee van een multinationaal Palestina vormt geen reële basis voor een levensvatbare staat.

9. Het bestaan van de staat Israël moet ook betekenen, dat de Palestijnen nationale rechten hebben.

10. Een van de merkwaardigste aspecten van de Nederlandse samenleving voor een buitenlander is de gewoonte de gordijnen van de woonkamer 's avonds open te laten. Deze gewoonte, hoe charmant ook, is eerder acceptabel, wanneer de ramen dubbel zijn uitgevoerd.
11. In het algemeen wordt "Brits Engels" gesproken met een meer beschaafd accent en rijker vocabulair en een elegantere stijl dan "Amerikaans Engels", met name wat betreft toespraken door politieke figuren.

12. Het is wenselijk, de borstvoeding terug te brengen als een volksgewoonte, in het westen, maar vooral ook in de ontwikkelingslanden; hiervoor is een betere kennisoverdracht betreffende de emotionele en fysiologische aspecten nodig.
